

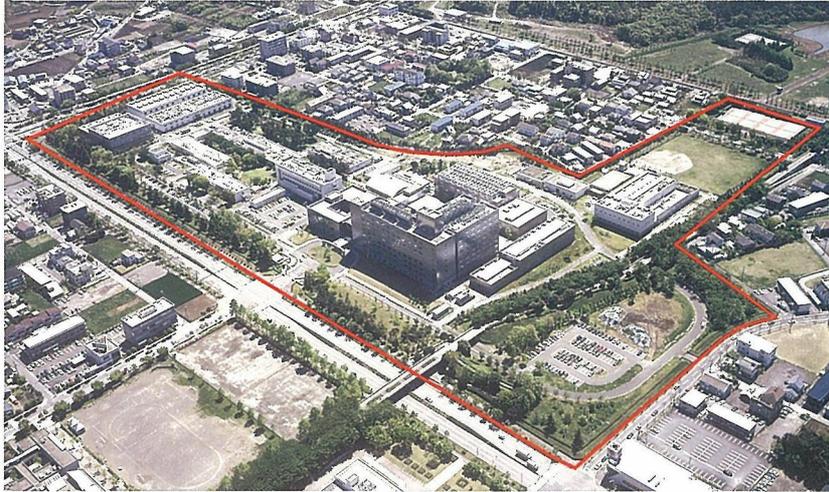
NRIM

Research Activities

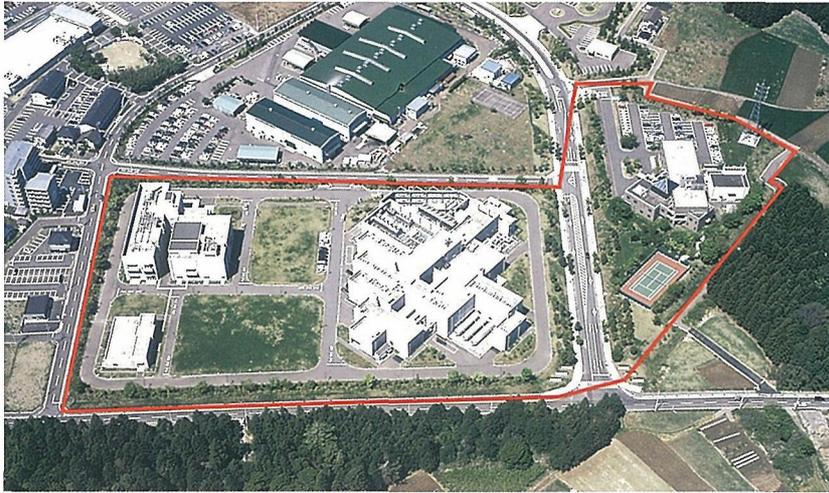
1999

National Research Institute for Metals

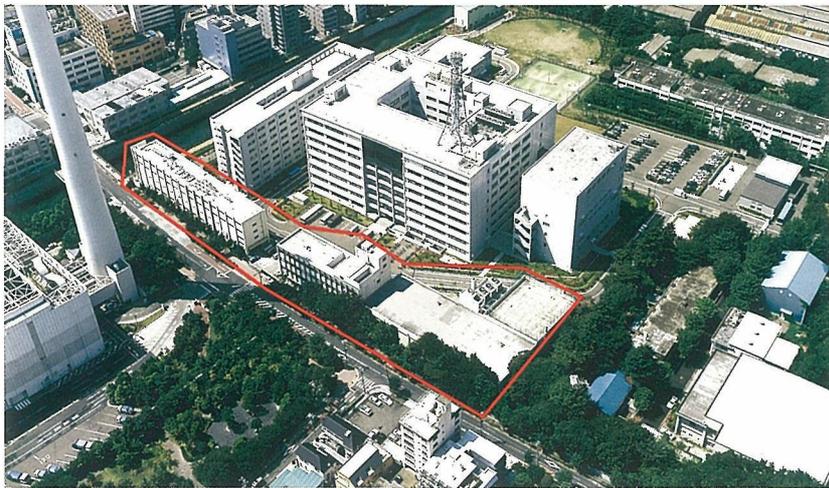
Japan



Sengen Site



Sakura Site



Meguro Site

Preface

This report covers the annual activities of the National Research Institute for Metals (NRIM), focusing on our research programs and the progress we have made from April 1, 1998 to March 31, 1999.

The research programs have been carried out based on the 5th Long-term Plan which started from April 1997. The 5th Long-term Plan has five main policies : the promotion of R & D for fundamental technologies and materials characterization in materials science ; the promotion of the research for the social-needs-oriented research project ; the promotion of the research in advanced physical field using large-scale research facilities ; the promotion of the research for constructing the databases of the materials-fundamental information based on long-term prospect ; constructing bases for international R & D.

The system of research in NRIM consists of the Core Research Branch with 5 divisions, 5 groups and 4 teams, the Center for Advanced Physical Field with 3 stations, and the Frontier Research Center for Structural Materials with 3 stations. We know that an international leadership and cooperation with industries and universities are important roles of the national institute. Therefore, we have the Center for Advanced Physical Field for fundamental materials research, and the Frontier Research Center for Structural Materials to create future "ultra steels". These Core Research Branch and Research Centers have cooperated among others.

This report reflects our services to all who interest in our activities. We continue to expand our activities for advanced materials research and improvement of reliability of the materials.



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

A handwritten signature in black ink that reads "Masatoshi Okada". The signature is written in a cursive style.

Dr. Masatoshi OKADA
Director-General

NRIM Research Activities 1999

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Research in Progress 1998-1999

□ A List of Research Program

1. Investigation on Synthesis and Characterization of Metal Complexes with High Electron-Spin Mulicity
2. Study on the Improvement of Analytical Technologies for Metallic Materials
3. Composition, Temperature and Pressure-Induced Structural Changes and Physical Properties of Materials
4. Angle-resolved Photoelectron Spectroscopy Study on Surface Structures and Electronic Properties
5. Evaluation of Structures with Trace Element Analysys
6. Coating of Photocathode and Fundamental Investigation of Photoelectron Emission from Laser Illuminated Photocathode for TEM
7. Development Program of New High Pressure Techniques and Investigation of New Magnetic Compounds and their Physical Properties
8. Atom Probe Microanalysis of Advanced Metallic Materials
9. Application of the High Magnetic Field to the Optical Research on Low Dimensional Systems
10. Studies on the Highly Correlated Electron Systems under Multiple Extreme Conditions
11. Study on the unusual metallic state and electronic structure of magnetic materials
12. Research for the Development of a New Type of Semiconductor Radiation Detector
13. Thermodynamic Analysis of Formation Processes of Metastable and Stable Phases
14. New Phenomena in Ultrathin Magnetic Films and Multilayer Systems
15. Computer simulation on the vortex states and phase transitions of high- T_c superconductors under an external magnetic field
16. A Computer-Simulation Study of the Plastic Deformation of Crystals
17. Numerical Simulation of Phase Separation
18. Theoretical study on atomic diffusion and electronic state in metal oxides
19. Theory of Thermal Reaction on Solid Surfaces
20. Development of Unification System for Distributed Materials Scientific Data utilizing Networking Enviornment
21. Development of Knowledge Database for High- T_c Superconducting Materials
22. Fundamental Studies of the Microbial Reaction with Inorganic Compounds
23. Fatigue Behavior and Microstructure of Metals
24. Fatigue Strength in a Corrosive Environment
25. Dynamic Microstructural Change and Mechanical Properties in Ceramics at High Temperatures
26. Fracture Mechanism of Welded Structure of Stainless Steel at Cryogenic Temperature
27. Fabrication of Ni_3Al -Base Intermetallic Compounds by Unidirectional Solidification
28. Search for Group IV Elements Compounds Including Alkaline-earth-metal Elements
29. Remaining Life Prediction for Weldments in FBR based on Creep Damage Evaluation
30. Improvement of Thermal and mechanical Properties in Tungsten-Based Materials
31. NRIM Creep Data Sheet Project-V
32. NRIM Long-Term Fatigue Data Sheet Project-I
33. Control of the Oriented Single Crystals of Refractory Metals through Solid State Processes
34. Selenium (VI) Removal from Wastewater by a Fluidized Bed Process
35. The Development of High Strength High Functional In-Situ Composite
36. Crystal growth and dissolution mechanisms in peritectic system
37. Application of Ionization Separation Technique to Gaseous Process
38. Fabrication and characterization of nano-structured materials

39. Diffusion Bonding between Transition Metals (Cr, Fe, and Ni) and Metals of Group IV~VI
40. Cladding or Coating Processes by Utilizing Semi-solid Processing
41. Effect of Interfacial Damage on the Fatigue Crack Propagation in Fiber-Reinforced Titanium Composite
42. Study on the Near Net Shaping of a Thick Film by the Deposition of Ultrafine Particles
43. Development of AgCu Alloy Sheathed Superconducting Wires/Tapes with High Mechanical Strength and Large Critical Current Density
44. Control of the In-plane Texture of High-T_c Superconducting Thin Films for Microwave Applications
45. Development of High-T_c Oxide Superconducting Wires and Tapes
46. Understanding of the Mechanism of Superconductivity in High Temperature Superconductors
47. Study on the Pinning Mechanism of Vortices in High Temperature Superconductors
48. Fabrication of Intrinsic Josephson Junctions and Evaluation of their Physical Properties
49. Characterization and Application of Superconducting Thin Films Synthesized by Atomic Layer-by-Layer and Epitaxial Growth Methods
50. Title : High-Resolution Real-Time Investigation on Defect Formation Processes under Surface- and Interface-reactions
51. Understanding and Improvement of Radiation-Induced Degradation in the Advanced Nuclear Materials
52. Influence of Nuclear Transmutations on Low Activation Structural Materials for Fusion Reactor Application
53. Isotope Separation and Its Application to Materials
54. Research on Utilization Technique of "Data-Free-Way" System for Nuclear Materials
55. Microstructure Control and Mechanical Property of Intermetallic Alloys in Ti-Al System
56. Development of Light Weight High Strength Ti₂AlNb Titanium Intermetallic Alloy
57. Development of Basic Superconducting Technology for High Field Micro-SMES
58. Energy Conversion Materials Fabricated with Composite Structure
59. Research and Development of High-Performance Light Alloys for Hydrogen Storage
60. Development and Total Evaluation of Advanced Metallic Membranes for Hydrogen Purification
61. Investigation of New Nonlinear Optical Crystals for Wavelength Modulation, Single Crystal Growth and Principle Technology Development for Optical Devices
62. Research on Surface Modification by Plasma Source Ion Implantation
63. Research on Quantum Magnetic Properties and Spinic Functions of Mesoscopic Magnetic Materials
64. Development of Advanced Shape Memory Thin Films by Sputtering
65. Creation of Multi-functional Materials by Assemblage of Primitive Functions
66. Preparation of Ion Conductors by Pressurization
67. Enhanced Durability of Structural Steels in Marine Environment
68. Design of Refractory Superalloys
69. Study on the Processing and Assessment of Ecomaterials
70. Formation of Amorphous Alloys and their Physical Properties
71. Study on Combustion Synthesis of Useful Intermetallic Compounds
72. The Improvement of the International Cooperation in the Center for Advanced Physical Fields
73. Fundamental Studies on Very High Magnetic Field Generation
74. Materials Development through Control of Phase Transformations by High Magnetic Field
75. Basic Research for the Control of Chemical Reactions by High Magnetic Field
76. Development of 1 GHz NMR Spectrometer
77. Evaluation of oxide superconductors
78. Development of Magnetic Separation System
79. New cryocooler system below 4 K refrigeration
80. Development of New Superconductors for Nuclear Fusion Use

81. Characterization and Control of the Opto-electronic Properties of Small Crystalline Materials with Electron Probe Analysis
82. Analysis/Evaluation of Atomic Scale Compositional Change in Materials Due to the Radiation Damage
83. Study on Detection, Evaluation and Utilization of Non-equilibrium Processes Under Extreme Particle Fields
84. Development of Fundamental Technologies for Excited Neutral Beams
85. Advanced characterization of micro and nano meter scale structure of materials by brilliant synchrotron x-rays at the SPring-8
86. Fabrication of Nanometer-Scale Structure on the Extremely High Vacuum Surface
87. Self-control of Surface Composition of Thin Film and Its Application to Field Emitter
88. Study on Melting of Refractory Metals by Cold Crucible Levitation Melting Method
89. Feasibility Study on Utilization of High Brilliance X-rays for Steel Characterization
90. Research and Development of Recyclable Simple-System Alloys
91. Study on Strengthening of Ferrite Matrix Steels for Welded Structures
92. Effect of Aging Degradation on Localized Corrosion of Structural Materials for Light Water Reactors
93. Advanced Ultra-High-Strength Steels (1500-MPa-plus class)
94. Mechanical Properties of Thin Films and Coatings
95. Computational Simulation of Mechanical Properties and Behavior of Materials for Atomic Power Plants by Taking Microstructures into Account
96. Long-term Creep-fatigue Properties of 316FR Stainless Steel for Fast Breeder Reactor
97. Strategic Research on Advanced Ferritic Steels for 650°C USC Boilers (R&D of Structural Materials for 21st Century)

□ Research Programme

Characterization/Properties

1 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 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, electrochem-

istry, 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 and A.B.P. Lever, *Bull. Chem. Soc. Jpn.*, 71 (1998) : 1039-1047.

An Adjacent Dibenzotetraazaporphyrin : A Structural Intermediate between Tetraazaporphyrin and Phthalocyanine, N. Kobayashi, H. Miwa, H. Isago and T. Tomura, *Inorg. Chem.*, 38 (1999) : 479-485.

Rapid Reactions of Phthalocyanines with Tellurium Tetrachloride in Non-Aqueous Solutions, Y. Kagaya and H. Isago, *J. Porphyrins Phthalocyanines*, in press.

2 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. Nakamura, K. Yamada, K. Ogawa, S. Itoh, K. Ide, S. Hasegawa, H. Yamaguchi, Y. Hasegawa and M. Amano, *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 in-

crease 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) on N and C has been carried out. Accurate analyses of nitrogen and carbon 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) 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, HR-TEM

Related Papers

- 1) Determination of Trace Aluminum in Iron and Steel Samples by Graphite Furnace Atomic Absorption Spectrometry. S. Hasegawa, T. Kobayashi and R. Hasegawa; J. Japan Inst. Metals, 62 (1998) : 1163-1168.
- 2) Measurement of Isotope Ratios of Boron and Silicon by Glow Discharge Mass Spectrometry Using a Small Quantity of Sample. S. Itoh and R. Hasegawa ; J. Japan Inst. Metals, 62 (1998) : 289-292.
- 3) Trace analysis of high-purity copper by total reflection X-ray fluorescence spectrometry. H. Yamaguchi, S. Itoh, S. Igarashi, K. Naitoh and R. Hasegawa ; Fresenius J. Anal. Chem., 362 (1998) : 395.
- 4) Determination of Trace Elements in Acidic Solution of Iron and Steels by Graphite Furnace Atomic Absorption Spectrometry. T. Kobayashi, S. Hasegawa and T. Yoshioka ; Tetsu-to-

Hagane, 85 (1999) : 40-44.

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

T. Hirata, Materials Physics Division

[April 1998 to March 2001]

Most materials undergo any structural change (s) when composition and temperature are varied or pressure is applied, predominating their physical and electronic properties. The current research is underway focussing on several issues as follows.

With respect to structure-related properties of materials, it is of interest to look into the octahedral distortion in the $\text{TiO}_2\text{-SnO}_2$ system based on bond-lengths and/or bond-angles. The information on this distortion might help us in understanding different and anisotropic compressibilities / thermal expansivities between TiO_2 and SnO_2 .

The temperature and pressure dependences of optic phonons for some materials are measured, to search for any phase transition (s) and to understand the dynamics of atomic displacements that are relevant to the phase transition.

The mode Grüneisen parameters are determined from the frequency changes of optic phonons on application of pressure for materials. This encourages us to estimate the Grüneisen parameters when the corresponding phonons are changed in frequency on a modification of materials composition, to assess similar or dissimilar effects of chemical and external pressure on the lattice distortions.

Infrared and Raman spectra of Si, Ge and $\text{Si}_{1-x}\text{Ge}_x$ incorporated with oxygen atoms are measured, in order to study their structural and vibrational properties.

Keywords : lattice distortions, phase transitions, phonons, infrared and Raman spectra

Related Papers

1. Pressure, temperature and concentration dependences of phonon frequency with variable Grüneisen parameter ; fits to the Raman-active E_g mode in TiO_2 and $\text{Ti}_{1-x}\text{Zr}_x\text{O}_2$ ($x \leq 0.1$), T. Hirata, Phys. Stat. Sol. (b) 209 (1998) 17.
2. 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.
3. Orientation dependence of infrared spectra on thermal oxidation and subsequent etching of single crystal Si, T. Hirata, Solid State Commun.

4 Angle-resolved Photoelectron Spectroscopy Study on Surface Structures and Electronic Properties

M. Shimoda, Materials Physics Division

[April 1998 to March 1999]

On the basis of structure studies with photoelectron diffraction^{1,2)} and STM³⁾, synchrotron radiation photoelectron spectroscopy (SRPES) has been performed to investigate the surface stoichiometry of the S-terminated GaAs(001)-(2×6) phase. Photoemission spectra of Ga 3d, As 3d and S 2p core levels at various temperatures are analyzed with a least-squares curve fitting procedure to extract the contribution from the surface composition. The S 2p spectra (Fig. 1) are satisfactorily described with a single fitting curve and show a significant decrease of the peak intensity with increasing the substrate temperature up to 530°C, which gives rise to a transition of the surface reconstruction from the (2×6) to a (2×3) phase by releasing the central pair of the five

dimers³⁾. The Ga 3d spectra (Fig. 2) are decomposed into a bulk component and more than one surface components. One of the surface components, which is attributed to a Ga-S bond, decreases in accordance with the change observed in the S 2p spectra. As for the As 3d photoemission spectra (Fig. 3), no surface component associated with As-As dimers is observed, and moreover, no significant change follows the transition to the (2×3) phase. These results strongly support the model that each pair of the five dimers in the (2×6) reconstruction consists of S-S dimers¹⁾⁻³⁾.

Keywords : Synchrotron radiation photoelectron spectroscopy, GaAs, sulfur-termination

Related Papers

- 1) M. Shimoda, S. Tsukamoto and N. Koguchi, *Surface Science*, 395 (1998) 75-81.
- 2) M. Shimoda, S. Tsukamoto and N. Koguchi, *Surface Science*, 402 (1998) 669-672.
- 3) S. Tsukamoto and N. Koguchi, *Jpn. J. Appl. Phys.* 33 (1994) L1185-L1188.

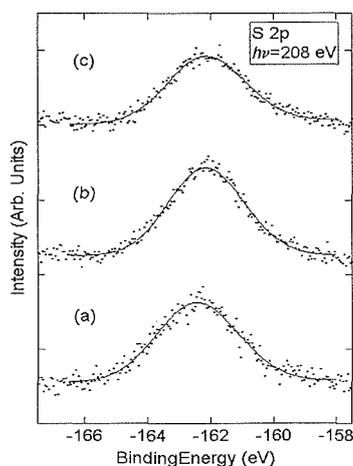


Fig. 1 S 2s photoemission spectra spectra.

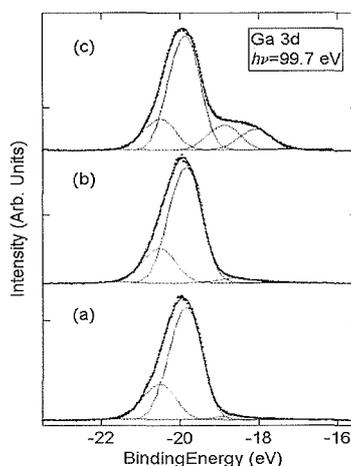


Fig. 2 Ga 3d photoemission spectra spectra.

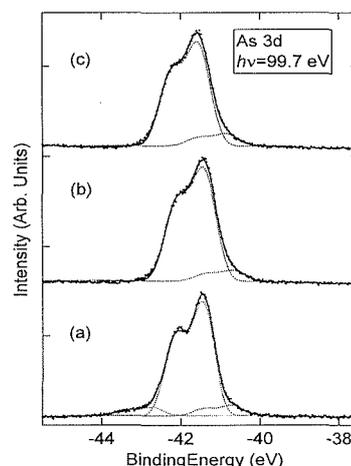


Fig. 3 As 3d photoemission spectra spectra.

5 Evaluation of Structures with Trace Element Analysis

M. Fukumachi and N. Ishikawa, 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 becomes easy to identify materials by

analyzing 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

6 Coating of Photocathode and Fundamental Investigation of Photoelectron Emission from Laser Illuminated Photocathode for TEM

T. Kimoto and M. Amano, Materials Physics Division

[April 1999 to March 2002]

The higher brightness electron source improves high resolution microscopy, electron holograph, microscopic ultimate analysis, coherent electron microdiffraction and so on in a transmission electron microscope (TEM). For this reason a Lanthanum hexaboride (LaB₆) tip whose brightness is about 10 times higher than a conventional Tungsten hairpin tip, was developed for a thermionic emission type electron source in the 1980's. In the 1990's a field emission type electron source whose brightness is about 10-100 times higher than LaB₆ tip source was developed for practical use, which enables us to perform electron holography.

It is estimated that a photocathode of high quantum efficiency illuminated by a laser beam could be an electron source for TEM whose brightness is 100-1000 times higher than a field emission type electron source. A few purely fundamental researches have been performed on the characteristics of laser illuminated photocathode so far, but few fundamental researches on the practical laser illuminated photocathode for TEM or other instruments have been carried on. It is necessary for the development of the practical photocathode to devise a special method to coat photocathodes such as Cs₃Sb onto the top of a cathode tip, because their quantum efficiency decrease rapidly just as they react chemically to small amount of oxygen¹⁾. It is also necessary to cool effectively the laser illuminated photocathode in the high vacuum and high voltage.

In the present research the fundamental experiment is aimed in order to get data for the development of a practical photocathode type electron source, a new type high brightness electron source for TEM. For this purpose, we will verify the effectiveness of the devised method of coating Cs₃Sb photocathode by vacuum evaporation and find the best coating condition. We will measure the temperature of laser illuminated photocathode which is cooled with a devised method for many experimental conditions. The effect of temperature of the photocathode, shape of the top of the photocathode tip, environmental vacuum and cathode voltage on the beam current of the photoelectron from the laser illuminated photocathode will be also examined. We

will use the Argon ion laser and the specially designed devices which were already made to carry out the present fundamental research.

Keywords : high brightness electron source, transmission electron microscope (TEM), coating of Cs₃Sb on cathode tip, quantum efficiency for photoelectric effect, laser illumination, Argon ion laser, vacuum evaporation, cooling of laser illuminated photocathode

Reference

Laser Illuminated High Current Photocathodes, L. R. Danielson, C. Lee and P.E. Oettinger, *Applications of Surface Science*, 16 (1983): 257-267.

7 Development Program of New High Pressure Techniques and Investigation of New Magnetic Compounds and their Physical Properties

A. Matsushita, J. Tang, J. Ye, T. Naka, H. Abe, S. Ishida and K. Maruyama, Materials Physics Division

[April 1996 to March 1999]

We have pursued for a number of years a research project in high pressure physics, centering around the physical properties of magnetic intermetallic compounds. One of the objects was Pr-Ba-Cu-O compounds. We investigated the effect of pressure on the superconducting transition temperature T_c of the superconducting Pr₁Ba₂Cu₃O_{7-δ} (Pr123) and found the pressure coefficient, dT_c/dP is positive and extremely large. This was in contrast to the previous results for (Y, Pr) 123, in which large negative values of dT_c/dP had been reported. It was surprising that a compound with the same chemical composition showed an opposite pressure dependence. In addition we found that the effect of oxygen re-ordering on T_c was not observed in superconducting Pr123 whereas it is remarkable in Y123. We also investigated the pressure effects on the electrical resistivity of Pr₁Ba₂(Cu, M)₄O₈ with M=Ni, Zn. Pr₁Ba₂Cu₄O₈ does not exhibit superconductivity but shows a interesting pressure dependence which reflects its characteristic transport mechanism. We found that the substitution effects were quite different between Ni and Zn, which was interpreted as a difference of substitution site. Another object was the pressure induced metal-insulator transition in CuIr₂(S, Se)₄. Last year we carried out a X-ray diffraction measurement under high pressure and low temperature using a diamond anvil cell and obtained an evidence that a structural transformation gives rise to the metal-insulator tran-

sition.

In these research projects we mainly used a piston-cylinder type pressure cell and a cubic anvil for generating high pressure. The maximum pressure obtained with these high pressure technique is 9GPa. In the new reasearch project started from this financial year we are aiming at higher pressures and will develop a new high pressure technique using a diamond anvil cell. We are planning two programs. One is a program to develop a technique of electrical resistivity measurement in a diamond cell. Another is a X-ray diffraction measurement at low temperatures using a diamond anvil cell.

In this new project we pursue another research that is to explore new 3d-compounds. In the former project we found some new 3d intermetallic compounds in which the magnetic behaviors strongly depend on heat treatments. We will investigate the origin of these phenomina and will search for new materials that exhibit similar properties.

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

Recent Publications

Effects of Pressure on the Electrical Resistivity of Iodine-doped Polyacetylene A. Matsushita, K. Akagi, T.-S. Liang and H. Shirakawa, Synthetic Metals, in press.

Evidence from High-Pressure Experiments that PrBa₂Cu₃Ox is a Normal Yba₂Cu₃Ox-like Oxide Superconductor, J. Ye, S. Sadewasser, J.S. Schilling, Z. Zou, A. Matsushita and T. Matsumoto, to be published in Physica C.

The Physical Properties of the New Quaternary Borocarbides RRh₂B₂C (R=Gd, Sm and Nd), S. Ishida, T. Naka, A. Matsushita, J. Ye, T. Shishido and T. Fukuda, to be published in Physica B.

8 Atom Probe Microanalysis of Advanced Metallic Materials

K. Hono, Materials Physics Division
[April 1996 to March 2001]

Properties of metallic materials are controlled by microstructures. Conventional structural materials such as steels, aluminum alloys, intermetallics and superalloys are all strengthened by controlling their microstructures. The microstructural scale of metallic materials are becoming smaller and smaller, and many microstructures in the modern industrial materials are in a subnanometer scale. Magnetic properties and other functional properties of metallic

materials are sensitive to their nanoscale microstructures and interfacial structures. Thus, microstructural characterizations of metallic materials in less than a nanometer scale resolution is essential for understanding the mechanisms of various novel properties in materials. This project aims to obtain better understandings of the underlying mechanisms of mechanical and magnetic properties of metallic materials by characterizing microstructures of advanced materials. For this purpose, we employ the atom probe field ion microscope (APFIM) technique which is capable of analyzing local chemical compositions with an atomic resolution. Unlike other analytical techniques, it can detect all alloying elements including light atoms such as Li, Be, B, C, N and O which often make key roles in controlling materials properites. By making use of a three dimensional atom probe (3DAP), it is possible to map out elemental distribution in alloys in a three dimensional real space with a near-atomic resolution. For complementary microstructural characterization, conventional transmission electron microscopy (TEM) and high resolution electron microscopy (HREM) techniques are also employed. Our research interests include nanocrystalline magnetic materials (Fig. 1), magnetic thin films, amorphous and nanocomposite alloys, microstructures and phase transformation in steels and aluminum alloys and other industrial metallic materials.

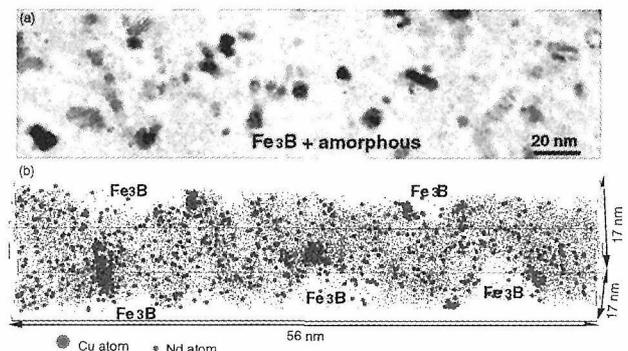


Fig. 1 (a) TEM bright field image and (b) 3DAP map of Nd and Cu atoms of a Nd₄₅Fe_{16.8}B_{18.5}Cu_{0.2} melt-spun alloy annealed at 530°C for 10 min. Nanocrystalline Fe₃B particles are dispersed in the amorphous matrix. Cu clusters are visible in direct contact with individual Fe₃B particles, suggesting that the Fe₃B primary crystals ate heterogeneously nucleated at the site of Cu clustets. This contributes to refinement of the Fe₃B/Nd₂Fe₁₄B nanocomposite magnet, and the resultant magnetic properties are significantly improved.

