

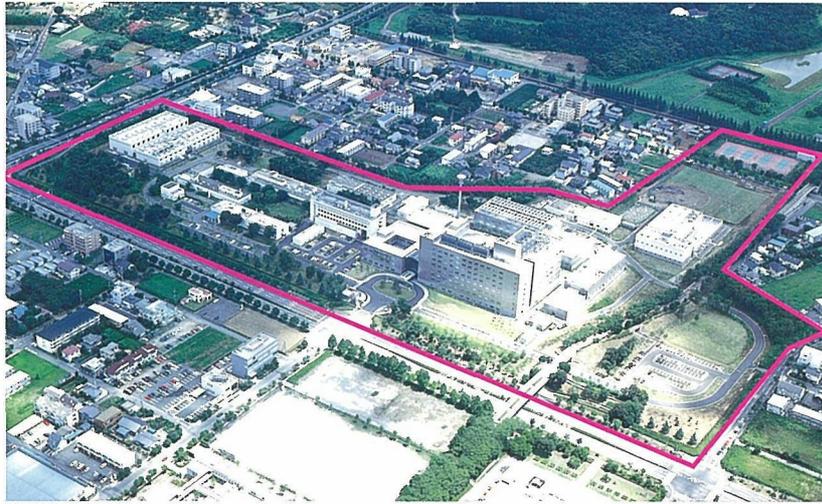
# **NIRIM**

## **Research Activities**

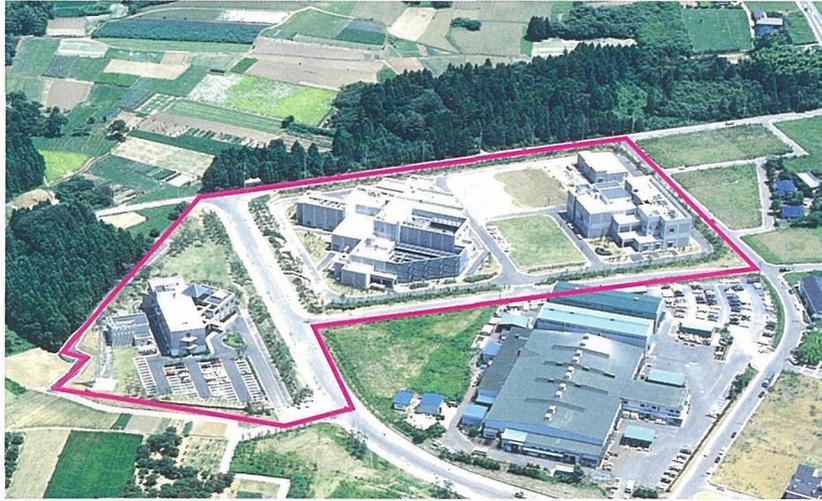
**1998**

**National Research Institute for Metals**

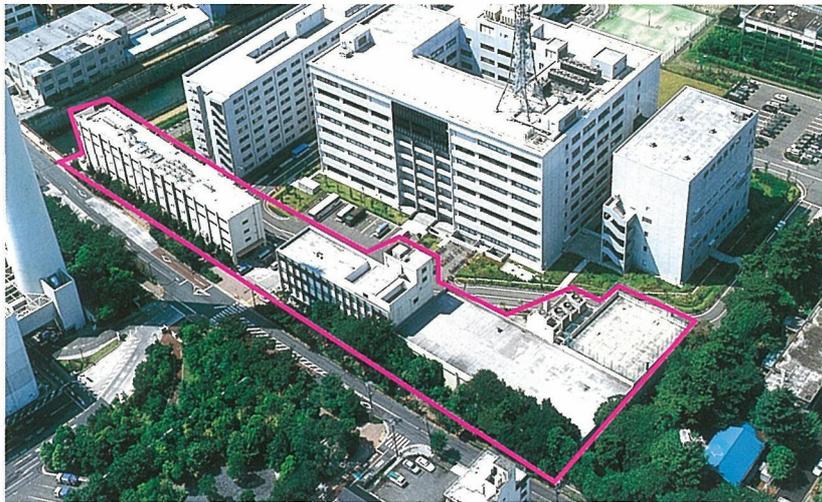
**Japan**



Sengen Site



Sakura Site



Meguro Site

## Preface

We hope you find the projects and related work described in NRIM Research Activities 1998 to be of interest.” This report summarizes the annual activities of the National Research Institute for Metals (NRIM). If all of you are useful even a few of this it is honor.

NRIM is a research institution attached to the Science and Technology Agency of the government of Japan and was established in 1956. Since then, NRIM has played an essential role in the field of research and development of metals, alloys and other materials. An ongoing effort has been to improve the reliability of existing materials, which is documented in the “NRIM Creep and Fatigue Data Sheet” series of publications. ‘NRIM Creep and Fatigue Data Sheet’ is likely to become the standard of the world regarding metal evaluation.

On July 1, 1995, NRIM moved its headquarters from Tokyo to Tsukuba Science City, where there are many world-class experimental facilities and various supercomputers. With the support and efforts of sponsors, staff, and the community, we have built a Center of Excellence for fundamental materials research in Tsukuba. Responding to the present social and economic needs of Japan.

We are establishing a “Frontier Research Center for Structural Materials” as part of “New Century Structural Materials Project.” We have already started to create future “ultra steels” at the center, making full use of the excellent resources available in social life. In this way, NRIM continues to expand its activities for advanced materials research.



To all of you, who have supported NRIM, we greatly appreciate your continued understanding and encouragement.

A handwritten signature in black ink, reading "Masatoshi Okada". The signature is written in a cursive, flowing style.

Dr. Masatoshi OKADA  
Director-General

# NRIM Research Activities 1998

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# Research in Progress 1997-1998

## □ List of Research Subjects

### Characterization/Properties

#### Materials physics Division

- 1 Effects of Pressure on the Physical Properties of Magnetic Materials
- 2 Investigation on Synthesis and Characterization of Metal Complexes with High Electron-Spin Multiplicity
- 3 Study on the Improvement of Analytical Technologies for Metallic Materials
- 4 Improvement of the Accuracy of Inductively Coupled Plasma-Mass Spectrometry through Sample Preparation and Isotope Dilution Analysis
- 5 Composition, Temperature and Pressure-Induced Structural Changes and Physical Properties of Materials
- 6 Two Dimensional Photoelectron Spectroscopic Studies on Surface Structures and Properties
- 7 Investigation on the Degenerate Electronic Ground State and Electronic Transitions of Metal Complexes with High Symmetry
- 8 X-ray Diffraction Study under High Pressure and Low Temperature Using Diamond Anvil Cell
- 9 Evaluation of Structures with Trace Element Analysis

#### Physical Properties Division

- 10 Spectroscopic Study of Low Dimensional System in High Magnetic Fields
- 11 Study on the unusual metallic state and electronic structure of magnetic materials
- 12 Studies on the Highly Correlated Electron Systems under Multiple Extreme Conditions

#### Computation Materials Science Division

- 13 Development of Knowledge Database for High-Tc Superconducting Materials

- 14 Theory of Thermal Reaction on Solid Surfaces
- 15 Theoretical Study on the atomic motions on surfaces
- 16 Thermodynamic Analysis of Formation Processes of Metastable and Stable Phases
- 17 Improvement of the Long Term Creep Strength of Ferritic Steels by the Minimum Alloying
- 18 Molecular Dynamics Study on Superplastic Deformation and Embrittlement due to Grain Boundary Segregation
- 19 Development of Unification System for Distributed Materials Scientific Data utilizing Networking Environment
- 20 Modeling and Simulation for the Prediction of Material Strength
- 21 A Computer-Simulation Study of the Plastic Deformation of Crystals
- 22 New Phenomena in Ultrathin Magnetic Films and Multilayer Systems

#### Mechanical Properties Division

- 23 NRIM Long-Term Fatigue Data Sheet Project- I
- 24 NRIM Creep Data Sheet Project-V
- 25 Relationships between Fatigue Behavior and TEM Structure of Titanium Alloys
- 26 Fatigue Strength in a Corrosive Environment
- 27 Effect of Cryogenic Temperature and Gas-environment on Deformation and Fracture Behavior
- 28 Characterization and Evaluation of Cryogenic Structural Materials
- 29 Fabrication of Ni<sub>3</sub>Al-Base Intermetallic Compounds by Unidirectional Solidification
- 30 Fundamental Studies of the Microbial Reaction with Inorganic Compounds
- 31 Improvements of High Temperature Properties in Materials for High/Ultra-high Temperature Use.

- 32 Remaining Life Prediction for Weldments in FBR based on Creep Damage Evaluation.
- 33 Dynamic Microstructural Change and Mechanical Properties in Ceramics at High Temperatures

**Materials Processing Division**

- 34 The Development of High Strength High Conductive Cu Base In-Situ Composite
- 35 Control of the Oriented Single Crystals of Refractory Metals through Solid State Processes
- 36 Selenium (VI) Removal from Wastewater by a Fluidized Bed Process
- 37 Study on combustion Synthesis
- 38 Synthesis and Utilization of Mesoporous Materials
- 39 Photocatalytic Properties of Ultrafine Particles
- 40 Micro Structure Control with Plastic Deformation under Mashy State
- 41 Diffusion bonding of Stainless Steel and Metals of Group IV~VI
- 42 The Development of High Strength and High Functional In-Situ Composite
- 43 Crystal growth and dissolution mechanisms in peritectic system
- 44 Application of Ionization Separation Technique to Gaseous Process

**Special Research Officer**

- 45 Solid State Interfacial Reactions and Surface Analysis of Thin Solid Films
- 46 A Study on the Durability of Coatings on Structural Materials
- 47 Preparation of Ionic Conductors by Pressurized Sintering

**1st Research Group : Superconducting Materials**

- 48 Understanding of the Mechanism of Superconductivity in High Temperature Superconductors
- 49 Study on the Pinning Mechanism of Vortices in High Temperature Superconductors
- 50 Fabrication of Intrinsic Josephson Junctions and Evaluation of their Physical Properties

- 51 Computer Simulation Study on the Mechanism of High Temperature Superconductivity
- 52 Development of High-Tc Oxide Superconducting Wires and Tapes
- 53 Development of a Superconducting Magnet for Magnetic Separation
- 54 Grain boundary control and Jc enhancement of Bi-2212/Ag tape conductors
- 55 Preparation of In-plane Textured Buffer Layers for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> Film Growth by Modified Bias Sputtering
- 56 Fundamental research on new materials of function-harmonized oxides
- 57 In situ TEM Observation and Structural Analysis of High Tc Superconductors for Fusion Reactor at Low Temperatures
- 58 Developments of high strength oxide superconductors for high magnetic field application
- 59 Fabrication of Ag-Cu Alloy Sheathed Oxide Superconducting Wires with High Strength and High Jc Properties
- 60 Study on surface modification by plasma source ion implantation

**2nd Research Group : Advanced Nuclear Materials**

- 61 Real-Time Investigation on Surface Reactions and Defect Growth Processes under Irradiation
- 62 Plasma reaction mechanism in advanced devices studied by large scale first principle molecular dynamics
- 63 Influence of Nuclear Transmutations on Low Activation Structural Materials for Fusion Reactor Application
- 64 Understanding and Improvement of Radiation-Induced Degradation in the Advanced Nuclear Materials
- 65 Isotope Separation and Its Application to Materials
- 66 Preparation of Isotopically Purified Silicon for Determining Standard Molar Mass
- 67 Research on Utilization Technique of "Data-Free-Way" system for Nuclear Materials

**3rd Research Group :  
Advanced High Temperature Materials**

- 68 Design of Refractory Superalloys

- 69 Design of High Temperature Alloys Based on Statistical Thermodynamics
- 70 Research and Development of High Temperature  $Ti_2AlNb$  Titanium Aluminide-Based Composites.
- 71 Microstructure Control and Properties of Titanium Aluminides
- 72 Numerical Simulation of Phase Separation

**4th Research Group : Energy Conversion Materials**

- 73 Development of Basic Superconducting Technology for High Field Micro-SMES
- 74 Search of New Nonlinear Optical Crystals for Wavelength Modulation, Single Crystal Growth and Principle Technology Development for Optical Devices
- 75 Development of Composition Graded Shape Memory Alloy and Wear Resistant TiAl Based Composites
- 76 Research and Development of High-Performance Light Alloys for Hydrogen Storage
- 77 Energy Conversion Materials Fabricated with Composite Structure
- 78 Energy Conversion Materials Fabricated with Functionally Graded Structure

**5th Research Group : Intelligent Materials**

- 79 Creation of Multi-functional Materials by Assemblage of Primitive Functions
- 80 Development of micro-cellular structural materials
- 81 Development of Advanced Shape Memory Thin Films by Sputtering

**Biomaterials Research Team**

- 82 Fundamental Study on Biocompatibility of Materials
- 83 Research on Creation on Biointegrated Materials to Improve Physically Handicapped People's Quality of Life

**Ecomaterials Research Team**

- 84 Study on the Processing and Assessment of Ecomaterials
- 85 Methodology of MLCA

- 86 Research on the generic interface of materials databases

**Center for Advanced Physical Field**

- 87 Analysis of stress strain curve of matrix containing second phase particles by large deformation FEM
- 88 Materials with Atomic Scale Structures (COE Project)

**High Magnetic Field Research Station**

- 89 Stability of Superconducting Materials
- 90 Development of 1 GHz NMR Spectrometer
- 91 Fundamental Studies for Developing Very High Field Superconducting Magnets
- 92 Test methods of superconductors
- 93 Development of Magnetic Separation Control system
- 94 Evaluation of oxide superconductors
- 95 Basic Research for the Control of Chemical Reactions by High Magnetic Field
- 96 Measurement technologies and reference materials for low temperature thermophysical properties of solids
- 97 Measurement technologies and reference materials for low temperature thermal expansion of solids
- 98 Fundamental Studies on Very High Magnetic Field Generation
- 99 Basic Research for the Improvement of Material by Structural Control in High Magnetic Field

**High Resolution Beam Research Station**

- 100 Surface Analysis Database
- 101 Surface Chemical Analysis
- 102 Characterization and Control of the Optoelectronic Properties of Small Crystalline Materials with Electron Probe Analysis
- 103 Analysis/Evaluation of Atomic Scale Compositional Change in Materials Due to the Radiation Damage
- 104 Study on Detection and Evaluation of Radiation Damage in Extreme Particle Fields
- 105 Development of Fundamental Technologies

for Excited Neutral Beams

- 106 Development of analytical techniques for characterization of nuclear materials using new generation synchrotron x-rays
- 107 Advanced characterization of micro and nano meter scale structure of materials by brilliant synchrotron x-rays at the Spring-8

#### **Extreme High Vacuum Research Station**

- 108 Fabrication and Characterization of Compound Semiconductor Nanometer Structures (Nanospace Laboratory Project II)
- 109 Fabrication of Nanometer-Scale Structure on the Extremely High Vacuum Surface
- 110 Self-control of surface composition of thin film and its application to field emitter
- 111 The Chamber Material for Standard Vacuum Pressure Measurement
- 112 The Evaluation and Control of Material Self-organization

#### **Frontier Research Center for Structural Materials**

- 113 Study on Strengthening of Ferrite Matrix Steels for Welded Structures
- 114 Advanced Ultra-High-Strength Steels (1500-Mpa-plus class)
- 115 Strategic Research on Advanced Ferritic Steels for 650 °C USC Boilers (R & D of Structural Materials for 21 st Century)
- 116 Development of Structural Steels Highly Durable to Marine Environments
- 117 Fabrication of Highly Functional Composite Casting Irons

#### **Materials Creation Research Station**

- 118 Study on Melting of Refractory Metals by Cold Crucible Levitation Melting Method
- 119 Research and Development of Recyclable Simple-System Alloys

- 120 Fabrication of Particles Dispersed Materials Through Controlling of Solidification Interfaces
- 121 Fine Microstructure Development in Plural Phases Alloy
- 122 Characterization of Recovery and Softening Process in Martensitic Steels at Elevated Temperatures
- 123 Feasibility study on utilization of high brilliance X-rays for steel characterization

#### **Joining and Interface Station**

- 124 Effect of the Interfacial Damage on Mechanical Properties for Ti-Based Matrix Composites
- 125 Evaluation of mechanical properties for metal matrix composites
- 126 Evaluation of corrosion damage at atomic level
- 127 Development of metal having environmental cleaning ability by photo catalysis reaction
- 128 Effect of Aging Degradation on Localized Corrosion of Structural Materials for Light Water Reactors

#### **Strenght and Evaluation Research Station**

- 129 Development of Nano Scale Characterization Technique of Grain Boundary and its Use to Analyses to Intergranular Fracture Mechnaism
- 130 Ductile versus Brittle Behavior of structural steels
- 131 Mechanical Properties of Thin Films and Coatings
- 132 Stability of Tetragonal Phase and its Effect on High-Temperature Mechanical Properties of Zirconia
- 133 Evaluation Method of High Temperature Fracture Property for Creep Brittle Materials
- 134 Long-Term Creep-Fatigue Properties of 316FR Stainless Steel for Fast Breeder Reactor

## □ Research Programme

### Characterization/Properties

#### Materials physics Division

##### 1 Effects of Pressure on the Physical Properties of Magnetic Materials

*A. Matsushita, J. Tang, J. Ye, T. Naka, H. Abe, S. Ishida and V.C.R.Turumella Materials Physics Division*

[April 1996 to March 1999]

We have been pursuing several research projects in high pressure physics, centering around the physical properties of magnetic intermetallic compounds.

One of the current research interests focuses on the physical properties of a 3d intermetallic compound,  $\text{Fe}_2\text{VAl}$ . This material exhibits interesting properties which resemble those of heavy fermion materials, such as an enhancement of specific heat at low temperatures, semiconducting temperature dependence of electrical resistivity and so forth. Recently we found that these properties are extremely sensitive to heat treatment. For example, a quenched sample exhibits a large enhancement of specific heat and does not exhibit magnetic ordering, while the enhancement of specific heat is suppressed and a ferromagnetic transition is observed for the samples which are annealed at low temperatures. These differences of physical properties are closely related to the mixture among Fe and V atoms.

Another research project is concerning the superconductivity of  $\text{Pr}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  (Pr123). This compound has been considered to be a non-superconductor for about 10 years. We found that the pressure coefficient of Tc,  $dT_c/dP$  is extremely large for the superconducting Pr123[2]. This is in contrast to the previous results for (Y, Pr) 123, in which large negative values of  $dT_c/dP$  have been reported. It is surprising that a compound with the same chemical composition shows an opposite pressure dependence. At present we are investigating the crystal structure of the superconducting Pr123 in detail.

Our program also encompasses developing high pressure techniques. We have constructed a diamond-anvil X-ray diffraction system equipped with a monochromator. With this system we can obtain excellent X-ray diffraction data under high pressures which are comparable to that obtained using synchrotron radiation facility.

**Keywords :** high pressure, magnetic materials, high-Tc superconductor

##### Recent Publications

Pressure Effects on Structure and Tc in Superconducting  $\text{PrBa}_2\text{Cu}_3\text{O}_x$ , J.Ye, Z.Zou, A.Matsushita, K. Oka, Y.Nishihara and T.Matsumoto, Rev. High Pressure Sci. Technol., 7 (1998) 577.

de Haas-van Alphen Effect Study of  $\text{CeRh}_2\text{Si}_2$ , H. Abe, H.Kitazawa and H.Aoki, J.Phys. Soc. Jpn., 67 (1998) 1852.

Pressure Effect on Metal-Insulator Transition in  $\text{Y}_{1-x}\text{Ca}_x\text{TiO}_3$ , T.Naka, T.Matsumoto, F.Iga and Y. Nishihara, Rev. High Pressure Sci. Technol., 7 (1998) 608.

Physical Properties of Heusler-type  $\text{Fe}_2\text{VAl}$  Compound, A.Matsushita and Y.Yamada, to be published in J. Magn. Magn. Mater..

Unusually Large Tc Enhancement in Superconducting  $\text{PrBa}_2\text{Cu}_3\text{O}_x$  under Pressure, J.Ye, Z.Zou, A. Matsushita, K.Oka, Y.Nishihara and T.Matsumoto, Phys. Rev. B58 (1998) R619.

##### 2 Investigation on Synthesis and Characterization of Metal Complexes with High Electron-Spin Multiplicity

*H. Isago, Y. Kagaya, Md. Hasan Zahir, and S. Nakajima\*, Materials Physics Division (\* : visiting researcher from Meiji College of Pharmacy)*

[April 1997 to March 2000]

Fabrication of molecular devices, where one molecule functions as one device, is one of the most challenging projects in current and future science. In a number of biological systems, such as enzymes, which can be considered as well-designed molecular devices, unusual electronic structures have often been observed in their reaction centers where some metal ions play an important role. In recent years, phthalocyanines and their metal compounds (MPcs), which are industrially important organic dyes, have attracted much attention in the field of electronics, nonlinear optics, and photosensitization in electron-transfer reaction. They are also of interest from the viewpoint of the similarity in their molecular and electronic structures to those of reaction centers of enzymes.

We have studied some MPcs as candidates for such materials. Quite recently, we have isolated

antimony (V)-phthalocyanine complex with unusual spectroscopic and electrochemical properties, which might be versatile in the field of non-linear optics, fuel cells, and so on. We have also studied spectroscopic properties of its one-electron-reduced species and have concluded that its ground state was orbitally doubly degenerate unlike the other known MPCs. Electrochemical investigations further supported this conclusion and even suggested that the ground state of its doubly reduced species might be a triplet; if this is true, this species could be a unit of a new type of molecular magnets which can be applied to magneto-optical devices. The latter suggestion, however, could not be confirmed due to chemical instability of the doubly reduced species. Efforts are being made in our laboratory to stabilize doubly reduced species of this type of complexes. Our main purposes in this project are to make compounds, which generate chemically stable, doubly reduced species and to verify the above speculations.

This research is being performed in collaboration with Meiji College of Pharmacy.

**Keywords ;** phthalocyanine, antimony, electrochemistry, spectroscopy, spin-multiplicity

### Recent Publications

Facile Reduction of Dichloro (phthalocyaninato) antimony (V) Cation, Y. Kagaya and H. Isago, *Chem. Lett.*, 1994: 1957-1960.

Spectroscopic Properties of One-Electron-Reduced-Species of Dichloro (phthalocyaninato) antimony (V) Cation, H. Isago and Y. Kagaya, *Bull. Chem. Soc. Jpn.*, 69 (1996): 1281-1288

Synthesis and NMR studies of a Single Isomer of an Alkynyl Substituted Binuclear Phthalocyanine, H. Isago, D.S. Terekhov, and C.C. Leznoff, *J. Porphyrins and Phthalocyanines*, 1 (1997): 135-140.

Synthesis of Dichloro (phthalocyaninato) antimony (V) Perchlorate, Tetrafluoroborate, and Hexafluorophosphate and Electrochemical Reinvestigation on the New Complex Salts, Y. Kagaya and H. Isago, *Bull. Chem. Soc. Jpn.*, 70 (1997): 2179-2185.

Aggregation Effects on Electrochemical and Spectroelectrochemical Properties of [2,3,9,10,16,17,23,24-Octa (3,3-dimethyl-1-butynyl) phthalocyaninato] cobalt (II) Complex, H. Isago, C. C. Leznoff, M.F. Ryan, R. Davids, A.B.P. Lever, *Bull. Chem. Soc. Jpn.*, 71 (1998): 1039-1047.

### 3 Study on the Improvement of Analytical Technologies for Metallic Materials

*T. Kobayashi, K. Sato, T. Kimura, K. Takahashi, M. Kiyokawa, T. Yoshioka, K. Honma, Y. Na-*

*kamura, K. Yamada, K. Ogawa, S. Itoh, K. Ide, S. Hasegawa, H. Yamaguchi, Y. Hasegawa, M. Koori, S. Suzuki, T. Ohkoshi, Materials Physics Division [April 1997 to March 2000]*

Systematic study on the improvement of various kinds of analytical technologies has been carried out to promote the research and development of new metallic materials. The aim of this study is to increase the adaptable range of samples and elements, and also to improve the detection limits and precision in the instrumental analytical methods.

#### (1) Direct Analyses

① For the glow discharge mass spectrometry (GD-MS), the study on the effects of preliminary discharge and pretreatment of sample surface on the relative sensitivity factors (RSF) of N and O has been carried out. Accurate analyses of nitrogen and oxygen will be possible by using the RSF.

② In order to determine trace amounts of each analyte in metallic materials by using the graphite furnace atomic absorption spectrometry (GF-AAS), direct atomization of the sample solution prepared only by the acid decomposition has been applied.

#### (2) Separation Analyses

① The inductively coupled plasma mass spectrometry (ICP-MS) has been applied after extracting by micellar liquid chromatography.

② High sensitive simultaneous determination procedure of trace impurity elements in high purity metallic materials has been established by using the inductively coupled plasma atomic emission spectrometry (ICP-AES).

③ In order to utilize the high sensitivity and the rapidity of the total reflection X-ray fluorescence spectrometry (TR-XRF) in the analyses of solution samples, the mounting method of solution samples on a silicon wafer has been applied.

#### (3) Microarea Analyses

① In order to reveal the segregation of small amount of each analyte in metallic materials a technique of computer-image processing has been applied to improve the resolution of concentration in the electron-probe microanalyzer (EPMA) X-ray images.

**Keywords :** GD-MS, GF-AAS, ICP-AES, ICP-MS, TR-XRF, EPMA, HRTEM

### Recent Publications

1) Evaluation of Electrothermal Vaporization, Emission Intensity-Time Wavelength Measurement and Time Resolution Combined with an Axially Viewed Horizontal inductively coupled Plasma Using an Echelle Spectrometer With Wavelength Modulation, Y. Nakamura, K. Ta-

kahashi, O. Kujirai and H. Okochi : J. Anal. At. Spectrom., 12 (1997), 349.

- 2) HREM Observations of Continuously Changing Intermediate Structures between f.c.c. and b.c.c. at the Austenite-Martensite Interface, K. Ogawa, T. Kikuchi and S. Kajiwara : J. PHYS. IV FRANCE 7 (1997) Colloque C5, Supplement au Journal de Physique III de novembre 1997
- 3) Phase Equilibria in the Tial-rich Portion of Ti-Al-Sb System at 1373 and 1573K, T. Kimura, H. Doi, K. Hashimoto, E. Abe and Y. Isobe : J. Japan Inst. Metals, 61 (1997), 385.

#### 4 Improvement of the Accuracy of Inductively Coupled Plasma-Mass Spectrometry through Sample Preparation and Isotope Dilution Analysis

*K. Sato, K. Ide, M. Kohri and R. Hasegawa*  
*Materials Physics Division*

[April 1997 to March 2001]

The study has been promoted to establish a primary analytical method to determine more accurately the trace elements in iron and steel standard samples. In order to do smoothly the production and business transaction of iron and steel materials, the international standardization of the chemical analysis methods is important. While, the establishment of the primary analytical methods, that is traceable to the SI unit "mol", is desired from the standpoint of the metrology of amount-of-substance. The combination of the isotope dilution (ID) and the inductively coupled plasma-mass spectrometry (ICP-MS) were selected as a primary analytical method. In this fiscal year, the preparation of analytical solutions by making use of microwave and the determination of trace lead by ID/ICP-MS were studied.

##### 1. Sample preparation

In the determination of trace elements in iron and steel standard samples, the first step is the preparation of a sample solution to be analyzed. A sample solution for ICP-MS is usually prepared by dissolving the sample in mineral acids such as hydrochloric acid, nitric acid, hydrofluoric acid and so on. However, some kinds of the iron and steel standard samples contain acid-insoluble inclusions, i.e., aluminum oxide, chromium oxide, silicon nitride, etc. which become residue on acid dissolution. The conventional processing of the acid-insoluble residue with flux is not only troublesome, but also a cause of increase of the background that disturbs the accurate determination. Hence, microwave assisted decomposition of the acid-insoluble residue has been studied using aluminum oxide, chromium

oxide, silicon nitride and a JSS iron and steel standard sample for one-element (aluminum) determination. In addition, a flow-injection system was examined as a means of the introduction of analytical solution.

① Nitric acid, hydrochloric acid and hydrofluoric acid could not significantly decompose aluminum oxide, although a difference in the recovery of aluminum measured by ICP-AES was found between the conventional processing method (1.83%) and the microwave assisted dissolution (4.60%). Then, the kind of the acid that is used to decompose the sample was changed to sulfuric acid, phosphoric acid and nitric acid. The recovery of aluminum was 38.9% for 8 hrs decomposition by the conventional procedure and 98.6% for 1 hr decomposition by microwave assisted dissolution. Thus, it was found that the microwave-assisted decomposition is effective to dissolve aluminum oxide depending on the kinds of acid.

A sample of chromium oxide was dissolved in sulfuric acid, hydrofluoric acid, perchloric acid, hydrochloric acid and nitric acid. The recovery of aluminum was 95.8% for 8 hrs decomposition by the conventional procedure and 97.1% for 1 hr decomposition by microwave assisted dissolution. Both procedures were effective and significant difference was not found between them.

② Microwave assisted decomposition was applied to the dissolution of silicon nitride samples (ESPI, TS-7). Analytical values of trace impurities in the solution agreed relatively well with those of the sample solution prepared by the conventional high-pressure dissolution in a PTFE vessel. However, the analytical values of Mg, Mo and W were slightly lower than those obtained from the sample solution prepared by alkali fusion. The time required for the microwave assisted decomposition was 1 hr at 250 °C. While, the decomposition time of conventional high-pressure decomposition was 20 hrs at 150 °C. Namely, the decomposition time was shortened to 1/20.

③ A JSS 332-3 [certified value of aluminum : 0.049<sub>2</sub>% (m/m)] standard steel sample for aluminum determination was provided to microwave assisted decomposition. The amount of residue decreased to 1/6~1/8 in comparison with the case of the conventional acid decomposition, but the complete dissolution was difficult. The same result was obtained for alloy steels. However, the influence on the certified values of aluminum is considered negligible, since the amount of residue is very small for these samples.

④ Using nitric acid, the influence of the acid concentration on the recovery of analyte was studied. For nitric acid of below 1.0M, the recoveries of various analytes were more than 95%. Subsequently,

the influence of the concentration of nitric acid could be disregarded. However, when the acid was hydrochloric acid, sulfuric acid, perchloric acid or hydrofluoric acid, the recovery lowered in the acid concentration above 0.5M. Accordingly, it is necessary to adjust the acid concentration to a value less than 0.5M.

⑤ As a means of sample introduction to ICP-mass spectrometer, flow injection system was studied. Injection volume of the sample solution was reduced to one-tenth in comparison with the volume required for the conventional spectrum measuring method. Consequently, it has become possible to reduce the interference caused by matrix. The observed values of relative standard deviation were less than 3% for the analytes from Li to Tl.

## 2. Determination by ID/ICP-MS

In general, isotope dilution uses a spike in which a particular isotope of the analyte was enriched. After the spike is added to the sample solution, the isotopic composition is measured and the amount of analyte is evaluated from the deviation of isotopic composition from the natural abundance. Therefore, the isotopic dilution analysis does not need the standard samples that are indispensable in the usual instrumental analysis. Determination of lead in the JSS CRM of high-purity iron, JSS 001-4 [certified value of lead: 0.2 ppm (m/m)] was carried out according to the analytical procedure given by the protocol of CCQM (the international committee of amount-of-substance). The observed value was  $0.20 \pm 0.10 \mu\text{g g}^{-1}$ , which was in good agreement with the analytical value of  $0.19 \pm 0.10 \mu\text{g g}^{-1}$  proposed by the analytical laboratory of the National Institute of Materials and Chemical Research (NIMC).

**Keywords:** ICP-MS, microwave-assisted decomposition, acid-insoluble residue, isotope dilution, lead in high-purity iron.

## 5 Composition, Temperature and Pressure-Induced Structural Changes and Physical Properties of Materials

*T. Hirata Metal Physics Div., 1st Study*  
[April 1998 to March 2001]

With changes in composition, temperature and pressure, materials undergo structural changes which dominate their physical and electronic properties as well. The research subject is composed of the following topics.

1. Octahedral distortion: we look into the distortion of octahedron  $\text{MO}_6$  in metal oxides upon replacement of the central ion in  $\text{MO}_6$  with another

cations. This is substantiated by determining bond-lengths and bond-angles to understand their anisotropic physical properties.

2. Dynamics of atoms in phase transitions: the temperature or pressure dependence of optical phonons is measured for the materials that exhibit any structural phase transition (s), in order to understand their mechanism focusing on atomic displacements.

3. Chemical pressure effect: it intrigues us to see if the chemical pressure exerts a similar effect upon application of the external pressure. This can be assessed by testing if the mode Grüneisen parameters obtained from the pressure dependence of optic phonon frequencies could reproduce the mode frequency changes upon doping.

4. Infrared/Raman spectroscopy of Si, Ge and  $\text{Si}_{1-x}\text{Ge}_x$ : we study vibrational properties of Si, Ge and  $\text{Si}_{1-x}\text{Ge}_x$  incorporated with some interstitials.

**Keywords:** octahedral distortion, phase transitions, chemical pressure, Infrared/Raman spectroscopy

## Recent Publications

Pressure, temperature and concentration dependences of phonon frequency with variable Grüneisen parameter: fits to the Raman-active  $E_g$  mode in  $\text{TiO}_2$  and  $\text{Ti}_{1-x}\text{Zr}_x\text{O}_2$  ( $x \ll 0.1$ ), T. Hirata, *phys. stat. sol. (b)*, 209, (1998) 17.

Oxygen concentration dependence of Raman active phonons with variable Grüneisen parameter in  $\text{YBa}_2\text{Cu}_3\text{O}_x$ , T. Hirata, *Physica B*. 263-264 (1999) 822.

## 6 Two Dimensional Photoelectron Spectroscopic Studies on Surface Structures and Properties

*M. Shimoda, Materials Physics Division*  
[April 1995 to March 1997]

The sulfur (S)-terminated GaAs (001) surface is a fundamental stage for droplet epitaxy, which is a potential technique to fabricate nano-scale structures on the GaAs surface. For developing this technique, correct knowledge of the structure and stoichiometry of this surface is essential. So far, STM studies have revealed that a (2x6) reconstruction is dominant and that the adsorbed S atoms form S-S dimers. In the present work, X-ray photoelectron diffraction (XPD) and Auger electron diffraction (AED) studies have been performed to investigate the surface structure and coverage of the S layer [1,2]. No forward scattering peak is found in the XPD image of S 2s core-level photoemission, indicating that adsorbed S atoms form a single layer. Comparing

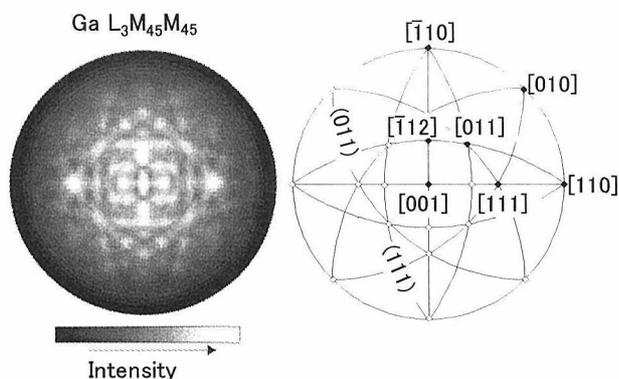


Fig. A Ga LMM AED image (left) with corresponding crystal axes and planes (right).

AED images of Ga and As LMM Auger electron with simulated images using a single scattering cluster model, the S-S bond length and interlayer distance between the S and Ga layer are determined [1]. Comparison of these images with each other reveals that a small amount of As remains after the initial S-treatment and that the residual As disappears by the second S-treatment. This result explains the reason why the S-treatment must be repeated to obtain more homogeneous and clean (2x6) reconstruction.

[1] Photoelectron and Auger Electron Diffraction Studies of a Sulfur-Terminated GaAs (001)-(2x6) Surface, M. Shimoda, S. Tsukamoto and N. Koguchi, *Surface Science* 395 (1998): 75.

[2] Coverage analysis of a sulfur-terminated GaAs (001)-(2x6) surface: the effect of double sulfur-treatment, M. Shimoda, S. Tsukamoto and N. Koguchi, *Surface Science* 402-404 (1998): 669.

**Keywords:** photoelectron diffraction, Auger electron diffraction, GaAs, sulfur-termination

## 7 Investigation on the Degenerate Electronic Ground State and Electronic Transitions of Metal Complexes with High Symmetry

*H. Isago, Y. Kagaya, and Md. Hasan Zahir, Materials Physics Division*  
[April 1998 to March 1999]

Fabrication of molecular devices, where one molecule functions as one device, is one of the most challenging projects in current and future science. In a number of biological systems, such as enzymes, which can be considered as well-designed molecular devices, unusual electronic structures have often been observed in their reaction centers where some metal ions play an important role. In recent years, phthalocyanines and their metal compounds (MPcs),

which are industrially important organic dyes, have attracted much attention in the field of electronics, nonlinear optics, and photosensitization in electron-transfer reaction. They are also of interest from the viewpoint of the similarity in their molecular and electronic structures to those of reaction centers of enzymes.

We have studied some MPcs as candidates for such materials. Although a typical MPc has a 4-fold axis and is highly symmetrical, it has been believed that its symmetry lowers upon Pc-ring reduction due to a significant Jahn-Teller effect (it is well known that the lowest unoccupied molecular orbital is doubly degenerate). Quite recently, we have isolated antimony (V)-phthalocyanine complex with unusual spectroscopic and electrochemical properties, which might be versatile in the field of non-linear optics, fuel cells, and so on. We have also studied spectroscopic properties of its one-electron reduced species and have suggested that its ground state was orbitally doubly degenerate unlike the other known MPcs. Electrochemical investigations further supported this conclusion and even suggested that the ground state of its doubly reduced species might be a triplet; if this is true, this species could be a unit of a new type of molecular magnets which can be applied to magneto-optical devices.

This project is being conducted in order to confirm experimentally the degeneracy of the electronic ground state, mainly based on spectroscopy at low temperatures.

**Keywords:** phthalocyanine, antimony, spectroscopy, orbital degeneracy

## Recent Publications

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Spectroscopic Properties of One-Electron-Reduced-Species of Dichloro (phthalocyaninato) antimony (V) Cation, H. Isago and Y. Kagaya, *Bull. Chem. Soc. Jpn.*, 69 (1996): 1281-1288.

Synthesis of Dichloro (phthalocyaninato) antimony (V) Perchlorate, Tetrafluoroborate, and Hexafluorophosphate and Electrochemical Reinvestigation on the New Complex Salts, Y. Kagaya and H. Isago, *Bull. Chem. Soc. Jpn.*, 70 (1997): 2179-2185.

## 8 X-ray Diffraction Study under High Pressure and Low Temperature Using Diamond Anvil Cell

*Jie Tang, Akiyuki Matsushita Material Physics Division*

It is very difficult to carry out the high pressure X-ray diffraction measurements because a typical sample diameter is only in the order of 100  $\mu\text{m}$ . Especially, for the case of that we put the sample in the diamond anvil cell (DAC) into a cryostat to cool the sample to low temperature, the X-ray beam has to go through two oppositely-facing diamonds. In this study, we put the DAC into an air-condition cryostat to cool the sample and did the powder X-ray diffraction experiments with an intense Mo rotor target as a X-ray source and collected the diffraction data with an image-plate detector by the angle-dispersive method.

With this system we studied the structure change in the spinel compound  $\text{CuIr}_2\text{Se}_4$ . In this compound an anomalous behavior that the electrical resistivity increases with increasing pressure has been reported. We found that this behavior is owing to a pressure-induced phase transition. High-resolution diffraction data with well behaved line shape and a wide dynamic range is essential for a successful structural analysis of powder samples, especially for  $\text{CuIr}_2\text{Se}_4$  sample with a large mass absorption coefficient.

**Keywords:** high pressure, low temperature, X-ray diffraction, structure change

## 9 Evaluation of Structures with Trace Element Analysis

*M. Fukumachi Materials Physics Division*  
[April 1998 to March 2000]

An application of trace-element analysis to the identification of compounds has been studied in this research project. Usually, precise measurements of concentrations on several elements are necessary to identify chemical compounds. Natural ores and materials produced with practical purposes contain trace elements with concentration less than 1 wt % as impurities. It seems easier to identify materials with the analysis of these trace elements. Because qualitative or semi-quantitative analysis of only one or two kinds of elements can be expected to give satisfactory results for the identification of materials.

The feasibility to use X-ray images of EPMA for this purpose has been studied with a numerical simulation method on the spatial resolution and on the precision of measurement of concentration. The trace-element analysis is expected to give a new simple-rapid-precise method for the identification and for the formation of map of metallurgical structures.

**Keywords:** trace-element analysis of metallurgical

structures, EPMA, computer image analysis of X-ray image

## Physical Properties Division

### 10 Spectroscopic Study of Low Dimensional System in High Magnetic Fields

*G. Kido, T. Takamasu, H. Kitazawa, K. Takehana, M. Oshikiri, H. Suzuki and Y. Imanaka*  
[April 1997 to March 1998]

For the study of low dimensional systems such as low dimensional magnetic materials and two dimensional electrons in the interface of semiconductors, we developed several optical measurement systems which can be used in the combination with a variety of magnets installed in High Magnetic Field Research Station of NRIM. Using these optical measurement systems, we performed spectroscopic study of low dimensional materials together with transport measurements, magnetostriction measurements and magnetization measurements.

In the region of far-infrared and millimeter-wave magneto-optical measurements, energy shift of phonons and cyclotron resonance of semiconductors are interesting objects to study in high magnetic fields. We have constructed measurement system for this frequency region using the FT-spectrometer (BOMEM DA-8) which covers wide spectral range from  $10\text{cm}^{-1}$  to  $50000\text{cm}^{-1}$ . Lamellar grating interferometer is also constructed to study the lower frequency range from  $40\text{cm}^{-1}$  down to  $3\text{cm}^{-1}$ . On the other hand, for the study of interband spectroscopy of semiconductors, measurements in the region of visible and near infrared light are needed. We can use the FT-spectrometer also in these regions, however, a newly constructed CCD camera system, which enables us to obtain magnetic field dependence of spectrum in a single shot of pulsed magnetic field, is mainly used in the recent experiments. Using these measurement systems, we have obtained many new results on magneto-optical study.

One of our new results in the far infrared region is about the one dimensional  $S=1/2$  antiferromagnet  $\text{CuGeO}_3$ , the first inorganic spin-Peierls material in which two neighboring spins are dimerized alternately below a critical temperature  $T=14\text{K}$ . We have found a new folded phonon mode at  $98\text{cm}^{-1}$  in the dimerized (D) phase and clarify its  $E//a$ -axis polarization property using a rotational grid polarizer. Furthermore, this folded phonon was found to be split into two components when the phase transition was occurred into the incommensu-

rate (IC) phase under high magnetic field above 12 T. With the polarization measurements, the absorption at  $312\text{cm}^{-1}$ , whose origin had been uncertain, was also made clear to be caused by a folded phonon. On the other hand, the absorption line at  $44\text{cm}^{-1}$ , was found to have strange polarization property and it is not straightforward to be explained as a magnetic excitation at  $\Gamma$  point in the reciprocal lattice.

As a low dimensional free electron system, we have intensively studied two dimensional electron gas in the interface of semiconductor heterostructure. In the GaAs/AlGaAs heterostructures, two dimensional electrons have very high mobility at low temperature and it shows variety of unique phenomena such as integer and fractional quantum Hall effects. Many researchers have been studying the low energy excitation property around Fermi energy of these phenomena by means of transport measurements. We have performed a combined measurement of optical and transport technique using CCD camera at low temperature  $T=400\text{mK}$ ; namely, current dependence of photoluminescence was measured. As shown in the figure, two dimensional electron system shows several photoluminescence peaks of electron-hole, electron-acceptor recombination. When the current is applied through the sample in the integer quantum Hall region, an additional peak (indicated by an arrow) appears and increases its intensity with increasing current. Current dependence of peak intensity (in the inset of the figure) shows nonlinear effect, suggesting that this peak is induced by the rise of electron temperature similar to the effect of current-induced breakdown of quantum Hall effect.

Concerning to the magneto-optical measurements of semiconductors, the quantum effect on the cyclotron resonance experiments is one of the most interesting objects. However such measurements have been limited to the electrons in GaAs/AlGaAs heterostructures, recent progress of the epitaxial growth technique enables us to obtain the high quality II-VI semiconductors which show clear quantum Hall effect. Using such high quality samples, we have studied quantum cyclotron resonance in CdTe/CdMgTe heterojunction whose mobility is about  $10\text{m}^2/\text{Vs}$ . The far infrared magneto-transmission spectra were observed up to 14T. We found that a single sharp cyclotron resonance at low temperatures splits into two resonant peaks with increasing temperature. This phenomenon can be explained by the quantum effect due to the electron-electron interaction. Furthermore, at low temperatures, effective mass of electrons reduced from the frequency of the cyclotron resonance was found to oscillate conspicuously as a function of the filling

factor. The qualitative explanation can be made in terms of electron-phonon interaction, however, further study is necessary for the quantitative theoretical analysis.

**Keywords :** low dimensional, spin Peierls, Semiconductor, high magnetic field

### Recent Publications

Magnetostriction measurements of CuGeO<sub>3</sub> in high magnetic fields, K. Takehana, T. Takamasu, M. Hase, G. Kido, K. Uchinokura, *Physica B* 246-247, 246-249, 1998

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Interband spectroscopy of p-type GaAs/(Al, Ga) As quantum wells at low hole densities, B.E. Cole, T. Takamasu, T. Takehana, R. Goldhahn, D. Schulze, G. Kido, J.M. Chamberlain, G. Gobsch, M. Henini, G. Hill, *Physica B*, 249-251 (1998) 607-611

### 11 Study on the unusual metallic state and electronic structure of magnetic materials

*H. Kitazawa and H. Suzuki, Physical Properties Division T. Matsumoto and N. Kato, Computational Materials Science Division [April 1998 to March 2001]*

The discovery of high  $T_c$  superconductive cuprates has stimulated much interest on the physics and chemistry of various compounds, such as ternary rare-earth transition-element oxides, chalcogenides and so forth. The materials exhibit a lot of interesting phenomena, such as superconductivity, colossal magnetoresistance, metal-insulator transition, charge density wave, spin density wave, charge ordering etc. The unusual properties are mainly explained by the electron correlation, hybridization with the ligands, and the low-dimensional effect. However, there is no exact consensus about the correct mechanisms.

One of the interesting problems of these materials is that the electronic state differs from the normal Fermi liquid. It is obvious that the anomalous metallic state should be originated from the electronic structure and the elementary excitations, in which the electron correlation plays an important role. So far, much work has been focused on the 3d transition-element oxides, while 4d or 5d transition-element compounds have not been paid much attention. This is due to what the electron correlation is relatively weak in the latter compounds. However,

the correlation strength can be altered by means of the constituent of the compounds, their structure and the applied conditions.

The spinel-type transition-metal chalcogenides show various properties, such as superconducting, ferromagnetic, and so on. The recent study on  $\text{CuIr}_2\text{S}_4$  and  $\text{CuIr}_2\text{Se}_4$  in which 5d transition element contributes mainly to the electronic conduction established that the non-metallic state becomes stable even at high pressure. In order to clarify the origin of the unusual behavior, we should perform detailed experimental research, such as structure and physical properties in high magnetic field. In addition, the systematic element-substitution study is also necessary.

**Keywords :** metal-insulator transition, electron correlation, 5d transition element, chalcogenides

## 12 Studies on the Highly Correlated Electron Systems under Multiple Extreme Conditions

*H. Aoki, 4th Research Group and Tsukuba Magnet Laboratories*

We have developed several types of high field magnets, such as a hybrid magnet, in the preceding project. The capabilities of the developed magnets are proved to be of the highest class in the world. The purpose of this project is to develop several types of high precision detection systems under low temperatures and high pressures for the high field magnets and is to apply them to the study of the highly correlated electron systems.

### (1) Developments

(a) We have developed a detection system of quantum oscillations under multiple extreme conditions of magnetic fields up to 20 T, temperatures down to 70 mK and pressures up to 20 kbar.

(b) Development of the nuclear double resonance spectrometer has been partly achieved with a specific feature of the wide frequency range 10-200 MHz which allows a double resonance between transition metal elements in a magnetic field up to 10 T.

### (2) Measurements

(a) The detection system under the multiple extreme conditions has been applied to the dHvA effect study of highly correlated f electron systems such as  $\text{CeSb}$ ,  $\text{CeB}_6$ ,  $\text{CeRu}_2\text{Ge}_2$ ,  $\text{CeRu}_2\text{Si}_2$  and  $\text{CeCo}_2$ . Unconventional pressure effects on the Fermi surface properties of these materials have been uncovered for the first time.

(b) NMR investigations on Cu oxide superconductors found that both the inter-chain and inter-plane susceptibilities have an effect suppressing the

total spin fluctuations at low temperatures, which shows that the dimension of the Cu spin system play a important role in the formation of the spin gap states.

(c) Spin echo nuclear double resonance measurement on anomalous metallic compound Rb-Cu sulfide revealed a microscopic evidence to show that a CDW state is formed in the anomalous metallic phase and that the conductivity is caused by spin-less solitons along the CDW.

**Keywords :** high magnetic field, low temperature, high pressure, highly correlated electron system

## Computation Materials Science Division

### 13 Development of Knowledge Database for High-Tc Superconducting Materials

*Y. Asada, Computational Material Science Division*  
[April 1995 to March 2000]

We have developed numerical database for high-Tc oxide superconductors. All the data in it are extracted from the papers reported in journals. The system has been improved for [www-usage](http://www-usage.nrim.go.jp). The home page address is "<http://asagiri.nrim.go.jp>". We have also developed database of standardized data (our original data) for typical high-Tc cuprate superconductors. One can access to the database through the home page mentioned above.

The papers contain many useful information as well as numerical data. These information are written in text style in abstract, summary or conclusion. It is desirable that researchers employed in designing new products and searching new materials retrieve these information from database and apply them to their purposes.

In this project we study how to store the information and how to construct knowledgebase for high-Tc superconductors. For this purpose we introduce 'matisse' and 'REX' as a main software. These are object-oriented database management system (ODBMS). We are developing the data acquisition system with semantic network. Thesaurus, especially semantic thesaurus, dictionary is very important for this purpose.

We developed Tc-prediction system for Y123-system by using Neural Network method. Neural Network was constructed using the data obtained by retrieving from the numerical database "SUPER-CON". The system predicts that Ca in Y-site have a valuable effect for high-Tc materials and Tc is higher

than that of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> if we choose the optimal content of Ca and O.

**Keywords** : oxide Superconductors, database, knowledgebase, net work

#### Related Papers

Database Development in Assistance of New Superconducting Materials: Y. Asada, E. Nakada: J. Jpn.Soc.Information and Knowledge (in Japanese), 5 (1995) 57.

Prediction of T<sub>c</sub> for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>z</sub> Doped with Ca Using Neural Network, Y. Asada, E. Nakada, S. Matsumoto, H. Uesaka, J. Superconductivity 10 (1997) 23-26.

### 14 Theory of Thermal Reaction on Solid Surfaces

*T. Ohno, Computational Materials Science Division*  
[April 1994 to March 2000]

The thermal reactions on solid surfaces play important roles in various surface processes including epitaxial growth, etching, and catalysis. The purpose of this work is to clarify theoretically the thermal reaction processes on several solid surface systems such as semiconductor surfaces and metal surfaces. The analysis is based on the density-functional electronic theory within local-density approximation, which provides a powerful tool to determine the dynamical behavior as well as the stable atomic arrangement of solid surfaces.

The optimum atomic arrangement of the Ga-rich GaAs (001)-(4x2) reconstructed surface has been theoretically investigated. It is shown that the Ga-rich GaAs (001) surface consists of two Ga dimers on the top layer and another Ga dimer at the third layer and that the simulated images of scanning tunneling microscopy are in good agreement with the observed ones.

The interaction of chlorine molecules with the reconstructed GaAs (001) surfaces has been examined. Chlorine is one of the most important halogens used in the semiconductor etching processes. The stable geometries of the GaAs (001) surfaces chlorinated by chlorine molecules have been determined theoretically, which are consistent with recent temperature programmed desorption measurements.

Recently, the Si adsorption on the monohydride terminated Si (001)-(2x1) surface has been theoretically investigated by using first-principles total-energy calculation techniques. We find that the Si adatom spontaneously segregates one H atom from a surface Si dimer during adsorption, and further

captures the remaining H atom of the same Si dimer during surface migration, leading to the most stable adsorption geometry. The migration of the Si adatom is assisted by the mobility of H atoms, being reduced compared with that on the bare Si surface. The reduction of the Si diffusion may have disruptive effects on the Si homoepitaxy.

**Keywords** : structural stability, chemisorption, reaction, solid surface

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Theory of Adsorption of Cl<sub>2</sub> Molecules on GaAs (001) Surfaces, T. Ohno, Surf. Sci. 357/358 (1996) : 322-326.

Adsorption and Diffusion of Si Atoms on the H-Terminated Si (001) Surface: Si Migration Assisted by H Mobility, J. Nara, T. Sasaki, and T. Ohno, Phys. Rev. Lett. 79 (1997) : 4421-4424.

### 15 Theoretical Study on the atomic motions on surfaces

*T. Sasaki, T. Ohno, T. Miyazaki, J. Nara, K. Kusunoki and X. Hu Computational Materials Science Division*  
[April 1996 to March 1998]

The atomic motion on material surfaces is a key to understand the fundamental processes which characterize the surface phenomena, such as corrosion, catalytic reactions and so on. In this study, we utilize one of the state-of-the-art computational materials science methods, the first-principles electronic structure calculation, to investigate the atomic motions on the surfaces of metals and semiconductors theoretically and to provide a chance to obtain a new idea toward the atomic control of the surface properties. We performed the calculations for the O<sub>2</sub>/Al (111) surface and the Cl/GaAs (001) surface. The former case is expected to elucidate the initial stage of the oxidation of metals. In the latter system, Cl is known as one of typical materials which are widely used in GaAs etching. The present study on this system is aimed to clarify the behavior of Cl atoms in the surface region, especially, subsurface region.

The calculation methods in the present study are mainly based on the density-functional theory and

the pseudopotential method, which are promising high reliability in its result for a wide range of materials. Generally, such a numerical electronic structure calculation for the surface requires large computation time. Thanks to the Numerical Materials Simulator installed in NRIM, NEC SX-4 and IBM SP2, we could obtain the results with high accuracy.

Little is known about the oxidization processes of the Al (111) surface, experimentally. Our study unveiled the physics of the initial stage of the oxidization, the dissociative adsorption of the molecule by presenting the potential energy surface and the electronic structures. The result exhibits that an oxygen molecule is easy to dissociate at high altitude from the surface and that this process is related not only to the electron transfer between the surface and the molecule but also to the change in the magnetic state of the molecule.

The density-functional calculations for the Cl/GaAs (001) surface have revealed a part of the etching processes: The Cl atom which is located at the subsurface region interacts strongly with the surrounding host crystal and is pushed out to the outer region breaking the covalent bonds of the host crystal. The analysis has indicated that it is due to the electrostatic forces originated in the electron transfer from the surface to the Cl impurity atom.

In this project, we also performed the electronic structure calculations for systems other than surfaces to examine the validity of the theory and the efficiency of the calculation techniques.

**Keywords:** surface, oxidation, etching, electronic structure, density-functional theory, first-principles calculation

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322.

## 16 Thermodynamic Analysis of Formation Processes of Metastable and Stable Phases

*H. Onodera, M. Ohnuma, M. Shimono, T. Abe and G. Tu, Computational Materials Science Division*

[April 1997 to March 2000]

A wide range of microstructural control can be realized through metastable structures using the transition process from amorphous state to crystalline state. For the effective utilization of these metastable phases to improve mechanical properties of materials, it is necessary to reveal the transition process from metastable to stable phases on the heat treatment. The target of this study is to make clear the formation process and the microstructure of metastable phases and the transition process from metastable to stable phases by experimental observations and molecular dynamics simulations.

A nanocrystalline Fe-Si-B-Nb-Cu alloy, known as FINEMET, is a very fascinating soft magnetic material exhibiting excellent permeability while maintaining a high saturation magnetization. This material is prepared by annealing a melt-spun Fe<sub>73.5</sub>Si<sub>13.5</sub>B<sub>9</sub>Nb<sub>3</sub>Cu<sub>1</sub> amorphous ribbon at the temperature range of 520-580 C. Hono et al. have reported formations of Cu-enriched clusters prior to the onset of the crystallization reaction based on the atom probe field ion microscopy (APFIM). The target of this paper is to clarify the spatial distribution and the size of Cu-enriched clusters by three dimensional atom probe (3DAP) analysis and small-angle neutron scattering (SANS) in the annealing process before the crystallization of the Fe-Si-B-Nb-Cu amorphous alloys. Cu clustering occurs prior to the onset of the primary crystallization reaction. The number of the clusters estimated by 3DAP is large enough to provide heterogeneous nucleation sites to all bcc/DO<sub>3</sub> Fe-Si crystals which appear at higher temperatures. This fact indicates that the distribution of nanocrystalline Fe-Si is strongly affected by that of the Cu-enriched clusters. The average diameter and interparticle distance of the Cu-enriched clusters estimated by SANS are about 1.8 nm and 6 nm, respectively.

