NRIM

Research Activities

1991

National Research Institute for Metals

Japan

Meguro Main Site

Tsukuba Laboratories

NRIM Research Activities

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National Research Institute for Metals, Japan

For the last several years, international scientific exchange between the National Research Institute for Metals (NRIM) and foreign research organizations through joint projects and exchange of scientists and information has increased considerably. We intend NRIM to be an open research center interacting even more actively with other research organizations all over the world. For this purpose, NRIM is to publish a new annual report "NRIM Research Activities" instead of the former English publication "Transactions of NRIM". This new journal is arranged to present up-to-date research activities in NRIM and other information such as its organization and budget. We hope that "NRIM Research Activities" will indeed be useful for your understanding of NRIM and will promote mutual scientific relationship.

NRIM Research Activities 1991

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Preface

NRIM was established in 1956 as an organization attached to the Science and Technology Agency of the Japanese Government. It was the time for Japan to make progress in industrial activities and to develop frontier expertise in science and technology for aircraft and atomic energy. A new national research organization was required to promote advance in science and technology of metals. Since then, our Institute has played an important role in research and development of metals and alloys as well as advanced materials. Now NRIM has a research staff of over 300 people with a budget of about 6.7 billion yen (FY 1990) and is located at two sites; one is the main site in Tokyo and the other is the branch in Tsukuba Science City.

The research activities of NRIM are concentrated in two fields. One is fundamental and applied research for advanced materials such as high performance heat-resisting alloys, workable intermetallic compounds, new superconductors, etc. The other is research on reliability of materials to ensure safety of structural components and facilities. It includes creep and fatigue testing, research on the failure mechanism, life prediction and so on.

During the past 35 years, we have made several contributions to materials science and technology, especially in the field of superconducting materials and superalloys. We have developed the bronze method to draw wire of metallic superconducting materials, and in 1988 our colleague found a new superconducting material of Bi-Sr-Ca-Cu oxide, which has a Tc higher than 100K. The computer aided design method for superalloys was newly constructed, and several excellent heat-resisting alloys have been developed. In the research on reliability of materials, we have been conducting very long term research programs on creep and fatigue properties, including creep rupture testing over 100,000 hr. We have been publishing these data as the series of NRIM Creep and Fatigue Data Sheets, which have been distributed to all of the important research organizations in the world. Through these programs, we have been working at

the progress in the life prediction technology and advanced material assessment technology.

Recently, the direction of research activities in NRIM has shifted from research providing scientific and technological basis for industries to research for fundamental science and frontier of material science. Together with the shift of direction of our research activities, a plan of relocation and reorganization is in progress by moving the main site in Tokyo to Tsukuba Science City. We expect that those changes bring about a new turn and development of NRIM.

Kazuyoshi Nii

Dr. NII, Kazuyoshi
Director-General

Research Topics

Development of High Resolution Magnet System and Applications

— A Step toward NRIM High Field Magnet Laboratories —

Aoki, H. : Materials Physics Division

Key words: High resolution magnet, Cooperative research, Quantum oscillation, NMR

Outline of NRIM High Field Magnet Project

A magnetic field is useful and powerful for research in many fields ranging from basic science such as physics, chemistry and biology to engineering and medical treatments. There are still increasing needs for magnetic field facilities which can provide higher magnetic fields and which are useful for versatile research purposes. The National Research Institute for Metals has been developing several types of high field magnet systems whose abilities are of the highest class in the world. These are hybrid magnet, long pulse magnet, large bore size magnet and high resolution magnet systems. These magnet systems will be installed in the high field facilities in Tsukuba in 1994 and will be open for both domestic and foreign researchers. In particular the high resolution magnet system has been nearly completed in 1990. Cooperative research programs with universities and other institutions as well as inhouse ones have started using the system.