Part of this project is conducted in collaboration with the Frontier Research Center for Structural Materials. The most up-to-date reports of this project can be found in the following WWW site :

<http://inaba.nrim.go.jp/apfim>

Related Paper

K. Hono, "Atom probe microanalysis and nanoscale microstructures in metallic materials"

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9 Application of the High Magnetic Field to the Optical Research on Low Dimensional Systems

G. Kido, H. Kitazawa, T. Shimizu, S. Uji, T. Takamasu, M. Oshikiri, T. Terashima, A. Goto, K. Takehana, H. Suzuki, Y. Imanaka and S. Kato, Physical Properties Division
[April 1995 to March 1998]

The quantum effect is one of the most interesting phenomena in the solid state physics and known to be remarkable in low dimensional systems. The high magnetic field is quite effective to investigate these magnetic systems since it controls the degree of quantum effect. We have constructed the optical research equipments to study in the high magnetic fields of the hybrid magnet, the high field superconducting magnets and the pulsed field magnets, which are provided in the High Magnetic Field Research Station of NRIM. We have applied the system to the optical research on low dimensional systems.

One of our topics is the magneto-optical studies on the spin-Peierls compound in the far-infrared region. The spin-Peierls transition occurs in the one-dimensional $S=1/2$ spin system with Heisenberg antiferro interaction, which follow a lattice distortion due to the dimerization of spin sites. This phase transition has been found in several organic conductors (TTF-CuBDT, MEM(TCNQ)₂ etc.) and inorganic materials CuGeO₃. An incommensurate lattice modulation is caused by the another phase transition under high magnetic field around 13T for CuGeO₃ and 20T for MEM(TCNQ)₂. Optical studies are useful method in investigating the structural change. We have found a new folded phonon mode on CuGeO₃, which the proof of the lattice dimerization. Moreover, the split of the folded mode was found in the incommensurate phase for the first time. This is the new phenomenon, so further investigation is needed to clarify the mechanism in more detail.

The integer and fractional Quantum hall effect were also investigated in two-dimensional electron systems of semiconductors. The accurate transport measurements were performed at very low temperatures in high magnetic fields so far. Recently, optical methods, such as a photoluminescence and a cyclotron resonance have attracted much attention as one of the method for investigating the Quantum hall system. We performed the magnetoluminescence experiments in the high mobility sample of GaAs/AlGaAs heterostructures and CdTe/CdMgTe quantum well up to 25T around 400 mK. We found very complicated optical spectra, originated from the

many-body effect. Moreover, the anomalous variation of the polarization were observed around the filling factor becomes unity in CdTe/CdMgTe QW. Far-infrared transmission experiments were also performed up to 18T. The coupling cyclotron resonance through the coulomb interaction was observed clearly in the temperature dependence of the cyclotron resonance.

Keywords : high magnetic field, optical studies, low dimensional system, spin-Peierls, Quantum hall effect

Related Papers

Magneto-optical measurements of CuGeO₃ in far-infrared region, K. Takehana, M. Oshikiri, T. Takamasu, M. Hase, G. Kido and K. Uchinokura, J. Magn. Mater. 177-181 (1998) 699.

Far-Infrared Spectroscopy in Spin-Peierls Compound CuGeO₃ under High Magnetic Fields, K. Takehana, T. Takamasu, M. Hase, G. Kido and K. Uchinokura, submitted to Phys. Rev. B.

Cyclotron Resonance in High Mobility CdTe/CdMgTe 2D Electron System at Integer Quantum Hall Regime, Y. Imanaka, T. Takamasu, G. Kido, G. Karczewski, T. Wojtowicz and J. Kossut, Physica B 256-258 (1998) 457.

10 Studies on the Highly Correlated Electron Systems under Multiple Extreme Conditions

G. Kido, Physical Properties Division
[April 1995 to March 2000]

The highly correlated electron systems such as high-Tc cuprates, heavy fermion compounds, organic metals, and mesoscopic systems have been the most important subject in material science. The strong electron-electron correlation is essential in understanding those fascinating materials and also for their future applications. The magnetic field is a very powerful tool to explore their physical properties and electronic structures, especially when it is combined with other experimental environments such as low temperatures and high pressures. At the early stage of the project, we devoted most of our efforts to the development of high-precision magnetic and transport measurement systems to be fitted with various high-field magnets installed at the NRIM and expanded our experimental access to multiple extreme conditions, high fields up to 36T, low temperatures down to 25 mK, and high pressures up to 20 kbar. In the last stage of the project, we, continuing the improvement of those systems, concentrate more on their application to researches in the highly cor-

related electron systems.

The main achievements of the year are as follows.

(1) Cu-Be high-pressure cells developed for the 20T superconducting magnet and dilution refrigerator system has extensively been used to study the pressure dependence of the Fermi surface in the heavy fermion compounds, CeRu₂Si₂, UPt₃, and CeCo₂ as well as the bulk quantum Hall effect in organic metals. We have also initiated an investigation of the Kondo semiconductor CeNiSn under the multiple extreme conditions.

(2) The search for quantum oscillations in the mixed state of type-II superconductors has been continued and we have succeeded in observing de Haas-van Alphen oscillations in the A15 superconductor V₃Si down to 11.4T below H_{c2}. Our results suggest that a conflict between two previous reports may be attributed to domain formation due to a structural phase transition. The present results, together with our previous data on the borocarbide superconductor YNi₂B₂C, offers a quantitative basis for theoretical considerations of still controversial origin of the quantum oscillation in the mixed state.

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

Related Papers

dHvA Effect Study of the Metamagnetic Transitions in CeRu₂Si₂ Transition Behavior of the dHvA Oscillations, H. Aoki, M. Takashita, T. Matsumoto, S. Uji, T. Terashima, K. Maezawa, R. Settai and Y. Onuki, in *Physics of Strongly Correlated Electron Systems*, JJAP Series 11 (19xx) : 3-5.

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

H. Kitazawa, Physical Properties 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 oxides and chalcogenides, which

exhibit superconductivity, colossal magnetoresistance, metal-insulator (M-I) transition, etc. One of the interesting problems of these materials is that the electronic state differs from the conventional Fermi liquid. It is obvious that the electron correlation should play an important role in the anomalous metallic state. 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 because of the weaker electron correlation.

Recently, it was found that the spinel-type chalcogenide CuIr₂S₄ exhibits the M-I transition at about 230 K, which is associated with a structural phase transition from a cubic to a tetragonal symmetry with decreasing temperature. More interestingly, the external pressure stabilizes the insulating phase, while according to the general band theory, the external pressure enhances the overlap of the related orbitals and leads to a tendency of metallization. The mechanism of the M-I transition of CuIr₂S₄ is still an open question. Ordering of charge on the Ir site caused by the electron correlation between 5d electrons is one possible origin of the M-I transition. Our aim is to clarify the origin of anomalous physical properties of CuIr₂S₄ and understand the electron correlation extensively by detailed experimental research.

We will first of all synthesize the spinel-type CuT₂X₄ (T : 5d transition element, X : S and Se) compounds. Then, the samples will be well characterized by the X-ray diffraction, electrical resistivity, magnetic susceptibility and specific heat, etc. The physical properties will be measured under various conditions (esp. high pressure and high magnetic field). Some spectral measurements should also be carried out to investigate the mechanisms. Finally, we wish to enlarge and/or enrich the understanding of electron correlation system.

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

12 Research for the Development of a New Type of Semiconductor Radiation Detector

T. Takamasu, Physical Properties Division
[April 1999 to March 2003]

In recent years, intensive studies to develop room temperature radiation detectors have been performed. Especially, semiconductor detectors are thought to be suitable candidates for the small and sensitive detector. However, conventional semiconductor detectors have a few important weak points.

One of these is that it is difficult to purify the crystal to get long enough mean free path of electron. To avoid such difficulty, we propose a new type of radiation detector which directly transfer the generated electron-hole pairs into visible light. For the basic study of this new type of detector, we adapt III-V semiconductors with rare earth impurity.

There are many combinations of materials of III-V semiconductors and rare earth. At present, we are studying basic properties of Yb doped InP and GaAs using visible optical measurement system under high magnetic field. Among these, we found Yb doped InP shows very strong photoluminescence (PL) signal. Efficiency of this PL suggests that the rare earth impurity has correlation with semiconductor band, which is not clarified up to now. To specify the physical origin of the PL, we are studying magnetic field dependence, which can resolve a PL peak into several peaks peculiar to the inner mode of rare earth atom. We think it is important to clarify the physical mechanism to find the best combination for the radiation detectors.

For the development of the detector, we plan to search the best combination using crystal growth technique and study basic physics of rare earth related PL at the same time. Furthermore, to enhance the efficiency of the detectivity, processing crystals into nanometer size structure is planned.

Keywords : Radiation Detector, Semiconductor, Optics

13 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.

The microstructure of Co-Al-O thin films which exhibit soft ferromagnetic and superparamagnetic properties have been studied by transmission electron

microscopy (TEM) and small angle X-ray scattering (SAXS). In the superparamagnetic specimens, high resolution electron microscope images show that isolated spherical Co particles are surrounded by an amorphous aluminum oxide matrix. However, in the soft ferromagnetic films, the shape of the Co particles is prolate ellipsoidal. SAXS intensities from the soft ferromagnetic specimens decrease inversely with the wave vector in the low wave-vector region, while an inter-particle interference peak has been observed in the superparamagnetic specimens. The scattering profiles of the soft ferromagnetic films imply that the Co particles have a cylindrical shape and are randomly oriented.

The transition process of Ti-Al amorphous alloys 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 fluctuation in the amorphous structure and nucleation site of the crystallization.

The microscopic mechanism of the martensitic transformation from a metastable fcc phase into a stable bcc phase in Fe-Ni alloys has been also studied by using the isobaric-isothermal molecular dynamics technique. We have found that a pair of interfering vortex type displacement of surface atoms evolves into a nucleus of martensite under a free boundary condition, while the physical process is always masked by a fictitious transformation induced by the deformation of the molecular dynamics cell under a periodic boundary condition.

Keywords : metastable structures, Co-Al-O thin films, small-angle X-ray scattering, molecular dynamics simulations, medium-range structures,

martensitic transformation

Related Papers

Microstructure of Co-Al-O Granular Thin Films, M. Ohnuma, K. Hono, E. Abe, H. Onodera, S. Mitani and H. Fujimori, *J. Applied Physics*, Vol. 82 (1997) : 5646-5652.

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.

14 New Phenomena in Ultrathin Magnetic Films and Multilayer Systems

X. Hu and Y. Nonomura, Computational Materials Science Division
[April 1997 to March 2000]

Micromagnetic theory formulated in the last two years is developed for multilayered structures of alternate anisotropy directions. Especially hysteresis loops during magnetization reversal processes are calculated numerically for systems of trilayer magnetic materials having an in-plane anisotropy defect between two perpendicular anisotropy layers. The shape of the hysteresis loop depends crucially on the magnetic parameters and the thickness of the in-plane layer. The sum of the anisotropy, exchange and Zeeman energy is also pursued in accordance with the reversal processes. When the energy required for the magnetization reversal is plotted as a function of the defect layer thickness, the energy accumulated in the defect indicates maximal value where the nucleation field bifurcates from the field necessary for the entire magnetization reversal.

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

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“New quantum Monte Carlo study of quantum critical phenomena with Trotter-number-dependent finite-size scaling and non-equilibrium relaxation”, Y. Nonomura, *J. of Phys. A : Math. and General*, 31 (1998) : 7939.

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“Magnetization hystereses in trilayer systems with an in-plane component defect”, T. Yoroza and X. Hu, *J. Appl. Phys.* 86 (1999) : 1581.

“Spin reorientation in ultrathin magnetic films with normal surface anisotropy”, X. Hu, *Condensed Matter News*, 7 (1998) : 18. (invited review article).

15 Computer simulation on the vortex states and phase transitions of high- T_c superconductors under an external magnetic field

X. Hu and Y. Nonomura, Computational Materials Science Division
[April 1999 to March 2004]

Using Monte Carlo simulations we have computed the phase diagram of a rotator model of the SO(5) symmetry between antiferromagnetism (AF) and d-wave superconductivity (SC). A bicritical point is observed at a finite temperature where the second-order AF and SC transition lines merge tangentially into a first-order line. The SO(5) theory in an external magnetic field is also investigated, and the following features are clarified : The long-range SC order is established through a first-order freezing transition of the flux-line lattice (FLL) ; The FLL of long-range SC order and the long-range AF order coexist at appropriate SO(5)-symmetry breaking fields ; Vortex cores are of larger AF amplitudes than elsewhere.

The mechanism of the FLL melting for the magnetic field along the c axis is clarified. From our simulation it becomes clear that the origin of this melting transition is the entanglement of flux lines. The finite-size scaling of the melting temperature T_m is found to be consistent with the one-dimensional character of the mechanism of the FLL melting.

Keywords : high- T_c superconductivity, antiferromagnetism, vortex state, flux-line lattice melting

Recent Publications

“Phase diagram of a superconducting and antiferromagnetic system with SO(5) symmetry”, X. Hu, T. Koyama and M. Tachiki, *Phys. Rev. Lett.* 82 (1999) : 2568.

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“Spin-gap phenomenon by an SO (5) model”, X. Hu, to appear in Physica B.

“Antiferromagnetism and superconductivity transitions with SO (5) symmetry”, X. Hu, to appear in J. Low Temp. Phys.

“Inter-layer phase difference of HTSC in B || c : Monte Carlo simulations”, Y. Nonomura and X. Hu, to appear in Physica B.

“Flux-line entanglement as the mechanism of FLL-melting transition in anisotropic HTSC”, Y. Nonomura and X. Hu, to appear in J. Low Temp. Phys.

“Thermodynamic properties of the SO (5) theory for the antiferromagnetism and d-wave superconductivity : a Monte Carlo study”, X. Hu, submitted to Phys. Rev. B.

“Vortex states and phase transition of high-Tc superconductors in a magnetic field viewed by computer simulation”, X. Hu, to appear in Butsuri (invited review article).

16 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. The many-body *EAM* (embedded atom model) potential which reproduces both the cohesive energy and the elastic constants of α -Fe is applied to construct sample crystals.

Under no periodic boundary condition, molecular-dynamics simulations of tensile tests were performed at various temperatures for α -Fe single crystals composed of about 2×10^4 to 7×10^4 atoms. The results are as follows. According to test conditions such as sample configuration, test temperature, and pulling speed, various types of deformation mode were observed as listed below ;

- a) plastic deformation and necking
- b) formation and development of crack (cleavage)
- c) generation, growth, and connection of voids (dimple fracture)
- d) primary recrystallization
- e) combination of the above

Here the mode a) and b) are also observed in the small systems composed of about 10^4 atoms. All of

the above deformation modes have been observed in real experiments, so it can be said that larger samples can, compared to small ones, reproduce more realistic results in the molecular-dynamics simulation of tensile test. Although definite explanation for the present relation between the test conditions and the resultant deformation modes is not made at moment, there seems to be some tendencies ; The smaller the pulling speed, the larger the reversion speed in the plastically deformed samples. Crack formation and development is prone to take place for lower test temperature, smaller pulling speed, and deeper notch depth.

Keywords : plastic deformation, atomistic model, molecular-dynamics, α -Fe

17 Numerical Simulation of Phase Separation

N. Akaiwa, Computational Materials Science Division

[April 1998 to March 2001]

Phase separation of two phase mixtures has been observed in a variety of systems. When the structures of the two phases are the same, the diffuse interface model (the Cahn-Hilliard model) has been 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 at the critical composition, and this spinodal structure is stable. At off-critical compositions spinodal structure initially generated is unstable. Morphological transition from the spinodal structures to a set of isolated particles occurs.

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 the 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 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.

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 concentration on the mesh points. The first method places the initial concentration using a random number generator. This initial condition generates the interconnected spinodal structure. The second method places isolated particles in the computational cell. In this case, the concentration 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 the Cahn-Hilliard model has two stable self-similar solutions at the critical composition.

Keywords : Spinodal decomposition, Nucleation and growth, Structure function

18 Theoretical study on atomic diffusion and electronic state in metal oxides

T. Sasaki, Computational Materials Science Division
[April 1999 to March 2002]

The properties of metal materials change by exposing its surface to air. The shiny surface of steel will corrode if it is not taken care of correctly; the rust will be made. On the other hand, aluminum surface can be protected by covering its surface by alumina. All these phenomena occur by the oxide formation. The study on the oxide formation on the metal surfaces has a long history. It contains not only the phenomenological analysis of the formation processes but also the model for the atomic diffusion and the chemical reaction. Nevertheless, the microscopic theory on the oxide formation, especially, based on the electronic theory has not been available. Previous studies have revealed that the oxide formation is governed by the atomic diffusion between oxides and the interior bulk metal. At this stage, the diffusion of atoms occurs with the help of vacancy or self-interstitial and their electronic states have significant influence to the diffusion. The present study aims to elucidate the diffusion processes of atoms in the oxides including defects theoretically, based on the state-of-the-art computation techniques; the first-principles electronic structure calculation methods in terms of the density-functional formalism. Thanks to the development of high-performance computers

and the progress in the computational technique, the modern electronic theory can be successfully applied to the materials to explain and predict various physical properties. However, there are still some unresolved problems. The metal oxides are the cases. This study includes the investigation to explore how far the present electronic theory can be applied in the metal oxides. The computations are performed on the Numerical Material Simulator System installed at NRIM, which consists of NEC-SX4/20 and IBM-SP 2/16.

Keywords : metal oxides, diffusion, electronic state, first-principles theory

19 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)-(4×2) 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 effect of hydrogen termination on the Si MBE homoepitaxy has been investigated. The adsorption of a Si atom on the monohydride terminated Si(001)-(2×1) surface is found to lead to formation of a SiH₂ species by capturing H atoms from the substrate Si atoms. The migration of the Si H₂ adatom is assisted by the release and capture of H

atoms, being reduced compared with that on the bare Si surface. The effect of steps on the diffusion of Si adatoms has been also examined on the H-terminated Si (001) surface, which is found to be qualitatively similar to that on the bare Si surface. Consequently, the reduction of the Si diffusion by the hydrogen termination may have disruptive effects on the Si homoepitaxy.

Keywords : structural stability, chemisorption, reaction, solid surface

Related Papers

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Theory of Adsorption of Cl₂ Molecules on GaAs (001) Surfaces, T. Ohno, Surf. Sci. 357/358 (1996) : 322-326.

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Theory of Adsorption and Diffusion of Si Adatoms on H/Si (100) Stepped Surfaces, J. Nara, T. Sasaki and T. Ohno, J. Crystal Growth 201/202 (1999) : 77-88.

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

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

[April 1995 to March 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 creating 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

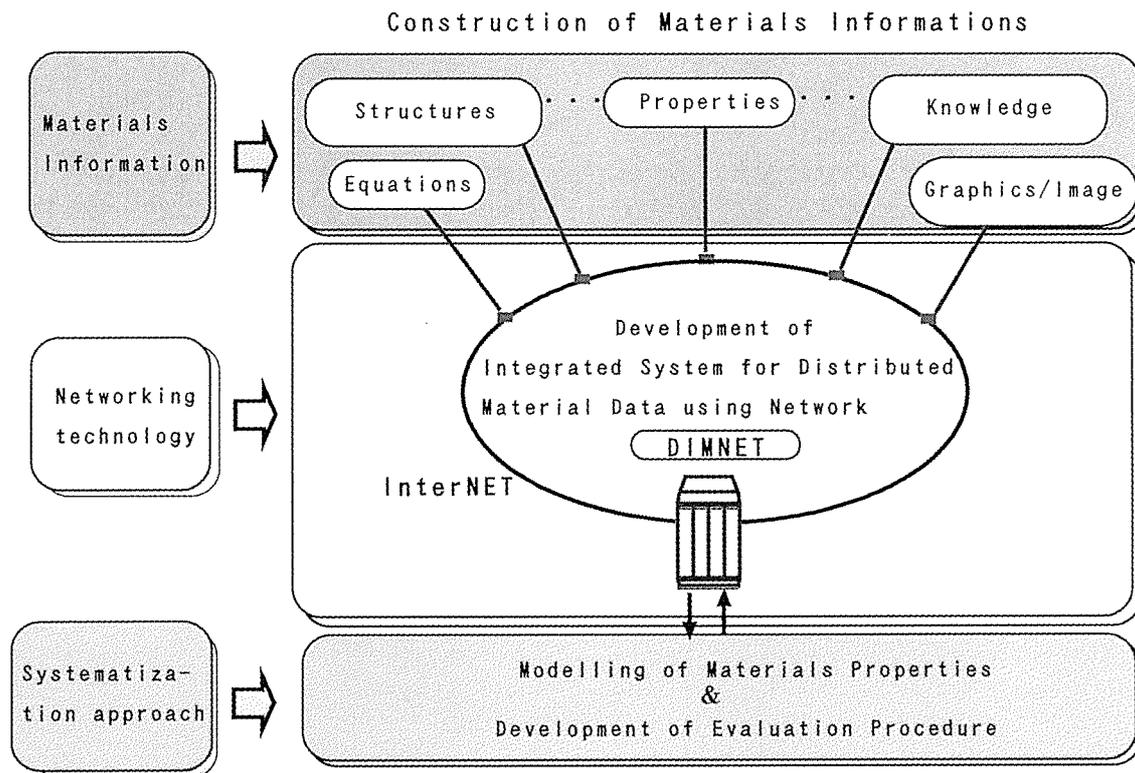


Fig. Systematic illustration for the research project

as NETSCAPE.

Figure shows the systematic illustration for this research project.

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, database, networking

21 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 reconstructed using "oracle" as a DBMS in order to clear "Year 2000 problem" and to improve for valuable web-usage. The URL of the home page is "http://asagiri.nrim.go.jp".

The papers contain many useful information as well as numerical data. These information are written in text style in abstract, summary or conclusion. In this project we study how to acquire useful information from the paper and how to construct a knowledgebase useful for researchers. For these purpose we introduced 'matisse' and 'REX' as a main software. These are object-oriented database management system (ODBMS). Using these ODBMS we are developing prototype of "Information Acquisition System". To know what kind of information are included in the paper is the important factor for the system. We made thesaurus, especially semantic thesaurus, dictionary in the field of high-Tc superconductors (HTSC). We can classify information according to their usage using the thesaurus dictionary. As a by-product we made word-database for HTSC and opened it through internet. "Word-database" contains the word of "JIS H705".

We have also developed database of standardized data (our original data) for typical high-Tc cuprate superconductors. In this project we measured superconducting properties, Hall coefficient, thermal conductivity, thermopower, specific heat for $\text{YBa}_2\text{Cu}_4\text{O}_8$ bulk, $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_z$ single crystal, $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_z$ bulk, and $\text{YBa}_2\text{Cu}_3\text{O}_7$ single crystal. These data are inputted into the database with the data of sample characterization and measuring

condition. One can access to the database through the home page mentioned above.

Keyword : oxide Superconductors, database, knowledgebase, net work

Related Papers

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22 Fundamental Studies of the Microbial Reaction with Inorganic Compounds

A. Aoki, Mechanical Property Division

[April 1996 to March 1999]

Certain species of microorganism accelerate the aqueous oxidation of metals and inorganic compounds. These are called chemolithotrophic bacteria and have played an important role in mining to extract metal valuables from ore. Much effort has been done to clarify and control the potential usefulness of microbiology in this field. However, the interfacial process of the interaction between the microorganism and the inorganic compound is still not sufficiently understood. To clarify this ambiguous point, as a first step, we previously investigated the characteristic of the microbial oxidation of iron sulfide (pyrite FeS_2 and pyrrhotite Fe_{1-x}S). *Thiobacillus ferrooxidans*, a typical microorganism of the chemolithotrophic type, was applied in this study. The result showed the significant catalytic influence of the microorganism in the oxidation process including the secondary solid phase on the surface.

We are subsequently trying to clarify the role of the crystallographic orientation of the sulfide on the reaction mechanism of the bacterial oxidation ; representative plane orientations of (100) and (111) of pyrite were adopted for this purpose. Microbial oxidation of the sulfide surface was carried out in an acid bacterial solution of pH 2.3 with H_2SO_4 in 9 K medium during 4 weeks at 30°C. At the beginning small amount of Fe^{2+} was added for energy source of the microorganism. It was shown by SEM measurement that the (100) plane would be more corrosive than the (111) plane because of the quantity of the pittings associated with the oxidation : tetragonal (Fig. 1A) and typical linear pittings of cubic on the

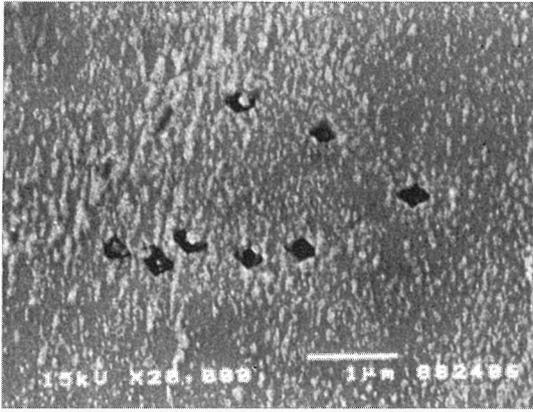


Fig. 1A

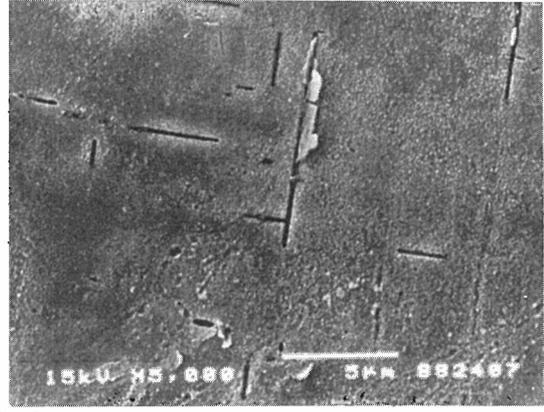


Fig. 1B

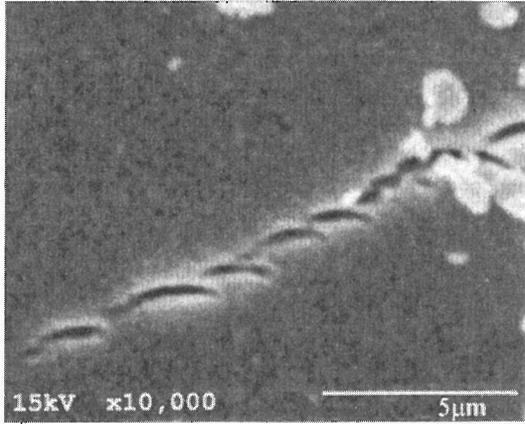


Fig. 2

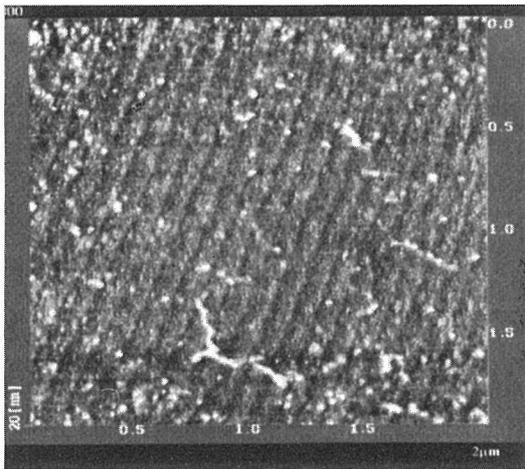


Fig. 3A

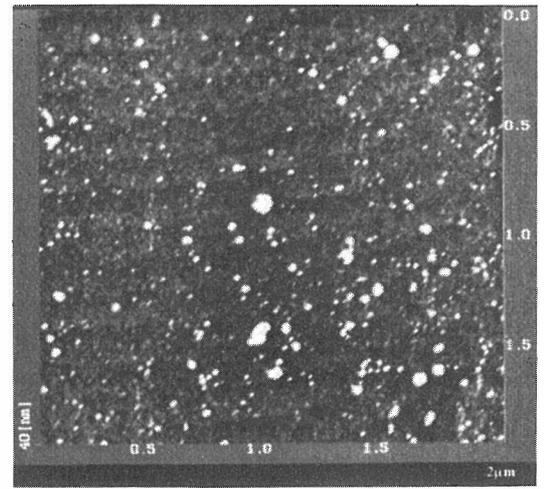


Fig. 3B

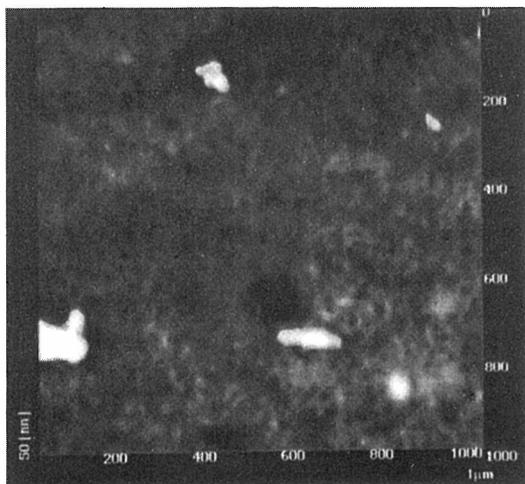


Fig. 4A

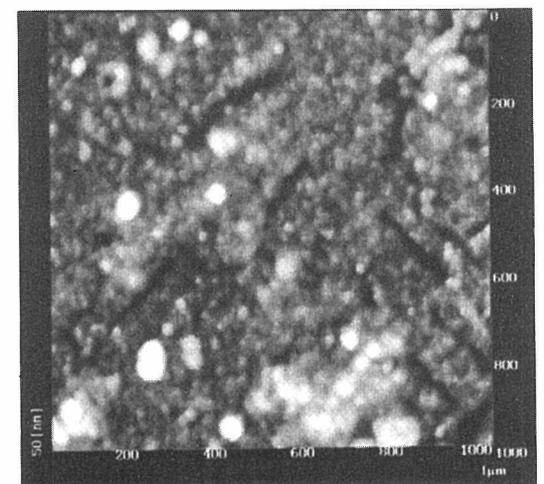


Fig. 4B

(100) (Fig. 1B) and rod type pittings on the (111) plane (Fig. 2). Subsequently, to examine the early stages of the oxidation AFM observation in tapping mode at the pyrite surface was carried out. As is in Fig. 3A untreated (100) surface was distinguished by a regular array of round humps at AFM. After 30 hours oxidation the round humps disappeared and etching pits were produced by the oxidation (Fig. 3 B). Figs. 4A and 4B illustrate the results of 7 days and 15 days oxidation, respectively. It was estimated that these pits are developing to becoming as is in Fig. 1A and 1B.