In the previous study, we have found the formation of metastable  $\alpha$  phase in preference to the stable  $\gamma$  phase in the crystallization process of amorphous Ti-Al alloys. Furthermore, small-angle X-ray scattering profiles of amorphous Ti-60at%Al alloy suggested the existence of concentration and/or density fluctuations in the sample. The formation of the unknown phase is considered to be closely related to

these fluctuations. Thus, in the present study, the transition process of sputter deposited Ti-Al amorphous alloy is studied by molecular dynamics simulations in view of the correlation between the nucleation site of crystalline phase and the structural and/or compositional fluctuation in the amorphous structure for the understanding of the transition mechanism in the atomistic scale. Liquid-to-amorphous transition and amorphous-to-crystal transition process of Ti-Al alloys are investigated by using constant-pressure, constant-temperature molecular dynamics techniques. Many-body interactions semi-empirically determined by Embedded Atom Method are used. Thermodynamic properties obtained in the simulations are in good agreement with experimental measurements. Especially, the present simulation can reproduce the experimentally observed concentration range of 40-85 at% Al for amorphous formation. Structure analyses have revealed that amorphous Ti-Al alloys formed by rapid cooling consist of three regions, the region having crystalline configuration of atoms, the region having an icosahedral configuration and the more disordered region having relatively large free volume. These three regions form medium-range structures of nanometer scale which seem to be closely correlated with the structural and/or compositional fluctuation in the amorphous structure. From the analysis on vibrational spectra of amorphous alloys, it is found that the more disordered regions are responsible for an excess density of low-frequency motions, the so-called boson peak which is a characteristic feature of the amorphous state. The reduction of boson peak height during structural relaxation and crystallization can be attributed to the reduction of the more disordered region.

**Keywords :** metastable structures, transition process, Fe-Si-B-Nb-Cu alloy, Ti-Al alloys, small-angle neutron scattering, Cu-enriched clusters, molecular dynamics simulations, medium-range structures, boson peak

**Related Papers :**

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Ti-52at%Al Alloy, M. Ohnuma, T. Abe and H. Onodera, MRS Symposium Proc. Series, Vol.400 (1996) : 209-214.

Molecular Dynamics Study on Liquid-to-Amorphous Transition in Ti-Al Alloys, M. Shimono and H. Onodera, Materials Trans., JIM, Vol. 39 (1998) : 147-153.

**17 Improvement of the Long Term Creep Strength of Ferritic Steels by the Minimum Alloying**

*H. Onodera, T. Abe and M. Ohnuma, Computational Materials Science Division*

*K. Kimura, Materials Creation Research Station*

*H. Kushima, Strength and Life Evaluation Research Station*

*K. Yagi, 2nd Research Group*

[April 1996 to March 1998]

The long term creep strength is one of important mechanical properties for the heat resistant ferritic steels in a power generator. The creep strength of ferritic steels converges to the constant inherent creep strength after a long time exposure by losing effects of precipitation strengthening, work hardening and so on, and the inherent strength depends mainly on the minute contents of Mo and C. The present authors have found a good correlation between the long term creep strength of carbon steels and the concentrations of Mn-C and Mo-C atomic pairs in the ferrite matrix. These atomic pairs seem to reduce the climb velocity of dislocations due to their large interaction energies with dislocations, suggesting that the long term creep strength of ferritic steels is controlled by these atomic pairs. However, the contribution of each atomic pair could not be made clear quantitatively because the carbon steels used in the analysis contained Mn, Cr and Mo simultaneously as impurities. Thus, in the present study, the effect of solute element, M, on the long term creep strength of ferritic steels was studied by using ternary alloys Fe-M-C (M=Mo, Cr and Mn) of ferrite single phase in view of M-C atomic pairs. The effects of M and M-C atomic pairs on the creep strain rate is discussed in terms of the dislocation climbing velocity.

*Table 1 The effect of solute atoms on the dislocation climbing rate at 973K.*

Element	Diffusion Rate $\frac{D_{Fe}}{D_M}$	Binding Energy		Climbing Rate		Concentration	
		$\Delta E^{M-C}$ (eV)	$\Delta E^M$	$\frac{V_{Fe}}{V_{M-C}}$	$\frac{V_{Fe}}{V_M}$	M-C (atppm)	M
Mo	1.17	0.33	0.19	10.3	2.5	3.1	1050
Mn	1.22	0.26	0.11	5.4	1.7	1.1	980
Cr	0.41	0.31	0.02	1.3	0.4	2.4	1060

Fe-0.01at%C and Fe-0.1at%M-0.02at%C (M=Mo, Mn and Cr) alloys of ferrite single phase were prepared as ingots of 1kg by vacuum induction melting. Ingots were swaged to a rod with a diameter of 12 mm at 1373 K and normalized at 1193 K for 20 min. The average grain diameter was about 1.0 mm for all specimens. Constant load creep tests were carried out at 973 K under an initial stress of 10 MPa in an Ar atmosphere to avoid excessive oxidation. The concentrations of atomic pairs were estimated by the central atoms model (CAM) which can calculate the atom configurations in the nearest neighbor atom shell.

Figure 1 shows the creep rate-time curves for Fe-0.01at%C and Fe-0.1at%M-0.02at%C (M=Mo, Mn and Cr) alloys of ferrite single phase. In all alloys, the creep rate decreases with increasing creep time. The onset of tertiary creep is not clear in Fig. 1 because the test was carried out under a constant load. The rapid increase in the final stage, however, seems to be attributed to tertiary creep for each alloy. In the Fe-C alloy, the minimum creep rate of about  $3 \times 10^{-7} \text{s}^{-1}$  was obtained in a creep time range from  $4 \times 10^2$  to  $8 \times 10^3$  s. The minimum creep rate was decreased by additions of Cr, Mn and Mo to the Fe-C alloy. The magnitude of decrement increased in this order and a remarkable strengthening was obtained in the Fe-Mo-C alloy.

The effect of solute atoms on the dislocation climbing rate was examined on the basis that the climbing velocity of the dislocation is controlled by a vacancy diffusion to jogs. According to the equation derived by Sandstrom, the ratio of the dislocation climbing velocity in a pure iron alloy (Fe) to that in a Fe-M-C alloy ( $V_{M-C}$ ) depends on the ratio of diffusion coefficients ( $D_{Fe}/D_M$ ) and the interaction energy between M and C atoms. Table 1 shows the  $V_{Fe}/V_{M-C}$  value for each M-C pair at 973 K. Parameters used in the calculation are also shown in

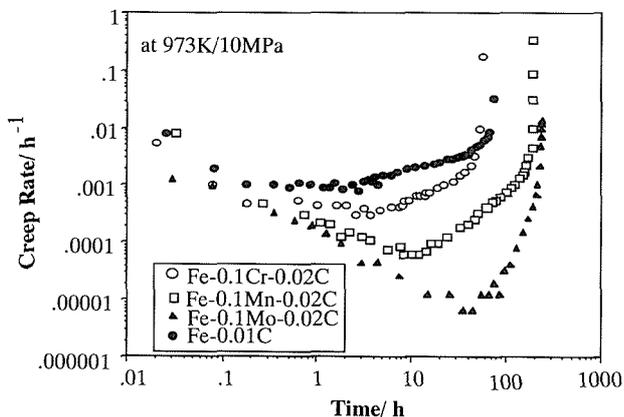


Figure 1 The creep rate-time curves for Fe-0.01at%C and Fe-0.1at%M-0.02at%C (M=Mo, Mn and Cr) alloys at 973K and 10MPa.

the table. The largest effect to reduce the climbing velocity was obtained by the Mo-C pair and the order of the magnitude by each M-C pair explains very well the effect of alloying element on the minimum creep rate in Fig. 1, while the effect of each solute element M ( $V_{Fe}/V_M$ ) is far smaller than that of M-C atomic pair. From these results, it is concluded that the minimum creep rate of Fe-M-C (M=Mo, Mn, Cr) alloys is controlled by the interaction between M-C atomic pairs and dislocations.

**Keywords:** heat resistant ferritic steels, inherent creep strength, the minimum creep rate, M-C atomic pairs, dislocation climbing velocity

#### Related Papers :

1. Effect of Minute Solute Elements in the Ferrite Matrix on the Inherent Creep Strength of Carbon Steels, H. Onodera, T. Abe, M. Ohnuma, K. Kimura, M. Fujita and C. Tanaka, *Tetsu-to-Hagane*, 81 (1995): 821-826; in Japanese.
2. Improvement of the EcoBalance of Ferritic Steels by the Minimum Alloying, T. Abe, H. Onodera, K. Kimura, K. Halada, and K. Ijima, in the Proc. of the 3rd Int. Conf. on Ecomaterials, Tsukuba, Japan, (1997): 47-50.

## 18 Molecular Dynamics Study on Superplastic Deformation and Embrittlement due to Grain Boundary Segregation

*H. Onodera and G. Tu, Computational Materials Science Division*

[April 1997 to March 2000]

The mechanical properties of materials are often limited to the cohesion of grain boundaries. Because the strength of grain boundaries is affected by the intergranular segregation of impurities, mechanical properties have been optimized by the control of segregation based on the thermodynamics. Increasing demands on mechanical properties in new technologies require a precise control of the grain boundary structure. Recently it has been reported that a minute content of sodium (Na) (less than 1atppm) can cause intergranular embrittlement in Al-Mg alloys as well as hydrogen (H) which is a well known intergranular embrittlement enhancer in aluminum (AL) alloys. Na is a simple metal which can be described by the free electron model. Thus, the target of the present study is to clarify the reason for the Na involved intergranular embrittlement by examining the effect of alkaline metals impurities such as Na and kalium (K) on the electronic structure at the grain boundary.

The DMol method which is a first-principle numerical method for solving the local density functional equations within cluster model is used to calculate the electronic structures of the clusters with and without impurity segregations. At first, a molecular dynamics simulation is performed to obtain a relaxed structure of tilt grain boundaries of pure Al by using the Finnes-Sinclair's many-body potential. The impurity atom of Na or K is placed at the point having the widest space in the relaxed grain boundary. The impurity atom and Al atoms around it form the cluster for the electronic structure calculation. From the eigenfunctions obtained self-consistently, we evaluate the overlap integrals and hence the overlap population between Al atoms and between Al and impurity atoms.

For all types of grain boundary structures,  $\Sigma 5$ ,  $\Sigma 7$  and  $\Sigma 11$ , investigated in this study, the cohesive energy becomes smaller when Na or K is placed into the cluster, indicating that the cohesion of the cluster is weakened by Na and K atoms. For evaluating the bond strength between Al atoms, we have calculated the change of the overlap populations between the Al atom nearest to the impurity atom and the other Al atoms when the impurity atom is placed into the cluster. The overlap population of Al atoms near the impurity atom decreases by Na and K impurity atoms as shown in Fig. 1. From these results we can conclude that a segregation of Na or K impurity atom to the grain boundaries of pure Al causes a redistribution of electron charge density resulting in the weakening of the bond between Al atoms.

**Keywords :** intergranular embrittlement, aluminum alloys, sodium, kalium, electronic structure, cohesive energy, overlap populations

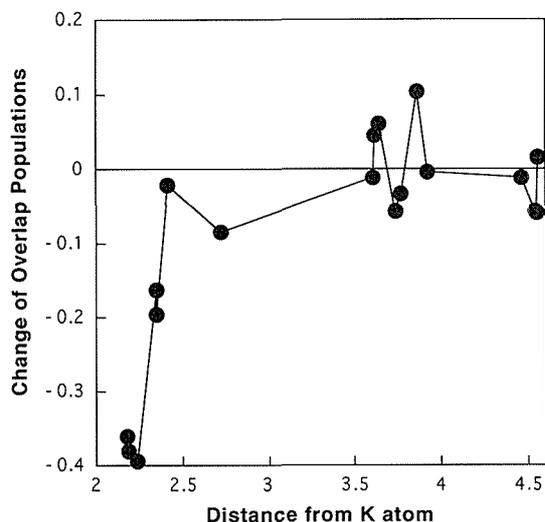


Fig.1 Change of the total overlap populations between Al atoms in a  $\Sigma 5$  tilt grain boundary due to a K impurity atom.

## Related Paper

Computer Simulation of Segregation of Alkaline Metals at the Grain Boundaries in Aluminum, G. Tu, K. Kyuno and R. Yamamoto, Proc. of Int. Workshop on Modelling and Simulation for Materials Design, Tsukuba, (1996) : 16-20.

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## 19 Development of Unification System for Distributed Materials Scientific Data utilizing Networking Environment

*M. Nihei and M. Sakamoto Computational Materials Science Division*

[Apr. 1995 to Mar. 2000]

Researches with a view of developing new evaluation technologies of materials strength through the utilization of the materials scientific databases are being conducted. The empirical systematization approach based on the combining the scientific understanding with the empirical one for material strength was successful for the development of the fatigue life prediction procedure in many heat treated structural steels, which constructs the new empirical equations related to the characterized items of materials by using the extracted data set from the factual database.

To apply this systematization approach for other materials properties and to use more efficiently other materials informations, we are developing the prototype of new unification system utilizing a networking environment and treating many different type of materials scientific database, which are located on many different sites bound with a network system such an INTERNET.

The developed system, DIMNET (now only usable in japanese version) will be soon accessible for some limited internet users through WWW browser such as NETSCAPE.

Figure illustrates the access image for this system through INTERNET.

The systematization approach using this system is also being conducted for the time-dependent creep rupture properties for heat resisted steels.

This research is being performed in collaboration with FUJI RESEARCH INSTITUTE CORPORATION.

**Keywords :** materials properties prediction,

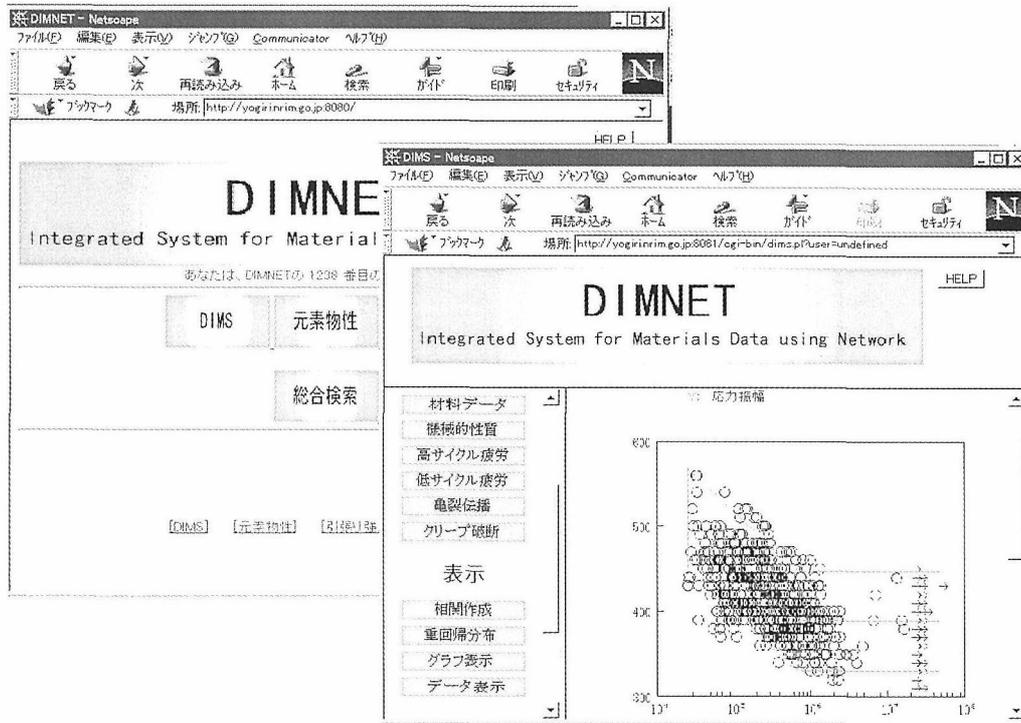


Fig. Access Image through INTERNET

database, networking

## 20 Modeling and Simulation for the Prediction of Material Strength

*M. Nihei, K. Hoshimoto and M. Sakamoto*  
Computational Material Science Division

*S. Matsuoka and K. Miyahara* The Strength and Life Evaluation Research Station

[April 1995 to March 1998]

The coordinated research program of the Science and Technology Agency (STA) to develop the virtual experimental technologies for the material design was carried out from April 1995. This research program aimed to promote the computational material science of Japan and to develop the new material design technology through the realization of a virtual experiment system. In this research program, the following three different phase of studies were conducted to develop the modeling and/or simulation method for the prediction of materials strength.

### 1. Development of nano-scopic material evaluation method

This aimed to develop the simulation method such as the nano-indentation tests using AFM of ultra-thin atomic layers applied for semi-conductors products. In this study, the calculation codes, based on the molecular dynamics and FEM respectively, were newly developed and the results calculated by

using these codes shows a good agreement with that of experiments.

### 2. Development of meso-scopic material evaluation method

This aimed to develop the meso-scopic simulation method using the continuum mechanics such as FEM and to analyze the microscopic deformation of poly-crystalline material. Figure shows the results of simulation and experiment. It was found from this figure that the strain distribution within a grain was caused by the effect of constraint from neighboring grains and that of the crystallographic orientation of each grain.

### 3. Development of virtual consulting expert system

This aimed to develop the expert system which offer a most suitable design tools for researchers and/or materials designers in the field of material design as the numerical values, texts, logical equations and calculation programs. In this study, for this purpose, some sub systems were newly developed such as the vague reference system, METIS system, which makes a summary of papers automatically and offers that to user, and KE system to translate the natural human language to the computer automatically.

**Keywords:** modeling, simulation, material evaluation, expert system

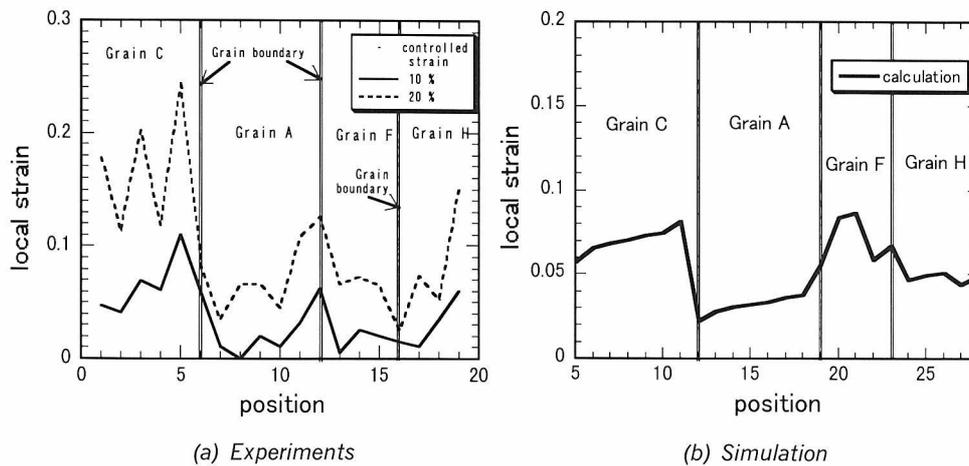
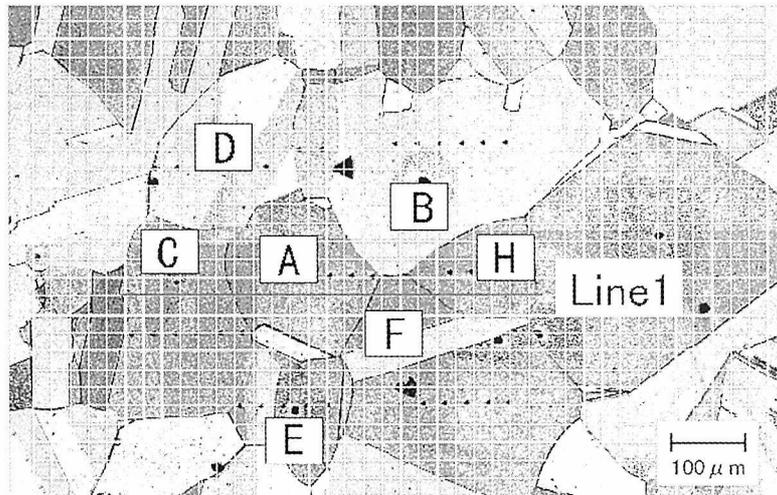


Fig. Local strain distribution (along Line 1)

## 21 A Computer-Simulation Study of the Plastic Deformation of Crystals

*K. Kusunoki, Computational Materials Science Division*

[April 1997 to March 2000]

With use of computer simulations, the present study aims to elucidate how the microscopic forces and displacements of atoms develop into a macroscopic plastic deformation. We made a simulator by which we carry out molecular-dynamics simulations of tensile tests for metals with simple crystal structures. Both the classical two-body interatomic potentials and the many-body *EAM* (embedded atom model) potentials are applied for the construction of sample crystals. Corresponding to each potential, the molecular-dynamics simulation was performed at room temperature without periodic boundary conditions. The size of the samples was  $20 \times 20 \times 40$  in units of the lattice parameter.

Tensile tests for  $\alpha$ -*Fe* single crystals, having  $\langle 001 \rangle$  axis parallel to the tensile axis, were done and the results are as follows. In case of samples without a

notch, a phase transformation from a bcc to an fcc structure took place. Although a similar phenomenon has been reported to occur for real *Li* metal with bcc structure, there is until now no report that the real  $\alpha$ -*Fe* makes such reverse-martensitic transformation under applied stress. So the present result may be attributed to the nature of the interatomic potentials or the size effect of the samples, in which the contribution of surface atoms to the total energy of the system is considered to be not negligible. In any case, definite explanation for the present result is not made at moment. We are now making preparations for tensile tests using much larger samples than the ones used in the present study. In case of specimens with a notch, plastic deformation initiated at around the notch took place. In this case the slip system was  $\{110\} \langle 111 \rangle$ . Also the notch blunting was observed. The blunting region was more noticeable for samples with larger cross sectional area.

All of the above results didn't depend on the type of the potentials used here. This suggests that the Cauchy force, which is exactly taken into consideration in the case of the many-body potential, does not change the deformation mechanism of metals with

simple crystallographical structures as used in the present study.

**Keywords :** plastic deformation, atomistic model, molecular-dynamics,  $\alpha$ -Fe

## 22 New Phenomena in Ultrathin Magnetic Films and Multilayer Systems

*X. Hu Computational Materials Division*

[April 1997 to March 2000]

The phenomenon of spin reorientation in ultrathin magnetic films is investigated. A micromagnetic theory is presented which reveals the competition between the in-plane shape anisotropy and the perpendicular surface anisotropy through a finite exchange stiffness. For small surface anisotropy, two continuous transitions in spin orientation are derived as the film thickness is increased : first from the uniform, normal configuration to a non-uniform, canting configuration, and then to the uniform, in-plane configuration. This theoretical result is in good agreement with experimental observations. For large surface anisotropy, it is derived theoretically that only the first spin reorientation occurs and the non-uniform, canting configuration remains stable even at large thickness limit. The critical value of the surface anisotropy is derived to be the square root of the product between the shape anisotropy and the exchange stiffness. From the good agreement between the scaled results of the discrete model and the results of the continuum model, it is concluded that the continuum approach is applicable to magnetic films as thin as of several atomic layers. The scaling relation is expected to provide a unified way for plotting experimental results on spin reorientation transitions in various magnetic films.

**Keywords :** ultrathin magnetic film, surface anisotropy, spin-reorientation transition, micromagnetics

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“Spin reorientation in ultrathin magnetic films with surface anisotropy”, X. Hu, *Condensed Matter News*, in press.

## Mechanical Properties Division

### 23 NRIM Long-Term Fatigue Data Sheet Project- I

*H. Irie, Mechanical Properties Division*

*S. Matsuoka, K. Yamaguchi, A. Ohta, T. Abe, K. Miyahara, N. Nagashima, H. Hirukawa, K. Kobayashi, M. Shimodaira, E. Takeuchi, T. Ohmura, M. Hayakawa, M. Kimura, N. Suzuki, H. Maeda, Strength and Life Evaluation Research Station, Frontier Research Center for Structural Materials*

*C. Masuda, Y. Tanaka, Joining and Interface Research Station, Frontier Research Center for Structural Materials*

[April 1997 to March 2002]

The project aims at the establishment of long term standard reference data on the fundamental fatigue properties of Japanese engineering materials most commonly used for machines and structures under fatigue conditions.

Since 1975, NRIM has established standard data base of conventional fatigue properties of various metals and their welded joints and published 83 data

sheets and 16 technical documents. In the documents, fatigue fact data of various metals, their relationships with basic mechanical properties such as elasticity, the fracture mechanism and so on were summarized and described under fundamental investigations on fatigue phenomena.

Recently the life of machines and constructions has been strongly required to be elongated from the ecological and economical points of view. According to the classical theory of fatigue, many of steels have their fatigue limit and there is no problem for any longer time if they will be used below the fatigue limit. However it has been pointed out that the fatigue limit decreases again for longer use, for instance at more than  $10^{10}$  cycles. Then we will start again the production of long term standard reference data even with some technical difficulties.

In this new project, (1) fatigue data of high strength steels for machine at more than  $10^{10}$  cycles, (2) fatigue data of heat resisting steels from low to high cycle fatigue regions under controlled strain, (3) fatigue data of titanium alloys for up to long term use and (4) fatigue data of welded joints for big constructions considering residual welding stress will be produced and published as data sheets. In addition, in each category of data production basic researches on fracture mechanism of metal due to fatigue from the micro and macro points of view and development of new evaluation methods will be carried out.

The data sheet project of NRIM has a programming system for deciding materials and testing methods in order data to be widely used. A committee, members of the which are selected from engineer and/or researchers of typical steel making and fabricating companies, is organized and discusses the testing program with NRIM.

In 1997, a new committee was organized and discussed a new testing program for long term fatigue data sheet. According to the decision, candidate materials for the program (1) was selected, middle carbon steel JIS S40C, low alloyed steels JIS SNCM439 and SCM440, steel for spring JIS SUP7, steel for bearing JIS SUJ2 and stainless steels JIS SUS403 and SUS631. The starting material was selected JIS SUP7 and testing began to be conducted. Candidate materials for the project (2) were selected JIS SB480, JIS SBV2, A4708, A387Gr. 11, A387Gr. 22, Mod. 9Cr-1Mo, stainless steels SUS403, SUS316 and SUS316FR, new heat resistant steels NCF800, NF616 and HCM12A. The starting materials were selected NF616 and HCM12A. Candidate materials for the program (3) were selected industrial pure titanium JIS-2, Ti-5Al-2.5Sn alloy, Ti-6Al-4V alloy, its Eli alloy, Ti-15V-3Al-3Cr-3Sn alloy and IMI834 alloy. The starting material was decided

Ti-6Al-4V alloy, and both high cycle and low cycle tests were started. Candidate materials for the program (4) were selected structural steels JIS SS400, SM490B, SM570Q, and HT790 and JIS A5083-O aluminum alloy. The starting material was decided SM590Q steel. Welded small rib cross joint and welded large cross joint of slit type were prepared and their fatigue tests are now being conducted.

**Keywords:** fatigue properties, standard reference data, steel, aluminum alloy, titanium alloy

## 24 NRIM Creep Data Sheet Project-V

*H. Irie, Mechanical Properties Division*

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*K. Kimura, S. Muneki, Materials Creation Research Station, Frontier Research Center for Structural Materials*

*M. Yamazaki, H. Hongo, T. Watanabe, Mechanical Properties Division*

[April 1996 to March 2001]

The major objectives of the NRIM Creep Data Sheet Project are to produce long-term creep and rupture data up to more than  $10^5$  hrs for heat resistant steels and alloys, which are produced in Japan, and to publish the data as a series of NRIM Data Sheets. This project has been continued since 1966 and the series of NRIM Data Sheets have been distributed not only in Japan but also in abroad. In fiscal year 1997, we published three sheets listed in the Table.

Among of these issues, both 19B and 10B are the final versions and very valuable data sheets due to creep rupture strength data more than 100,000 hrs. The data sheet No. 19B is of Cr-Mo ferritic steel widely used in heat exchanger and boiler and contains long-term creep rupture data up to 130,000 hrs, tables of creep rupture property, typical microstructures of fractured steels, results of statistical analysis of creep rupture data and so on. The data sheet No. 45 is of stainless steel SUS 316-HP, recently developed attracting notice and contains creep rupture data up to 50,000 hrs and properties of as-received specimen. The data sheet No. 10B is of heat resisting steel bar JIS SUH 616-B for turbine blade. It contains long-term creep rupture strength data up to 170,000 hrs, long-term creep strain data up to 160,000 hrs, tables of creep rupture property, tables of creep property, typical structures, results of statistical analysis of creep rupture data and so on.

Table Summary of NRIIM Data Sheets in fiscal year 1997

Materials	Number	Issued
9Cr-1Mo steel tubes and steel plates for boilers and heat exchangers (STBA 26)	19B	September 30, 1997
Hot rolled 18Cr-20Ni-Mo-middle N-low C stainless steel plates (SUS 316-HP)	45	September 30, 1997
Heat resisting 12Cr-1Mo-1W-0.3V steel Bars for turbine blades (SUH 616-B)	10B	March 31, 1998

In parallel with the testing and publication program, we have done researches on long term creep and rupture behavior of heat-resistant steels and alloys.

On the basis of inherent creep strength concept, creep rupture test results of high strength 9 to 12Cr ferritic steel were analyzed. Steels, which have more stable microstructure at higher temperature and longer use revealed stronger creep rupture property with respect to long creep behavior.

Creep deformation behavior of a 2.25Cr-1Mo steel, which was used in a practical plant for about 200,000 hrs, were investigated. The creep rupture strength of this used steel is inferior to that of new steel. And the decrease rate with time of creep rate ( $-\text{dlog } \epsilon / \text{dlog } t$ ) in the transient region of the used steel was smaller and showed constant value with respect to stress. It was cleared that these behaviors closely relate with decrease in dislocation density during long use.

Change in chemical composition and morphology of  $\sigma$  phase, which is the major precipitation at grain boundary formed in long creep tested SUS 304 austenitic stainless steel were investigated. At 700°C, the nose temperature of precipitation,  $\sigma$  phase grew along grain boundary and Cr condensed with time while Fe content decreased and Ni content did not change.

**Keywords:** long-term creep, creep rupture, stress relaxation, microstructural evolution

## 25 Relationships between Fatigue Behavior and TEM Structure of Titanium Alloys

T. Kainuma, Mechanical Properties Division  
[April 1997 to March 1999]

The dislocation arrangement introduced in aluminum, copper and iron by fatigue has been studied by a number of workers using TEM techniques. (1-5)

There is general agreement that fatigue moderate stresses result in a widespread formation of sub-

grains. Segall reported that if the stress was sufficiently low, no subgrain formation was observed but that dislocations existed in patches with a rather large concentration of dislocation loops being present.

The change of the width or area of the hysteresis loop during the fatigue testing of materials at constant stress amplitude is taken usually as a measure of dynamical changes in mechanical properties. By testing at stress amplitudes higher than the yield stress of annealed materials, fatigue hardening only takes place in alloys as well as pure metals (decrease in the width of hysteresis loop). While at stress amplitudes lower than the yield stress of cold-worked materials, fatigue softening occurs. Details of fatigue softening behavior have been reported for the materials such as aluminum(3), copper(4) and iron(5).

The aim of this work is to reveal the mechanisms of fatigue softening and hardening behavior of titanium alloys (hcp, bcc structure), fcc metals (copper, nickel, 304 stainless steel) and bcc metals (iron, mild steel, molybdenum, niobium) in connection with the characteristics of crystal structures, using transmission electron microscope (TEM).

### 1. Fatigue behavior of bcc metals

We examined fatigue softening and hardening behaviors using Ti-3Al-8V-6Cr-4Mo-4Zr alloy ( $\beta$ -type titanium alloy) and mild steel (Fe-0.2C). Also we examined the stress ratio ( $R=1$ ,  $R=0.1$ ) dependence of fatigue softening and fatigue hardening behaviors.

The experiments for the fatigue softening and hardening phenomena were carried out on work-hardened and annealed materials, respectively.

In fatigue of the work-hardened materials under  $R=-1$  stress ratio, the fatigue softening existed typically in the mild steel, but hardly in the  $\beta$ -type titanium alloy.

Under  $R=0.1$  stress ratio, no fatigue softening existed in both materials.

In fatigue of annealed materials under both stress ratios, the fatigue hardening existed typically in the mild steel, but hardly in the  $\beta$ -type titanium alloy.

### 2. Fatigue behavior of fcc metals

We examined fatigue softening and hardening behavior using pure nickel and 304 stainless steel.

In fatigue of the work-hardened materials under  $R = -1$  stress ratio, the fatigue softening existed typically in pure nickel, but did not exist in 304 stainless steel.

Under  $R = 0.1$  stress ratio, no fatigue softening existed in both materials.

In fatigue of annealed materials under both stress ratios, the fatigue hardening existed typically in both materials.

### 3. Transmission electron microscopic structure

In TEM observation, the structure of fatigue softening in mild steel and pure nickel was subgrain formation.

In the TEM structure of fatigue hardening under  $R = -1$  stress ratio in mild steel and pure nickel, at low stress amplitude the loop patches formation was observed, but at high stress amplitude the subgrain formation was observed.

**keywords:**  $\beta$ -type titanium alloy, mild steel, pure nickel, 304 stainless steel, TEM structure, fatigue softening, fatigue hardening, stress ratio dependence

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## 26 Fatigue Strength in a Corrosive Environment

*R. Hamano, Mechanical Properties Division*  
[April 1997 to March 2000]

Fatigue crack is nucleated along persistence slip bands, persistent Luders bands (PLBs), or at grain boundaries where slip bands impinge. The nucleat-

ed fatigue crack propagates over two successive stages-stage I (shear mode) and stage II (normal mode).

To improve the resistance to corrosion fatigue cracking which is sensitive to microstructures, we must clarify first; the mechanisms of how corrosive environments assist fatigue damages in the processes such as microstructure-sensitive stage I crack initiation and transition of fatigue crack growth from stage I to stage II. The present work was concerned with determining the crystallography of cyclic deformation of iron single crystals and age-hardenable Al-2wt% Li alloy.

The specimens of a gauge section of 2.0mm in thickness  $\times$  4.0mm in width  $\times$  6.0mm in length, oriented for two fold slip deformation were cut from a sheet of single crystals of iron. The axis of the specimen was close to [013]. A closed loop servohydraulic machine was used under grip distance control. The grip distance was measured by a SHIM-AZU differential transformer. The total strain means the relative displacement of the grips divided by the gauge length of the specimen. Fatigue tests were carried out in air and in a 3.5 pct NaCl aqueous solution at a cathodic potential of  $-1.1V$  against Ag/AgCl reference electrode at  $295 \pm 1K$ , using a sinusoidal wave with a frequency of 1Hz, a load ratio of  $-1$ , and a total strain of  $5 \times 10^{-3}$ . Specimens were immersed in a 3.5pct NaCl aqueous solution for 86.4ks at a cathodic potential of  $-1.1V$  against Ag/AgCl before being fatigued. The interference optical microscopy of slip band configuration on the surface of (031) showed that hydrogen-related environments affect the dislocation distribution of single crystal iron. The present result seems to correspond with the observation of highly dense dislocations of hydrogen-charged Fe-3.5pct. Si single crystals.

The experimental result that the transition of fatigue crack growth from stage I to stage II is accelerated in a hydrogen-related environment was discussed in terms of hydrogen induced dislocation multiplication near a crack tip. The microstructures less susceptible to environmental damages was examined, using an age-hardened Al-2wt% Li alloy.

**Keywords:** stag I and II crack initiation, environmental damage, fatigue strength

## 27 Effect of Cryogenic Temperature and Gas-environment on Deformation and Fracture Behavior

*T. Ogata and T. Yuri, Mechanical Properties Division*

[April 1996 to March 1999]

To promote the application of clean energy and space technology, there are projects of constructing large scale facilities to transport and store liquid hydrogen. It is very important to evaluate the mechanical properties of the materials including weld metals to keep the reliability of large scale structures used at cryogenic temperatures and in hydrogen gas environment. It is required to comprehend the mechanical properties such as continuous data of fracture toughness from room temperature to liquid helium temperature, and the clarification of effects of hydrogen-gas environment at low temperatures on deformation and fracture behavior of structural materials for the design of structure and selection of materials. Especially, hydrogen embrittlement at low temperatures in the large scale structures of stainless steels is an important subject. In this study, we are going to establish the testing technique of tensile, impact properties, and fracture toughness to evaluate the effects of low temperature and gas environment from room temperature to liquid helium temperature, and investigate the effects of microstructure, grain size,  $\delta$  ferrite, and hydrogen gas environment on tensile, impact, fatigue properties, and fracture toughness of austenitic stainless steels from room temperature to cryogenic temperature. In 1997, we have carried out high cycle fatigue tests of base and weld metals of SUS304L and SUS316L in order to evaluate the long-life reliability of the structural materials and the effects of welding structure and  $\delta$  ferrite on the fatigue properties at cryogenic temperatures. The S-N curves of base and weld metals shifted to higher stress or longer life side with a decrease in test temperature. The ratio of fatigue strength at one million cycles to tensile strength of the weld metals were 0.35 to 0.7 and getting lower than those of base metals with decreasing temperature. Fatigue crack initiation site of SUS304L weld metals initiated almost at blow holes of approximately 200~700 $\mu$ m diameter, and that of SUS316L weld metals initiated at a virtual crack. A virtual crack of SUS316L weld metal was caused by carbides of  $M_{23}C_6$ , and Al/Mn oxides, which were formed at weld pass interface boundary during welding. The decrease in fatigue strength at one million cycles at cryogenic temperatures was due to very small welding defects and a virtual crack. Although  $\delta$  ferrite reduces toughness at cryogenic temperatures, the effects of  $\delta$  ferrite on high cycle fatigue properties are not clear or significant.

We also performed detail evaluation of fracture toughness of each part of weld joints of SUS304L and SUS316L using a newly developed fracture toughness evaluation method by round bar with

circumferential notch. Fracture toughness of weld metal at 4K decreased significantly with an increase of  $\delta$  ferrite content compared to the toughness of base metal. Fracture surface of 10%  $\delta$  ferrite weld metals appeared a brittle dendrite structure with  $\delta$  ferrite.

This research was performed in collaboration with the Japan Research and Development Center of Metals and Mitsubishi Heavy Industry Co. Ltd.

Cryogenic High Cycle Fatigue Properties of Weld Metals for Austenitic Stainless Steels, T. Yuri, T. Ogata, M. Saito, Y. Hirayama, *Tetsu-to Hagane* Vol. 84 (1998), p. 888-895, (in Japanese)

**Keyword:** structural material, stainless steel, cryogenic temperature, tensile properties, fatigue properties, hydrogen embrittlement

## 28 Characterization and Evaluation of Cryogenic Structural Materials

*T. Ogata and T. Yuri, Mechanical Properties Division*

[April 1997 to March 2000]

For design and development of large scale cryogenic applications, such as a nuclear fusion reactor, a superconducting power generator, a superconducting magnetic levitated train, and so on, it is very important to construct intellectual infrastructure through international pre-standardization for promoting practical use of advanced cryogenic structural materials, high-strength stainless steels, high-Mn steels, and large thickness weld joints. This research has been carried out with a close contact with the VAMAS Technical Working Area (TWA) 17, cryogenic structural materials, which has been organized in the Versailles Project on Advanced Materials and Standards to promote the prestandardization program on material properties tests of glass fiber reinforced polymer (GFRP) composite materials and alloys at liquid helium temperature. The base is to develop an understanding of mechanical-property determinations at liquid-helium temperature (4.2K) and establish a unified method. A series of international interlaboratory comparisons of both tensile and fracture toughness tests for high-strength stainless steels, a titanium alloy, and an aluminum alloy, and compression and shear tests for composite material G-10CR were performed so far. Fourteen research institutes from seven nations have participated in these project of TWA 17.

In this research we are going to establish and report pre-standard testing methods of a) tensile test in high magnetic field, b) an advanced fracture

toughness evaluation method by round bar with circumferential notch, and c) interlaminar shear test of G-10CR, glass fiber reinforced plastic, at cryogenic temperature. Main backgrounds and objectives of these research items are as follows:

In 1997, we have performed investigation, analysis, and preliminary tests on testing conditions and procedures of each research subjects, and prepare materials and instruction manuals for international round robin tests. As a chairman and the office of TWA 17, we held the Technical Working Party meeting twice in USA and Japan attended by participants to this programs from each country, discussed and agreed the results so far and details of testing items and procedures of these round robin tests.

This research was performed in collaboration with the University of Tokyo, Tohoku University, National Institute of Fusion and Science, and Osaka University in Japan, FZK in Germany, RAL in United Kingdom, NHMFL, CTDI, and UCLA in USA, SEP in France, EMPA in Switzerland, Tech Univ. in Vienna in Austria.

VAMAS Round Robin Tests on Composite Material and Solder at Liquid Helium Temperature, T. Ogata, D. Evans, and A. Nyilas, published in *Advances in Cryogenic Engineering Materials* Vol. 44 (1998). p. 269-276

**Keyword:** structural material, cryogenic temperature, standardization, tensile test, fracture toughness test, shear test

## 29 Fabrication of Ni<sub>3</sub>Al-Base Intermetallic Compounds by Unidirectional Solidification

*T. Hirano, M. Imai, T. Mawari, and M. Demura  
Mechanical Properties Division  
[April 1997 to March 1999]*

So far, we found that unidirectional solidification using a floating zone (FZ) method is effective in improving the ductility of polycrystalline Ni<sub>3</sub>Al without addition of alloying elements such as boron. Also, we successfully grew high quality single crystals of stoichiometric Ni<sub>3</sub>Al which had been considered to be impossible to grow. The results indicate that the FZ method is a powerful technique not only to fabricate ductile intermetallic compounds but also provide us single crystals necessary for fundamental study of deformation mechanism.

The objective of this study is twofold. First is to improve high-temperature strength of Ni<sub>3</sub>Al. Since the brittleness of Ni<sub>3</sub>Al is almost overcome as mentioned above, one of the remaining problems is lack of high-temperature strength. Our target is to

develop Ni<sub>3</sub>Al-base intermetallic compounds strengthened by alloying or second phase precipitation. We apply the FZ method to fabrication of these compounds. Second is to study the deformation mechanism of Ni<sub>3</sub>Al using single crystals grown by the FZ method. The effect of stoichiometry on the deformation is focused. It is because in our preliminary study we found some interesting deformation behaviors which are characteristic of binary stoichiometric Ni<sub>3</sub>Al.

**Keywords:** unidirectional solidification, floating zone method, Ni<sub>3</sub>Al, mechanical properties, deformation mechanism

### Recent Publications

Stress Response by the Strain-Rate Change in Binary, Stoichiometric Single Crystal Ni<sub>3</sub>Al, M. Demura and T. Hirano, *Phil. Mag. Lett.*, 75 (1997), 143-148.  
Stress Response by the Strain-Rate Change in Binary, Stoichiometric Ni<sub>3</sub>Al Single Crystal, M. Demura and T. Hirano, *Mat. Res. Soc. Proc.*, 460 (1997), 549-554.

Effect of Alloy Stoichiometry on Grain Boundary Chemistry and Fracture Behavior of Directionally Solidified Ni<sub>3</sub>Al, E.P. Geroge, M. Imai, and T. Hirano, *Intermetallics*, 5 (1997): 425-432.

Effect of Directional Growth-Rate on the Mechanical Properties of Ni<sub>3</sub>Al, T. Hirano, T. Mawari, M. Demura, and Y. Isoda, *Mater. Sci. Eng. A239-240* (1997), 324-329.

Compressive Flow Stress of a Binary Stoichiometric Ni<sub>3</sub>Al Al Single Crystal, D. Golberg, M. Demura and T. Hirano, *Scripta mater.*, 37 (1997), 1777-1782.  
High-Temperature Yield Strength of Binary Stoichiometric and Al-rich Ni<sub>3</sub>Al Single Crystals, D.V. Golberg, M. Demura, and T. Hirano, *Proc. of 2nd International Symposium on Structural Intermetallics*, 1987. 9. Champion.

Single Crystal Growth and Characterization of Binary Stoichiometric and Al-Rich Ni<sub>3</sub>Al, D. Golberg, M. Demura and T. Hirano, *J. Cryst. Growth*, 186 (1998), 624-628.

Effect of Al-Rich Off-Stoichiometry on the Yield Stress of Binary Ni<sub>3</sub>Al Single Crystals, D. Golberg, M. Demura and T. Hirano, *Acta Mater.*, 46 (1998), 2695-2703.

Structure and Yield Strength of Directionally Solidified Ni<sub>3</sub>Al Al Intermetallic Premelted with MoSi<sub>2</sub>, D. Golberg, M. Demura and T. Hirano, *Intermetallics*, 7 (1999), 109-114.

## 30 Fundamental Studies of the Microbial Reaction with Inorganic Compounds

A. Aoki, *Mechanical Property Division*

[April 1996 to March 1998]

The bacterially catalyzed  $Fe_{1-x}S$  oxidation process with *Thiobacillus ferrooxidans* was studied to characterize the particles secondarily formed on the sulfide surface. By using XRD, biooxidation products were revealed to be K-jarosite  $KFe_3(SO_4)_2(OH)_6$ , shwertmanneite-akaganetite type compound of similar crystallography to  $Fe_8O_8(OH)_6SO_4$  and elemental sulfur; whereas nothing but small amounts of goethite type iron oxyhydroxide  $FeOOH$  and elemental sulfur in the chemical medium. Morphology change of the particles obtained was then observed by using SEM and discussed with the results of XRD, FTIR and TG/DTA. The product after 30 days was spherical, several  $\mu m$ s in diameter and uniform in shape and size; very different from those in the chemical process in which the particles were spherical but having numerous fibrous spicules on the surface. These fibrous substance was also found at the early stages of the bacterial medium, however, most of them changed into two kinds of crystals on the surface; plate-like and small rod type crystals. The spicules were identified to be goethite by XRD; the numerous fibrous substances would be poorly crystallized goethite containing relatively large amount of  $H_2O$  compared to those in the bioprocess, which was estimated by FTIR and TG/DTA. Accordingly, it could be also understood morphologically the difference in the oxidation rate between bacterial and chemical reaction: various kinds of powders for a functionally important materials could be obtainable, if the reaction processes above mentioned are possibly controlled. Further, some organic compounds out of the microorganism (extracellular substance-e.g. phospholipid which is known as a surface-active agent) would affect on the reaction rate as well as the structure of the product particles in the biooxidation.

**Keywords:** bacterially catalyzed process, *Thiobacillus ferrooxidans*,  $KFe_3(SO_4)_2(OH)_6$ ,  $Fe_8O_8(OH)_6SO_4$ , extracellular substance

### Recent Publication

Characterization of the secondarily particles formed during the biooxidation of pyrrhotite, A. Aoki, Proceedings of IBS '97, Sydney (1997) PM31

## 31 Improvements of High Temperature Properties in Materials for High/Ultra-high Temperature Use.

T. Tanabe, *Mechanical Properties Division*

[April 1996 to March 1999]

### 1. Materials for high temperature use.

Effects of microstructures on the creep rupture properties of Ti-49at.%Al and-51at.%Al were investigated in a high purity helium environment at temperatures ranging from 1023K to 1373K. In Ti-49at.%Al, steady state creep rate was the lower in the specimens with the larger  $\gamma$  grain size in the single phase  $\gamma$  alloys. It was found that fully lamellar microstructure is not the strongest at 1273K, especially at lower stresses. Further it was recognized that  $\alpha_2$  phase in the  $\gamma$  grain interior does not improve the creep resistance but the one at the  $\gamma$  grain boundaries does improve the resistance. Meanwhile in Ti-51at.%Al, rupture lives and steady state creep rates of the alloy depended on its microstructures. The specimens with the larger  $\gamma$  grain size showed the longer lives and the lower steady state creep rates than the specimens with the smaller grain size throughout the test temperatures. The existence of  $\alpha_2$  phase improved the ductility of the alloy at 1023K, while the phase at the  $\gamma$  grain boundaries improved the creep resistance at temperatures higher than 1173K. Dynamic recrystallization occurred at higher temperatures higher than 1173K, leading to the increase of rupture elongation of the alloy.

### 2. Materials for ultra-high temperature use.

In order to examine the change of properties in W due to transmutation of W to Re after heavy neutron irradiation, the effect of Re content (up to 25mass%) on the thermal shock resistance, mechanical properties and thermal diffusivity of W-Re alloy was investigated. The results obtained were as follows; (1) Heat load test: With increase of Re content, the incubation time for erosion of the alloy decreased and their eroded volume increased. The results indicate the superiority of W to W-Re alloy as a plasma facing material. (2) Mechanical properties: In the three-point bend test, maximum bend stress and ductility increased with increase of Re content. (3) Thermal properties: Thermal diffusivities of W-Re alloy decreased with increase of Re content at room temperature. With increase of temperature, the thermal conductivity of W decreased, while those of W-Re alloys increased.  $10^{19}n/cm^2$  neutron irradiation did not alter the thermal diffusivity of W-Re alloys.

**Keywords:** intermetallic compounds, TiAl, creep, plasma facing material, thermal shock resistance.

## Related Papers

Effect of Microstructures on the creep rupture properties of Ti-49at/%Al, I. Mutoh, Y. Kawano, T. Tanabe and M. Nakamura, Proc. Int. Conf. on Materials and Mechanics 97 (1997) 335-336.

High Heat Load Test on Tungsten and Tungsten-Rhenium Alloys, M. Fujitsuka, I. Mutoh, T. Tanabe and T. Shikama, Proc. 1997 Fall Meeting of the Atom. Ener. Soc. of Japan, vol1 (1997) 144

## 32 Remaining Life Prediction for Weldments in FBR based on Creep Damage Evaluation.

*T. Tanabe, Mechanical Properties Division*  
[April 1996 to March 2001]

(1) Heterogeneity in creep properties of welds on 304 stainless steel thick plate was investigated. A butt-welded joint was fabricated using 25mm thick plates of 304 stainless steel and 308 welding wires by a submerged arc welding method. Creep rupture tests of base metal, weld metal and welded joint were conducted at 823K. Creep specimens for weld metal and welded joint were cut out (parallel and perpendicular to the weld line, respectively) from the welded plate at locations of  $1/4t$  and  $3/4t$  from the front side of the plate. It was shown that microstructure of the weld metal part of the welded joint is influenced by the built-up sequence of the bead and the existence of the constraint at the welding performance, with the result that 0.2% proof stress and creep properties are different in the specimens at different sampling locations. The difference remained after several hundreds hours. These results suggest that heterogeneity of mechanical properties in the welds should be taken into account when the strength evaluation and the simulation for the life prediction of the weldments are conducted.

(2) Creep behavior of 16Cr-8Ni-2Mo weld metal part of the welded joint in low carbon-medium nitrogen type 316 steel (316L) was investigated and the data were compared with those of 316L weld metal part in the 316 welded joint. The welded joints used were narrow gap welded joints and were fabricated from type 316L steel thick plate of 50mm thickness using type 16-8-2 filler metals by gas tungsten arc welding. Creep rupture tests were done at 823 and 873K. 16-8-2 type weld metal in the as welded condition had a two phase microstructure consisting of austenitic  $\gamma$  phase matrix and  $\delta$  ferrite precipitates. Though creep rupture strength of type 316L weld metal is larger than that of 16-8-2 weld metal, rupture elongation of the latter at longer test times was larger than that of the former. Residual  $\delta$

ferrite content after rupture at 873K at longest times was reduced to almost zero. The same trend was also observed in 316L weld metal, however, the metal contained much more  $\sigma$  phase than 16-8-2 weld metal. This could be the reason why rupture ductilities of 16-8-2 are larger than those of 316L weld metal.

**Keywords:** creep damage, welded joint, weld metal, stainless steel, microstructure, FBR

## Related Papers

Local Variability of Creep Properties for 304 Stainless Steel Welds, M. Yamazaki, H. Hongo, T. Watanabe, J. Kinugawa, T. Tanabe and Y. Monma, Proc. 35th Sympo. on Strength of Materials at High Temperatures (1997) 169-173.

Creep Behavior of Low Carbon-Medium Nitrogen Type 316 weld metal, H. Hongo, M. Yamazaki, T. Watanabe, J. Kinugawa, T. Tanabe and Y. Monma, *ibid* (1997) 164-168.

## 33 Dynamic Microstructural Change and Mechanical Properties in Ceramics at High Temperatures

*K. Hiraga, Mechanical Properties Division*  
[April 1998 to March 2001]

Most of polycrystalline ceramic materials show plasticity at high temperatures under the aid of grain boundary sliding accommodated by matter transport through or across the boundaries. The failure of such accommodation at localized boundary regions leads to the occurrence of intergranular cavities, which grow into facet sized ones and coalesce to form intergranular microcracks. This study aims to get basic information on microstructural factors relating to such deformation and fracture processes. Special attention is placed on the effects of dynamic microstructural changes on constitutive behavior and cavitation damage during deformation at relatively low tensile stresses ( $\sigma/E=10^{-4}$ ), at temperatures higher than 1600K. The followings are within the scope of the present study.

(1) modeling of dynamic grain growth in alumina and relating materials with and without second phases: an analysis based on strain energy stored during deformation and its depletion through grain growth and cavitation is underway.

(2) microstructural aspects of deformation in zirconia: the effects of intergranular segregation and/or small amounts of a silicate are under examination using HRTEM, internal friction experiments and creep tests, where concurrent tensile strains at

gauge portion can be measured directly by an optical method.

(3) cavity nucleation and growth behavior in materials with second phases: stereological analysis of cavity size distributions is undertaken to get basic information on the effects of second phases on the elemental process of intergranular damage.

(4) tensile failure in superplastic ceramics: the occurrence of microcracks followed by final failure is under examination in connection with such microstructural changes as dynamic grain growth and the precipitation of glass phases at multiple junctions, stress concentration, relaxation of stress by diffusion, and crack extension behavior.

**Keywords:** particle dispersion, amorphous phase, grain growth, tensile creep, cavitation, microcrack, modeling

## Materials Processing Division

### 34 The Development of High Strength High Conductive Cu Base In-Situ Composite

*H.G. Suzuki, and E. Takakura, Materials Processing Division*

[April 1996 to March 1998]

The effect of the addition of Zr and Ti on the mechanical as well as physical properties of Cu-15% Cr composite was studied. Effect of Fe as an impurity element was also studied.

1) The addition of 0.1 to 0.2wt% of Zr causes the retardation of recovery and recrystallization of dislocation structures introduced by a heavy cold rolling and resulted in a banding structure. This effect leads to the increment of strength by about 100MPa compared with that of Cu-15%Cr. Precipitation hardening and the recovery of electrical conductivity are remarkable by aging treatment.

By optimizing the process variables such as cold rolling and aging treatment, the strength level of 1150MPa and the electrical conductivity of 71% IACS were attained in the Cu-15%Cr-0.15%Zr alloy.

2) The effort of practical application is undergoing. Vacuum induction melting of a size of 150kg ingot scale and wire making by works level are successful in The Furukawa Electric. Co., LTD.

**Keywords:** Cu alloy, high strength, electrical conductivity, cold rolling, composite

#### Recent Publications

Y. Jin, K. Adachi, T. Takeuchi, and H.G. Suzuki, *Materials Sci. & Engineering*, A212 (1996), 149-156,

"Microstructural evolution of a heavily cold-rolled Cu-Cr in situ composite"

Y. Jin, K. Adachi, T. Takeuchi, and H.G. Suzuki, *Applied Physics Letters*, 69 (1996), 1391-1392, "Cu precipitation in Cr ribbon of Cu-15%Cr in situ composite"

Y. Jin, K. Adachi, T. Takeuchi, and H.G. Suzuki, *J. Mater. Science*, 33 (1998), 1333-1341, "Aging characteristics of Cu-Cr in situ composite"

Y. Jin, K. Adachi, T. Takeuchi, and H.G. Suzuki, *Mater. Letters*, 32 (1997), 307-311, "Correlation between the cold working and aging treatment in a Cu-15%Cr in situ composite"

### 35 Control of the Oriented Single Crystals of Refractory Metals through Solid State Processes

*T. Fujii, K. Honda and K. Kamihira Materials Processing Division*

[April 1997 to March 1999]

Molybdenum and tungsten, b.c.c refractory metals, have many advantages such as high melting points, useful elevated temperature strength, high thermal and electrical conductivity, low thermal expansion and good resistance to liquid metal corrosion. Thus, at the present, molybdenum, tungsten and their alloys are widely utilized in the fields of electrical and electronic industries, high temperature vacuum and chemical industries. However, such refractory metals undergo a severe loss of ductility after recrystallization, welding or heavy neutron irradiation. It is generally accepted that such a problem is due to intergranular embrittlement. This is the greatest weak point of these metals.

Recently, NRIM (National Research Institute for Metals) have succeeded in establishing a new technology to develop commercial scale molybdenum and tungsten single crystals and their multilayer crystals from hot-rolled sheet doped with a certain amount of oxides by means of secondary recrystallization. However, no research and development for preparation of the single crystals with desired orientation by a solid state process have been carried out.

Thus, the main purpose of this study is to develop a new technology for preparation of the oriented single crystals of refractory metals such as a molybdenum or a tungsten through solid state processes.

**Keywords:** oriented single crystal, refractory metal, solid state process

#### Recent Publications

Preparation of Molybdenum Single Crystal with a

Desired Orientation by Means of Zone Annealing, K. Kamihira, K. Honda and T. Fujii. *JSPM*. 44 (1997) 770-774.

### 36 Selenium (VI) Removal from Wastewater by a Fluidized Bed Process

*K. Goto, Materials Processing Division*  
[April 1997 to March 1999]

The Japanese government office enacted in 1994 that the effluent water quality standard for selenium was 0.1mg/l. This was an important problem in the copper refineries, because they discharge a large amount of effluent containing the selenium ions higher than the standard. A provisional standard of 20mg/l has been applied to the industries, and the moratorium will finish within a few years. In order to clear the general standard, various methods were examined and investigations were carried out. According to their efforts, it becomes clear that Se (IV) can be removed but Se (VI) cannot. In the laboratory, Se (VI) can be removed by the reduction and the coprecipitation with ferrous and ferric ions. The cost is, however, too expensive and the method cannot be applied to the wastewater treatment from the practical viewpoint.