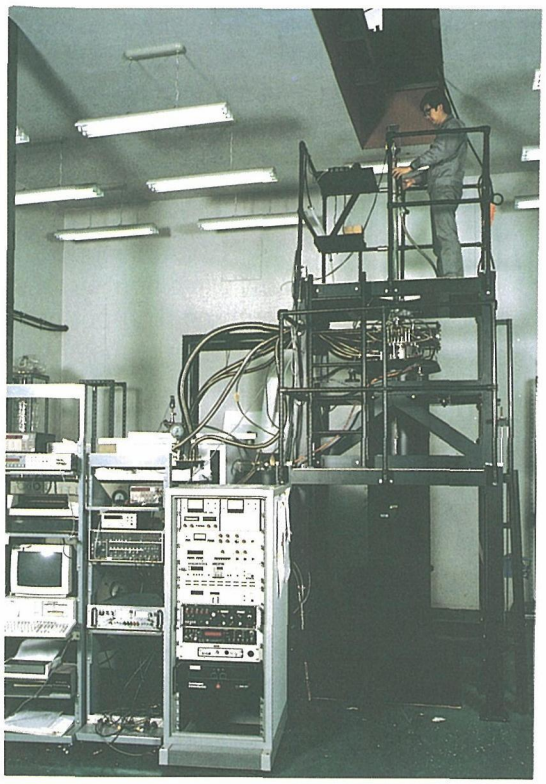


Fig. 1 High resolution magnet system-subsystem 1

High Resolution Magnet System

The high resolution magnet, which can produce a magnetic field of high homogeneity and stability, is indispensable for such experiments as magnetic resonance measurements and detection of quantum oscillations. However, the specifications required for the magnet system are different depending on the type of the experiment. The high resolution magnet system of NRIM consists of three different sub-systems to meet various requirements.

The first one can produce a magnetic field up to 16T with a homogeneity of 10^{-4}/10mmdsv and is equipped with a top-loading dilution refrigerator which can cool a sample space of 25 mm in diameter below 30 mK (Fig. 1). The magnet system is also equipped with a modulation coil so that the sensitive detection technique of modulation method can be applied. This system is particularly suitable for detection of quantum oscillations and can be used also for ordinary transport and magnetic measurements.

The second one is designed for broad band nuclear magnetic resonance (NMR) and other magnetic resonance experiments. The magnet can produce a magnetic field up to 15.5 T with a homogeneity of 10^{-5}/10 mmdsv and stability of 10^{-5}/hr in the sample space of 50 mm in diameter. The NMR probes for temperatures from 1.5K to 800K have been developed and th eprobe for a He^3 system will be ready in 1991. An NMR detection system which is capable of magnetic field sweep and frequency sweep masurements has been completed. A new automatic frequency tuning device has been also developed to make the experimental time shorter.

The third one is a 500 MHz high resolution solid state NMR system with room temperature bore size of 89 mm. The magic angle spinning frequency can be increased up to 10 kHz and the temperature of

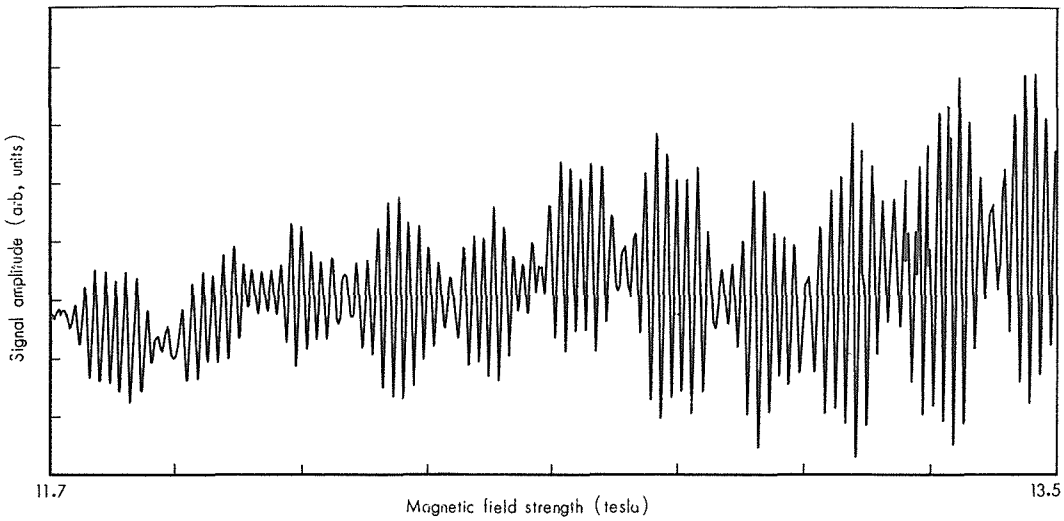


Fig. 2 De Haas-van Alphen effect of the heavy Fermion compound UGe_2. This work has been done in collaboration with Prof. Onuki of Tsukuba University.

the sample space can be varied from 100°C to −100°C. A broad band NMR system covering the temperature range from 1.5 K to 800K will be also equipped with the 500 MHz magnet system for such experiments that need much data accumulation in 1991.

Applications

The high resolution magnet system can be applied to research in various fields. Several cooperative and in-house research projects have started or will start from 1991: (1) NMR/NQR studies of the high Tc oxides, (2) de Haas-van Alphen (dHvA) effect studies of heavy Fermion compounds and organic superconductors. (3) high resolution NMR studies of organic compounds, (4) transport properties of single crystals of the high Tc oxides, thin films and semiconductors, (5) magnetic field effects on biological beings.