The results obtained here, at the same time, will be received wide application to solve the environmental problems by the microorganism ; bacterial corrosion of the metals or acidic drainage of the closed mines.

Keywords : chemolithotrophic bacteria, Thiobacillus ferroxidans, interfacial process, redox potential, SEM, AFM

23 Fatigue Behavior and Microstructure of Metals

F. Morito, Mechanical Properties Division

[April 1999 to March 2002]

When pure metals are subjected to cyclic plastic strains, they may harden or soften depending on their initial structures. Thus, metals in the annealed state usually become harder while those that are cold worked generally soften. Such a fatigue softening or hardening in deformation resistance can be detected by corresponding changes in indentation hardness, flow stress, damping response and the cyclic stress-strain response of the material.

Fatigue damage process develops preferentially at the sites of cyclic strain localization. As a direct consequence of strain localization, therefore, crack nucleation occurs and crack growth proceeds in the material.

In order to understand changes in the deformation resistance and the strain localization during fatigue, we must study the dislocation structure as well as the surface slip pattern associated with cyclic deformation process. It is also necessary to clarify any obvious correlation between the interior dislocation structure and the surface slip band structure.

We examined the fatigue behavior in pure nickel and 304 stainless steel with FCC structure. Specimen was bar type of 80 mm total length with 4 mm ϕ and 8 mm gauge length. Fatigue tests were carried out at a frequency of 4 Hz in the load control mode and a stress ratio of $R=0.1$ or -1 at room temperature.

In fatigue of the work hardened materials under R

$= -1$, the fatigue softening existed typically in pure nickel, but it did not occur in 304 stainless steel. Under $R=0.1$, no fatigue softening existed in both materials. In fatigue of annealed materials under both stress ratios, the fatigue hardening existed in both materials.

In the fatigue softened pure nickel, the microstructure was mainly subgrain formation. In the fatigue hardened pure nickel under $R = -1$, the loop patch formation was observed in low stress amplitude, while the subgrain formation was observed in high stress amplitude. In the fatigue hardened 304 stainless steel under $R = -1$, oriented dislocations and stacking faults were recognized in low stress amplitude, while cell-like structure with high dislocation density existed in high stress amplitude. The reason why no fatigue softening occurred under $R = -1$ in work hardened 304 stainless steel is considered that cross-slip deformation was difficult due to lower stacking faults energy.

Based on the above results, particular attention is paid on the fatigue behavior and microstructure in niobium and molybdenum with BCC structure. We examine details of the surface slip band structure, dislocation arrangement, crack nucleation and their relations during fatigue deformation. We compare the characteristics of fatigue damage process in BCC crystals with those in FCC crystals. It is possible to reveal the mechanisms of fatigue softening and hardening behavior.

Keywords : fatigue softening, fatigue hardening, stress ratio, microstructure

24 Fatigue Strength in a Corrosive Environment

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[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 nucleated 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-2 wt% Li alloy.

The specimens of a gauge section of 2.0 mm in thickness \times 4.0 mm in width \times 6.0 mm 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 SHIMAZU 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 -1.1 V against Ag/AgCl reference electrode at 295 ± 1 K, using a sinusoidal wave with a frequency of 1 Hz, a load ratio of -1 , and a total strain of 5×10^{-3} . Specimens were immersed in a 3.5 pct NaCl aqueous solution for 86.4 ks at a cathodic potential of -1.1 V 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 to the observation of highly dense dislocations of hydrogen-charged Fe-3.5 pct. 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 in a 2.5% H₂SO₄ aqueous solution at a cathodic current density of -10 mA/cm², using tensile or fatigue specimens of coarse grain of Al-2 wt% Li alloy.

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

25 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 1600 K. 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 and creep tests, where concurrent tensile strains at gauge portion can be monitored directly with a resolution of $5 \mu\text{m}$ using an optical extensometer.
- (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

26 Fracture Mechanism of Welded Structure of Stainless Steel at Cryogenic Temperature

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[April 1999 to March 2002]

In the applications of cryogenic technology, there are projects of constructing large scale facilities of superconducting magnets at liquid helium temperature (4 K) and clean energy to transport and store liquid hydrogen (20 K). It is very important to evaluate the mechanical properties of the materials including weld metals in practical environment to keep the reliability of large scale structures used at cryogenic temperatures and in high magnetic field. It is required to comprehend the mechanical properties such as continuous data of fracture toughness from room temperature to liquid helium temperature, and also to clarify the effects of hydrogen-gas envi-

ronment 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 carry out high-cycle and low cycle fatigue tests on stainless steel welds with delta ferrite but less weld defects and clarify the effects of brittle structure on fatigue properties, carry out the J-evaluation tensile tests by round bar with circumferential notch on the specimens sampled from the welds and hydrogen-charged to evaluate fracture toughness of the welds in detail and effects of hydrogen on the welded structure, and carry out tensile and fracture toughness tests from room temperature to liquid helium temperature in high magnetic field and investigate the effects of high magnetic field and weld structure on the mechanical properties of unstable austenitic stainless steels at each temperature.

Keywords : structural material, stainless steel, cryogenic temperature, magnetic field, tensile properties, fatigue properties, hydrogen embrittlement

27 Fabrication of Ni₃Al-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 Ni₃Al without addition of alloying elements such as boron. Also, using the FZ technique, we successfully grew high quality single crystals of stoichiometric Ni₃Al which was regarded as impossible to grow. The results prove that the FZ method is a powerful technique not only in engineering area but also in fundamental research.

The objective of this study is twofold. First is on the high-temperature materials based on Ni₃Al. Since the brittleness of monolithic Ni₃Al is overcome as mentioned above, one of the remaining problems is its insufficient high-temperature strength. Our target is to establish an engineering foundation in developing Ni₃Al-base intermetallic compounds strengthened by alloying or second phase precipitation. We apply the FZ technique to fabrication of the composites. Second is on study the deformation mechanism of Ni₃Al using single crystals. The effect of stoichiometry on the deformation is focused. In our preliminary study we found some interesting

results, for example compliance to Schmid law and stress response due to strain rate change, which are considered to be characteristic of binary stoichiometric Ni₃Al.

Keywords : unidirectional solidification, floating zone method, Ni₃Al, mechanical properties, deformation mechanism

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28 Search for Group IV Element Compounds Including Alkaline-earth-metal Elements

M. Imai and T. Hirano, Mechanical Properties Division

[April 1999 to March 2001]

Si is still one of the important materials in the present LSI technology. With progress of the technology, the problems arise that cannot be solved with the materials used conventionally. Therefore, search for new Si-related materials with new function and properties becomes more important. Silicides are one of the potential constituents of microelectric and optoelectronic device. Among the silicides, silicides including alkaline-earth-metal elements have unique structures like a layer-by layer packed structure, clathrate structure, and so on. For the reasons above, we studied alkaline-earth metal disilicides (M_ASi_2 , $\text{M}_A = \text{Ca}, \text{Sr}, \text{Ba}$) for recent several years. We synthesized metastable phases of alkaline-earth metal disilicides BaSi_2 under high-pressure and high-temperature condition, and studied structure and electronic properties of these phases. BaSi_2 was chosen as samples because of their unique atomic configurations and large compressibility of Ba atoms. BaSi_2 was found to be a semiconductor with an orthorhombic structure at ambient conditions. We synthesized BaSi_2 with a cubic structure and a trigonal structure, and found that trigonal BaSi_2 is a hole metal while cubic BaSi_2 is an n-type semiconductor. It is rarely known that high-pressure metallic phase is quenched at ambient condition. Furthermore, it was found that trigonal BaSi_2 is a superconductor with onset temperature of 6.8 K. We also observed pressure-induced structural phase transition with in situ X-ray diffraction measurements, and discussed the similarity among the transformation sequence under pressure in three M_ASi_2 .

In this project, we are studying Si clathrate compounds, and CaAl_2Si_2 , which has a layer-by-layer packed structure, and related materials.

The Si clathrate compounds were discovered in

alkaline-metal-Si system for the first time, and their physical properties were investigated many years ago. Crystal structure of the Si clathrate compounds consists of Si polyhedral cages, and alkali-metal atoms are incorporated inside the cages. After recent discovery of superconductivity of alkali-metal-doped fullerenes, the Si clathrate compounds has attracted attention again. This is because the shape of polyhedral cage is close to that of fullerene, and the expected Debye frequency for the tetrahedrally coordinated Si network seems to be favorable for the superconductivity of the BCS mechanism. Now two Si clathrate compounds, $(\text{Na}, \text{Ba})_8\text{Si}_{46}$ and $(\text{K}, \text{Ba})_8\text{Si}_{46}$, are known as superconductors. In this study, we are trying to synthesize the Si clathrate compounds in the other system, and investigate their physical properties.

Keywords : silicides, alkaline-earth metals, electrical resistivity

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29 Remaining Life Prediction for Weldments in FBR based on Creep Damage Evaluation

T. Tanabe, M. Yamazaki, H. Hongo and T. Watanabe, Mechanical Properties Division, J. Kinugawa, Joining and Interface Research Station

[April 1996 to March 2001]

Creep behaviors of austenitic and ferritic steel welded joints for Fast Breeder Reactor (FBR) were investigated and the following results were obtained.

(a) The relation between creep behavior and microstructural change was investigated in detail on

SUS304 steel plates of which maximum lives reached over one hundred thousand hours. Creep rate-time curves changed its shape complicatedly reflecting the precipitation of carbides and/or σ phase. Microstructural observation revealed that after one hundred thousand hours, neither sub boundary nor dynamic recrystallization was recognized. (b) Creep rupture test results on the welded joints of 2.25 Cr-1 Mo steel multi-layer weldment showed that the fracture position shifted from base metal, via heat affected zone to weld metal part, as the stresses decreased (rupture lives increased). (c) Creep damage in 316FR steel loaded at a given stress was inspected ultrasonically by using creep specimens interrupted periodically. Relations between creep rate, density, hardness or dislocation density and, sound velocity change, loss of sound propagation energy and frequency response function were examined. Positive correlations were found between the velocity change and density, and the propagation energy and creep rate. From these results and those obtained last year, it can be safely said that in the austenitic stainless steels, the assessment of creep damage by ultrasonic inspection is possible. (d) When multi-axial stress state at the weldment due to residual stress on welding is taken into account as multi-axial stress influence factor, the creep curves and rupture lives of multi-layer welded joints for SUS 304 thick plates can be successfully simulated with use of a simple analysis model developed at NRI.

Keywords : creep damage, welded joint, ferritic steel, austenitic steel, microstructure, FBR

Related Paper

Long Term Creep Rupture Properties and Microstructural Change in Welds of 2.25 Cr-1 Mo Steel Thick Plates, T. Watanabe, M. Yamazaki, H. Hongo and T. Tanabe, Progress in Mechanical Behaviour of Materials, ICM8, Vol. II (1999) 658.

30 Improvement of Thermal and mechanical Properties in Tungsten-Based Materials

T. Tanabe I. Mutoh and M. Fujitsuka, Mechanical Properties Division
[April 1999 to March 2002]

Tungsten (W) is considered as one of the candidate materials for structural applications in fusion reactors. However, it has low room temperature ductility and low recrystallization temperature. These disadvantages are improved to some extent with addition of rhenium (Re). Further, Re is one

of the products in the transmutation of W after heavy neutron irradiation. Recently, it has been reported that W with dispersed TiC at grain boundaries has better tensile ductility and strength, and higher recrystallization temperature than pure W. Further, improvement is recognized in the toughness after neutron irradiation. In view of these situations, it is important to examine the effect of dispersed particles on the thermal and mechanical properties of W-based materials.

In the study, effect of neutron irradiation using JMTR reactor on thermal and mechanical properties of W and W-Re alloys will be investigated firstly. Then, improvement of their properties will be made by dispersed particles through powder metallurgical method. The species of dispersed particles considered are TiC, TiB₂, HfC and HfB₂. Effect of neutron irradiation on thermal and mechanical properties of these dispersion strengthened W-based materials is our primary concern.

Keywords : Tungsten, Tungsten-Rhenium Alloy, Dispersion strengthening, Thermal diffusivity, Tensile ductility, Neutron irradiation

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31 NRI Creep Data Sheet Project-V

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M. Yamazaki, H. Hongo and T. Watanabe, Mechanical Properties Division
[April 1996 to March 2001]

The major objectives of the NRI Creep Data Sheet Project are to produce long-term creep and rupture data up to longer than 10⁵ hrs for heat

resistant steels and alloys, which are produced in Japan, and to publish the data as a series of NRIIM Data Sheets. This project has been continued since 1966 and the series of NRIIM Data Sheets have been distributed not only in Japan but also in abroad. In fiscal year 1998, we published 4 sheets listed in the Table.

Among of these issues, 26B is the final versions and very valuable data sheet due to creep rupture strength data longer than 10,000 hrs. The data sheet No. 26 B is of Fe based superalloy steel widely used in heat exchanger and contains long-term creep rupture data up to 14,000 hrs, tables of creep rupture property, typical microstructures of received and fractured steels, results of statistical analysis of creep rupture data and so on. The data sheet No. 46 is of 9 Cr-2 Mo heat resisting ferritic steels, Mod. STBA 27 and Mod. SFVA 27 for power plant and contains creep rupture data up to 40,000 hrs and properties of as-received specimen. The data sheet No. 41A is of Ni-based superalloy bar, plate and tube NCF 600 for corrosion resisting and heat resisting materials. It contains long-term creep rupture strength data up to 120,000 hrs, tensile strength at high temperature, microstructure of as received and creep ruptured specimens and so on. The data sheet No. 47 is of the stress relaxation properties at between 600 and 750°C and also contained creep rupture data up to 30,000 hrs and creep strain data up to 50,000 hrs.

The data sheet No. M-1 is the first issue of metallographic atlas of long-term crept materials. It contains a lot of microstructures taken by optical

microscopes and electron microscopes at three portions of SUS 304H-TB crept stainless steel specimens, head, under creep stressed and near creep ruptured portions. According to creep fracture mechanism of the creep rupture data sheet (No. 4B, 1986), metallic carbides and sigma phase are also quantitatively analyzed and summarized.

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.

Long-term creep deformation behavior of ferritic Cr-0.5 Mo and 2.25 Cr-1 Mo steels has been investigated and also microstructural changes in creep stressed austenitic stainless steel (18 Cr-8 Ni) have been quantitatively investigated.

- 1) In the time region, when a S curvature in stress-rupture time relationship was observed, a curvature was also observed in strain rate-time relationship. Under higher stress than that which revealed S curvature, the creep strength remarkably decreased by preheat aging, while the lower stress and longer creep test showed no effect of preheat aging.
- 2) Before the time when the S curvature appeared, strengthening factors of fine carbides and dislocations disappeared and the creep strength is governed the inherent creep strength.
- 3) The influence of initial microstructures on long-term creep deformation behavior became smaller at lower stress. In 2.25 Cr-1 Mo steel, it

Table Summary of NRIIM Data Sheets in fiscal year 1998

Materials	Number	Issued
Iron based 21Cr-32Ni-Ti-Al alloy for heat exchanger seamless tubes (NCF 800H TB)	26B	September 30, 1998
9Cr-2Mo ferritic steels for power plant boiler tubes and forged plates (Mod. STBA 27 and Mod. SFVA 27)	46	September 30, 1998
Nickel based 15.5Cr-8Fe superalloy For corrosion-resisting and heat-resisting superalloy bars(NCF600-B) and plate(NCF 600-P) and seamless Ni-Cr-Fe alloy heat exchanger tube(NCF 600 TB)	41A	March 31, 1999
Stress relaxation properties of Fe-based 21Cr-32-Ni-Ti-Al for corrosion resisting superalloy bar(NCF 800H-B)	47	March 31, 1999
Micrographs and microstructural Characteristics of crept specimens of 18Cr-8Ni stainless steel for boiler and heat exchanger seamless tubes (SUS 304H TB)	M-1	March 31, 1999

could not be found at less than 100 Mpa.

- 4) The fact that there did not exist the difference of deformation among steels at low stress and long testing time indicated that the strength reached the inherent one which does not depend on microstructure, due to the recovery of microstructure and the disappearance of precipitation strengthening effect. The difference in creep strength due to initial microstructure could be explained by the difference of the strain rate coefficient α in the modified θ method.

The results of investigation on creep behavior in austenitic stainless steels are as follows.

- 1) The amount of σ phase increased at the head portion (low stress portion) with time, but its size did not change, while it hardly changed and remarkably grew at the gauge portion. This result indicates that precipitation of σ phase is governed by nucleation under low stress, but the nucleation tends to occur at the grain boundary at which the stress loads in the nearly normal axis.
- 2) In $M_{23}C_6$ particle, Cr content increased with time, while Fe content decreased. On the other hand, in σ phase all of content of Cr, Fe and Ni did not change. The equilibrium composition of Cr in $M_{23}C_6$ is much higher than that in matrix and it precipitates at short time. Then $M_{23}C_6$ with low Cr content precipitates at first and its content gradually increases to the equilibrium value. As Cr content in σ phase is higher than that of matrix but lower than that of $M_{23}C_6$, it is nearly the equilibrium value at the early stage of creep.

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

32 NRIM Long-Term Fatigue Data Sheet Project-I

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[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 which are selected from engineer and/or researcher 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, the following fatigue tests were conducted.

- 1) Long-term fatigue test at room temperature

The first candidate of steel JIS SUP 7 for spring material began to be tested by rotary bending type testing facilities aiming 10^{10} cycles fatigue data. As conventional fatigue data of this steel was already published by the NRIM fatigue data sheet No. 53. The testing has been being carried out on the basis of this sheet, using steels tempered at 430 and 500°C, and testing frequency is 100 to 150 Hz. In this test, the fracture mode and fractography are also observed. In addition to this normal test, fatigue tests with a ultra-sonic fatigue facility with 20 kHz have been tried and compared with the normal tested results in

order to shorten the long-term testing. The S-N curve by ultra-sonic testing machine shifted at higher stress level from that of normal test. The exact calibration of stress and others of the ultra-sonic test will be carried out and the possibility of use of these results in a data sheet. The nano-indentation technique with AFM, developed by NRIM will be used to make clear the relationship between the fracture orientation and inclusion inside of metal.

2) Long-term high temperature fatigue test

Recently developed and nearly practically used high temperature steel NF616 and HCM12A for power plant were begun to be tested under a strain control up to 10^5 cycles (partly 10^6 cycles). Testing temperatures were room temperature, 400 to 700°C. In 1998, the partly tests up to 10^5 cycles were finished. At more than 10^4 cycles, the S-N curve folded to the higher stress level.

3) Fatigue test of Ti alloys

Specimens of 3 heats of Ti-6Al-4V alloy have been fatigue tested from low cycle to high cycle fatigue region. The S-N curves were classified into two types, especially in low to middle region of fracture cycle. However, the fatigue limit of all heats was nearly the same value. The cause of difference in S-N curve has not been clear and investigation are being carried out. Fatigue tests of Ti-6Al-4V alloys, which microstructures are different from each other, will be conducted.

4) Fatigue test of welded joint

In order to obtain basic fatigue properties of practical arc welded construction, fatigue test of large scale specimen were carried out and at the same time the influence of residual stress on fatigue properties has been investigated, by measuring residual stress. Large scale specimen and small rib cross welded joint of JIS SM590Q steel were produced. In large scale specimen, the slit type welding was carried out in order to get the maximum residual stress. Comparing of fatigue test results using both welded joint indicated that the small size rib welded joint can simulate practical large scale joint if residual stress is correctly evaluated. The same fatigue test will be carried out with specimens of JIS SM400B steel.

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

33 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 advantage 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 undergoes 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

Related Papers

- 1) 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.
- 2) Crystallographic Orientation Relationship between the primary and Secondary Recrystallized Grains in Multi-layer Molybdenum Crystals, K. Honda and T. Fujii. JSPM. 45 (1998) 801-805.

34 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 0.1 mg/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 20 mg/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 amorphous 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

35 The Development of High Strength High Functional In-Situ Composite

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

Recent years, the further strengthening of the Cu-base alloys for the lead frame and the pulse magnet is strongly sought. Cu-base in situ composite that has high strength and high electrical conductivity is promising material. We have developed Cu-base in situ composite which has the strength of 906MPa and the electrical conductivity of 76%IACS, as far. The advantage of this alloy is lower cost than other Cu-base in situ composites such as Cu-Ag alloy. However, the cost of this alloy is not so low because of the high purity raw materials. Therefore, in this study we aimed to clarify the effects of the impurities on the mechanical property and the electrical conductivity of the Cu-Cr alloy in order to utilize the low purity raw materials.

It is clarified that Fe is the main impurity of the alloy and is scavenged into the Cr fiber. Furthermore, this is resulted in the increment of the hardness in the fiber. The maximum electrical conductivity of the aged low purity alloy is almost the same as of the high purity one at 800 K.

It was confirmed by these results that the low purity Cu and Cr materials are applicable as the starting materials to produce high strength and high electrical conductivity Cu-15wt%Cr alloy.

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

36 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 (NO₃)₂-H₂O 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 (NO₃)₂ phase and Sr (NO₃)₂·4H₂O 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 Enkevort and P. Bennema, *J. Crystal Growth* 186 (1998) : 214-223.

Atomic force microscopy observations of hollow cores on the {111} and {100} faces of barium nitrate, M. Plomp, K. Maiwa and W.J.P. van Enkevort, *Journal of Crystal Growth* 198/199 (1999) : 246-256.

37 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 were 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 research 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.

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Study of Even-Parity Autoionization States of Lutetium Atom by Laser Resonance Photoionization Spectroscopy, Y. Ogawa and O. Kujirai, J. Phys. Soc. Japan, 68 (1999)428-433.

38 Fabrication and characterization of nano-structured materials

Y. Sakka, K. Ozawa, T. Uchikoshi, T. S. Suzuki, and O.O. Vasylykiv*, *Materials Processing Division*

* STA fellow

[April 1999 to March 2002]

Nano-structured materials can be classified into two general categories. One category consists of materials of only nanosized materials. The other consists of materials where nanosized particles are distributed within the intra- and/or inter-grains of micronsized grains. These nano-structured materials have been receiving increasing attention due to their unique chemical and physical properties which cannot be obtained from the conventional materials. However, the processing of the nano-structured has

not been established. In this study two types of processing are conducted to fabricate nano-structured materials. One is synthesized by consolidating fine powders through a colloidal processing followed by sintering. The other is nano-porous materials with layered perovskite structures through the soft chemical processing i.e. a sol-gel or a hydrothermal processing.

The colloidal processing is a useful tool for consolidating nano-sized particles with desired pore size distribution. An important factor is to control the interparticle interaction in liquid. Alumina and/or zirconia compacts with a narrow pore size distribution, which was determined by mercury porosimetry, was produced by slip cast, pressure filtration or electrophoretic deposition technique. Sintering characteristics of the green compacts and mechanism of preparing nano-structured materials are examined.

Powder and film of antimonic acid are prepared by a direct reaction of $\text{Sb}(\text{O}-n\text{-C}_3\text{H}_7)_3$ or Sb metal with H_2O_2 aqueous solution. Three types of antimonic acids ($\text{Sb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) films : (111)-oriented and non-oriented polycrystalline films of cubic antimonic acids and amorphous antimonic acid films, were prepared on quartz glass substrates with a spin-coating technique. The electrical conductivity of the (111)-oriented film is approximately one order of magnitude larger than those of the non-oriented and amorphous films. Bismuth doped antimonic acids were also prepared by reacting an H_2O_2 aqueous solution with $\text{Sb}(\text{O}-i\text{-C}_3\text{H}_7)_3$ and $\text{Bi}(\text{O}-i\text{-C}_3\text{H}_7)_3$. The conductivity of $\text{Sb}_2\text{O}_5 \cdot 0.1\text{Bi}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ was found to be high ($1.0 \times 10^{-3} \text{Scm}^{-1}$). Effect of the water vapor pressure and nano-pore structure on the proton conductivity is studied.

Keywords : nanoparticle, colloid, antimonic acid, sintering, nanocomposite

Related papers

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

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39 Diffusion Bonding between Transition Metals (Cr, Fe, and Ni) and Metals of Group IV~VI

T. Kasugai, K. Ei, *Materials Processing Div.*

[April 1999 to March 2002]

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 bonding zone between Ni-Cr alloy or stainless steel and metals of group IV.

In this study, joinability of the diffusion bonding between transition metals (Cr, Fe, and Ni) and metals of group IV to VI, the formation of metallic compounds in the bonding zone between transition metals (Cr, Fe, and Ni) and metals of group IV to VI, diffusion processes, and bonding crack are investigated in the connection with the periodic table.

Keywords : Diffusion bonding, Cr, Fe, Ni, Metals of Group IV, Metals of Group V, Metals of Group VI, Metallic compound

Related paper

T. Kasugai, K. Ei and H. Irie ; "Diffusion Bonding of Zirconium and Stainless Steel", Proc. of IIW Asian Pacific Welding Congress Vol. 1, (1996) 271.

40 Cladding or Coating Processes by Utilizing Semi-solid Processing

T. Dendo, T. Shiota and T. Kimura, Materials Processing Division

[April 1999 to March 2002]

In the recent years, much interest has been arisen in composite or combined materials because requirements of engineering materials become more and more severe and versatile. Accordingly, various processing techniques have been attempted for manufacturing composite materials or for combining dissimilar materials. We also have proposed new methods for combining dissimilar materials, in which cladding and forming are simultaneously performed by utilizing semi-solid processing.

This study consists of two sub-themes ; one is on cladding process combined plastic working of solid metal with squeeze forming of semi-molten metal ; and another is on coating process with particle-

dispersed composite by means of pressure infiltration under semi-molten state. Through the former process, cylindrical bars or shaped parts clad in a skin of dissimilar metal are manufactured, and through the latter, blocks or parts coated partially in a composite layer are fabricated.

The work has just started from this fiscal years, and we are investigating feasibility and problems of the new methods proposed so as to establish fundamental techniques in these processes.

Keywords : semi-solid processing, cladding, coating, composite, plastic working, infiltration

41 Effect of Interfacial Damage on the Fatigue Crack Propagation in Fiber-Reinforced Titanium Composite

C. Masuda, Y. Tanaka and Y.-F. Liu, Materials Processing Division

[April 1999 to March 2002]

Continuous fiber-reinforced titanium matrix composites are promising structural materials because of their high specific modulus and specific strength as well as good stability at moderately high temperature. Such applications often require resistance to a repeated mechanical loading condition. For a composite specimen under an intermediate level of applied stresses, the fiber bridging mechanism is believed to improve the resistance to fatigue crack propagation at room and high temperatures. Interface debonding and sliding are required to achieve fiber bridging, and the interface debonding may be initiated due to localized stress intensification when the matrix crack front reaches the fiber-matrix interface in a notched specimen and/or due to the brittle reaction layer cracking between the matrix and outermost carbon coating in an unnotched specimen. In contrary, the fiber failure was believed to be a dominant initial fracture mode in unnotched composites and eventually evolved into microcracks in the matrix if the applied stress was high. Surface fiber breaks also occurred at a low or intermediate level of cyclic loading at various temperatures. After some initial fracture event in the form of matrix crack propagation, reaction layer cracking or fiber break, a situation of the crack tip touching the interface occurs ; the crack arresting at the interface may then propagate through deflection or penetration. A two-dimensional idealization of fiber-reinforced systems was considered to address the crack deflection and penetration competition. As reviewed above the interface property has significant impact on stress transfer and fracture behavior under various situa-

tions.

However, the mechanism of interfacial damage evolution under fatigue conditions, particularly at high temperature, is unclear. The effect of test temperature and applied stress on the interfacial damage evolution has not been fully understood. They will be investigated in this study focusing on the following subjects.

(1) Fatigue tests are carried out in a scanning electron microscope chamber to observe fatigue crack growth behavior and to discuss the mechanism. Meanwhile, measurement of crack growth rate and crack opening displacement is planned.

(2) Interfacial properties are to be evaluated with a high temperature fiber pushout test apparatus developed by the authors. The relation between fiber pushout stress and fiber displacement can be obtained to calculate interface bonding energy and frictional sliding stress. Besides, atomic force microscope (AFM) is used to explore the interfacial damage behavior including roughness and wear change and frictional property evolution.

(3) Fatigue crack growth model will be developed with the interfacial damage considered.