The aim of this study is to develop the new method to remove the selenium ions. We propose a new fluidized bed process, which involved reduction of Se (VI) to Se (IV) or to crystal selenium. The research will be carried out to verify that Se (VI) is reduced by the fluidized bed process, and to decide the optimum conditions of the process.

**Keywords :** selenium, removal, wastewater, fluidized bed

### 37 Study on combustion Synthesis

*Y. Kaieda, Process Control Division*  
[April 1996 to March 1999]

The fundamental study to reveal the reactions in combustion synthesis is carried out. The propagation of the reaction front and the synthesis process of the materials synthesized through the reaction are also studied. Investigation by the thermal analysis with rising temperature at constant speed and/or in alternating speed is carried out to reveal the conditions for the initiation of the reaction, the propagation and the synthesis. The influence of pressure and convection on the phenomena in the reaction process of the system containing gaseous phase or liquid

phase is studied using a high gaseous pressure apparatus.

The selection of the combinations of elements, which is focused in the present study, will be investigated. The system of the combination that might exhibit the effect of convection and pressure during the reaction and synthesis process is selected considering the system that performs the effect of liquid and gaseous phase. The system of elements, in which the safety during the experiment is assured, is selected.

Most intermetallic compounds are conventionally produced by the processes including high frequency induction vacuum melting and casting. It is difficult to control accurately the chemical components of intermetallic compounds produced by the conventional process. Homogeneous intermetallic compound is produced by the industrial process including a combustion synthesis method, which is a newly developed manufacturing process in this institute. The chemical components, the impurities industrially produced by the process are revealed. These properties are vitally important when the combustion synthesis method is applied to an industrial mass production process for producing intermetallic compounds.

**Keywords :** combustion synthesis,

### 38 Synthesis and Utilization of Mesoporous Materials

*Y. Sakka, K. Ozawa, T. Uchikoshi, T.S. Suzuki, and K. Sodeyama\*, Materials Processing Division, \*Kagoshima Prefectural Institute of Industrial Technology*

[April 1996 to March 1999]

Two types of porous materials are used for fabricating nanocomposite, heterogeneous phases, hierarchically structured materials, etc. One is synthesized by consolidating fine powders through a colloidal processing. The other is microporous materials with layered perovskite structures, which are synthesized by soft chemical processing i.e. a sol-gel or a hydrothermal processing.

The colloidal processing is a useful tool for preparing mesoporous materials with desired pore size distribution. An important factor is to control the interparticle interaction in liquid. Porous alumina or zirconia body with a narrow pore size distribution, which was determined by mercury porosimetry, was produced by slip cast of dispersed suspension followed by low temperature sintering. Infiltration of metal solutions into the porous mate-

rials and sintering result in the advanced materials.

Intercalation or ion-exchange reaction in host materials results in a novel electronic material which is not synthesized by heating at high temperatures. Vanadium oxide-organic composite is synthesized by a hydrothermal method. The lithium insertion characteristics were examined. The reaction was influenced by the micro-pore size of the host-material.

Powder and film of amorphous antimonite are prepared by a direct reaction of  $\text{Sb}(\text{O}-n\text{-C}_3\text{H}_7)_3$  with  $\text{H}_2\text{O}_2$  aqueous solution. Three types of antimonite acids ( $\text{Sb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ) films: (111)-oriented and non-oriented polycrystalline films of cubic antimonite acids and amorphous antimonite acid films, were prepared on quartz glass substrates with a spin-coating technique. The electrical conductivity of the (111)-oriented film, which increases from  $1.69 \times 10^{-5}$  to  $2.89 \times 10^{-3} \text{ } \Omega\text{cm}^{-1}$  as the relative humidity changes from 11 to 85%, is approximately one order of magnitude larger than those of the non-oriented and amorphous films. Effect of the water vapor pressure and micropore structure on the proton conductivity is studied.

This research was performed in collaboration with Kagoshima Prefectural Institute of Industrial Technology.

**Keywords:** soft chemistry, micro-pore, colloid, vanadium oxide, antimonite acid

#### Recent publications

*Water Sorption-Desorption Characteristics of Proton-Conducting Antimonite Acids with Cubic and Monoclinic Structures*, Y. Sakka, K. Sodeyama, T. Uchikoshi, K. Ozawa and M. Amano, *J. Am. Ceram. Soc.* 79 (1996): 1677-80.

*Preparation and Electrical Conductivity Measurement of Amorphous Antimonite Acid*, K. Ozawa, Y. Sakka and M. Amano, *J. Ceram. Soc. Japan* 104 (1996): 756-59.

Processing and some properties of Shirasu/alumina lightweight composites, K. Sodeyama, Y. Sakka, Y. Kamino and K. Hamaishi, *J. Ceram. Soc. Japan* 105 (1997): 815-20.

Preparation and electrical conductivity of three types of antimonite acid films, K. Ozawa, Y. Sakka and M. Amano, *J. Mater. Res.* 13 (1998): 830-33.

#### 39 Photocatalytic Properties of Ultrafine Particles

*S. Ohno, H. Okuyama, Y. Sakka and T. Uchikoshi, Materials Processing Division*

*K. Honma, Materials Physics Division*

*K. Halada and K. Minagawa, Ecomaterials*

#### Research Team

[April 1996 to March 1998]

It is well known that the ultrafine particles (UFP) have many excellent physical and chemical properties. In particular, UFP of oxide semiconductors is a very promising material as a photocatalyzer.

In this study, titanium oxide ( $\text{TiO}_2$ ) UFP synthesizes by oxidation of Ti vapor in the tail flame of an argon RF-Plasma, and their activity for photocatalytic hydrogen evolution in aqueous suspensions has been investigated.

Synthesized  $\text{TiO}_2$  UFP is composed of the particles having both the rutile phase and the anatase phase, and anatase content in UFP varies from about 35 to 75 mass% with the oxygen content and the injection point of a reaction gas. The photocatalytic activity of  $\text{TiO}_2$  UFP increases drastically with decreasing anatase content, and reaches a maximum at about 40 mass% anatase. The maximum activity is 1000 times larger than that of a commercial anatase UFP.

**Keywords:** ultrafine particle, arc plasma, RF-plasma,  $\text{TiO}_2$ , photocatalytic property

#### 40 Micro Structure Control with Plastic Deformation under Mashy State

*T. Dendo, T. Shiota, T. Kimura, Advanced Materials Processing Division*

[April 1996 to March 1998]

Processing under semi-solid or semi-molten state i.e. mashy state has attracted the attention as an exotic technique for refinement of the micro structure and/or for creation of new composite materials. In the procedure of the above processing, plastic working is mostly inevitable. Plastic working under mashy state in which solid and liquid phases coexist, however, induces unfavorable problems such as segregation due to the flow of the liquid component and/or difficulty of the shape retention during handling of work piece. In order to solve the above problems, a new metal working process is proposed, in which the semi-molten metal is inserted in a solid hollow metal and worked plastically together with the hollow metal that suppresses the flow of the liquid component and retains the shape of mashy metal. The work piece fabricated through this process is consequently clad with the hollow metal.

Experimental study is carrying out to grasp the comprehensive feasibility of the above process. In the present study, several kinds of Al-Si alloy are adopted as the semi-molten metal, and the pipes of

aluminum, copper and 304 stainless steel are used as the hollow metal. Through some experiments, loading characteristics, formability of the hollow metal and bondability at the cladding interface are investigated with respect to the process parameters such as working temperature, solid fraction of semi-molten metal and degree of plastic deformation. As for the worked pieces obtained, microscopic morphology of the bonding interface and the interior material is examined.

On the other hand, the preferred orientation in crystalline introduced by plastic deformation under mashy state is explored so as to aim at developing new method of texture control. In this study, cast pieces of Al-Si alloys are compressively deformed under semi-molten state, and texture developments due to the deformation are discussed in relation to the solid fraction. It is found that the preferred orientation parallel to the compressing plane varies from (110) to (100) according as the solid fraction decreases.

**Keywords :** mashy state, plastic working, clad metal, preferred orientation

#### Recent Publications

An Attempt for Fabrication of Clad Parts through Semi-Molten Processing, T. Dendo, T. Shiota, B. Han, T. Kimura, Proc. of 5th Int. Conf. on Semi-Solid Processing (1998): 131-138.

#### 41 Diffusion bonding of Stainless Steel and Metals of Group IV~VI

*T. Kasugai and K. Ei Advanced Materials Processing Div.*  
[April 1996 to March 1999]

It is difficult to apply fusion welding processes, such as an arc welding or an electron beam welding, to dissimilar metals joining because a large amount of brittle metallic compounds form in the weld metals. On the other hand, the size of metallic compounds and diffusion layer in dissimilar metal joints can be easily controlled by a solid state diffusion bonding.

The basic metallurgical knowledge on the dissimilar metal bonding zone has been scarce until now, and it is difficult to estimate the size/kind of metallic compounds at the bonding zone based on phase diagrams. The diffusion process in the bonding zone of dissimilar metals, moreover, is not simple, but a few negative diffusion or up-hill diffusion phenomena have been observed in metals of group IV.

In this study, joinability of the diffusion bonding of stainless steels and metals of group IV~VI, the

formation of metallic compounds in the bonding zone of the these steels and metals, diffusion processes, and bonding crack are investigated in the connection with the periodic table.

**Keywords :** Diffusion bonding, Stainless Steel, Group IV metals, Group VI metals, Group VII metals, Metallic compound

#### 42 The Development of High Strength and High Functional In-Situ Composite

*E. Takakura and H.G. Suzuki Materials Processing Division*  
[April 1998 to March 2000]

High strength and high electric conductive material has a strong application potential in the electrical and electronic industries. We have developed Cu-15wt%Cr in situ composite that has a strength of 1000MPa and an electrical conductivity of 70% IACS so far.

The present study aims at improving the mechanical property of this material. In addition we also plan to improve that of the titanium alloy in the similar way. At first, we plan to clarify the relation between the microstructure and the mechanical property in detail in order to quantify the effects of reinforcement, grain refinement, precipitation hardening and solid solution hardening on the strength. Furthermore, we also plan to improve processes by optimizing the process variables such as casting, hot forging, cold rolling and aging treatment.

**Keywords :** high strength, electrical conductivity, cold rolling, composite

#### Recent Publications

Correlation between the Electrical Conductivity and Aging Treatment for a Cu-15 wt%Cr Alloy Composite Formed in-situ, Y. Jin, K. Adachi, T. Takeuchi and H.G. Suzuki, Materials Letters 32 (1997): 307-311.

Ageing Characteristics of Cu-Cr in-situ Composite, Y. Jin, K. Adachi, T. Takeuchi and H.G. Suzuki, J. Mater. Sci. 33 (1998): 1333-1341.

#### 43 Crystal growth and dissolution mechanisms in peritectic system

*K. Maiwa, K. Goto and T. Fujii*  
[April 1998 to March 2000]

We intend to clarify the mechanisms of crystal growth and dissolution in a peritectic system in this

subject. For this purpose, we chose Sr (NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O peritectic system as an example, in which the crystal growth and dissolution processes can be observed in situ in a transparent liquid at room temperature. Above and below the peritectic temperature,  $T_p=29.3^\circ\text{C}$ , Sr (NO<sub>3</sub>)<sub>2</sub> phase and Sr (NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O phase are equilibrium with the liquid in this system, respectively. A peritectic reaction is expected at peritectic point in equilibrium. It was observed, however, that in the liquid of the composition of the peritectic point at the temperatures below  $T_p$ , both solid phases could grow. In these conditions, the growth rate of the low-temperature phase was much larger than that of the high-temperature phase and the difference in the growth rate between two phases increased with the decrease of the temperature. It is followed that the latter was engulfed in the former simply due to the difference in growth rate, which resulted in a 'peritectic texture'.

**Keywords :** peritectic reaction, incongruent melting, crystal growth

#### Recent Publications

AFM Observation of Barium Nitrate {111} and {100} Faces : Spiral Growth and Two-dimensional Nucleation Growth, K. Maiwa, M. Plomp, W.J.P. van Enckevort and P. Bennema, *J. Crystal Growth* 186 (1998) : 214-223.

#### 44 Application of Ionization Separation Technique to Gaseous Process

*Y. Ogawa and O. Kujirai, Materials Processing Division*

[April 1998 to March 2001]

Ionization separation methods are effective to remove impurities from a gaseous matrix by electrostatic field. The objective of this study is to investigate basically photoionization and surface ionization as the separation technique. It was found using photoionization that there many unknown high-lying energy levels in lutetium which is the last member of the rare-earth elements and has the filled 4f electron shell. Light and middle rare-earth atoms have an unfilled 4f electron shell and complex spectral configuration. The research of unknown high-lying energy levels of these atoms is important to understand energy transition and electron configuration of rare-earth atoms and to apply photoionization to them.

The reaserch is composed of the following two subjects.

1. Study of high-lying energy levels of light and

middle rare-earth atoms by resonance photoionization.

2. Study of the basic features and characteristics of the surface ionization as the separation method.

**Keywords :** laser, resonance photoionization, surface ionization, high-lying energy level, rare-earth elements

#### Related Papers

Laser Material Purification of Neodymium, Y. Ogawa et al., *J. Jpn. Inst. Met.* 55 (1991) : 545-552.

Observation of Even-Parity Autoionization States of Lutetium atom by Opto-galvanic Spectroscopy, O. Kujirai and Y. Ogawa, *J. Phys. Soc. Japan*, 67 (1998) 1056-57.

Study of Even-Parity Autoionization States of Lutetium Atom by Laser Resonance Photoionization Spectroscopy, Y. Ogawa and O. Kujirai, submitted.

### Special Research Officer

#### 45 Solid State Interfacial Reactions and Surface Analysis of Thin Solid Films

*S. Hofmann, Special Research and Extreme High Vacuum Station (coworker : Dr. A.Rar, COE fellow)*

[April 1997 to 31. March 1998 (23 July 1998)]

Out of the major aims of our project, namely surface and thin film analysis, and thin film deposition and processing, the focus of our small research group was mainly on the first topics. The low energy ion gun for direct fabrication of nitride coatings is currently being tested.

Aiming at the determination of the composition of thin films with a precision of the order of one atomic monolayer, depth profiling by ion sputtering in combination with Auger electron spectroscopy was optimized using new GaAs/AlAs reference samples [1-3]. The investigations were directed to finding the dependence of the main parameters of the depth resolution function, namely atomic mixing, surface roughness and information depth, on the instrumental settings of the Microlab 310F used in our experiments [4]. The new GaAs/AlAs sample had the structure : (Thickness in atomic monolayers) : 48 GaAs/1AlAs/48GaAs/4AlAs/46GaAs/20AlAs/GaAs (substrate) with atomically sharp interfaces checked by transmission electron microscopy [4,5].

Argon (Ar), Xenon (Xe) and Sulfur Hexafluor-

ide ( $\text{SF}_6$ ) were used as Sputter Gases. The primary ion energy was varied from 5 keV to 500 eV with the ion incidence angles 70 and 85 deg. Ultrahigh depth resolution with ( $z=1.6$  nm) was obtained for  $\text{SF}_6$  and 500 eV, 85 deg. [6]. Application of the mixing-roughness-information depth (MRI) model for quantitative profile evaluation discloses the different contributions of atomic mixing, roughness and information depth to the depth resolution. Although at optimum conditions ( $\text{SF}_6$ , 500 eV, 85 deg.) the roughness is still dominating with an rms value of 0.7 nm, a record low value of 0.4 nm was found for the mixing zone length. This corresponds to less than two monolayers and opens the way to layer-by-layer sputtering without atomic mixing. Characterization of thin films and interfaces with atomic monolayer accuracy is an important contribution to our COE-project on nanostructures.

The theoretical model for the mixing influence modified to include surface roughness and information depth, the so called MRI-model (from Mixing - Roughness - Information Depth) was further developed and a Visual Basic version was set up which will be soon available for the members of the Surface Analysis Society of Japan [7]. High accuracy profile reconstruction can be achieved by careful experimental determination and theoretical modelling of the depth resolution function. One of the important parameters, namely surface roughness, can be determined by Atomic Force Microscopy (AFM). AFM measurements on the sample surface after profiling showed that the roughness is about a factor of two smaller than the MRI determined roughnesses. A major contribution to the MRI model was attributed to the gradually decreasing mixing zone. Further investigations, including the effect of original interface roughness, are planned using Glancing Incidence X-ray Reflectivity (GIXR). It is also planned to introduce nonlinear effects in the concentration-intensity relation and effects such as sputtering induced segregation in combination with preferential sputtering.

Depth profiling using Auger electron spectroscopy evaluation with respect to the chemical bonding state was used to analyze the formation of silicides in Si samples implanted with energetic Ca and Mg ions by ion induced thin film reactions. This research is part of an ongoing cooperation with the Electrotechnical Laboratory in Tsukuba.

**Keywords:** Depth Profiling, Depth Resolution, Thin Films, surfaces, Interfaces, Ion-Solid Interactions, Sputtering, Auger Electron Spectroscopy, Atomic Force Microscopy (AFM)

#### Related Papers :

- [1] S. Hofmann  
Sputter depth profiling of thin films High Temp. Materials and Processes 17, 13-28 (1998)
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Quantitative Auger electron spectroscopy in sputter depth profiling Vacuum 48, 607-612 (1997)
- [3] Ultimate depth resolution in sputter profiling J. Surface Analysis 3, 389-393 (1997)
- [4] S. Hofmann, K. Min and J. Schubert  
Depth Profiling: High accuracy profile reconstruction using experimental and theoretical depth resolution functions. in: Proceedings of ECASIA 97, Gothenburg, eds.: I. Olefjord, L. Nyborg and D. Briggs, Wiley, Chichester (1997) pp. 419-422
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Ultrahigh resolution in sputter depth profiling with Auger electron spectroscopy using ionized  $\text{SF}_6$  molecules as primary ions Jpn. J. Appl. Phys. 32, L758-L760 (1998)
- [7] S. Hofmann, Applications of the MRI-model in sputter depth profiling J. Surface Analysis 4, 9 (1998)

#### 46 A Study on the Durability of Coatings on Structural Materials

*T. Kodama, H. Baba, A. Tahara, and H. Katayama*

[April 1996 to March 1998]

##### 1) Atmospheric Degradation and Corrosion Resistance of Organic-coating

Most of steel structures are used under a painted condition in the atmosphere partly because of esthetic reasons and partly for corrosion protection. The degradation rate of organic-coatings is much faster in outdoor atmosphere than indoor, since ultraviolet (UV) rays of sun light plays a great role in the scission process of polymer coatings. In this study, the degradation process for alkyd and epoxy coatings is regularly monitored by gloss retention. Ac impedance has been also applied to study the corrosion protection of organic coatings. Exposure test was conducted to evaluate atmospheric degradation and corrosion resistance of alkyd and

epoxy coatings. The gloss of all coatings was measured at regular intervals, and some samples were collected at different periods of exposure time for the measurement of contact angle, ac impedance and surface analyses. The pigmented coatings showed high level of corrosion resistance owing to surface segregation of pigments even after the gloss retention and the contact angle decreased to the minimum level. Corrosion resistance started to decay, at the time when the loss of pigment started. On unpigmented coatings, on the other hand, cracks were observed to propagate in the early stage of exposure: showing poor corrosion resistance. A mechanism of atmospheric degradation is proposed based on impedance data. It is demonstrated that AC impedance is a very powerful tool to evaluate atmospheric degradation and corrosion resistance of organic-coatings.

## 2) Organometallic Coating and its Chemical Bonding to Metal

Two different methods were used for improving the anticorrosive characteristics of organic films on copper; potentiostatic anodization which accelerates polymerization of thiol radicals, resulting in improved adhesion properties of the film and film production by anodic reaction of copper, and modification of triazinedithiol (TDT). In the latter case alkyl amino groups having a hydrophobic group of a long carbon chain was introduced to the TDT as a substitution radical (-R), which modified the copper surface to give a highly corrosion-resistant and water-repellent nature.

In this study, we have focused on TDT having-N ( $C_8H_{17}$ )<sub>2</sub> as a substitution group (-R), for which the corrosion inhibition effect has been reported elsewhere. We evaluated the effect of electrode potential, solution concentration and electrolysis time on the corrosion inhibition of copper. Electrochemical analyses of the anodized films were carried out, and the relationship between the carbon number in the substitution group of TDT was also investigated.

When copper was anodized in solutions containing various concentrations of ( $C_8H_{17}$ )<sub>2</sub>N-TDT the anodic polarization curves showed duplex current peaks. By anodizing copper in 5 mM ( $C_8H_{17}$ )<sub>2</sub>N-TDT solution at the potential equal to the second current peak, 1.25 V (SCE), the polymerization of the thiol groups proceeded with the simultaneous outward growth of film, which resulted in the corrosion inhibitive properties of the copper. By the introduction of long alkyl chains to TDTs, highly corrosion-resistant and water-repellent films were obtained.

## 3) Evaluation of Defects in Metallic Coating

For the measurement of electrode potential of metals covered with thin solution film, the Kelvin

technique was applied, in which a silver wire of 0.5 mm diameter with a AgCl coating was used as the Kelvin probe for potential detection. The probe placed in air was oscillated sinusoidally with respect to metal surface. It is thus possible to measure relative electrode potential without touching the electrolyte. A galvanic couple model comprising of iron and zinc was used for demonstrating potential transition at the interface. Experiments were carried out under pure water to 0.5% NaCl solution layer with 100 and 400  $\mu$ m thick. Under the solution films, potential on zinc was about -1.2 V while that on iron was about -0.7 V. Under the pure water film of 100  $\mu$ m thick, the zone of potential transition was 3 to 4 mm wide from the boundary into Fe surface. The width of potential transition was influenced by both solution film thickness and salt concentration. The width of potential transition zone under the film of the NaCl solution was larger than under pure water. This indicates that galvanic effect reaches further into Fe surface in salt solutions. The effective distance of corrosion protection by zinc is proportional to a square root of  $\delta/\rho$ , where  $\rho$  is a resistivity and  $\delta$  is a thickness of a solution film. Potential distribution at Zn/Fe boundary was explained in terms of "transmission line model".

**Keywords:** atmospheric degradation, corrosion, organic-coatings, exposure test, ac impedance, pigments, Kelvin probe, galvanic couple, transmission-line model

## 47 Preparation of Ionic Conductors by Pressurized Sintering

*H. Nakamura, Team of Director of Special Research*

[April 1995 to March 1998]

There have been many reports on solid-state oxygen ionic conductors that can be used for an oxygen sensor. For monitoring pollutants in air such as SO<sub>x</sub> and NO<sub>x</sub>, there is an increasing demands for stable sensors consisting of solid state electrolytes or ionic conductors. Very few reports have yet been available partly because of the difficulty in the search of compounds that show chemical selectivity to specific chemical species. Moreover the compounds that show selective affinity to pollutants are liable to thermal decomposition at elevated temperature. In our previous research, however, we have shown that several solid-state and glassy electrolytes gave electrochemical potential indicative of SO<sub>x</sub> concentration in air: The electrolyte consisted of oxides and sulfates. It was demonstrated that the sensor was

successfully applied for the monitoring SOx level in exhaust gases.

In this study, for the synthesis of complex solid-state electrolytes a technique of pressurized sintering was developed to suppress the thermal decomposition of otherwise readily degradable compounds (especially nitrates). The technique allowed the synthesis of solid electrolytes consisting of a solid solution that shows complete ionic conduction and sufficiently high conductivity even at relatively low temperatures. The solid-state electrolyte thus prepared showed sufficient selectivity for the quantitative measurement of corrosive gases and could be applied for the monitoring of NOx gas.

**Keywords :** pressurized sintering, ionic conductor, solid electrolyte, electrical conductivity

## 1st Research Group : Super conducting Materials

### 48 Understanding of the Mechanism of Superconductivity in High Temperature Superconductors

*K. Hirata, T. Mochiku, H. Takeya, M. Tachiki, X. Hu, T. Yokoya and T. Takahashi 1st Research Group*

[April 1995 to March 2000]

To understand the mechanism of superconductivity in high temperature superconductors (HTS), enormous amount of experiments and theoretical analysis have been performed after the discovery. Recently, high quality single crystals of HTS have been grown and the experimental data have become more reliable and definite. In our group, single crystals of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  (Bi-2212),  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  and  $\text{YNi}_2\text{B}_2\text{C}$  with high quality in crystallinity have been grown by travelling solvent floating zone technique. Among of them, Bi-2212 single crystals were used for high-resolution angle-resolved photoemission spectroscopy (ARPES). Preparing samples with a different kind of hole-doping from under-doped to over-doped, careful ARPES experiments have been performed and remarkable results have been obtained. We have found the energy gap in normal and superconducting state of these samples. In optimally doped samples, the gap closes in the vicinity of the superconducting transition temperature ( $T_c$ ). However, in the under-doped samples, the gap still remains above  $T_c$  and closes in the normal state. The magnitude of the gap increases with decreasing a carrier doping. The gap has a finite

density of states in normal state, which is therefore called as a “pseudo-gap”. The pseudo-gap seems to be changed continuously to the superconducting gap ( $\Delta$ ). Furthermore, it is noted that the magnitude of superconducting gap is irrelevant to the doping level, whereas the  $T_c$  is different with a carrier doping. So, this indicates that  $2\Delta/k_B T_c$  ( $k_B$ ; the Boltzmann constant) increases with decreasing a carrier doping. By ARPES measurements, we could obtain the wave-number dependency of the “pseudo-gap”. The symmetry of the “pseudo-gap” is same as that of the superconducting gap. So, it suggests that the origin of the “gap” is the same in superconducting and normal states. This will be a great clue for further development to understand the mechanism of superconductivity in HTS.

This research project aims also to understand the characteristic phenomena observed in the superconducting state of HTS in a magnetic and an electric field. They may mainly come from their layered structures, composed of the superconducting  $\text{CuO}_2$  layers sandwiched with the insulating or less-conductive layers. The electrons or holes are confined into a quasi-two-dimensional state, which causes the electronic state to be anisotropic. The Josephson effect has been found as an intrinsic nature of these materials in the voltage-current characteristics. The characteristics are studied by numerical analysis to calculate the differential equation of the phase in the Josephson current. The multi-branches in the characteristics were well reproduced by numerical calculations, assuming the charge distribution in the superconducting layers.

The magnetic phase diagram of the HTS also reveals quite different features from those of the conventional superconductors. One of the distinct results is the distribution of the vortices, when a magnetic field is applied along  $\text{CuO}_2$  layers. It was considered that the vortices distribute according to the penetration length of the magnetic fields along c-axis and perpendicular to the axis, and the distorted Abrikosov lattice may be formed. However, by the numerical analysis and Monte-Carlo simulation, a chain-like distribution has been obtained. This was also confirmed experimentally by a Bitter Pattern technique. These results will make the Josephson plasma and the Josephson current perpendicular to the c-axis to be reanalyzed and reconsidered.

Understanding these characteristics phenomenologically, we will reconstruct and refine the model to make clear the real mechanism of superconductivity in HTS and the physical properties of HTS in electromagnetic field.

This research has been made in collaboration with Tohoku University.

**Keywords:** high temperature superconductors, mechanism of superconductivity, magnetic & electronic properties

**Publications ;**

Anisotropy and Doping-Dependence of Energy Gap in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ : T. Yokoya, H. Ding, T. Takeuchi, T. Takahashi, J. Campuzano, M. Randeria, M. Norman, T. Mochiku, and K. Kadowaki, *Advances in Superconductivity IX*, Springer Verlag Tokyo (1997), p. 133-137.

Destruction of the Fermi Surface in Underdoped High TC Superconductors: M. Norman, H. Ding, M. Randeria, J. Campuzano, T. Yokoya, T. Takahashi, K. Kadowaki, P. Guptasama, and D.G. Hinks, *Nature* 392 (1998) 157-159.

**49 Study on the Pinning Mechanism of Vortices in High Temperature Superconductors**

*K. Hirata, T. Mochiku and H. Takeya 1st Research Group*

[April 1995 to March 2000]

High temperature superconductors (HTS) have been studied intensively on their physical properties after the discovery. Distinct features of these materials have been obtained, compared with the conventional metal or intermetallic superconductors. There have been found a higher critical temperature, a higher critical current density and a higher upper critical magnetic field. Two dimensionality of their crystal structure is a significant feature, which has been recently recognized in superconducting properties. For the application of these materials, it is really essential to use at liquid nitrogen temperature 77K. However, the upper critical current density, for example, is reduced drastically under a magnetic field. Superiority to the conventional superconductors can be found only around liquid He temperature. The reason is that there have been found no pinning centers effective at 77K or at higher temperatures. However, most of the obstacles come from the nature of the HTS themselves, for example, two-dimensional electronic states, large anisotropy, short coherence length, superconducting quantum fluctuation, etc. Therefore, it is of necessity for the application of the HTS to understand the pinning mechanism of vortices in HTS single crystals at first, and then, to introduce effective pinning centers into the materials artificially.

This research program aims to find the effective pinning centers by understanding the pinning mechanism in these superconductors. First of all, we have to know the intrinsic properties of high quality

single crystals. We have developed our crystal growth techniques with various methods. Based on the fundamental studies on the high quality single crystal, we have introduced the pinning centers, artificially, such as defects (dislocations, columnar defects by a heavy ion irradiation and other phases), impurities. Recently, we have found distinct features in the heavy-ion irradiated Bi-2212 single crystals. By measuring the Josephson plasma resonance, new phase boundary has been observed above the irreversibility line, in which the vortices are considered to be in the liquid state. The new boundary exists at  $B_\phi/3$  ( $B_\phi = n \times \Phi$ ;  $n$ : density of columnar defects,  $\Phi$ : magnetic flux quantum), which is independent to temperature. Below the boundary, the vortices are in the liquid state. Above that, the coupling between the superconducting layers becomes strong, which indicates that the vortices become a line-like structure with increasing magnetic field. This field-induced transition has been also confirmed by the Monte-Carlo simulations. Furthermore, it has been shown that this boundary penetrates into the irreversibility region independent to temperature. This was observed as a peak effect at the magnetic field of  $B_\phi/3$  in the magnetization curves.

Magnetic phase diagram of single crystalline  $\text{YNi}_2\text{B}_2\text{C}$  has been studied by ac susceptibility and dc magnetization measurements. At higher magnetic fields, peak effect has been observed clearly, and, at lower fields, a vortex line lattice melting has been appeared in ac susceptibility. This characteristics are studying as a general property of type II superconductors, when the crystallinity becomes better with less pinning centers.

Arrangement of the vortices in HTS has been observed by the Bitter decoration technique. When the magnetic field is applied perpendicular to the superconducting layers, clear Abrikosov lattice has been observed. Inclining the magnetic fields to the layers, a chain-like structure appears at some angle besides the Abrikosov vortex lattice. The structure is analyzed in relation to the interaction between the vortices and the layerness of the materials. A distinct distribution of vortices appears, when the magnetic field is applied parallel to the layers. Arrangement of the vortices is not a distorted Abrikosov vortex lattice, considered from the penetration length of the fields perpendicular and parallel to the layers. It shows meshes of vortices line. This suggests that the interaction among the vortices is somewhat different from the model considered before, and, the Josephson plasma and the Josephson current are reconsidered to take account of the distribution of the vortices.

This research has been made in collaboration with Tokyo Institute of Technology.

**Keywords :** high temperature superconductors, vortex pinning, vortex dynamics

### Recent Publications

Coupling Transition of Vortex Liquid in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  with Columnar Defects, M. Kosugi, Y. Matsuda, M.B. Gaifullin, L.N. Bulaevskii, N. Chikumoto, M. Konczykowski, J. Shimoyama, K. Kishio, K. Hirata and K. Kumagai, *Phys. Rev. Letters* 79 (1997) 3763-3766.

Magnetization Measurements on  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  Single Crystal with Columnar Defects, K. Hirata, T. Mochiku and N. Nishida, *Advances in Superconductivity X*, Springer-Verlag Tokyo (1997) 553-556.  
Peak Effect and Vortex Line Lattice Melting in Single Crystalline  $\text{YNi}_2\text{B}_2\text{C}$ , K. Hirata, H. Takeya, S. Miyamoto, T. Mochiku and K. Togano, *Chinese J. of Physics* 36 (1998) 215-221.

### 50 Fabrication of Intrinsic Josephson Junctions and Evaluation of their Physical Properties

*K. Hirata, T. Mochiku and H. Takeya 1st Research Group*

[April 1995 to March 2000]

Most of high temperature superconductors have been found to show a large anisotropy in their magnetic and electronic properties, in contrast with the conventional metal or intermetallic superconductors. This anisotropy comes from their crystallographic structures, which are composed of superconducting  $\text{CuO}_2$  layers, sandwiched with the insulating layers or less-conductive layers. The electrons or holes are confined in two-dimensional system, and the coherence length perpendicular to the layers becomes very short ( $\sim 1 \text{ \AA}$  or less for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  (Bi-2212)). This structural anisotropy causes interesting phenomena. The dc-Josephson effect has actually been observed in the voltage-current characteristics, and the ac-Josephson effect has recently been observed, too. High temperature superconductors is confirmed to have the Josephson effect as their own properties without any artificial insulating layer. The layeriness of these materials leads also to the peculiar characteristics in magnetic and electronic properties; magnetic phase diagram, the Josephson plasma resonance, second peak effect (fish tail), and so on.

This research program is planned to utilize the intrinsic properties of high temperature superconductors for the application, such as the Josephson effect, and to find a new characteristic feature in these materials under various circumstances. For this purpose, it always becomes a key to grow a large

single crystal of high quality. We have developed our technology in growing single crystals of high temperature superconductors mainly by traveling solvent floating zone method. Large single crystals have been obtained with a size of 5mm in width, longer than 10mm in length. The evaluation of the crystallinity has been performed to make a feedback to the crystal growth. By the measurements of a double crystal X-ray diffraction, single crystal of Bi-2212 shows about 70 arcseconds in the full width of the half maximum. There is also less misalignment in the diffraction plane, which was confirmed by a double crystal X-ray topography. Magnetic and electronic properties (resistivity under magnetic fields, ac susceptibility, dc magnetization, Hall coefficients, heat capacity, etc) are measured on these single crystals in normal and superconducting state.

For the current-voltage ( $I-V$ ) measurements, a fine structure is essential to avoid a heating effect. We have fabricated the mesa-structured junctions by an ion-milling with a diameter from 30 to 6  $\mu\text{m}$  and with a height from 200 to 50 nm on the cleaved surface of Bi-2212 single crystals. Measuring on the mesa-structured junctions, multi-branches have been obtained in the  $I-V$  curves without applying a magnetic field and a microwave. Under the microwave, a Shapiro step, which is usually observed in the normal Josephson junction, has not been seen in this junctions. Instead, a fine structure in the  $I-V$  curves has been found at low voltage (current) or zero crossings region. This fine step is considered as an influence of the coherent vortex flow. Even the junction is smaller than the magnetic penetration depth, there might be a phase variation of Josephson current in this mesa-type structure. To understand the step, the measurements has been done under a magnetic field. But, there have been found no fine step at various magnetic fields. Under magnetic fields and microwave, there are still ambiguous characteristics observed. Further experiments will be needed to develop a technique for the fabrication of micro-structured junctions.

Based on these results, the intrinsic properties of the Josephson junction in HTS will be analyzed numerically by a computer simulation, and, for the application of HTS, new function will be proposed.

This research has been made in collaboration with Technical University of Munich.

**Keywords :** high temperature superconductors, intrinsic Josephson junction, Josephson devices

### Recent Publication

Intrinsic Josephson Junctions under Microwave Irradiation. W. Prusseit, M. Rapp, K. Hirata and T. Mochiku, *Physica C* 293 (1997) 25-30.

## 51 Computer Simulation Study on the Mechanism of High Temperature Superconductivity

*K. Hirata, T. Mochiku, H. Takeya, M. Tachiki, X. Hu, R. Sugano, T. Onogi, Y. Matsuda, T. Koyama and Y. Ohashi 1st Research Group*

[October 1997 to March 1999]

This research project aims to study theoretically on the physical properties of high temperature superconductors (HTS) in a magnetic field and an electric field, by using a computer simulation. For this purpose, we have developed algorithm and programs for the calculation by super-computer to compare quantitatively with experiments. We have performed the calculation (Monte-Carlo and molecular dynamics method), based on the Lawrence-Doniach model and London-Maxwell model, which are assumed from the layer-structures of HTS. To enhance the critical current density, for example, we have tried to understand the quantum vortex state, and the Josephson plasma, which may be applied to communications. From these studies, following significant results are obtained ;

1) In heavy-ion irradiated Bi-2212 single crystals, it was shown by the plasma resonance experiments that the vortices are in a coupled state along the c-axis with increasing a magnetic field. This was well understood by the numerical analysis that the transition occurs at  $B_{\phi}/3$  ( $B_{\phi} = n \times \Phi$ ;  $n$ : density of columnar defects,  $\Phi$ : magnetic flux quantum) both in the reversibility and irreversibility region. From the analysis, anomalous peak effect has been confirmed by the precise magnetization measurements.

2) First order phase transition of the vortices is obtained from the Abrikosov vortex line lattice to the liquid state as a melting in thermodynamics by computer simulation. This is well coincided with experiments. Furthermore, it is shown that the liquid is in a decoupled state without any coherence in superconductivity between the superconducting layers.

3) Josephson plasma mode has been analyzed numerically on the frequency-dependence of reflectivity and transmissivity in the magnetic and electric field, when the magnetic field is applied parallel to the superconducting layers. It is shown that reflectivity and transmissivity oscillate as a function of frequency, when the frequency is larger than the plasma frequency. It is concluded that this is caused by the reflection and interference of the transverse electro-magnetic wave to the both surfaces. It is also proposed that generation of the microwave is possible to excite the plasma wave by virtue of the vortex flow with flowing a current perpendicular to the superconducting layers.

4) In the superconducting state, Goldstone mode (collective excited mode) has been analyzed, which is caused by a spontaneous breakdown of the continuous symmetry. Taking account of the Landau damping of quasi-particles, which was not considered well before, it is shown that the Goldstone mode can be observed only in a dirty system.

This research has been made in collaboration with Advanced Research Laboratory at Hitachi, Ltd, Institute for Solid State Physics at Tokyo University, Research Institute for Materials at Tohoku University and Tsukuba University.

**Keywords :** high temperature superconductors, computer simulation, mechanism of superconductivity, vortex pinning, Josephson plasma

### Recent Publications

Field-Driven Coupling Transition in the Vortex State of Irradiated  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ : Computer Simulation Study, R. Sugano, T. Onogi, K. Hirata and M. Tachiki, Phys. Rev. Letters 80 (1998) : 2925-2928.

## 52 Development of High-Tc Oxide Superconducting Wires and Tapes

*H. Kumakura, 1st Research Group*

[April 1995 to March 1999]

Bi-based oxide superconductors are very promising for high-field superconducting magnets because of their extraordinarily high upper critical fields  $H_{c2}$  and high irreversibility fields. In case of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  (Bi-2212), c-axis grain oriented microstructure is easily obtained by slow solidification from a partially molten state on silver tapes. This grain alignment significantly increases the critical current density,  $J_c$ , even in magnetic fields well above 20T where it is difficult to use conventional metallic superconductors because of their lower  $H_{c2}$ . We have developed high- $J_c$  Bi-2212/Ag superconducting tapes by the combination of this melt-solidification method and a dip-coating method.

Recently, we found that the application of Pre-Annealing and Intermediate-Rolling (PAIR process) before the melt-solidification improved the microstructure of Bi-2212 layer and significantly enhanced  $J_c$  values. This PAIR process is promising for the fabrication of high- $J_c$  long tape conductors. First, an oxide/Ag tape was prepared by the dip-coating using a slurry containing Bi-2212 powder, and was pre-annealed in pure oxygen gas at a temperature between 800 and 880°C for 1 hour. By this pre-annealing, organic materials in the slurry were

completely removed from the oxide layer. Then, the pre-annealed tape was cold-rolled. The deformation rate of Bi-2212 layer was  $\sim 25\%$ . After the PAIR process, the conventional melt-solidification was applied in order to obtain grain oriented microstructure of Bi-2212 phase. By the application of this PAIR process,  $J_c$  values were significantly enhanced. The tapes prepared with PAIR process showed  $J_c$  values above  $3 \times 10^5 \text{ A/cm}^2$ , while the tapes prepared with only the conventional process (without PAIR process) showed  $J_c$  values of  $1\text{-}1.5 \times 10^5 \text{ A/cm}^2$ .

Ac susceptibility measurement indicated that the superconducting transition width of the PAIR processed tape was less sensitive to ac field amplitude than that of the conventionally processed tape. This result suggests that the grain coupling of Bi-2212 is improved by the application of the PAIR process. This improvement in the grain coupling contributes to the  $J_c$  enhancement mentioned above. We observed the microstructure of the Bi-2212 layer using a scanning electron microscope. The amount of impurity phases in the PAIR processed tapes was smaller than that in the tapes prepared without the PAIR process. Moreover, the uniformity of the Bi-2212 layer was significantly improved by the application of the PAIR process. The rolling process decreased the Bi-2212 layer thickness, indicating the increase of the Bi-2212 layer density. In the PAIR processed tapes, more highly aligned grain structure was observed. This higher grain alignment can be explained by both the smaller amounts of impurity phases and smaller Bi-2212 layer thickness.

**Keywords:** Bi-based oxide, pre-annealing, cold-rolling, grain coupling

#### Related Papers

1. H. Kumakura, H. Kitaguchi, K. Togano and N. Sugiyama, "Effect of high oxygen partial pressure heat treatment on the superconducting properties of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x/\text{Ag}$  tapes", *J. Appl. Phys.*, 80 (1996) 5162-5168.
2. H. Kumakura, H. Kitaguchi, K. Kato, K. Nomura, N. Inoue, K. Inoue and K. Togano, "Development of Bi-2212 tapes and coils applying the dip-coating process", *Adv. Cryogenic Engr.*, 42 (1996) 777-784.
3. H. Miao, H. Kitaguchi, H. Kumakura and K. Togano, "Fabrication of high current carrying Bi-2212/Ag superconducting tapes by the pre-annealing and cold rolling process", *Cryogenics*, 38 (1998) 257.

### 53 Development of a Superconducting Magnet for Magnetic Separation

*H. Kumakura, 1st Research Group*

[April 1995 to March 1999]

Magnetic separation has been used for many years to correct magnetic particles such as iron ore. For the efficient magnetic separation, field gradient  $\nabla B$  should be large because the magnetic force is proportional to  $\nabla B$ . High Gradient Magnetic Separators (HGMS) use a finely divided ferromagnetic matrix to create large gradient and to correct even paramagnetic materials. In most cases, however, conventional copper electromagnets are being used for HGMS, and the magnetic fields available are limited to  $\sim 2$  Tesla by the saturation of iron. In addition, generation of magnetic fields in a large volume is costly in terms of electric power, iron and copper. For example, a large electromagnet for kaolin separation may consume as much as 500kW electric power, all of which is converted into heat. For these reasons superconducting magnets for magnetic separation were proposed as early as 1970. The advantage of superconductivity is the lack of electric power dissipation at a constant field. However, conventional metallic superconducting magnets usually require expensive liquid helium for cooling, which hinder the significant decrease of the running cost. Furthermore, separator magnet users are not accustomed to use liquid helium. High-Tc oxide superconductor is promising for a helium-free magnet. Cryocooler can be used effectively to cool down an oxide superconducting magnet.

In this research program, we will develop the prototype of an oxide superconducting magnetic separator which can be operated with a cryocooler. Bi-based oxides seem to be most promising for the magnet. Recently, we have fabricated small  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  (Bi-2223) pancake magnet with 79mm bore, 130mm outer diameter and 130mm height using 20m-long Bi-2223 tape conductors, and tested it using a GM cryocooler in order to investigate the applicability of the Bi-based oxides to the magnetic separation system. The voltages and temperatures of the pancake magnets were measured as a function of time at various operating currents. At 30K, the maximum operating current density was  $8,600 \text{ A/cm}^2$ . This current generated a field of 1 Tesla at the center of the magnet. At 20K, we repeated the excitation of the magnet up to 1.1 Tesla, and we found the magnet was stably operated. All these results indicate that a Bi-2223 magnet is promising for the magnetic separation system. We have started the scale-up of the Bi-2223 tape conductors to construct a prototype magnet for a magnetic separation system.

**Keywords:** Bi-based oxide superconductors, critical

current density, cryogen-free magnet, stability

### Related papers

1. K. Kato, J. Sato, S. Kuma, H. Kitaguchi, H. Kumakura, K. Togano and N. Inoue, "Bi-2212 tapes and coils fabricated using Ag-Mg-Zr substrates" *Adv. Superconductivity*, VIII (1996) 937-940.
2. T. Hasegawa, Y. Hikichi, T. Koizumi, A. Imai, H. Kumakura, H. Kitaguchi and K. Togano, "Fabrication and characterization of Ag-Mg sheathed Bi-2212 multilayer superconducting tapes and coils", *Adv. Superconductivity*, IX (1997) 871-874.

## 54 Grain boundary control and $J_c$ enhancement of Bi-2212/Ag tape conductors

H. Kumakura, 1st Research Group

[April 1998 to March 1999]

A Bi-2212/Ag composite tape is one of the promising materials for the application to superconducting power devices. C-axis grain oriented Bi-2212 layer is easily obtained by the slow cooling from the melting state, and this grain-oriented microstructure can sustain high critical current density ( $J_c$ ). We have been engaged in the development of the Bi-2212/Ag tape conductors by applying a dip-coating process and a powder-in-tube process, and succeeded in the fabrication of small coils that can generate high magnetic fields in combination with a conventional superconducting magnet. The microstructure and the superconducting properties of Bi-2212/Ag tapes are influenced by the heat-treatment parameters. Oxygen partial pressure ( $pO_2$ ) during the heat treatment is one of the parameters on which  $J_c$  of the tape sensitively depends.  $J_c$  of the Bi-2212/Ag tape increases with increasing  $pO_2$  if the tape is heat treated at an optimum temperature for each  $pO_2$  value. However, the origin of this  $J_c$  increase is not clear. The volume fraction of Bi-2212 phase in the oxide layer increases with increasing  $pO_2$  for  $pO_2$  up to 0.2atm, but the volume fraction becomes almost constant for  $pO_2$  above 0.2atm. However,  $J_c$  for  $pO_2=1.0$ atm is obviously higher than that for  $pO_2=0.2$ atm. Ac susceptibility measurements indicate that the superconducting transition width becomes less sensitive to ac field amplitude with increasing  $pO_2$ , suggesting that the grain couplings of Bi-2212 are improved by the heat treatment under high  $pO_2$ . Preliminary observations using a transmission electron microscope (TEM) indicate that some Bi-2212 grain boundaries contain non-superconducting amorphous thin layers and that the population of

grain boundaries having amorphous layers decreases with increasing  $pO_2$ . This implies that the modification of grain boundary structure of Bi-2212 is possible by the  $pO_2$  control during the heat treatment.

In this study, we will make precise analyses on the grain boundary structure of the Bi-2212 prepared at various  $pO_2$  values using high-resolution TEM technique. We will measure the distribution of the misalignment angle of the boundaries having the amorphous layers, and we will analyze how the distribution changes with increasing  $pO_2$ . From the obtained results, we will discuss the possibility of the modification of grain boundary structure through the  $pO_2$  control and the possibility of the  $J_c$  enhancement by this modification of grain boundary structure.

**Keywords:** Bi-based oxide, oxygen partial pressure, grain boundary, amorphous layer

### Related Papers

1. H. Kumakura, H. Kitaguchi, K. Kiyoshi, K. Inoue, K. Togano, M. Okada, K. Fukushima, K. Tanaka, K. Kato and J. Sato, "Performance tests of Bi-2212 insert magnets fabricated by Ag sheath method and dip-coating method", *IEEE Trans. Appl. Supercon.* 7 (1997) 646-649.
2. H. Kumakura, H. Kitaguchi, K. Togano and N. Sugiyama, "Effect of high oxygen partial pressure heat treatment on the superconducting properties of  $Bi_2Sr_2CaCu_2O_x$ /Ag tapes", *J. Appl. Phys.*, 80 (1996) 5162-5168.
3. H. Fujii, H. Kitaguchi, H. Kumakura and K. Togano, "Effect of oxygen partial pressure on grain boundaries in Bi-2212/Ag tapes", *Physica C*, 282-287 (1997) 2567-2568.

## 55 Preparation of *In-plane* Textured Buffer Layers for $YBa_2Cu_3O_y$ Film Growth by Modified Bias Sputtering

M. Fukutomi, First Research Group

[April 1995 to March 2000]

Much work has been undertaken to develop techniques for fabricating  $YBa_2Cu_3O_y$  (YBCO) superconducting films on flexible metallic substrates using various buffer layers such as MgO and yttria-stabilized zirconia (YSZ). Since the quality of the YBCO films depends strongly on the crystallographic orientation of the buffer layers, control of grain orientation of the buffer layers is very important. In particular, since critical current density ( $J_c$ ) is primarily limited by the grain boundary misorientation of YBCO films, preparation of buffer layers with an

*in-plane* texturing on which YBCO films epitaxially grow is vital to obtaining high  $J_c$  superconducting films. Recently, an ion-beam assisted deposition (IBAD) process has been developed to grow *in-plane* textured YSZ buffer layers on polycrystalline metallic substrates, resulting in a significant step towards fabrication of high- $J_c$  YBCO coated conductors. Success in obtaining high- $J_c$  films by the IBAD process was followed by the recent marked development in processing textured YBCO coated conductors. In the IBAD process, the occurrence of *in-plane* texturing in the films is believed to be due to directional ion-bombardment effects during deposition. This has led us to the development of modified bias sputtering (MBS) process, which enables to deposit *in-plane* textured YSZ thin films on polycrystalline metallic substrates as a buffer layer for deposition of YBCO films. The principle of developing an *in-plane* texturing by this technique is basically the same as that of ion beam assisted deposition; an *in-plane* texturing occurs by *off-normal* ion beam bombardment because of the higher sputtering yields of all orientations other than the channeling direction. In our process, however, a flux of energetic particles impinging on the growing film is generated using specially devised negatively biased electrodes installed in a magnetron sputtering system in stead of a separate ion-source in IBAD. So far a X-ray  $\Phi$ -scan width of  $18^\circ$  was attained for YSZ films on Hastelloy tapes. Epitaxial YBCO films grown on these buffer layers using pulsed laser deposition showed the  $J_c$ 's exceeding  $10^5 \text{ A/cm}^2$  (77K, 0T). The optimization of the bias sputtering technique has been done to obtain the textured films on large area substrates. Although the proposed process offers a very convenient method to grow textured films, more efforts must be made to increase growth rates of the films (currently  $\sim 0.1 \text{ nm/s}$ ) for large-scale applications of YBCO films.

**Keywords:**  $\text{YBa}_2\text{Cu}_3\text{O}_y$  film, *in-plane* textured buffer layer, modified bias sputtering critical current

### Recent Publications

Preparation of In-Plane Textured Buffer Layers for  $\text{YBa}_2\text{Cu}_3\text{O}_y$  Film Growth by Modified Bias Sputtering, M. Fukutomi, M. Saitoh, K. Komori And K. Togano, Applied Superconductivity, 4 (1996): 447-454.

Fabrication of  $\text{YBa}_2\text{Cu}_3\text{O}_y$  Thin Films on Textured Buffer Layers grown by Plasma Beam Assisted Deposition, M. Fukutomi, S. Kumagai and H. Maeda, Aust. J. Phys., 50 (1997): 381-389.

## 56 Fundamental research on new materials of function-harmonized oxides

M. Yata, T. Hatano, A. Ishii 2nd Research Group, 1st Research Group  
[April 1997 to March 1999]

Metal oxides exhibit various interesting properties such as dielectricity, ferroelectricity, superconductivity, giant magnetoresistance and so on. The combination of these properties gives one the opportunities to create new functional materials towards "oxide electronics". In order to achieve the harmonic integration for functional metal oxide, the growth control of metal oxide layers with atomic layer accuracy is necessary. Recently the techniques for unit-cell layer-by-layer growth or atomic layer-by-layer growth of metal oxide films have been progressed by modifying molecular beam epitaxy. The growth mechanism involving oxidation reactions, however, has not been understood in detail.

We have investigated the oxidation reaction process on Cu surface as well as formation mechanism of Cu-O 2-dimensional lattice using supersonic molecular beam technique, low energy electron diffraction and Auger electron spectroscopy.  $\text{O}_2$  molecule adsorbs dissociatively on Cu (001) clean surface at the surface temperatures above room temperature (R.T.). The initial dissociative sticking probability of  $\text{O}_2$  molecule increases with the translational energy of incident  $\text{O}_2$  molecule. The probability is dependent of incident angle of  $\text{O}_2$  molecule and the scale follows a normal energy scaling. At the initial stage O atoms adsorb randomly on the Cu surface. The reconstructed surface structure ( $2\sqrt{2} \times \sqrt{2}$ ), namely Cu-O 2-dimensional lattice, is formed in a disorder-order phase transition with increasing coverage, where critical nucleation takes place at an oxygen coverage 0.34. The saturation coverage in the ( $2\sqrt{2} \times \sqrt{2}$ ) surface is 0.5. Further adsorption of oxygen forms  $\text{Cu}_2\text{O}$  clusters on the ( $2\sqrt{2} \times \sqrt{2}$ ) surface. The higher surface temperature and the lower translational energy of the incident  $\text{O}_2$  molecule enhance the formation rate of the  $\text{Cu}_2\text{O}$  cluster. If the surface temperature is low and the translational energy of the incident  $\text{O}_2$  molecule is enough high, the oxygen adsorption stops after the completion of ( $2\sqrt{2} \times \sqrt{2}$ ) surface reconstruction and  $\text{Cu}_2\text{O}$  clusters are not formed on the surface, which we call "self-limiting reaction". Thus it is found that the initial oxidation process can be controlled by controlling the translational energy of the incident  $\text{O}_2$  molecule and surface temperature.

**Keywords:** Surface reaction dynamics, Metal oxides, Supersonic molecular beam

## Recent Publications

- 1) Kinetics of oxygen surfactant in Cu (001) homoepitaxial growth, M. Yata, H. Rouch and K. Nakamura, *Phy. Rev. B* 56 (1997) : 10579-10584.
- 2) Surface segregation of O atoms on Cu (001)-(2 $\sqrt{2}\times\sqrt{2}$ )-O during Cu homoepitaxial growth, M. Yata, H. Houch and K. Nakamura, *J. Surf. Sci. Soc. Japan*, 19 (1998) : 92-97.
- 3) Role of oxygen adatoms on homoepitaxial growth of Cu (001), M. Yata, H. Rouch and K. Nakamura *Mater. Res. Soc. Proc.*, 528 (1998) : 59-65.
- 4) An interpretation on the temperature dependent growth mode of Cu on Cu (001)-(2 $\sqrt{2}\times\sqrt{2}$ )R45°-O surface, K. Nakamura and M. Yata, *Surface Sci.*, 417 (1998) : 268-280.
- 5) Control of the initial oxidation on Cu (001) surface by selection of translational energy of O<sub>2</sub> molecules, M. Yata and H. Rouch, *Appl. Phys. Lett.*, 75 (1999) : 1021-1023.

## 57 In situ TEM Observation and Structural Analysis of High Tc Superconductors for Fusion Reactor at Low Temperatures

*T. Kimoto, 1st Research Group*

[April 1994 to March 1999]

Few principles for the development of high Tc superconductors for fusion reactors have been found because the mechanism of their superconduction has not been understood so far. The image resolution limit of a transmitted electron microscope (TEM) is extremely low at low temperature because of specimen drift due to the unstable temperature control and specimen vibration due to evaporation and circulation of liquid helium. The first objective of our research is to improve the resolution limit of TEM imaging at low temperatures in order to observe O and Cu atoms in the future in high Tc superconductors near or above Tc where abnormal lattice distortion occurs which could reveal the mechanisms of their superconduction. The other objective is to develop the method to examine the long-range order (LRO) parameter in the microscopic region of high Tc superconductors and to develop the analytical method to measure the abnormal lattice distortion from the convergent beam electron diffraction (CBED) pattern.

We developed in 1994 the high-speed CCD camera system whose minimum exposure time is 50 nano sec. It was found that a short-time exposed imaging from a drifting specimen improves TEM resolution at low temperatures to some extent, but that the

reduction of S/N ratio due to the short-time exposure makes the image unclear. We developed a new imaging system for TEM and software for image processing to solve this problem in 1995 and 1996. By using the developed imaging system, we take the short-time exposed TEM images of 1018 $\times$ 1000 pixels sequentially at a speed of 5 images/sec. With the developed software for image processing, the computer calculates the distance and direction of the image-shift between images, which are taken from a drifting specimen with the developed imaging system, shift these images to be adjusted with each other and then finally add these shifted images to get a clearer image by increasing S/N ratio. A new method to control the specimen temperature by controlling liquid helium circulation instead of using a heater was also developed to suppress the specimen vibration. However, the new temperature control method increases the speed of specimen drift because the specimen temperature becomes more unstable. In 1997, the new software was developed which enables the computer system including the A/D converter (DASBOX) and the sun workstation to suppress the drift of TEM image by controlling the magnetic field for the TEM function of "image shift", which shifts TEM image very slightly, even if the TEM specimen drifts. By using the newly developed software for computer control of the function of "image shift", the previously developed imaging system mentioned above, and the new method for temperature control, we are able to take a fine and high-resolution TEM image at low temperatures.