Figure 2 shows an example of the cooperative work, the de Haas-van Alphen effect of UGe_2, which utilizes the capability of the high resolution magnet system. UGe_2 is one of the so-called heavy Fermion compound. In order to observe a sufficiently large dHvA signal from heavy Fermion compound, a high homogeneous magnetic field and low temperature is indispensable as well as a single crystal of high quality.

More research projects will start in 1991 and proposals for cooperative researches are welcome.

Fabrication of Quantum Well Box Systems by Droplet Epitaxy for Advanced Optoelectronic Devices

Koguchi, N., Takahashi, S., Chikyow, T. and Ishige, K. : Surface and Interface Division

Key words: Quantum well boxes, Molecular beam epitaxy, Droplet epitaxy

Quantum Well Boxes—Artificial Quasi-zero Dimensional System

Recently, artificial low-dimensional semiconductor structures with nanometer sizes such as quantum well wires and quantum well boxes have received considerable attention, owing to their interesting physical properties and potential application in very-high performance devices. For example, emission of low threshold and high-monochromized laser light is expected by using these artificial nanostructures. The calculated optical gain coefficient of the InGaAs/InP laser with different type of active layer is shown in Fig. 1. The optical gain coefficient increases by reducing the sample dimensionality. Also, prediction of enhanced electron mobility has been made for quantum well box systems. An other promising candidate for artificial quasi-zero dimensional system is a modulation doped spherical semiconductor heterostructure which is called a "Superatom". It has been speculated that the system could have a quasiatomic electronic structure and, therefore, that we can design and fabricate a variety of artificial molecules or crystals using these superatoms as building blocks.

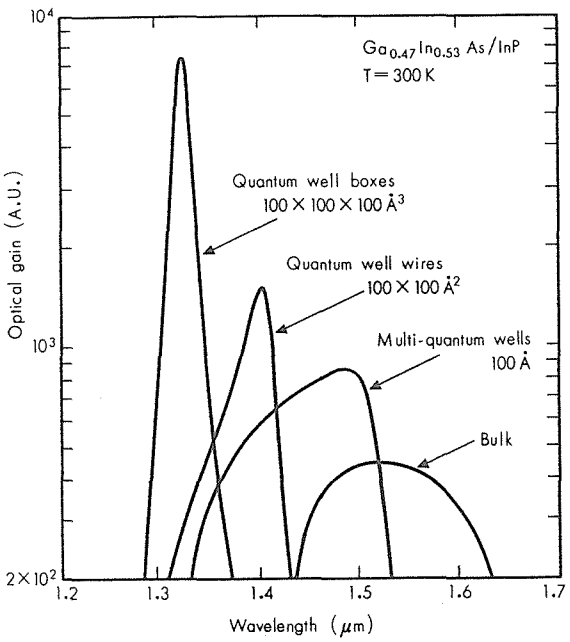


Fig. 1 The caluculated optical gain coefficient of the InGaAs/InP laser with different type of active layer.

Fabrication Method of the Quantum Well Boxes—Present Status

In spite of the fundamental interest in making quantum well boxes, progress in their fabrication has been slow. To date, electron beam lithography followed by dry etching has been most commonly used to define these nanostructures. However, the quantum well wires and boxes produced by these two techniques often have exposed side walls damaged by the etching process. This damage is found to strongly reduce the structure luminescence efficiency at reduced future sizes, probably due to a high density of surface defects acting as nonradiative recombination centers.