(4) Repetition of Items (1)~(3) to establish a sound model having prediction capacity.

Keywords : Fiber-Reinforced Titanium, Fatigue, Interfacial Damage

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42 Study on the Near Net Shaping of a Thick Film by the Deposition 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 1999 to March 2001]

It is well known that the ultrafine particles (UFP) have many excellent physical and chemical properties. It has the possibility which can get a new functional film when a three-dimensional thick film (1-10 mm thick) is composed by UFP.

In this study, we are aiming at higher adhesive and agglomerative properties of UFP from the viewpoint of the moldability, and examine the formation of the thick film having a near net shape by using UFP synthesized from the thermal plasma process such as a DC-arc plasma or an RF-plasma.

Keywords : ultrafine particle, near net shape, thick film

43 Development of AgCu Alloy Sheathed Superconducting Wires/Tapes with High Mechanical Strength and Large Critical Current Density

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

Since superconductors in applications such as superconducting magnets are subjected to mechanical loads, influences of stress/strain on superconducting properties are one of the major concerns in developing superconducting wires/tapes for the magnet use. Ag-sheathed oxide superconducting tapes made by the widely used powder-in-tube method consist of the Ag matrix and the oxide core embedded in the matrix. It is reported that superconducting properties of Ag-sheathed oxide superconducting tapes are easily degraded due to stress because of weak mechanical strength of the Ag sheath and the brittle nature of the oxide superconductor. It is objective of this study to develop the oxide superconducting wires/tapes with high mechanical strength and large critical current density, using AgCu alloy sheath.

In this year the mechanical properties and effects of stress/strain on the superconducting properties of Ag- and AgCu alloy-sheathed Bi (2212) oxide super-

conducting tapes were investigated. Specimens were prepared by the power-in-tube method ; pure Ag and Ag-10at%Cu tubes were filled with the composition of Bi₂Sr₂Ca_{0.64}Cu_{1.64}O_x oxide powders made by the co-precipitation technique. These composites were drawn and rolled into tapes of 0.15 mm in thickness and 2.3-2.7 mm in width with intermediate annealings in vacuum. Finally, heat treatments of partially melting process were made in air at 875-880°C for 15 min, followed by the slow cooling at a rate of 5°C/hr. and simultaneously tensile strain dependences of the critical current as well as stress-strain relations for these Bi (2212) monocoresh tapes were measured at 4.2 K and a magnetic field of 5 T. The critical current was defined as a current where the electric field of 1 μV/cm occur across the voltage taps soldered on the specimens. These composite tapes showed some differences in mechanical properties. Strains where the linearity between stress and strain start to deviate were about 0.2% and 0.45% for Ag- and AgCu alloy-sheathed tapes, respectively. Furthermore, AgCu alloy-sheathed tapes showed about the 0.2% proof stress of 60 MPa that was about three times as high as Ag- sheathed tapes. Thus, AgCu-sheathed tapes showed improved mechanical properties compared to Ag-sheathed tapes. These improvements can be attributed to the reinforcement of the sheath resulting from the dispersion of the Cu oxides precipitated during partially melting process in air through the sheath. In Fig.1 the results of strain effects on the critical current are shown. Ag-sheathed tapes showed that critical currents initially remained unchanged and started to rapidly degrade when strain was increased beyond about 0.3%. On the other hand, degradation of the critical current occurred through 3 stages for AgCu-sheathed tapes. On straining a drop in the critical current occurred, followed by gradual decrease in the critical current until strain reached to about 0.5%. Finally the critical current degraded rapidly with further increasing strain.

In conclusion, it was found that mechanical properties of AgCu-sheathed tapes were improved com-

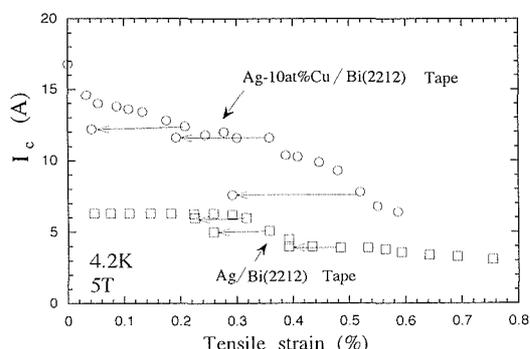


Fig. 1 Critical current, I_c as a function of tensile strain for Ag- and AgCu-sheathed Bi (2212) tapes

pared to Ag- sheathed tapes. Furthermore, there were some differences in strain dependences of the critical current between Ag- and AgCu- sheathed Bi (2212) superconducting tapes. In relation to the cause of these changes in mechanical and superconducting properties under strain, further study is to be planned.

Keywords : Bi (2212) superconducting oxide tapes, stress/strain effects, critical current

44 Control of the In-plane Texture of High-Tc Superconducting Thin Films for Microwave Applications

M. Fukutomi, 1st Research Group

[April 1998 to March 2001]

High temperature superconducting (HTS) thin films have great potential in microwave applications. To date, most work in this field has been done using single crystal substrates such as LaAlO₃ and NdGaO₃. These substrates are, however, very expensive and available only in small sizes, and all have limitations for the microwave applications. Various other HTS film/substrate combinations should be surveyed from now on.

The HTS thin films dealt with in the present study falls into two categories : 1) YBCO thin films on lattice-mismatched substrates such as MgO, sapphire and silicon ; and 2) YBCO thin films on substrates having no template for epitaxial growth such as polycrystalline metal, ceramic or amorphous substrates. The development of these films would have important consequences particularly for HTS microwave applications. To successfully obtain these films, high-angle grain boundaries resulting from in-plane misorientations need to be kept to a minimum because they are known to severely increase the microwave surface resistance R_s of the film. We must, therefore, control as strictly as possible the in-plane texture of the YBCO films grown on these substrate materials. For this purpose, the study on films in the first category is directed toward searching for desirable multi-buffer layers, especially with respect to the in-plane epitaxy. For the use of polycrystalline substrates of the second category, we have tried to fabricate in-plane textured templates for the subsequent growth of the YBCO films using a modified bias sputtering technique (MBS), which we previously proposed as an alternative to the ion beam assisted deposition (IBAD), the widely used method to grow in-plane textured films.

The R_s values of the films obtained has been measured using a HTS film- sapphire rod resonator technique. So far we have succeeded in developing

YBCO films with a fairly low R_s on polycrystalline copper substrates with a Cr/MBS-YSZ double buffer layer. A strong correlation was observed between in-plane misorientations and the R_s values of the films. More effort is under way to further reduce the R_s values by improving the degree of texturing of the films. Another goal of this study is to obtain microwave quality YBCO films over large areas. A new laser scanning ablation method has also been attempted to this end.

Keywords : YBCO thin film, buffer layer, in-plane texture, microwave surface resistance

45 Development of High- T_c Oxide Superconducting Wires and Tapes

H. Kumakura, H. Kitaguchi, H. Fujii, A. Matsumoto and K. Togano
[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 20 T where it is difficult to use conventional metallic superconductors because of their lower H_{c2} . In the past years, 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 have developed a new method of PAIR (Pre-Annealing and Intermediate-Rolling) process in order to improve current carrying properties of Bi-2212/Ag tapes. We applied this PAIR process to multilayer Bi-2212/Ag tapes prepared by a lamination method. Silver tapes were coated with slurry containing Bi-2212 powder. Three coated tapes were stacked and laminated with a Ag-0.2at% Mg alloy foil. We used the Ag-Mg alloy foil for the lamination in order to enhance mechanical strength. By applying PAIR process before the melt-solidification, Bi-2212 grain alignment and intergrain connectivity were much improved, and a large J_c enhancement was obtained. The key factor of the PAIR process is to increase the density of the oxide layer before the heat treatment (melt-solidification). In the conventional process, organic materials in the slurry were removed during the heat treatment and oxide layer became porous. In the PAIR process, organic materials were removed by the pre-annealing

and porosity was much decreased by the subsequent intermediate rolling. This high density of oxide layer is effective to obtain excellent grain alignment by the melt-solidification.

PAIR processed tapes show better J_c reproducibility than no-PAIR processed tapes. Typical J_c at 4.2 K of the PAIR processed short tapes was $\sim 4 \times 10^5 \text{ A/cm}^2$ in a field of 10 T parallel to the tape surface with highest J_c values over $5 \times 10^5 \text{ A/cm}^2$. These J_c values are two or three times higher than those of no-PAIR processed tapes. 10 m long tapes were also fabricated by applying the PAIR process. J_c values of the 10 m long tapes were somewhat lower than the J_c values of short tapes due to the temperature inhomogeneity in the large furnace used for the heat treatment.

In addition to high J_c values, excellent E (electric field) -J (current density) characteristics is also an important factor from the viewpoint of practical applications. For example, energy dissipation in the tape is closely related to the E-J characteristics. PAIR process is much effective to improve E-J characteristics of Bi-2212 tapes. This improvement can also be explained by the improved microstructure of the PAIR processed tapes.

As is well known, grain oriented Bi-2212/Ag tapes show fairly large anisotropy in J_c with respect to the magnetic field direction. In a field perpendicular to the tape surface, J_c is 1/2-1/3 of the J_c in parallel field. This low J_c in the perpendicular field is inconvenient for practical applications. PAIR processed tape show larger J_c anisotropy than the no-PAIR processed tapes because of the improved grain alignment. However, J_c in perpendicular field of the PAIR processed tape is higher than that of the no-PAIR processed tape. Thus, PAIR processed tapes show higher J_c values than the no-PAIR processed tapes in entire field directions.

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

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46 Understanding of the Mechanism of Superconductivity in High Temperature Superconductors

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

[April 1995 to March 2001]

To understand a mechanism of superconductivity in high temperature superconductors (HTSCs), enormous amount of experiments and theoretical analysis has been performed after the discovery of the materials. Recently, high quality single crystals of HTSCs have been grown and the experimental data have become more reliable and definite. In this 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 with a travelling solvent floating zone method. Among of them, Bi-2212 single crystals have been used for high-resolution angle-resolved photoemission spectroscopy (ARPES). Preparing samples with a different kind of hole-doping level from under-doped to over-doped, careful ARPES experiments have been performed and remarkable results have been obtained. We have found a “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 “dpseudo-gap”. The pseudo-gap seems to be changed continuously to the superconducting gap (Δ). 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 $2\Delta/\kappa_B T_c$ (κ_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 clue for further developments to understand a basic mechanism of superconductivity in HTSCs.

This research project aims also to understand the characteristic phenomena observed in the superconducting state of HTSCs in a magnetic and an

electric field. They may come mainly from their layered structures, composed of the superconducting CuO_2 layers and the non-superconducting 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 the numerical analysis to calculate the differential equation of the phase. The multi-branches in the characteristics were well reproduced by numerical calculations, assuming the charge distribution in the superconducting layers. In a magnetic field parallel to the Cu-O planes, a distribution of Josephson vortices has been simulated numerically, when the current flows along the c-axis. We found that there are in-phase and out-of-phase configurations in the distribution of vortices, which causes an abrupt increase of the Josephson current in the in-phase condition.

Magnetic phase diagram of HTSCs reveals also 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 parallel to Cu-O layers. It has been 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, with the numerical analysis and the Monte-Carlo simulation, a chain-like distribution has been obtained. This was also confirmed experimentally by a Bitter decoration technique. From these results, the Josephson plasma and the Josephson current perpendicular to the c-axis were analyzed and discussed.

Understanding these characteristics phenomenologically, we construct and refine the model to make clear a real mechanism of superconductivity and the physical properties of HTSCs in electromagnetic fields.

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

47 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 2001]

In high temperature superconductors (HTSCs), distinct features have been recognized, compared with the conventional metal and intermetallic super-

conductors. Two dimensionality of their crystal structures causes significant features in the electromagnetic field. For the application of these materials, it is really essential to use at liquid nitrogen temperature 77 K. 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 77 K or at higher temperatures. However, most of the obstacles come from the nature of the HTSCs 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 HTSCs to understand the pinning mechanism of vortices in HTSC 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 of vortices in HTSCs. First of all, we have to know the intrinsic properties of high quality single crystals. We have developed our crystal growth techniques in various methods. Based on the fundamental studies on the high quality single crystals, 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 $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi-2212) single crystals. By measuring the Josephson plasma resonance, new phase boundary has been observed above the irreversibility line. The new boundary exists at around $B_\phi/3$ ($B_\phi = n \times \Phi$; n : density of columnar defects, Φ : magnetic flux quantum), which is independent to temperature. Below the boundary, the vortices are in the liquid state, and above that, the vortices become a line-like structure with increasing a magnetic field. This field-induced transition has been confirmed in the Monte-Carlo simulations. Furthermore, 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, which is also confirmed by the dynamical calculation of current flow in a magnetic field.

Even in the Bi-2212 single crystals with high quality in crystallinity, there observed pinning effect at low fields and low temperatures below 30 K, measured by a Bitter decoration technique. With increasing a magnetic field, vortices form a hexagonal lattice as the magnetic interaction becomes larger to overcome the pinning force. At higher magnetic fields than 2D-3D transition field, a depinning of the

vortices has been observed in magnetization curves, which causes a new phase boundary in the irreversibility region. The magnetic phase diagram of Bi-2212 becomes a complicated, but reveals the real system to reflect the existence of the pinning centers.

This research has been made in collaboration with Tokyo Institute of Technology, Institute for Solid State Physics, the University of Tokyo, and Hitachi Advanced Research Laboratory.

Keywords : high temperature superconductors, vortex pinning, vortex dynamics

Recent Publications

Josephson Coupling in the Vortex-Liquid State of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ with columnar defects, M. Kosugi, Y. Matsuda, M.B. Gaifullin, L.N. Bulaevskii, N. Chikumoto, M. Konczykowskii, J. Shimoyama, K. Kishio and K. Hirata : Phys. Rev. B 59 (1999) 8970.

Columnar Defects in Heavy-Ion Irradiated $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$, ---New Magnetic Phase Transition in Vortices---, K. Hirata : Nuclear Instruments and Methods B, 156 (1999) 12.

48 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]

High temperature superconductors (HTSCs) 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 crystal structures, which are composed of superconducting CuO_2 layers and insulating layers or less-conductive layers. The electrons or holes are confined in two-dimensional superconducting layers, and the coherence length perpendicular to the layers becomes very short (~ 2 Å or less for $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi-2212)). This structural anisotropy causes interesting phenomena. DC-Josephson effect has been observed in the voltage-current characteristics, and the ac-Josephson effect has been observed, too, which indicate the existence of Josephson effect in the materials intrinsically. So, HTSCs are confirmed to have the Josephson effect as their own properties without any artificial insulating layers. 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 HTSCs for the application, such as the Josephson effect, and to find a new characteristic feature in these materials under various circumstances. For these purposes, it always becomes a key to grow large single crystals of high quality. We have developed our technology in growing single crystals of HTSCs mainly by traveling solvent floating zone method. Large single crystals have been obtained with a size of 5 mm in width, longer than 10 mm 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 maxima. 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 micro-structure is essential to avoid a heating effect. We have fabricated the mesa-structured junctions by an ion-milling on the cleaved surface of Bi-2212 single crystals. Measuring on the mesa-structured junctions, multi-branches have been observed in the I - V curves. Under the microwave, a Shapiro step, which is usually observed in the normal Josephson junction, has not been seen in the curves. Instead, a fine structure has been found at low voltage (current) or zero crossings region. This fine step is considered as an influence of the coherent vortex flow. To confirm the step under a parallel magnetic field, the measurements has been done, but, there have been found no fine step at various magnetic fields.

Generation of microwave has been tried to excite the Josephson plasma with an injection of quasi-particles into the junctions in an equilibrium condition. In the minus resistance regime in the I - V curves, the microwave emission has been observed. This preliminary result enforces us to try new methods in the excitation of the Josephson plasma for obtaining a coherent emission.

Based on these results, the intrinsic properties of the Josephson junction in HTSCs are analyzed numerically by a computer simulation, and, for the application of HTSCs, new function will be tried to find.

This research has been made in collaboration with Technical University of Munich and Tokyo Institute of Technology.

Keywords : high temperature superconductors, in-

trinsic Josephson junction, Josephson devices

Recent Publication

High Frequency Microwave Emission from BSCCO Intrinsic Junctions, W. Wang, K. Lee, I. Iguchi, K. Hirata and T. Mochiku : to be published in IEEE Trans. Appl. Superconductivity (1999).

49 Characterization and Application of Superconducting Thin Films Synthesized by Atomic Layer-by-layer and Epitaxial Growth Methods

T. Hatano, 1st Research Group

[April 1995 to March 2002]

Synthesis of extremely thin ribbon-shaped films

New synthesis route to grow $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (2212) ribbon-shaped films has been developed. The ribbon-shaped films have been grown under ambient pressure from 2212 powder material on a silver substrate by so called "partial melt and slow cooling" heat treatment procedure. The ribbons are extremely thin and stuck firmly to the silver substrates. The ribbon-like films showed superconducting transition with the onset temperature of about 80 K.

Recrystallization of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ films accompanying *in-plane* crystalline rotation.

In order to keep better surface morphology and *in-plane* orientation, thin films of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (2212) and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (2223) were deposited by pulsed laser ablation onto MgO (100) and LaAlO₃ (100) single crystal substrates at temperature about 50–100 K lower than the decomposition point of 2212 or 2223 phases. To get the effect of *ex-situ* annealing on the *in-plane* orientation and T_c , the films were accurately post-annealed in oxygen potential controlled furnace. The results showed that the T_c of the annealing films reached to 75–80 K depending on the *in-situ* substrate temperature before annealing. The annealed 2223 films showed homogeneous intergrowth mixing of 2212 phase by 10–20% and showed the T_c at 100–105 K.

We found that the *in-plane* orientation of the 2212 films on MgO (100) substrates depends on the substrate temperature during deposition. The films deposited at higher substrate temperature have either 2212[100]//MgO[100] $\pm 11^\circ$ and 2212[100]//MgO[100] relation or 2212[100]//MgO[100] $\pm 11^\circ$. While the film deposited at lower substrate temperature showed only the 2212[100]//MgO[100] $\pm 11^\circ$ epitaxial relation. After annealing, the *in-plane* direction completely rotated by 45° , and only the 2212 [100]//MgO[100] epitaxial relation became observable. On the other hand, from the films deposited on

LaAlO₃ substrate, only the strong 2212[100]//LaAlO₃[100] *in-plane* epitaxial relation was observed independent of the substrate temperature and post-annealing.

Atomically layer-by-layer deposition

Superlattice films of bismuth-based oxide superconductors, for instance

Bi₂Sr₂Ca₃Cu₄O₁₂/Bi₂Sr₂Ca₁Cu₂O₈ and Bi₂Sr₂Ca₄Cu₅O₁₄/Bi₂Sr₂CuO₆, have been synthesized by sequential sputtering of bismuth-oxide, strontium-copper-oxide and calcium-copper-oxide monolayers. Crystal structures, superconducting transition temperatures and hole concentration of the films were studied by x-ray diffraction, Meissner effect and Hall effect measurements. It was observed that the superconducting transition temperatures were enhanced by forming superlattice films of over doped (Bi₂Sr₂Ca₁Cu₂O₈, Bi₂Sr₂CuO₆) and under doped (Bi₂Sr₂Ca₃Cu₄O₁₂, Bi₂Sr₂Ca₄Cu₅O₁₄) phases. The results can be understood by stress induced changes in the hole concentration between the over and the under doped phases derived from the epitaxial formation of the superlattice films.

Keywords : high- T_c , superconductor, thin film, annealing, pulsed laser ablation, layer-by-layer growth, Bi₂Sr₂Ca_{n-1}Cu_nO_{2n+4+δ}, intergrowth, lattice mismatch, surface morphology, *in-plane* orientation

50 Title : High-Resolution Real-Time Investigation on Defect Formation Processes under Surface-and Interface-reactions

M. Kitajima, K. Ishioka, A. Nakamura (Itakura), and M. Hase, 2nd Research Group-mail : kitajima@nrim.go.jp, T. Hirano, M. Demura, Mechanical Properties Division. [April 1999 to March 2004]

A control of reaction at the atomic level on the solid surface and/or film/substrate interface is essential for developing materials with higher quality and microscopic devices. This study is to elucidate kinetics and dynamics on reactions of ions, neutral atoms and plasmas with solid materials. There are two main targets in this study :

1) Using a pump/probe technique with ultrashort pulse laser, we are going to develop an equipment for observation of lattice vibration on a time scale of 10 -100 fs. This could give us direct information to understand lattice dynamics for defect formation and carrier excitation in damaged materials. The coherent phonons of Bi having a slow vibrational motion are being observed. We also discuss the relation of the dynamic information, such as decay

time, amplitude and phase, with static structure of defects.

2) We are also going to measure the mechanical properties of Ni₃Al bicrystal specimens in hydrogen ion and hydrogen plasma environments, in order to examine the effect at interface defects induced by hydrogen atoms from a viewpoint of kinetics. An equipment for the in situ measurements of the mechanical properties is now being designed. Methods of detection of changes in surface mechanical properties will be also studied.

Keywords : defect, ultrashort pulse laser, coherent phonons, hydrogen

Related papers

“Effects of crystal disorder on the molecular hydrogen formation in silicon”, M. Kitajima, K. Ishioka, S. Tateishi, K. Nakanoya, N. Fukata, K. Murakami, S. Fujimura, S. Hishita, M. Komatsu and H. Haneda, Mater. Sci. Eng. B58, 13 (1999).

“Effect of ion irradiation on coherent phonon dynamics in bismuth”, K. Ishioka, K. Ushida, K.G. Nakamura, S. Hishita and M. Kitajima, Jpn. J. Appl. Phys. 38, L446 (1999).

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

J. Nagakawa, Y. Murase, N. Yamamoto, Y. Fukuzawa and K. Yagi, 2nd Research Group K. Fukutomi 1st Research Group [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 significantly influence 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 nuclear materials to be used in the advanced nuclear energy sources like the fusion reactors and the next-generation light water reactors. Emphasis is placed on the understanding of deformation and fracture properties of the advanced materials under irradiation, and also on the development of new methods to suppress the radiation-induced degradation.

Damage by energetic particles causes atomic displacements 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 levels¹⁾.

It is, on the other hand, well known that a metal fatigue is one of the crucial mechanical properties to decide the life of structural components. We have revealed that the fatigue fracture is affected by the simultaneous irradiation and further by the additional radiation-induced creep in 316 stainless steel²⁾. The fatigue life, i.e., the number of cycles to failure, under irradiation with 17 MeV protons at 60°C was larger by several times than that of the thermal case in a load-controlled tensile-tensile fatigue of side-notched specimens. 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.

There are two stages where the significant irradiation-induced deformation can influence the fatigue phenomena. One is the crack initiation stage and the other is the crack propagation stage that follows the former. The latter stage is clearly affected by the irradiation as the crack propagation rate revealed by the spacing of the striation pattern, reflecting the crack propagation step made each cycle, is smaller under irradiation. In order to examine the effect of *in-situ* irradiation on the fatigue crack initiation, the Finite Element Analysis has been applied to the stress development at the notch-tip portion prior to the crack initiation in both irradiated and unirradiated conditions. The plastic deformation rate of the significant plastic creep under irradiation at 60°C was experimentally obtained and was included in the calculation. The results indicate that the development of stress localization in front of the crack-tip is slowed down due to the very active irradiation-induced deformation. However, the reduction is not particularly significant even after 3,000 cycles and it does not seem to make a large difference in the number of cycles to start a fatigue crack. This analysis appears to indicate that the delayed crack propagation may play a rather important role in the longer fatigue life under irradiation, together with the suppression effect of irradiation on the crack initiation.

Keywords : radiation damage, point defects, deformation, fatigue

Recent Publications

1. Theoretical and Experimental Study on the Significant Creep Deformation of SUS 316 Induced by Irradiation at 60°C, J. Nagakawa, Y. Murase, N. Yamamoto and Y. Fukuzawa, (to be published in the Proc. CFEMS-8).
2. Creep-Fatigue Response of 20%CW 316 SS under Irradiation at 60°C, Y. Murase, J. Nagakawa, N. Yamamoto and Y. Fukuzawa, (to be published in ASTM STP 1366).

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

N. Yamamoto, J. Nagakawa, Y. Murase and Y. Fukuzawa, 2nd Research Group
[April 1996 to March 2001]

Radio-activation of materials has been recognized as one of the most crucial issues in the field of nuclear fusion technology from the standpoint of waste management, environmental safety and public acceptance. The problem is much pronounced for first wall/blanket structural materials used in a prototype reactor and the beyond, due to large radiation doses of fusion neutrons. Since such heavy irradiation causes material deterioration in many cases, the development of radiation-resistant structural materials with low activation characteristics has been hence strongly demanded for the progress of fusion reactors. In order to contribute such material development, we have investigated the influence of nuclear transmutational elements on material integrity using accelerator irradiation technique with a primary concern on gaseous elements (helium and hydrogen) which are known to often induce severe grain boundary embrittlement.

The method of α -particle irradiation with a cyclotron was adopted to simulate neutronic generation of helium by (n, α) reactions in reactors. Through this technique, helium was implanted into a representative low activation martensitic steel, F 82 H (Fe-8 Cr-2 W-V, Ta), which had been selected as a reference material for a round-robin test organized by IEA (International Energy Agency). The implantation was carried out at 823 K, a desired high temperature limit of martensitic steels for fusion use. Creep tests were subsequently conducted at the same temperature on specimens containing 100 appmHe and 300 appmHe. Ruptured samples were fractographically examined to clarify the effect of helium on failure modes.

The creep rupture strength and elongation of 100

appmHe implanted samples were mostly identical to those of corresponding helium free control specimens. On the other hand, samples implanted with 300 appmHe showed roughly five times larger creep life in comparison with unirradiated references, while rupture elongation values of both sets again remained within a normal experimental error band. No degradation of rupture strain was therefore perceived up to 300 appmHe implantation. In addition, all the specimens including implanted and unimplanted ones ruptured perfectly in a transgranularly ductile fashion and any indication of grain boundary embrittlement caused by helium was not appreciated. These facts mean that this material, F 82 H, may withstand helium-induced mechanical degradation in the fusion reactor environment.

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

Recent Publications

Helium Embrittlement of Ti and P added Austenitic Alloys Crept at 923 K, N. Yamamoto, J. Nagakawa, Y. Murase and H. Shiraishi, *Fusion Engng. Des.* 41 (1998) 111-117.

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Effect of Combined Addition of Ti and P on Creep Rupture Properties of Helium Implanted Fe-25%Ni-15%Cr Alloy, N. Yamamoto, J. Nagakawa, Y. Murase and H. Shiraishi, *J. Nucl. Mater.* 258-263 (1998) 1634-1638.

An Evaluation on Helium Embrittlement Resistance of Low Activation Ferritic/Martensitic Steel F 82 H, N. Yamamoto, J. Nagakawa and K. Shiba (to be published in *J. Nucl. Sci. Technol.*).

Creep Rupture Properties of Helium Implanted Low Activation Martensitic Steel for Nuclear Fusion Application, N. Yamamoto, J. Nagakawa and K. Shiba (submitted to *Key Engng. Mater.*).

53 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 CO₂ 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 CO₂ laser is limited in emission of wavenumber as 931-956 cm⁻¹, 966-983 cm⁻¹, 1,033-1,057 cm⁻¹ and 1,069-1,085 cm⁻¹. If ¹²C or ¹⁶O is replaced by the other isotope such as ¹³C or ¹⁸O, then new emission lines appear due to the different stretching and bending modes of isotopic CO₂ from those of usual CO₂ gas.

In order to achieve the isotope laser, a closed-cycle CO₂ laser system is examined. It is necessary to use isotope CO₂ effectively because of its high cost. When the laser is emitted by discharge, isotope CO₂ is consumed with the reaction as



Then the catalyzer composed of CuO is installed in the circulation system to recombine CO and O₂ to return CO₂. 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 5-30 μm (333-2,000 cm⁻¹) and at 5 MW. The use of this laser also is being examined under the cooperation with the FOM institute and Los Alamos National Laboratory. The enrichment of silicon isotopes in the SiF₄ formed and residual Si₂F₆ was observed in 10, 12 and 25 μm absorption bands.

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_4 or Si_2F_6 gas to examine various physical properties of isotopically controlled silicon and its compounds. Silicon flake was deposited by a plasma CVD method. Natural SiF_4 gas was used to find the optimum condition of Si film formation prior to isotopically enriched gases. Microwave of 2.45 GHz with a power of $8.4 \times 10^{-4} \text{ Wm}^{-2}$ was applied to the gas at 13.3 Pa-266 Pa at a flow rate of 30-500 SCCM. Ar and H_2 are added as a plasma assisting and scavenging gases, respectively. The substrate temperature was kept at 523-873 K. The films formed were examined with SEM, XRD and weighed for measuring formation rates. 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 623-723 K. The maximum conversion efficiency from fluoro-silane to silicon metal was 28%.

Natural boron is composed of ^{10}B of 19.9% and ^{11}B of 80.1%. Since relative mass difference between ^{10}B and ^{11}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}B and 99% ^{11}B powders. After isostatically pressed to a cylindrical shape under hydrostatic pressure of 2,000 kgW/cm², the isotopic boron powders were sintered in a vacuum at 1,873 K. The sintered rod was then zone melted on the seed crystal under flowing Ar gas. Finally isotope boron single crystals with a size of 10 mm ϕ \times 40 mm could be formed (see photo 1). 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}B , 99% ^{11}B and natural boron (19.9% ^{10}B and 80.1% ^{11}B).