We started in 1996 to develop a new type of electron source by using a CW laser, which could produce high intensity electron beam for TEM. The new type of electron source could not only improve S/N ratio of the short time exposed TEM image but also improve the abilities of a TEM, an electron accelerator, X-ray generator because it produces electron beam of high intensity. For this purpose, we constructed the device to produce an CW Ar ion laser and developed a vacuum chamber to examine the fundamental technical problem such as converging of a laser beam, cooling of the area irradiated by a laser beam with the Peltier cooling method, and so on. In 1997, we designed and constructed a chamber for TEM electron source which allows us to irradiate laser beam onto a tip of the cathode for electron source. The specially designed evaporation device was also constructed in 1997 in order to coat Cs<sub>3</sub>Sb which has high quantum efficiency for visible light on a tip of the cathode.

In 1997, we also developed the method to determine a long-range order parameter of high Tc superconductors and started to develop the method to

measure an abnormal lattice distortion from the convergent beam electron diffraction (CBED) method.

**Keywords :** resolution limit of TEM at low temperatures, high  $T_c$  superconductors, short-time TEM imaging, CCD camera, signal and noise (S/N) ratio, image processing of "shift and addition, Image-shift control by computer, high-intensity electron source

## 58 Developments of high strength oxide superconductors for high magnetic field application

*Y. Tanaka and T. Kuroda*  
[April 1995 to March 1997]

Bi-2212 Ag-sheathed wires with round cross-section have been developed for the application to high field superconducting magnets. Round cross-sectional wires with 7-, 19- and 37-cores where each core consists of double tubes of oxide layers have been successfully fabricated by the powder-in-tube technique and show a critical current,  $I_c$ , value of over 200A at 4.2K and in the magnetic field of 12T. In this fiscal year, in succession to the results obtained so far, effects of the number of cores and the cooling rate from sintering temperature on  $I_c$  have been studied. Furthermore, influences of bending in wires before heat treatment on  $I_c$  have been investigated as a preliminary test to construct small coils. Overall critical current densities,  $J_c$ , were increased with increasing number of cores up to 37 but further improvements were not obtained with wires containing 61 cores. However, scatter of  $I_c$  values were smaller for 61-core wires than that for 7-, 19-, 37-core wires. On the other hand, the smaller was the cooling rate, the higher was overall  $J_c$ , irrespective of number of cores. The highest overall  $J_c$  at 4.2K and 12T of  $2.8 \times 10^4 \text{ A/cm}^2$  was obtained for 37-core wires cooled at the rate of  $1.5^\circ\text{C/hr}$  from  $902^\circ\text{C}$  to  $820^\circ\text{C}$ , followed by furnace cooling. As to bending test, overall  $J_c$ 's decreased with increasing bending strain. Normalized overall  $J_c$ 's to their initial values of unbent samples were 87% and 57% at a bending strain of 5% for pre-annealed and non pre-annealed samples, respectively.

This research was performed in collaboration with Sumitomo Heavy Industries, Ltd and Sukegawa Electric Co. Ltd.

**Keywords :** Bi (Pb) SrCaCuO, Ag sheath, Powder-in-tube, Multifilamentary wires

### Recent Publication

Bi-2212 Ag-Sheathed Round Cross Section Wires, K.

Miura, Y. Abe, Y. Suga, Y. Tanaka, T. Kuroda, M. Ishizuka, T. Yanagiya and S. Yasuhara, *Advan. in Superconductivity X (1997)* : 829-832.

## 59 Fabrication of Ag-Cu Alloy Sheathed Oxide Superconducting Wires with High Strength and High $J_c$ Properties

*Y. Tanaka and T. Kuroda, 1st Research Group*  
[April 1998 to March 2000]

Bi-system high temperature oxide superconducting wires have been of great interest for high current and high magnetic field applications such as current leads, power transmission cables and high field magnets. Producing conductors with high critical current density,  $J_c$ , high critical current,  $I_c$ , long length and high mechanical strength have been the key-technology to realize these applications. The  $J_c$  property is in general strongly dependent on many kinds of microstructural defects of an appropriate size and distribution which are spread over within oxide grains and grain boundaries. Higher  $J_c$  can easily be obtained primarily with increasing grain alignment and high grain connectivity or decreasing electrical resistivity between well aligned plate-like grains.

In the present project fabrication techniques for both Bi-2212 and Bi-2223 round-cross-sectional multi-filamentary wires will be studied with emphasis on high  $J_c$  property and increased mechanical strength. Round-cross-sectional multifilamentary wires are fabricated by the so-called oxide powder-in-tube-technique. Elementary wires consisted of two concentric Ag-Cu alloy tubes with a centered Ag-Cu wire and oxide powder layers between them are first prepared then numbers of these elementary wires are assembled and inserted into a Ag-Cu alloy tube to form a multifilamentary composite. These composites are fabricated to thin wires by drawing and subjected to heat treatment to produce superconducting wires. Ag-Cu alloy has higher mechanical strength than that of pure Ag. In the present study, further, a small amount of third elements are doped into Ag-Cu alloy to enhance the grain alignment, consequently to attain high  $J_c$  performance. For winding high homogeneity magnets round-cross-sectional multifilamentary wires become very important with benefits of no anisotropy in  $J_c$ , contrary to the conventional tape-shaped wires, and easiness of fabrication process.

This project will be performed through a collaboration with Sumitomo Heavy Industries, Ltd, 63-30, Yu-higaoka, Hiratsuka, Kanagawa and Sukegawa Electric Co. Ltd, 3-19-5, Namerikawa-honmachi,

Hitachi, Ibaraki.

**Keywords:** Bi-oxide wires, powder-in-tube technique, element addition, high- $J_c$ , high strength

## 60 Study on surface modification by plasma source ion implantation

*H. Shinno, 4th Research Group*

[April 1995 to March 1998]

Ion implantation method has been used for surface modification of metals, ceramics, polymers etc. The surface layers formed using ion implantation has excellent adhesion since gradient layers are formed between the surface layers and the substrates and essentially there are no clear interfaces between them. Conventional ion implantation method uses ion beams, so that substrate materials are ion-implanted from one side. In order to treat all surfaces of three-dimensional materials, rotational manipulation of the materials is necessary.

Plasma source ion implantation (PSII) (or plasma immersion ion implantation (PIII)) method is a novel ion-implantation method which was developed by Conrad et al.<sup>1)</sup>. This method is characterized by substrates immersed in plasma and negative high-voltage pulses applied to the substrates. Ions in the plasma are accelerated by the negative high-voltage pulses to the substrates and implanted into the surfaces of the substrates. PSII method has an advantage to the conventional beam-line ion implantation that all surfaces of three-dimensional materials can be treated simultaneously without rotational manipulation, because ions are implanted normally to the surfaces of the target materials.

However, thickness of the surface layer varies substantially around sharp edges, narrow grooves or small holes on the surfaces of materials treated by PSII. This problem becomes severe as the sizes of these grooves or holes become smaller than a critical size, which is determined by the thickness of the plasma sheath. One of purposes is to study these geometrical effects on the thickness of the surface layers. Auxiliary electrodes will be used in order to change the thickness distribution of the surface layer, and their effects will be investigated.

In the case of the beam-line ion implantation, ion energy is constant, but in the case of PSII, the ion energy has a broad spectrum. A dynamic process of the plasma during the high-voltage pulses determines the energy spectrum. This causes differences in the depth distribution of the implanted ions and the properties of the surface layer between PSII and the

beam-line ion implantation. To clarify the energy spectrum and the depth distribution of ions in the case of PSII and to compare them with those in the case of the beam-line ion implantation are also purposes of this study.

To implant ions in gas plasma such as nitrogen ions by PSII, the target materials are immersed in the gas plasma and negative high-voltage pulses are applied to the target. On the other hand, to implant metal ions, vacuum arc sources are used to generate metal ions. Vacuum arc sources consists of metal cathodes and filters to eliminate neutral atoms and metal droplets ejected from the arc spots on the cathode surfaces. The metal ions from the vacuum arc source are accelerated to the target material by the negative high-voltage pulse bias applied to the target. Since metal ions from the vacuum arc source come from one side of the target, it is necessary to use many vacuum arc sources, which surrounds the target, to treat all the surfaces of the three-dimensional material simultaneously.

Hard and adhesive diamond-like carbon (DLC) films are formed on various target materials using PSII and vacuum arc sources of carbon. This hard coating is expected to be useful to reduce friction coefficient substantially and reduce friction erosion of the material. In this case, how to keep the homogeneity of film thickness on the surfaces of the three-dimensional materials is a problem to be solved. C-N films formed using PSII and carbon vacuum-arc source with the presence of nitrogen ions are expected to become harder than DLC films. The development of the hard C-N coatings is also one of purposes of this study. Theoretically,  $C_3N_4$  is expected to be as hard as diamond.

Ion beam assisted deposition (IBAD) technique is a combined technique of ion implantation and physical vapor deposition (PVD), which has been used to fabricate adherent films with good quality. The ion beam irradiation during the film deposition improves the structural completeness, the performance, and the adhesion of the deposited films. In this study, IBAD techniques using PSII instead of the beam-line ion implantation will be developed and all surfaces of three-dimensional materials will be coated simultaneously with the adherent PVD films with good quality.

The excellent adherence of the IBAD films is due to the atomic mixing at the interface region between the film and the substrate by the ion beam. As the result of the atomic mixing, gradient layer is formed between the film and the substrate, and the adherence is improved. The adherence of the films depends on the depth profile of the composition and the structure of the gradient layer. Relation between the adherence and the compositional profile of the

gradient layer will be investigated in this study.

Recently, requirements of metal, ceramics and carbon coatings on materials with low melting points such as silicon, glasses and polymers have been increasing. The combined IBAD and PSII technique may meet with these requirements, since adherent films with good quality can be formed at room temperature with this method, and also all surfaces of three-dimensional materials can be coated simultaneously.

In these applications, homogeneous distribution of film thickness and film properties may be required on complex shaped surfaces of target materials. For this purpose, many vapor sources may have to be arranged properly around the target material. From this point of view, widely spread vapor sources such as sputtering target may be suitable. The development of the IBAD&PSII method using sputtering vapor source and its application to form various coatings on materials with low melting points are also purposes of this study.

**Keywords:** plasma source ion implantation (PSII), surface modification, ion beam assisted deposition (IBAD)

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## 2nd Research Group: Advanced Nuclear Materials

### 61 Real-Time Investigation on Surface Reactions and Defect Growth Processes under Irradiation

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[April 1994 to March 1999]

Dynamics and kinetics of reactions on material surfaces under irradiation of ions, plasma, molecular beams and light are being investigated. It is also a target of this project to develop fast analytical techniques that enable real-time observation of dynamic processes. Resonance enhanced multiphoton ionization (REMPI) measurements have been carried out to obtain the internal-state distributions of SiO and GeO molecules desorbing from Si and Ge surfaces respectively in reaction with O<sub>2</sub> beam. We have extended the multiphoton ionization (MPI) work to

the reactive scattering of O<sub>2</sub> on carbon surface under a condition of laser-ablation, and determined the translational energy distribution of CO produced in the infrared-laser-assisted reaction. Real-time ellipsometry has been successfully applied to the determination of threshold energy of erosion of tungsten with neon plasma, which was a result of the collaboration work with SANDIA Laboratory. We have started a basic study for measuring technique of surface stress change induced by thin film growth in a plasma condition. The reflectance on material surface is also being measured with femtosecond time-resolution using the optical-heterodyne method. We have finished an initial stage on this technique, and detected coherent optical phonon signals for Bi polycrystalline. For the next stage, we will study effects of defects in crystal on the dephasing. For H<sub>2</sub> in silicon, we have made Raman measurements on crystalline Si implanted with 200 keV Si<sup>+</sup>. The signal intensity of H<sub>2</sub> at 4160 cm<sup>-1</sup> decreased with the phonon coherent length in the samples after a hydrogen plasma treatment, suggesting that the H<sub>2</sub> molecule is not trapped with defects such as vacancies but in the voids in well-ordered crystalline phase. A detailed study on the relation with a new Raman signal H<sub>2</sub> at 3600 cm<sup>-1</sup>, which has been recently detected, is being carried out to understand the formation mechanism of H<sub>2</sub> in crystalline Si.

**Keywords:** irradiation, surface reaction dynamics, growth process of surface defect, real-time observation

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### 62 Plasma reaction mechanism in advanced devices studied by large scale first principle molecular dynamics

*M. Kitajima, K.G. Nakamura, A. Miyamoto (Tohoku Univ.), M. Kubo (Tohoku Univ.), and K. Terai-shi (Tohoku Univ.)*

[April 1996 to March 1999]

For the purpose of optimizing the plasma processes used in the advanced semiconductor device manufacturing, computational chemistry techniques such as quantum chemical calculations and molecular dynamics simulations were performed to investigate the mechanisms of plasma reactions on the semiconductor surfaces. In order to investigate the reaction mechanism during the plasma oxidation of silicon, the insertion of oxygen were traced one by one up to five atoms by means of quantum chemical calculation using cluster models. In the case of Si (100)-2x1, because the surface dimer sites are not directly connected to each other, oxidation of neighboring dimer sites and that of distant dimer sites are energetically almost equal. In the case of Si (111)-1x1, surface Si atoms are connected to each other to form a network structure, and oxygen is favorably inserted so as to be connected to the Si which is already bonded to the preceding oxygen. When five oxygen atoms are inserted, the oxide growth to the third layer and the oxidation at a distant dimer site are energetically almost equal on Si (100)-2x1. On the other hand, the insertion of oxygen so as to be connected to the Si which is already bonded to oxygen is preferred energetically to the oxidation at an isolated site or the growth of the oxide toward deeper layer. It is expected from these results that the oxide nuclei would be highly dispersed and oxidation proceed uniformly on Si (100)-2x1, while the oxide would grow locally in lateral direction on Si (111)-1x1. Furthermore, accelerated quantum molecular dynamics (Tight-binding molecular dynamics) program has been developed and applied to analyze the dynamics of the surface oxidation. With regard to the hydrogen plasma reactions, the stability, the migration energy, and the vibrational frequency of H<sub>2</sub> in silicon crystal were determined by ad initio molecular orbital calculations.

**Keywords :** quantum chemical calculation, semiconductor surface, plasma reaction, oxide film formation

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press).

### 63 Influence of Nuclear Transmutations on Low Activation Structural Materials for Fusion Reactor Application

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[April 1996 to March 2001]

For the purpose of contributing to the development of irradiation resistant low activation structural materials for first wall and/or blanket use in future nuclear fusion systems, such as prototype reactors and beyond, the influence of nuclear transmutational elements on material integrity has been investigated using ion irradiation with a cyclotron. The emphasis is focussed on effects of gas species (helium and hydrogen) on mechanical properties, due to their strong tendency of inducing embrittlement.

Creep rupture tests after hot helium implantation (100 appm) by  $\alpha$ -particle irradiation at 823 K were conducted at the same temperature on a low activation ferritic steel, F82H (Fe-8Cr-2W-V,Ta), which had been chosen as a reference material for IEA round-robin examination. The creep rupture strength and elongation of helium implanted samples were mostly identical to those of corresponding controls. In addition, all the specimens including implanted and unimplanted ones ruptured perfectly in a transgranularly ductile fashion and no indication of grain boundary embrittlement by helium was observed. These facts mean that this material can withstand helium-induced mechanical degradation in the parameter range investigated.

On the other hand, modeling of helium embrittlement phenomenon has been proceeded. The critical size of intergranular helium bubbles, beyond which they become energetically unstable and continue to grow up to fracture, was evaluated through direct computation of the bubble growth rate and compared to the results of microstructural observations on Fe-25%Ni-15%Cr austenitic alloys. In these alloys the average distances of grain boundary bubbles with super-critical radii stay within the order of hundreds of nm, and coincide with the spacings of cavity traces on the surfaces of intercrystalline fracture. This correspondence probably mirrors grain boundary separation led by the instability of helium bubbles.

**Keywords :** helium embrittlement, hydrogen embrittlement, ferritic steel, vanadium alloy

## Recent Publications

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Microstructural Observation of Helium Implanted and Creep Ruptured Fe-25%Ni-15%Cr Alloys Containing Various MC and MN Formers, N. Yamamoto, J. Nagakawa, Y. Murase and H. Shiraiishi, (to be published in J. Nucl. Mater.)

## 64 Understanding and Improvement of Radiation-Induced Degradation in the Advanced Nuclear Materials

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[April 1998 to March 2002]*

Changes in microstructure and degradation in mechanical properties induced by the irradiation with energetic particles are critically important for the structural materials of nuclear application. They influence significantly the endurance of structural components of nuclear reactors. In this research project, deformation and fracture of materials under irradiation are being studied experimentally and theoretically for the advanced nuclear materials to be used in the future nuclear energy sources like the fusion reactor. Emphasis is placed on the development of a new method to suppress the radiation-induced embrittlement, and also on the understanding of deformation and fracture properties of the advanced materials under irradiation.

Damage by energetic particles causes atomic displacement and introduces migrating point defects and stable defect agglomerates in the material. Migration of point defects, especially the interstitial atom that has a very stronger strain field, is influenced by the external stress field and induces various material degradation phenomena. One of the most important degradation for the nuclear reactor materials is the radiation-induced deformation. Unusually large plastic deformation is produced by the synergistic effect of irradiation and external stress even at rather low temperatures and stress levels. This phenomenon has been extensively examined for austenitic stainless steels, i.e. the most widely used materials in the commercial light-water reactors and experimental fast breeder reactors. However, little is

known for the advanced nuclear materials such as low activation vanadium alloys and SiC/SiC composites for the fusion reactors. Recently, we have revealed that the fatigue fracture is affected by the simultaneous irradiation and further by the radiation-induced deformation in 316 stainless steel<sup>1)</sup>. In the fusion reactors, atomic displacement and radiation-induced deformation are expected to be more significant compared with those in the fission reactors. It is, therefore, very critical to investigate the radiation-induced deformation and the fatigue fracture behavior under irradiation for the advanced materials of fusion reactor application. Using the NRIM cyclotron accelerator and the in-beam creep-fatigue machine, radiation-induced deformation and fatigue under irradiation will be investigated for the various advanced nuclear materials in this research project.

Radiation damage also introduces stable defect agglomerates that hinder the propagation of dislocations and consequently the dissipation of impact energy during accidental stressing on the reactor components. This phenomenon is known as the radiation embrittlement and regarded as quite detrimental, leading to the initiation of cracks and subsequent fracture. It'll be very valuable for the development of fusion reactors and for the prolongation of light-water reactors if this phenomenon can be prevented or suppressed. Our previous HVEM observation<sup>2)</sup> showed that dislocations absorb the defect agglomerates, that are essentially dislocation loops, when the Burgers vector is the same, or push them aside if the Burgers vector is different. By this way, a clear channel zone is formed in the radiation-hardened material and dislocation can propagate through this channel until the dislocation multiplication is stopped due to the back-stress from residual dislocations piled-up on the channel wall. Therefore, even the radiation-hardened materials may deform reasonably well if the channel could be continuously formed all over the material. In this research project, study has been initiated to find a new method to effectively and continuously introduce massive amount of dislocation channels in the irradiated materials.

**Keywords :** radiation damage, point defects, deformation, fatigue

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## 65 Isotope Separation and Its Application to Materials

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[April 1997 to March 2002]

### 1. Introduction

Materials composed of isotopically selected elements realize the essential solution of subjects such as induced activity, He embrittlement, and compositional change caused by reactions with energetic particles. Moreover, the isotopically controlled materials have been pointed out to improve various physical properties of crystallines.

The objectives of the program are (1) to develop CO<sub>2</sub> laser with oxygen isotope, which expands the infrared wavenumber region of the laser emission and to search infrared laser with a wide range of wavenumber, (2) to synthesis isotopically controlled materials such as silicon and boron compounds, and (3) to utilize isotopes by transmutation, including simulation studies.

### 2. Main Results

#### 2.1 Development of isotopically controlled laser and searching infrared laser with a wide range of wavenumber

Usual pulse CO<sub>2</sub> laser is limited in emission of wavenumber as 931-956cm<sup>-1</sup>, 966-983cm<sup>-1</sup>, 1033-1057cm<sup>-1</sup> and 1069-1085cm<sup>-1</sup>. If <sup>12</sup>C or <sup>16</sup>O is replaced by other isotopes such as <sup>13</sup>C or <sup>18</sup>O, then new emission lines appear due to the different stretching and bending modes of isotopic CO<sub>2</sub> from those of usual CO<sub>2</sub> gas.

In order to achieve the isotope laser, a closed-cycle CO<sub>2</sub> laser system is examined. It is necessary to use isotope CO<sub>2</sub> effectively because of its high cost. When the laser is emitted by discharge, isotope CO<sub>2</sub> is consumed with the reaction as



Then the catalyzer composed of CuO is installed in the circulation system to recombine CO and O<sub>2</sub> to return CO<sub>2</sub>. The system is now being manufactured. Free Electron Laser (FEL) is also examined to be used as the other laser covering a wide wavenumber region. The one which is available in the infrared

wavenumber region and has a considerable high power is the FELIX of the FOM in the Netherland. The FELIX emits the infrared laser at 5-30μm (333-2000cm<sup>-1</sup>) with 5MW. The use of this laser also is being examined under the cooperation with the FOM institute and Los Alamos National Laboratory.

#### 2.2 Synthesis of isotope silicon films and growth of isotope single crystals

It is necessary to take out silicon metal from isotopically concentrated SiF<sub>4</sub> or Si<sub>2</sub>F<sub>6</sub> gas to examine various physical properties of isotopically controlled silicon and its compounds.

Silicon flake was deposited by a plasma CVD method. Natural SiF<sub>4</sub> gas was used to find the optimum condition of Si film formation prior to isotopically enriched gases. Microwave of 2.45GHz with a power of 8.4x10<sup>-4</sup>Wm<sup>-2</sup> was applied to the gas at 13.3Pa-266Pa at a flow rate of 30-500SCCM. Ar and H<sub>2</sub> are added as a plasma assisting and scavenging gases, respectively. The substrate temperature was kept at 523-873K. The films formed were examined with SEM, XRD and weighed for measuring formation rates.

Fig. 1 shows the X-ray diffraction patterns of silms formed at various temperatures. It is found that polycrystalline Si films were formed in the present experimental temperature range. That is, silicon can be produced through the decomposition reactions of fluoro-silane gases by the plasma CVD. The optimum temperature to obtain silicon films with a high efficiency was 623-723K. The maximum conversion efficiency from fluoro-silane to silicon metal was 28%.

Natural boron is composed of <sup>10</sup>B of 19.9% and <sup>11</sup>

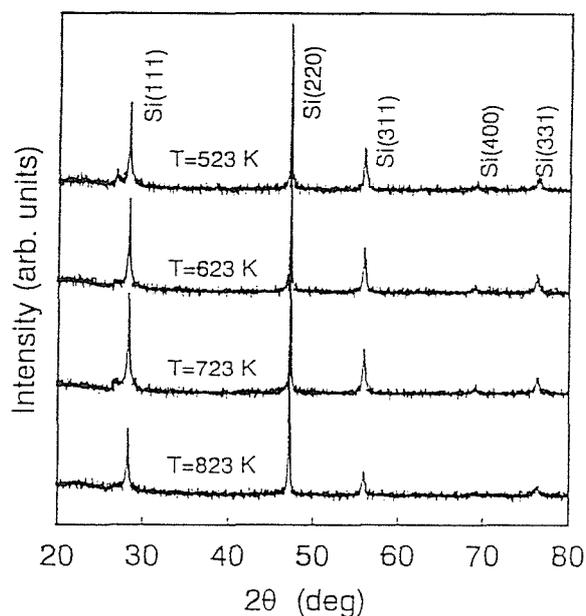


Fig.1 X-ray diffraction patterns of Si films formed at various temperatures.

B of 801%. Since relative mass difference between  $^{10}\text{B}$  and  $^{11}\text{B}$  is very large, mass effect on physical properties of boron is expected. In the present study, single crystalline isotope boron was tried to be prepared using zone melting technique. The starting materials were 99.5% $^{10}\text{B}$  and 99% $^{11}\text{B}$  powders. After isostatically pressed to a cylindrical shape under hydrostatic pressure of 2000kgW/cm<sup>2</sup>, the isotopic boron powders were sintered in a vacuum at 1873K. The sintered rod was then zone melted on the seed crystal under flowing Ar gas. Finally isotope boron single crystals with a size of 10mm $\phi$ x40mm could be formed. The observation of the cross section of the crystals indicated a smooth surface and the growth direction was identified to be  $\langle 100 \rangle$  by X-ray Laue back reflection analysis. The boron single crystals prepared are 93.2% $^{10}\text{B}$ , 99% $^{11}\text{B}$  and natural boron (19.9% $^{10}\text{B}$  and 80.1% $^{11}\text{B}$ ).

Physical properties such as lattice constant, thermal diffusivity, and heat capacity for boron single crystals are being measured.

### 2.3 Utilization of isotopes by transmutation

The simulation code, IRAC, calculating transmutation was improved by combining with a neutron transport calculation code and introducing multi-step reactions to predict more precisely the transmutation of materials including isotopically controlled materials. FENDL2.1 was introduced as a newest nuclear data file covering both stable and unstable nuclides for various nuclear reactions. Using the improved calculation code, synthesis of new materials through the transmutation and annihilation of radioactive nuclides with a long half-life are being examined.

SiC has excellent nuclear properties and has been considered as a structural material of fusion reactors. Since SiC itself is intrinsically brittle, SiC composites with a high purity and favorable mechanical properties are being developed using chemical vapor infiltration process.

**Keywords:** isotopically controlled materials, isotope separation, free electron laser, silicon, boron, chemical vapor infiltration, silicon carbide, transmutation

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## 66 Preparation of Isotopically Purified Silicon for Determining Standard Molar Mass

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[October 1997 to March 2002]

### 1. Introduction

Silicon is produced in the form of highly purified and perfect crystal. Recent progress in measuring physical constants requires the precise determination of Avogadro constant. Silicon single crystal is believed as the most reliable material for this purpose. However, natural silicon is composed of 92.23% $^{28}\text{Si}$ , 4.71% $^{29}\text{Si}$  and 3.1% $^{30}\text{Si}$ . Since isotope effect on physical properties appear in lattice constant, volume and molar mass, isotopically purified silicon is needed to improve the accuracy of molar mass measurement.

Among several isotope separation methods, isotope selective decomposition of  $\text{Si}_2\text{F}_6$  gas using infrared laser makes it easy to conduct the concentration of silicon isotopes.

In the present study, the objectives are 1) to concentrate  $^{28}\text{Si}$  using infrared laser multi-decomposition of  $\text{Si}_2\text{F}_6$ , 2) to convert isotopically concentrated fluoro-silane to silicon, and finally to prepare the highly purified silicon enriched with  $^{28}\text{Si}$ .

## 2. Main results

### 2.1 Concentration of $^{28}\text{Si}$

The effect of several parameters such as the wavenumber and the power of  $\text{CO}_2$  laser, and the gas pressure and the flow rate of  $\text{Si}_2\text{F}_6$  on the enrichment of  $^{28}\text{Si}$  is examined and optimum conditions to obtain fluoro-silane enriched with  $^{28}\text{Si}$  is determined.

$\text{CO}_2$  pulse laser with an output power of 1.62-3.2J was used for the enrichment of  $^{28}\text{Si}$  isotope. The reaction cell is a cylindrical tube of stainless steel with a size, 60mm in diameter and 2m in length. The laser beam was focused to be about 6x7mm by ZnSe with a 1.5m focal distance at the central part of the reaction tube. The pressure and the flow rate of  $\text{Si}_2\text{F}_6$  gas were kept at 10.7~266.6Pa and  $8.3 \times 66.7 \times 10^{-7} \text{mm}^2/\text{s}$ , respectively. As the result,  $\text{SiF}_4$  which mainly contained  $^{29}\text{Si}$  and  $^{30}\text{Si}$  was formed at  $950\text{--}956\text{cm}^{-1}$  and  $^{28}\text{Si}$  was concentrated in the residual  $\text{Si}_2\text{F}_6$ . At  $956\text{cm}^{-1}$ , the  $\text{Si}_2\text{F}_6$  gas containing 97%  $^{28}\text{Si}$  was produced under the flow rate of  $16.7\text{mm}^3/\text{s}$  and the pressure of 133Pa conditions. The enrichment of  $^{28}\text{Si}$  increased with increasing the laser power and in addition introducing an inert gas like He, Ar, and Kr simultaneously. Under the conditions of the wavenumber of  $953\text{cm}^{-1}$  and the power of  $7.47\text{kJ}/\text{m}^2$ , and the Ar flow rate of  $83.5\text{mm}^3/\text{s}$ ,  $\text{Si}_2\text{F}_6$  gas with 99.72%  $^{28}\text{Si}$  was obtained continuously at about 4% yield. However, the yield of the  $\text{Si}_2\text{F}_6$  enriched with  $^{28}\text{Si}$  decreased with increasing the  $^{28}\text{Si}$  concentration. It was found that the yield exceeded 50%, if the  $^{28}\text{Si}$  concentration of about 95% is satisfactory.

### 2.2 Conversion of fluoro-silane enriched with $^{28}\text{Si}$ to metallic silicon by using plasma CVD

Fluoro-silane gases are thermodynamically stable and are difficult to be reduced to silicon even using hydrogen. In general, after converting fluoro-silane to silane, then Si is obtainable by the thermal decomposition of the silane. However, the final Si yield decreases with the steps of the process. Therefore, it was tried to directly convert fluoro-silane to metallic silicon by plasma CVD. The quartz pipe of  $30\text{mm}\phi$  was used as a reaction cell. Microwave with about 360W was applied to mixed gases of  $\text{SiF}_4$  or  $\text{Si}_2\text{F}_6$ , Ar and  $\text{H}_2$  at 523-723K so that fluoro-silane is decomposed. Si film was deposited on the inner wall. Below 523K,  $\text{SiF}_2$  was formed and Si films once deposited was etched by  $\text{SiF}_x$  above 723K. After collecting Si films, the isotope abundance was measured with glow discharge mass spectrometer (GDMS). It was confirmed that silicon film was produced with the same isotope composition as for the fluoro-silane enriched with  $^{28}\text{Si}$ . It was then concluded that the plasma CVD was effective as a method for directly converting from fluoro-silane to

metallic silicon.

**Keywords:** isotopically controlled silicon, isotope separation, molar mass, plasma chemical vapor deposition

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## 67 Research on Utilization Technique of "Data-Free-Way" system for Nuclear Materials

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[April 1995 to March 2001]

Material information system a having huge database and effective computer aided tools are required for the alloy design or selection of advanced nuclear materials. However there are limitations in storing numerous material properties into the database and developing a variety of the tools in one research institute. Thus, under corporation among National Research Institute for Metals (NRIM), Japan Atomic Energy Research Institute (JAERI) and Power Reactor and Nuclear Fuel Development Corporation (PNC) with different special field, the pilot distributed database system for development of nuclear materials called "Data-Free-Way" has been built since 1990. The project on the second stage was started in 1995 under collaboration among NRIM, JAERI, PNC and Japan Science and Technology Corporation (JST). The aim of this project is to store the data in the database and to develop useful computer utilized tool for data analysis and simulation codes for various phenomena under irradiation environments.

The method of the connection among the

database of each organization in “Data-Free-Way” system changed from private line to the Internet. Using tools used in the Internet, users can easily refer to simultaneously any necessary information by accessing to the four databases in NRIM, JAERI, PNC and JST with WWW browser without taking account of in which database site the required data exit.

The construction of welding database using the technique used in “Data-Free-Way” system is carried collaboratively out between NRIM and JST in database development support program. The database consists of more than 200 CCT diagrams measured by same experimental method and the prediction system of heat cycle at each point in welded zone based on the conductivity of welding heat. The optimum of welding conditions and the selection of suitable steels for welding are easily using the database.

**Keyword:** Data-Free-Way, distributed database, advanced nuclear materials, data share, welding database

### 3rd Research Group: Advanced High Temperature Materials

#### 68 Design of Refractory Superalloys

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[April 1995 to March 2000]

The temperature capability of the Ni-base superalloy has been improved by 400 °C since it was introduced in 1945; the capability of the latest single crystal superalloys is approaching 1100 °C. However, it is obvious that there will be a limitation which comes from the melting points (~1350 °C) of the Ni-base superalloys.

In this project we design “Refractory Superalloys” which is defined by us as alloys with fcc/L12 coherent microstructures similar to Ni-base superalloys and yet with considerably higher melting points. Metallic elements with high melting points, such as Ir and Rh, have been examined experimentally for possible use as the base metal in the refractory superalloys. It has been shown that both Ir and Rh can be precipitation hardened by L12 phase to exhibit high yield strengths, e.g., 220MPa at 1800°C for Ir-15at%Nb alloy. Characterisation of the microstructure and evaluation of the ultra-high temper-

ature creep strength/oxidation resistance are being carried out. A computer modelling based on statistical thermodynamics is employed in the alloy design. Theoretical predictions on the equilibrium state of the alloys have become possible for selected binary, ternary and quaternary systems. The model is being used to search for alloys with optimum microstructure to exhibit further superior high temperature strengths.

**Keywords:** iridium, rhodium, refractory superalloy, high temperature strength, computer modelling

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#### 69 Design of High Temperature Alloys Based on Statistical Thermodynamics

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*H. Onodera, T. Abe, M. Ohnuma, M. Shimono, T. Yamagata, T. Yokokawa, and T. Kobayashi, Computational Materials Science Division*  
[April 1995 to March 1997]

The equilibrium state in multi-component single crystal (SC) Ni-base superalloys was estimated by computer modelling using Cluster Variation Method (CVM) and Monte Carlo (MC) simulations. The microstructures in the Ni-base superalloys were also analysed by an Atom Probe Field Ion Microscope (APFIM) equipped with a Three Dimensional Atom Probe (3D-AP). The state of  $\gamma/\gamma'$  phase equilibrium, including atomic configuration in the  $\gamma'$  phase, has been determined. A good agreement was obtained between the calculations and the experimental result. CVM has been successfully applied to the development of 3rd generation Ni-base SC superalloys with further superior temperature capabilities.

In order to develop an alloy design system for intermetallic titanium aluminides, TiAl (L1<sub>0</sub>) and

Ti<sub>3</sub>Al (DO<sub>19</sub>), based on the CVM, formulations of the CVM for the DO<sub>19</sub> and L1<sub>0</sub> structures were performed on the tetrahedron approximation. The phase equilibrium between the h.c.p. phase and the ordered DO<sub>19</sub> phase in the Ti-Al system was examined by Monte Carlo simulations. Obtained results suggested that at least the second nearest neighbour distance should be taken into consideration in order to reproduce the  $\alpha/\alpha_2$  phase boundaries.

Many-body interactions semi-empirically determined by the Embedded method were used to simulate liquid-to-amorphous transitions in Ti-Al alloys. The present simulation could reproduce the experimentally observed concentration range for amorphisation (40-85at%Al) by sputtering.

**Keywords :** Ni-base superalloy, Ti-base alloy, TiAl, Ti<sub>3</sub>Al, phase equilibrium, atomic configuration, computer modelling

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Molecular Dynamics Study on Liquid-to-Amorphous and Amorphous-to-Crystal Transitions in Ti-Al alloys, *Trans MRSJ*, 20 (1996) : 803-807.

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## 70 Research and Development of High Temperature Ti<sub>2</sub>AlNb Titanium Aluminide-Based Composites.

*M. Hagiwara, Third Research Group*  
[April 1997 to March 2001]

Titanium alloys and titanium aluminides are of great technological interest because of their low density and high temperature strength. One main drawback of these titanium-related materials for structural application is that the service temperature is limited to 760°C due to a degradation of tensile strength, creep resistance, thermal stability and environmental resistance. Moreover, they exhibit lower stiffness and poorer abrasion-related properties than nickel-based alloy. However, for future aircraft design, there are still demands for advanced light-weight alloys having superior combinations of mechanical properties in the temperature range up to

1,000°C.

The fabrication of titanium aluminaide-based composites reinforced with ceramic particulate creates considerable potential for improvement in various properties. These particulate metal matrix composites (MMC's) have isotropic characteristics and can be processed more cheaply using the conventional net shape technologies.

Recently, a new class of titanium aluminide based on the ordered orthorhombic phase Ti<sub>2</sub>AlNb has been developed. Because of its attractive combination of room temperature ductility and elevated temperature strength compared to Ti<sub>3</sub>Al ( $\alpha_2$ ) and TiAl ( $\gamma$ ), Ti<sub>2</sub>AlNb can be considered as a potential matrix alloy for particulate composites.

The objective of this research program is to produce Ti<sub>2</sub>AlNb-based MMC's reinforced with both relatively large-sized ceramic particulate such as TiC and TiB and very fine oxide particulate such as Er<sub>2</sub>O<sub>3</sub> using advanced P/M processes, and creep and fatigue properties will be evaluated with emphasis on relating microstructural characteristics to these high temperature mechanical properties.

**Keywords :** titanium aluminide, particulate-reinforced, composites, powder metallurgy, mechanical properties

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2. Modulated Microstructure in Ti-22Al-11Nb-4Mo Alloy, F. Tang, S. Emura and M. Hagiwara, *Scripta Mater.*, 40 (1999) : 471-476.

## 71 Microstructure Control and Properties of Titanium Aluminides

*M. Nobuki, K. Hashimoto, K. Kasahara, T. Kumagai, E. Abe, M. Nakamura, T. Tsujimoto\*, K. Niinobe\* and H. Yamamoto\*\*, H. Moriya\*\* 3rd Research Group, \* : Ibaraki Uni., \*\* : Chiba Inst. Tech.*

*T. Kimura, Physical Properties Division*  
*T. Tanabe and I. Muto, Mechanical Properties Division*

[April 1997 to March 2001]

We have continued overall research systematically connected with processing, characteristic evaluation

and detailed structure analyzing. The objective of this work with respect to TiAl  $\gamma$  based and L12 modified Al<sub>3</sub>Ti  $\tau$  based alloys is to improve the mechanical properties for structural application.

The phase, structure and compositions of Al-Mn-Ti-X (X=Zr, V, Ag, Ga) alloys were studied by X-ray diffraction and Electron Probe Microanalyzer (EPMA). The solubility of X (X=Zr, V, Ag < Ga) element into the L1<sub>2</sub>-type  $\{(AlMn)_3Ti\}$  (1-n) Xn trialuminides at 1450 K was varied from 6.8Zr to 12.9Ga. It was found that the resultant quaternary alloys had the region of the single phase of the L1<sub>2</sub>-type  $\{(AlMn)_3Ti\}$  (1-n) Xn trialuminides for all additional elements. Its single phase region was shown in the quaternary phase diagram of Al-Mn-Ti-X alloys. When Zr, V, or Ga was added into the L1<sub>2</sub>-type (AlMn)<sub>3</sub>Ti trialuminide, they occupied the Al- and Ti- sublattice in the L1<sub>2</sub> crystal. The lattice parameter of the resultant quaternary trialuminide was smaller than that of the ternary counterparts, except for trialuminide with Zr addition. On the other hand, the Ag occupied the Al-sublattice in the L1<sub>2</sub>-type (AlMn)<sub>3</sub>Ti trialuminides when it was added into the L1<sub>2</sub> crystal. The lattice parameter of the resultant quaternary trialuminide with Ag or Zr addition was larger than that of the ternary counterparts. The variation of lattice parameter of the L1<sub>2</sub>-type  $\{(AlMn)_3Ti\}$  (1-n) Xn trialuminide can be explained by the atomic size effect.

We have discussed the  $\alpha \rightarrow \gamma$  phase transformations of a Ti-48Al (mol%) alloy accomplished within a very short time on quenching/heating based on the results in a series of our studies, which have been made by examining the characteristic features of the microstructure in detail using high-resolution electron microscopy.

(a) Fine lamellae formation :  $\alpha \rightarrow \alpha_2 + \gamma$ . 1) Partial dislocation ledges to accomplish the fundamental lattice change of h.c.p. to f.c.c. are observed at the  $\alpha_2$ - $\gamma$  interfaces in the growth edge of the  $\gamma$ -plate. 2) The  $\alpha_2$ - $\gamma$  interfacial lattice misfit is very small, and the  $\alpha_2$ - $\gamma$  interfaces and  $\gamma$ - $\gamma$  twin boundaries are atomically flat in a wide range. Partial dislocation ledges are hardly recognized at the  $\alpha_2$ - $\gamma$  interfaces, which are known to be observed in high-density for lamellar structures formed by relatively slow cooling. 3) Antiphase domain boundaries (APDBs) are formed both in the  $\alpha_2$  and  $\gamma$ -plates, and they are continuous across the  $\alpha_2$ - $\gamma$  interfaces and  $\gamma$ - $\gamma$  twin boundaries at the atomic level. 4) Considerable compositional change has occurred between the  $\alpha_2$  and  $\gamma$  phases during quenching. On these bases, the formation process of the present fine lamellar structure is described as  $\alpha \rightarrow \alpha_2 \rightarrow \alpha_2 + \gamma$ . Although a long-range diffusion process is involved in this transformation, it is concluded that the mechanism is

strongly dominated by the atomic movement involving shear displacements.

(b) Massive transformation :  $\alpha \rightarrow \gamma_m$ . 1) High-density of microtwins which are aligned parallel to one another is formed in some places. Extremely thin h.c.p. plates with the thickness of about 0.8-2.0 nm are found to exist in the massively transformed  $\gamma$  phase, which are also aligned to the microtwins mentioned above. 2) Twin boundaries are irregular and are not on the (111) mirror plane of the twinning operation. Large ledges with the height of about a few tens nm are formed at the twin boundaries. These features are attributed to the pile up of twinning partial dislocations. 3) Extremely thin rotated domain walls are mostly formed at the APDBs. These rotated domains are considered to be grown from the simple APDB in order to reduce the high APB energy of the  $\gamma$  phase. From these facts, it is concluded that the mechanism of the present massive transformation is based on the h.c.p. to f.c.c. shear displacement, although the mobility of individual atoms is high due to a nature of high-temperature transformation. Short-range diffusion process must be involved in the present massive transformation, which accomplishes the rearrangement of atoms including ordering for the L1<sub>0</sub> and growth of rotated domains.

(c) Formation of the  $\alpha_2$  plate from the  $\gamma_m$  phase :  $\gamma_m \rightarrow \alpha$  ( $\alpha_2$ ). 1) By isothermal aging at 1473K, the fine  $\alpha_2$  plates are formed in the grain interiors lying on the  $\{111\}$  planes of the  $\gamma$  phase. The formation process is described as  $\gamma_m \rightarrow \gamma + \alpha \rightarrow \gamma + \alpha_2$ . 2) In the early stage of the  $\alpha_2$  plate growth (a few nm in thickness), the  $\alpha_2$ - $\gamma$  interfaces are nearly lying on the  $\{111\}$  planes, although the interfaces are not flat but having a complex structure. The  $\alpha_2$ - $\gamma$  interfacial lattice misfit is relatively large. 3) As plates thickened (about 100 nm), macroscopically the  $\alpha_2$ - $\gamma$  interfaces partially become curved and not on the  $\{111\}$  planes. This is due to formation of high-density of ledges at the interfaces. These facts indicate that this transformation mechanism is also based on the f.c.c.-h.c.p. change accomplished by migration of ledges. The complex interface structure is considered to be responsible for the thermal stability of the  $\alpha_2$  fine plates.

**Keywords :** titanium aluminide, particulate-reinforced, composites, powder metallurgy, mechanical properties

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H. Yamamoto, K. Hashimoto, T. Kimura, H. Moriya, M. Nobuki and N. Khono : JIM, (1997), in

print.

## 72 Numerical Simulation of Phase Separation

*N. Akaiwa, Computational Materials Science Division*

[April 1998 to March 2001]

Numerical simulations of phase separation are generally performed using diffuse and sharp interface approaches. When the structures of the two phases are the same, the diffuse interface approach (the Cahn-Hilliard model) is used for theoretical and numerical studies. In this case, the free energy of the system is composed of a single curve with two minima. The Cahn-Hilliard model generates interconnected spinodal structures near the critical composition, while near the coexistence line the system consists of a set of isolated particles which are generated by nucleation. Between those two regions morphological transition from the spinodal-like structures to a set of isolated particles occurs.

On the other hand, when the structures of the two phases are different, the free energy of the system is composed of two different curves. In this case, isolated particles are formed by nucleation at any quench positions, so that spinodal decomposition does not occur. After the nucleation stage the particles grow in supersaturated solutions. When the supersaturation becomes small or the volume fraction of the particle phase becomes almost constant, large particles grow at the expense of small particles. This process is known as coarsening or Ostwald ripening, and sharp interface model is used for theoretical and numerical studies.

In the late stage of phase separation, both of the phenomena are driven by reduction in total surface area through diffusion, resulting in an increase of the average domain size. It is well known that the scaling laws hold in the late stage. For example, the structure functions scaled by the characteristic length become time independent. We have found previously that all of the qualitative features in the structure function for the spinodal structure generated by the Cahn-Hilliard model and a set of isolated particles generated by the sharp interface model are the same even though the domain structures are quite different. The structure function can be obtained experimentally by X-ray, neutron or light scattering and gives information about the domain structure in Fourier space. However, it is not easy to relate the scattering intensity profile to the real space structure.

In this project we perform numerical simulations of phase separation at the critical composition using the Cahn-Hilliard model in two dimensions. The

simulations are performed using two methods for placing the initial order parameter on the mesh points. The first method places the initial order parameter using a random number generator. This initial condition generates the interconnected spinodal structure. At the critical composition, the morphological transition from the spinodal structure to a set of isolated particles does not occur. Thus, the spinodal structure is stable. The second method places isolated particles in the computational cell. In this case, the order parameter is 1 on the mesh points inside the particles and  $-1$  outside the particles. We find that the structures consisting of isolated particles are also stable. This suggests that there exist two stable solutions at the critical composition. The purpose of this project is to obtain the relationships between the domain structures in the real space and the structure functions.

**Keywords :** Spinodal decomposition, Nucleation and growth, Structure function

## 4th Research Group : Energy Conversion Materials

### 73 Development of Basic Superconducting Technology for High Field Micro-SMES

*K. Inoue, Y. Yoshida, Y. Iijima, and A. Kikuchi. 4<sup>th</sup> Research Group*

[April 1997 to March 2002]

Because the stored energy density of SMES (Superconducting Magnetic Energy Storage) is increased rapidly with increasing the magnetic field, the increase of the operation field make the fabrication of micro-SMES (compacted SMES) possible. The operation field is determined mainly by the  $J_c$ -B properties of superconducting wire used for SMES. There are two kinds of commercialized superconducting wires ; Nb-Ti wires for low fields and Nb<sub>3</sub>Sn wires for high fields. Although Nb<sub>3</sub>Al, Nb<sub>3</sub>Ge, Nb<sub>3</sub>Ga, Ni-2212, and Bi-2223 have not yet been commercialized, they are the most promising candidate superconducting materials for increasing the operation field of SMES because of their large potentialities due to higher  $H_{c2}$  (4.2K)'s than that of Nb<sub>3</sub>Sn. Recently we found that the Nb<sub>3</sub>Al multifilamentary wire, fabricated through the rapid-heat, quench, and transformation (RHQT) process, showed 2-5 times larger  $J_c$  in high fields than that of commercialized Nb<sub>3</sub>Sn multifilamentary wire and excellent strain tolerances. The large  $J_c$  in high fields and the excellent strain tolerance are the most

required properties for the superconductor used for the micro-SMES. In this study we are investigating the coil fabrication technique, stabilization, superconducting junction, and improvements of superconducting properties for the Nb<sub>3</sub>Al multifilamentary wire and other high-field superconductors. Superconducting current lead and superconducting magnetic shield are also being studied as the basic technologies for the micro-SMES.

We tried the fabrication of Nb<sub>3</sub>Ga wire through the RHQT process by using mixed powder of Nb-Ga intermetallic compound as a precursor. However we could not obtain the excellent superconducting properties for the Nb<sub>3</sub>Ga wire, because the poor heat conductivity of the powder prevented the samples from rapid heating and quenching. We also studied the Ge addition to the Nb<sub>3</sub>Al multifilamentary wire, which improved remarkably not only T<sub>c</sub> from 17.6 K to 19.4 K, but also H<sub>c2</sub> (4.2K) from 27.6 T to 40 T, but reduced J<sub>c</sub> (4.2K) a little. The additional effects of Ge to Nb<sub>3</sub>Al should be studied in more detail.

In order to fabricate a large-scaled superconducting Bi-2223 magnetic shield through plasma spraying, we are developing the junction technique between the Bi-2223 films. By spreading Bi-2223 powder between the junction and then heat treating the junction under uniaxial compressive stress, we could obtain an excellent junction between Bi-2223 films, which shows good magnetic shielding properties.

This research was performed in collaboration with Hitachi Cable Co. Ltd.

**Keywords:** Nb<sub>3</sub>Al, Bi-2223, Rapid-Heat, Quench, Transformation, J<sub>c</sub>, Superconducting Junction.

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Critical Current Density Characteristics of Nb<sub>3</sub>Al multifilamentary Wires Continuously Fabricated by Rapid-Quenching, Y. Iijima, M. Kosuge, T. Takeuchi, and K. Inoue, Proc. of ICEC16/ICMC (1997): 1659-1700.

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### 74 Search of New Nonlinear Optical Crystals for Wavelength Modulation, Single Crystal Growth and Principle Technology Development for Optical Devices

*H. Kimura, A. Miyazaki, T. Fukuda\*<sup>1</sup>, T. Sasaki\*<sup>2</sup>, M. Sato\*<sup>3</sup>, T. Katsumata\*<sup>4</sup>, S. Yoda\*<sup>5</sup>, X. Jia\*<sup>6</sup> and R. Sakai\*<sup>7</sup>: 4th Research Group*  
[April 1997 to March 2001]

Single crystals for nonlinear optical materials are important for frequency modulation devices. It is usually required for this purpose that single crystal should have crystal asymmetry. However, it is generally difficult to grow single crystals having crystal asymmetry even if new materials are discovered. It would be possible to obtain single crystals having crystal symmetry by means of the substitution of constituent elements for another elements in order to form the asymmetry surroundings of substituent elements in micro-scale. In this work, single crystal growth of these substituted materials having crystal asymmetry are tried by the Czochralski method and the floating zone method from their melts and the crystal quality is improved by means of controlling the crystal growth conditions. Furthermore, optical properties of the crystals, such as transmission and harmonic generation etc., are evaluated using the single crystals grown.

In this year, single crystals of BaB<sub>2</sub>O<sub>4</sub>, substituted Al or Ga for B, were grown by a new double ring-shape halogen lamp floating zone pulling down furnace (DRFz). Transparent single crystals with 1 mm $\phi$  x 20 mm could be grown by this technique as shown in Fig. 1, despite the single crystals by the Czochralski method were opaque. Their nonlinear optical properties, such as a SHG (second harmonic generation) intensity, were superior to the BaB<sub>2</sub>O<sub>4</sub>.

On the other hand, it is important to study an origin of the SHG because its data is useful for investigation of new oxides for the SHG. So we are

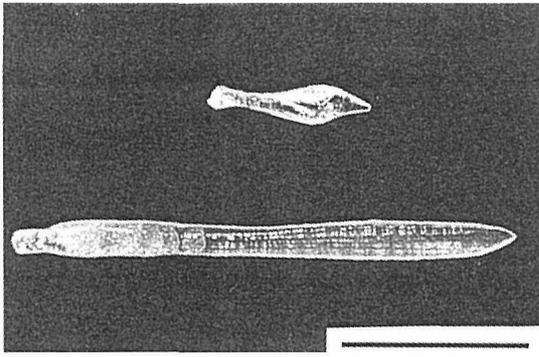


Fig.1 Example of crystals grown substituted Al for B as 5%. Upper crystal is grown by normal type floating zone pulling down furnace (DEFz), lower one is by DRFz. Scale is 10 mm.

studying the origin of the SHG on single crystals of  $BaB_2O_4$ , substituted Al or Ga for B, as a refractive index and a dielectric constant viewpoints. We expect that the refractive index and the dielectric constant will be increased with the increase of Al or Ga content.

This article also introduces another research program of "Investigation of Wavelength Modulation on Nonlinear Optical Oxides by Atomic Distribution Control" (April 1998 to March 1999).

In addition, this research was performed in collaboration with the Institute for Materials Research, Tohoku University, and the Institute of DEO for a crystal growth and a characterization on nonlinear optical oxides.

**Keywords:** frequency modulation, crystal asymmetry, substitution, refractive index, dielectric constant

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- (1) Melt supercooling behavior and crystal growth of  $Ba(B_{1-x}M_x)_2O_4$  (M: Al or Ga), H. Kimura, T. Numazawa and M. Sato, *J. Cryst. Growth* 174 (1997): 308-312.
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### 75 Development of Composition Graded Shape Memory Alloy and Wear Resistant TiAl Based Composites

*H. Sasano, S. Uehara and S. Ikeno, 4th research group*

[April 1997 to March 1999]

One of the purposes of this research program is to develop the fabrication method of composition graded shape memory alloy. If the composition is delicately changed along the longitudinal direction of the material, we can obtain the material possessing unique properties. We successfully made zinc concentration graded Cu-Zu-Al shape memory alloy by locally regulating temperature of Cu-Al wire in zinc vapor. We tried to control the concentration of titanium in TiNi shape memory alloy by the chemical transportation technique using transporting medium of titanium chloride. We have obtained narrow strips of concentration graded NiAl shape memory alloy.

Another purpose of the program is to develop wear resistant intermetallic compounds. In order to increase wear resistance of TiAl and to lower the friction coefficient of TiAl, two kinds of TiAl based composites, TiAl-Ti<sub>2</sub>AlN and TiAl-MoS<sub>2</sub>, are studied in this work. TiAl based composites are prepared by powder metallurgical method, using TiAl, TiN and MoS<sub>2</sub> powder. Ti<sub>2</sub>AlN in TiAl is formed by the interaction of TiN and TiAl. Ti<sub>2</sub>AlN is stable up to 1273K and suitable as a hardening particle for TiAl based composites. MoS<sub>2</sub> particles on the surface of TiAl-MoS<sub>2</sub> composite decrease the friction

coefficient of the composite. The TiAl composites have been developed for a sliding or rotating parts in high vacuum system.

**Keywords :** shape memory alloy, intermetallic compound, chemical transportation, composite, wear resistance, TiAl, TiNi

## 76 Research and Development of High-Performance Light Alloys for Hydrogen Storage

*C. Nishimura, H. Numata and M. Komaki, 4th Research Group*

*M. Amano, Materials Physics Division*

[April 1997 to March 2001]

Hydrogen can be regarded as an ideal energy intermediary for the following reasons: (1) it is almost inexhaustible, (2) clean and tender to ecology, (3) easy to be stored and transported. There is no doubt that hydrogen will play an important role in the near future after the fossil-energy era. In scope of the large-scale use of hydrogen as an energy intermediary, it is inevitable to establish the technological fundamentals of materials related to hydrogen-energy applications. In this study, it is aimed to give guidelines for developing high-performance light alloys for hydrogen storage, based on Mg, which can be applied in automobiles as gas-containers or batteries.

A new melting furnace has been introduced in order to melt and cast Mg alloys, which are difficult to melt because of high vapor pressure and oxidation problem of Mg. In this furnace, Mg alloys can be melt, with Mg vaporization being suppressed by Ar atmosphere. Molten alloys can be mixed and alloying elements can be additionally charged during melting. We started the melting and casting of Mg-Ni based alloys using this new furnace. Characterizations of the alloys are in progress.

Basic data on hydrogen diffusion will give important guidelines to develop high-performance alloys for hydrogen storage. Reports on hydrogen diffusion are, however, scarce for Mg alloys. That is true even for pure Mg. Here, hydrogen diffusion behaviors in pure Mg have been investigated by means of a gas-phase permeation technique. Permeation measurements were performed in an equipment with ultra-high vacuum system over a pressure range from 1.0 to 25 kPa (1 to 200 torr) and a temperature range of 463 to 503K. Thickness of membrane specimens were 2 to 3 mm. Hydrogen diffusivity,  $D$ , show no dependence on hydrogen pressure applied on the entrance side. Steady-state hydrogen permeability,  $\Phi$ , keeps constant up to a certain value of hydrogen

pressure, but decreases at higher pressures. This observation implies that hydrogen dissolution deviates from Sieverts' law at higher pressures. Hydrogen diffusion coefficients determined in this investigation,  $3.4 \times 10^{-9} \text{ m}^2\text{s}^{-1}$  at 473K for an example, are one-order higher than those extrapolated from the previous data [1] determined at higher temperatures for Mg-2mass%Ce alloy.

This research is performed in collaboration with Yokohama National University, Science University of Tokyo, and Institute of Industrial Science, and the University of Tokyo.

**Keywords :** hydrogen, hydrogen storage, magnesium, diffusion and permeation

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## 77 Energy Conversion Materials Fabricated with Composite Structure

*I.A. Nishida, 4th Research Group*

[April 1996 to March 2002]

Thermoelectric (TE) materials have been widely used for the purpose of direct conversion of thermal energy to electric power without noise and cooling system. Recently, the thermoelectric generators are mainly used for the electric source in space, marine and polar regions, and the thermoelectric cooling systems are mainly used for the precise temperature control in the semiconductor processing, optical and electronic devices. Therefore, it is important to develop TE materials with a high figure of merit  $Z$ .

The good TE materials are given by  $Z$  with high thermoelectric power  $\alpha$  and electric conductivity  $\sigma$  and low thermal conductivity  $\kappa$ . For a given TE materials with homogeneous matrix and dopant

concentration, the optimized  $Z$  can only be obtained in the relative narrow temperature range. In other temperature range, the TE conversion efficiency  $\eta$  becomes comparatively small. However,  $Z$  can be increased by controlling the dopant, composition and grain size of the functionally graded Material (FGM), because the lattice contribution to the thermal conductivity can be decreased by phonon scattering at the lattice defects such as crystal distortion and grain boundary.