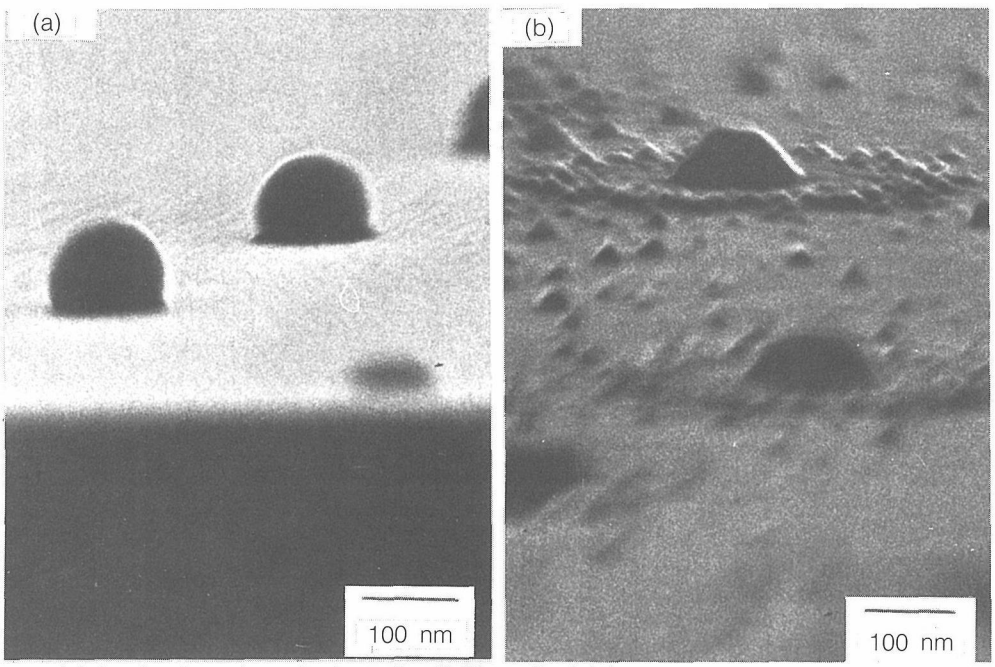
Thus, it is highly desirable to look for alternative methods to fabricate quantum well boxes without air-exposed and etch-damaged interfaces. Several different methods are currently applied to manipulate the dimensions of semiconductor crystals and to control their size in the nanometer regime. Two alternative strategies have turned out to be most promising for the realization of such ultrasmall semiconductor microcrystallites, suspended in a dielectric matrix which serves as confining potential. This method inherently produces zero-dimensional systems, but it has the drawback of the structural environment being amorphous. Consequently, the surface of a suspended microcrystallite is quasi-free; i.e., it forms by necessity surface states (dangling bonds) which act as centers for nonradiative recombination. The second approach is the controlled epitaxial growth of semiconductor multilayers on terraced substrates; i.e., so-called "Fractional Epitaxy". In principle, this concept offers the possibility to directly fabricate one-dimensional structures by the preferential nucleation of adatoms on the step edges. However, the inevitable fluctuation of the growth rates usually results in a poor control of the geometrical configuration and thus the electronic and optical properties of the fabricated structures.

Droplet Epitaxy—New Fabrication Method for Quantum Well Boxes

Molecular beam epitaxy (MBE) is successful in growing finely layered structures, but it has not yet been able to achieve comparable success in production of structures for quantum well boxes.
In this laboratory, we proposed a new molecular beam epitaxial growth method for InSb quantum well boxes surrounded by CdTe which has a nearly equal lattice constant to InSb. We termed this method as "Droplet Epitaxy" which was characterized by Sb incorporation into In droplets deposited on a CdTe epitaxial layer in an ultra high vacuum.
The MBE system used in this work was a conventional system with a cluster of boron nitride effusion cells in a common liquid nitrogen shroud and an electron gun for reflection high energy diffraction (RHEED). Elemental In and Sb and compound CdTe in the Knudsen cells were used as molecular beam sources. An InSb (001) wafer was used as a substrate. At first, an InSb buffer layer was grown onto the substrate. Then the CdTe epitaxial layer was grown onto the InSb buffer layer. Next, In was deposited on the CdTe epitaxial layer. After deposition of the In droplets, an Sb flux was supplied.
In this method, numerous In droplets were formed on the CdTe epitaxial layer because the substrate temperature was kept above the melting point of In during deposition and because of the inertness of the CdTe epitaxial layer surface for the monolayer adsorption of the In with zinc-blend structure. The photographs of In droplets on the CdTe epitaxial layer and the surface of the specimen after the Sb molecular beam radiation taken by high resolution scanning electron microscope (HRSEM) are shown in Fig. 2. The shape of the In droplets is hemispherical and the average diameter of the droplets is 1200 Å. The standard deviation of the size distribution of the In droplets is about 10%. These In droplets changed to pyramidal shape InSb microcrystals which were truncated (111) and (100) facets after the Sb flux radiation. The size of the InSb microcrystals depends on the size of the In droplets. The size of In droplets decreases with decreasing substrate temperature and/or increasing intensity of the In molecular beam. The quantum well box system may be fabricated by growing the CdTe epitaxial layer over the InSb microcrystals.

Application of Droplet Epitaxy to Other Materials

The key point of the "Droplet Epitaxy" is making a inert surface for the III and V column elements monolayer adsorption. We are now trying to fabricate quantum well boxes by Droplet Epitaxy for the system of GaAs/ZnSe as a combination of III-V and II-VI compound semiconductors. We are also challenging to fabricate quantum well box systems composed of the III-V compound semiconductor microcrystals surrounded by other III-V compound semiconductors by using VI-column element terminated III-V compound semiconductor substrates. In this case, the inert surface of the III-V compound semiconductor is expected to be obtaied by the VI-column element termination.