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

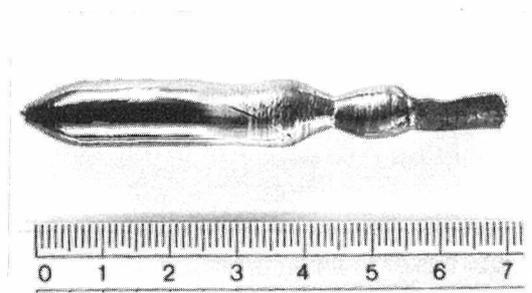


Photo. 1 β -Boron single crystal enriched with 99% ^{10}B .

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. FENDL 2.1 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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54 Research on Utilization Technique of "Data-Free-Way" System for Nuclear Materials

M. Fujita, J. Kinugawa, T. Noda and K. Yagi, 2nd Research Group

[April 1995 to March 2001]

Material information system having huge database and effective computer aided tools is 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 Japan Nuclear Cycle Development Institute (JNC) with different special field, the pilot distributed database system for development of nuclear materials called "Data-Free-Way (DFW)" has been built since 1990. The project on the second stage was started in 1995 under collaboration among NRIM, JAERI, JNC and Japan Science and Technology Corporation (JST). The aim of this project are to store the data in the database and to develop useful computer utilized tool for data analysis and simulation codes from various phenomena under irradiation environments.

The method of the connection among the database of each organization in DFW system changed from private line to the Internet. Using tools used in the Internet, users can easily refer to any necessary information by accessing to the fore database with WWW browser without taking account of in which database site the required data exit. The final target of the usage of the WWW for the present study will be the development of a data information system for designing and selecting nuclear materials.

Some trails of the WWW server of each sites in DFW to supply the information on nuclear materials are introduced. Several databases and tools for the system are provided in the WWW of the NRIM site (<http://inaba.nrim.go.jp/>), which has main functions of material database, on-line simulator and remote experiment. Databases consist of DFW, transmutation under neutron irradiation and decay, diffusion information in Iron or Aluminum matrix, Ni superalloy properties, CCT diagram for welding, SiCf/SiC composite materials. The compositional simulators are prediction of the chemical changes and radioactivation under neutron transmutation, evaluation of mechanical properties at high temperature in Ni-base super-alloys and calculation of welding heat cycle. Moreover, between NRIM and Staatliche Materialprüfungsanstalt (MPA) Stuttgart was discussed to exchange mutually the material information using DFW system in 1998 German-Japanese Workshop on Chemical Information at Karlsruhe on the programing of German-Japanese Meeting of the Panel for Information and Documentation.

Keywords : Data-Free-Way, distributed database, advanced nuclear materials, data share, simulator, remote experiment

55 Microstructure Control and Mechanical Property of Intermetallic Alloys in Ti-Al System

K. Hashimoto, 3rd Research Group

[April 1997 to March 2001]

The mechanical properties of intermetallic alloys change drastically with microstructure. Thus the microstructure control is a key to improve the mechanical properties and/or to decrease the manufacturing cost for practical use. Among them, γ -TiAl based alloys have been paid considerable attention in recent years from automotive industry as a potential material for making rotating and reciprocating components to produce a more efficient engine. Although titanium trialuminide alloys exhibit brittle fracture at ambient temperature, the alloys are also promising materials for high temperature applications. Thus the ductility improvement of the alloys is one of the most important problems for practical use.

To examine the effect of compositions and deformation processing on the microstructure and deformability of γ -base alloys with compositions of Ti-(37-44 at %) Al-(3-9 at %) Cr, the alloy ingots were produced by vacuum induction melting. The ingots were cut into tetrahedral blocks and homogenized at 1,273 K for 604.8 ks. All of the blocks were isothermally forged in three steps. At the first-step they were deformed to 50% at 1,473 K under strain rate of 10^{-3}s^{-1} . At the second- and third-steps, they were deformed to 50% at 1,473 K and 1,273 K under strain rate of 10^{-3}s^{-1} , respectively, in such a way that their forging directions became perpendicular from each other. The tensile test for the forged alloys was carried out in a temperature range of 1,223-1,473 K and in a strain rate range of 10^{-2} - 10^{-4}s^{-1} . The forged alloy with fine spherical shaped γ and α_2 phases in the β phase matrix has exhibited superplastic elongation of 1,100% at 1,273 K and it also exhibited the elongation of more than 300% even at a high strain rate of 10^{-2}s^{-1} . Meanwhile, the effect of heat treatment on the microstructure of Ti-48 at % Al-3.5 at % Cr has been examined by changing cooling-rate during phase transition from α single phase region to the $\alpha+\gamma$ two phase region. Transmission electron microscopy revealed that a feathery microstructure is composed of lamellar colonies (5-10 μm), which are crystallographically tilted slightly with their neighbors, and can be produced through a simple slow-cooling.

The phase, structure and composition of L 1₂-type titanium trialuminide (AlMn)₃Ti-X (X=Zr, V, Ag, Ga) alloys heat-treated at 1,450 K have been studied by X-ray diffraction and electron probe microanalysis. From the microstructure analysis, the L 1₂-type {(AlMn)₃Ti}_(n-1)-X_n single phase region was shown in the quaternary phase diagram. For those alloys, the minimum load for crack initiation during hardness measurements has been examined by optical and scanning electron microscopy after hardness tests and the residual strain which was induced during milling of the alloy into powder has been examined by X-ray diffraction analysis. The residual strain exhibited a positive correlation with the minimum load. The quaternary alloys containing V showed the maximum value of the residual strain. In the ternary alloys the relatively high residual strain was obtained in the vicinity of the center of Al and Mn-rich corner of the single phase region. To examine the effect of V addition on the ductility of the L 1₂-type (AlMn)₃Ti alloys, the alloys with addition of V from 4 to 7 at % have been examined by three-point bend testing. The V addition up to 6 at % increased the tensile strain in the tension surface of the bend test specimen.

Keywords : intermetallics, gamma-titanium aluminide, L 1₂-type titanium trialuminide, superplasticity, room temperature ductility

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56 Development of Light Weigfht High Strength Ti₂AlNb Titanium Intermetallic Alloy

M. Hagiwara, Third Research Group

[April 1999 to March 2003]

The ordered orthorhombic Ti₂AlNb (O-phase)-based titanium intermetallic alloys are considered as potential materials for aircraft engine applications due to their higher room temperature strength, ductility and fracture toughness than conventional Ti₃Al (α₂) and TiAl (γ) alloys. Among various Ti₂AlNb-based alloys, two phase O+β₀ (B2 type ordered phase) alloys such as Ti-22 Al-27 Nb are said to have the best balance of tensile, creep and fracture toughness. One main drawback of these Ti₂AlNb-based alloys is that the service temperature is limited to 750°C due to a degradation of tensile strength, creep resistance, thermal stability and environmental resistance. Moreover, they exhibit lower elastic modulus and higher density compared to those for α₂ and γ alloys.

The objective of the present research project is to develop advanced light weight Ti₂AlNb-based alloys having superior combinations of mechanical properties in the temperature range up to 1,000°C by the compositional and microstructural modification and the homogenous dispersion of fine ceramic particulate such as TiB and Er₂O₃.

So far, we have examined in a systematic way the change of density and elastic modulus in a Ti-22 Al-27 Nb alloy upon substituting other transition elements such as Mo, W and V for a part of Nb. This compositional modification was based on achieving a same beta stability as a Ti-22 Al-27 Nb alloy. According to the literatures, the beta phase stabilizing tendency of Mo, W and V is 3.60, 1.44 and 2.4 times stronger, respectively, than that of Nb, which means that one percent addition of Mo, W and V corresponds to the replacement of the 3.60, 1.44 and 2.4 percent of Nb, respectively. Using this guideline, various compositionally modified alloys such as Ti-22 Al-11 Nb-4 Mo, Ti-22 Al-14 Nb-4 W and Ti-22 Al-21 Nb-4 V have been newly developed. The high temperature mechanical properties such as creep and low cycle fatigue are now being evaluated for these modified alloys.

Keywords : titanium intermetallics, particulate composites, powder metallurgy, microstructure, mechanical properties

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57 Development of Basic Superconducting Technology for High Field Micro-SMES

K. Inoue, Y. Yoshida, Y. Iijima and A. Kikuchi, 4th 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 (compact 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 Nb³Sn wires for high fields. Although Nb₃Sn, Nb₃Ge, Nb₃Ga, 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} (4.2 K)'s than that of Nb₃Sn. Recently we found that the Nb₃Al multifilamentary wire, fabricated through the rapid-heat, quench, and transformation (RHQT) process, showed not only 2-5 times larger J_c in high fields than that of the commercialized Nb₃Sn multifilamentary wire but also 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, and improvements of superconducting properties for the Nb₃Al 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 studied the Ge addition to the Nb₃Al multifilamentary wire, which improved remarkably not only T_c from 17.9 K to 19.4 K, but also H_{c2} (4.2 K) from 26.2 T to 40 T, but drastically reduced J_c (4.2

K). On the hand the Mg addition to the Nb₃Al multifilamentary wire reduced T_c from 17.9 K to 17.4 K, but increased H_{c2} (4.2 K) from 26.2 K to 27.3 K with improving J_c (4.2 K) a little. The additional effects of Ge and Mg to the Nb₃Al wire should be studied in more detail.

For stabilizing the superconductivity of Nb₃Al wire, we studied pure-Cu coating on the wire. At first we tried Cu-electroplating on the Nb₃Al wire rapidly-heated/quenched. However, the firm Nb oxide layer on the Nb surface, which has large electrical resistance and thermal one, prevent the stabilization of the Nb₃Al wire. Therefore we studied Cu-ion plating on the Nb₃Al wire in the next step. We found that the Cu-ion plating with thicker than 1 μm in thickness removed the Nb oxide layer efficaciously, and prevented the reformation of oxide layer on the Nb surface. We found that Cu-electroplating after Cu-ion plating on the Nb₃Al wires stabilized their superconductivity remarkably.

In collaboration with Nippon Keiki Works, Ltd. and Mitsui Mining & Smelting, Co. Ltd., we fabricated a large-scaled superconducting Bi-2223 magnetic shield through plasma spraying. In a large zero-field chamber surrounded by the magnetic shield, we have succeeded in measuring the magnetic pulsed fields caused by human brain activities. These measurements will be very promising for understanding the brain activities and medical examination of brain disease. However, the Bi-2223 shield is not so effective to shield the high leakage fields produced by SMES, because of its low irreversible field at 77 K.

The current lead, transporting current from an ac-dc converter at room temperature to a superconducting magnet at cryogenic temperature in the SMES, must be high conductive for current, and low conductive for heat. In many oxide superconductors, Y-123 film is the most promising material for the current lead in SMES, because of its high J_c (77 K) in high fields. However, only Y-123 films with good similarity among crystal orientations show high J_c. We studied on the fabrication process of Ni substrates with similarity among crystal orientations for using them the substrates of Y-123 films.

Keywords : Nb₃Al, Bi-2223, Rapid-Heat, Quench, Transformation, J_c, Superconducting Shield, Current Lead.

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58 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 α and electric conductivity σ and low thermal conductivity κ . 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 η 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.

The properties of unidirectionally solidified p-type AgSbTe₂ and Ag_{0.208}Sb_{0.225}Te_{0.517} boules have been evaluated to develop FGM with complex structure of Ag₂Te and Sb₂Te₃. The boules 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 Ag₂Te 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 AgSbTe₂ above 633 K revealed its high potential of power generation. The effective maximum power of Ag_{0.208}Sb_{0.225}Te_{0.517} boule was four times as large as that of AgSbTe₂ at a temperature difference of 350 K and also equaled that of the segmented Pb_{1-x}Sn_x newly developed. These results suggest that there is a high possibility to realize superior FGM by controlling structure and composition.

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

Related Paper

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

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[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 automatic equipment has been introduced in order to characterize the alloys for hydrogen storage. Pressure-composition isotherms for four distinct samples can be obtained at a time by this equipment. Characterizations of the Mg-Ni-X 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 503 K. Thickness of membrane specimens was ranged from 0.6 to 3 mm. For thicker specimens (thickness > 2 mm), the permeation process was rate-controlled by the diffusion of hydrogen in bulk magnesium. The diffusion coefficient was determined to be : $D = 1.54 \times 10^{-6} \exp(-24,100/RT)$ in $\text{m}^2 \cdot \text{s}^{-1}$. The steady state hydrogen permeability was determined to be : $\Phi_{ss} = 2.77 \times 10^{-7} \exp(-35,700/RT)$ in $\text{mol of H}_2 \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1/2}$. D and Φ_{ss} were independent of applied hydrogen pressures, suggest-

ing that D is independent of hydrogen content and the solubility of hydrogen obeys Sieverts law. We believe that the present data are the first data on hydrogen diffusion coefficient in pure magnesium, determined by a dynamic method.

This research is performed in collaboration with Japan Science and Technology Corporation, Science University of Tokyo, and Ibaraki University.

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

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60 Development and Total Evaluation of Advanced Metallic Membranes for Hydrogen Purification

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[April 1999 to March 2004]

Purity of hydrogen gas affects the lifetime of fuel batteries and hydrogen storage alloys, which play key roles in hydrogen-related energy conversion. So, production of high purity hydrogen-gas is an important technical matter associated with energy and environment problems for the future. Palladium-silver (Pd-Ag) alloy membranes have been used for decades to provide hydrogen gas of 99.99999% purity or more, mainly for semiconductor manufacture and laboratory use. However, Pd-Ag alloy has two shortcomings : (1) palladium is as expensive as platinum, (2) and hydrogen permeability of the alloy is insufficient at lower temperatures. Thus, Pd-Ag alloy has not been used for large-scale hydrogen

purification.

Vanadium is one of the most hydrogen-permeable metals, because of its high hydrogen diffusivity and solubility. The intrinsic hydrogen permeability of vanadium is much higher than that of Pd-Ag alloy. Vanadium has, however, not been recognized as a possible membrane material for hydrogen purification; hydrogen embrittlement and surface problems have precluded the application of vanadium to the membrane material. We have searched alloying elements to eliminate the hydrogen embrittlement problem without reducing the high hydrogen permeability of vanadium, significantly. We have found that addition of 10 to 30 mol% of nickel, cobalt and molybdenum is effective. We showed that Pd-coated disks of V-Ni, V-Co and V-Mo alloys kept a high hydrogen permeability even at a low temperature of 473 K, and showed a good resistance to the hydrogen-induced cracking during a run of the permeation test [1-3]. We have proposed Pd-coated membranes of V-15 Ni alloy as a promising candidate for new hydrogen-purification membranes.

From 1999, we have started a project to establish the technical fundamentals for the practical application of vanadium alloys to hydrogen purification membranes. Investigations have been started to develop vanadium alloy membranes having high performance and good durability. At the beginning, we have investigated the effect of thinning on the hydrogen permeation characteristics of Pd-coated alloy membranes. There was no difference in steady-state hydrogen-permeability for 1 mm thick membrane and 0.1 mm thick membrane, suggesting possible achievement of high performance for hydrogen purification, inversely proportional to the membrane thickness. We have also checked the durability of Pd-coated V-15 Ni alloy membrane. After a continuous permeation test at 573 K for two weeks, the membrane showed little (2%) decrease in hydrogen permeability. The permeability has been completely recovered by a baking treatment.

Keywords : hydrogen, vanadium, permeation, purification, membrane

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Recent Publications

Hydrogen Permeation through Magnesium, C. Nishimura, M. Komaki and M. Amano, (to be published in J. Alloys and Compounds).

61 Investigation of New Nonlinear Optical Crystals for Wavelength Modulation, Single Crystal Growth and Principle Technology Development for Optical Devices

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[April 1997 to March 2001]

Single crystals of nonlinear optical materials are important for frequency modulation devices. It is usually required for this purpose that single crystals should have crystal asymmetry. However, it is generally difficult to grow single crystals, which have crystal asymmetry, even if new materials are discovered. It would be possible to make an asymmetric part in micro-scale, even single crystals which have crystal symmetry. The method is a substitution of the small constituent element for another large element to form an asymmetry in surroundings of a pair of the large and small elements. In this work, single crystals of these materials, which have crystal asymmetry, are grown by the Czochralski method and the floating zone pulling down method. Furthermore, optical properties of the crystals, such as a refractive index and a harmonic generation, are evaluated using the single crystals grown.

In this year, single crystals of BaB₂O₄ substituted Al for B, such as Ba (B_{1-x}Al_x)₂O₄, were grown by a new double ring-shape halogen lamp floating zone pulling down method (Fz-PD). Transparent single crystals with 1 mm ϕ \times 20 mm could be grown by this method up to 0.05 of x despite the single crystals grown by the Czochralski method were opaque. The crystal transparency of the Ba (B_{1-x}Al_x)₂O₄ was depends on the crystal diameter, and was summarized as shown in Fig. 1. Their nonlinear optical properties, such as a SHG (second harmonic generation) intensity, were superior to the BaB₂O₄. We think one of the reasons that the crystal asymmetry is emphasized by the substitution in micro-scale.

On the other hand, it is important to study an origin of the SHG because its data is useful to investigate new oxides for the SHG. Therefore, we are studying the origin of the SHG on single crystals of the BaB₂O₄ substituted Al for B from the viewpoints of a refractive index and a dielectric constant. We expect that the refractive index and the dielectric constant will be increased by the substitution.

For the application of the BaB_2O_4 substituted Al for B, it is important to fabricate an optical waveguide structure. It is required for the optical waveguide that the refractive index of a core part is larger than that of a matrix part. The refractive index is increased by the substitution. Therefore, it is possible to fabricate the waveguide by means of the $\text{Ba}(\text{B}_{1-x}\text{Al}_x)_2\text{O}_4$ on the BaB_2O_4 structure. Fig. 2 shows a SHG image radiated Nd : YAG laser to the trial waveguide fabricated by a reaction diffusion method using the BaB_2O_4 single crystal and the BaAl_2O_4 crystal.

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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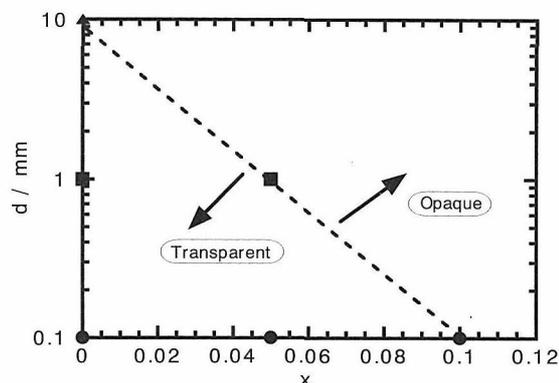


Fig. 1 Crystal state as a transparent or an opaque depending on crystal diameter, d , and Al content, x , on $\text{Ba}(\text{B}_{1-x}\text{Al}_x)_2\text{O}_4$.

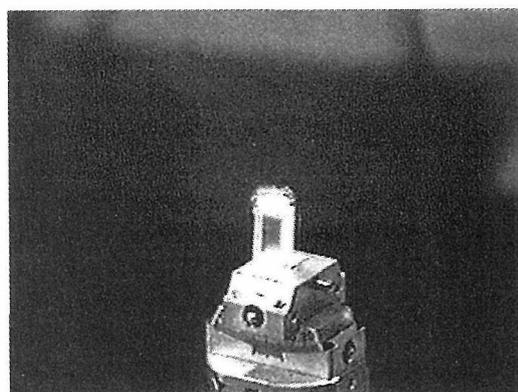


Fig. 2 SHG image radiated Nd : YAG laser to a crystal fabricated with a trial waveguide.

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62 Research on Surface Modification by Plasma Source Ion Implantation

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[April 1998 to March 2001]

Implantation of accelerated ions into a surface layer of a material causes compositional and microstructural changes in atomic scale. Therefore, materials which are unable to be synthesized in thermal equilibrium are created by the ion implantation method. In this study, surface modification of materials by a new ion implantation method called plasma-source ion-implantation will be performed. Further, surface layers of innovative materials such as C_3N_4 , Bi-based high temperature superconductor, and modified layer on TiAl-based materials will be synthesized using a conventional beam-line ion-implantation method and characterized.

The plasma-source ion-implantation is a new ion-implantation method by which materials are immersed in plasma and implanted with positive ions accelerated by negative high voltage pulses. This

method has characteristics that all the surfaces of three-dimensional material are able to be ion-implanted simultaneously, while conventional beam-line method only implant ions from one side of the materials.

A high voltage pulse generator for plasma-source ion-implantation was constructed. Fig. 1 shows the pulse circuit and the experimental apparatus schematically. High-voltage and high-current pulses were generated using a dc high-voltage generator and a tetrode (4PR1000A) as a switching device of the high voltage. The pulse voltage was -5 kV to -20 kV , maximum current was 1 A , pulse width was 10 to $20\mu\text{s}$ and the pulse repetition frequency was 100 to 1000 Hz . The rise time of the pulse was $0.5\mu\text{s}$, the decay time was $1.5\mu\text{s}$, and the pulse-voltage deviation was 0.7% , when a load resistance of $20\text{ k}\Omega$ was connected to the output terminal. The plasma was generated using a radio frequency generator (13.56 MHz , 300 W), in a magnetron sputtering apparatus, by applying a radio frequency power to a substrate terminal. The high voltage pulses were introduced through a high-voltage feed-through. The electrode of the feed-through in the vacuum chamber was insulated with a glass tube except the tip, and a small sample was attached to the tip of the electrode.

Preliminary experiments using a mixed gas of Ar and C_2H_2 showed that when the gas pressure was 0.1 to 1 Pa , plasma spread throughout the entire chamber and the condition was favorable for usual plasma source ion implantation. On the other hand, when the gas pressure was higher, plasma was localized around the substrate terminal of the sputtering apparatus and did not reach to the sample. However, in the case of the latter, another localized plasma was generated which enveloped the sample and the electrode-tip of the feed-through by the pulse voltage. It may be probable that the second plasma will be used for plasma ion implantation into small complex-shaped three-dimensional material that is hard to implant even by the usual plasma ion implantation.

Recently, research on carbon-base materials has progressed, and ultra-hard films such as DLC (Diamond Like Carbon) and c-BN (cubic boron nitride) have been developed as a new wear resistant coating material. Especially, $\beta\text{-C}_3\text{N}_4$ (hexagonal carbon nitride) is noticed. The value (427 GPa) of the bulk modulus of $\beta\text{-C}_3\text{N}_4$ is equivalent to value (435 GPa) of diamond. Ion assisted deposition and reactive sputtering method, etc. have been used as synthesizing methods of $\beta\text{-C}_3\text{N}_4$. However, the hardness has been $\sim 60\text{ Gpa}$, and the synthesis of the C-N crystal has not been achieved yet. $\alpha\text{-C}_3\text{N}_4$ (trigonal carbon nitride) has seemed to be formed in most films in these cases, since $\alpha\text{-C}_3\text{N}_4$ is energetically more stable than

$\beta\text{-C}_3\text{N}_4$. Therefore, the synthesis of $\beta\text{-C}_3\text{N}_4$ was tried using ion-implantation technique in the non-equilibrium state. First, carbon films were prepared using RF magnetron sputtering. Then, nitrogen ions were injected into the films in order to synthesize $\beta\text{-C}_3\text{N}_4$ by an ion implantation method. However, clear evidence of $\beta\text{-C}_3\text{N}_4$ phase has not been obtained yet. In the future, we need to establish identification methods of product materials and the way of measuring hardness.

Measurements of critical magnetic field of Bi-base high-temperature super-conducting films were also conducted using a superconducting magnet, and effects of ion implantation into the films on critical magnetic field were investigated.

New wear-resistant materials of TiAl complex alloys were also investigated. TiAl shows higher wear resistance than the ordinal metals. However, lower surface hardness restricted use of TiAl as wear-resistant substance especially for low friction velocities. Matrix of TiAl complex alloys was strengthened by SiC or TiC particles. Furthermore, hard surface layers of TiN and Ti_2AlN are formed by N ion implantation.

Key words : plasma source ion implantation, high voltage pulse, C_3N_4 , TiAl

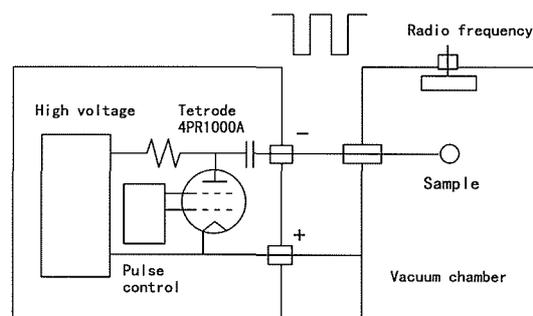


Fig. 1 Experimental Apparatus of a plasma source ion implantation.

63 Research on Quantum Magnetic Properties and Spinic Functions of Mesoscopic Magnetic Matetials

I. Natatani, T. Furubayashi and H. Mamiya, 4th Group 3rd Sub-group

[From April 1996 to March 2003]

The objective of the project is to explore the basic research, technology, and applications of novel magnetic materials with mesoscopic sizes. In all sort of fundamental phenomena on magnetism, there exist corresponding characteristic length, e.g. distance of exchange interaction, distance of magnetic dipole interaction, magnetic domain size, spin diffusion length, and so on. The project includes three types

of magnetic materials with mesoscopic sizes of dimensions in around 100 nm, 10 nm and 1 nm regime, respectively. This work has two main components.

First, there is the exploration of fabrication method for the following three types of mesoscopic magnetic materials. These are nanostructures of ferromagnetic substances fabricated by an electron-beam nanolithography into dimensions of several hundreds nm or sub-100 nm, magnetic colloids (magnetic fluids) of ferromagnetic ion-nitride particles of sub-10 nm in diameter dispersed in liquids of mineral oils, and nanogranular magnetic materials that ferromagnetic fine particles with several nm or 1 nm in size are embedded in solid matrix of insulator.

Second, there is the challenge that one can explore mesoscopic magnetic phenomena, from classical to the quantum limit. Although its roots are in the quantum description of solids, new fabrication techniques for sophisticated materials described above allow to making widespread studies of the phenomenon and the development of device applications.

Keywords : ferromagnetic material, electron-beam lithography, micro fabrication, magnetic fluid, nanogranular magnetic material

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64 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 micro-machines such as micromanipulators and fluid micro-valves. 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. We also succeeded in evaluating the mechanical properties, including yield stress and elongation, of sputter deposited thin films. The mechanical test showed that a sputter-deposited thin film of Ti-50 at.% Ni exhibits 40 percent elongation before fracture. These results prove that sputter-deposited thin films of Ti-Ni possess stable shape memory effect and reliable mechanical properties for practical applications. However, it is likely that film thickness affects various properties such as shape memory effect and mechanical properties. We investigated, therefore, the effect of film thickness on shape memory behavior. Ti-50 at.% Ni thin films with various thicknesses of 0.5, 1, 3, 5, 7 μ m were prepared by magnetron sputtering. The shape memory effect of these films was evaluated at stresses of 100 MPa and 200 MPa. Figure 1 shows the transformation and plastic strains obtained at 100 MPa. It was found that these strains show the

maximum values at a thickness of $2\mu\text{m}$. This result can be explained by the microstructure of a $2\mu\text{m}$ thick film. Transmission electron microscopy showed that this film has a bamboo structure. The transformation temperatures were constant at thicknesses of more than $2\mu\text{m}$, but decreased with thickness if the thickness is less than $2\mu\text{m}$. The decrease in transformation temperatures is attributable to oxidation of a Ti-Ni film which seems to occur during oxidation. These results indicate that the effect of film thickness can not be ignored in a thin film with a thickness of less than $2\mu\text{m}$. The film thickness is also likely to affect the mechanical properties of sputter-deposited Ti-Ni thin films. This evaluation will be carried out soon. In order to apply a shape memory thin film to practical use, further studies including fabrication process are clearly needed. In our laboratory such investigations are under way. It is believed that microactuators with shape memory thin films are becoming increasingly feasible.

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

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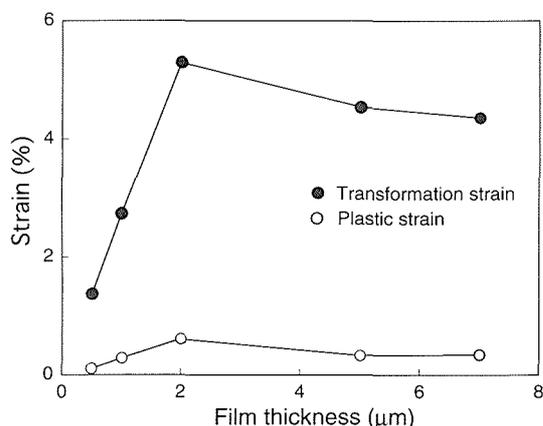


Fig. 1 Transformation and plastic strains of a Ti-50 at. % Ni thin film at a stress of 100 MPa.

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

Background

Research on intelligent materials is one of the most important frontiers in the material science. The intelligent materials are the materials which have systematized and cooperative functions. They work as mechanical parts or electronic devices.

We proposed a particle assemblage to create intelligent materials. We must give materials multiple functions and make the functions work coactively. 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 micrometer 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.