TE properties of unidirectionally solidified p-type AgSbTe<sub>2</sub> boule have been evaluated to develop FGM with complex structure of Ag<sub>2</sub>Te and Sb<sub>2</sub>Te<sub>3</sub>. The boule had two kinds of different structures in it ; one is Widmannstatten structure near the surface of boule, and another is eutectic structure in the center of boule. The eutectic structure contained more Ag<sub>2</sub>Te precipitates. Both the structures showed the different temperature dependence of thermoelectric properties, which were strongly affected by the transformation at 418 K and also 633 K. High temperature phase of AgSbTe<sub>2</sub> above 633 K revealed its high potential of power generation. These results suggest that there is a high possibility to realize superior FGM by controlling structure.

**Keywords :** energy conversion, thermoelectric materials, composite materials, thermal conduction, thermoelectric conversion, thermoelectric cooling system

#### Related Paper

Development of FGM Thermoelectric Materials in Japan-State of Art-, I. Shiota and I.A. Nishida, Proc. 16th Int'l. Conf. Thermoelectrics (ICT '97), Dresden, Germany (1997) : 364-370.

### 78 Energy Conversion Materials Fabricated with Functionally Graded Structure

*I.A. Nishida, 4th Research Group*  
[April 1993 to March 1998]

Thermoelectric (TE) materials have been widely used for the purpose of direct conversion of thermal energy to electric power without noise and cooling system. For a given TE material system with homogeneous matrix and dopant concentration, the optimized figure of merit  $Z$  can only be obtained in a narrow temperature range. In other temperature range, the TE conversion efficiency  $\eta$  becomes comparatively small. Since the temperature of the thermocouple legs changes continuously from the top (high temperature) end to the bottom (low temperature) end, the large value of  $\eta$  will be obtained if the carrier concentration in the TE material changes

continuously along the thermocouple legs, i.e., functionally gradient TE materials. By preparing these materials, the effective value of  $\eta$  is estimated to increase a more than double. In addition,  $Z$  can be increased by controlling the composition and grain size of the FGM, because the lattice contribution to the thermal conductivity can be decreased by phonon scattering at the lattice defects such as crystal distortion and grain boundary.

The effective maximum powers for the two stepped FGMs of n-type PbTe with different electron concentration and p-type PbTe-SnTe solid solutions with different Sn-composition were found to be larger 24% and 28% than those for the optimized homogeneous materials at a temperature difference of 320K, respectively.

**Keywords :** energy conversion, thermoelectric materials, functionally graded materials (FGM)

#### Related Paper

Highly Efficient Thermoelectric Materials in FGM Program, I.A. Nishida, Proc. Japan-Russia-Ukraine Int'l. Workshop on Energy Conv. Materials (ENCOM 95), Sendai Japan, January (1995) : 1-10. Development of FGM Thermoelectric Materials in Japan -The State of the Art-, I. Shiota and I.A. Nishida, Proc. of 16th Int'l. Conf. on Thermoelectrics (ICT '97), Dresden, Germany, August (1997) : 364-370.

## 5th Research Group: Intelligent Materials

### 79 Creation of Multi-functional Materials by Assemblage of Primitive Functions

*N. Shinya, M. Kobayashi, T. Dan, M. Egashira, T. Konno, S. Kishimoto, H. Fudouzi, M. Hase, and J. Kyono 5th Research Group*  
[April 1997 to March 2002]

#### Background

Intelligent material research is one of the most important frontiers in the material science. The materials have the ability to respond to environmental circumstances. We can, therefore, replace mechanical parts and electronic devices with them.

Various approaches are studied to create such materials. We proposed a particle assemblage as follows. As the intelligent function is considered to be a systematically coordinated multiple functions, it will be realized through accurate three dimensional arrangement of various particles, each of

which has a primitive function such as sensor, processor and actuator. In other words, we consider that micro-meter sized particles are the unit of materials and unit of function.

A key of the particle assemblage is a method to integrate various kinds of particles. Each kind of the particles must be placed at a prescribed position. More accurate positioning is required than achieved by the conventional methods. Thus, we have developed three methods, i.e., ordered mixture, manipulation by a microprobe, and particle arrangement using electron/ion beams. Detail of each method is described in the following section. Figure 1 shows the conceptual process to create intelligent materials through the newly developed methods of particles' integration.

#### Integration methods of particles

Each of three methods shown in Fig. 1 has a potential so as to find its application fields as described below. Our final goal, however, is to create intelligent materials in cooperation with the three methods.

The first one is a fabrication of ordered mixtures, in which two kinds of particles are combined. The composite particle is formed by an electrification method. Two kinds of particles are separately enclosed in metallic vessels. The particles are electrified positively and negatively, respectively, by applying high DC voltage to the vessels. When both particles are sprayed in the same space at the same time, the composite particles are formed by the electrostatic force. In comparing with the conventional method of mechanical mixing, the electrification method has an advantage that homogeneity of the composite is assured.

Using this method, new PTC materials are devel-

oped. A packed bed of semiconducting  $\text{BaTiO}_3$  particles showed the similar PTC properties with those for the sintered bulk. The resistance of the packed bed, however, is more than 100 times higher. It is attributed to high contact resistance between the semiconducting particles. While a packed bed of the ordered mixture of semiconducting  $\text{BaTiO}_3$  and In particles showed the same PTC properties and the same resistance with those for the bulk. The reason is that In particles existing between the  $\text{BaTiO}_3$  particles remove the high contact resistance. It opens the door to the shape free forming of ceramics.

The second one is a particle manipulation using a micro-probe. The manipulation system is composed of a tungsten microprobe, a probe positioning system, stages for movement of substrates, and a CCD camera for the observation.

Both metallic particles and polymer particles of less than  $100 \mu\text{m}$  can be adsorbed to the tip of the probe and detached from it by controlling the applied voltage between the probe and the substrate. The probe can, therefore, carries particles to any positions on the substrate. Furthermore, it can weld metallic particles by applying high voltage so as to make the glow discharge. Five metallic particles were stacked and welded by the probe system as an example of three dimensional microstructures.

The third one is a particle arrangement using an electron beam and an ion beam. In contrast to the manipulation by the micro-probe, it can process a large number of particles at a time.

The electrified pattern is drawn on insulating substrates by radiation of an electron beam or an ion beam. The substrate is dipped into a suspension, where particles to be arranged were dispersed. Since the particles are attracted to the electrified pattern by

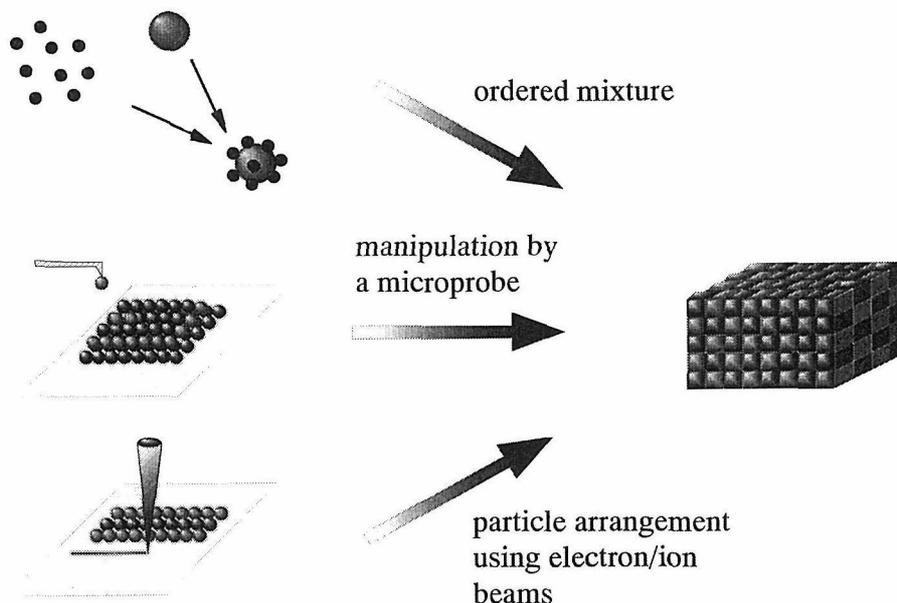


Fig.1 Concept of particle assemblage

the electrostatic force in the suspension, the particles are arranged as the electrified pattern. Fixing of the arranged particles are needed to repeat the above arranging process for the fabrication of three dimensional microstructures. Experiments showed that formation of thin polymer film and a heat treatment are both effective to the fixing.

**Keywords :** Intelligent materials, multiple functions, particle assemblage.

## 80 Development of micro-cellular structural materials

*S. Kishimoto, N. Shinya, M. Kobayashi, T. Dan, and J. Kyono*

[April 1998 to March 1999]

### INTRODUCTION

Recently, passive and active damping technologies are becoming increasingly important in terms of vibration control<sup>1</sup>, and also energy-absorbing systems are being required to protect a person from impact in a traffic accident. The key technologies of these research fields are energy-absorbing materials<sup>2</sup>. Particularly, cellular materials are receiving renewed attentions as structural and functional materials. Cellular materials have unique thermal, acoustic and energy absorbing properties that can be combined with their structural efficiency<sup>3</sup>. Therefore, many kinds of cellular materials have been tried for use as damping and energy absorbing materials. However, most of the cellular materials are open cellular polymers and woods. Though the closed cellular materials are thought to have many abilities and applications for the vibration control and the energy-absorbing systems, there is a lack of technique to produce such fine closed cellular materials except for gas foaming<sup>4</sup> or honeycomb structures<sup>3</sup>.

In this study, in order to solve these problems, a new method to produce a metallic closed cellular material such as three dimensional micro-honeycomb structural materials has been developed.

### CONCEPTUAL PROCESS

The schematic process flow of the closed cellular material production is shown in Fig. 1. The process is as follows ; 1) powder particles of the polymer are coated with a metal layer using electroless plating, 2) the powder particles are assembled and the green compacts are formed by cold isostatic pressing, and 3) after sintering at high temperature in a vacuum, the closed cellular material was produced.

### MICRO-CELLULAR STRUCTURAL MATERIAL

Powder particles of polystyrene, which is a ther-

mal plastic polymer, were used to produce the micro-cellular structures. Polystyrene particles of 10  $\mu\text{m}$  diameter were coated with a 0.46  $\mu\text{m}$  thick nickel-phosphorus alloy layer using electroless plating. These powder particles of polystyrene were pressed into green compacts by isostatic pressing at 180°C. This temperature is higher than the glass transition temperature of polystyrene. After this, these green compacts were sintered for 1 h at 800°C in a vacuum. Figure 2 shows an SEM image of the cross-section of the cellular material after sintering, and it was observed that the shape of the cells of this material is polyhedral.

Though the volatilized temperature of polystyrene is lower than the sintering temperature (800°C)<sup>5</sup>, the cross-section observation shows that almost cells of this material contain polystyrene. These results show that the closed cellular solid including the polymers can be produced by using this powder particle assembling technique.

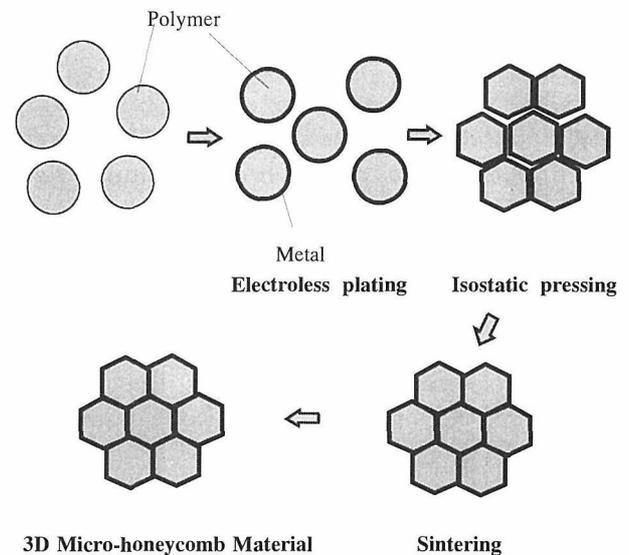


Figure 1. Flow diagram of closed cellular solid fabricating process.

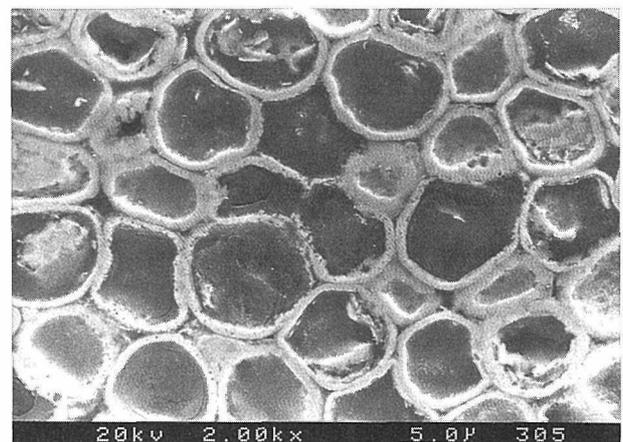


Fig.2 Cross-section of a closed cellular material.

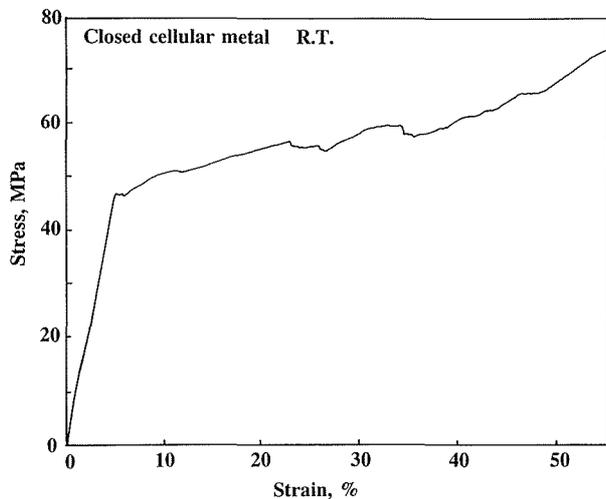


Fig.3 Compressive stress-strain curve.

The density of this material is about 2.0-2.3g/cm<sup>3</sup>, this value is smaller than that of aluminum (2.7g/cm<sup>3</sup>). Compressive tests were carried out and a typical example of the compressive test result is shown Fig. 3. The stress-strain curve shows a linear elastic region, a long plateau where the stress gradually increases and a wavy region where the stress rapidly fluctuates. The shape of the curve in the linear elastic and plateau region is the same as the typical stress-strain curve of open cellular solid material<sup>4,6</sup>. The shape of the curve in the next region, is the same as the stress-strain curve of a brittle ceramic foam<sup>6</sup>. It is suggested that the fracture initiates from a defect in the cellular solid. Therefore, if the closed cellular material has only a few defects, the plateau area of the stress-strain curve will continue further during the compressive test. As the presence of the plateau in the compressive stress-strain curve is responsible for the high energy absorption, this closed cellular solid seems to have a high energy absorbability.

#### CONCLUSION

A closed cellular material containing polystyrene particles has been developed. This cellular material has a high energy absorption. The results obtained emphasize that the closed cellular material can be utilized for the energy absorbing and the passive damping systems.

**Key words:** closed cellular solid, high strength to weight ratio, energy absorbing

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Development of Three Dimensional Micro-Honeycomb Materials, S. Kishimoto and N. Shinya, Proceedings of the 4th International Conference on Intelligent Materials (1998), 54-57.

#### 81 Development of Advanced Shape Memory Thin Films by Sputtering

A. Ishida and M. Sato 5th Research Group  
[April 1997 to March 2002]

Recently sputter-deposited thin films of Ti-Ni are expected to be used as microactuators for micromachines such as micromanipulators and fluid microvalves. Since 1993 we have been successful in showing that sputter-deposited thin films of Ti-Ni display perfect shape memory effect, superelasticity and two-way shape memory effect. Lately we succeeded in evaluating the mechanical properties, including yield stress and elongation, of sputter deposited thin films. Figure 1 shows the stress-strain curves of sputter-deposited Ti-48.3, 50.0 and 51.5at.% Ni thin films. The Ti-50.0at.%Ni thin film shows a large plastic deformation and fractures after an elongation of 40%, whereas the Ti-51.5at.%Ni thin film fractures before yielding. The stress yield of the Ti-51.5at.%Ni thin film is estimated to be above 1.5GPa and that of the Ti-50.0at.%Ni thin film is determined to be 700MPa. The high yield stress of the thin films is partly owing to the small grain size in the films. The grain size in the films was a few micrometers, whereas that of bulk specimens is reported to be several tens of microns. Figure 1 shows

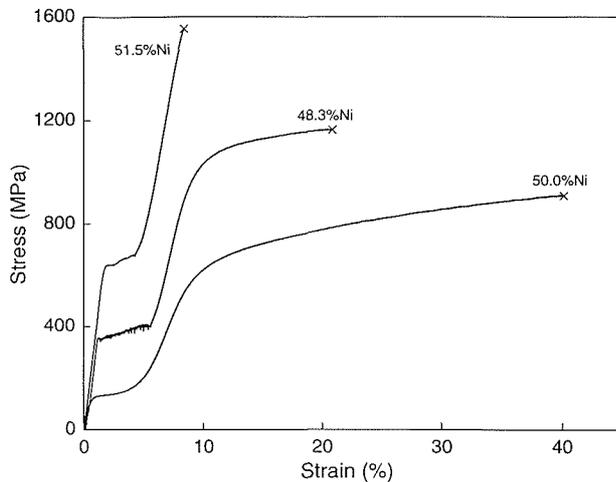


Fig.1 Stress-strain curves of Ti-48.3, 50.0, 51.5at.%Ni thin films at 315K. The Ti-48.3, 50.0at.%Ni films were annealed at 773K for 300s and for 3.6ks respectively, and the Ti-51.5at.%Ni film was aged at 673K for 3.6ks after solution treatment at 973K for 3.6ks.

clearly that sputter-deposited thin films possess enough ductility and strength for practical applications. Furthermore, it is of importance to note the deformation behavior of the Ti-48.3at.%Ni thin film. The yield stress of this film is 1.1GPa, being significantly higher than that of the Ti-50.0at.%Ni thin film. On the other hand, the elongation of the film is as large as 20%. As a result, the Ti-48.3at.%Ni thin film shows a good balance between ductility and strength. This is surprising, since a bulk specimen with the same composition has not been reported to show any ductility. A detailed observation of the microstructure in this film was made with a transmission electron microscope. The thin film showed different microstructure to that of bulk specimens. In bulk specimens the grain boundaries of TiNi are decorated by blocky precipitates of  $Ti_2Ni$ , resulting in the brittleness of the bulk specimens. In contrast, no precipitates are observed in the grain boundaries of the Ti-48.3at.%Ni thin film. Instead of grain boundary precipitates of  $Ti_2Ni$ , fine GP zones were formed within the TiNi grains. This difference in microstructure is considered to be responsible for the excellent ductility of Ti-48.3at.%Ni thin films.

The results from the mechanical tests prove that sputter-deposited thin films of Ti-Ni possess stable shape memory effect and reliable mechanical properties for practical applications. In order to apply these shape memory thin films to practical devices, further research work is under way.

**Keywords:** microactuator, shape memory effect, thin film, Ti-Ni, sputtering

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Stress-strain curves of sputter-deposited Ti-Ni thin films, A. Ishida, M. Sato, T. Kimura and S. Miyazaki, *Phil. Mag. A* (1999), in press.

## Biomaterials Research Team

### 82 Fundamental Study on Biocompatibility of Materials

M. Sumita<sup>1</sup>, K. Nakazawa<sup>1</sup>, N. Maruyama<sup>1</sup>, A. Yamamoto<sup>1</sup>, S. Hiromoto<sup>1</sup>, M. Ying<sup>1</sup>, T. Kobayashi<sup>2</sup>  
<sup>1</sup> Biomaterials Research Team, <sup>2</sup> Mechanical Property Division

[April 1994 to March 1999]

Rapid progress of aged society in Japan derives the importance and urgency of a research on biomaterials. Increasing needs for biomaterials induces elongation of the implanting periods of biomedical devices, which reveals the insufficiency on their durability and biocompatibility. Biomaterials are required to have non-toxicity, optimal affinity for tissues, high fatigue strength, and high resistance to wear and corrosion. Metallic biomaterials currently used, however, have troubles on their biocompatibility, affinity for tissues, and durability, because they have originally been developed for industrial uses and then diverted for biomedical uses. Therefore, new and superior metallic biomaterials are required to be developed, but it is difficult to obtain a sufficient amount of fundamental data necessary for the development of new metallic biomaterials. The object of this research is the accumulation of fundamental data necessary to develop new and superior metallic biomaterials.

*Research on quantitative and systematic evaluation of cytotoxicity of materials*

Toxicity data of metallic elements have been accumulated by evaluating metal salts' cytotoxicity using cell culture technique. Cytotoxicity of 43 metal salts was already examined for cell lines der-

ived from murine tissues. However, difference in metal salts' cytotoxicity between species has not been studied before. In order to investigate the effects of these metallic elements on human beings, cytotoxicity of 12 metal salts was evaluated using human epithelial carcinoma. Obtained results were compared with those for murine fibroblasts and osteoblastic cells. Consequently, the tendency of the metal salts' cytotoxicity corresponded well between the human cell line and the murine cell lines.

*Research on the evaluation of materials' affinity for cells*

Biomaterials are required to have optimal affinity for cells or tissues because response of the cells adhering to material surface induces reactions of a living system to the material, which sometimes results in failure of the implantation. In order to develop new metallic biomaterials with optimal affinity for cells, quantitative evaluation of the adhesive properties between cells and material surface are necessary. In this research, a new system has been developed to measure directly the shear force necessary to detach a single cell from material surface. Using this system, the adhesive properties of a murine fibroblast to glass surface were determined. As a result, the cell adhesive shear force and the cell detachment energy differ with the shapes of the cell ; round, spindle-shaped, or thin-spreading.

*Research on the mechanical properties of biomaterials*

Corrosion fatigue and fretting corrosion fatigue are some of the causes for failure of surgical implants such as artificial hip joints and bone plates with screws. Fatigue and fretting fatigue properties, however, have not been studied even for metallic biomaterials currently used. In this research, fatigue and fretting fatigue properties of commercially pure titanium and Ti-6Al-4V alloy were already examined in air and under a quasi-biological environment. In this year, fatigue properties of forged Co-Cr alloy (ASTM F75-92) were also examined in air and under the quasi-biological environment. As a result, the fatigue strength of the Co-Cr alloy under the quasi-biological environment decreased than those in air at lower cycles.

*Research on the standardization of the testing method for artificial hip joints by a hip simulator*

Artificial hip joints currently used have insufficiency in wear resistance of their bearing parts, which induces patients to have revision of hip arthroplasty. However, no standardized testing method is determined for them. In this research, the effect of the maximum load on wear of artificial hip joints were examined by a hip simulator developed here. The joints used were composed of the head of COP alloy and the cup of UHMWPE. Wear test of the

joints were performed in 0.9mass% NaCl at 37°C. Consequently, the cup hardly wore at the maximum load of 1960N but at 2940N. The cup wore most at +20°, presumably by the load at the peak corresponding to the touch of a heel to ground.

**Keywords :** cytotoxicity, cell-material adhesion, fatigue and fretting fatigue properties

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A new technique for direct measurement of the shear force necessary to detach a cell from a material, A. Yamamoto, S. Mishima, N. Maruyama, and M. Sumita, *Biomaterials*, 19, 871-879 (1998).

**83 Research on Creation of Biointegrated Materials to Improve Physically Handicapped People's Quality of Life**

M. Sumita<sup>1</sup>, K. Nakazawa<sup>1</sup>, N. Maruyama<sup>1</sup>, A. Yamamoto<sup>1</sup>, S. Hiromoto<sup>1</sup>, M. Ying<sup>1</sup>, T. Kobayashi<sup>2</sup>, A.P. Tsai<sup>3</sup>

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[April 1997 to March 2000]

Biomaterials currently used have troubles on their biocompatibility, bioaffinity, corrosion resistance, and durability. Furthermore, staples, bone plates with screws, artificial joints, and sensors are strongly demanded to be smaller in size because they are implanted between tissues: no space is originally remained for them. Amorphous alloys generally have higher resistance to corrosion, higher tensile strength, and lower Young's modulus than crystalline alloys. These features of amorphous alloys are favor for biomaterials. Therefore, the objective of this research is development of new biointegrated amorphous alloys with superior biocompatibility, bioaffinity, resistances to corrosion and wear, and fatigue strength. For this purpose, fundamental data of cytotoxicity, affinity for cells, corrosion resistance, and durability of various metallic materials are systematically accumulated. On the basis of the obtained data, then, bulky amorphous alloys are explored thermodynamically and material structurally.

*Research on the cytotoxicity of metallic biomaterials*

Dependence of metal ions' cytotoxicity on the

kind of cells was investigated using several cell lines. Cytotoxicity of 12 metal salts were evaluated using murine macrophage and human neuroblastoma by colony formation method. The obtained results were compared with those already obtained for murine fibroblasts, murine osteoblastic cells, and human epithelial carcinoma. Consequently, metal ions' cytotoxicity correlated well between these 5 cell lines (correlation coefficients were 0.7-0.9). This fact indicates that metal ions tend to have low dependence on cell lines concerning their ability to inhibit cell proliferation.

#### *Research on the material affinity for cells*

Adhesive property between a cell and material surface was evaluated as cell adhesive shear force and cell detachment energy. These indexes were measured by detaching a single cell from material surface in a cell culture medium applying shear force to the cell using a cantilever. The cell adhesive shear force is defined as the maximum force necessary to detach the cell, and the cell detachment energy is defined as the total energy required to completely detach the cell. As a result, cell adhesive shear force and cell detachment energy of murine fibroblast adhering to collagen- or fibronectin-coated surface is more than twice as high as those of the cells adhering to uncoated polystyrene.

#### *Research on corrosion resistance of amorphous alloys under a quasi-biological environment*

Corrosion resistance of new amorphous alloys was evaluated under a quasi-biological environment and compared to that of crystalline alloys with the same chemical composition and commercially pure (CP) titanium, a representative of the metallic biomaterials currently used. The laminary specimens of new amorphous alloys with chemical composition of  $\text{Pd}_{78}\text{Si}_{16}\text{Cu}_{6x}\text{Cr}_x$  were prepared by liquid-quenching method. Then, polarization curves of the specimens were measured in phosphate-buffered saline [PBS(-)] bubbled with argon gas. The corrosion current density, critical passivation current density, and passivation current density of amorphous alloys were lower/smaller than those for the crystalline alloys and the CP titanium, indicating that newly prepared amorphous alloys have higher resistance to corrosion under the condition tested.

#### *Development of the fretting fatigue testing machine for a small specimen*

A new fretting fatigue testing machine is designed and manufactured for a small specimen of amorphous alloys under a quasi-biological environment. This machine can evaluate fretting fatigue strength of a small specimen with 35mm between chucks in PBS(-) under controlled concentration of dissolved oxygen at 37°C.

**Keywords :** amorphous alloys, cytotoxicity, cell adhesive strength, corrosion resistance, fatigue strength

#### **Recent publications**

Correlation of metal salts' cytotoxicity between 6 cell lines, A. Yamamoto, R. Honma, A. Tanaka, and M. Sumita (submitted to J. Biomed. Mater. Res.)

Quantitative evaluation of cell attachment to glass, polystyrene, fibronectin- or collagen-coated polystyrene by measuring cell adhesive shear force and cell detachment energy, A. Yamamoto, S. Mishima, N. Maruyama, and M. Sumita (submitted to J. Biomed. Mater. Res.)

## **Ecomaterials Research Team**

### **84 Study on the Processing and Assessment of Ecomaterials**

*K. Halada, K. Minagawa, K. Ijima, H. Yoshizu*  
*Ecomaterials Research Team*

[April 1997 to March 2002]

ECOMATERIALS, which have high recyclability and give less environmental load to the eco-sphere without deteriorating their properties, are expected to be coming materials adapting to the sustainable development. It is an approach from materials science and engineering to the Industrial Ecology towards the coming Sustainable Society. The coming paradigm of the Post mass production is often called Dematerialization. This comes from the re-consideration of mass production, in which it was believed that the resources were infinite and the capacity of global environment was also infinite. Dematerialization means to decrease the mass of materials which the mankind uses, but does not mean the unnecessary of materials. Materials will circulate mainly among producers and service providers to realize effective circulation system to decrease the input/of material from/to the environment. In this coming era, the material technology will become more important, because we have to circulate materials and products with higher quality adequately. Materials should have the properties of 1) lower environmental loading, 2) flexibility of production, 3) long life and the possibility of progressive maintenance.

The basis of this study is to seek the direction of the appropriate processes and materials in the coming era. In this service oriented society, the thinking of "product out" will be ancient manner of the mass production era which push out the great amount of

products to consumers. Materials should be organized and assembled in according to the demanded service to the user. This means the importance of the flexibility of processing of materials. The manner by which the producer of materials product out steel sheet or slabs and entrust the treatment to the following dealer will not succeed no longer. Surface treatment, near-net-shape processing, semi-solidus processing, or other complex flexible processing will become inside of material producer, in order to response the demand from user flexibly. Materials processing is necessary to acquire 1) purposive, 2) autonomouns 3) efficient feature.

This study consists of two parts in concrete. One part is the experimental feasibility study on the new processing technology for the dematerialization era. The processing with higher materials efficiency is the key concept of this study. The materials efficiency does not means the direct amount of materials per product, but the total amount, in which fuel materials and raw materials are included, of materials in the lifecycle per intended service. The expected processing technology is not only the process with lower energy consumption nor lower emission but the process which can control the microstructure of material to assemble into proper part of the aimed material. From this viewpoint, powdermetallurgical technology is selected as one of the most available process. At the first part of the study, Fe-Fe composite as higher recyclable composite is investigated.

Preparation of fiber reinforced porous Fe-Fe composite composed from SCIFER (highly drawn iron fiber) and Fe powder was investigated as an attempt of production of ECOMATERIAS by P/M technology. This Fe-Fe composite is expected to have high recyclability because the microstructure of SCIFER reinforces the matrix without using any alien material nor any alloying elements. In order to utilize the cold-worked structure of SCIFER, sintering temperature was limited under 450°C. UFP (ultra-fine powder) of Fe was used for the acceleration of sintering in lower temperatures. SCIFER fiber and Fe-powder were covered and embellished with Fe-UFP by wet dispersion method. Sintering behavior of embellished SCIFER and Fe powder mixture was examined, and raptured microstructures were observed. Fe-Fe composite had 30kg/mm<sup>2</sup> of Fracture resistance strength by sintered at 400°C, while sintered Fe-powder had 10.3kg/mm<sup>2</sup> by sintered at the same temperature. SEM observation showed that Fe-UFP improved the interconnection of SCIFER fiber and Fe powder at lower temperature.

The other part of this study is to establish the assessment technology of ecomaterials. In the earlier work on ecomaterials, MLCA (materials life cycle

analysis) was established as an assessment method, and the environmental load data of metals and alloys were calculated and collected into database. In this work, further development of MLCA is investigated to give the guideline of DfE (design for environment) and Eco-Design of products to the user of materials. As the utilization of MLCA in future should be used as an environmental element of life cycle engineering, the exchangibility of data with CAD and STEP is seeked. And, the predictability of the environmental data change in the improvement of the process is also the required property of the database in order to deal with the development of flexible processes. At the first part of the study, the retrieval interface and the data structure of "the environmental load database of steel alloys" is modified.

The database is composed of three unit ; 1) CO<sub>2</sub>, SO<sub>x</sub>, NO<sub>x</sub> emissions of preceeding alloying element processing and each processes of steel making, 2) process flow in production of steels, 3) composition of steels in JIS classification. System I is the primitive datasystem which gives the emission data corresponding to the input data of the composition of subjected steels. However this is useful to use these data in the field of materials design, product designer cannot use these data without the knowledge of composition of steels. In System II, the retrieval system of alloys from the purpose of usage is modified. Another table of the purpose of usage and the JIS code are prepared and related together corresponding with the input from selection window of the purpose of usage. Furthermore, System III is developed as to design new product. In the System III, alloys are once selected corresponding to the input data of the properties such as yield strength or hardness. A designer can select or compare the materials from the environmental data of System III from the selected alloys.

**Keywords :** ecomaterials, materials efficiency, recyclability, powder processing, materials environmental life-cycle analysis, computerized materials data

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## 85 Methodology of MLCA

*K. Halada, K. Ijima, K. Minagawa and K. Yagi\**  
*Ecomaterials Research Team and \*2nd research*  
*Group*

[April 1996 to March 1998]

Global environmental issues originate from strains existing in a large amount of materials and energy consumption. Although man-made materials have supported the society bringing advantages and conveniences to human life, they also impose a wide variety of burdens on the environment through each and every step of production, processing, consumption, usage, recycling and disposal. Ecomaterials which would harmonize with the environment and minimize environmental load have to be developed as a new concept of materials design and materials technology. In the project of "Study on Design and Assessment Technology for Ecomaterials", three subjects; assessment technology, materials design and recyclable design are being conducted. This work, methodology of LCA, corresponds to the share of assessment technology of the project.

The development of assessment method for environmental load through the life cycle of materials is a very important subject in this research. The objective of this work is to construct basic database and their frame in order to establish a new ecobalance evaluation method in which environmental load and materials properties are evaluated. A new evaluation method named MLCA (Materials environmental Life-Cycle Analysis) is established, and the data of the environmental load of materials are accumulated.

The methodology of LCA inventory analysis is discussed to develop a common procedure of inventory analysis. Description rule of inventory-tree, treatment of recycling, discrepancy of physical allocation method, and quantitative expression of data quality are subjected to develop LCI as a scientific method with repeatability.

As results of the work, a description procedure which can easily connect to a matrix of process flow is proposed. Concurrentness of the close-loop-recycling and the open-loop-recycling is insisted in real recycling system. A model case of physical allocation is examined to disclose the discrepancy depending on the depth of allocation. Wide data distribution in the same industrial process is shown. The necessity of a quantitative parameter of data quality is mentioned to utilize globally distributed data system with different data quality. Two recommendations are proposed; 1) stocks of material, which are carried out or in beyond a system boundary, 2) preliminary LCI procedure, in which domi-

nant data uncertainty will be indicated to improve the data in order to achieve gradually to an agreeable result.

MLCA is intended to evaluate from the both sides of properties of material and life-cycle environmental load. The way to evaluate the environmental load relating to the mechanical properties or functions are investigated. As the result, the environmental load through life cycle is expressed as follows; (environmental load)=(environmental load for unit mass)

\*(mass-saving ratio by superior property)\*  
(maintenance-saving ratio by long life)

Furthermore, material-design is developed to link with MLCA, to design the composition of the material which brings least environmental load with sufficient mechanical properties demanded in the intended utilization. Phase calculation is subjected for a given composition, and gives the prediction of properties; density, yield strength, metal loss by hot corrosion and creep rupture life. Predicted properties, e.g. density, yield strength, metal loss by hot corrosion and creep rupture life, were compared with a given demand of mechanical performance; e.g. to sustain 1MN force, to endure during 1000h at 1040°C with 137MPa, to protect from corrosion 0.8 times effective than IN738. From these both values of demanded properties and predicted ones, mass of material which is required to satisfy the demand and frequency of maintenance which will be necessary to repair after the predicted life span of material. Then, total weight of material through life-cycle can be calculated by multiplying required mass and maintenance frequency. On the other hand, environmental load per unit weight can be known from a database by giving the composition. The database which gives environmental load has been constructed as a series of materials Eco-Sheet. The total environmental load is obtained by multiplying the environmental load data associated with composition and the total weight through life-cycle. The composition which gives the minimum value of the calculated total environmental load is the best composition both for performance and for environment.

In order to support MLCA, the data of environmental load have to be estimated by using the same method and from published data which everybody can access, while various types of data are collected and comprehensively accumulated in common PLCA. In this work, data subjected to analysis are emission of CO<sub>2</sub>, SO<sub>x</sub>, and NO<sub>x</sub>, consumption of energy and resource, and recyclability of alloys. The consumption of energy and resources are estimated from the data of the unit requirement of fuels and of raw materials. The generation of airborne, such as CO<sub>2</sub>, SO<sub>x</sub>, or NO<sub>x</sub>, are calculated by multiplying the

unit fuel requirement by its emission factors of each substances from the peculiar furnaces and boilers of the process. In the case of CO<sub>2</sub>, emission per unit production is assumed to be equal to the emission amount. Removal factor is accounted for SO<sub>x</sub> and NO<sub>x</sub> when the objective system is equipped with removal facilities.

The calculated environmental data are arranged with detailed description of alloys in the database, which is named Materials ECO-sheet. We can read out that alloy steels have different levels of environmental load each other. This means that it is impossible to discuss them collectively. Materials ECO-sheet will give the information of environmental load of each alloys. In addition, the method to calculate the environmental load of alloy provides the estimation method to calculate that of alloy with arbitrary composition and processing. When the property is given for a alloy with any composition, we can assess it from the viewpoint of Ecomaterial by using the Materials Eco-sheet.

**Keywords:** ecomaterials, environmental load, LCA, Materials LCA, database

#### Related Papers

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MLCA helps Eco-design of Materials, K. Halada, H. Harala, K. Ijima, & T. Yokokawa, *Proc. of the 2nd Intnt. Conf. On EcoBalance, (1996); 453-458*

Environment Load database of Alloys on the Network K. Ijima, K. Halada and K. Yagi, *Proceedings of The Second International Conference on EcoBalance (1996) p. 564*

#### 86 Research on the generic interface of materials databases

*K. Halada, H. Yoshizu Ecomaterials research team [April 1997 to March 1999]*

The recent rapid progress and the expansion of internet and computer technologies involves every engineering fields to process various information. Materials science is one of the most expected field of utilization of information technology.

Many databases exist on the internet, and aimed information of each user can be obtained by accessing to these databases. However, these databases have its unique independent interfaces of the datasystem. Even the description procedures of the data in

the similar materials field does not standardized. Furthermore, each database has independent data structures. Not only the computerized data exchange but also the mutual retrieval of data are difficult in the present state of materials database.

In this study, the establishment of the technical basis of the interface for data exchange is aimed to create an open datasystem of materials property data. The open datasystem should be accessible and exchangeable among different viewpoints of materials sciences; namely materials-designing, processing/developing of materials, evaluation of materials, and utilization of materials for product designing. Since each user or constructor of database from different viewpoints requires its specialized data structure, generic platform of databases is targeted in this study to share and exchange the data from each database, instead of creating the generic data-or database-format of materials data.

The main activity in the first year was to collect information of materials database and computerized material property data-book issued from the institute all over the world by the use of internet or other media. The interface structure of the databases and the description procedure of materials property data are investigated.

Based on the result, the problem on the materials database for computerized exchange is extracted.

1) Extract of problem for the collected materials database and materials property data-book. In the current state, the followings are found by now.

Material databases have each own special original format and structure. This is the reason that the common procedure to retrieved and use the data from databases does not exist. The material names which is a typical retrieval item of the database are also used differently in the description in each database. For example, they are described some UNS (Unified Numbering System) of E527/E1388/ASTM standards, JIS (Japanese Industrial Standard) or DIS in another time. However UNS was expected to be a domain standard, it is not used thorough the world excluding the United States.

From the results of survey, the common or standardized procedure for data exchange system should be developed as the "interface of the platform", on which data can be treated without consciousness of the structure of the original database.

2) Development of the database.

As a case study, the database using the creep-rupture data which has been constructed and published by NRIM is developed. The structure of the interface of the material database is analyzed using this database. The structure of this database is composed of three parts of specimen information, test results and data concerning analytical-model

evaluation. ASTM standards are described as one item for the test results and data concerning analytical-model evaluation. Each data file is to be examined simplify as much as possible to have an approach structure corresponding to the structure of each data file. The data analysis program should be added as an outside system, as various analysis will be subjected depending on the published user.

The retrieval item which should be developed with priority are following ; material name, product form, application and rupture strength (for example, 100000 hour rupture strength is designated).

Furthermore, the development of the test system which becomes the prototype of the open data system is scheduled in the future.

**Keywords :** materials database, interface for data exchange, material property data

### Related Papers

Construction of Open System for Materials Database-Development of Creep Rupture Database-, H. Yoshizu, K. Halada, Proceedings the 35 th Symposium on Strength of Materials at High Temperatures (1997) : 144-148

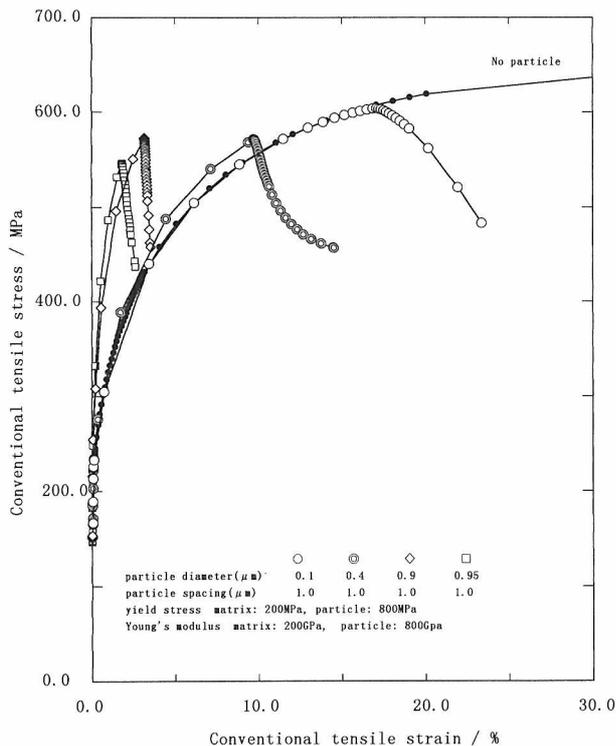


Fig.1 Effect of particle size on stress strain curve in dispersion strengthened material

## Center for Advanced Physical Field

### 87 Analysis of stress strain curve of matrix containing second phase particles by large deformation FEM

H. Shiraishi *Advanced Physical Fields*

[April 1994 to March 1999]

The stress strain curve of the matrix containing second phase particles is analyzed by the large deformation finite element method. Model consists of the infinitely arrayed circular holes in a plate. This is a two dimensional approximate of the real three dimensional material. Mises yield condition, J2 flow theory, n-th power work hardening law and periodic boundary condition are assumed. In this calculation, the following stress strain relationship is assumed for the matrix.

$$\sigma = E\varepsilon, \quad \sigma \leq \sigma_y$$

$$\sigma = C(\varepsilon_0 + \varepsilon_p)^n, \quad \sigma > \sigma_y$$

The material constants in the above equations are determined to correspond to the case of the austenitic stainless steel. The Young's modulus and the yield stress of the second phase particle is set 4

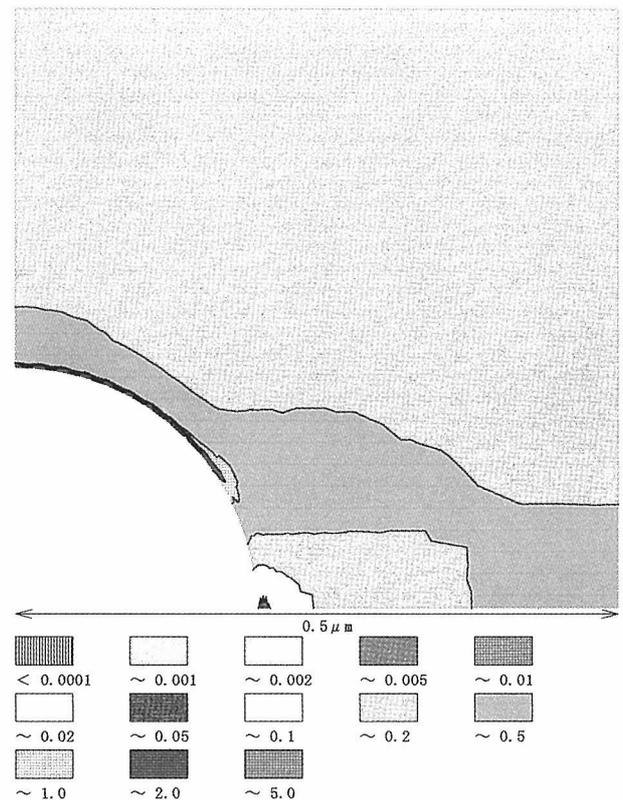


Fig.2 Distribution of equivalent true strain around particle. Work hardening exponent : 0.3, Particle diameter : 0.4μm, Particle spacing : 1.0μm

times of the those of the matrix.

Figure 1 shows the effect of the particle size on the stress strain curves of composite in the case of particle spacing fixing to 1  $\mu\text{m}$ . When the particle size is small, no effect is seen on the work hardening behavior but the uniform elongation is reduced to the half of the no particle case. With increase of size of the particle, the 1% flow stress increases and the uniform elongation decreases sharply to 1.8% in the extreme case of particle of 0.95 $\mu\text{m}$  diameter. Figure 2 illustrates the equivalent true strain distribution around the particle at the final stage. The calculation was interrupted when the present load reduced to 80% of the maximum load. The strain distribution inside the particle is not shown because the state almost remained elastic throughout the calculation. The direction of load is up to down and normal to the paper plane. At first, the plastic strain appears backward of the particle. At the point of the maximum load, the strain reduces clockwise from y to x axis's. After this plastic instability point, the region of the large concentration of strain is formed behind the particle, as illustrated in Figure 2. Also, this strain pattern shows that the inter particle necking appears and this is the reason of the reduction of the uniform elongation.

**Keywords:** stress strain curve, composite, finite element method, continuum mechanics

## 88 Materials with Atomic Scale Structures (COE Project)

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[April 1995 to March 2000]

Under its 5-year plan implemented in 1995, National Research Institute for Metals (NRIM) is conducting researches on the creation of advanced materials with atomic-scale structures exhibiting quantum phenomena. This research is promoted as one of the Center of Excellence Development Program (COE Project) of the Japanese Government, and is financed with the special coordination fund from the Science and Technology Agency (STA).

The main part of our COE Project is progressed at the Center for Advanced Physical Fields (APF) of NRIM, equipped with some stations which provide extreme experimental environments such as high magnetic fields, high resolution beams and extreme high vacuum. The project is in fact designed to make use of the advantages of these facilities in researches on advanced materials.

The COE Project is roughly divided into two parts. One is "Improvement of techniques to establish extreme physical fields". The techniques provided by the Center for APF are important to carry out research on the creation of materials with atomic scale structure. We call this research "COE supporting research". The other one is "Creation and physical properties of atomic scale structure materials". We call this research "COE core research". Atomic scale structure materials are categorized into quantum dot, quantum wire and thin film. Therefore, we divided "COE core research" into 6 sub projects, which cover quantum dot, quantum wire and thin films. We have created new nano dimension crystals, fabricated single atomic width lines which exhibited electron transport properties, and found interesting quantum phenomena in the high magnetic fields. The main results of these 6 sub-projects are as follows: The structural observation of nano-materials with TEM has been developed, and the determination of shape and atomic arrangement was successfully demonstrated. Application of negative ions to colloid formation has been tried and this procedure may lead to fabrication of 2D-like distribution. Various attempts have been done to realize atomic-and nano-scale structures which are connected to electric pads for measuring electron transport properties. The boron nitride film has

been proved to be a good substrate for the fabrication of the nano-structure material. The measuring systems for experiments in the high field magnets have been set up and have been used for a variety of experiments. The unique characteristic phenomena of the low dimensional systems and highly correlated electron systems were investigated in high magnetic fields.

Since the start point the project, the research fellow positions of COE project have been opened to the world. Over 20 fellows are employed from all over the world. However, the number of fellows is still not sufficient, though participation of young scientists both from foreign countries and from Japan is substantially increased. To encourage the mutual communication, International Symposia on Advanced Physical Fields were held in NRIM once a year, and they will enhance the research activities in this research field.

**Keywords :** advanced physical fields, atomic scale structures, quantum phenomena

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## High Magnetic Field Research Station

### 89 Stability of Superconducting Materials

#### H. Wada, High Magnetic Field Station

[April 1994 to March 1999]

The main purpose of this study is to define stabilities of superconducting materials under various condition they may experience when wound to superconducting magnets. Stabilities of new, promising superconducting materials, developed for fusion reactor magnets such as Nb<sub>3</sub>Al and a series of high-temperature oxide superconductors, are examined in terms of temperature, magnetic field intensity/direction and mechanical stress/strain.

Nb<sub>3</sub>Al has been considered as an alternative to Nb<sub>3</sub>Sn for nuclear fusion use, since excellent strain tolerance has been demonstrated for jelly-roll (JR) and rod-in-tube (RIT) processed Nb<sub>3</sub>Al conductors. However, non-Cu J<sub>c</sub> of this Nb<sub>3</sub>Al conductor is much smaller than that of Nb<sub>3</sub>Sn conductors, probably due to the deviation of Nb<sub>3</sub>Al phase composition from A15 stoichiometry. Recently, we have developed a new fabrication technique for Nb<sub>3</sub>Al multifilamentary superconductors with very high stoichiometry and fine grains to attain the enhanced high-field J<sub>c</sub> performance by exploiting the transformation from supersaturated bcc-solid-solution Nb (Al)<sub>ss</sub>. The strain sensitivity of J<sub>c</sub> of A15 phases was explained to increase dramatically with long-range atomic order parameter. If this is the case, the above mentioned J<sub>c</sub>-enhancement in highly stoichiometric Nb<sub>3</sub>Al would trade off the excellent strain tolerance. In fiscal year 1997 the strain sensitivity of the transformed Nb<sub>3</sub>Al conductors with nearly-stoichiometric composition was examined in comparison with that of conventionally heat-treated Nb<sub>3</sub>Al conductors to see if these transformed Nb<sub>3</sub>Al conductors can be a realistic alternative to Nb<sub>3</sub>Sn conductors in high-field and large-scale applications.

The I<sub>c</sub> maximum is believed to occur at  $\epsilon_{a, \max}$  where the thermal differential axial strain is canceled by the externally applied strain and the intrinsic strain  $\epsilon_i (= \epsilon_a - \epsilon_{a, \max})$  is zero. The critical current normalized to the I<sub>c</sub> maximum is plotted as a function of the intrinsic strain  $\epsilon_i$  in Fig. 1(b), comparing the strain sensitivity with the conventional JR processed Nb<sub>3</sub>Al and the ITER Nb<sub>3</sub>Sn conductors at 12T. The upper critical field B<sub>c2</sub><sup>\*</sup>, obtained by extrapolating the Kramer plot, is also given in Fig. 1(a). B<sub>c2</sub><sup>\*</sup>(0) of the transformed RIT Nb<sub>3</sub>Al conductor is larger by about 5T than that of the conventionally heat treated Nb<sub>3</sub>Al which is known to be off-stoichiometric and of high strain-tolerance. The B<sub>c2</sub><sup>\*</sup> degradation with -0.7% intrinsic-strain is 8% for the transformed RIT Nb<sub>3</sub>Al, and almost comparable to conventionally heat treated Nb<sub>3</sub>Al. In line with the prediction by Flukiger et al, the high stoi-

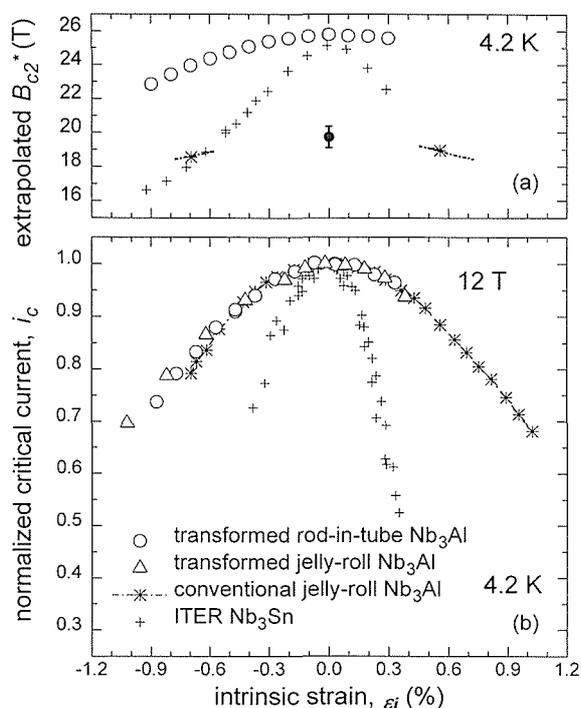


Fig.1 Strain dependence of (a) the upper critical field  $B_{c2}^*$  extrapolated from the Kramer plot, and (b) the normalized critical current  $i_c$  at 12 T and 4.2 K. In order to compare the conventionally heat-treated JR Nb<sub>3</sub>Al conductor and the ITER Nb<sub>3</sub>Sn conductors, the data are plotted against the intrinsic-strain. Closed circle is the  $B_{c2}^*$  of the conventionally heat-treated rod-in-tube Nb<sub>3</sub>Al conductor without applied-strain.

chiometry achieved in the present transformed-Nb<sub>3</sub>Al-conductors seems to have slightly increased the strain sensitivity of the  $B_{c2}^*$ . However, since  $J_c$  strongly depends on  $B_{c2}^*$  ( $\epsilon_i$ ) itself as well,  $J_c$  at a given magnetic-field may look less sensitive to strain if  $B_{c2}^*$  ( $\epsilon_i$ ) is larger. It should anyway have sense from the practical standpoint to compare the strain-sensitivity of  $J_c$  at 12T among different conductors, since this is a designed operation field for fusion magnets. The  $J_c$  degradation with  $-0.7\%$  intrinsic strain is only 20% for the both transformed RIT and JR Nb<sub>3</sub>Al conductors, almost the same in magnitude as that for the conventional JR Nb<sub>3</sub>Al conductor that has a  $B_{c2}^*$  lower by 5T. The degradation of  $J_c$  at 12T in these Nb<sub>3</sub>Al conductors is much smaller than that of the ITER Nb<sub>3</sub>Sn conductors. Consequently, it is concluded that in the transformed Nb<sub>3</sub>Al conductors the excellent strain-tolerance is compatible with substantially improved high-field performance.

**Keywords :** transformed Nb<sub>3</sub>Al, negligible anisotropy, angular dependence, critical current

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H. Aoki, T. Shimizu, T. Terashima and S. Uji, Physical Properties Division  
H. Kumakura and H. Kitaguchi, 1st Research Group, K. Inoue, 4th Research Group  
[April 1995 to March 2002]

High  $T_c$  oxide superconductors (HTS) are expected to be able to induce much higher magnetic fields than low  $T_c$  metallic superconductors (LTS) when used at 4.2K. We have initiated a program in which we will develop a 1 GHz superconducting NMR spectrometer including a 23.5T superconducting magnet; such magnet must be constructed using HTS coils in combination with LTS coils. In fiscal year 1997, engineering design of the NMR magnet was done and fabrication of NbTi and Nb<sub>3</sub>Sn conductors has been started.

In our design the LTS coils are operated in persisting mode at a field of 21.1T in a 132mm diameter bore. The HTS coil is expected to generate an additional field of 2.4T in a 54mm room temperature bore. The cryostat has been designed to replace the HTS coil when necessary. This enables parallel development of the LTS and HTS coils. Those coils are cooled with atmospheric superfluid helium at 1.8K.

Development of high performance metallic superconductors is one of the key issues of this program. LTS coil conductors need to have high yield strength as well as high critical current density in order to be wound compact. Improvement of a high critical current density Nb<sub>3</sub>Sn conductor and a Ta reinforced Nb<sub>3</sub>Sn conductor was carried out. A critical current density of 119 A/mm<sup>2</sup> was obtained at 4.2K and at 18.5T.

Since HTS coil development requires a lot of technological challenges, we have fabricated HTS coils with an outer diameter of ca. 160mm. It is designed as the innermost coil of a 21T superconducting magnet developed at the NRIM. Its performance will be confirmed in a back up field of 18T and at 1.8K in autumn of 1998. Field stability is one of the most important requirements for an NMR magnet. A Bi-2212 pancake coil made of 16 pancakes was developed for this purpose. It was wound continuously and included no joint between the pancakes.

**Keywords :** NMR spectrometer, high field magnet, oxide superconductor

### Related Papers

Current Decay Evaluation of Closed HTS Coil

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## 91 Fundamental Studies for Developing Very High Field Superconducting Magnets

*H. Wada, K. Itoh, T. Takeuchi, M. Kosuge, Y. Sakai, H. Ohtsuka, M. Yuyama, T. Kiyoshi, T. Asano, T. Ohara, H. Abe, K. Takazawa, A. Sato, T. Numazawa, H. Nagai and F. Matsumoto High Magnetic Field Research Station*

*Y. Tanaka and H. Kitaguchi 1st Research Group  
Y. Iijima and K. Inoue 4th Research Group*

[April 1997 to March 1998]

Development of new superconductors for very high fields is one of the key issues to realize the very high field superconducting magnets. Nb<sub>3</sub>Al by rapid heating and quenching process and Bi-2212 conductors are considered the most promising for such application.

Critical currents of Nb<sub>3</sub>Al and Nb<sub>3</sub>(Al, Ge) conductors were measured in the National High Magnetic Field Laboratory (NHMFL) and the National Research Institute for Metals (NRIM). They were fabricated at the NRIM using a rod-in tube process and rapid heating and quenching treatment. Their critical currents below 28T were measured at the Tsukuba Magnet Laboratory (TML) of the NRIM. By using a water-cooled magnet of the NHMFL, critical currents at 33T were measured. These measurements proved that the Nb<sub>3</sub>(Al, Ge) conductors could maintain superconducting state even over 33T. The coincidence of the experimental results measured in both laboratories suggested that the high field magnets in both laboratories were well characterized.

High field performance of a Bi-2212 single pancake coil fabricated by the NHMFL was measured with a 21T superconducting magnet developed at the TML of the NRIM. The engineering current density of 70.5A/mm<sup>2</sup> is required for the planned innermost coil of the 1GHz NMR magnet that is under development at the TML of the NRIM. The coil could maintain the critical current density over 90A/mm<sup>2</sup> even at 21T.