(a) In droplets deposited on the CdTe epitaxial layer
(b) InSb microcrystals grown by the Sb molecular beam supply to In droplets
Fig. 2 HRSEM photographs

Creep Data Activities as Reference Data for Engineering Materials

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Key words: 100,000 hours creep rupture data, Heat-resistant steels and alloys, NRIM Creep Data Sheets

High temperature structural machinery such as thermal power generation plants, nuclear reactors, petrochemical and synthetic chemical plants are generally operated for 10 to 30 years under high temperature and high pressure conditions. In order to secure the safety and reliability of the structural materials in these plants, it is necessary to understand the long-term creep properties accurately. With the remarkable progress of Japanese industries in the 1950's, the service temperature and pressure of these plants was raised. The availability of long-term creep data of domestic high temperature materials, however, was very limited. In view of this background, with strong demand and support from industries and academic societies, it was planned to conduct systematic material tests in NRIM from the neutral standpoint in order to obtain high-temperature strength properties of commercial heat-resistant metallic materials manufactured in Japan. It was also planned to publish the results as the NRIM Creep Data Sheets series (NRIM/CDS).

Since 1966 we have conducted the systematic testing program of creep and creep-rupture tests up to 100,000 hours (over 11.5 years) for 41 kinds of heat-resistant steels and alloys. For this program we installed 878 single-type creep testing machines, 144 multiple-type creep testing machines and 30 special-type creep testing machines. The testing materials for NRIM/CDS were sampled from commercial stocks manufactured by 24 companies in Japan, and the total number of heats was 361. Table summarizes the testing materials, testing conditions and the data obtained. The table also includes the NRIM/CDS in publication. We have already published 15 CDS (designated 3B, 4B, 5B, 7B, 8B, 9B, 12B, 14B, 15B, 16B, 18B, 23B, 24B, 29B and 30B) that contain the long-time data up to 100,000 hours. The NRIM/CDS containing 100,000h creep rupture data of 19 kinds of materials will be published in the next 10 years.

The NRIM/CDS are sent to 375 R & D organizations of 39 countries on an exchange basis. The NRIM data are also available to the general public via JICST (Japan Information Center of Science and Technology) on-line service of factual database: ENSTAL. The NRIM/CDS are now considered to be one of commonly referred high temperature strength data and they contribute to determine the design allowable strength, to ensure the safety and reliability and to evaluate the life an residual life prediction of high temperature structural components.

Long-term creep strain-time data and stress relaxation data are also necessary for inelastic design analysis. Long-term creep strain tests and long-term stress relaxation tests are conducted on 2.25Cr-1Mo steel, 304, 316, 321 stainless steels and 800H alloy. In the new program, modified 9Cr-1Mo and 9Cr-2Mo steels are added to the existing 41 testing materials of NRIM/CDS. These data will be published as NRIM/CDS in the near future.

Many investigations have been conducted concerning the creep fracture and deformation properties in connection with the NRIM/CDS program. Followings are some of the subjects of published research work;

(1) Development of extrapolation method for long-term creep rupture strength
(2) Analysis of microscopical creep fracture mechanism and construction of fracture mechanism map
(3) Evaluation of creep damage and analysis of creep damage rule
(4) Evaluation of creep strain data for inelastic design analysis
(5) Prediction of creep deformation curves using modified θ projection concept
(6) Evaluation of high temperature strength of welded joints
(7) Analysis of drift in PR thermocouple after long-term creep testing
(8) Analysis of long-term stress relaxation behavior
(9) Analysis of creep-fatigue interaction and microscopical damage mechanism
(10) Evaluation of creep crack growth behavior using large size specimen
(11) Evaluation method of materials strength data for database building
(12) New materials testing technique
(13) International collaborative researches: for example, VAMAS project, JICA project concerning collaborative research between Japan and Korea