Integration methods of particles

Each of three methods 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 or more 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.

The ordered mixture of composite particles and another kind of particles can be fabricated by repeating the process.

Using this method, new PTC materials are developed. A packed bed of semiconducting 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 BaTiO₃ 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 BaTiO₃ particles remove the high contact resistance. It opens the door to the shape free forming of ceramics.

Furthermore, the resistance of the ordered mixture of PTC particles, NTC particles and In particles showed "V"-type dependence on the temperature. It is an example of the integration of functions by the particle assemblage.

The second one is a particle manipulation using a microprobe. 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.

Particles of less than 100 μm on a metallic substrate can be adsorbed to the tip of the probe by applying voltage between the probe and the substrate. The probe can, therefore, carries the particle to any positions on the substrate. Furthermore, the metallic particle can be welded by applying high voltage so as to make the glow discharge. It is shown that two-step discharge makes a tough bond between the particle and the substrate. High voltage of about 10 kV is applied to the probe in touch with the particle. The probe is lifted up for about 50 μm, and 2 kV is applied again to the probe.

Five metallic particles were stacked and welded by the probe system as an example of three dimensional microstructures.

The third 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 process is as follows. An electrified pattern is drawn on insulating substrates by irradiation of an electron beam or an ion beam. A suspension is prepared from the particles to be arranged and an inert non-polar solvent. The substrate is dipped into the suspension for about 30 seconds. Since the particles are attracted to the electrified pattern by the electrostatic force in the suspension, they are arranged as the electrified pattern.

Silica particles of 5 μm can be arranged on a electrified line. The line composed of the particles is about 30 μm wide. The arranged particles are fixed by a heat treatment or by a coating treatment. The fixing is necessary to repeat the above arranging process for the fabrication of three dimensional microstructures.

Keywords : Intelligent materials, multiple functions, particle assemblage

66 Preparation of Ion Conductors by Pressurization

H. Nakamura, Team of Director of Special Research

[April 1998 to March 2000]

There have been many examples of research related to solid electrolytes which use various ion conductors found in oxide ceramics ; some of these electrolytes have been put into practical use as oxygen sensors. In order to obtain real-time measurements of the chemical species characteristic using solid electrolytes, it is necessary to synthesize solidified high-ion conductors related to these species. However, many if not most of the compounds of chemical species related to air pollutants break down easily at high temperatures, so there has been no attempt to synthesize complex compounds that can indicate ion conductivity.

In this study, pressurized baking was used to suppress the breakdown of otherwise easily degradable compounds (such as nitrates) for synthesis. This made it possible to increase the types of solid electrolytes derived from complex compounds that can indicate ion conductivity, so electric conductivity was high at relatively low temperatures. The purpose of this study is to produce solid electrolytes for selectively classifying and quantitatively measuring corrosive gases.

Keywords : ionic conductor, solid electrolyte, charge carrier, electrical conductivity

67 Enhanced Durability of Structural Steels in Marine Environment

T. Kodama,

[April 1997 to March 2001]

Among structural steels for the use of marine environment we have concentrated our effort on the development of stainless steels and coatings that show corrosion resistance in splash zone, and low alloy weathering steels for marine atmosphere use. In the case of stainless steels, its performance in seawater was evaluated by the tendency to localized corrosion tests since it is more serious problem than general corrosion. In the latter case it is thought to be most advantageous to develop in advance acceleration tests that simulate actual atmospheric corrosion process and are capable of differentiating the cor-

rosivity of steels in marine atmosphere. Several candidate elements for alloying are proposed for new weathering steels using a new acceleration test. This method is extended for standardization and is expected to reduce the evaluation time for the development of new steels.

Materials Creation Studies

In the creation of new stainless steels highly resistant to marine corrosion, we have placed focus on the structural cleanliness and nitrogen addition. For obtaining the cleanest structure a levitation smelting by means of a cold crucible technique was used. The enhancement of corrosion resistance by nitrogen addition was motivated from the preservation of less common metals such as Ni, Cr or Mo and the development of fully austenitic, resource-saving steels with the minimum addition of Ni. In this case as a starting and referencing material we used 316L type steel, to which nitrogen was added by various methods. Conventionally nitrogen enrichment has been carried out at normal pressure by simultaneous melting of Mn with solid nitrides. Usually 16 to 20% of Mn is added simultaneously for this purpose, since Mn reduces activity of nitrogen in stainless steel melt. Additional process for N-enrichment was gas diffusion, in which high-pure 316L sheet of 2 mm thick is heated in flowing nitrogen gas for 24 hrs at 1200°C. Fig. 1 shows change in pitting potential as a function of nitrogen content both for high and very low Mn contents of N-bearing steels. Evidently pitting potential shifts in nobler direction with an increase in N content and is also influenced by Mn content. The deteriorated pitting resistance is partly because of the increased amount of non-metallic inclusions and partly because of the deteriorated protectiveness of passive film. The results suggest that the corrosion resistance of nitrogen addition is the most effective when structural purification is attained to extreme level. For this purpose we investigate cold-crucible method for small-scale production and pressure electroslag refining (PESR) production. By the latter method the nitrogen enrichment and inclusion removal are attained simultaneously.

Surface Coating

Spray coating technology gives a promising technique for the production of corrosion-resistant materials, where our goal is to develop a spray coating method that may substitute the titanium cladding. We employed high velocity oxy-fuel (HVOF) spray method that generates high velocity to particles to be sprayed at relatively low temperature resulting in the formation of pore-free film with improved adherence. Particles of stainless steels and nickel base alloys were sprayed on carbon steels to form corrosion resistant coatings by means of HVOF. For comparison also plasma spray was employed. Fig. 2 shows change in

corrosion potential with time when the coated steel samples are immersed in synthetic seawater. Samples coated with pore-free films retain potential at a nobler value. For samples with higher porosity potential drops to a value close to that of carbon steel when penetrated seawater reaches the coating/substrate interface. The penetrated seawater induces galvanic corrosion to substrate metal, which leads to the peeling of the coating. Fig. 2 demonstrates that the combination of HVOF and Hastelloy C as a coating metal gives good corrosion performance. For the further improvement of the coating property post-treatments such as rolling and heat-treatment are to be scheduled. Also basic studies will be conducted for the elucidation of improved galvanic behavior of nickel-base alloys.

Evaluation of Atmospheric Corrosion and Development of Low-Alloy Steels

It was almost impossible to differentiate the corrosivity of low-alloy steels by conventional acceleration corrosion tests of wet-and-dry cycles, in which the wet cycle consists of saltwater spray while in the dry cycle the atmosphere in a chamber is heated so as to avoid condensation to occur on metal surface. The development of acceleration tests was initiated from a very basic standpoint; phenomenological but nanoscale analyses of water condensation on metal surfaces and rust nucleation on metal surface. The instrumental techniques included atom-force microscopy (AFM) and Kelvin force microscopy (KFM), which are applied in-situ measurement in actual corrosion environments of wet atmosphere of atmospheric corrosion.

In parallel with the nanoscopic measurements macroscopic structural analyses and electrochemical techniques have been carried out. In the presence of high level of salinity in rust, unstable β -FeOOH is the major ferric product which is readily reduced to Fe₃O₄ or green rust consisting of Fe(II)-Fe(III) mixture under wet cycle. Acceleration of atmospheric corrosion exists in the catalytic redox reaction through β -FeOOH. In the simulation of marine atmosphere simple dry-and-wet cycle is not sufficient since wet (aqueous) process of redox reaction proceeds even dry cycle. In addition to the dry-and-wet cycle a cycle of water spray should be added for the removal of accumulated salinity in rust. When water spray cycle was inserted in the acceleration cycle, the corrosivity order of low-alloy steels agreed with that in natural exposure. Fig. 3 shows results obtained for low-alloy steels evaluated by the new acceleration test. Time for evaluating atmospheric corrosivity, which otherwise required from several years of outdoor exposure, has been reduced to one month by using the new acceleration test. The acceleration test is to be applied for the development of

new weathering steels and is extended for the future standardization.

For macroscopic evaluation of atmospheric corrosion, a high-accuracy testing facility for atmospheric test was installed within NRIM. Other than NIRM site atmospheric exposure tests are in progress at marine and subtropical sites of Japan Weathering Test Center (JWTC). Exposed specimens include both standard low alloys and developed alloys. The former consists of steels with a basic/simple composition and is to be served for database.

Conclusion

In the development of stainless steels for marine use a new facility of pressure electroslag remelting (PESR) was installed by which the production of high nitrogen stainless steel with $N > 1\%$ is now possible. The new alloy is to be tested for corrosion, mechanical properties and weldability. In the field of low alloy steel the focus is to be shifted to the alloy development on the basis of basic studies and acceleration tests.

Keywords :

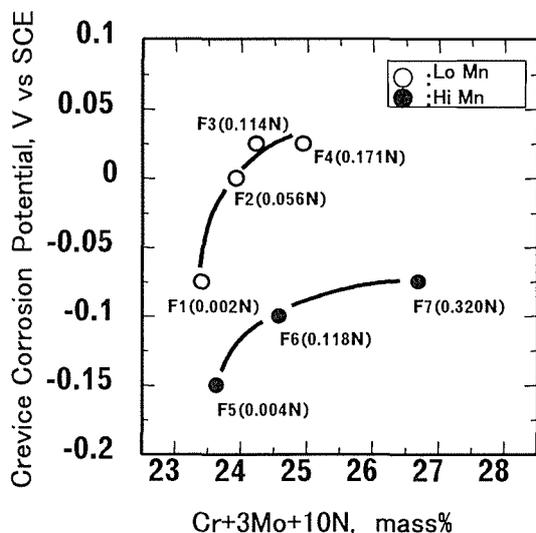


Fig. 1 Effect of N and Mn addition to 316L type steels on the crevice corrosion potential in synthetic seawater.

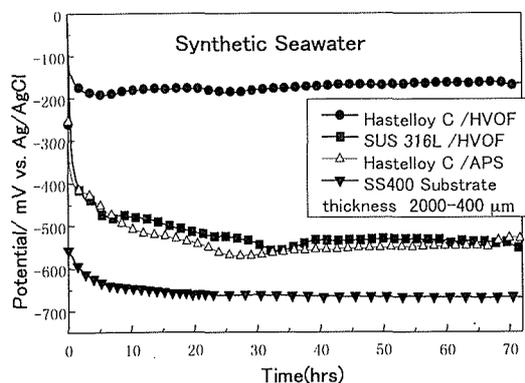


Fig. 2 Performance of spray coated steel in synthetic sea water. Higher potential indicates better corrosion resistance.

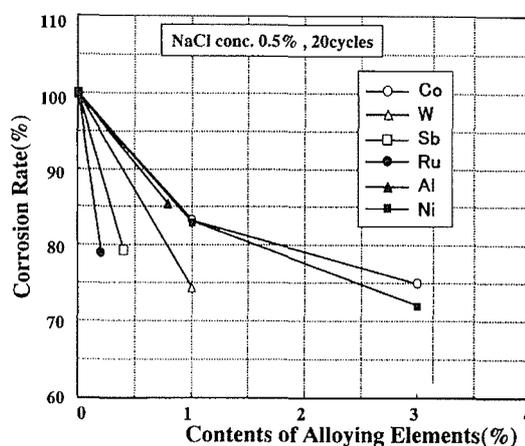


Fig. 3 Relative corrosion rate of low alloy under an accelerated conditions of wet (0.5% NaCl), dry and water spray cycles.

68 Design of Refractory Superalloys

H. Harada, Y. Yamabe-Mitarai, Yuefeng Gu, Xi-Hong Yu, Y. Ro, T. Maruko, Y. Koizumi, H. Murakami, T. Yokokawa, S. Nakazawa, T. Kobayashi and T. Yamagata, High Temperature Materials 21 Project

[April 1995 to March 2000]

The temperature capability of the Ni-base superalloy has been improved by 400°C since its introduction to a jet engine in 1940s; 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, has 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., 220 MPa at 1800°C for an Ir-15 at% Nb alloy. Characterisation of the microstructure and evaluation of the ultra-high temperature creep strength/oxidation resistance are being carried out. A computer modelling based on statistical thermodynamics is employed in the alloy design. Theoretical predictions for 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 an optimum microstructure to exhibit further superior high-temperature strengths.

Keywords : iridium, rhodium, refractory superalloy,

high temperature strength, computer modelling

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69 Study on the Processing and Assessment of Ecomaterials

K. Halada, K. Minagawa, K. Ijima, H. Yoshizu, Ecomaterials Research Team
[April 1997 to March 2000]

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 needlessness of materials. Materials will circulate mainly among producers and service providers to realize effective circulation system to decrease the input/output 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.

This study consists of two parts in concrete. One part is the experimental feasibility study on the new processing technology for the coming dematerialization era. The processing with higher materials efficiency is the key concept of this study. The materials efficiency does not mean 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, powder-metallurgical 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 ECOMATERIALS 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 ruptured microstructures were observed. Fe-Fe composite had 30 kg/mm² of fracture resistance strength by sintered at 400°C, while sintered Fe-powder had 10.3 kg/mm² 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 exchangeability of data with CAD and STEP is sought. 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) CO₂,

SO_x, NO_x emissions of preceding 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 data-system 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

Recent Publications

Estimation of the emissions of CO₂, Ox, and NO_x of steel alloys, K. Halada, K. Ijima and K. Yagi, *J. Mater. Res.*, 13 (1998) : 2514.

Recyclability and Life Cycle Environmental Loading of PM Products, K. Halada, K. Ijima and K. Minagawa, *Proc. 1998 Powder Metallurgy World Congress, Granada, Spain, October 18-22.*

The requirements of LCI data model as a tool of life cycle engineering, K. Halada, *Proc. 3rd Intl. Conf. on EcoBalance 1998 Tsukuba, (1998).*

70 Formation of Amorphous Alloys and their Physical Properties

A. P. Tsai, Aperiodic Materials Research Team
[April 1997 to March 2000]

1. Dynamic Mechanical Properties of Amorphous Alloys

Dynamic tensile properties have been studied on an amorphous Pt₆₀Ni₁₅P₂₅ alloy, below and close to glass temperature range. The storage and loss tensile moduli, as well as the dynamic tensile viscosity, are found to obey the time-temperature superposition principle in the temperature range. The three quantities display Arrhenius temperature dependences

with similar activation energies and indicate that the alloy has an intermediate fragility strength in the general scheme for glass-forming liquids. The master curves reflect a very broad distribution of microscopic relaxation times. The results obtained in this study indicate a very high degree of dynamic heterogeneity in the tensile relaxation process for the amorphous alloy.

2. Quasicrystalline Composites

Nanocomposites comprising of nanoparticles embedded in a matrix of another phase can be prepared by phase separating the liquid prior to solidification, using rapid solidification technique. We embedded the nano-Pb particles in a matrix of amorphous phase and in a quasicrystalline phase, in an Al₇₅Cu₁₅V₁₀ alloy. In the Al-Cu-V alloy, the amorphous phase formed by rapid solidification can be transformed to the quasicrystal on annealing. Thus if the Pb particles were embedded in this alloy, the effect of the amorphous phase and quasicrystal on melting and solidification behavior of the particles can be directly compared. In the amorphous phase, Pb particles show a lowering of melting temperature by about 20 K, which is comparable to the melting temperature of free nanoparticles of about the same size. In quasicrystalline phase, Pb particles reveal a lowering temperature by about 6 K. The lowering of melting temperature is attributed to the loss of coherency at interphase interface.

3. Growing Single Quasicrystals

Current interest of study on quasicrystals has been focussed on the structure and physical properties of a single quasicrystal. We have grown a single decagonal quasicrystal with a size of cm in an Al₇₂Ni₁₂Co₁₆ alloy, by floating zone method. On the other hand, a single icosahedral Zn-Mg-Ho quasicrystal have been grown by Bridgman method in an originally designed furnace. The single quasicrystals have been characterized by back-Laue X-ray diffraction as well as neutron diffraction and verified to have high perfection in structure.

4. Neutron Scattering on Single Quasicrystals

Magnetism in a single icosahedral Zn-Mg-Ho quasicrystal has been studied by neutron scattering. No any long-range magnetic order but short-range order characterized by the magnetic diffuse scattering, was observed in the single quasicrystal. It was found that the diffuse scattering appears as satellites from intense nuclear Bragg reflections. This indicates that corresponding spin correlations can be regarded as a sort of development among spins on six-dimensional hyperspace lattice. A magnetic modulation vector for the correlations is proposed as $q^{6D}_m = (3/4, 0, 0, 1/2, 3/4, 1/2)$.

On the other hand, the dynamics of the decagonal phase has been investigated on a single Al₇₂Ni₁₂Co₁₆

quasicrystal using inelastic neutron scattering. The decagonal structure is viewed as a periodic stacking of quasiperiodic planes. The anisotropy between the modes propagating in the periodic and quasiperiodic directions is found to be much weaker than theoretically predicted. A strong resonance splitting is observed at an energy transfer of 15 meV for transverse modes polarized in quasiperiodic plane.

5. Atomic Structures of Quasicrystals Studied by Electron Microscopies

In a high-resolution transmission electron microscopy study on the Frank-Kasper decagonal quasicrystal in Zn-Mg-RE (RE : rare earth metals) alloy, we found that the decagonal structure can be simply described by the Penrose tiling decorated by individual atoms on quasiperiodic plane. It is striking that there is no large atomic cluster in the decagonal phase, being against the idea of linking atomic clusters which has been available described the structure of quasicrystal in last decade. In some case, the structure of the decagonal structure can be described by the *quasi-unit-cell* picture. Furthermore, we have observed a reversible phase transformation between the icosahedral phase and hexagonal phase in an Zn-Mg-Y alloy, accompanied with a minute concentration change. The hexagonal phase has been clarified to have a structure without large icosahedral atomic cluster, implying that structural unit such as the Mackay or Bergman type cluster does not exist in the icosahedral phase in the Zn-Mg-RE system.

Keywords : amorphous alloy, dynamic property, quasicrystal, composite, nano-particle, neutron scattering, electron microscopy, atomic cluster

71 Study on Combustion Synthesis of Useful Intermetallic Compounds

Y. Kaieda and N. Oguro, Combustion Synthesis Research Team

[April 1999 to March 2002]

The fundamental study to reveal the reactions in combustion synthesis of intermetallic compounds is carried out. The propagation of the reaction front and the synthesis process of the intermetallic compounds synthesized through the reaction are also studied. Investigation by the thermal analysis with rising temperature at constant and/or in alternating velocity 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.

The processes including high frequency induction vacuum melting and casting conventionally produce most intermetallic compounds. It is difficult to control accurately the chemical components of intermetallic compounds produced by the conventional process. The industrial process including a combustion synthesis method, which is a newly developed manufacturing process in the present institute, produces homogeneous intermetallic compound. The chemical components and the impurities in the specimens 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, intermetallic compound

Related Paper

Morphology Change in the Optical Microscopic Microstructure of Titanium by Nitriding Reaction and Combustion Synthesis Under Normal and Microgravity, Y. Kaieda, J. Mater. Synthesis Process 7 (1999) : 67-82.

72 The Improvement of the International Cooperation in the Center for Advanced Physical Fields

K. Yoshihara,

The Center for Advanced Physical Fields has three stations such as High Magnetic Field Station, High Resolution Beam Station and Extreme High Vacuum Station. Most advanced facilities have been integrated at the Center for Advanced Physical Fields. NRIM intends to open these facilities to all over the world. The first step of this program is to open High Magnetic Field Station. This station has a series of the most advanced high-field magnets such as "Large scale magnets", "Pulsed field magnets", "High precision magnets" and "Small scale superconducting magnets". NRIM invites scientists who wish to use these facilities. A scientist who wishes to use these

facilities should present the proposal to the office of the Center for Advanced Physical Fields. The committee in NRIM will assess the presented proposals, and the machine time will be allocated to the scientists when their proposals are accepted by the assessment committee.

This process will be applied to other stations in the Center for Advanced Physical Fields in future.

Keywords : international cooperation, Advanced Physical Fields, High Magnetic Field Station

73 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, High Magnetic Field Research Station

[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 operation. It is cooled down to 3.6 K with two G-M refrigerators. This magnet generates uniform magnetic force field up to $224 \text{ T}^2/\text{m}$ 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%. Experiments on protein crystal growth in magnetic force environment have been carried out using this magnet.

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

74 Materials Development through Control of Phase Transformations by High Magnetic Field

H. Ohtsuka, High Magnetic Field Research Station

[April 1998 to March 2001]

A helium free type superconducting magnet has been developed, which has made it easier to get high magnetic field. As a result, new type of experiments such as the heat treatment at high temperatures in high magnetic field or deformation in high magnetic field have become possible. In iron-based alloys, there are many solid/solid phase transformations such as recovery, recrystallization, precipitation, ordering, spinodal decomposition, diffusional transformations and martensitic transformation. In these phase transformations, not only the difference of magnetic moment but also magnetocrystalline anisotropy, shape magnetic anisotropy, induced magnetic anisotropy and magnetostriction affect the nucleation and growth rate, transformation kinetics, variants and microstructure of product phases. Therefore transformation behavior and microstructure is expected to be affected by magnetic field. In this research, effects of magnetic field on diffusional transformation behavior and structure have been investigated in iron-based alloys. The specimens used in this study are Fe-0.4C (wt%) and Fe-1.5Mn-0.1C-0.05Nb for ferrite transformation, and Fe-0.8C for pearlite transformation. Both ferrite and pearlite transformation kinetics are remarkably accelerated by magnetic field. The Fe-C phase diagram was calculated under various magnetic fields using the susceptibility of ferrite and austenite at high temperatures, and it was found that A_3 temperature increases with increasing magnetic field. The A_{r3} temperature of pure iron in a magnetic field of 10 T was experimentally determined by the recalescence during cooling, and it was found that the A_{r3} temperature increases by 7 K, which is in a good agreement with the calculated value. The direction of lamella of pearlite observed on the specimen surface was affected slightly by magnetic field.

Keywords : phase transformation, high magnetic field, kinetics, microstructure, ferrite, pearlite

Related Papers

1. J. Choi, H. Ohtsuka and Ya Xu : "Diffusional Transformations in High Magnetic Field", Proc.

Workshop on the Development of High Performance Structural Steels for 21st Century, Posco Technical Research Laboratories, Korea, p. 191-221.

2. Ya Xu, H. Ohtsuka, K. Anak, S. Miyazaki, K. Itoh and H. Wada : "Effects of high magnetic field on recrystallization texture in Fe-3% Si steel", Proc. the Second Symposium on New Magnetic Science (SNMS'98), p. 239-246.

75 Basic Research for the Control of Chemical Reactions by High Magnetic Field

H. Abe and K. Takazawa, High Magnetic Field Research Station

[April 1996 to March 2000]

With the aim of producing new materials in the high magnetic fields more than 10 T, 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 2 T 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 40 T 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 (355 nm, 15 ns). 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 0-29.6 T.¹⁾ Large magnetic field effects were observed for both of the lifetime of radical pairs and the yield of escape radicals. More-

over, we have observed new saturation phenomenon of magnetic field effects due to the Δg mechanism under high fields up to 28 T.²⁾ This saturation phenomenon has predicted theoretically to occur at extremely large magnetic field of 10^3 T.

(2) Dynamic behavior of electronically excited molecules in the gas phase under high magnetic fields up to 10 T. 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 10 T, 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. Moreover, in order to observe the electronic structures of paramagnetic radicals under high magnetic fields, which are the intermediates of gas phase reactions such as CN, OH, CH, C₂, etc., we are constructing microwave discharge flowing afterglow apparatus.

As the first step to the excitation to the highly excited state, the electronic spectra of gaseous NO $X^2\Pi \rightarrow A^2\Sigma$ transition were observed under magnetic fields up to 10 T. Large Zeeman effects on the spectra were observed. A quantum mechanical calculation was carried out to obtain the eigen-function of each Zeeman perturbed level and at the result, both transition energies and the intensities of all spectral lines could be completely reproduced.³⁾ 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.⁴⁾ Cooling effect of molecular beam under high magnetic fields was observed for NO molecule, resulting about 10 K of the rotational temperature.

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3) K. Takazawa and H. Abe, J. Chem. Phys., 110, 9492 (1999).

4) K. Takazawa and H. Abe, J. Chem. Phys., i 110, 11687 (1999).

Keywords : high magnetic field, chemical reaction, photo-dissociation, photo-ionization, reaction intermediate, photoreduction

76 Development of 1 GHz NMR Spectrometer

H. Wada, T. Kiyoshi, T. Takeuchi, K. Itoh, A. Sato, T. Numazawa, M. Yuyama, M. Kosuge, H. Nagai and F. Matsumoto, High Magnetic Field Research Station

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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 4.2 K. We have initiated a program in which we will develop a 1 GHz superconducting NMR spectrometer including a 23.5 T 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 Nb₃Sn conductors has been started.

In our design the LTS coils are operated in persisting mode at a field of 21.1 T in a 132 mm diameter bore. The HTS coil is expected to generate an additional field of 2.4 T in a 54 mm 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 1.8 K.

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. The required conductors except Ta reinforced Nb₃Sn conductors were fabricated. We have started to wind them into coils.

Since HTS coil development requires a lot of technological challenges, we have fabricated a Bi-2212 double-pancake coil with an outer winding diameter of 147 mm. It is designed as the innermost coil of a 21 T superconducting magnet developed at the NRIM. It generated central magnetic fields up to 21 T in a back up field of 18 T and at 1.8 K. After the test operation, this coil has been used to generate fields up to 21 T as a part of the user facilities. We proved that a Bi-2212 coil could be applied to a high-field insert coil.

Construction of the cryostat was finished. Its test operation without LTS and HTS coils will be scheduled in 1999.

Keywords : NMR spectrometer, high field magnet, oxide superconductor

Related Paper

Development of 1 GHz Superconducting NMR Magnet at TML/NRIM, T. Kiyoshi, A. Sato, H. Wada, S. Hayashi, M. Shimada and Y. Kawate, IEEE Trans. Appl. Superconductivity, vol. 9 (1999), 559-562.

77 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 2002]

To realize a magnet made of a high- T_c oxide superconductor (HTS), it is indispensable to have a long 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 research 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 1 GHz 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 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 has been also established and used by many groups engaged in development of HTS materials and/or the conductors for the 1 GHz NMR magnet system.

Major evaluation systems established in this project are listed below with brief introduction and specification.

1) Measurement System for Magnetic Field Angle Dependence of I_c

We have established two measurement systems for this purpose. Specification of each system is as follows ;

#1-1) Magnetic field : $-15\sim 15$ T (Split type superconducting magnet)

Temperature range : $1.8\sim 100$ K (helium gas cooling)

Sample length : 70 mm (30 mm in homogeneous field)

Rotation angle : $-360\sim 360^\circ$ and more

Current capacity : 200 A (300 A for very limited period)

#1-2) Magnetic field : $0\sim 8$ T (Axial solenoid type superconducting magnet)

Temperature range : 4.2 K (liquid helium) and $10\sim 100$ K (helium gas cooling)

Sample length : 50 mm (whole part is in homogeneous field)

Rotation angle : $-30\sim 210^\circ$ (0° : B//sample support)

Current capacity : 400 A (600 A for very limited period)

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 specimen is mounted on a U-shape holder and attached to the movement mechanism. The feature of this system is that strain can be changed continuously from -1% (compressive strain) to 1% (tensile strain).

This type of evaluation system is unique in Japan. 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 obtained. 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.

Magnetic field : $0\sim 8$ T (Axial solenoid type superconducting magnet)

Temperature range : $4.2\sim 100$ K (helium gas cooling)

Sample length : 60 mm (center part of ~ 10 mm can be deformed with homogeneous strain)

Strain range : -1% (compressive strain) $\sim 1\%$ (tensile strain)

Current capacity : 300 A (500 A for very limited period)

3) Variable Temperature Large Current Capacity I_c Measurement System

Because of the progress in HTS conductor development, I_c characterization at high temperatures ($10\sim 30$ K) with large current becomes essential. We established a measurement system for this purpose.

Magnetic field : $0\sim 8$ T (Axial solenoid type superconducting magnet)

Temperature range : 4.2 K (liquid helium), $10\sim 77$ K (helium gas cooling)

Sample length : 70 mm (whole part is in homogeneous field)

Current capacity : 800 A (1,000 A for very limited period)

4) High Field Performance Test System

By utilizing TML hybrid magnet system, we can perform I_c characterization in high field up to 30 T.

Magnetic field : $0\sim 30$ T (Hybrid magnet system in TML)

Temperature range : 4.2 K (liquid helium)

Sample length : 35 mm (whole part is in homogeneous field)

Current capacity : 500 A

Keywords : oxide superconductor, evaluation, measurement technique

78 Development of Magnetic Separation 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 Tc sc magnets to magnetic separation. One of them is an optimization method of an sc solenoid for High Gradient Magnetic Separation (HGMS) systems to minimize the quantity of sc wire used in the 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. MC has a possibility to analyze ultra-fine particles with diameters of several tens nanometers, which are too large for conventional chromatography techniques. Our MC systems use ferromagnetic wires in a strong magnetic field to create high magnetic field gradients. The fluid velocity is low near the wires, so that particles with high magnetic susceptibility are drawn to the wires, and are separated from the particles of low susceptibility. Because MC columns can be easily cleaned by switching off the applied magnetic field, MC systems generate no secondary waste, which is a common problem with conventional chromatography systems. Our MC simulator modeled the transient behavior of the particles by taking into account the fluid flow field, magnetic field, particle diffusion, and particle size distributions. Our simulation results 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 which is caused with the channel length increasing method. 3) It is possible to make magnetic field distribution most suitable for MC by adjusting a ferromagnetic wire arrangement. 4) As the size distribution widens, the steady-state particle concentration increases near the ferromagnetic wires, and decreases the separation efficiency at low flow velocities.