This study was carried out in cooperation with the National High Magnetic Field Laboratory

(NHMFL), Tallahassee, Florida, U.S.A.

**Keywords:** niobium aluminum superconductor, bismuth oxide superconductor, high field magnet, NMR magnet

## Recent Publications

Nb<sub>3</sub>(Al, Ge) Multifilamentary Conductor Fabricated by Continuous Rapid-Heating/Quenching by Process, Y. Iijima, K. Inoue and T. Takeuchi, Proceedings of the Fifteenth International Conference on Magnet Technology, 1040-1043 (1998).

## 92 Test methods of superconductors

*H. Wada, K. Itoh, A. Sato, T. Takeuchi, M. Yuyama and M. Kosuge High Magnetic Field Research Station*

*H. Kitaguchi, T. Kuroda and K. Kumakura 1st Research Group*

[April 1997 to March 2000]

It is very important to establish and standardize the test methods in order to promote the development and utilization of metallic and oxide superconductors. In this study we work on pre-standardization of test methods in conjunction with a large number of domestic and overseas research laboratories in the framework of VAMAS. Results obtained will be the base of the standards discussed and decided at the IEC/TC90; an international organization responsible for standards of superconductors.

In this study we intend to establish and pre-standardize;

1) critical current measurement methods of Ag-sheathed oxide superconductors,

2) critical current measurement methods under mechanical strain and

3) coupling loss measurement methods.

In addition to this, we intend to establish a data-base system containing electromagnetic, thermal and mechanical property data of superconducting and other materials which are necessary for designing superconducting and cryogenic devices.

In fiscal year 1997, we summarized the results obtained before in the domestic round robin tests on the critical current measurement method of oxide superconductors. We were troubled with the critical current degradation in samples, probably caused by thermal cycling, transportation and aging. However, we found that fixing the sample to the measurement holder is quite effective to reduce the degradation. We finally drafted a measurement standard (guideline) and submitted it to the VAMAS and then to

the IEC/TC90.

As for the strain effect measurement methods, we focused the target to the uniaxial tensile test method and constructed a facility to test it. As for the data-base system, we investigated the scope, data format, accessibility, etc. and constructed a small test system.

**Keywords :** standard, metallic superconductor, oxide superconductor, measurement method, critical current, strain effect, data-base

### 93 Development of Magnetic Separation Control System

*T. Ohara, Strong Magnetic Field Research Station*  
[April 1995 to March 2000]

Progress in applied superconductivity technologies has resulted in the development of superconducting (sc) magnets with excellent operability. One of the promising application fields is magnetic separation. The primary advantages, those being energy saving, compact size, and increased speed becomes visible only after the system is superconductorized. The full-scale application of this process will also contribute greatly to the preservation of global environments.

We have developed the key system technologies of application of high  $T_c$  sc magnets to magnetic separation. One of them is an optimization method of a superconducting solenoid for High Gradient Magnetic Separation (HGMS) systems to minimize the quantity of superconducting wire used in the HGMS systems. We developed two computational techniques to simulate the magnetic field created by the solenoid: a detailed numerical model, and a simplified graphical method. Comparing with the case where an HGMS filter and a solenoid have the same length, our optimization technique shows that a large amount of wire reduction is possible.

We proposed magnetic chromatography (MC) as a new technique for ultra-fine particle separation which separates chemically similar but magnetically dissimilar materials, such as lanthanide and actinide elements. Our MC simulator modeled the transient behavior of 300 Å and 500 Å particles by taking into account the fluid flow field, magnetic field, and particle diffusion. Using the simulator, we discussed three factors of the flow velocity and channel length, the magnetic field strength, and the magnetic field distribution, which directly affect the separation efficiency. The result showed the following: 1) Particle staying time in the channel is an important factor to decide the separation efficiency. 2) Increasing

the applied magnetic field strength improves the separation efficiency, and has the advantage of no degradation of particle concentration. This point is different from the channel length increasing method. 3) It is possible to make magnetic field distribution most suitable for MC by adjusting a ferromagnetic wire arrangement.

We conduct this research in collaboration with the Electrotechnical Laboratory, AIST, MITI.

**Keywords :** ultra-fine particles, high  $T_c$  superconducting magnet, high gradient magnetic separation, magnetic chromatography, Computer Simulation

### Recent Publications

Optimization of a Superconducting Solenoid for High Gradient Magnetic Separation Systems, T. Ohara, K. Kaiho and T. Kiyoshi, *IEEE Trans. Magnetics* 32 (1996): 5103-05.

Feasibility of Magnetic Chromatography for Ultra-Fine Particle Separation, T. Ohara, S. Mori, Y. Oda, Y. Wada and O. Tsukamoto, *Trans. IEE of Japan* 116-B (1996): 979-86.

Computer Simulation of Magnetic Chromatography System for Ultra-Fine Particle Separation, X. Wang, T. Ohara, E.R. Whitby, K.C. Karki, C.H. Winstead, *Trans. IEE of Japan* 117-B (1997): 1466-74 in Japanese.

### 94 Evaluation of oxide superconductors

*K. Itoh, T. Kiyoshi, M. Yuyama, M. Kosuge, and H. Wada, High Magnetic Field Research Station*  
*H. Kitaguchi, T. Kuroda, and Y. Tanaka, 1st Research Group*

*K. Inoue, 4th Research Group*

[April 1995 to March 2000]

To realize a magnet made of a high- $T_c$  oxide superconductor (HTS), it is indispensable to have along wire with high quality and homogeneity. We often use short specimens cut from the different positions of the whole length of a wire to check the quality and homogeneity. However, such technique does not only waste a wire but also disable to use it for magnet winding.

In this study we develop and establish efficient techniques to measure superconducting properties such as the critical current ( $I_c$ ) as a function of field, temperature, mechanical strain, etc. In addition, we develop measurement techniques on long and/or coil shaped specimens, and compare the results with those obtained by the techniques on short specimens. Such comparison would be useful for the development of wire fabrication and winding techniques.

Another objective of this project is to prepare, to establish, and to manage various testing systems for superconducting properties such as  $I_c$  which are necessary for conductor and magnet development. By using these systems, we help other groups in the multi-core project for their test of prototype products and possible candidates of conductors. For example, we tested various kinds of metallic and oxide superconductors, which were developed for the 1GHz NMR magnet and the magnet for magnetic separation. We also perform extensively many collaboration projects with superconductor research groups in universities and companies in order to utilize our facilities more efficiently and to progress scientific research on superconductors (HTS as well as metallic superconductors).

Since the beginning of this project, we have established the evaluation system for field angle dependence of  $I_c$  (up to 15T) and measured the relation between field angle and  $I_c$  for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  (Bi-2212) and  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  (Bi-2223) silver sheathed HTS tapes. We found that the field angle dependence of these conductors was dominated by the field component normal to the tape surface except for fields nearly parallel to the tape surface. Results obtained should be useful for the design of HTS magnet, at the end parts of which the normal component of field becomes large and for the evaluation of field irreversibility against coil current. A  $I_c$  test system for high field and high current (up to 28T, 400A) has been also established and used by many groups engaged in development of HTS materials and/or the conductors for the 1GHz NMR magnet system.

Major achievement of this year is as follows:

1) Local  $J_c$  Distribution in Superconducting Oxide Layer of Bi-2212/Ag Tapes

The relationship between  $I_c$  and the thickness of oxide layer of Bi-2212/Ag composite superconductor was studied to clarify local critical current density ( $J_c$ ) distribution in the oxide layer. Oxide layer thickness of Bi-2212/Ag monolayer tape was reduced by a mechanical polishing from the initial thickness of 25 micron to 2-20 micron and  $I_c$  was measured. The first derivative of  $I_c$ -thickness relation gives local  $J_c$  as a function of thickness. Microstructure observation was performed to examine the relationship between local  $J_c$  and Bi-2212 grain alignment. Local  $J_c$  exceeds  $300,000\text{A}/\text{cm}^2$  at 4.2K, 10T for the region near oxide/silver interface where Bi-2212 grains align well. On the contrary, in the middle region (5-20 micron apart from the interface) of the oxide layer where the grain alignment is bad, local  $J_c$  (4.2K, 10T) stays below  $50,000\text{A}/\text{cm}^2$ . The results indicate that  $I_c$  of the whole tape is mainly achieved by the contribution of the region

within 5 micron from the oxide/silver interface with highly oriented microstructure. The results also indicate that the higher  $J_c$  can be expected with decreasing the thickness of oxide layer or with increasing the thickness of Bi-2212 well-aligned region along oxide/silver interface.

2) Strain Effect Measurement System

For magnet applications, strain effect of conductors is very important. However, information on this matter stays insufficient for HTS. In order to perform a systematic study for HTS, we installed a measurement system for strain effect by which  $I_c$  can be measured under strain. The strain can be changed continuously from  $-1\%$  (compressive strain) to  $1\%$  (tensile strain). The system is also equipped with a temperature controlling system. By using this system, 4 dimensional ( $I_c$  magnetic field, strain and temperature) information can be expected. Installation of the system was completed lately and preliminary test has been performed successfully. The further improvement is scheduled in next year. In addition, this system is expected to be utilized also for a fatigue test, in which the relationship between  $I_c$  degradation and the number of strain cycle is examined under alternative strain.

### Recent Publications

High Field Performance Tests for Bi-2212 Magnets with 30 mm Bore, H. Kitaguchi, H. Kumakura, K. Togano, M. Okada, K. Tanaka, J. Sato, *Cryogenics* 38 (1998) 181-186.

Critical Current Density Distribution in Superconducting Oxide Layer of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x/\text{Ag}$  Composite Tapes, H. Kitaguchi, H. Miao, H. Kumakura, K. Togano, and B. Chenevier, *Physica C* 301 (1998) 111-115.

Fabrication and Transport Properties of Bi-2212/Ag Multifilamentary Coils for High Magnetic Field Generation (II); High Field Performance Test, H. Kitaguchi, H. Kumakura, K. Togano, M. Okada, K. Tanaka, K. Fukushima, K. Nomura, and J. Sato, *Inst. Phys. Conf. Ser.* 158, Applied Superconductivity 1997, (Inst. Phys. Publishing, Bristol, 1997), 1543-1546.

Study on Reproducibility of Transport Critical Current for HTSC, H. Kitaguchi, K. Itoh, H. Wada, and K. Togano, (to be published in *Advances in Cryogenic Engineering Materials*, 44).

Critical Current Density Distribution in Superconducting Oxide Layer of PAIR Processed  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x/\text{Ag}$  Composite Tapes, Y. Hishinuma, H. Kitaguchi, H. Miao, H. Kumakura, K. Itoh, and K. Togano, (to be published in *Superconductor Science & Technology*).

**Keywords:** oxide superconductor, evaluation, mea-

surement technique

## 95 Basic Research for the Control of Chemical Reactions by High Magnetic Field

*H. Abe and K. Takazawa, High Magnetic Field Research Station*

[April 1996-]

With the aim of producing new materials in the high magnetic fields more than 10T, we have started to investigate a possibility of controlling chemical reactions by the high magnetic fields. Taking advantage of availability of high magnetic fields in Tsukuba Magnet Laboratory, we are to develop a methodology to measure magnetic field effects on each elementary process in chemical reactions. Such studies hitherto have been performed in the fields up to 2T and have given a clear ground for the interpretations of many aspects of the magnetic field effects on the photochemical reactions in solutions and on the dynamic behavior of electronically excited molecules in the gas phase. The aim of this project is not an extension of such studies to high fields, but exploitation of new research field, "the dynamics of excited molecules in high magnetic fields", which may be a basic research for magnetic field control of chemical reactions.

Two apparatus are used for the following experiments.

(1) Mechanism of photochemical reactions in solutions under 40T class pulsed magnetic field. The reaction is initiated with the excitation of target molecule to the electronically excited state by the third harmonic of a pulsed YAG laser (355nm, 15ns). The creation and annihilation of the resultant reaction intermediate such as triplet state, radical pair, and bi-radical is observed by its transient absorption. The monitor light source is a Xe flash lamp. Trigger timing of the laser and the flash lamp is controlled to synchronize with the maximum field strength of the pulsed magnet.

Using this apparatus, the photoreduction of benzophenone in micellar solutions was investigated under magnetic fields of 0-29.6T.<sup>1)</sup> Large magnetic field effects were observed for both of the lifetime of radical pairs and the yield of escape radicals.<sup>2)</sup>

(2) Dynamic behavior of electronically excited molecules in the gas phase under high magnetic fields up to 10T. Target molecule is excited to a specific energy level located around its predissociation threshold by a tunable pulsed laser. Another tunable pulsed laser is used to detect a resultant dissociation fragment by observing a laser induced fluorescence. Changing time interval between the

firing of the lasers, time evolution of the creation and annihilation of the fragment is measured under magnetic fields up to 10T, which is applied by a liq. He free superconducting magnet. Magnetic field effects on the elementary processes of combustion reaction and photo-ionization will be also investigated. We have also constructed molecular beam apparatus within the magnet bore. Using it, we are to measure the spin relaxation rates of paramagnetic molecules through cooling effect in the supersonic beam.

As the first step to the excitation to the highly excited state, the electronic spectra of gaseous  $\text{NO } \times \text{ } ^2\Pi \rightarrow \text{A } ^2\Sigma$  transition were observed under magnetic fields up to 10T. Large Zeeman effects on the spectra were observed. A quantum mechanical calculation was carried out to obtain the eigenfunction of each Zeeman perturbed level and at the result, both transition energies and the intensities of all spectral lines could be completely reproduced.<sup>3)</sup> Now, we have succeeded to get preliminary data of the magnetic field effects on the level structure of Rydberg molecule, auto-ionization rate (which probably comes from the dissociation rate) from the level, and Landau level above the ionization potential, which is the first observation for molecule.<sup>4)</sup>

**Keywords:** high magnetic field, chemical reaction, photo-dissociation, photo-ionization, reaction intermediate, photoreduction

<sup>1)</sup> Nishizawa et al. Chem. Phys. Lett. 267 (1997) 501-506.

<sup>2)</sup> M. Wakasa, K. Nishizawa, H. Abe, G. Kido, and H. Hayashi, J. Am. Chem. Soc., 120 (1998) 10565.

<sup>3)</sup> K. Takazawa and H. Abe, J. Chem. Phys., 110, 9492 (1999).

<sup>4)</sup> K. Takazawa and H. Abe, J. Chem. Phys., in press.

## 96 Measurement technologies and reference materials for low temperature thermophysical properties of solids

*A. Sato, T. Numazawa, F. Matsumoto and H. Nagai*

[April 1997 to March 1999]

A national project has been started in 1997 to establish measurement technologies and reference materials for thermophysical properties of solids. We have joined the project for low temperature properties of solids on heat capacity and thermal conductivity. Since it is required to clarify the uncertainty in measurements and the characters of materials for reliable thermophysical property of data, we started

to develop the both measurement systems by using the latest technologies. For heat capacity system, we used a heat relaxation method in the temperatures between 0.5K and 200K and the magnetic field up to 12T. By introducing newly developed helium 3 refrigerator, the temperature region will be extended down to 0.3K. For thermal conductivity system, a steady heat flow method was used and it covered the temperatures from 2K to 200K with the magnetic field of 5T. The measurement range will be extended from 0.5K to 300K and up to 8T. Several candidates of reference materials have been measured. Some garnet, ortho-aluminate and vanadate oxide crystals including rare-earth elements have been chosen and measured from the view point on the sharp magnetic transition peaks in the heat capacity and on the large magnetic field dependence of the thermal conductivity. The measured data now are being analyzed.

**Keywords :** measurement technology, reference materials, low temperature thermophysical properties

#### Recent Publications

Thermal Conductivity of Rare-earth Oxides for Heat Switch Application, T. Numazawa, A. Sato and K. Shimamura, Proc. of ICEC16, The Cryogenic Society of Japan, Tokyo, Japan (1997)

Thermal Conductivity of  $RAI_3$  (R=Dy, Er and Ho), T. Numazawa, A. Sato and K. Shimamura, J. of Material Science, vol. (1998): 827-831

#### 97 Measurement technologies and reference materials for low temperature thermal expansion of solids

*A. Sato, T. Numazawa, F. Matsumoto and H. Nagai*

[April 1997 to March 1999]

A national project has been started in 1997 to establish measurement technologies and reference materials for thermophysical properties of solids. We have joined the project for low temperature thermal expansion property of solids. We started to develop a thermal expansion measurement system in low temperatures between 1K and 20K. A strain gage method is considered here because of ease of measurement for various test samples. The cold stage which controls the sample temperature between 1K and 20K has been built by using a helium 3 refrigerator. It could set the sample temperature within 0.01K error. Several materials have been listed to measure the thermal expansion below 20K. Since most materials show very small amount of thermal

expansion change below 20K, the selected materials are considered from some unique magnetic properties such as a sharp lambda magnetic transition in RSb system (R=Ho, Dy, Gd) or Yahn-Teller effect in  $DyVO_4$ . In particular, magnetic regenerator materials including RSb are important for cryocooler application below 10K, a data base is being constructed on the thermal properties including thermal expansion data.

**Keywords :** measurement technology, reference materials, low temperature thermal expansion

#### 98 Fundamental Studies on Very High Magnetic Field Generation

*T. Kiyoshi, T. Asano, M. Kosuge, M. Yuyama, A. Sato, F. Matsumoto, H. Nagai, T. Numazawa, T. Takeuchi, K. Itoh and H. Wada*

[April 1998 to March 2001]

Generation of very high magnetic fields is expected to open new frontiers of science and technology. To realize such high fields, continuous studies on magnet design, magnet fabrication, cooling system and materials should be performed.

New applications of magnetic fields often require special magnets based on new concept. Uniform magnetic force field magnets are now under development for a new application to structural biology. A magnet is usually designed and fabricated to achieve uniform magnetic field as well as uniform magnetic field gradient. In this new application, uniform magnetic force field is important because it has recently been found that the growth of protein crystals is affected by the presence of magnetic force.

Uniform magnetic force field magnets are superconducting magnets because they must be continuously run for several days to grow protein crystals. The first magnet wound with NbTi is now under construction. This magnet is designed to generate uniform field of 240 T<sup>2</sup>/m in a cylindrical space of 10 mm in diameter and 10 mm in height, and the magnetic force field fluctuation along z-direction is better than 0.4%. Its performance was confirmed in liquid helium. This magnet will be cooled with a G-M refrigerator and used for studies on protein crystal growth in magnetic force environment.

This study has been carried out in cooperation with the National Institute of Bioscience and Human-Technology and the National Institute of Materials and Chemical Research and partially supported by CREST of JST.

**Keywords :** high magnetic field, superconducting magnet, water-cooled magnet, uniform magnetic

force field

### Recent Publications

Superconducting Magnets for Generating Uniform Magnetic Force Field, T. Kiyoshi, O. Ozaki, H. Nakayama, H.B. Jin, H. Wada, N.I. Wakayama and M. Ataka, IEEE Trans. Appl. Superconductivity, Vol. 9 (1999): 362-365.

## 99 Basic Research for the Improvement of Material by Structural Control in High Magnetic Field

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*\* Domestic Research Fellowship*

[April 1995 to March 1997]

Magnetic field affects most of the solid/solid phase transformations in Fe-based alloys mainly due to the difference of magnetic moment of product and parent phase. It is expected that nucleation and growth rates of product phase, transformation kinetics, transformed structure and mechanical properties of product phase are remarkably influenced by magnetic field. Therefore magnetic field is also useful for structural control of Fe-based alloys. In this research, effects of magnetic field on martensitic transformation, spinodal decomposition, recrystallization and gelcasting in magnetic field have been investigated.

1 Effects of magnetic field and/or tensile stress on martensitic transformation in Fe-Ni-C alloys has been studied at 4.2K. Number density, length of martensite plates and fraction transformed were measured, and the size of nucleus of martensite was calculated. The contribution of autocatalytic nucleation was also obtained, and experimental results were well explained by this calculation.

2 Aspect ratio of martensite formed at 4.2K was measured in Fe-Ni-C alloys. The aspect ratio has a close relationship with driving force, mechanical behavior of product and parent phase, etc. Many data of aspect ratio have been obtained so far, and they are on a straight line as a function of temperature, but it was found that the data below 77K are larger than those on the line. This is because very small amount of transformation strain is accommodated in martensite below 77K.

3 An Fe-Ni-Al alloy was aged in magnetic field and magnetic moment was measured. It was found that the magnetic moment is decreased by the aging in magnetic field, which is due to the change of precipitation, ordering and spinodal decomposition kinetics in magnetic field.

4 Effects of magnetic field on recrystallization was studied in Fe-3%Si alloy. Recrystallization and coarsening behavior after recrystallization were found to be retarded by magnetic field. Therefore magnetic field can be used to prevent coarsening during heat treatment.

5 A lamella structure of textured phase, which has been made by gelcasting in magnetic field, and non-textured phase of Fe<sub>2</sub>TiO<sub>5</sub> was produced. It was shown that the toughness is remarkably improved by gelcasting in magnetic field.

**Keywords:** martensitic transformation, diffusional transformation, aspect ratio, spinodal decomposition, gelcasting, recrystallization

### Recent Publications

Growth Behavior of Martensite Plates in Fe-Ni-C Alloys Formed under High Magnetic Field and Tensile Stress at 4.2K, H. Ohtsuka, G. Ghosh, K. Nagai and H. Wada, Journal of the Japan Institute of Metals, 61 (1997), 1337.

Aging of an Fe-Ni-Al Alloy in Magnetic Field, H. Ohtsuka, G. Ghosh, H. Mamiya and H. Wada, *ibid.*, 61 (1997), 1333.

## High Resolution Beam Research Station

### 100 Surface Analysis Database

*K. Yoshihara, High Resolution Beam Station.*

*M. Yoshitake, Extreme High Vacuum Station*

[April 1998 to March 1999]

About 20 years has passed since commercial AES and XPS apparatuses appeared. Since that time, a number of spectral data for surfaces were obtained by many scientists and engineers. However, almost all of them were not shared and not stored as databases. Nowadays, it becomes important to stock these knowledge or data as databases, because we are aware that these data are very useful to characterize unknown surfaces. To create spectral database, we have to establish the system to share spectral data taken on different machines.

NIST has published a database for XPS peak positions. AVS is publishing Surface Science Spectra. Manufacturers have their own spectral databases and distributed to their customers. Usually, the objective of these databases is to provide users with spectral data of clean surfaces of pure materials. However, the concept of this database is that "If we store the all spectral data of all surfaces taken on all machines, we can characterize any surfaces and

calibrate any analyzers without difficulty". This concept is different from those of other existing databases, and we consider this database should be open to public. Nowadays the usefulness of Internet is increasing. If the database is connected to Internet, a number of scientists can freely access the accumulated scientific property.

In 1994 the Science and Technology Agency (STA) of Japanese Government launched a project to interconnect networks under various ministries and agencies. As a site of this network we are implementing a network-oriented database for surface chemical analysis such as AES and XPS spectra. We asked the Surface Analysis Society of Japan (SASJ) to provide the spectral data, and to control its quality. Internet spectral data now has about 2,000 spectra of metals, semi-conductors and ceramics. The file structure of spectral data is based on ISO FDIS 14976 and ISO CD 14975, and is fully compatible with VAMAS Standard Data Transfer Format. Because this file structure can carry the information on specimens, calibration and data-processing, we could construct a GUI searching system for Internet database.

A workstation was installed in National Research Institute for Metals to collect the spectral data with VAMAS/ISO format from different analysis machines via computer networks. Collected spectra are stored in the database. If a personal computer is connected to Internet, one can access the database, address of which is <http://sekimori.nrim.go.jp>. When <http://sekimori.nrim.go.jp> is opened, one can select the database menu and retrieve a spectrum from the selection menu. The retrieved spectrum will be displayed and can be downloaded if a user is a member of SASJ.

Spectral data have been collected through the voluntary work of the members of SASJ using certified materials. The quality of spectra is checked by the committee of SASJ. The committee checks the calibration procedures for energy and intensity scales of a supplier's analyzer, and rate a spectrum sent from a supplier. We are intending to construct an automatic spectra acquiring system for database using Internet. If this system is established, one can easily send one's spectral data to SASJ database through Internet. The spectra will be used to identify the surface chemistry of new materials by comparing it with an observed spectrum.

The spectra database has an index for each spectral data. When a spectra is registered in the database, the index is renewed and its information is registered. If a spectrum follows VAMAS/ISO format, the necessary information to register is automatically attached. The index is created using "Oracle" database engine, and easily retrieved by SQL lan-

guage. However, it is impossible for a person who does not know SQL language to retrieve a spectrum. Therefore, the spectra database provides a user with an graphical user interface (GUI), and the viewer named Common Data Processing System for the downloaded spectral data. When a user inputs or selects searching conditions for spectra, the list of the spectra which corresponds to the selection is shown. When a user selects one of the spectra from the list, the retrieved spectrum is shown on the screen. If a user is a member of SASJ, the retrieved spectrum can be downloaded and processed or compared with other spectral data.

Since 1989, we have been constructing the spectral data processing system under VAMAS (Versailles Project on Advanced Materials and Standards) umbrella. This system is called Common Data Processing System (COMPRO). COMPRO is designed to be a program to convert an original spectral data file structure to common one, to assess the data processing procedures proposed by scientists, to calibrate energy and intensity scales, to check a spectrum, and to build both spectra and correction factor database. In this system, the spectral data acquired on different instruments and/or computers can be compared to one another. COMPRO is designed to be a program to assess the data processing procedure provided by scientists, to check a spectrum, and to build both a spectra and a physical property databases. To achieve these objectives, COMPRO provides a tool for converting spectral data taken on different instruments to common one. COMPRO (present version is 5.4) runs on Windows 95 and can be downloaded from <http://sekimori.nrim.go.jp>.

In future we hope all computers of the surface analysis machines can be connected to the system so that every surface analyst worldwide can share the spectral data to characterize surfaces of materials.

**Keywords :** AES, XPS, Database, Internet

### Recent Publications

Database for Surface Analysis, M. Yoshitake and K. Yoshihara, *J. Korean Vac. Soc.* 5 (1996), 57-60  
Sharing of AES and XPS Spectral Data through Internet, K. Yoshihara and M. Yoshitake, *J. Vac. Sci. Technol.*, A16 (1998), 1388-1393

### 101 Surface Chemical Analysis

*K. Yoshihara, High Resolution Beam Station*  
*M. Yoshitake, Extreme High Vacuum Station*  
*S. Hofmann, Director in Special Research*  
[April 1998 to March 2000]

Surface chemical analysis is a relatively new field, starting embryonically in 1968 in a few University departments. The major growth in applications of the techniques occurred in the last decade as the instrumentation developed. During this period the field of applications of surface analysis, both in academic research and in industry, grew widely to range from failure processes in advanced materials to the development of catalysts and microelectronics.

The above studies include not only the analysis of the surface atom layers but also compositions in the near surface layers to a depth of 1  $\mu\text{m}$  or so. To analyze these regions four main techniques have evolved: X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS) and sputtered neutral mass spectrometry (SNMS). XPS and AES are the simpler of the techniques, XPS providing chemical state data whilst AES provides spatial resolution to sub-micron levels. The advantages of SIMS and SNMS lie in their greater sensitivities although this is coupled with a greater difficulty in analysis of the data.

Prior to the initiation of the VAMAS program, in which the Surface Chemical Analysis Technical Working Area is a founder activity, the extent of internationally co-ordinated work was small. At the outset it was recognized that, if this TWA were to cover the whole surface chemical analysis field effectively, it would need subdivision into a series of semi-autonomous sub-projects led by the relevant expert in one of the Member States. Large, all-embracing, projects were avoided so that individual points could be addressed and solved at rates governed by the activities of relatively small groups of workers. Groups could build on each others' results but were not dependent on them for completing their projects.

Within the above structure three main objectives were defined. (i) to provide the measurement infrastructure required for setting standard methods of specifying surface chemical analysis. (ii) to develop an agreed base for principles, definitions and equations for relevant aspects of surface analysis techniques and (iii) to identify reference procedures for materials, data, instrumentation and measurement methods. To meet these objectives, 31 sub-projects have now been established in VAMAS community. It is easier to understand the structure of this program if we note that the work naturally falls into one or more of five distinct areas. (i) the development or validation of the basic theory for the physical process involved in the techniques. (ii) the understanding and calibration of the measuring instruments. (iii) the development or calibration of software for data reduction and for communication. (iv) the development of reference materials and (v) the deter-

mination of reference data. Below we describe, briefly, developments in these areas.

In 1992, ISO/TC201 committee has been established, the objective of which is the standardization of surface chemical analysis. This committee has liaison with VAMAS Surface Chemical Analysis group and the fruits of VAMAS activities are transferred to ISO/TC201 as the ISO standards.

Since the VAMAS project has started in 1982, we have investigated the reliability of the quantification with AES and XPS with round robin, and proposed calibration procedures for the energy and intensity scales. Since 1989, we have also been constructing the spectral data processing system. This system is called Common Data Processing System (COMPRO). COMPRO is designed to be a program to convert an original spectral data file structure to common one (VAMAS standard data transfer format), to assess the data processing procedures proposed by scientists, to calibrate energy and intensity scales, to check a spectrum, and to build both spectra and correction factor database. In this system, the spectral data acquired on different instruments and/or computers can be compared to one another. By using this software, users of surface analytical machines can easily use the calibration process proposed by the VAMAS community.

Nowadays, it becomes very important to analyze the small area of surfaces, so that primary beam current density increases and may deteriorate the surface structure, and gives wrong information on surfaces. So it becomes important to estimate the degradation and to find the procedure to minimize the damage of surfaces. Since 1997, we have started a new research project on the damage induced by the primary beam.  $\text{SiO}_2$  will be reduced by the irradiation of electron beam. Therefore, when one wants to analyze a thermally oxidized silicone surface, one can not identify precisely the interface between the oxidized surface and substrate. We investigated the degradation behavior of  $\text{SiO}_2$  by the irradiation of electron beam, and found the procedure how to minimize the degradation.

During the time that it takes to collect XPS data, every material will be exposed to experimental conditions that can cause minor or major changes in the chemical composition and/or the physical structure of the surface region. The results of the changes to a material are defined as the degradation of a material. Therefore, we estimated the degradation of PVC film by measuring the change of C12p peak heights during the irradiation of X-ray. We found that the C12p peak height decreases exponentially with irradiation time of X-ray. However, we should confirm this degradation behavior by round robin, because the behavior may be influenced by the

measurement conditions. Therefore, we will propose the new round robin on polymers degradation under the influence of X-ray illumination in VAMAS/TWA2 community.

**Keywords :** VAMAS, Standardization, AES, XPS

### Recent publications

Compositional and Chemical State Analysis of Layered Intermetallic Compounds by Line Scanning of Etched Crater with Scanning XPS, M. Yoshitake and K. Yoshihara, *J. Surf. Anal.*, 3 (1997): 478-482  
Round Robin on Spectrometer Transmission Calibration for AES in the Common Data Processing System, M. Yoshitake and K. Yoshihara, *Surf. Interface Anal.*, 25 (1997): 209-214

## 102 Characterization and Control of the Optoelectronic Properties of Small Crystalline Materials with Electron Probe Analysis

*K. Furuya, Y. Fukuda, M. Tanaka and K. Yoshihara, High Resolution Beam Research Station*  
[April 1995 to March 2000]

It is possible to characterize and control the specific optoelectronic properties of very small crystalline materials by enclosing the crystals with a different kind of materials, or by terminating the conducting electrons inside particles. This type of small structures is feasible by burying nanometer-sized crystals into materials and covering the surface of one material with other material.

We are trying to create those small "hetero structures" and to characterize their structures.

Porous silicon is chosen for one example of non-equilibrium nanocrystals embedded in the bulk matrix. A highly porous silicon (PS) made by anodization is known as a material with efficient visible photoluminescence (PL) at room temperature. The quantum confinement model can explain the PL in the visible light range. However, a number of experimental data inconsistent with this model have also been observed and alternative explanations proposed. For example, siloxene derivatives, SiH<sub>2</sub>, or oxide defects on the surface of Si particles are suggested to be responsible for the PL. It is therefore considered that the visible PL may be ascribed to not only the nanosize effect but also to some surface state. However, few studies have been reported on the PL properties related to both chemical states and microstructures of PS layer.

In this year, the correlation among PL properties, chemical states, and microstructures in PS layers treated with NaOH solution has been investigated to

clarify the origin of PL. PS samples were prepared by anodizing p-type Si (100) wafers with 0.04-0.06Ωcm resistivity. The anodization was performed in a 50%HF-ethanol (1 : 1) solution at room temperature at a constant current density of 0.35A/cm<sup>2</sup> for 10 seconds. In addition, PS samples aged for 15 months were used. The chemical treatment of PS was carried out by immersion in 0.05% aqueous NaOH at room temperature. The chemical states and microstructures of PS layers were studied using Fourier transform infrared spectroscopy and electron microscopy. PL spectra were measured at room temperature by using a nitrogen laser pulse (337 nm) as an excitation source. As-prepared PS exhibited red PL. The red PL was almost quenched by NaOH treatment for 10 seconds, while a lightly oxidized outer surface layer of about 100 nm was removed. Aged PS showed stronger red PL than as-prepared PS. The PL of aged PS became weak gradually as the Si—O bond content in PS decreased with NaOH treatment time, but was stronger than that of as-prepared PS even after treatment for 450 seconds. In this case, although micro pores were widened, the thickness of PS layer did not change and the outer surface layer remained in part. These results suggest that the oxidized outer surface layer of Si nanocrystals in PS is responsible for the red PL.

Photoluminescence Change of As-prepared and Aged Porous Silicon with NaOH Treatment, Y. Fukuda, W. Zhou, and K. Furuya, submitted to *J. Electrochem. Soc.*

**Keywords :** Small crystalline materials, surface terminated particles, porous silicon, photoluminescence

## 103 Analysis/Evaluation of Atomic Scale Compositional Change in Materials Due to the Radiation Damage

*K. Furuya, M. Song, T. Noda and T. Saito, High Resolution Beam Research Station*  
[April 1995 to March 1999]

Radiation damage in materials is characterized by the atomic displacements associated with the destruction of crystalline structure, transmutation by nuclear reaction and radiation induced solute segregation by the irradiation of energetic particles such as neutrons and ions. In addition to the formation of many types of defect clusters produced by this atomic process and the resultant microstructural changes, enhanced diffusion associated with these defect reactions results in the local change in the concentration of solute atoms, the segregation at

grain boundaries and surfaces, and the precipitation of secondary phases. For the basic understanding of radiation damage and compositional changes, an analytical TEM consists of 1 MeV electrons with two ion accelerators, energy dispersive X-ray spectroscopy (EDS) and energy loss spectroscopy (EELS), so-called "SUBNANOTRON", is used in this research. In this year, the researches on the advantage of the extensive usage of EELS at higher voltages and on the chemical analysis of Ni silicide epitaxially formed on Si (100) surface were investigated.

A post-column type energy filtered imaging system made of GATAN Ltd. was installed below a camera chamber of a JEM-ARM1000 high-voltage transmission electron microscope (HVTEM). The addition of the optical deflection lens for the detection system to eliminate stray X-rays makes it possible to take HV-EELS spectra and energy filtered TEM (EFTEM) at 1000 kV. The energy resolution of EFTEM was measured from zero-loss peak obtained from the HV-EELS system operated at 1000 kV. The full width at half maximum (FWHM) of the peak was 0.7 eV for unsaturated filament, which indicates the limitation of spectral analysis. HV-EELS spectra were obtained for Si  $L_{2,3}$ -edge and Ni M-edge with the detection area of about 10 nm in diameter and followed by EFTEM in the same region.

Ni silicide structures were prepared by electron beam evaporation of Ni onto Si (100) TEM thin films in an ultra-high vacuum chamber (base pressure of  $2 \times 10^{-8}$  Pa). The average thickness of Ni was 3 nm and the deposition rate was 0.01 nm/s at 573K. High-resolution transmission electron microscopy (HRTEM) was performed with JEM-ARM1000 high-voltage electron microscope. Ni silicide forms islands with the size ranging from 50 to 200 nm. HRTEM images of the boundary region between silicide and Si indicates the difference in the contrast due to the structural difference. Multi-slice image simulation supports this change in contrast, namely the contrast of Ni column is lower than that of Si column. Energy filtered images were taken at 400 and 1000 kV to perform two dimensional chemical analysis of Si and Ni. The results clearly indicated the distribution of Ni as islands similar to those in HRTEM observation. However, atomic scale mapping of Ni was prevented by the chromatic aberration of electron beams and the vibration of the specimen.

**Keywords:** SUBNANOTRON, EELS, Ni silicide, compositional mapping

## 104 Study on Detection and Evaluation of Radiation Damage in Extreme Particle Fields

*N. Kishimoto, H. Amekura, Y. Takeda, K. Kono, C. G. Lee, H. Shiraishi and T. Saito High Resolution Beam Research Station*

[April 1992 to March 1999]

Hybrid particle fields of ion and photon exert strong interactions with materials and are potent not only to detect elementary processes but to explore novel properties of materials. Especially if both high energy and high density of ion and photon are attained, unexplored non-equilibrium effects will be expected, by virtue of their contrasting effects of momentum, energy and excitation modes. The extreme particle field is also an important aspect for practical environments of high energy devices, such as fusion reactors etc. The main purpose of this research program is to detect and evaluate non-equilibrium processes of materials in the extreme-particle-fields (EPF), associated with radiation damage.

In this fiscal year, the program concentrated on system integration of the EPF generator, especially on Phase-IV, i.e., a photon-field generator and optical devices installed into one of the two irradiation chambers. The photon-field generator, i.e., a high-performance YAG laser, employed the image-relay transport and attained 5 J/pulse at the specimen. Concurrently, beam-material interactions in the low-energy/high-current ion fields were studied by use of the negative-ion beam-line. The intense particle flux, comparable with vacuum evaporation methods, occurred unusual material kinetics, such as spontaneous colloid formation without thermal annealing.

Technologies of in-situ measurements were developed for particle-induced conductivity, DLTS and plasma spectroscopy. Particle-induced conductivity (PIC) under proton irradiation was measured in comparison with photoconductivity (PC), i.e., photon-induced charge transport. The in-situ conductivities manifested similarity and difference between ions and photons. Either PIC or PC was caused by electronic excitation, but there appeared a difference in excitation intensity dependence: the PIC was proportional to the square root of beam intensity, differently from the linearity of the PC. The apparent difference was understood in the identical regime, by taking account of difference in excitation intensity. Practical beam densities, e.g.  $\sim 10$  nA/cm<sup>2</sup>, gives a strong excitation condition, where electron-hole recombination becomes dominant. Needless to say, a principal difference of PIC results from atomic displacements due to nuclear energy deposition. The PIC is subject to perpetual

deterioration due to accumulated defects. It was also found that, above the critical fluence, the decreasing rate of PIC against fluence was  $10^3$  times larger than PC. In-situ DLTS confirmed that VO- and  $V_2$ -centers were responsible for the deterioration and that other deep centers of carbon-defect complex coexisted in a metastable manner. It is thus revealed with those in-situ measurements that dynamic coupling between defects and impurities plays important roles under the hybrid particle fields.

**Keywords:** extreme particle field, high current, heavy ion, in-situ measurement

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High Current Implantation of Negative Copper Ions into Silica Glasses, N. Kishimoto, V.T. Gritsyna, K. Kono, H. Amekura, T. Saito, Mater. Res. Soc. Symp. Proc., Mater. Mod. & Synth. by Ion Beam Processing, Vol. 438, (1997): 435-440.

Particle-Induced and Photo-Conductivities in Amorphous Si: H Under Proton Irradiation, N. Kishimoto, H. Amekura, K. Kono and T. Saito, Mater. Res. Soc. Symp. Proc., Microstructure Evolution During Irrad., Vol. 439 (1997): 679-684.

Evaluation of Proton-Induced Deep Levels in n-Si, K. Kono, N. Kishimoto, H. Amekura, T. Saito, Meeting, Mater. Res. Soc. Symp. Proc., Defects in Electronic Mater. II, Vol. 442, (1997): 287-292.

### 105 Development of Fundamental Technologies for Excited Neutral Beams

*Y. Yamauchi, Neutral Beam Unit, High Resolution Beam Research Station*  
[April 1997 to March 2002]

The electronic states of surfaces play significant roles in chemical reactions and crystal growths on surfaces of materials. The excited neutral beams are promising probes to get information from exactly outmost surfaces rather than electron or photon beams. Fundamental technologies to generate excited neutral beams are being developed.

In spite of the fact that photoelectron spectra or electron-excited secondary electron spectra include the information on the outmost layer, photons and electrons penetrate through the outmost layer and reach to more deeper layers. Those spectra contain the information on deeper layers where the ejected electrons are generated. Thus some ambiguity remains whether any features of spectra are originated from the outmost layer or the deeper layers. On the other hand excited neutrals also may release their internal energy to the surface electrons. The slow

neutrals with a kinetic energy of several tens meV are reflected by the potential which comes from the surface atoms and never reach to the deeper layers. The ejected electrons pick up only the information on the electronic state outside of the top-most layer. Therefore slow excited neutrals are essentially sensitive to the electronic state of adsorbed molecules or states spatially extended wave function from the surface to the vacuum. Further the spin selected neutral beams enable us to understand surfaces more precisely.

The present project includes two kinds of technologies, i.e., generating techniques for excited neutral beams and detecting techniques for secondary particles ejected from irradiated surfaces. As regarding to the beam forming, a beam system creating high density neutral beams under a clean vacuum environment, exciting atoms by electron impacts, removing ions and high Rydberg atoms, selecting the velocities, and polarizing the electron spins of atoms will be developed. Means to measure the energy angular distribution and the spin polarization of ejected low energy electrons will also be investigated.

To concretely design a neutral beam system, a preliminary study has been conducted using a prototype apparatus for beam generation and excitation. The direct excitation by a discharge between an electrode inside a nozzle made of insulating materials and a skimmer, i.e., nozzle-skimmer discharge produces intense beams and its simplicity is beneficial. However nozzle-skimmer discharge sources produce not only metastable atoms but also emit photons of appreciable amount. Therefore time-of-flight (TOF) method and mechanical chopping of atom beams are combined to eliminate the effect of photons but the additional mechanism loses the advantage of their simple structure. Although the pulsed discharge may enable us to get pulsed beams without mechanical chopping and to keep the flight distance between a source and a target small, no pulsed discharge of nozzle-skimmer discharge source has been reported. This is due to the fact that the ignition condition of a discharge is largely different from its steady operation. While several hundreds volts is enough to sustain the discharge, several thousands volts is normally required to start it. In some cases the gas pressure is risen up higher or the nozzle is moved closer to the skimmer for the ignition. The standard method to obtain a stable discharge is to control one of the major discharge parameters, the discharge voltage, the gas pressure, and the distance between electrodes. Practically the voltage is easiest to vary in the pulse durations of 10-100  $\mu$ S among them. Therefore, to secure a stable pulsed discharge, the electric field of the source was

controlled by the third electrode between the nozzle and the skimmer. The maximum total flux in the pulse duration which is equivalent to a continuous beam flux to be chopped mechanically is estimated to be  $1.7 \times 10^{15} \text{ s}^{-1} \text{ sr}^{-1}$  considering the duty factor of the pulses. This intensity is comparable to that reported for a high power source operated at a power of 100 W and is one order of magnitude larger than that of other conventional low power sources. On the other hand the pulsed discharge allows higher peak powers while the average power remains low leading to a long lifetime and retaining the advantage of its simple structure. The continuous metastable atom beam most of which is scattered by a mechanical chopper in a conventional system is squeezed up to a pulsed beam in the present source and its peak intensity increases with the duty ratio of the pulsed discharge.

The oxygen adsorption on a polycrystalline titanium surface at room temperature was studied to examine the capability of the MDS. MDS, UPS and AES spectra were measured by the prototype apparatus. From the analysis of the spectra, the followings were revealed: (1) With increasing oxygen exposure at 0-2L, the local density of states (LDOS) of the first atomic layer, i.e., the surface density of state (SDOS) at 0-1eV below the Fermi level ( $E_F$ ) decreases more steeply than that of deeper layers. (2) The SDOS at 5-8 eV below  $E_F$  remains small at 0-2 L, and begins to increase at 2L while the LDOS of sub surface layer increase first. These results support that the adsorbed oxygen atoms occupy subsurface sites at 0-2 L. The ultimate surface sensitivity of MDS and its potential for the surface electronic analysis were

successfully confirmed.

**Keywords:** neutral beam, metastable atom, excited neutral, surface

### Recent Publications

A Metastable Helium Atom Source Directly Pulsed by a Nozzle-Skimmer Discharge, Y. Yamauchi, M. Kurahashi and N. Kishimoto, *Meas. Sci. Technol.* 9 (1998): 531-533.

A Metastable-Atom Deexcitation Spectroscopy (MDS) Study on the First Atomic Layer of a Polycrystalline Titanium Surface, M. Kurahashi and Y. Yamauchi, *Mat. Res. Soc. Symp. Proc. Vol. 501* (1998): 67-72.

### 106 Development of analytical techniques for characterization of nuclear materials using new generation synchrotron x-rays

*K. Sakurai and H. Eba, High Resolution Beam Research Station*  
[April 1994 to arch 1999]

Synchrotron light source can provide tunable-monochromatic, well-collimated and polarized intense X-rays. Such properties are quite attractive from a viewpoint of materials characterization. The present program aims to develop feasible analytical techniques in both hardware and software. Our recent activities have been placed on the nano-meter-scale morphology on the mirror-polished surface by grazing incidence X-ray scattering.

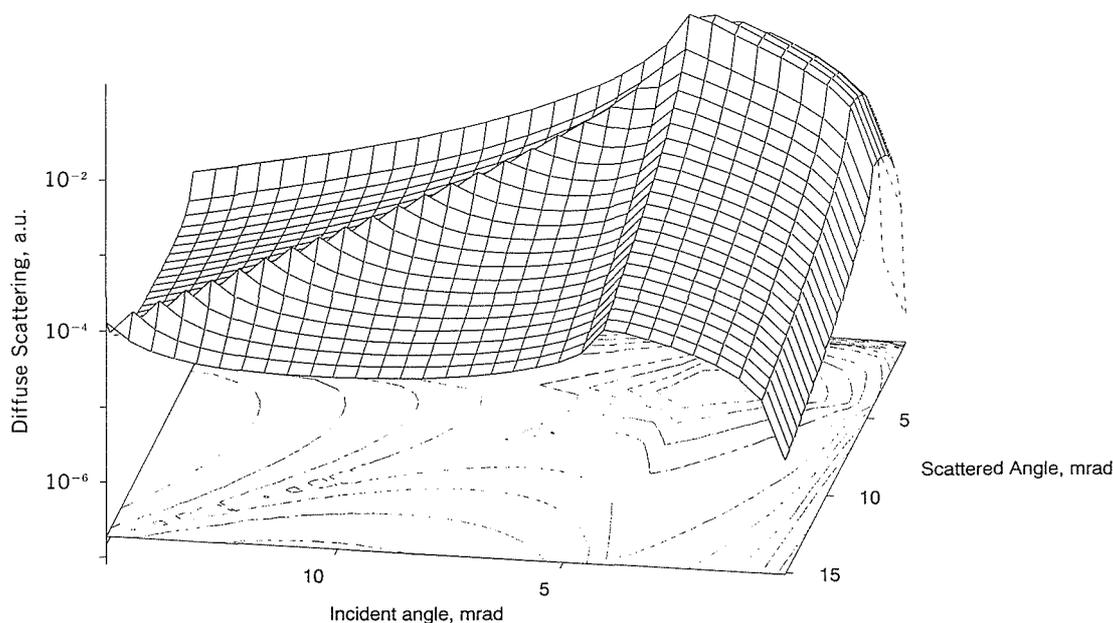


Fig.1 Simulation of X-ray diffuse scattering from synthetic quartz surface (rms roughness 1nm, correlation length 300nm, fractal dimension 2.8, X-ray energy 8.047keV).

X-rays are totally reflected at flat smooth surfaces when impinged at an extremely shallow angle, and it indicates that X-ray techniques can be extended to the surface and interface study. Recent rapid advances in theory of X-ray surface scattering are demonstrating that both specular reflection and diffuse scattering give significantly detailed information on the physical shape of the surface and interfaces. While angular profile of specular reflectivity is related to the density change along the depth, diffuse scattering enables the analysis in the lateral direction, such as a fractal parameter and a correlation length. In the present program, we have developed a specially designed reflectometer for measuring X-ray scattering at grazing incidence. Not only the instrument but also software for simulation and data analysis is important to perform the precise surface morphologic study. The software developed here works on Windows 95 PC, and can analyze the isotropic self-affine rough surface. The DWBA (Distorted Wave Born Approximation) theory has been implemented. One advantage of the software is a capability of the combined fitting for different types of diffuse scattering data, such as transverse and radial scans. The reflectometer and the software are now successfully applied to the evaluation of the super-polished engineering surface of synthetic quartz.

**Keywords :** synchrotron radiation, materials characterization, instrumentation, surface morphology, reflectometer, diffuse scattering, software

### Recent Publications

Review on grazing incidence X-ray spectrometry and reflectometry, K.N. Stoev and K. Sakurai, *Spectrochim. Acta B* 54, 41-82 (1999).

Recent performance of laboratory-scale x-ray absorption fine structure instruments, K. Sakurai and X. Guo, *Spectrochim. Acta B*, in B54, 99-107 (1999).

Trace heavy element analysis using X-ray fluorescence with quasi monochromatic high-energy photons: Iodine in an environmental sample, M. Harada and K. Sakurai, *Jpn. J. Appl. Phys.* 37, 2740 (1998).

Recent theoretical models in grazing incidence X-ray reflectometry, K. Stoev and K. Sakurai, *Rigaku Journal* 14, 22 (1997).

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Study on diluted magnetic semiconductors  $Zn_{1-x}Mn_xB$  ( $B=S, Se$ ) synthesis and structural characterization, S.D. Deshpande and K. Sakurai, *J. Surf. Anal.* 3, 494 (1997).

## 107 Advanced characterization of micro and nano meter scale structure of materials by brilliant synchrotron x-rays at the SPring-8

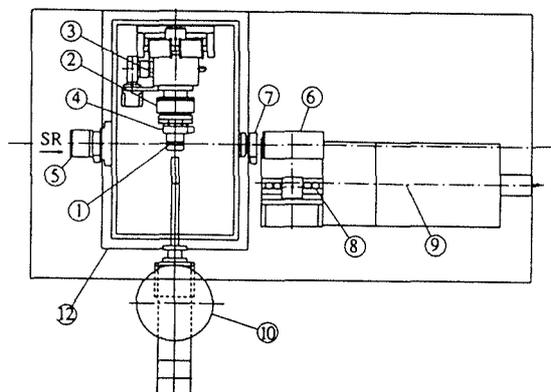
*K. Sakurai and H. Eba, High Resolution Beam Research Station*

[April 1997 to March 2002]

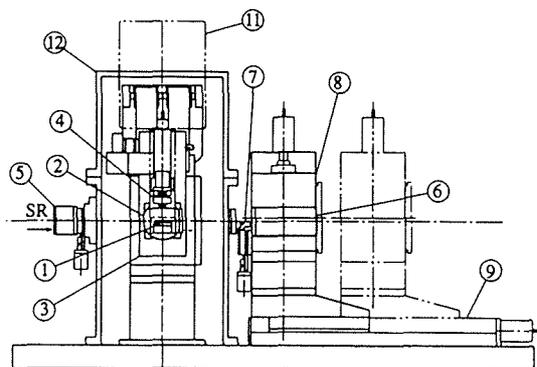
The present research program aims to establish new techniques for analysis with super precision and high resolution to evaluate micro and nano meter scale structure of materials. We are involved in the construction and commissioning of the physico-chemical analysis beamline at the SPring-8, which is a new brilliant synchrotron facility just started in October, 1997. A new grazing incidence X-ray spectro-reflectometer (Figure 1) has been very recently installed, and some preliminary experiments are being carried out during the commissioning.

The measurement was done using 10 keV monochromatic X-rays (ID Gap 14.46 mm), and higher order harmonics were rejected by the beamline Pt mirror (5 mrad). Two ionization chambers ( $N_2$  for incident monitor and Ar for reflection/scattering detection) were used. A Si (Li) detector is placed at 160 mm distance from the sample. The chamber is evacuated (around 100 mTorr) to reduce air scattering of the incident beam. To minimize a parasitic fluorescent X-rays, the sample holder has been carefully designed, and also a part of the inside wall is covered with Teflon plates.

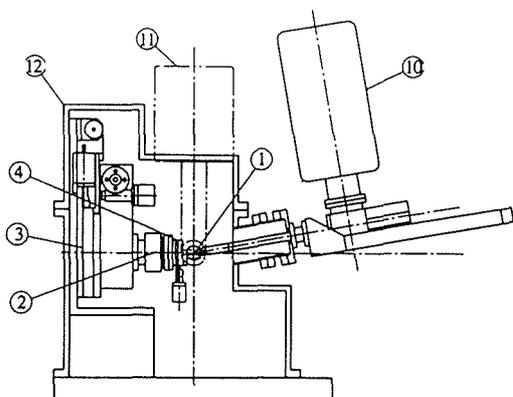
Figure 2 shows the X-ray fluorescence spectrum of a Si wafer, of which surface is intentionally contaminated by several 3d transition metals. The concentration is around  $3 \times 10^{11}$  atoms/cm<sup>2</sup>. One can confirm that almost all metals are detected very easily, and in this case, the scattering does not restrict the detection limit. When the concentration is lowered to  $10^9$  or  $10^8$  atoms/cm<sup>2</sup>, the low-energy-side tail of the scattering becomes a main part of the background again. It has been found that optimization of the geometry can enhance signal to background ratio further, and in the future, we plan to renew the record of the detection power for trace metals. Figure 3 shows specular reflection and diffuse scattering from Cr/Au thin film. Because of the interference effect caused by multiple reflection at each interface, Kiessig fringes were observed in specular reflection, which includes information on the layer thickness and interface roughness. One can find the interference oscillation in diffuse scattering as well. It is possible to determine the nm-scale shape of the surface and interfaces based on the self-affine description. In the next opportunity, we would plan combined measurements of diffuse scattering and fluorescent X-rays from trace metals, which



(a)



(b)



(c)

Fig.1 Grazing incidence X-ray spectro-reflectometer installed at the BL-39XU, SPring-8 (horizontal axis geometry). 1. Sample, 2. Goniometer, 3. Stage for positioning the goniometer center, 4. Stage for positioning the sample surface, 5. Incident X-ray monitor with entrance slit, 6. Reflection detector with receiving slit, 7. Direct beam stopper and the stage, 8. Stage for reflection detector scan, 9. Stage for adjusting angular resolution, 10. Fluorescence detector, 11. Fluorescence detector (direction convertible type), 12. Vacuum chamber.

could give detailed information of interfaces.

**Keywords :** synchrotron radiation, beamline, materials characterization

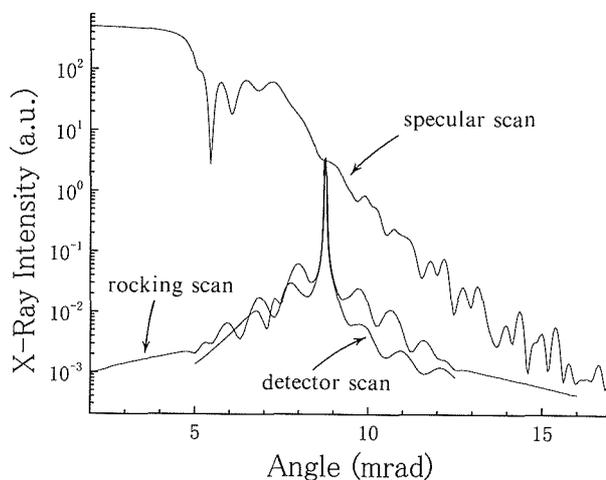


Fig.2 Grazing incidence specular reflection and diffuse scatter from Cr[51.8nm]/Au[100nm]/Cr[20nm]/Glass (Sub) sample.

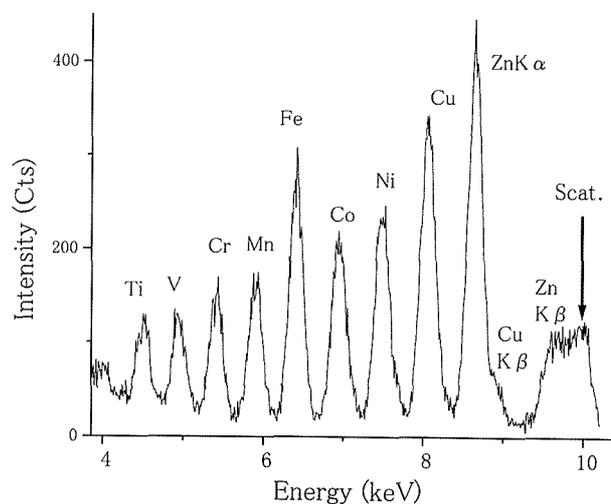


Fig.3 Total-reflection X-ray fluorescence spectrum of trace 3d transition metals on a Si wafer. The concentration is  $3 \times 10^{11}$  atoms/cm<sup>2</sup>.

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Grazing incidence reflectometer for BL-39XU at SPring-8, K. Sakurai, S. Uehara and S. Goto, J. Synchrotron Rad. 5, 554-556 (1998).