Table Status of NRIM/CDS data file as of March 1992

NRIM CDS No.	Material (Nominal Composition)	Specification (JIS) Form*	No. of Heats	Latest Issue	Creep-Rupture Data	
					Test Temperature	Data Size
1A	1Cr-0.5Mo	STBA22, T	11	Sep. 1976	500– 650	300
2A	1.25Cr-0.5Mo-Si	STBA23, T	10	Sep. 1976	500– 650	268
3B	2.25Cr-1Mo	STBA24, T	12	Dec. 1986	500– 650	408
4B	18Cr-8Ni	SUS304HTB, T	9	Dec. 1986	600– 750	319
5B	18Cr-10Ni-Ti	SUS321HTB, T	9	Dec. 1987	600– 750	332
6A	18Cr-12Ni-Mo	SUS316HTB, T	9	Mar. 1978	600– 750	337
7B	0.2C	STB42, T	9	Mar. 1992	400– 500	228
8B	0.5Mo	STBA12, T	12	Sep. 1991	450– 550	252
9B	1Cr-1Mo-0.25V	ASTM A470–8	11	Mar. 1990	500– 650	291
10A	12Cr-1Mo-1W-0.3V	SUH616, B	9	Mar. 1979	500– 650	261
11A	2.25Cr-1Mo, NT	SCMV4-NT, P	7	Sep. 1980	500– 650	185
12B	5Cr-0.5Mo	STBA25, T	9	Mar. 1992	500– 650	229
13A	12Cr	SUS403-B, B	9	Mar. 1980	450– 600	236
14B	18Cr-12Ni-Mo	SUS316-HP, P	2	Mar. 1988	600– 850	60
15B	18Cr-12Ni-Mo	SUS316-B, B	6	Sep. 1988	600– 850	166
16B	25Cr-20Ni-0.4C	SCH22-CF, T	14	Sep. 1990	800–1050	276
17A	0.3C	SB49, P	8	Mar. 1981	400– 500	122
18B	1.3Mn-0.5Mo-0.5Ni	SBV2, P	5	Dec. 1987	450– 550	108
19A	9Cr-1Mo	STBA26, T	11	Mar. 1981	550– 700	264
20A	0.5Cr-0.5Mo	STBA20, T	9	Sep. 1981	450– 600	240
21A	1.25Cr-0.5Mo-Si, NT	SCMV3-NT, P	14	Sep. 1981	500– 650	344
22A	Fe-15Cr-26Ni-Mo-Ti-V	A286	4	Sep. 1982	550– 700	103
23B	Fe-20Cr-20Ni-20Co-W-Mo-(Nb+Ta)	S590	3	Mar. 1989	650– 800	84
24B	Ni-15Cr-28Co-Mo-Ti-Al	Inconel 700	2	Mar. 1989	700– 850	55
25A	High strength steel	SPV50, P	21	Sep. 1983	400– 550	349
26A	Fe-21Cr-32Ni-Ti-Al	NCF800HTB, T	6	Mar. 1983	600–1050	171
27A	Fe-21Cr-32Ni-Ti-Al	NCF800HP, P	6	Mar. 1983	600–1000	157
28A	18Cr-12Ni-Nb	SUS347HTB, T	9	Sep. 1983	600– 750	267
29B	Ni-13Cr-4.5Mo-0.75Ti-6A1-2.3 (Nb+Ta)-Zr-B	Inconel 713C	8	Mar. 1990	850–1000	192
30B	Co-25Cr-10Ni-7.5W-B	X45, C	4	Sep. 1988	750– 950	101
31A	1Cr-1Mo-0.25V	ASTM A356-9, C	9	Sep. 1984	450– 600	178
32	18Cr-8Ni	SUS304HP, W	45	Mar. 1982	500– 650	623
33	Fe-21Cr-20Ni-20Co-3Mo-2.5W-(Nb+Ta)-N	N155, C, F	9	Mar. 1984	550– 850	158
34A	Ni-19Cr-18Co-4Mo-3Ti-3Al-B	U500, C, F	9	Sep. 1989	700–1000	206
35A	1Cr-0.5Mo, NT	SCMV2-NT, P	8	Sep. 1990	450– 650	204
36A	2.25Cr-1Mo, QT	ASTM A542, P	7	Mar. 1991	450– 650	248
37	25Cr-12Ni-0.4C	SCH13, C	5	Oct. 1985	700– 950	85
38A	25Cr-35Ni-0.4C	SCH24, C	7	Sep. 1991	850–1100	94
39	Ni-15.5Cr-2.5Ti-0.7Al-1Nb-7Fe	NCF 750-B, B	4	Mar. 1988	600– 900	96
40	0.2C-1.3Mn	STB52, T	2	Sep. 1989	400– 500	31
41	Ni-15.5Cr-8Fe	NCF600, T, B, P	5	Mar. 1991	600–1000	96
	Total Heat and Data Size		368			8724