We conduct this research in collaboration with the Electrotechnical Laboratory, AIST, MITI.

Keywords : ultra-fine particles, high Tc super-

conducting magnet, high gradient magnetic separation, magnetic chromatography, computer simulation

Related Papers

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.

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Computer Simulation of Magnetic Chromatography System for Ultra-Fine Particle Separation, X. Wang, T. Ohara, E.R. Whitby, K.C. Karki and C.H. Winstead, Trans. IEE of Japan 117-B (1997) : 1466-74 in Japanese.

79 New Cryocooler System Below 4K Refrigeration

A. Sato, T. Numazawa, F. Matsumoto and H. Nagai

[April 1999 to March 2004]

A number of devices that requires cryogenic cooling below 4 K are considerably increasing because of the progress in cryogenic system using magnetic regenerators. Liquid helium temperatures have been achieved with two-stage GM coolers by using rare-earth intermetallic compounds. Recently, much lower temperatures below 4 K are required for cooling such as superconducting magnet system which needs high current density and stability in our laboratory. We have started to investigate a new cryocooler system, which refrigerates below 4 K. First, the system down to 2 K region has been considered in GM or Stirling cycle with new magnetic regenerator materials. The test machine is under constructing with high efficient heat exchanges and mass flow system. The scope of the refrigerator is to test for superconducting magnet cooling at 2 K. Second, we will construct another sub-1 K refrigeration. A new helium 3 regenerator cycle will be used in the system. The final goal of this study is to establish a conventional sub-1 K refrigeration system without liquid helium. Study for magnetic materials used in the regenerator will be also done. The study will be also focussed on high heat capacity materials below 4 K region.

Keywords : cryogenic system, GM cycle, Stirling cycle, pulsed tube cycle, regenerator

T. Takeuchi, High Magnetic Field Station

[April 1999 to March 2004]

The main purpose of this study is to develop the new superconductors to be used for the nuclear fusion reactor. The superconducting conductors for the nuclear fusion are required to have (1) large critical current density (J_c) in high fields, (2) high tolerance to mechanical stress and strain, (3) large current carrying capacity, (4) low sensitivity to radiation, (5) high stability to electromagnetic disturbances, (6) low ac losses. Recently, we have developed a new Nb₃Al multifilamentary superconductor, which is based on a Jelly-Rolled (JR) Nb/Al composite and fabricated by rapid-heating and quenching a wire of such composites with subsequent transformation annealing to form Nb₃Al phase. In contrast to the conventionally fabricated Nb₃Al conductors, the transformation from super-saturated bcc-solid-solution Nb(Al)_{ss} enables the highly stoichiometric A15-Nb₃Al to form with fine grains, and the J_c characteristics are significantly improved over the whole range of magnetic fields, in particular, in the fields more than 20 T. The resulting substantially improved high-field performance is compatible with the excellent strain tolerance. Thus, the transformed Nb₃Al conductor is promising as a realistic alternative to Nb₃Sn for the fusion reactor use.

The current carrying capacity is, however, currently too small for such large-scale application uses. In the present study, various cross-sectional structures for the multifilamentary billet, with different Nb-matrix ratios, JR-filament configurations, etc., were designed to enhance the current capacity. Figure 1 shows the transversely cross-sectional images of the JR Nb/Al composites examined. The specifications of these conductors are given in Table I. The Nb-matrix ratio is decreased from 1.5 to 0.52, adjusting the filament sizes d_f to $\sim 100 \mu\text{m}$ for 1.25 mm Φ wires. In order to ensure high cooling-rate in the rapid-quenching process, the diameter of a JR Nb/Al composite wire (d_w), however, used to be below 0.5 mm, limiting the current carrying capacity of this type of conductor. The increase in d_w is most likely direct and effective way to enhance the current capacity. Thus, d_w was increased from 0.5 to 1.25 mm. The maximum d_w of 1.25 mm is currently limited by the performance of the electric power supplier for continuous self-heating. The critical current (I_c) was proportionally enhanced by increasing d_w , almost without degrading non-Nb J_c . A decrease in the Nb-matrix ratio from 1.5 to 0.52 further enhanced the I_c

for the 1.25 mm Φ samples. Consequently, I_c for a monolithic conductor at 21 T and 4.2 K has now been enhanced to 166 A which used to be 15 A, by increasing d_w to 1.25 mm and decreasing the Nb-matrix-ratio to 0.52.

Keywords : transformed Jelly-rolled Nb₃Al, current carrying capacity, Nb-matrix ratio, wire diameter

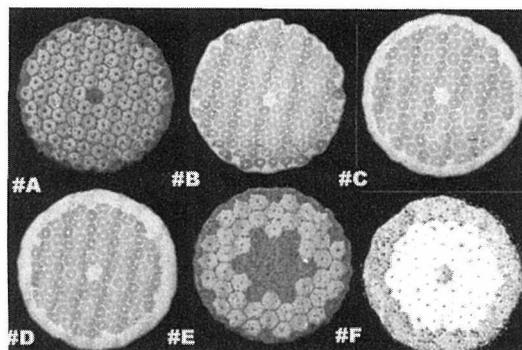


Figure 1. Transversely cross-sectional views of the JR Nb/Nb(Al)_{ss} multifilamentary conductors.

Table I Specifications of the JR processed Nb/Al composites

Sample	d_w (mm)	Nb matrix ratio	Number of filaments	d_f (μm)	filament location
#A	1.25	0.52	84	112	center
#B	1.25	0.56	120	92	center
#C	1.25	0.82	84	103	center
#D	1.25	1.0	84	92	center
#E	1.25	1.06	42	139	outer shell
#F	1.25	1.5	36	136	center
#F1	1.0	1.5	36	109	center
#F2	0.5	1.5	36	55	center

81 Characterization and Control of the Optoelectronic Properties of Small Crystalline Materials with Electron Probe Analysis

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[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, SiH₂, or oxide defects on the surface of Si particles are suggested to be responsible for the PL. However, many points are still unclarified.

In this year, the correlation among PL properties, chemical states, and microstructures in PS layers treated with NH₃ solution has been investigated to clarify the origin of PL. PS samples were prepared by anodizing p-type Si (100) wafers with 0.04-0.06 Ω cm resistivity. The anodization was performed in a 50% HF-ethanol (1 : 1) solution at room temperature at a constant current density of 0.35 A/cm² for 10 seconds. The chemical treatment of PS was carried out by immersion in 0.14% aqueous NH₃ at room temperature. The microstructures and chemical states of PS layers were studied using transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), and Fourier transform infrared spectroscopy (FTIR). 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 NH₃ treatment for 1 minute, while the sponge-like structure in the PS top surface region disappears. The PS treated for 5 minutes shows strong yellow PL, while a new sponge-like structure is formed in the top surface region. TEM and EELS observations suggest that the sponge-like region consist of oxidized Si nanoparticles. FTIR analysis reveals that there is no direct correlation between chemical states and PL properties. These results suggest that the red PL in as-prepared PS arises from the original sponge-like structure and the yellow PL in NH₃-treated PS is ascribed to the newly formed sponge-like structure.

Keywords : small crystalline materials, surface terminated particles, porous silicon, photoluminescence

82 Analysis/Evaluation of Atomic Scale Compositional Change in Materials Due to the Radiation Damage

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[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 spectra and EFI were investigated.

It is known that when inert gas Xe ions are implanted into solid materials such as metals and semiconductors, they usually form crystalline precipitates with a FCC or HCP structure. Xe precipitates in Al have a FCC structure with the same crystal orientation with the Al matrix. The lattice structure and the shape of the Xe precipitates have been clearly observed by means of high-resolution electron microscopy using so called off-axial condition. However, little work has been carried out on the structural and chemical aspects of Xe precipitates at high temperature.

In the present work, we conducted structural and chemical analyses of Xe precipitates in Al in-situ, as a function of temperature, using of electron energy loss spectroscopy (EELS) and energy filtered imaging (EFI) techniques.

Al specimens were implanted with 50 keV Xe at 423 K and 473 K to a dose up to 2.6×10^{21} ions·m⁻² in a SUBNANOTRON. EELS spectra were measured and EFI images were taken at room temperature, 773 and 858 K using a post-column imaging filter system (GIF) made by Gatan.

In order to make the Xe precipitates observable in EFI mode, specimens were implanted at 423 and 473 K. Extra SAD spots at positions between the center spot and Al {111} or {200} spots were identified to be those from Xe precipitates. Precipitates in size from less than 10 nm to about 30 nm are seen in both zero-loss and core-loss images. The shape and distribution of Xe precipitates in EFI images are consistent with those observed in TEM diffraction contrast. Though there are some noises seen as small white spots (about 1 nm in size), the contrast of large precipitates is usually better than that of small ones. This indicates that the signal/background ratio in the

image depends on the number of Xe atoms in the precipitates.

Crystalline Xe precipitates changed to a non-crystalline state as the temperature increased. The diffraction spots from the Xe precipitates start to become weaker at about 623 K and weakened further with increasing temperature. The spots disappeared completely at about 773 K.

Xe-M_{4,5} core loss spectra also show a change when the temperature increased from 300 to 773 K. At 300 K, the experimentally obtained Xe-M_{4,5} edge has three peaks at energy losses of 683, 698 and 712 eV, while in the spectrum obtained at 773 K only two peaks seen clearly at 688 and 700 eV respectively. The Xe-M_{4,5} edge obtained at 773 K has a similar shape and peak positions to a spectrum obtained from gaseous Xe. This suggests that the Xe precipitates are in gas state at 773 K. A final confirmation requires on the further study.

Keywords : SUBNANOTRON, EELS, Xe, precipitate, EFI

83 Study on Detection, Evaluation and Utilization of Non-equilibrium Processes Under Extreme Particle Fields

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[April 1999 to March 2003]

Hybrid particle fields of ion and photon exert strong interactions with materials and are potent not only to detect elementary processes but also 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 features of momentum, energy and excitation modes. Up to present, we have attained ion beams over 6 MeV × mA for heavy ion species and have combined with a 5J/pulse laser. The hybrid state of the ions and photons is called an Extreme Particle Field (EPF), emphasizing the hybrid features of particle environments highly interactive with materials. The EPF 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. Utilization of the non-equilibrium processes is further aimed at.

In this fiscal year, high-current ion irradiation into insulators, amorphous/crystalline SiO₂, and MgO · Al₂O₃ spinel have become capable by use of applying negative ions and have demonstrated dose-rate de-

pendent changes in nanocrystal formation. Metal nanoparticles embedded in insulators are promising for optical devices, such as optical switches and logic elements. We have focused on non-equilibrium processes either in-beam or after irradiation. In-situ spectroscopy of ion-induced photons has been conducted and detected synergistic beam-material interactions including a strong plasma continuum and line spectra of sputtered ions. Existence of the plasma indicates strong beam-surface interactions induced by high-flux ions, primarily surface sputtering process. The line spectra are evidence of ion-induced mass transport from the intra-solid to the vacuum, dependent on the ion flux. Another in-situ device of particle emission, i.e., secondary electrons and ions, was installed into a high-vacuum chamber. The device meets various surface analyses, i.e., XPS, AES, SIMS and SPM under ion irradiation. The post-irradiation optical properties due to nanocrystals were also evaluated with a pump-probing method, employing a femto-sec laser of titanium-sapphire. The measurement of the plasmon absorption gives time-resolved understandings of electrons confined within metal nanoparticles. The result of as-irradiated specimens showed absence of a pico-sec component in plasmon absorption and that the major component is a few hundreds pico-sec. After thermal annealing, the faster component of plasmon recovered. The faster component was hindered by defects due to high-flux ions. The changes in optical properties were correlated with microstructural changes observed by cross-sectional TEM.

Other in-situ techniques of measurements are also in progress : A fast beam chopper accomplished pulsation of 6 MeV ions, down to a pulse width of several tens nanosec, which will be used for beam-induced time-resolved measurements. Material irradiation techniques of a high-power laser has been developed after optimizing the optics to reduce the beam load onto the window glasses and employing a double-sided optical window. Development of in-situ conductivity measurements focused on co-irradiation effects of high-energy protons and photons on semiconductors. The results showed nonlinear dependence of particle-induced conductivity on the beam flux. The ion-induced nonlinearity indicates the pronounced recombination process due to strong excitation of electrons and holes. These technologies integrated for the EPF are now in use to reveal the highly non-equilibrium processes.

Keywords : non-equilibrium process, extreme particle heavy ion, in-situ measurement

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84 Development of Fundamental Technologies for Excited Neutral Beams

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[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.

Based on the preliminary study which had been conducted using a prototype apparatus for beam generation and excitation, improvements of metastable atom beam source has been attempted. A hollow cathode discharge was introduced to a nozzle-skimmer discharge helium metastable atom beam source with a trigger electrode between a nozzle and a skimmer. A hollow cathode is contained inside of a quartz glass nozzle of 20 mm in diameter. The aperture of the nozzle is 0.5 mm in diameter. The distance between the nozzle and the skimmer is 7 mm. A pulsed high voltage is applied to the hollow cathode through a high speed FET switch and a stabilizing resistor of 2 k Ω from a capacitor of 1 μ F charged by a constant current power supply of 3 kV in maximum voltage. The atom source was successfully operated at variable pulsed discharge currents up to 1 A running through the hollow cathode behind the nozzle and the skimmer anode. The total flux of the continuous beam with mechanical chopping equivalent to the pulsed beam measured at a mean discharge current of 10 mA was estimated at $1.2 \times 10^{15} \text{ s}^{-1} \text{ sr}^{-1}$. The intensity of the metastable helium beam increased proportionally with the increase of the mean discharge current up to 50 mA. Higher discharge currents which could be achieved by an active cooling mechanism are expected to produce more intense metastable atom beams.

Spin polarization of metastable atoms was performed by an optical pumping method. The photon intensity required for getting a sufficient polarization is strongly depends on the accuracy of its wave length. The wave length of the pumping laser diode was stabilized to the saturated absorption by an helium discharge cell. The degree of polarization was confirmed by a Stern-Gerlach measurement with a compact Rabi type magnet which was also developed newly. A laser diode of rating power of 25 mW was enough to polarize the most of triplet atoms when its frequency was stabilized. For applications of the spin polarized metastable deexcitation spectroscopy such as magnetic properties of outermost surfaces of transition metals the stray field

around a sample has to be taken into account. Therefore the spin state change of He 2^3S_1 atoms skimming over a Fe single crystal surface were carefully examined. The spin flip of He 2^3S_1 atoms was found to be avoided by magnetizing the sample anti-parallel to the defining field.

The adsorption of oxygen on a polycrystalline zirconium surface at room temperature has been studied by metastable deexcitation spectroscopy (MDS) and ultraviolet photoelectron spectroscopy (UPS) using the pulsed metastable atom beam source developed. From the analysis of the measured spectra of MDS, UPS and Auger electron spectroscopy, followings were clarified; (1) At the initial stage of oxygen adsorption (exposure < 1.2 L), the surface density of states (SDOS) of zirconium changes little at around the Fermi level (E_F), while it decreases appreciably at 1-2 eV below E_F ($E_B = 1-2$ eV) by oxygen adsorption. (2) The SDOS at $E_B = 0-2$ eV decreases with increasing oxygen exposure at > 1.2 L and disappears at > 8 L. (3) The oxygen 2p states ($E_B = 5-8$ eV) are localized at the subsurface then grows with increasing exposure 0-2 L. (4) The ZrO_2 phase appears at the outermost zirconium surface at around 2 L, then grows with increasing exposure, and finally dominates at > 8 L. It is suggested that two different phases (ZrO_2 phase and that in which oxygen occupies subsurface sites) coexist at the outermost surface at 2-8 L. The ultimate surface sensitivity of MDS and its capability for the surface electronic analysis were successfully demonstrated.

Keywords : neutral beam, metastable atom, excited neutral, surface

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85 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. Developing a new X-ray fluorescence spectrometer is one of the most significant activities for such advanced analysis, because the conventional Si (Li) spectrometer does not have sufficient performance to make full use of highly brilliant synchrotron X-ray source. It often leads to unsuccessful separation from the scattering background or different X-ray peaks, and one could encounter the saturation of the detector system as well.

Photo 1 shows the spectrometer, which has been designed and assembled at our laboratory. A Ge (220) analyzing crystal (Rowland radius 350 mm) and a NaI : Tl detector with a 0.15 mm receiving slit were employed. The spectrometer is equipped with 3 linear stages and a 1-axis goniometer for angular scan. The experiment was carried out on undulator beamline BL-39XU at SPring-8. Undulator radiation was monochromatized by a Si (111) rotated-inclined double crystal monochromator, and higher-order harmonics were rejected with a single, flat platinum-coated mirror at a glancing angle of 5 mrad. The width of the entrance slit of the chamber was 0.2 mm, and the beam size at the sample position was 0.2 (H) \times 2 (V) mm². Figure 1 shows an XRF spectrum of Cu-Ta alloy powder. The sample is fixed on thin polymer tape, with the quantity being a few mg/cm². Though the Cu $K\alpha$ and Ta $L\alpha$ lines are rather close and usually overlap in a spectrum obtained by a Si (Li) detector, they were observed as completely separate peaks. Even Cu $K\alpha_1$ and $K\alpha_2$, or Ta $L\alpha_1$ and $L\alpha_2$, were clearly separated. The present energy resolution is estimated as 8 eV at Cu $K\alpha_1$ (8.04 keV). Figure 3 shows the XRF spectra of Cu foil (6 μ m) measured as a function of incident X-ray energy around the X-ray absorption edge (8.96 to 9.02 keV). The near-edge absorption spectrum, which provides information on the chemical state of the elements, is obtained by measuring the total XRF yield. This time, not only the integrated intensity but also the spectral profile were obtained, and therefore more detailed information is available. Faint peaks of X-ray Raman scattering are seen at 8.98 keV or lower energy.

The present Johansson-type curved crystal spectrometer is feasible and promising for XRF analysis with monochromatized undulator radiation. The energy resolution is much better than that of a Si (Li) detector, and is sufficient to avoid the overlapping of the low-energy tails of scattering X-rays. Although XRF intensity obtained in the present study is fairly strong because of the extreme brilliance of undulator radiation, further enhancement of the signal is necessary to measure trace systems. Optimization of the spectrometer for detection efficiency is currently in

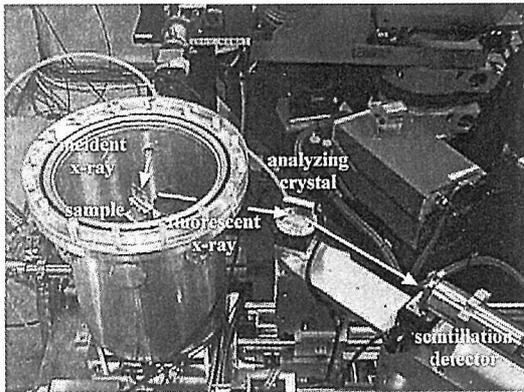


Photo 1 NRI Johansson-type XRF spectrometer.

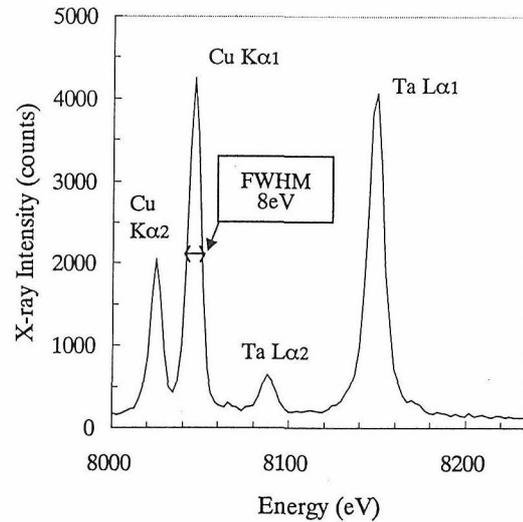
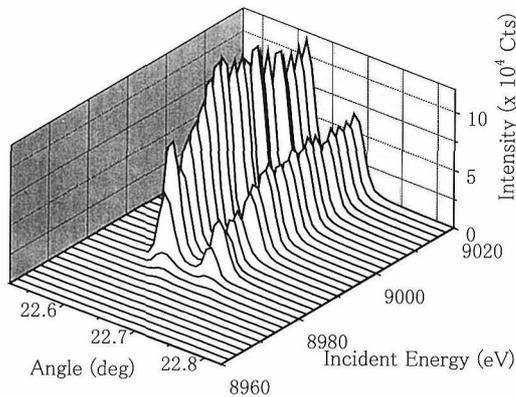
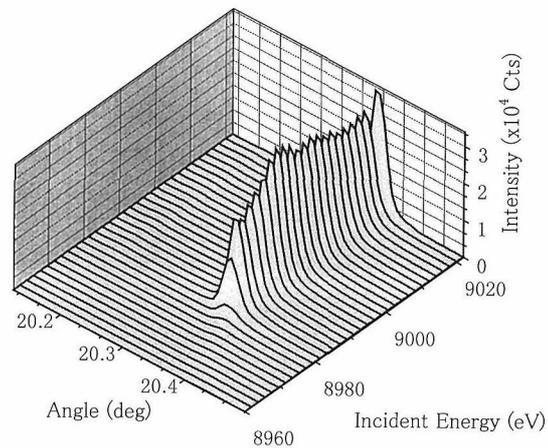


Fig. 1 XRF spectrum of Cu-Ta alloy powder (10 keV excitation). Measuring time 25 min.



(a)



(b)

Fig. 2 Resonant XRF spectra from 6 μ m Cu foil. (a) Cu K β , (b) Cu K α . Measuring time for one XRF spectrum is ca. 3 min.

progress.

Keywords : synchrotron radiation, materials characterization, spectrometer, X-ray fluorescence

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86 Fabrication of Nanometer-Scale Structure on the Extremely High Vacuum Surface

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We have reported our success in observing standing wave (Friedel oscillation) on the surface of gold single crystal (111) by using a scanning tunneling microscope. The standing wave was observed more significantly on a peculiar structure called a herring-bone structure on the reconstructed surface of gold (111). By cooling down the gold (111) sample to 30 K, we found out two things : the surface standing waves were found to be elongated over 70 nm ; their amplitudes on the surface were not uniform but rather complicated due to the formation of potential modulation caused by the surface structures such as the herring-bone and steps. There exists the surface state called Shockley state on the reconstructed surface of gold (111). Since electronic state on the surface can be regarded as two-dimensional free electron gas and the electron-wave is scattered by its steps as well as defects of the surface, the wave shows several interference patterns.

Furthermore, taking the above outcome into consideration, we have analyzed the standing wave in the wave-number space by applying two-dimensional Fourier transform to the real-space STM images. By this method, we were able to visualize the anisotropic two-dimensional Fermi surface. By this method, the observed k-space image can be attributed to the local Fermi electronic state on the surface in a nano-scale order. The phenomenon may be caused by the peculiar nature of the reconstructed surface.

The method to evaluate the transformation from the STM image into wave-number space by the Fourier transformation is more interesting, compared to another method that evaluates the electronic state on the surface in the wave-number space by angle resolved ultraviolet photoelectron spectroscopy (ARUPS). Since the method with ARUPS requires the ultraviolet radiation toward the sample surface with its large area beam diameter, the observed information corresponds to the averaged value over the quite wide area (millimeter). On the contrary, the method to Fourier-transform the STM image enabled us to evaluate the electronic state in a considerably small area (micrometer to nanometer).

In addition to the above research, our current interest is magnetic features of minute magnetic substance. By utilizing electron beam lithography, we have fabricated sub-micron magnetic wire. By measuring the electronic resistance, we have observed the changes in the resistance affected by the magnetic domain wall as well as the movement of the wall itself. Since similar experiments have performed quite actively in these days, it is known that the electronic resistance declines with the invasion of magnetic domain wall. We now attempt to control the movement of magnetic domain wall by fabricating multiple constrictions in this system, and examine

the effect of magnetic domain wall more in detail.

From now on, taking an advantage of those magnetic features, we will examine the effect of the magnetic structures on the electronic transport phenomena.

Keywords :

87 Self-control of Surface Composition of Thin Film and Its Application to Field Emitter

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[April 1995 to March 2000]

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. The time dependence of Ti surface concentration has been analyzed by introducing two parameters, the diffusion coefficient of Ti in Nb film and surface segregation possibility of Ti atom under surface. It is shown that those two parameters in any elemental combination can be obtained by fitting the experimental results on surface concentration variation of substrate element at certain temperature. 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. The electronic state of Cu under surface segregation was observed with XPS. It is concluded that in both cases electron is partially transferred from Cu to Ti, and that the direction of electric dipole for each case corresponds to the tendency of work function change.

Keywords : surface segregation, saturated surface composition, self-composition control, work function, field emitter

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88 Study on Melting of Refractory Metals by Cold Crucible Levitation Melting Method

A. Fukuzawa, K. Sakuraya, T. Watanabe, S. Iwasaki and Y. Kobayashi, Material 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 heating of the materials. Since we have succeeded reducing the oxygen in molten titanium by this new 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 Metallic Ball in Cold Crucible Simultaneous Supplied Two Frequencies, K. Sakuraya, T. Watanabe, S. Iwasaki, A. Fukuzawa, M. Yamazaki, T. Take and M. Fujita, *Tetsu-to-Hagane*. 81 (1995) : 179-84 (in Japanese).

89 Feasibility Study on Utilization of High Brilliance X-rays for Steel Characterization

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[April 1998 to March 2000]

The third generation storage ring, SP ring-8 (Super Photon ring-8 GeV) has been constructed at the Harima Science Garden City. The beamline BL24 XU 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.

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

90 Research and Development of Recyclable Simple-System Alloys

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[April 1996 to March 2001]

Because of various additives, the recycling of metallic materials used for automobiles parts and other aspects should be solved. Nowadays, the recyclability of materials should be fulfilled in developing new structural materials. In the present research, four kind of metallic materials and processing methods for improving recyclability are concerned.

The {101} type twin boundaries have been considered as an important factor that contributes to the high damping capacity of MnCu alloys. Crystallographic studies of the twinning boundaries are

conducted to clarify the structural features which affect the mobility of the boundaries when a cyclic external stress is applied. Damping capacity of alloys are sensitive to the measuring conditions, such as frequency, strain amplitude, temperature and vibration mode. A concise measuring method is designed to coordinate the factors in determining the damping capacity of alloys.

In order to develop recyclable high-strength sintered steels a powder-deposition equipment has been installed in NRIM. By altering atomizing pressure, distance between the gas outlet and centrifugal board, as well as the rotation rate of the centrifugal board, the factors that affect the particle size distribution of produced powder and the particle refinement will be confirmed through the application to Al. In addition, the sedimentation process of fine droplets could also be clarified.

Aluminum casting alloys without addition of grain refining elements present a higher recyclability. Instead of the grain refining elements, a strong stirring of ultrasonic vibration during the solidification is capable of refining the microstructure of castings. And effects of the vibration on the formation of primary crystals in a molten Al-Si alloy are examined. In the Al-6%Si alloy, the primary crystals are obviously destroyed by the vibration. As a result, dendrites are segmented, and a granular microstructure is formed. Ultrasonic vibration is also effective to refine the primary Si of Al-18%Si. Vibration of molten metal and the large acoustic stream formed in molten metal should promote the nucleation and segmentation of primary dendrite crystals.

Pb free-cutting steels are used for machine products and vehicles parts. Steel containing Pb will be prohibited due to the environmental pollution and the poor recyclability. New free-cutting steels containing no Pb are required keenly. A Ti deoxidation steel that shows the hardness of HV350 by the introduction of martensite microstructure is developed. The machinability of the steel is examined by the properties of tool abrasion, cut resistance, chip-disposability. Since the steel has a high tensile strength of about 1000Mpa, a high-strength free-cutting steel is prospective to meet the light-weight and compact requirement of vehicles parts and mechanical products.

Keywords : High damping alloys, Ultrafine steel particles, Ultrasonic vibration casting, Chip-disposability, Martensite microstructure

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91 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, M. Saito, T. Shimizu, 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, K. Sasabe, S. Meguro, T. Ohtani, 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 under 1

micron and double the tensile strength from 400 MPa to 800 MPa. In a small-size sample of a 0.15 wt% C steel (SM 490 grade) with about 1 mm thickness, an ultra-fine grain ferrite-pearlite structure was created with a ferrite grain size of 1 micron. Through warm groove rolling process developed in the present study, ultra-fine grain ferrite microstructure with a ferrite grain size of less than 1 micron was created for 12 mm square rods, which showed tensile strength of 680 MPa and ductile-to-brittle transition temperature of 77 K. In addition, 'Oxsteel', iron with finely-dispersed oxides, was also created with a ferrite grain size of less than 1 micron through the warm groove rolling of a compaction of mechanically-milled commercial pure-iron powders.