## Extreme High Vacuum Research Station

### 108 Fabrication and Characterization of Compound Semiconductor Nanometer Structures (Nanospace Laboratory Project II)

N. Koguchi, S. Tsukamoto, T. Chikyow, and K. Ishige, Extremely High Vacuum Research Station ;

*T. Ohno, Computational Materials Science Division ; M. Shimoda, Materials Physics Division*  
[April 1997 to March 1999]

With the continuous reduction in the dimension of electronic devices, quantization effects become dominant and may disturb the function of the device. Nanometer research, however, makes constructive use of quantum effects. Tunneling, single-electron transfer and wave interference can be used as a basis for novel devices. In 1994, Science and Technology Agency has organized several institutes and universities for a new research project, named 'Nanospace Laboratory Project'. The target of this project is to fabricate and characterize the material structures with dimensions down to a few nanometers. In this project, we are researching the fabrication and characterization of compound semiconductor nanometer structures. In order to fabricate these structures with high qualities, we need to establish a real-time in-situ growth monitoring system with atomic-scale resolutions, observing real-space semiconductor growth fronts.

Recently, the combined molecular beam epitaxy (MBE) and scanning tunneling microscopy (TM) system has proven to be a very powerful technique for the observation of real-space semiconductor surfaces with extremely high lateral and vertical resolution. Using this system, samples need to be cooled in MBE chamber and transferred to a cleaner environment for STM analysis. This procedure allows the surface to evolve, and no longer be representative of the true growth front. In this project, we study real-time in-situ STM observations of Ga adatoms on the MBE growth front, GaAs (001) (2×4)-As surface, with a system which STM and MBE are completely one. It is found that the Ga adatoms are relatively located near not A-but B-type step edges. Filled state STM images of Ga adatoms near B-type stepped terrace were observed at 15sec, 250sec and 500sec after the supply of 0.1 ML Ga at 200 °C. The Ga atoms form a dimer like surface structure with two Ga adatoms about one unit cell far from the B-step edge and on a missing dimer row. Then, with the addition of one Ga atom, this dimer like structure changed into trigonal like surface structure. After 250sec, this trigonal changed into a tetragonal like structure with the addition of one more Ga atom. It seems that this position attracts the Ga atoms. There are theoretical calculations which predict the migration potentials of Ga adatoms near step edges. These calculations show that the lowest migration potential value on a stepped GaAs (001) (2×4) surface was located at the position of one unit cell far from the B-step edge and on a missing dimer row. The experiment well agrees with these theoretic

cal results.

**Keywords:** nanometer structures, in-situ, GaAs, molecular beam epitaxy, scanning tunneling microscopy

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N. Koguchi, S. Takahashi, and T. Chikyow, "New MBE Growth Method for InSb Quantum Well Boxes", *J. Cryst. Growth*, 111 (1991): 688-692.

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S. Tsukamoto and N. Koguchi, "Observation of Sulfur-terminated GaAs (001)-(2×6) Reconstruction by Scanning Tunneling Microscopy", *Appl. Phys. Lett.*, 65 (1994): 2199-2201.

S. Tsukamoto, T. Ohno, and N. Koguchi, "Scanning Tunneling Microscopy and First-Principles Investigation on GaAs (001) (2×6)-S Surface formed by molecular beam epitaxy", *J. Cryst. Growth*, 175/176 (1997): 1303-1308.

S. Tsukamoto and N. Koguchi, "Real-time in-situ Scanning Tunneling Microscopy Observation on GaAs (001) Surface during Molecular Beam Epitaxy Growth", *Abstracts of the 5th International Colloquium on Scanning Tunneling Microscopy*, (1997): 27.

M. Shimoda, S. Tsukamoto, and N. Koguchi, "Photoelectron and Auger Electron Diffraction Studies of Sulfur-terminated GaAs (001)-(2×6) Surface", *Surf. Sci.*, 395/1 (1998): 75-81.

S. Tsukamoto and N. Koguchi, "Atomic-level in-situ Real-Space observation of Ga adatoms on GaAs (001) (2×4)-As surface during Molecular Beam Epitaxy growth", to be published in *J. Cryst. Growth* (1999).

#### **109 Fabrication of Nanometer-Scale Structure on the Extremely High Vacuum Surface**

*H. Nejo, D. Fujita, T. Uchihashi, T. Yakabe*  
*Extremely High Vacuum Station*

[April 1995 to March 2000]

We reported that we observed standing waves on a single crystal Au (111) surface by scanning tunneling microscope (STM). Herring-bone reconstruction

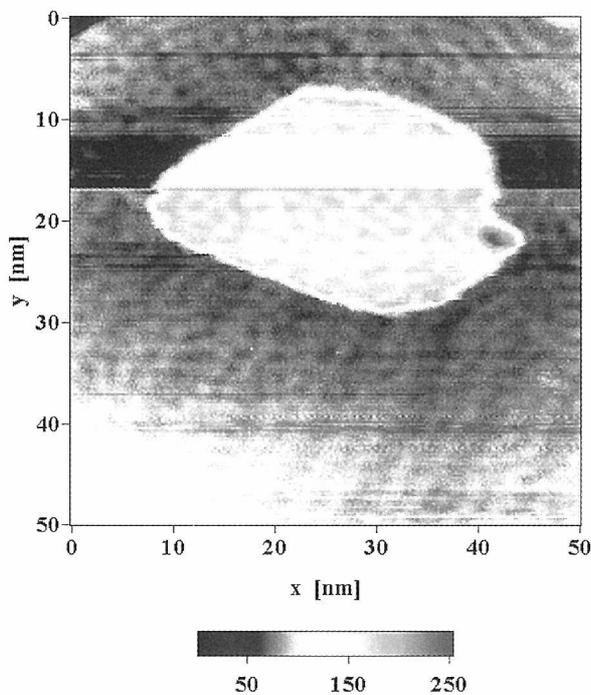


Fig.1 STM Image of Standing Waves on Au (111) at 30K

structure which is peculiar to gold surface was observed. We discovered that the wavelength of standing waves was 70nm at 30K. Since the surface structures; herring-bone structure, steps and so on modulated the potential surface, the standing waves were not isotropic and had complicated structures. There is Shockley's type surface states on reconstructed Au (111) surface. Since the surface electrons can be considered as 2D electron gas, they can show interference pattern with scattering by surface steps, defects and so on.

Furthermore, we analyzed the wave vector spaces of STM images by 2D Fourier transform. Figure 1 is an STM image of Au (111) surface. Since its bias voltage was very small ( $-3\text{mV}$ ), it showed a local density of state around Fermi level. The bright area around center is one atomic step higher than others. The stripes from left up to right down and the other ones from left down to right up are so called soliton walls which are peculiar to herring-bone structures. Two domains which have soliton walls of different directions make a boundary around center of island in Fig. 1. Ripples are standing waves which we observed on this Au (111).

Figure 2 shows Fourier transform to wave number space from Fig. 1. There is an ellipse around the center in Fig. 2. If the surface electrons are isotropic, the 2D Fermi surface should be simply a circle. We think that this elliptic ring pattern shows local 2D Fermi surface on nano-scale region of Au (111) surface. From Fig. 2, the short and long radius are  $3.0\sim 3.4\text{nm}^{-1}$ . Since a wave number of a standing wave is  $2K_F$  ( $K_F$ : Fermi wave number), the

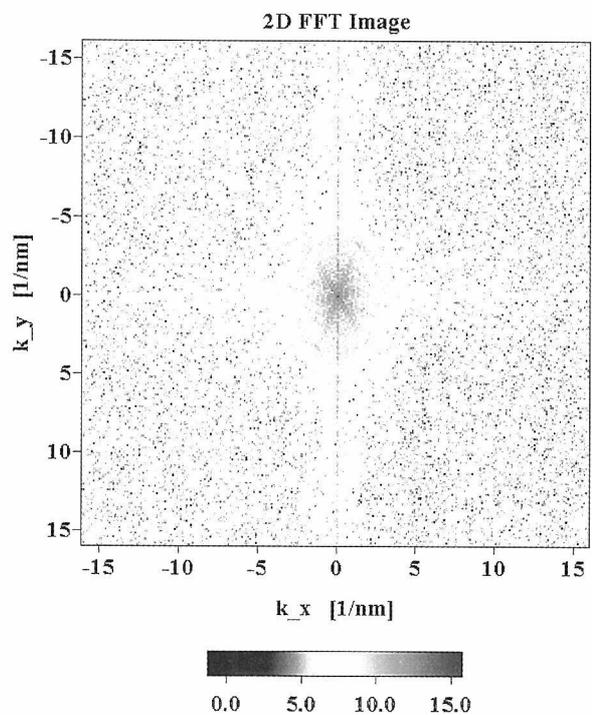


Fig.2 2D FFT Image of Standing Wave on Au (111) at 30K

observed wave number is consistent with  $K_i=1.73\text{nm}^{-1}$ , observed by angled resolved ultra-violet photoelectron spectroscopy (ARUPS).

It is very interesting to point out that the evaluation method by Fourier transform from STM images into wave number spaces gives finer information compared with ARUPS which evaluates electron density of states into wave number spaces. ARUPS takes the averaged data from microscopic size (millimeter order) because of the beam radius. On the other hand this method can take from microscopic size (nano or micrometer order).

**Keywords:** standing wave, 2D Fourier transform, wave number space

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1. D. Fujita, T. Yakabe, H. Nejoh, T. Sato and M. Iwatsuki, Surf. Sci. 366 (1996) 93.
2. D. Fujita, K. Amemiya, T. Yakabe, H. Nejoh, T. Sato and M. Iwatsuki, Phys. Rev. Lett. 78 (1997) 3904
3. D. Fujita, K. Amemiya, T. Uakabe, H. Nejoh, T. Sato and M. Iwatsuki, "Observation of two-dimensional Fermi surface of a reconstructed Au (111) surface using k-space imaging scanning tunneling microscopy" submitted to Surf. Sci.

#### 110 Self-control of surface composition of thin film and its application to field emitter

M. Yoshitake, M. Tosa, A. Kasahara, and K.

When deposited metal film on substrate was heated in a vacuum, it was observed that substrate element diffused to the surface of film. The surface concentration of segregant was always constant. Even if the segregated layer was removed by argon ion sputtering, the segregated layer of the saturated concentration was formed again by re-heating. Therefore, the surface composition of the segregated layer on metal film is expected to have a self-controlling property.

It is well known that the surface adsorption of metal changes the work function of a solid surface. Therefore, it is expected to change the work function by the surface segregation. The work function varies with coverage of adsorbed materials. However, if we use the self-controlling property of segregation behavior on metal film, then the stable work function on the surface, i.e., stable field emission current can be expected and we can produce a field emitter of high performance. It has been shown by authors that Nb film with Ti surface segregation works as a getter for residual gas in ultra high vacuum, in which environment a field emitter functions.

In this study, the stability of surface composition has been quantitatively analyzed in the wide range of temperature, and the change of work function by segregation has been measured. Until now, the recovering rate of the surface composition during Ar ion sputtering in case of Ti segregation on Nb thin film was measured. At first, ion sputtering rate was precisely calibrated quantitatively. The concentration of Ti remains constant if the removal rate of Ti by ion sputtering balances with the supply rate of Ti by diffusion from substrate. By observing the condition of the balance, the rate of Ti supply at various temperatures was determined. The work function change by the surface segregation of Cu on Ti film and of Ti on Cu film has been measured. Work function decreased approximately 0.3 eV by the surface segregation of Cu on Ti film and slightly increased by the surface segregation of Ti on Cu. The amount of work function decrease caused by Cu segregation is reproducible when surface is once removed and Cu segregates again by heating. Therefore, it is shown that the original idea of getting stable work function by using features of segregation phenomenon is working.

**Keywords :** surface segregation, saturated surface composition, self-composition control, work function, field emitter

## Recent Publications

Electric States of Segregated Metal Atom on Metal Surfaces and potential Use for Field Emitter, M. Yoshitake and K. Yoshihara, *J. Vac. Sci. Technol. A13* (1995): 2407-2411.

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Measurement of Work Function Change with Surface Segregation of Substrate Element on a Deposited Film, M. Yoshitake and K. Yoshihara, *J. Vac. Soc. Jpn.*, 41 (1998): 320-323.

The Surface Segregation of Ti-Nb Composite Film and Its Application to a Smart Getter Material, Michiko Yoshitake and Kazuhiro Yoshihara, *Vacuum*, 51 (1998): 369-376.

Measurement of Work Function Change with Surface Segregation of Substrate Element on a Deposited Film M. Yoshitake and K. Yoshihara, *Appl. Surf. Sci.*, 146 (1999): 97-100.

## 111 The Chamber Material for Standard Vacuum Pressure Measurement

*M. Tosa and A. Kasahara ; Extreme High Vacuum Station*

*K. Yoshihara ; High Resolution Beam Station*

[April 1997 to March 2000]

Calibration of standard vacuum pressure gauge requires the surface modification method to generate the standard pressure field with accurately controlled constant pressure and the study of the interaction among the chamber wall material surface and the hydrogen behavior of deposition and permeation and residual gas molecules. The main residual gas in the vacuum chamber mainly contains hydrogen molecules in the ultra high vacuum. The reduction of the hydrogen behavior is therefore inevitable for the generation of standard stable vacuum field for the calibration of standard vacuum pressure gauge and the project aims the development of advanced surface modification of the vacuum chamber wall material which can reduce the hydrogen behavior to disturb the steady standard vacuum field.

The improvement of surface modification is studied by the application of surface segregation of hexagonal boron nitride (h-BN) on the copper surfaces. Copper metal is excellent in low hydrogen solution, high thermal and electric current conductivity and high vacuum packing but suffers from easy oxidation which becomes large outgassing source. The surface of h-BN is excellent in low gas adsorp-

tion but is brittle and the preparation of BN layer on the substrate is not so easy. The co-sputtering deposition process with BN sintered porous disc and pure copper disc and the following in situ vacuum annealing is developed and discussed in order to prepare the h-BN compound layer for the low gas adsorption on the surface and the low permeation through the substrate carried out by hydrogen.

BN can cover the surface of the substrate almost uniformly and adsorbs low gas molecules about less than one-third of the surface compared with the copper substrate without BN layer on the surface. Lower atomic attractive force is also observed on the surface of the BN covered substrate with less than about 1 nN though the substrate without BN surface layer shows over about 20 nN with an atomic force microscopy. Scanning tunneling microscope also shows higher dielectric behavior on the BN partly that the BN surface segregation layer on the substrate mixed with BN and copper can well improve low gas adsorption of the surface of the chamber wall for the steady standard vacuum field.

**Keywords:** gas adsorption, gas permeation, gas desorption, standard pressure gauge, surface segregation, co-sputtered film, hexagonal boron nitride

## 112 The Evaluation and Control of Material Self-organization

*M. Tosa and A. Kasahara; Extreme High Vacuum Station*

*K. Yoshihara; High Resolution Beam Station*

[April 1996 to March 1999]

Hexagonal boron nitride (h-BN) segregated on the surfaces of metals or alloys doped with boron and nitrogen can form the preferred (0001) crystal basal plane parallel to the base substrate material surface. The binding force between c planes is much smaller than those of other planes and the friction force on the plane will be small in case of the horizontal force due to easy slide of the plane. The property of the small adsorption force of segregated h-BN layer will be applied to the micro scanning probe system without large sliding friction which leads to the development of the advanced memory media disc system with a huge amount of memory volume. This study therefore aimed the fabrication of h-BN layer with preferred (0001) crystal plane parallel to the base substrate by means of the control of surface segregation using strain energy.

The co-sputtering deposition process and the following vacuum annealing can prepare the h-BN compound layer on the surface of the sputtered film

substrate with BN and alloy targets. Segregated BN can cover the film substrate prepared by the co-sputtering copper and BN. Auger scanning probe analysis shows that the distribution of B and N is uniform and less carbonate adsorbs on the BN segregated surface in spite of about 60% BN coverage and atomic force microscopy also shows that attractive force reduced on the surface of the segregated BN film compared with no BN segregates substrate.

Tribological property of prepared BN films is evaluated with sliding friction force. We developed the vacuum micro-friction measuring device which can measure sliding friction force in range of from an atmospheric pressure down to ultra high vacuum pressure of  $10^{-8}$  Pa by a tandem turbo molecular pumping system. The range of loading weight can be also changed from about several 10 N down to less than 100  $\mu$  N in the same range of vacuum pressure.

The friction coefficient of the substrate of mixture of BN and copper partially covered with h-BN can be less than one-third compared with no BN covered substrate in an atmospheric pressure and in the ultra high vacuum. Lower loading weight increases the friction coefficient of no BN covered substrate by several ten while that of BN partially covered substrate can keep almost constant without increase. This shows therefore that the BN surface segregation can well improve micro-tribological property of the substrate.

**Keywords:** self-organization, surface segregation, co-sputtered film, vacuum tribology, hexagonal boron nitride

## Frontier Research Center for Structural Materials

### 113 Study on Strengthening of Ferrite Matrix Steels for Welded Structures

*K. Nagai, S. Torizuka, H. Nakajima, T. Hayashi, T. Hanamura, T. Mitsui, J. Takahashi, N. Sakuma, T. Saito, T. Shimizu, Y. Muramatsu, S. Wanikawa, M. Otaguchi, T. Ohashi, T. Inoue, and N. Tsuchida, Materials Creation Research Station, S. Tsukamoto, G. Asai, K. Hiraoka, A. Okada, T. Nakamura, R. Itoh, Y. Kawaguchi, Y. Muramatsu, H. Yamawaki, T. Fukuhara, I. Uetake, and C. Shiga, Joining and Interface Research Station, A. Ota, N. Suzuki, Y. Maeda, and N. Nguyen, Strength and Life Evaluation Research Station, and H. Irie, Mechanical Properties Division*

[April 1997 to March 2002]

Building steel is one of major mass-produced items in the steel market. Easier recyclability, more efficient and less skilled welding and enhanced mechanical properties will be required for the building steels in the next century to construct sustainable infrastructure. However, present high strength steels of 600-800 MPa in tensile strength contain the alloying elements undesirable for recycle, and their welded joints show very poor fatigue strength, i.e. only one-tenth of tensile strength.

Low strength C-Si-Mn ferritic steels are potential alternatives, since they are desirable for recycle and easy to weld. To overcome the low strength, in the present study, new thermo-mechanical processing is developed to refine the ferrite grain size into  $1\mu\text{m}$  and double the tensile strength from 400 MPa to 800 MPa. In a small-size sample with about 1mm thickness, an ultra-fine grained ferrite-pearlite structure was created with a ferrite grain size of 2 micron-meter, no crystallographic texture, and a high ratio of high angle boundaries. About 40% increase in strength is expected with this refinement. In addition, ultra-fine grained ferrite microstructure with finely-dispersed second phase particles was also created with a ferrite grain size of less than 2 micron-meter through a warm deformation processing of martensite microstructure as well as a newly developed compaction processing of commercial pure-iron powders.

In order to keep the ultra-fine grains in the HAZ on welding process, the function of finely-dispersed particles like oxides is investigated in terms of pinning sites for grain growth as well as nucleation sites for ferrite transformation from austenite.

High speed and no defect welding has to be developed coincident with preserving the ultra-fine grained microstructure from its heat in the heat-affected-zone (HAZ). In arc welding, an ultra-narrow gap arc welding processing is developed with an idea of simultaneous control of low heat distribution and large electricity input to make the HAZ as narrow as possible. With this concept, 20 mm thick steel plates were joined with a 5 mm gap by 2 passes, although the narrowest gap was 10 mm in conventional methods. And further, a high-power CO<sub>2</sub> laser one-pass welding has been elucidated. A main problem is that plasma generation due to metal evaporation deteriorates the efficiency of laser beam heat. A preliminary study demonstrated that the plasma generation is well suppressed by controlling the focus height of the incident laser beam.

Welded specimen large enough to simulate the conditions for service is subjected to mechanical tests with a large capacity of power to evaluate the fatigue property. The lower fatigue strength of welded joints is tried to basically increase by using a

newly designed welding rod with a lower transformation temperature. With a decrease in the tensile residual stress at the welded joints, the fatigue strength of high tensile steel's joint was drastically improved by a factor of two.

Defects might be introduced into the materials and their joints through welding process. Tolerable size of the defects becomes smaller under higher stress conditions expected. Hence, more reliable inspection technique is desired in a nondestructive or a non-contacting manner. Laser beam, supersonic wave, and magnetic flux leak are tried to utilize for detection and characterization of the small defects and the microstructural evolution. Laser speckle technique was able to follow the strain change at high temperature during welding process.

Computer simulation of the microstructure evolution in the steels studied and the deformation and fracture behavior of welded points is also studied. Fundamental approach has been made to model the meso- as well as macro-level plastic behaviors of plural microstructure in tensile deformation.

**Keywords :** ferritic steels for welded structures, grain refinement, welding process, heat-affected-zone, residual stress, welded joint, tensile strength, fatigue strength, simulation

#### **114 Advanced Ultra-High-Strength Steels (1500-MPa-plus class)**

*S. Matsuoka, Frontier Research Center for Structural Materials, Strength and Life Evaluation Research Station*

[April 1997 to March 2001]

There is an increasing demand for ultra-high-strength steel that has a tensile strength exceeding 1500 MPa, for example in the use of higher-strength bolts in the construction industry and in the weight reduction of automobile parts and main cables of long-span suspension bridges. The key to practical implementation does not lie in the achievement of the high strengths but rather in preserving the necessary reliability in the delayed fracture and giga-cycle fatigue properties of the steel.

In the search for advanced ultra-high-strength steels, the center is trying to develop new martensitic steels that contain carbide-free boundaries and hydrogen trap sites to give high delayed fracture resistance. Other martensitic steels containing a large amount of nitrogen is also developed in order to attain a high fatigue resistance. Studies of the mechanisms of delayed fracture and fatigue will reveal new concepts for material design. Such

studies require atomic-scale analysis of fine precipitates and interphase boundaries by AP-FIM and nanoscopic analysis of deformation and fracture structures by AFM and nanohardness tester. Other works will include standardizing the evaluation of delayed fracture and constructing a database that contains fatigue property data for  $10^{10}$  cycle tests.

In the recent year, experimental facilities have been equipped for this study. A small sample of martensitic steel with carbide-free boundaries, which will give high delayed fracture resistance, was obtained by applying the ausforming process. High strength wires have been analyzed in an atomic scale with AP-FIM. The analysis revealed new strengthening mechanisms of the wire.

**Keywords:** martensitic steel, delayed fracture, gigacycle fatigue, AP-FIM, SPM, nanohardness tester

### **115 Strategic Research on Advanced Ferritic Steels for 650 °C USC Boilers (R&D of Structural Materials for 21<sup>st</sup> Century)**

*Fujio Abe, Strength and Life Evaluation Research Station*

[April 1997 to March 2002]

The critical issues for the development of ferritic steels for 650 °C USC boilers are the improvement of oxidation resistance as well as long-term creep rupture strength. For the improvement of long-term creep rupture strength of ferritic steels, the stabilization of initial microstructure is required for up to long times. The logarithm of creep rupture strength of simple 0.1C-9Cr-W steels increased linearly with increasing W concentration up to 3% W for up to long times at temperatures between 550 and 650 °C, suggesting that W can be maximized up to about 3% in the 9Cr steel. The strengthening by W resulted from the stabilization of  $M_{23}C_6$  and lath subgrains for up to long times. The addition of austenite stabilizing elements is required to prevent from the  $\delta$ -ferrite formation for the steels containing Cr higher than 9% or Si higher than 0.5%. Of the austenite stabilizing elements, the high melting point element Ir is promising for strengthening and stabilizing the matrix of martensite. Indeed, the creep strength of 0.08C-9Cr-3.3W-0.2V-0.05Nb-0.005B-0.05N steels increased with increasing Ir concentration. The weight gain of 0.15C-8.5Cr-2W-0.2V-0.05Nb steels during oxidation in air decreased with increasing Si concentration from 0 to 1%, resulting from a change in morphology of oxide scale from porous to compact. Ti and Y can be used to substitute for a part of Si.

**Keywords:** ferritic heat resistant steel, ultra-supercritical power plant, alloy designing, creep, steam oxidation, fatigue, welded joint

### **Recent Publications**

Alloy Design of Advanced Ferritic Steels for 650 °C USC Boilers, F. Abe, M. Igarashi, N. Fujitsuna, K. Kimura and S. Muneki, Proc. of Intern. Conf. on Advanced Heat Resistant Steels for Power Generation, (1998): 84.

Research and Development of Advanced Ferritic Steels for 650 °C USC Boilers, F. Abe, M. Igarashi, N. Fujitsuna, K. Kimura and S. Muneki, Proc. 6<sup>th</sup> Liege Conf. on Materials for Advanced Power Engineering, (1998) 259.

Microstructure Control of Martensitic Phase Matrix in Advanced Ferritic Steels for USC Boiler to Achieve Long Term Stability, M. Igarashi, S. Muneki and F. Abe, Proc. 6<sup>th</sup> Liege Conf. on Materials for Advanced Power Engineering, (1998) 637.

Microstructure Control of Martensitic Phase in Advanced Ferritic Steels for USC Boilers to Achieve Long Term Stability at High Temperatures, S. Muneki, M. Igarashi and F. Abe, 11<sup>th</sup> Congress of Intern. Federation for Heat Treatment and Surface Eng., (1998) 265.

### **116 Development of Structural Steels Highly Durable to Marine Environments**

*T. Kodama, K. Sakuraya, Y. Katada, H. Uno, K. Kuroda, H. Masuda, T. Nishimura, M. Yamamoto, T. Watanabe, S. Iwasaki, Y. Kobayashi, K. Kurosawa, S. Ohashi, T. Fukushma, H. Sumiyoshi, M. Abe, N. Washizu, K. Noda, K. Hiraoka, A. Fukuzawa, H. Nakamura, H. Baba, A. Tahara, H. Katayama*

In Japan, there is a great activity in new infrastructure construction in marine and offshore environments because the inhabitable coastal zones are already heavily burdened by the population. However, marine environment is extremely aggressive to steels. For example, weathering steels that are resistant to rural and industrial environments show poor corrosion resistance in a marine/coastal atmosphere. Similarly, stainless steel suffers in the sea from various forms of localized attacks such as pitting, stress corrosion cracking, and crevice corrosion. The aim of this study is to develop high- and low-alloy steels, and protective coatings resistant to marine environments. The principle of our materials development is to avoid using expensive or exotic materials that have heretofore been used to develop corrosion-

resistant alloys : instead we improve corrosion resistance by purification and homogenization of matrix metals. In addition, techniques of nanoscopic measurement of corrosion and passive film scale is to be carried out. This basic research allows us developing new methods of accelerated corrosion tests.

### 1. Improved Corrosion Resistance of Stainless Steel by Increasing Purity

Phosphorus in stainless steel known to degrade its corrosion resistance. However, in the smelting process of stainless steels, it is difficult to remove phosphorus originated from ferrochrome, one of the principal raw materials of stainless steel. Since chromium removal occurs simultaneously with oxidative dephosphorization conventional smelting cannot be applied for the phosphorus removal from stainless steels.

An innovative method of cold-crucible levitation smelting allows non-contact melting and solidification of metals. Contamination does not occur from the crucibles in the cold-crucible smelting. In addition, there is no restriction in selecting slag composition because of the non-contact nature between the slag and crucible : the cold-crucible smelting, therefore, makes it possible to utilize the hitherto unusable metal-slag systems. We applied the cold-crucible levitation smelting to create a low-phosphorus stainless steel.

Figure 1 shows an examples of phosphorus reduction when 800g of type 316L stainless steel was processed with 5g of Ca-CaF<sub>2</sub> flux in levitation smelting. Phosphorus concentration in commercial 316L is reduced from original 0.026% to 0.001% or even less by smelting with the Ca-containing flux. The Figure also shows the removal of P by increasing the repeated number of smelting processes. The

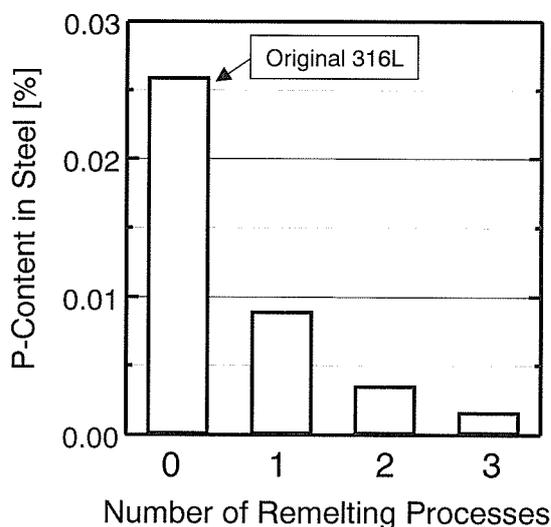


Fig.1 Removal of P in 316L SS by successive cold-crucible remelting using 5g of Ca-CaF<sub>2</sub> flux and 800g of steel.

phosphorus level was reduced to less than 0.002% after three processes of the smelting.

Future researches on this line include the determination of the lowest phosphorus level accessible, the mechanism of phosphorus removal, and the most effective flux composition for this reaction. At the same time, corrosion behaviors of the low-phosphorus stainless steels are to be examined in various environments.

### 2. Development of Stainless Steels Containing High-Nitrogen

Investigations are being conducted on the development of stainless steels that require smaller amount of alloying elements such as Cr, Ni or Mo. In our previous study we have proven that austenitic stainless steel showed better corrosion resistance particularly to localized corrosion in chloride media with increasing N addition to the steel and purification of matrix metal. In FY 1998, we plan to pressurized remelting for the production of high-nitrogen stainless steels. Prior to the enhancement of nitrogen under high pressure, we prepared high nitrogen steel by annealing the 316L steel in a pure-nitrogen environment at normal atmospheric pressure.

The specimens were prepared from low-Mn 316L-like steel (F4: 16.5 mass% Cr ; 14mass% Ni ; 2mass% Mo ; 0.17 mass%N). In the nitrogen atmosphere, 2mm-thick annealed specimens were thermally processed at 1200°C. Specimens thus processed were tested for local corrosion such as pitting and crevice corrosion, and electrochemical polarization measurements were carried out in seawater. Figure 2 shows the pitting potential as a function of the nitrogen content of 16.5 mass% Cr-14mass% Ni-2mass% Mo steel. The F4N steel (0.51 mass% N) in

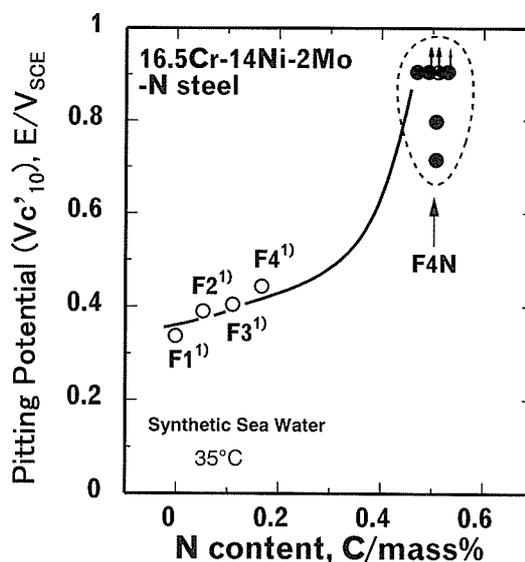


Fig.2 Effect of N addition on the pitting potential of high-purity type 316L steels.

this figure is thermally processed F4 steel (0.17 mass%) at 1200°C for 24 hours in nitrogen atmosphere. A sharp enhancement of the pitting potential (indicating more resistant to pitting corrosion) was observed with an increase in nitrogen content. In future experiments, it is expected to develop stainless steels with higher nitrogen content using pressurized ESR.

### 3. Protective Coating by Improved Thermal Spray Technology

High-velocity oxygen-fuel (HVOF) flame spray technique was applied to produce protective films of 316L stainless steel, Hastelloy C, and WC-Co on steel. During the spray process in-situ measurement of residual stress in film was carried out by measuring curvature of substrate metal. The stress monitoring proved that the unfused particles collided at a high speed to the substrate metal, resulting in compression in metal film.

Furthermore, we examined the structure, stress, porosity and corrosion resistance of spray film as functions of the velocity and temperature of SUS316L particles and substrate temperature. The compression introduced into the film was directly related to the kinetic energy of the particles, and the film porosity could be reduced to less than 1% at optimal conditions. Corrosion resistance was evaluated in synthetic seawater by electrochemical polarization and impedance measurements. The results showed HVOF were much better than those with plasma spray films but less protective than bulk materials.

### 4. Detailed Analysis of Saline Particle and Laboratory Reproduction (Nanoscope observation of rusting and atmospheric corrosion)

Atmospheric corrosion of metals initiates in large part from deposited saline particles that are carried by wind and adherent on metal surfaces. Existing acceleration tests employ conditions that could rarely occur in natural conditions. Actual saline particles were collected to conduct a detailed analysis. As a result, it was found that saline particles of up to about 20 $\mu$ m in diameter were carried in particulate form by the wind; at a relative humidity of 75% or less, they existed in NaCl crystals and in saturated MgCl<sub>2</sub> solution, while at higher humidity they were found in droplets. An attempt was made to reproduce saline particle adherent to metals; particles of nearly of the same morphology as natural ones were successfully created on the metal surface.

Then, using high-precision metallurgical microscope and AFM, saline particle was investigated at various temperature. For accurate morphology measurement, layered graphite and gold mirror surfaces were exposed for several days in a coastal area.

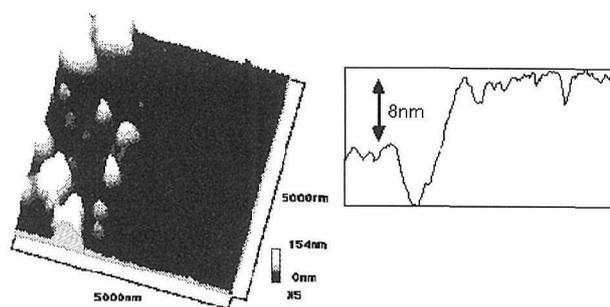


Fig.3 AFM image of a saline particle adherent on gold surface.

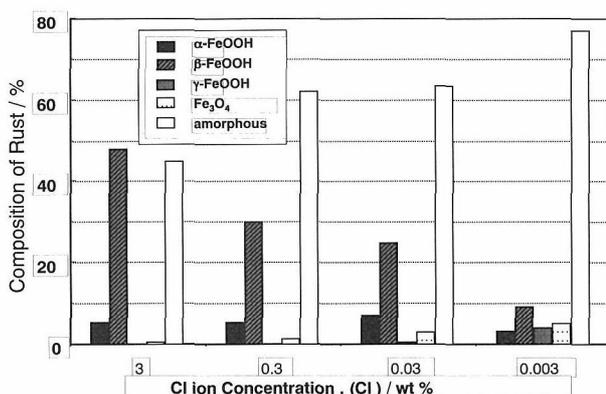


Fig.4 Effect of Chloride Ion on the Composition of Rust

Figure 3 shows an atomic force microscope (AFM) image of saline particles adhered to gold surface at 40% humidity. The crystalline NaCl particles observed here ranged 5-30  $\mu$ m in diameter. when viewed under AFM magnification, there was a height gap of 8nm between the discolored and colored sections, which was not apparent with an optical microscope. We could also see that there was a liquid substance (MgCl<sub>2</sub> solution) covering the entire discolored portion.

### 5. Characteristics of Iron Rust Occurring in Coastal Environments (Development of low-alloy weathering steels)

For the simulation of marine atmosphere a new wet-and dry cycle was proposed: 0.4L/m<sup>2</sup> of an aqueous chloride solution was dripped onto a carbon-steel specimen, then dried for 12 hours in a thermostatic incubator at 25°C and a constant relative humidity of 60%. The steel slats were washed with pure water immediately before dripping the solution to prevent the accumulation of salt over time. To investigate the effect of chloride in rust, four types of NaCl solutions with different concentrations were used. Also test solutions with different Na/Mg ratio and the same Cl concentration were used.

The structural analysis of rust was carried out using an innovative X-ray diffraction (XRD)

method. After 20 wet-and dry cycles, the rust phase was quantitatively analyzed using the internal standard method.

The corrosion on carbon-steel increased with an increase in environmental chloride concentration. As shown in Figure 4, among the rust phases, the occurrence of  $\beta$ -FeOOH was especially remarkable with increasing Cl, which suggests the non-protective nature of rust formed in a coastal environment.

On the other hand, the structure of rust is not dependent on Na/Mg ratio as far as Cl level was maintained constant. In the process of  $\beta$ -FeOOH formation, Cl ion plays a catalytic role and therefore it is not trapped in the final product of  $\beta$ -FeOOH.

**Keywords :** marine corrosion, weathering steel, stainless steel, nitrogen in steel, atomic-force microscope, saline particle

## Materials Creation Research Station

### 117 Fabrication of Highly Functional Composite Casting Irons

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The present study, as one theme in the "Living and Social Basis Project" jointly researched in some institutes, universities and corporations, was started in 1996. Fabrication of ceramics particles dispersed casting iron is being tried in NRIM, with a compocasting technique used to produce composite materials by adding various particles into the solid-liquid co-existing slurry. Simultaneously, a CVD coating method is attempted to the particles and iron powder to improve the wettability with molten cast iron and the dispersion state of the particles. Alumina, silica and silicon carbide are possibly used as dispersion particles in cast iron. Although alumina is the most promising one, the unsatisfactory wettability of alumina with cast iron makes it necessary to coat with some other compound such as silica, silicon carbide, to improve the wettability. Therefore, a chemical vapor deposition technique in fluidized bed is applied to make coating layers on alumina particles. The coating of silica on alumina substrate and on the cast iron powder is proceeded in a gas mixture of Tetramethylsilane and water. The deposited silica layer is an amorphous silica. The amorphous silica solitary is stable up to 1393K,

however, when the particles are mixed with calcium hydroxide, the amorphous silica layers are found to crystallize into  $\alpha$ -quartz crystals at 1300K, and to cristobalite at 1500K. The coating of silicon carbide on alumina particles is also proceeded in a gas mixture of silicon tetrachloride and methane. Finally, the mechanical properties of the fabricated composite materials are characterized, intending to qualify the materials to different applications. The compocasting technique, usually used for alloys with lower melting temperatures, has been improved and applied to the creation of cast irons, through solving some processing problems and designing suitable apparatus.

**Keywords :** Cast iron, Compocasting, Alumina particles, stirring, CVD, SiO<sub>2</sub>

### 118 Study on Melting of Refractory Metals by Cold Crucible Levitation Melting Method

*A. Fukuzawa, K. Sakuraya, T. Watanabe, S. Iwasaki, and Y. Kobayashi Materials Creation Research Station [April 1997 to March 2000]*

A cold crucible type levitation melting method using high frequency electric power is known as a non-contacting melting method. Therefore, from the point of view of high pure material creation, this melting method is advantageous for melting of high purity metals, chemically reactive metals and refractory metals. As for the refractory metals, there have never been means for melting of refractory metals by using crucible made of common oxide refractories.

In these several years, we have already developed the new control technique for cold crucible levitation melting; the two different frequencies are simultaneously supplied to two work coils that are wound to the water cooled crucible. Rather lower frequency is supplied to lower coil for levitation of melting materials mainly and the higher frequency is supplied to upper coil for heating of the materials. Since we have succeeded reducing the oxygen in molten titanium by this new control technique of cold crucible levitation, so next we are challenging to melt refractory metals and its alloys by mean of the cold crucible levitation device.

The purpose of this study is the creation of molten refractory metals and its alloys by the cold crucible levitation melting method and the origination of homogeneous solidified structures that have been never gotten by the usual melting methods for refractory metals for instance, electron beam remelting, plasma arc remelting.

As the most of refractory metals have not only high melting point but also high density and high thermoconductivity, it is considered that levitation of refractory metals and its alloys is not easy. So the optimum levitating conditions such as the shape of the cold crucible, high frequency coil and the electric output power are to be examined, and we are going to design and manufacture trial of the cold crucible devices for this purpose.

**Keywords :** cold crucible, levitation melting, refractory metal, high frequency

### Recent Publication

Levitation and Heating of Metallic Ball in Cold Crucible Simultaneously Supplied Two Frequencies, K. Sakuraya, T. Watanabe, S. Iwasaki, A. Fukuzawa, M. Yamazaki, T. Take and M. Fujita, *Tetsu-to-Hagané*. 81 (1995): 179-84 (in Japanese)

### 119 Research and Development of Recyclable Simple-System Alloys

*A. Sato, Frontier Research Center for Structural Materials, F. Yin, Domestic Research Fellowship, K. Kawahara, O. Ohashi Guest Researcher, K. Minagawa, K. Harada, Ecomaterials Research Team, Y. Ohsawa, G. Arakane, S. Takamori, Materials Creation Research Station, S. Yamamoto, Materials Processing Division*  
[April 1996 to March 2001]

Because of the various additives, recycling of the metallic materials used for the parts of automobiles and other aspects remains a question awaiting to solve. Nowadays, the recyclability of materials should be fulfilled in the development of new structural materials. In the present research, 4 kind of metallic materials and processing methods for improving recyclability are concerned.

(1) Changes of logarithmic decrement with temperature were measured in Mn 19.2Cu4Ni2Fe, Mn18Cu5.19Ni2Fe and Mn18Cu5.98Ni2Fe (at%) alloys, which were solid solution treated at 900°C and subsequently cooled to room temperature in 10h. The microstructure the treated alloys contains three phases, i.e. a matrix Mn-rich fct  $\gamma$  Mn phase, a fine Cu-rich phase and a small amount of retained  $\gamma$  fcc phase. Below the Tt temperatures, both magnetic domain boundary damping and (011) twinning boundary damping contribute to the obvious increases in logarithmic decrement. Higher Ni content in alloys tends to shift both damping peaks to lower temperatures, however, improve the magnitudes of domain damping and flatten the twinning

boundary damping peak. (011) twin packets have showed very different dimensions and packing configuration in the three alloys, and some reoriented fractions, deviated from the original twinning orientation by a few degrees, appear inside the twinned plates or as an abnormal twinning plate in the packet. The mobility of (011) twinning boundaries may be prohibited by those reoriented fractions, and consequently a sharper main damping peak is resulted in the alloys with a lower Ni content.

(2) Many structural parts made by powder metallurgy are well used in vehicles. Another elements are added to the conventional material for the performance enhancement of the sintered materials, through the refinement of microstructure and improvement of material property. However, the separation of the additives is quite difficult, when the recycling is considered. Therefore, the manufacturing of Fe-Fe composite materials made of the iron powder as the matrix and reinforced fibers, becomes instructive in the development of recyclable sintered alloys. A 2 patterns sintering processes (250°C×30min-400°C×30min) has been reached which attains a strength of as high as 50kg/mm<sup>2</sup> in the Fe-Fe composite materials.

(3) Aluminum casting alloys without addition of the third alloying elements present a higher recyclable property. Instead of the grain refinement effects of the third elements, strong stirring of ultrasonic vibration during the solidification process of the alloys is expected capable of refining the microstructure of castings. In order to apply the ultrasonic vibration in the molten metal, the SiALON ceramic is used as horn material. And the effects of such a horn on the formation of primary crystals in a molten Al-Si alloy is examined. In the Al-6%Si alloy, the primary crystals are obviously destroyed by adding the vibration, as a result, the dendrites are segmented, and a granular dendrite microstructure is formed. Ultrasonic vibration is also effective to refine the primary Si of Al-18%Si.

(4) The study on improvement of the tool life has been carried out this year to develop the alternative material instead of lead free cutting steel. According to the cutting test in which titanium oxide dispersed material was machined, the oxide covers the surface of tool and protect it from abrasion by chips. But chip-disposability and cutting resistance are not improved in this Ti deoxidized steel. In order to improve these properties, heat treatment was carried out to obtain martensite mixed structure. This heat treated steel shows superior chip-disposability and tool wear and cutting resistance.

**Keywords :** high damping alloys, Ultrafine Fe particles, Ultrasonic vibration casting, Chip-

disposability, martensite microstructure

### Paper list

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- (3) Effect of solid solution treating on the microstructure and damping behavior of MnCuNiFe alloy ; Fuxing Yin, Yoshiaki Ohsawa, Akira Sato and Kohji Kawahara ; J. Mater. Sci. Technol., 14 (1998), 299-307.

## 120 Fabrication of Particles Dispersed Materials Through Controlling of Solidification Interfaces

*A. Sato Frontier Research Center for Structural Materials Y. Osawa, G. Arakane, S. Takamori Materials Creation Research Station F. Yin Domestic Research Fellow Y. Jiao STA Fellowship S. Yoda Visiting Researcher*  
[April 1997 to March 1998]

Particles such as fine ceramics are often used for particle dispersed metals to prevent the progress of crack and to increase the strength and toughness of the material. In this study, the materials in which ceramic particles were uniformly dispersed were unidirectionally solidified, and the behavior of the particle at the solidification interface was analyzed.

The particle dispersed material was produced from pure aluminum powder and alumina powder, by mechanical mixing and alloying using the planetary ball-mill for mechanical alloying, and then unidirectional solidification experiment was carried out on this material. Furthermore, the behavior of the oxide particle at the solidification interface was examined by the visualized model experiment.

Powders were mixed and compacted, then swaged for unidirectional solidification. The solidified samples show unidirectionally solidified structure. But oxide film on Al powder did not dissolve and constructs oxide network through the sample. This oxide network was torn off during unidirectional solidification, and was pushed up together with alumina powders by solid/liquid interface. Unidirectional solidification structure was

observed only where oxide network was eliminated.

The mechanical alloying was carried out on the powders. Pellets were produced by this method. These pellets are very hard because of work hardening, and have firm oxide film on the surface. So compaction could not be done using this pellet. These pellets were introduced into the melt of Al-4.5wt%Cu. These were easily introduced into the melt without floating. But the oxide film on the pellet surface is too firm to dissolve into melt, so the alumina particles did not disperse uniformly in the melt.

In the visualized model experiment, the behavior of the particle at the unidirectional solidification interface using succinonitrile which is a transparent organic substance with the same surface property as metallic material.

As a result of the observation on condition of the smooth solid/liquid interface, particles were not entrapped by the interface, but pushed out. On condition of the dendritic solidification, particles were not entrapped, but the particle located between dendrite arms as if it was entrapped in the matrix.

Oxide particle dispersed material was produced and solidified unidirectionally to examine the behavior of the particle at the solidification interface. It was not possible to eliminate the oxide network produced on the surface of aluminum powders during sintering. But we found that Alumina powders are likely to be pushed out at solid/liquid interface. This means this kind of particles exist at grain boundary or interdendritic region on normal casting condition.

**Keywords :** solidification, solidification processing,

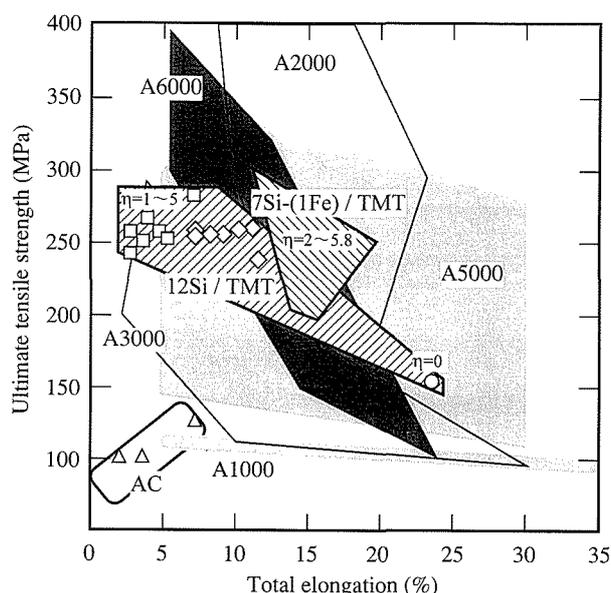


Fig.1 Illustration of strength-elongation balance map for the Al-Si(Fe) materials.

unidirectional solidification, composite, particle dispersion

## 121 Fine Microstructure Development in Plural Phases Alloy

*K. Nagai and O. Umezawa, Materials Creation Research Station*

[April 1996 to March 1998]

In the present aluminum (Al) material flow of recycle stage, few reclaimed scraps are reborn as wrought products. Major secondary products are castings. The cast Al alloys are brittle and show very poor formability. When the cast alloys might have as high formability as the wrought alloys, the Al material flow would change from one-way close-loop system.

In the present study, Al-Si (silicone) system alloys as most typical and practical one of the Al cast alloys were attempted to attain a sufficient formability through a newly designed thermo-mechanical processing. The main concept to turn brittle into ductile is to create "recyclable micro-complex microstructure". The Al-Si system has two-phase microstructure of Al matrix with dispersed Si crystals. The brittleness of coarse Si crystal results in the poor ductility of the alloy system. When the Si crystals become small enough not to break under workings, the alloys is expected to reveal a good formability.

The alloys examined were Al-7mass%Si, Al-12% Si, and Al-20%Si for Al-Si binary system and Al-7% Si-1%Fe, Al-11%Si-2%Fe, and Al-14%Si-2%Fe for ternary system. Iron (Fe) is one of main impurities mixed in recycling process. These alloys have brittle second phases: fine needle-like eutectic Si crystal, coarse needle-like intermetallic compounds (Al<sub>5</sub>SiFe) and coarse primary Si crystal. Hence, they showed the small fracture strain between 0.3 and 7% and a poor cold-formability.

By a given amount of cold-swaging after the sample was cooled in liquid nitrogen (77K), all the brittle phases cracked into smaller pieces and decreased their size. Intermediate heat-treatment of annealing for 3.6 ks at 793 K and water-cooling followed the swaging. Until when the accumulative reduction in the sample section was achieved about 80% by the repetition of the thermo-machanical treatment (TMT), the sample became so ductile that more than 90% reduction could be given in cold-deformation.

The brittle phases were refined into about a fifth in size compared with those in the as-cast (AC) materials. Even if the refined brittle phases cracked

in cold-deformation, the cracking did not develop into the Al matrix and only micro-voids formed around the refined particles.

The TMT materials had higher strain-hardening rate than the AC materials, and eventually their uniform elongation was remarkably improved. Furthermore, higher tensile strength was given and therefore strength-elongation balance was evidently superior to the AC materials. Figure I demonstrates the good strength-elongation balance of the TMT materials compared with various wrought alloy systems. Some of Al-Si alloys by the present TMT show comparable properties with practical materials for wrought products.

Most interesting phenomenon in the newly developed processing is "healing" of cracks in coarse primary Si crystal introduced in cold-swaging. These cracks did not perfectly disappear by the subsequent annealing. However, almost all the cracks were extinguished during the repetition of TMT. The authors discussed that easily deformed Al matrix might fill up the cracked space plastically and that the voids diffusion in the recovery of deformed Al matrix by annealing could accelerate this healing process.

Microstructural Design and Processing of Plasticized Hyper-eutectic Al-Si-Fe Alloys, O. Umezawa and K. Nagai, Proc. Third Inter. Conf. on ECOMATERILAS, (1997): 59-62. Microstructural Design of Hyper-eutectic Al-Si Alloy and Its Deformation Behavior, O. Umezawa and K. Nagai, Proc. Third Inter. Conf on ECOMATERILAS, (1997): 91-94. Microstructural Control of recyclable Al-Si-Fe Alloys by Low Temperature Working Process, C. Y. Lim, O. Umezawa and K. Nagai, Proc. Third Inter. Conf. on ECOMATEILAS, (1997): 99-102. O. Umezawa and K. Nagai, Japanese Contract 10-48382 (1998). O. Umezawa and K. Nagai, Japanese Contract 10-51111 (1998).

**Keywords:** Al-Si cast alloys, recyclable design, thermo-mechanical treatment, refinement, formability

## 122 Characterization of Recovery and Softening Process in Martensitic Steels at Elevated Temperatures

*M. Igarashi, S. Muneki, K. Kimura (Materials Creation Research Station) and F. Abe (Strength and Life Evaluation Research Station)*

[April 1998 to March 1999]

High Cr ferritic steels such as 9Cr-1MoVNb steel

(ASME SA335 P91) have successfully been used for large diameter and thick section boiler components such as main steam pipe and header in super critical (SC) boilers in fossil-fired power plants. Recent trend to utilization of clean energy leading to protection of global environment has been accelerating application of ultra super critical (USC) boilers, which are operated with higher efficiency in power generation than in conventional ones and thus release less amount of carbon dioxide etc. The USC boiler requires heat resistant materials with improved creep rupture strength at elevated temperatures over 600 °C, because of increase in operating temperature and pressure of the steam used. We added high Cr ferritic steels such as 9Cr-0.5Mo-1.8WVNb (ASME SA335 P92) and 12Cr-0.4Mo-2WCuVNb (ASME SA335 P122) steels have already been developed for the USC boilers up to around 610 °C and are being produced for actual applications. The expected goal of the USC boilers is, however, now considered to be 630 °C and 30MPa, which might be the applicable limit of the conventional ferritic steels regarding creep strength and steam-oxidation resistance.

The ferritic steels with 9-12% Cr developed for USC boilers are basically used after normalizing and tempering to obtain long-term creep rupture strength with enough toughness. A typical microstructure of the steels normalized and tempered consists of lath-martensite matrix and  $M_{23}C_6$  (M; Cr, Fe, Mo, W etc.) type carbides along prior austenite grain boundaries and lath boundaries,  $MX$  (M; V, Nb, etc. and X; C, N) type carbonitrides inside lath-martensite grain. The addition of W to the steels enhances precipitation of intermetallic compounds such as *Laves* and  $\mu$  phases mainly along prior austenitic grain boundaries and lath boundaries, and also inside grain during long term exposure at high temperatures.

Creep deformation of the ferritic steels during service exposure at high temperatures is controlled by recovery and softening process of the tempered martensite described above, which strongly depends on the constitution of the microstructure and its change with time. It is, thus, important to understand the detail of the constitution of the microstructure and its change with time by changing the alloying elements, to clarify the creep deformation process at higher temperatures over 630 °C.

This research program is thus proposed to clarify first the effects of alloying elements on the relevant phase equilibria of the steels in question at the corresponding temperatures using a thermodynamic software, *Thermo-Calc*. Then, as a new attempt, the transformation and precipitation behavior of the steels are experimentally measured using DSC (Dif-

ferential Scanning Calorimetry). The results would be analyzed in relation to the change in microstructure and the creep related properties such as diffusion coefficient during creep deformation.

**Keywords:** martensitic transformation, ferritic steels, creep resistance, recovery

### 123 Feasibility study on utilization of high brilliance X-rays for steel characterization

*O. Umezawa\**, *T. Takahashi\*\**, *K. Tsuzaki\**, *Y. Yamauchi\*\*\**, *K. Kimura\**, *M. Hayakawa\*\**, *T. Omura\*\**, and *T. Hara\**

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[April 1998 to March 1999]

The third generation storage ring, SPring-8 (Super Photon ring -8 GeV) has been constructed at the Harima Science Garden City. The beamline BL24XU which Hyogo prefecture supports is designed for providing the highly brilliant microbeam and phase contrast imaging.

Regarding on the microstructural characterization of steels, transmission electron microscopy has been usually employed. However, the analyses have to be done by thin foil and are invalid for bulk information. Thus the three-dimensional distribution of tiny precipitate and/or microcrack in bulk sample interior has been hardly clarified. The improved resolution of topographic images with hard X-ray is expected for an advanced characterization of steels.

We have collaborated with the Center for Advanced Science and Technology, Hyogo, and have investigated the feasibility of phase contrast imaging for steels' study in the following aspects:

1. Microstructural characterization of steels

Imaging tiny precipitates like carbides, nitrides, and intermetallic compounds in low alloy steels,

2. Analysis for delayed fracture in steels

Imaging intergranular cracks and grain boundary structure in high strength steels, damaged by delayed fracture,

3. Analysis for the microcrack and local stress field in high-cycle fatigue

Imaging interior microcracks and local stress distribution introduced by fatigue damage.

**Keywords:** synchrotron radiation, steels, precipitates, intergranular crack, delayed fracture, fatigue crack and deformation

## Jointing and Interface Station

### 124 Effect of the Interfacial Damage on Mechanical Properties for Ti-Based Matrix Composites

*C. Masuda, A. Fukuhara, I. Uetake, H. Yamawaki, Y. Tanaka and Y.F. Liu Interface and Joining Division*

[April 1996 to March 1999]

Silicon-carbide (SiC) fiber reinforced titanium alloy matrix composites are attractive for structural applications such as gas turbine engines, because of their high specific modulus and strength, and good stability at high temperature. There are many reports on the fabrication methods and mechanical properties of those composites. It is well known that the major problem during processing is fiber degradation due to the unavoidable nature of active reaction behavior between the fiber and matrix, that is, the reaction layer thickness was related to the degradation of mechanical properties. The effect of the reaction layer thickness on the mechanical properties could not be deduced by the micromechanics, because the mechanical properties of reaction layer could not be obtained.

(I) Fatigue crack initiation and propagation mechanisms tested at room temperature are as follows; (1) a fiber cracking and the initiation at the tip of it in the reaction layer, (2) interfacial debonding between the reaction layer and outer carbon layer, (3) a wearing between carbon layer and reaction layer, and (4) matrix cracking. Fatigue mechanisms tested at high temperature in vacuum was nearly the same as those tested at room temperature. But the life duration for the formation of the debonding between outer carbon layer and reaction layer was longer at high temperature than that at room temperature under the same stress level. It is suggested that the fatigue life at high temperature is higher than that at room temperature due to the formation of debonding.

(II) As revealed experimentally, the interface region between the fiber, reaction layer and matrix plays an important role in damage initiation and propagation, therefore modeling and analysis of the interfacial damage initiation and propagation have been carried out. Analytical and numerical results are obtained regarding 3 types of damage interaction between interface bonding/debonding and a crack in fiber-reinforced metals, namely, a circumferential crack approaching a fiber-matrix interface, crack deflection and penetration at an interphase, 3-

dimensional plasticity growth around a crack tip and interface. These results are summarized as follows: (1) bonding interface may hinder or accelerate the growth of an approaching crack depending on the combinations of fiber and matrix material properties, (2) properties and thicknesses of the interphase are very important to crack deflection and penetration conditions at interphase interfaces, (3) plasticity growth is likely to occur preferentially around and interface because of thermal stresses induced during composite processing, and this complicates debonding conditions.