* : T=Tube, P=Plate, B=Bar, C=Casting, F=Forging, W=Welding

Fatigue Fracture in Ceramic Materials

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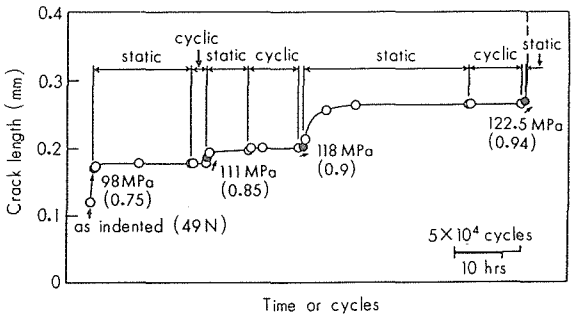
Key words: Cyclic fatigue, Ceramics, Crack growth, Indentation, Asperity-contact, Trans-granular fracture, Intergranular fracture

Nowadays it is of common knowledge that fatigue in metals and alloys under cyclic loading is primarily attributable to their plastic deformation characteristics associated with dislocation movement. For a long time, therefore, it has been taken for granted that brittle ceramics in which plastic deformation is effectively absent cannot be fatigued. However, the latest active works have made it clear that crack growth occurs under cyclic loading conditions in some ceramics and can not be explained by the subcritical cracking mechanism due to static fatigue (environmentally-assisted cracking process) alone.

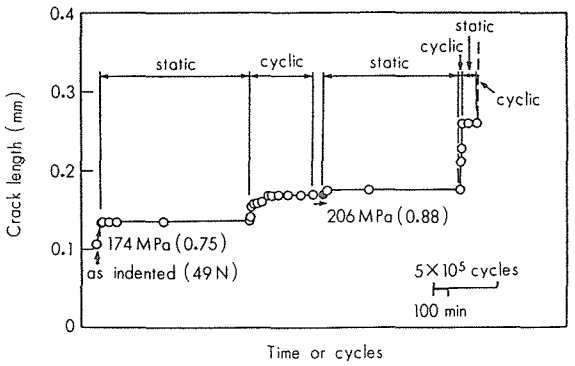
Fatigue Mechanism

What kinds of ceramics are damaged under cyclic loading conditions? As an example, Fig. 1 shows crack growth behavior in two types of silicon carbide loaded statically and cyclically by turns. One material is characterized by transgranular fracture mode while another is of intergranular fracture type. These data suggest that cyclic fatigue occurs only in the intergranular fracture type material; in other words, a crack sited along grain boundaries can propagate under stress reversals whereas a crack situated on the cleavage-surface cannot propagate. Similar behavior was observed also in silicon nitride systems. Since the toughened ceramics with high K_{IC} are usually characterized by intergranular cracking mode, such a tendency appears to be a serious problem for engineering practices.

On the basis of the experimental results above mentioned and other data available, the mechanism illustrated in Fig. 2 was proposed as the most plausible model for the fatigue in brittle non-transforming ceramics. In this figure, the fatigue crack growth mechanism of ceramics is schematically shown in comparison with that of metallic materials, specifically, the plastic blunting and resharpening mechanism for producing striations. It is assumed that during the tensile part of the loading cycle in ceramic materials where cyclic fatigue is observed, stable crack growth followed by crack arrest should occur. Such crack resistance in non-transforming ceramics is mainly due to micros-cale-crack branching and crack-path deflection. During unloading, asperity-contacts on crack surfaces develop. Such asperities are presumably produced because of the release of localized residual stresses created by thermal contraction anisotropy and/or trapping of debonded particles inside of cracks. Accordingly, local compressive stresses develop at the asperity-contacts, which lead to activation of the crack tip area such as lateral crack formation. Therefore, it has been considered that cyclic fatigue in ceramics is caused by the repetition of "crack resistance" during tensile part of loading and "crack reactivation" during unloading.



(a) Trans-granular fracture type material (sintering additives: B, C)



(b) Intergranular fracture type material (additives: Al_2O_3)[1)2)]

Fig. 1 Fatigue crack growth behavior during static and cyclic loadings in silicon carbide.

Indentation Fatigue

We are also examining the damage caused by cyclic application of local compressive stress onto the material surface which gives rise to lateral crack growth and the resultant chipping phenomenon.