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 was developed with an idea of simultaneous control of low heat distribution and large electricity input to make the HAZ as narrow as possible. The progress has been made to develop a phase controlling system. And further, a high-power CO₂ 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. The preliminary study to obtain the high efficiency is almost finished to introduce a high-power machine.

The small samples with ultra-fine grain microstructure was subjected to simulated welding processing like arc welding and spot welding. The arc welding simulated samples showed 'softening' at the HAZ according to input heat. The spot welding simulated sample revealed almost ideal hardness distribution without any specific hardened region at the whole joint.

Welded specimen large enough to simulate the conditions for service was subjected to mechanical tests with a large capacity of power to evaluate the fatigue property. The lower fatigue strength of welded joints has been tried to basically increase by using a newly designed welding rod with a lower transformation temperature. With introducing compressive residual stress at the welded joints, the fatigue strength of high tensile steel's joint was successfully improved by a factor of three. The fatigue strength of structure member of box section 3.5 m long beams was also improved by inducing compressive residual stress on longitudinal corner weld.

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 techniques have been developed like supersonic

CT scanning of defects in a welded joint and magnetic flux leak detection by DTF for surface flaws. Laser speckle technique was advanced to follow the strain change at a bead both on heating and on cooling during welding process.

Finite Element Method was successfully applied to clarify the relationship between strain given in the thermo-mechanical processing and evolved ferrite grain size. And a simulation system to predict the deformation and fracture behavior of welded points has been also developed by combining calculation of stress and strain distribution and experimental tensile tests.

Keywords : ferritic steels for welded structures, grain refinement, welding process, heat-affected-zone, residual stress, welded joint, tensile strength, fatigue strength, simulation

92 Effect of Aging Degradation on Localized Corrosion of Structural Materials for Light Water Reactors

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[April 1996 to March 2000]

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 cracking (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. Environmentally assisted cracking of Alloy 600 in high temperature water

Interaction between corrosion fatigue (CF) and stress corrosion cracking (SCC) of Alloy 600 were investigated under three loading modes in high temperature water. Type 1 was a cyclic loading condition at constant stress ratio. Type 2 was a monotonic loading condition and Type 3 was a combined loading condition of Type 1 and Type 2. As a result, the crack growth rate under Type 3 was almost equal to the linear summation of those under Type 1 and

Type 2. It was found therefore that there was no striking interaction between CF/SCC in Alloy 600. Further investigation using sensitized Alloy 600 is now being investigated under relevant conditions.

2. Mitigation for the enlargement of local damage by laser beam technique

As one of the evaluations for corrosion behavior of weld metal of SUS 304 stainless steel, which was post-treated by CO₂ laser beam technique, electrochemical approach was conducted by using a micro vibration electrode in 8 N-HNO₃ solution. It was found that the post-treating by laser beam technique for the HAZ was able to suppress the initiation of corrosion pits. Further investigation for the effect of laser beam will be carried out using thermally aged materials, which simulate sensitized welded region.

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. Since 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 investigated at first. As a result, it was found that high-speed measurement of local strain was successfully made by using a pin-hole, shielding light cylinder and filters.

Keywords : aging degradation, localized corrosion, light water, reactor, weld joints, laser beam

93 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 10¹⁰ cycle tests.

In the recent year, the activities are summarized in the following.

1. Delayed fracture resistance for 450°C tempered SCM 440 steel was evaluated. The relationships between diffusible hydrogen content and rupture time were dependent on the specimen configuration and loading conditions.

2. Delayed fracture resistance for ausformed SCM 440 steel was also evaluated. The delayed fracture resistance, i.e., critical diffusible hydrogen content, was much higher for ausformed SCM 440 steel than for 450°C tempered one.

3. AFM observations and ultra-micro hardness measurements were conducted for 450°C tempered SCM 440 steel. It was newly found that the martensitic steel was strengthened mainly by block boundaries. The difference in microstructures and strength mechanisms between 450°C tempered and ausformed SCM 440 steels is being investigated by the two techniques. This will clarify the high resistance of delayed fracture for ausformed steels.

4. Additions of more than 0.2 mass% nitrogen and 2 mass% molybdenum decreased the fatigue crack growth rate and increased the fatigue threshold for 316 type austenitic stainless steel. AP-FIM analysis showed that it is Mo-N pairs that improve the fatigue resistance for the stainless steel. The study on establishment of the mechanism for martensitic steels was started.

5. It was confirmed that an ultra-sonic fatigue testing machine with a frequency of 20 kHz was useful to obtain the fatigue strength at 10¹⁰ cycles.

Keywords : martensitic steel, delayed fracture, giga-cycle fatigue, AP-FIM, SPM, nanohardness tester

94 Mechanical Properties of Thin Films and Coatings

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[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 this financial year, DSI was carried out for gold and platinum thin films on a hard substrate of sapphire. The results obtained were compared with those for aluminum films which had been measured in the last year. Pop-in phenomena which are usually seen on the load-penetration depth curves for aluminum films, did not occur for both gold and platinum films. Auger electron spectroscopy revealed that the natural oxide layer existed on the surface for aluminum films, whereas the oxygen did not detect for gold and platinum films. It is concluded from these results that the pop-in phenomena for aluminum films are due to the oxide layer on the specimen surface.

Keywords : Thin films, Coatings, Elastic modulus, Hardness, Depth sensing indentation

95 Computational Simulation of Mechanical Properties and Behavior of Materials for Atomic Power Plants by Taking Microstructures into Account

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[April 1999 to March 2004]

The materials used in atomic power plants degrade due to the initiation and growth of various kinds of damages induced by neutron irradiation, creep and so on. The present study aims to develop the programs to simulate the initiation and growth behavior of damages and mechanical properties of damaged materials by using micro, meso, and macroscopic computational method. The material designing method to prevent the embrittlement and the evaluation method of material reliability will be discussed.

1. Dynamical process of irradiation-induced defects and their effects on materials properties

With use of computer simulations, this study aims to elucidate how the microscopic defects such as vacancies, interstitials, and their complex in irradiated materials develop into macroscopic ones such as voids and bubbles. Also we study how these defects affect the mechanical properties of the materials. For these purposes, we perform two types of calculations. One is the calculation for a microscop-

ic region where the initial process of irradiation-induced defects plays important roles on the overall fortune of the materials. For this region we carry out calculations based on atomistic models such as the molecular-dynamics and the Monte Carlo simulations. The other is for a mesoscopic region where aggregation and diminishing of voids and bubbles, which are regarded as products in very early stage of the macroscopic region, are thought to be most important for the mechanical properties of materials. For this region we perform calculations based on continuum models such as diffuse and sharp interface models.

2. Computational analysis for deformation and fracture of damaged materials at high temperatures

In the previous research theme, the prediction method for tensile properties of materials including He bubbles by using FEM analysis has been developed. In the present research, we investigate the prediction method for creep and fracture properties of materials including damages such as He bubbles, creep voids and cracks. The effects of morphology and distribution of He bubbles on creep properties are investigated by FEM analysis. The diffusive growth and cohesion to precipitates of He bubbles will be taken into account for the simulation. The growth rate of damages under creep condition will be computed by taking the microscopic mechanism such as diffusion and sliding into account. The growth rate of damages is accelerated under multi-axial conditions. The creep and fracture properties under multi-axial conditions in welded joints including irradiation and creep damages are also investigated.

Keywords : computer simulation, irradiation damage, molecular-dynamics, Monte Carlo simulations, diffuse and sharp interface models, helium embrittlement, creep fracture, finite element method

96 Long-term Creep-fatigue Properties of 316FR Stainless Steel for Fast Breeder Reactor

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[April 1995 to March 2001]

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, a simple and accurate analysis method for evaluating the low cycle fatigue life of the 316FR steel is required, because the main components of the reactor are subjected to cyclic thermal stresses. One of the objects in this research is to

apply a parametric analysis method for time-dependent low cycle fatigue life data of the 316FR steels. This method was developed by the authors and was successful to represent the temperature- and strain rate-dependences of the fatigue life for many kinds of conventional engineering heat resisting materials at the strain rate up to 10^{-5} /sec. The fatigue tests for 316FR steel are now running at 500, 550 and 600°C under the strain rates from 10^{-2} /sec up to 10^{-6} /sec.

Second object is to evaluate creep rupture and creep-fatigue properties for modified 316FR steels which is now developing by a steel maker and fabricators. So the testing data would be useful to the materials design. In the first half of this research the effects of the chemical composition such as C, N, Mn, P, Cr, Ni, Mo, Si and microstructure such as grain size on the high temperature strength properties are examined. In the second half a development of prediction method of the creep-fatigue life is aimed by using the data of monotonic creep rupture properties such as creep rupture ductility.

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

Related paper

High Temperature Fatigue Properties of the 316 FR Steel, K. Kobayashi and K. Yamaguchi, Trans. Japan Soc. Mech. Eng., 64 (1998) : 545-549.

97 Strategic Research on Advanced Ferritic Steels for 650°C USC Boilers (R & D of Structural Materials for 21st Century)

F. Abe, Strength and Life Evaluation Research Station

[April 1997 to March 2002]

The creep rupture strength has been improved to develop advanced 9Cr steels for application to large diameter and thick section boiler components such as main steam pipe and header of ultra-supercritical (USC) plant which will be operated at 650°C and 350 atmospheric pressure. The main results are summarized as follows ;

(1) The maximization of W concentration up to about 3% in the martensitic phase and the small addition of MX forming elements effectively improved the creep rupture strength of tempered martensitic 9Cr steels.

(2) Of the austenite stabilizing elements, the high melting point elements Ir and Pd are promising for further strengthening and stabilizing the matrix of martensite of the 9Cr-3W base steel by solid solution and precipitation strengthening, respectively. The fine precipitation of Fe-Pd intermetallic compound having L1₀ ordered structure occurred homogeneously in the matrix during creep as well as during tempering. The effect of Pd addition on the improvement of creep rupture strength becomes more significant at higher temperature.

(3) In Mod.9Cr-1Mo steel, the recovery of martensitic microstructure proceeded preferentially in the vicinity of prior-austenite grain boundaries at low stresses and long rupture time conditions above 10⁴h. The preferential recovery accelerated the onset of acceleration or tertiary creep and degraded the creep rupture strength. Therefore, for the improvement of long-term creep rupture strength, special attention should be paid to the suppression of preferential recovery of the microstructure near grain boundaries. An indication of the degradation in creep rupture strength at long times was easily seen in the creep rate - true strain curves in short times before rupture. The strain to reach a minimum creep rate shifted to small values when preferential recovery occurs.

(4) The creep rupture time of HAZ simulated materials of HCM 12A had its minimum after A_{C3} heating. The fine grains produced by the A_{C3} heating were responsible for the minimum time to rupture.

Keywords : ferritic heat resistant steel, ultra-supercritical power plant, alloy designing, creep, steam oxidation, fatigue, welded joint

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279. M. Igarashi, S. Muneki and F. Abe, *Gakushin-123 Committee*, 39(1998) : 355-362.
280. K. Kubo, M. Tabuchi, K. Yagi, H. Yokobori (Tohoku Univ.) and A. Fuji (IHI), Evaluation of Creep Crack Growth Property of High Temperature TiAl Intermetallic Compound, *Gakushin-123 Committee*, 39-3 (1998) : 237-243.
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□ **NRIM Publications (Apr. 1998 to Mar. 1999)**

1. Bulletin of National Research Institute for Metals, in Japanese No. 21 (Mar. 1999)
2. Annual Report of National Research Institute for Metals, in Japanese For fiscal year of 1997 (Mar. 1999)
3. Kinzaigiken News, in Japanese No. 4 to 12 (1998) and No. 1 to 3 (1999)
4. NRIM Research Activities, in English (Mar. 1999)
5. Material Strength Data Sheet, in English NRIM Creep Data Sheet No. 26B and No. 46 (Dec. 1998)
6. Guide to National Research Institute for Metals, in Japanese and in English For fiscal year of 1998 International Collaboration Research Apr. 1998 to Mar. 1999

International Exchange

Apr.1998 to Mar. 1999

International Collaboration Research

Australia

1. Studies on conductor fabrication Processes of high-Tc BiSrCaCuO super-conductors (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. Processing 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 Ni₃Al 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)
10. Enhancement of Superconducting Properties in Bi₂Sr₂Ca₂Cu₃O_x/Ag Wires and Tapes (Northwest Institute for Metal Research)
11. Comparison Researches of Materials Life Cycle Assessment (MCLA) Between Japan and China (Sichuan

Union University)

12. Atomic-scale Structure Fabrication using Scanning Tunneling Microscope (STM) (Beijing Laboratory of Vacuum Physics)
13. Composition and Structure OF Nitride Interfaces (Institute of Metal Research, Academia Sinica)
14. Environmentally Assisted Cracking (EAC) of Structural Materials for Light Water Reactors (Shanghai Research Institute of Materials)

EU

1. Research on Materials for Nuclear Fusion Reactor (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)
4. Evaluation Model of the Characterization Data of Materials (Institute for Advanced Materials, Petten Site)

France

1. Superconducting and cryogenic magnetic materials (Service National des Champ 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)
4. Structural Study of Disordered System by Synchrotron Radiation X-rays (Centre de Recherche sur la Physique des Hautes Temperature)

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 Eisenforschung GmbH, Universität 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, Et = v = s 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 Thermophysics & Cryogenics Sec.)
2. Intercomparison of methods and materials for strain measurements at cryogenic temperatures (Istituto di Metrogia "G. Colonnetti"-C.N.R.)
3. Metallic materials (Istituto per la Tecnologia dei Materiali Metalici Non Tradizionzli)

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 Fabrication and Evaluation Technique for Semiconductor Nano -Structure (Korea Research Institute for Science and Standard)
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)
7. Characterization of High-field and Strain-tolerance Performances for Super-conductors (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. Investigation and Development of Highly Parallel Algorithms for Materials Science Calculations (Kingston University)
3. Measurement and Evaluation Methods for Critical Current in High Temperature Superconductors (Cambridge University)
4. Advancement of Levitation Melting and Refining Technology (National Physical Laboratory)
5. Assessment of Ultra-Long-Term Creep Rupture Strength of Heat Resisting Steels (GEC Alstom 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 microstructural 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 (Northwestern University)
 12. Studies on mechanisms of nanoscale microstructural evolution in advance metallic materials (University of Virginia)
 13. Study on the mechanical properties of directionally solidified intermetallic 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 Superconductors (Argonne National Laboratory)
 18. Physical Properties of the Transition Metal Compounds under High Pressure (Carnegie Institution of Washington)
 19. Development of Nb₃Al Multi-filamentary Superconductor (Ohio State University)
 20. Analysis and Numerical Modeling of High Energy Beam Welding Phenomena (New Mexico State University)

□ List of Visiting Foreign Researchers

*STA Fellowship

Country and Name	Affiliation	Term	Research Subject
Argentina			
Miguel Ipohorski Lenkiewicz	Comision Nacional Energia Atomica	1998.1.13~1998.1.30	Electron Microscopy and Surface Technique
Australia			
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 Engineering, Monash Univ.	1997.12.1~ 1997.12.20	Atom Probe and TEM Studies of the Precipitation Processes of High Strength Aluminum Alloys
Austria			
Hans Kirchmayr	Technical Univ. of Vienna	1997.10.25~ 1997.10.29	Testing and Evaluation Methods of Superconductors
Brazil			
Marcelo Ferreira Moreira	Institute de Pesquisas Technologicas (IPT)	1997.9.3~1997.10.30	Surface Quality on Cast Superalloys (Directional Solidified and Single Crystal superalloys)
Belgium			
Josef Cornelis	Vlaamse Instelling voor Technologisch Onderzoek	1997.10.26~ 1997.10.29	Testing and Evaluation Methods of Superconductors
Bulgaria			
Dimitar Stoyanov Tchankov*	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
China			
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

Country and Name	Affiliation	Term	Research Subject
Zhou Wei	Tsing Hu University	1997.9.20~ 1997.12.24	Aging Behavior of Porous Silicon
Yuefung Gu*	Shanghai Jiao Tong Univ.	1997.10.1~1999.9.30	Grain Boundary Structures and Ductility Improvement of Platinum Metals based Refractory Superalloys
Lanting Zhang	Shanghai Jiao Tong University	1997.10.13~ 1997.12.12	Synthesis of TiNi ₂ Single Crystal
Qing Chen	Beijin Univ. of Science and Technology	1997.10.31~ 1998.2.28	Structural Investigation of Nanocrystalline Pb, In and Ge on Silicon
Zhang Xuanjia	Physics Department, Zhejiang University	1997.11.13~ 1997.12.27	Study on the CDW Film and High Temperature Superconductivity Film
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	Study on the Formation and Characterization of High Temperature Superconductor Films
Xie Huimin*	Department of Mechanics, Tsinghua University	1998.3.16~1999.3.15	Measurement of Micro-deformation using Electron Moire Method and AFM Moire Method
Czech			
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
Denmark			
Erik Johnson	University of Copenhagen	1997.10.13~ 1997.10.26	Structural Determination of Metastable Pb Inclusions in Metal Matrix
Finland			
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
France			
Evelyne Peron Gonia*	Ecole National Superiour 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 Materiaux et du Genie 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 Materiaux et du Genie 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

Country and Name	Affiliation	Term	Research Subject
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 Appication of Superconducting Thin Films Synthesized by Atomic Layer-by-layer and Epitaxial Growth Methods
Germany			
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
Hungary			
Reich, Lajos	Department of General Physics, Etovos Univ.	1997.10.1~ 1998.11.11	Three Dimensional Atom Probe Studies of the Precipitation Processes of High Strength Alminum Alloys
India			
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
Israel			
Mosche Kuznietz*	Nuclear Research Center-Negev	1998.1.24~1998.4.22	Magnetism and Superconductivity of the (Pr, Dy) Ni ₂ B ₂ C Solid Solutions
Korea			
Hong, Moon Hi	JST Domestic Fellow	1997.4.1~1998.2.28	Atom Probe and TEM Studies of the Microstructures of Pearlistic Steel Wires
Ahn Jeon Ju*	Yeungnam Univresity	1997.4.21~1998.8.26	Fatigue Properties for SiCw/AC4CH and SiCw/AC ₈ 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

Country and Name	Affiliation	Term	Research Subject
Yang Hae Un	Chonnam National Univ.	1998.1.19~1998.2.28	Microstructure Control of Intermetallic Compounds in Ti-Al System
Malaysia			
Md. Hasan Zahir*	Universiti Sains Malaysia	1997.11.5~1999.11.4	Synthesis and Characterization of Noble Phthalocyanine Species
Myanmar			
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
New Zealand			
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
Russia			
Olga Tkachenko	Novosibirsk State University	1997.9.10~1997.9.17	Photon-assisted Tunneling Phenomenon Solid State Interfacial Reactions and Surface Analysis of Thin Solid Films
Andrei Rar		1997.10.1~2000.3.31	
Slovakia			
Michal Rabara	The Univ. of Tokyo	1997.5.20~2000.3.31	Critical Current Density Characteristics for Bi ₂ Sr ₂ Ca ₃ Ox Tape Conductors
Switzerland			
Markus Buttiker	Geneva University	1997.7.22~1997.7.26	Tunneling Time in Magnetic Field
Ukraine			
Yulia Vitaševna Bosova*	Institute for Sorption and Problems of Endoecology	1997.5.18~1997.8.5	Research on Measuring Technics for the Electrochemical Property of Active Carbon
United Kingdom			
Bryan Edward Cole	University of Salford	1997.9.16~1998.2.28	D 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
U.S.A.			
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 Inset Magnets with High T _c Superconductors
Loren F. Goodrich	National Institute of Standards and Technology	1997.10.24~ 1997.11.1	Testing and Evaluation of Superconducting Materials

Country and Name	Affiliation	Term	Research Subject
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.	mes Laboratory, Iowa State University	1998.1.10~1998.1.19	Single Crystal Growth of Boro-carbide 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

Nationality and Name	Affiliation	Site	Date
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China Yan Luguang, Sha Ciwen	Institute of Electrical Engineering, Academia Sinica, Director and Dipurity director of MHD division	20.	Apr.1998
India Dr. Dpankar Benerjee	Defence Metallurgical Reseach Laboratory, India	20.	May.1998
Brazil Mr. Denilson Jose do Carmo	Marcelino Corradi Foundry Technology Center, Technoogical Assistance Area/Mechanical Engineer	2.	Jul.1998
U.S.A Dr. Shih Chi Liu	National Science Foundation, Program Director Division of Civil & Mechanical Systems	14.	Jul.1998
India K. A. Natarajan	Indian Institute of Science, Professor	21.	Jul.1998
China Pan Wei	Qing Hua Univ, Dept. of Material Science	7.	Aug.1998
U.S.A Dr. Timothy J. Renk	Sandia National Laboratories, Principal Member of Technical Staff	22.	Sep.1998
ロシア Oleg A. Plaksin	Institute of Physics & Power Engineering, Senior Scientist	14.	Oct.1998
U.S.A S. K. Guharay	Univiersity of Maryland, Group Leader, Associate Reseach Professor	26.	Oct.1998
China Yang Deze	China Metallurgical Information & Standardization Institute, President	29.	Oct.1998
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Mexico Ms. Estela Gonzalez Caballero	Enginering and Industrial Development Center, Material Characterization Division, Material Technology Dept.	30.	Nov.1998

Nationality and Name	Affiliation	Site	Date
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Ms. Maria Judit Rivera Montevalvo	Engineering and Industrial Development Center, The Chief of the general sffaiarc department division	5.	Mar.1999
China			
Hai Jin-Tao	Academy of Mechniry Science & Technology, General Director	11.	Mar.1999
England			
Laurence Eaves	Department of Physics,University of Nottingham	11.	Mar.1999
China			
Zhiming Liu	Hebei Technological University, Deputy President	24.	Mar.1999

□ Brief Introduction of STA Fellowship Program

In response to growing calls from the international community for greater international 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.

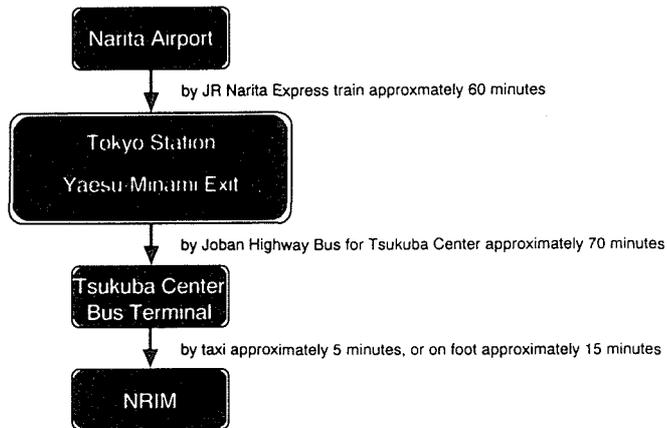
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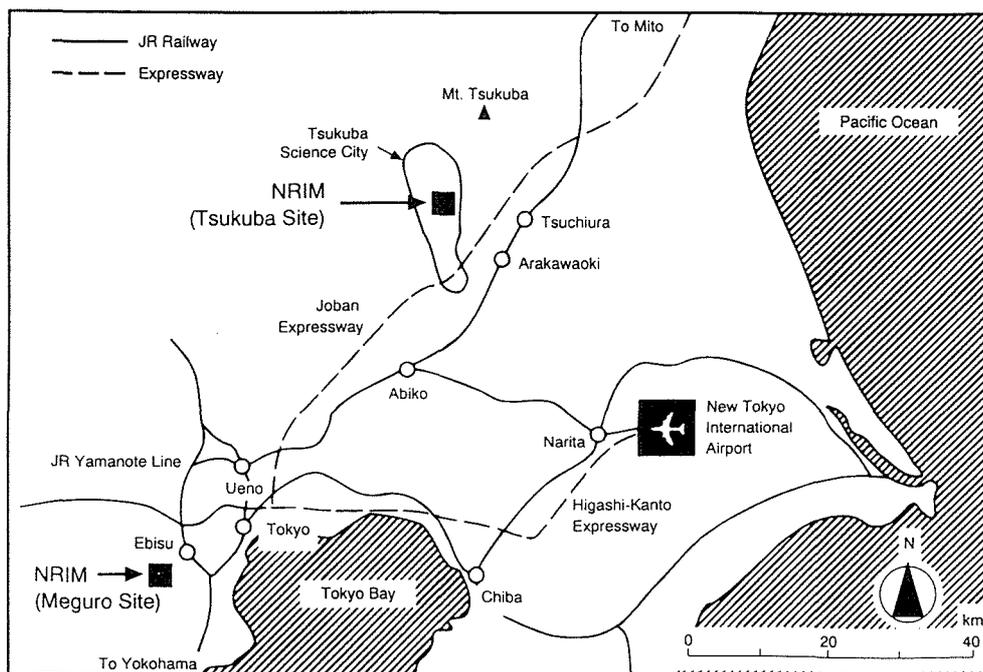
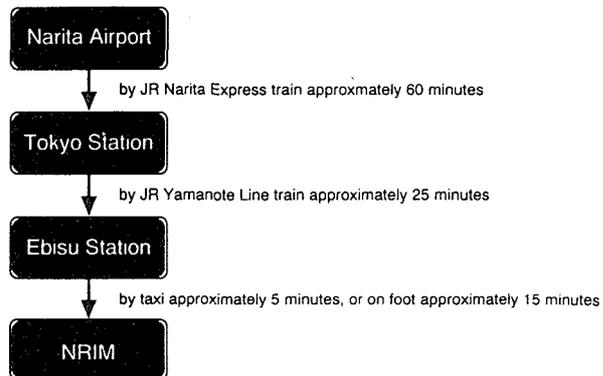
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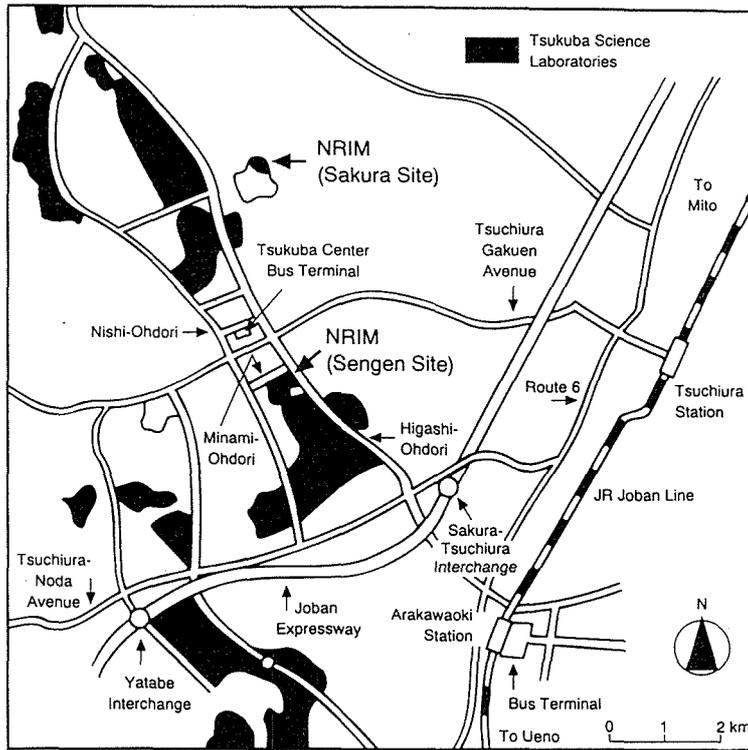
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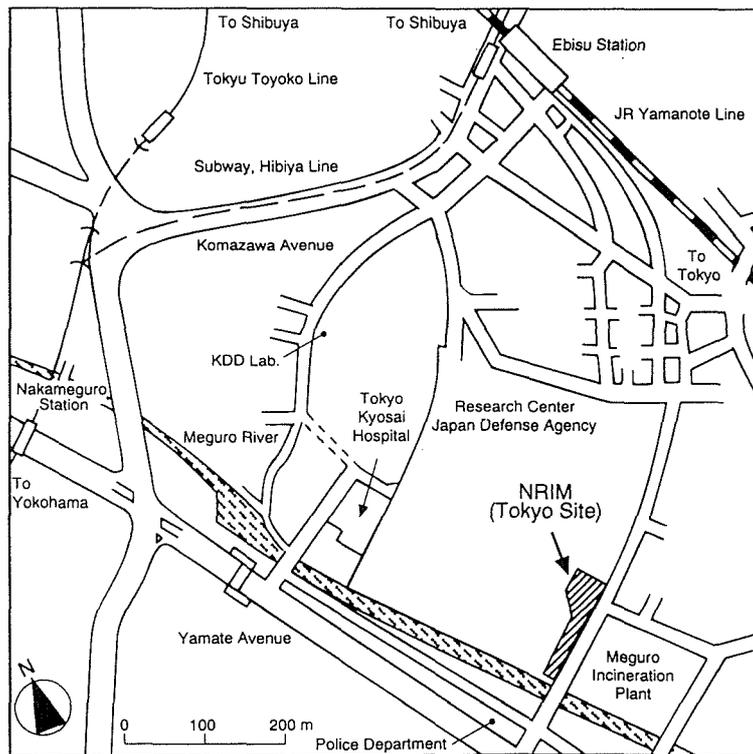


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Tsukuba Site



Tokyo Site

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