**Keywords:** metal matrix composite, fatigue fracture mechanism, interfacial debonding, wearing, FEM analysis

#### Recent Publications

- 1) Y.F. Liu, C. Masuda and Y. Tanaka, "Analysis of a fiber-matrix axisymmetrical model with a circumferential crack", *Int. J. Fracture*, 88 (1998) p87-105.
- 2) Y.F. Liu, C. Masuda and R. Yuuki, "Effect of microstructural parameters on the fracture behavior of fiber-reinforced ceramics, *Mechanics of Materials*, 29 (1998) p111-121.
- 3) Y. Tanaka, Y. Kagawa and C. Masuda, "Observation of fatigue damage process in SiC fiber-reinforced Ti-15-3 composite at high temperature, *Met. and Mat. Trans.*, 30A (1999) p221-229.

### 125 Evaluation of mechanical properties for metal matrix composites

*Chitoshi Masuda, Yoshihisa Tanaka Joining and Interface Research Station*  
[April 1996 to March 1999]

As metal matrix composites have anisotropic structures, those mechanical properties are significant depended upon the fiber direction in the composites in comparison to the convention steels, aluminum alloys and so on. In order to obtain the reliable data of mechanical properties for metal matrix composites and to propose the test standard to ISO and so on, it has been continued since 1992 to proceed an international cooperative research for the round robin test (RRT) of mechanical properties for metal matrix composites. About eight organizations in United State of America, United Kingdom, Germany, France, and Japan are assisted for the members of this technical working area of VAMAS Project.

Up to now a tensile test was carried out for a silicon carbide whisker reinforced aluminum alloy

matrix composite supplied from NASA at room temperature. Data obtained from RRT were analyzed and the tensile test method for metal matrix composite at room temperature was proposed to ISO.

Moreover, the tensile test at high temperature for the same composite was performed and analyzed the data obtained by about 6 organizations in the world. The modulus and tensile strength data showed very large scatters, because of the difference of the test procedure among the organizations. The second test was organized to check the effect of the strain rate on the tensile strength and modulus. The second test has finished now, but all data were not gathered yet. According to our results, the tensile strength increased with increasing strain rate, although the effect of the strain rates was not made clear yet. Fatigue test will be organized for silicon carbide whisker reinforced aluminum alloy matrix composite at room and high temperatures. The test condition has already been discussed, but the specimen configuration was not yet decided.

Titanium alloy matrix composite will be tested for the tensile and fatigue condition at high temperature. For that purpose the materials have already obtained and test conditions have also decided. Because the reference fatigue data were not obtained, those data are necessary to take now. RRT will be started after the test stress level is decided.

**Keywords :** metal matrix composites, standardization of test methods, tensile test, fatigue test, aluminum alloy matrix composites, titanium matrix composites

## 126 Evaluation of corrosion damage at atomic level

*H. Masuda, Frontier structural material center*  
[April 1996 to March 1998]

Previous AFM observation showed that small water droplets and water film were observed on the surface when pure water or aqueous solution was poured on graphite or mica. However when the specimen surface was dirty and too rough to observe very thin water film like roughly polished metal surface, we cannot decide whether the water film exists or not. The possibility of measurement of water film distribution by surface potential measurement was studied. As the results it is proved that surface potential becomes low when water film is existed and thin water film which cannot be distinguished from the surface shape can be observed by measuring the surface potential distribution.

**Keywords :** Corrosion, KFM, Potential

### Related paper

Possibility of observation of water film by measuring surface potential distribution : H. Masuda, J. Japan Inst. Metals Vol, 62 No. 12 (1998) 1183-1188

## 127 Development of metal having environmental cleaning ability by photo catalysis reaction

*H. Masuda, Frontier structural material center*  
[April 1996 to March 1998]

Previous AFM observation showed that small water droplets and water film were observed on the surface when pure water or aqueous solution was poured on graphite or mica. In this experiment, pouring pure water and 0.01 M  $\text{CuSO}_4 + \text{H}_2\text{SO}_4$  aqueous solution on graphite, adsorbed water observed by AFM was tried to detect by the FT-IR microscope. The existence of adsorbed water on the surface of gold and pure iron was also examined by the FT-IR microscope and AFM. The results showed that the peak of water was observed near  $1590 \text{ cm}^{-1}$  on the surface of graphite, gold and pure iron. The existence of liquid film of which thickness is 2 nm was confirmed by the AFM observation. From these results, there is the high possibility that the water film exists on the metal surface used for present experiment.

**Keywords :** Water droplet, AFM, FT-IR

### Related paper

Observation of Adsorbed Water on Various Materials by AFM and FT-IR : H. Masuda, J. Japan Inst. Metals, Vol. 62, No. 7 (1998) 617-620

## 128 Effect of Aging Degradation on Localized Corrosion of Structural Materials for Light Water Reactors

*Y. Katada, S. Ohashi, K. Kurosawa, J. Kinugawa, Y. Muramatsu, Y. Asai, Joining and Interface Research Station*  
*H. Irie, Mechanical Properties Division*  
*T. Kasugai, K. Ei, Materials Processing Division*  
[April 1996 to March 2001]

Life management of Nuclear Power Plant (NPP) for the acquisition of renewal license is one of the worldwide primary concerns. From the viewpoint of the integrity evaluation of structural materials, therefore, the interaction between aging degradation of the materials and environmentally assisted crack-

ing (EAC) is one of the important issues to be investigated.

The objectives of the research are to investigate the interaction between aged structural materials and environmentally assisted cracking (EAC) such as stress corrosion cracking, corrosion fatigue in high temperature water, and to mitigate the enlargement of local damage in weld joints by using a laser beam technique.

#### 1. Interaction between aged materials and EAC

Sulfur (S), which exist as a form of MnS inclusion in materials, is one of the important factors for evaluation of EAC behavior in high temperature water. The dissolution of MnS results in lowering pH in the vicinity of a crack tip. In this year the effects of MnS and Temperature on corrosion loss of low alloy steel in high temperature water were investigated. As a result, it was found that the trend of corrosion loss was subjected to the series of test condition : aeration+MnS>aeration+no MnS>deaeration+MnS>aeration+no MnS. In addition, it was also found that in the case of aeration+MnS, the corrosion loss was the largest at 175°C, which was probably due to the formation of stronger oxide film of magnetite at higher than 175°C.

#### 2. Mitigation for the enlargement of local damage by laser beam technique

TEM observation was conducted for a helium doped heat affected zone (HAZ) of stainless steel from 2-200 appm in amount of helium, on which surface was post-treated by electron beam technique simulating a laser beam processing. It was found that helium bubbles were observed in the case of higher doping more than 20 appm, and its behavior showed various appearances such as tiny bubbles scattered in grains or large bubbles gathered in grain boundary, which depended upon its input heat condition.

As one of the evaluations for corrosion behavior of weld metal of stainless steel which was post-treated by laser beam technique, electrochemical approach was conducted by using a micro vibration electrode in 3% NaCl solution. Although corrosion pits were observed in HAZ, it was found that the post-treating by laser beam technique for the HAZ was able to suppress the initiation of corrosion pits. The mechanism of the initiation of corrosion pits is now being investigated.

In-situ observation by a laser speckle method has been applied in order to measure the local strain behavior of weld metal in laser processing. It was found that the precision of strain measurement decreased due to the very high intensity of radiation by the plasma of laser beam. Optimization of measurement conditions was, therefore, primary concerns at present.

**Keywords :** aging degradation, localized corrosion, light water, reactor, weld joints, laser beam

## Strenght and Evaluation Research Station

### 129 Development of Nano Scale Characterization Technique of Grain Boundary and its Use to Analyses to Intergranular Fracture Mechnaism

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[April 1997 to March 2000]

Grain boundary is the most important factor of metallurgical structures which control mechanical properties of metals such as delayed fracture and stress corrosion cracking as well as strength and toughness.

It is essential to have informations about microstructures and fracture behaviour at grain boundary and the mechanical properties in the immediate vicinity of grain boundary in order to clarify the mechanism of intergranular fracture.

Scanning electron microscopy (SEM), Auger electron spectroscopy (AES) and transmission electron microscopy (TEM) are typical methods for microscopic analysis of grain boundary structures. However, capabilities of these methods are not enough to reveal the details of microstructures and fracture behaviour at grain boundary, that is, SEM and AES do not have sufficient resolution to observe very small precipitates less than 10 nanometer and TEM is not adequate for a three-dimensional analysis of microstructures.

This study has the following four aims.

1. Development of the technique for a three-dimensional nanoscopic characterization of grain boundaries.
2. Analysis of the effect of grain boundary microstructures on the mechanical properties in a very small area near grain boundary by nano-indentation method developed at NRIM.
3. Analysis of the relationship between grain boundary microstructures and the strength and the intergranular fracture based on above informations.
4. Establishment of the guide principle to improve the resistance to intergranular fracture.

The scanning probe microscope (SPM) is appropriate for nanoscopic analyses of grain boundary microstructures, because the SPM has the atomic scale resolution. However, it is hard to observe very

small precipitates on the specified grain boundary surface of intergranular fractured specimen by the conventional SPM because of its large surface roughness of more than  $10\mu\text{m}$ .

This study began with the development of a new probe and a lever for atomic force microscope (AFM) which enable the nanoscopic characterization of grain boundary. A newly developed probe has a height of 1 mm taller than conventional one of  $20\mu\text{m}$  and a new lever has a width of  $400\mu\text{m}$  wider than a conventional one of  $50\mu\text{m}$ . Next, in order to resolve problems related to reduction of measuring accuracy of height due to increase of lever weight and related to increase of spring constant, the shape of a lever is newly designed and the new material is used for a lever. The new material is also adopted for a probe to improve resolution. Moreover, a SEM is incorporated into the AFM to make possible to observe the specific grain boundary surface.

Preliminary observations of fractured surface of the quenched steel of 0.53% carbon was carried out by use the conventional AFM to verify that the AFM was effective tool for nanoscopic analyses of microstructures of the fractured surface. It was confirmed that nanoscale precipitates could be observed by AFM which were not observed by SEM with the highest quality.

In 1998, the following studies are scheduled.

1. Analysis of the grain boundary microstructure by newly developed apparatus.
2. Analysis of the grain boundary microstructure on the mechanical properties in the vicinity of the grain boundary by nanoindentation technique.
3. Analysis of the relationship between the grain boundary microstructure and the intergranular fracture.
4. Improvement of the performance of newly developed apparatus.

**Keywords :** grain boundary, delayed fracture, nanoscale, scanning probe microscopy (SPM), atomic force microscopy (AFM), intergranular fracture

### 130 Ductile versus Brittle Behavior of structural steels

*S. Matsuoka, Frontier Research Center for Structural Materials, Strength and Life Evaluation Research Station*

[April 1996 to March 1998]

Many steel structures were damaged on Hanshin-Awaji great earthquake of January 17, 1995. One typical example was the buckling of steel columns in highways and another was the brittle fracture of steel

box columns in high-rise buildings. Such a difference in damage modes is closely related to the ductile versus brittle behavior of the structural steel.

SEM fractography showed that the cleavage appearance was observed in large-scale specimens fractured under load sequence simulating Hanshin-Awaji earthquake. This confirmed that steel structure components were brittle-fractured on Hanshin-Awaji earthquake. Ductile fracture specified by dimples was formed ahead of brittle fracture in large-scale specimens. Similar phenomena were observed in small specimens of Charpy impact tests. Based on these results, We proposed that the toughness of steel structural components was equal to the Charpy impact energy, when the ductile crack length was the same each other.

**Keywords :** Hanshin-Awaji earthquake, buckling and brittle fracture of steel components, fractography

### 131 Mechanical Properties of Thin Films and Coatings

*S. Matsuoka, Frontier Research Center for Structural Materials, Strength and Life Evaluation Research Station*

[April 1997 to March 1999]

Mechanical properties of thin films and coatings become a subject of much concern, because they are widely used in a large number of industrial fields. In this study, depth sensing indentation (DSI) technique is developed to measure hardness and elastic modulus of thin films and coatings. The study is closely related to the new technical working area TWA 22 "Mechanical properties of thin films and coatings" among VAMAS projects.

In the financial year, DSI was carried out for aluminum thin films on a hard substrate of alumina which were prepared in the previous year. Pop-in phenomena were occurred because the oxide film was formed on aluminum thin films. An empirical equation was developed, so that Vickers hardness was estimated from DSI data. The equation was useful for evaluating the hardness of the metallic thin film.

**Keywords :** thin films, coatings, elastic modulus, hardness, depth sensing indentation

### 132 Stability of Tetragonal Phase and its Effect on High-Temperature Mechanical Properties of Zirconia

*Fujio Abe, Strength and Life Evaluation Research*

## Station

[April 1996 to March 1999]

Transformation-toughened zirconia ( $ZrO_2$ ) base ceramics have been of much interest in recent years, because of the considerable potential of these ceramics in structural applications. The author and co-workers have revealed for a partially stabilized zirconia (PSZ)  $ZrO_2$ -9.7 mol% MgO that the tetragonal (t) to monoclinic (m) phase transformation occurred in the two distinct stages at 1000-1200 K and 400-700 K on cooling. The low-temperature stage was caused by martensitic transformation of the ellipsoidal particles of the t-phase in the cubic phase matrix. The high-temperature stage was caused by martensitic transformation of the low-MgO-content m- and t- phase containing 1-2 mol% MgO produced by eutectoid decomposition of cubic phase. In this research, the transformation behavior has been compared with that in another PSZ,  $ZrO_2$ -8 mol% CaO, and in tetragonal zirconia polycrystal (TZP),  $ZrO_2$ - (2-3) mol%  $Y_2O_3$ . The  $ZrO_2$ -8 mol% CaO and  $ZrO_2$ - (2-3) mol%  $Y_2O_3$  showed martensitic transformation corresponding to the high-temperature and low-temperature stages, respectively, in the  $ZrO_2$ -9.7 mol% MgO. The present results suggest that the transformation behavior in zirconia ceramics strongly depends on the microstructure.

The relationship between fracture toughness  $K_{IC}$  and Vickers hardness  $H_v$  has been investigated for the  $ZrO_2$ -9.7 mol%MgO and  $ZrO_2$ -2 mol% $Y_2O_3$  in the temperature range between room temperature and 1173 K. The volume fraction of the m-phase in the specimens was changed from 0 to 0.987 for the  $ZrO_2$ -9.7 mol%MgO by various heat treatments. The present results showed that the  $K_{IC}$  was inversely proportional to the  $H_v$ , similar as those in the maraging steels and Ti alloys which were already published by Muneki et al. The zirconia ceramics were located in low  $K_{IC}$ -high  $H_v$  side, while the metallic materials in high  $K_{IC}$ -low  $H_v$  side.

**Keywords :** partially stabilized zirconia, transformation, fracture toughness

### Related papers :

High Temperature Hardness and Toughness of MgO Partially Stabilized Zirconia and  $Y_2O_3$  Tetragonal Zirconia Polycrystal, S. Muneki and F. Abe, Ceramic Processing 97 (1997) in press.

Relationship between hardness and fracture toughness of a 9.7 mol% MgO partially stabilized zirconia alloy and high specific strength metallic materials, S. Muneki, F. Abe, Proc. 5th Japan International SAMPE Symposium (1997) 547.

Impurity Control in Heat Resisting Steels and Evaluation of Their Radioactivity, F. Abe and T. Noda, 8th International Conference on Fusion Reactor Materials (1997) 198.

### 133 Evaluation Method of High Temperature Fracture Property for Creep Brittle Materials.

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[April 1997 to March 2000]

It is necessary to establish the test method of creep crack growth in order to evaluate the reliability and residual life of high temperature components. VAMAS international collaborative research for creep crack growth has been conducted since 1986. Based on the results of this research project, the testing standard concerning creep crack growth of creep ductile metals have been adopted by ASTM as E1457-92. However, the test method should be modified in order to adapt to advanced heat resisting materials because they show different creep crack growth behavior from ductile metals. Therefore VAMAS Technical Working Area 19 on High Temperature Fracture of Creep Brittle Materials was established in 1993. This research aims to conduct the collaborative research in VAMAS TWA19 and to establish the standard test and evaluation method of creep crack growth for creep brittle materials.

The round robin tests on titanium aluminides (Ti-33.4wt%Al) intermetallic compound which have fully lamella microstructure and coarse grain have been conducted. We have proposed the guideline of creep crack growth test method for TiAl based on the round robin test results. This guideline was discussed in VAMAS TWA19 meeting.

Fatigue pre-cracking was recommended in conventional fracture mechanics tests method. However, the fatigue pre-cracks grew to the direction along the lamella structure and deviated more than 20° from the notch plane. It was experimentally and numerically indicated that the sharp V-notch specimen was useful in stead of pre-cracked specimen in order to get creep crack growth rate for this creep brittle material. Micro cracks induced by electrical discharged machining (EDM) affected the stability of creep crack initiation behavior. Therefore we recommended the V-notch machined by hard tool cutter as a standard starter notch. The notch tip angle should be smaller than 30° and notch tip radius should be smaller than 0.1mm. The side-grooves were effective in order to prevent the deviation and tunneling of creep crack. Creep crack length could be measured by direct current electrical

potential method within the accuracy of 5%. The method to unite the potential leads with specimen was investigated in detail because the potential must be measured for long time at high temperature.

Creep crack growth tests were conducted at 973K ~1123K. For the creep brittle materials,  $C^*$  integral could characterize the creep crack growth rate better than stress intensity factor. The creep crack growth rate of TiAl was higher than that of creep ductile Cr-Mo steel and was lower than that of more brittle Ni-base superalloy. Therefore, it is considered that the reasonable value was obtained according to this test guideline. The creep crack growth mechanism of TiAl was dependent on temperature. While creep crack grew along the interface of lamellar structure at 973K, crack grew on grain boundaries at higher than 1023K. At 1073K and 1123K where the dynamic recrystallization was observed on grain boundaries, the creep crack growth rate showed a higher value.

We are also planning to conduct the round robin tests on TiAl (Ti-34Al-1.8Fe-1.6V-0.09B) which has duplex structure and fine grain. The effect of specimen configuration, specimen size, load, temperature, microstructure of materials and fracture mode on creep crack growth properties will be investigated. The standard test and evaluation method will be discussed.

**Keywords :** creep crack growth, TiAl, standardization of tests method, VAMAS project

### Recent Publications

Testing Method and Evaluation of Creep Crack Growth for High Temperature Brittle Materials, M. Tabuchi, A. Fuji, A.T. Yokobori and K. Kubo, Proc. of the 42th Japan National Symposium on Strength, Fracture and Fatigue (1997) 37-44 (in Japanese).

Results of a Japanese Round Robin on Creep Crack Growth Evaluation Methods for Ni-base Superalloys, M. Tabuchi, K. Kubo, K. Yagi, A.T. Yokobori and A. Fuji, (submitted to Engineering Fracture Mechanics).

### 134 Long-Term Creep-Fatigue Properties of 316FR Stainless Steel for Fast Breeder Reactor

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[April 1995 to March 2000]

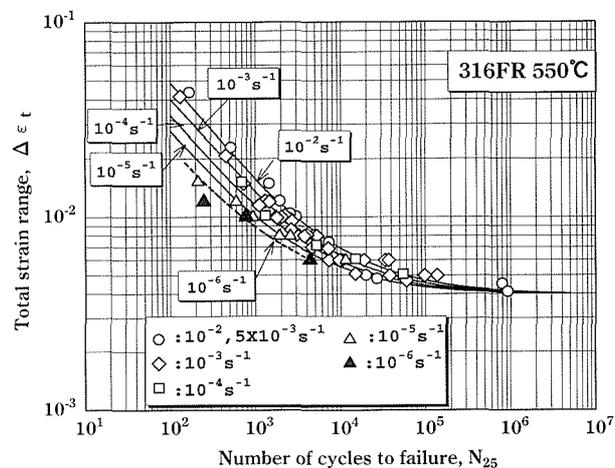


Figure 3 Strain rate-dependence of the fatigue life for 316FR steel.

The 316FR stainless steel has been developed as a candidate material for fast breeder reactor of twenty first century. For the structural design of components of the reactor, evaluation of fatigue life data for the 316FR steel is important to represent the temperature- and strain rate-dependence of the fatigue life design curves. Because the main components of the reactor are subjected to cyclic thermal stresses due to start-up and shut-down of the system. Figure shows the strain rate-dependence of the fatigue life of 316FR steel at 550°C. The S-N curves are the results of parametric analysis which was proposed by the authors.

Another object is to develop the new material with longer creep-fatigue life by modifying the 316FR steel. Twenty seven heats of the materials with different chemical compositions varying the elements such as C, N, Mn, P, Cr, Ni, Mo, Si and with different grain size are being tested.

This research is performed in collaboration with Mitsubishi Heavy Industry Ltd., Nippon Steel Corp. and The Japan Atomic Power Co.

**Keywords :** low cycle fatigue, fast breeder reactor, 316FR stainless steel

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## □ **NRIM Publications (Apr. 1997 to Mar. 1998)**

1. Bulletin of National Research Institute for Metals, in Japanese.  
No. 20 (Mar. 1998)
2. Annual Report of National Research Institute for Metals, in Japanese.  
For fiscal year of 1996 (Mar. 1998)
3. Kinzaigiken News, in Japanese.  
No. 4 to 12 (1997) and No. 1 to 3 (1998)
4. NRIM Research Activities, in English. (Mar. 1998)
5. Material Strength Date Sheet, in English.  
NRIM Creep Date Sheet,  
No. 19B and No. 45 (Sep. 1997)
6. Guide to National Research Institute for Metals, in Japanese and in English.  
For fiscal year of 1997 (1997)

## International Exchange

Apr. 1997 to Mar. 1998  
International Collaboration Researcherch

### Australia

1. Studies on conductor fabrication Processes of high-TCP BiSrCaCuO superconductors (University of Wollongong)
2. A comparison of high energy density beam and arc welding technique for joining advanced materials of both the metal-matrix composite and intermetallic compound types (CSIRO)
3. Process technology and characterization of advanced metal matrix Composites (CSIRO)

### Bulgaria

1. Characterization of thin films using X-ray total reflection (Institute on Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences)

### China

1. Investigation of high temperature Titanium alloy for application over 600°C (Northwest Institute for Non-Ferrous Metal Research)
2. Studies on structural control and superconducting properties of high Temperature superconductors (Institute of Metal Research, Chinese Academy of Science)
3. Fundamental study on the improvement of superconductivity for high-Tc oxides (Northwest Institute for Non-Ferrous Metal Research)
4. Studies of local corrosion damage of corrosion resistant alloy in high Temperature aqueous solution (Shanghai Jiao Tong university)
5. Study on the improvement of brittleness of Ni<sub>3</sub>Al and NiAl by Unidirectional Solidification (Institute of Metal Research, Chinese Academy of Science)
6. Environmental life cycle analysis of materials (Lanzhou University)
7. Study of TiAl Base Alloys (Northwest Institute for Non-Ferrous Metal Research)
8. Fundamental research on TiAl base intermetallic compounds (University of Science and Technology, Beijing)
9. Studies on Crevice Corrosion of Low Alloy pressure vessel steels in high Temperature aqueous solution (Institute of Corrosion and Protection of Metals)

### EU

1. Research on Materials for Nuclear Fusion Reac-

tor (KFK Juelich etc.)

2. Evaluation Model of the Characterization Data of Materials (Institute for Advanced Materials, Petten Site)
3. Development of High-Field Pulse Magnets (Grenoble High Magnetic Field Laboratory)

### France

1. Superconducting and cryogenic magnetic materials (Service National des Champus Intenses, CNRS)
2. Mechanical properties for short fiber reinforced metal matrix composites (Conservatoire National des Arts et Matiers)
3. First Order Phase Transitions in Magnetic and Superconducting Materials At Low Temperatures (CNRS)

### Germany

1. High Performance Superconducting Materials (Forschungszentrum Karlsruhe)
2. Development of Documentation Panel Numerical data (Fachinformationszentrum Karlsruhe)
3. Designing of New Continuous Refining Process (Haus der Technik e.v. Essen)
4. Nanoscopic Evaluation of Material Properties (Max-Planck-Institut für Eisen-forschung GmbH, Universit (t des Saarlandes)
5. In Vitro and In Vivo Biocompatibility of Biomaterials (Free University of Berlin)

### Hungary

1. Studies on Mechanisms of Nanoscale Microstructural Evolution in Advance Metallic Materials (Department of General Physics, Etövös university)
2. Noise Analysis of Single Electron Transister (Department of Physics, Jozses Attila University)

### India

1. Studies of quasi-crystalline based composites (Indian Institute of Science)

### Italy

1. Superconducting properties of advanced superconductors in time-varying magnetic fields (CISE SPA, Technologia Innovative Thermo-

physics & Cryogenics Sec.)

2. Intercomparison of methods and materials for strain measurements at cryogenic temperatures (Istituto di Metrologia "G. Colonnelli" -C.N.R)
3. Metallic materials (Istituto per la Tecnologia dei Materiali Metallici Non Tradizionali)

## Korea

1. Development of the aluminum base intermetallic compounds for structural application at high temperature (Korea Institute of Machinery and Materials)
2. Performance characterization of materials at high temperature (Korea Research Institute of Standards and Science)
3. Development of metallic superconducting material (Korea Research Institute of Standard Science)
4. Thermoelectrics research for advanced intermetallic compounds (Rapidly Solidified Materials Research Center)
5. Evaluation of the high temperature properties for titanium-based particulate Composites (Korea Advanced Institute of Science and Technology)
6. Studies on the fabrication of Bi-2223 superconducting wire and its application (Korea Institute of Machinery and Metals)

## Netherlands

1. Studies for Measuring Technique of Quantum Effect and for Strongly Correlated Electron System (Amsterdam University)
2. Study on Magnetic Properties of Steels at High Temperature (Delft University of Technology)
3. Assessment of Environmental Loading of Materials (Center of Environmental Science Leiden University)
4. Interface Roughness and Thickness of Thin Film Multi-layer Structures (FOM Institute for Atomic and Molecular Physics)
5. Study on Electronic Instabilities in Magnetic Materials With F-electrons Under Multi-extreme Conditions (University of Amsterdam)
6. Design and Evaluation of Super-alloys for Gas Turbine Applications (University of Twente)

## Poland

1. Magnetization and magnet-optics in diluted magnetic semiconductors in high magnetic fields (Polish Academy of Science)

## Russia

1. Eco-balance analysis in life cycle of materials (Russian Research Center for standardization, Information and Certification of Materials)
2. Study on electron transport through atomic scale tunnel junctions (Novosibirsk State University)

## Sweden

1. Fabrication and characterization of semiconductor quantum dots (Lund University)
2. Atomic-scale Single Electron Transistor (Chalmers University of Technology)

## Switzerland

1. Research and Development of High Performance Ceramic Super-conducting Wires (University of Geneva)

## U.K.

1. Prediction technology of life and remaining life of huge structures under service condition and its application to design (The Welding Institute)
2. Research and Development of High Performance Multifilamentary Ceramic Superconducting Wires (Cambridge University)
3. Investigation and Development of Highly Parallel Algorithms for Materials Science Calculations (Kingston University)
4. Measurement and Evaluation Methods for Critical Current in High Temperature Superconductors (Cambridge University)
5. Advancement of Levitation Melting and Refining Technology (National Physical Laboratory)
6. Assessment of Ultra-Long-Term Creep Rupture Strength of Heat Resisting Steels (GEC Alsthom Generators Ltd.)

## U.S.A.

1. Research and development on systems and materials for magnetic refrigeration (Francis Bitter National Magnet Laboratory, MIT)
2. Databases on high temperature superconducting materials (National Institute of Standards and Technology)
3. Studies of high-strength/high-conductive materials and their application to high-field magnets (Francis Bitter National Magnet Laboratory, MIT)
4. Fundamental studies on the conductor fabrication of high temperature oxide superconductors

- (National High Magnetic Field Laboratory)
5. Measurement and evaluation methods for superconducting properties (National Institute of Standards and Technology)
  6. Developments and applications of extremely high-field magnets and magnet systems (National High Magnetic Field Laboratory)
  7. Study of nano-composites magnetic materials for cryogenics (National Institute of Standards and Technology)
  8. Joint Research on the "in-situ" analysis/evaluation of atomic and micro-structural changes in materials (Argonne National Laboratory)
  9. Fundamental studies of vortex state in high Tc superconductors (Argonne National Laboratory)
  10. High pressure research on strongly correlated electron systems (University of California)
  11. Effect of high magnetic field on solid/solid phase transformations (North-western University)
  12. Studies on mechanisms of nanoscale micro-structural evolution in advance metallic materials (University of Virginia)
  13. Study on the mechanical properties of directionally solidified inter-metallic compounds (Oak Ridge National Laboratory)
  14. Evaluation of thick coatings formed by advanced thermal spray processes (New York State University)
  15. Photolysis of Silicon Compounds by Infrared Free Electron Laser (Los Alamos National Laboratory)
  16. Basic Studies on Mechanisms of Micro-structural Evolution in Next Generation Steels (Virginia Polytechnic Institute and State University)
  17. Study on the Flux-line States and Josephson Plasma in High-Tc Super-conductors (Argonne National Laboratory)
  18. Physical Properties of the Transition Metal Compounds under High Pressure (Carnegie Institution of Washington)
  19. Development of Nb3Al Multi-filamentary Super-conductor (Ohio State University)
  20. Analysis and Numerical Modeling of High Energy Beam Welding Phenomena (New Mexico State University)

### □ List of Visiting Foreign Researchers who came to NRIM from Apr. 1997 to Mar. 1998

\*STA Fellows

Country and Name	Affiliation	Term	Research Subject
<b>Argentina</b>			
Miguel Ipohorski Lenkiewicz	Comision Nacional Energia Atomica	1998.1.13~1998.1.30	Electron Microscopy and Surface Technique
<b>Australia</b>			
Yuan Chang Guo*	The University of Wollongong	1997.5.20~1998.8.16	Improvement of Electrical and Mechanical Properties in High Temperature Superconductors
Ninh the Nguyen*	The University of Adelaide	1997.9.1~1999.8.31	Assessment of Fatigue Strength of Welded Joint in a Residual Stress Field
Ringer, Simon P.	Department of Materials Engineer- ing, Monash Univz	1997.12.1~1997.12.20	Atom Probe and TEM Studies of the Precipitation Processes of High Strength Aluminum Alloys
<b>Austria</b>			
Hans Kirchmayr Brazil	Technical Univ. of Vienna	1997.10.25~1997.10.29	Testing and Evaluation Methods of Superconductors
<b>Brazil</b>			
Marcelo Ferreila Moreira	Institute de Pesquisas Technologicas (IPT)	1997.9.3~1997.10.30	Surface Quality on Cast Superal- loys (Directional Solidified and Single Crystal superalloys)
<b>Belgium</b>			
Josef Cornelis	Vlaamse Instelling voor Tech- nologisch Onderzoek	1997.10.26~1997.10.29	Testing and Evaluation Methods of Superconductors
<b>Bulgaria</b>			
Dimitar Stoyanov Tchan- kov*	Technical University of Sofia	1997.4.9~1998.4.8	Random Fatigue on Notched Plates

Krassimir Nedialkov Stoev	Institute of Nuclear Research and Nuclear Energy Bulgarian Academy of Sciences	1997.8.1~1997.10.29	Theoretical Analysis of Surface X-ray Scattering from the Randomly Rough Surface
<b>China</b>			
Ping Dehai	Institute of Metal Research, Chinese Academy of Science	1997.5.1~1998.4.30	Crystal Structure Analysis
Guo Junqing Feng Tang*	Harbin Institute of Technology	1997.6.1~2001.11.30 1997.8.1~1998.12.31	Fabrication of Quasicrystals Synthesis of Light Weight Composites and Evaluation of their High Temperature Properties
Yang Wen	Nuclear Power Institute of China	1997.8.25~1998.2.23	Synthesis and Evaluation of Irradiation Effects of SiC Composites Prepared by CVD and CVI Technique
Yingda Yu	Institute of Metal Research	1997.8.29~1998.2.28	Relation between Microstructure and Photoluminescence of Porous Silicon
Ya Ku	Japan Science and Technology Corporation (JST)	1997.9.1~2000.8.31	Effects of High Magnetic Field on Crystallization Behavior in Fe-based Alloys
Li Ye Xiao	National High Magnetic Field Laboratory	1997.9.19~1998.3.30	Quench Stability of High Temperature Superconducting Coils
Zhou Wei Yuefung Gu*	Tsing Hu University Shanghai Jiao Tong Univ.	1997.9.20~1997.12.24 1997.10.1~1999.9.30	Aging Behavior of Porous Silicon Grain Boundary Structures and Ductility Improvement of Platinum Metals based Refractory Superalloys
Lanting Zhang Qing Chen	Shanghai Jiao Tong University Beijin Univ. of Science and Technology	1997.10.13~1997.12.12 1997.10.31~1998.2.28	Synthesis of TiNi <sub>2</sub> Single Crystal Structural Investigation of Nanocrystalline Pb, In and Ge on Silicon
Zhang Xuanjia	Physics Department, Zhejiang University	1997.11.13~1997.12.27	Synthesis and Physical Properties of High- <i>t<sub>c</sub></i> Superconducting Single Crystals and their Films
Zhang Wen	Institute of Advanced Energy, Kyoto Univ.	1998.1.5~1999.1.4	Interfacial Control and Evaluation of SiC/SiC Composites by CVI Technique
Yuning Jiao*	Institute of Metal Research, Chinese Academy of Science	1998.2.1~2000.1.31	Solidification Phenomena in Casting Process
Jiao Zhengkuan*	Physics Department, Zhejiang University	1998.3.1~1998.5.31	A Study on the Relation between Structure and Applied Properties of High-Tc Thin Films Synthesized by Various Deposition Methods
Xie Huimin*	Department of Mechanics, Tsinghua University	1998.3.16~1999.3.15	Measurement of Microdeformation using Electron Moire Method and AFM Moire Method
<b>Czeck</b>			
Paval Lejcek	Metal Physics Division, Czech Academy of Science	1997.10.27~1997.11.22	Solid State Interfacial Reactions and Surface Analysis of Thin Solid Films
<b>Denmark</b>			
Erik Johnson	University of Copenhagen	1997.10.13~1997.10.26	Structural Determination of Metastable Pb Inclusions in Metal Matrix
<b>Finland</b>			
Franco Mancini*	Department of Geology and Mineralogy, Univ. of Turku	1997.8.25~1997.9.29	Crystallographic Investigation on Fe-Mg-Si Minerals Produced in Scandinavia
<b>France</b>			
Evelyne Peron Gonia*	Ecole National Supérieur des Mines de Paris	1997.4.3~1998.4.2	Microscopic Deformation Analysis Around the Ceramic Reinforcement for SiCw/Al Composites
Bernard Chenevier	Laboratoire des Matériaux et du Génie Physique, CNRS	1997.10.12~1997.11.16	Study on Superconducting Properties and Microstructure for YBCO Films Prepared with Modified CVD and Sputtering Processes
Francois Weiss	Laboratoire des Matériaux et du Génie Physique, CNRS	1998.3.9~1998.3.14	(ditto)

Stephane Odasso*	Research Center on the Mechanism of crystal Growth	1997.5.1~2000.3.31	Lead Chain Fabrication on Si (111) Surface
Nathalie Bergion*	National Institute of Applied Sciences of Lyon	1997.5.8~1998.8.31	Atomic Force Microscopy Study of Fe-based Shape Memory Alloys
Luc Ortega*	European Synchrotron Radiation Facility	1997.6.16~1998.8.7	Grazing-incidence X-ray Scattering Studies on the Initial Stages of Metallic Thin Film Growth
Claude Landron	Centre de Recherche Sur la Physique des Hautes Temperature, CNRS	1998.3.1~1998.3.15	X-ray Absorption Fine Structure (XAFS) Analysis of Refractory Oxides
Stephane Labat*	University of Marseille	1998.3.31~1999.8.17	Characterization and Application of Superconducting Thin Films Synthesized by Atomic Layer-by-layer and Epitaxial Growth Methods
<b>Germany</b>			
Hans J. Steffen	University of Applied Sciences in Mannheim	1997.8.14~1997.9.26	Ion Beam Synthesis of Silicides Studied with AES Depth Profiling
Arman Nyilas	Forschungszentrum Karlsruhe	1998.3.22~1998.3.27	Characterization and Evaluation of Cryogenic Structural Materials
<b>Hungary</b>			
Reich, Lajos	Department of General Physics, Eotvos Univ.	1997.10.1~1998.11.11	Three Dimensional Atom Probe Studies of the Precipitation Processes of High Strength Aluminum Alloys
<b>India</b>			
Ram Gopal Sharma	National Physical Laboratory	1997.7.2~1997.7.23	Studies on High Tc Superconducting Tapes
Venkatachalapathy Saravanan	Anna University	1997.9.1~1997.9.30	Effects of High Magnetic Field on Crystallization Behavior in Fe-based Alloys
Chandrasekhar Rao V. Turumella*	Bhabha Atomic Research Center	1998.1.8~1999.1.7	Physical Property Research under the Superconducting Pressure
<b>Israel</b>			
Mosche Kuznietz*	Nuclear Research Center-Negev	1998.1.24~1998.4.22	Magnetism and Superconductivity of the (Pr, Dy) Ni <sub>2</sub> B <sub>2</sub> C Solid Solutions
<b>Korea</b>			
Hong, Moon Hi	JST Domestic Fellow	1997.4.1~1998.2.28	Atom Probe and TEM Studies of the Microstructures of Pearlitic Steel Wires
Ahn Jeon Ju*	Yeungnam University	1997.4.21~1998.8.26	Fatigue Properties for SiCw/AC <sub>4</sub> CH and SiCw/AC <sub>8</sub> C Composites
Byung Deok Yu	Fundamental Research Laboratories, NEC	1997.6.1~2000.3.31	Atomic Structures of Metal-semiconductor Interfaces
Kyoun Sub Lee	Sungkyunkwan University	1997.9.1~1998.2.28	Fabrication of Monolayer Thin Film for Advanced Substrate
Bae Jogsuck	Tohoku University	1997.10.1~1998.3.30	Electron Interaction with Evanescent Field
Hong-Boem Jin	Korea Electrotechnology Research Institute	1997.12.15~1998.12.14	Design of Superconducting Magnet
Lim Yun Soo	Korea Atomic Energy Research Institute	1998.1.6~1998.3.31	A Microscopic Study on Initiation of Corrosion Pits by Using Atomic Force Microscopic in Aqueous Solution
Sung Joon Kim	Korea Institute of Machinery and Materials	1998.1.12~1998.1.19	Evaluation of the High Temperature Properties for Titanium-based Particulate Composites
Soo Woo Nam	Korea Advanced Institute of Science and Technology	1998.1.19~1998.1.25	Evaluation of the High Temperature Properties for Titanium-based Particulate Composites
Yang Hae Un	Chonnam National Univ.	1998.1.19~1998.2.28	Microstructure Control of Intermetallic Compounds in Ti-Al System
<b>Malaysia</b>			
Md. Hasan Zahir*	Universiti Sains Malaysia	1997.11.5~1999.11.4	Synthesis and Characterization of Noble Phthalocyanine Species
<b>Myanmar</b>			

Thi Thi Lay	Japan Science and Technology Corporation (JST)	1997.9.1~2000.8.31	Development of Measuring Techniques for Nanostructural Q Effects by Photon Probe Methods
<b>New Zealand</b>			
Dealing L. Zhang*	University of Waikato	1997.12.9~1998.2.28	The Study of the Mechanism of Tensile Strength and Fracture of Cu Base in-situ Composites
<b>Russia</b>			
Olga Tkachenko	Novosibirsk State University	1997.9.10~1997.9.17	Photon-assisted Tunneling Phenomenon
Andrei Rar		1997.10.1~2000.3.31	Solid State Interfacial Reactions and Surface Analysis of Thin Solid Films
<b>Slovakia</b>			
Michal Rabara	The Univ. of Tokyo	1997.5.20~2000.3.31	Critical Current Density Characteristics for Bi <sub>2</sub> Sr <sub>2</sub> Ca <sub>3</sub> Ox Tape Conductors
<b>Switzerland</b>			
Markus Buttiker	Geneva University	1997.7.22~1997.7.26	Tunneling Time in Magnetic Field
<b>Ukraine</b>			
Yulia Vitaïevna Bosova*	Institute for Sorption and Problems of Endo-ecology	1997.5.18~1997.8.5	Research on Measuring Technics for the Electrochemical Property of Active Carbon
<b>United Kingdam</b>			
Bryan Edward Cole	University of Salford	1997.9.16~1998.2.28	2D Electron System in Semiconductors in High Magnetic Fields
Stephen E. Donnelly	Nottingham University	1997.9.20~1997.10.4	Defect Interaction of Metastable Xe Precipitates
Timothy M. King	Kochi Univ. of Technology	1998.3.1~2000.3.31	The Research Concerning Upgrade of Materials Data System
David Evans	Rutherford Appleton Laboratory	1998.3.22~1998.3.27	Characterization and Evaluation of Cryogenic Structural Materials
<b>U.S.A.</b>			
Robert C. Birtcher	Argonne National Laboratory	1997.9.15~1997.10.4	Effect of Ion Radiation on the Structural Stability of Metastable Xe Precipitates
Justin Schwartz	National High Magnetic Field Laboratory (NHMFL)	1997.10.15~1997.10.25	High Temperature Superconductors
Yusuf Hascicek	NHMFL	1997.10.20~1997.10.24	Development of High Field Insert Magnets with High Tc Superconductors
Loren F. Goodrich	National Institute of Standards and Technology	1997.10.24~1997.11.1	Testing and Evaluation of Superconducting Materials
Edward W. Collings	The Ohio State University	1997.10.26~1997.10.29	Testing and Evaluation Methods of Superconductors
Yeon Soo Sung*		1997.10.30~1999.10.29	Microstructure Control and Jc Enhancement of Bi-based Oxide Superconductors
John L. Lyman*	Los Alamos National Laboratory	1997.11.3~1997.12.20	Photo-decomposition of Hexa Fluoro Disilane by IR Laser Irradiation
K.A. Gschneidner, Jr.	Ames Laboratory, Iowa State University	1998.1.10~1998.1.19	Single Crystal Growth of Borocarbide Superconductors and Their Physical Properties
Steven W. Van Sciver	NHMFL	1998.2.8~1998.2.13	Levitation of Non-magnetic Objects in High Gradient Magnetic Fields
David Larbalestier	Applied Superconductivity Center, Univ. of Wisconsin	1998.3.21~1998.3.29	Development of HTS Conductors
Bruce Brandt	NHMFL	1998.3.21~1998.3.29	Magnet Technology
Robert P. Walsh	National High Magnetic Field Laboratory (NHMFL)	1998.3.22~1998.3.27	Characterization and Evaluation of Cryogenic Structural Materials
Ronald E. Cohen	Geophysical Laboratory, Carnegie Institution of Washington	1998.3.23~1998.3.26	Seed-seeking on Physical Properties Measurements for Sub-micron-size Samples
Charles W. Allen	Argonne National Laboratory	1998.3.27~1998.3.31	Effect of Electron Irradiation on the Structural Stability of Metastable Xe Precipitates

## □ List of Visitors

T : Tsukuba Site M : Meguro Site

Nationality and Name	Affiliation	Site	Date
<b>Finland</b>			
Ms. Sisko Sipila her party	TEKES	T	Apr. 1997
<b>Colombia</b>			
Prof. G. Gaviria his party	University of Antioquia	T	May. 1997
<b>France</b>			
Germain Sanz his party	IRSID	T	May. 1997
<b>Brazil</b>			
Mr. Vicente de Paulo	QIFTSMSI	T	May. 1997
<b>Poland</b>			
Dr. Leszek B. Magalas	University of Mining and Metallurgy	T	Nov. 1997
<b>U.S.A</b>			
Pat Mcginley	JEOL U.S.A	T	Nov. 1997
Lee Heatherly	ORNL	T	Feb. 1998

## □ Brief Introduction of STA Fellowship Program

In response to growing calls from the international community for greater inter-national cooperation, the STA Fellowship program was established to provide foreign researchers with opportunities to conduct research at Japanese national laboratories and public corporations which are not part of the university system.

The program is managed by the Japan Science and Technology Corporation (JST) Which is one of the key organizations for implementing policies of the Science and Technology Agency (STA) in cooperation with the Japan International Science and Technology Exchange Center (JISTEC). Fellowship qualifications are as follows :

1. Possession of Ph.D. or equivalent qualifications.
2. Long term fellowship is less than 35 years of age. Short term fellowship is no limitation of age.
3. Good health to do research-work and live in Japan.

4. Skillful language of Japanese or English words.

The tenure is from 6 months to 2 years (long term Fellowships), or 1~3 months (short term Fellowships).

JST provides fellowships with a round-trip airline ticket, a monthly living expenses, a family allowance, an initial international moving allowance, accommodations (long term fellowships), accommodations allowance (short term fellowships).

And to the long term fellowships it is paid the travel cost in Japan related to research activities but it is not applied to the short-term fellowships. Research expenses will be paid to the host institutes.

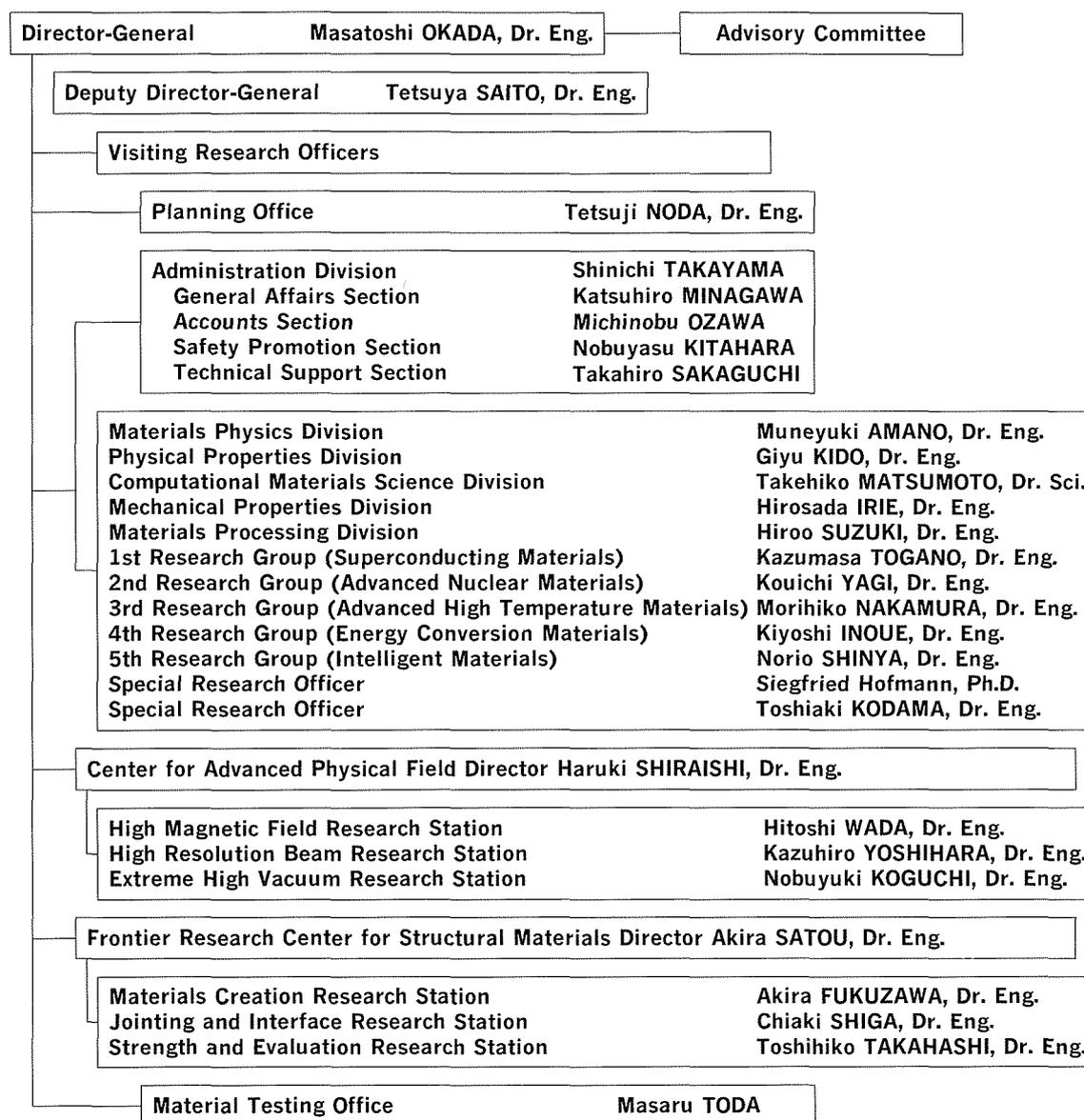
Further information can be obtained at JISTEC : 2-20-5, Takezono, Tsukuba City, Ibaraki Pref. 305-0032, Japan.

Phone +81-298-53-8250

Fax +81-298-53-8260

# Organization of NRI

## Organization



## Budget and Personnel in Fiscal Year of 1998

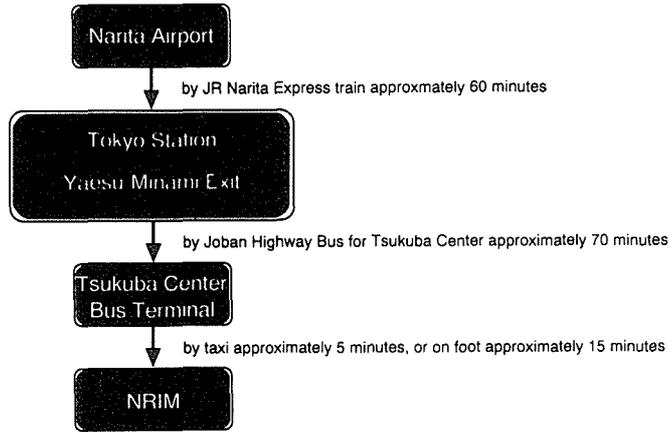
Budget		Personnel	
Research and facilities	5,677	Administrative staffs	79 (7)
Personnel expenses	3,783	Researchers	317 (7)
<b>Total</b>	<b>9,460</b>	<b>Total</b>	<b>410 (14)</b>

unit: million yen

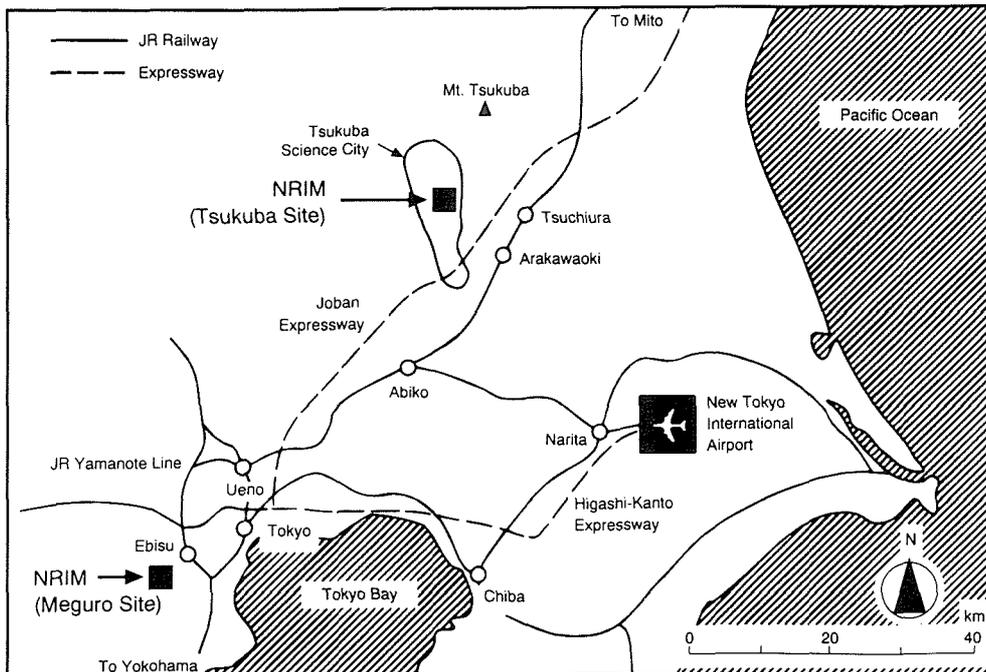
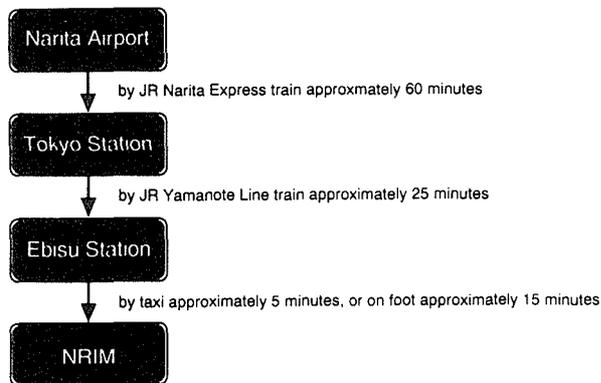
Number in parenthesis: Material Testing Office

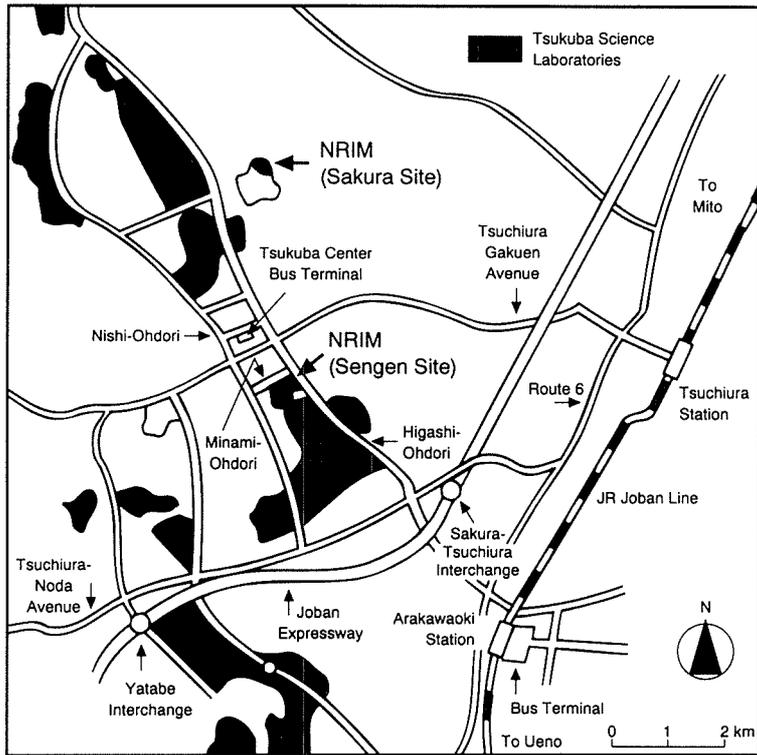
# How to get to NRIM

To NRIM Tsukuba Site  
 1-2-1 Sengen, Tsukuba-shi, Ibaraki 305  
 Phone +81-298-53-1000, Fax +81-298-53-1005

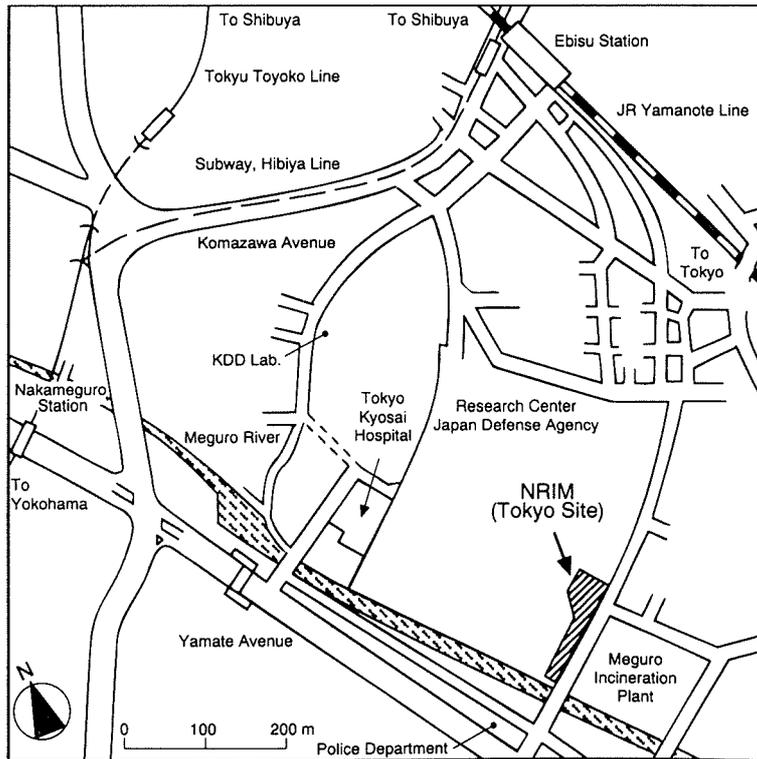


To NRIM Meguro Site  
 2-2-54 Nakameguro, Meguro-ku, Tokyo 153  
 Phone +81-3-3719-2271, Fax +81-3-3719-2177





Tsukuba Site



Tokyo Site



Cu-enriched clusters	14	fatigue strength	23,63,90
CVD	95	fatigue test	100
cytotoxicity	62,63	FBR	27
		Fe <sub>8</sub> O <sub>8</sub> (OH) <sub>6</sub> SO <sub>4</sub>	26
		FEM analysis	99
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molar mass	49	pigments	33
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