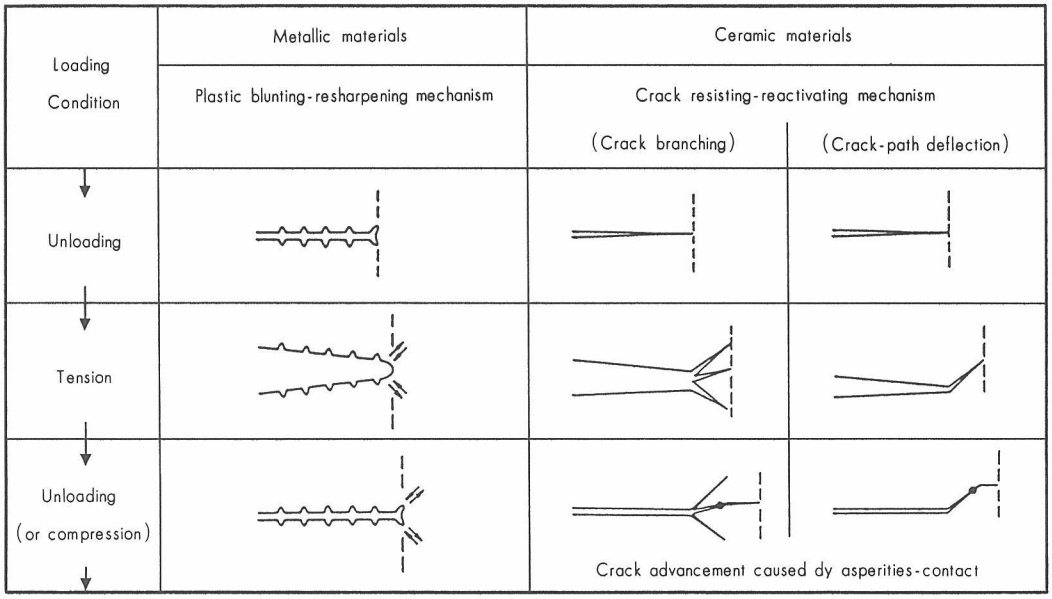


Fig. 2 Schematic presentation of cyclic fatigue crack growth mechanism of ceramic materials in comparison with that of metalic materials[2].

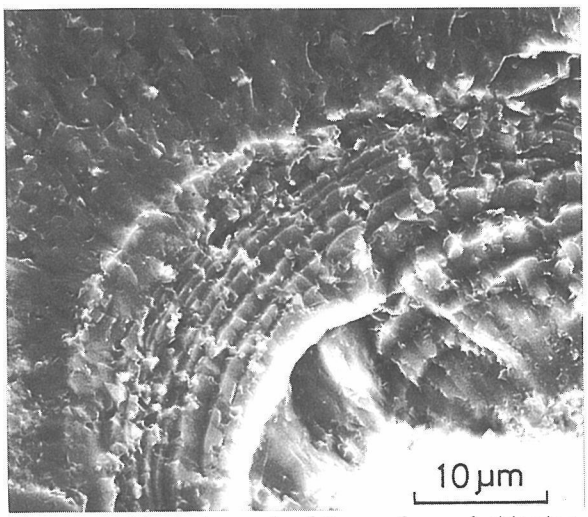


Fig. 3 SEM photograph of the surface of chipping area produced in the silicon nitride with transgranular fracture characteristic.

This kind of damage accumulation, which is called indentation fatigue, is supposed to be very important, because it is unfavorable from an engineering viewpoint. Moreover, it is also significant for fundamentally understanding the fatigue mechanism in ceramic materials such as the damage accumulation in the crack asperity contact area described above. Figure 3 presents the surface of chipping area produced in silicon nitride with trans-granular fracture characteristic. Interestingly, striations are seen. It is supposed that they were produced in every indentation cycle, owing to the difference between the stress fields during loading and unloading for each cycle.

Besides the above mentioned research technique, ultrasound fatigue testing facilities are employed in order to deeply understand the fatigue mechanism in ceramic materials.

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Control of Trace Elements Effect in TIG Arc Welding

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Key words: Trace elements effect, TIG arc welding, Anode, Vaporization, Current density distribution, Wedge shaped electrode

In the VAMAS project "Weld Characteristics" which dealt with the effect of surface active trace elements in TIG are welding, many reports were discussed from the point of view of surface tension driven flow (Marangoni flow) on a molten pool. This study was done from the view point of anode area behavior due to vaporization phenomena from the molten pool surface. To prove the effect of anode area behavior on melting phenomena, it is necessary to obtain the current density distribution on molten pool.

Measurement of Current Distribution on Molten Pool

Regarding anode phenomena of the arc, current density distributions on the anode have been investigated very thoroughly for the tungsten cathode/water-cooled copper anode combination by Nestor (1962). In the case of a molten anode, however, the current density distribution on the molten pool surface has not yet been measured. It is conjectured that the distribution will be different from that on a water-cooled cooper plate, because the ionization potentials of metal vapours are much lower than those of the environmental gases and consequently, the distribution will depend on the local vaporization from the molten pool. If the distribution could be measured, vaporization phenomena at the molten pool of metals could be better understood.

A method was developed for the measurement of the current density distribution on the molten pool of which the diameter is 10mm at most under a stationary TIG arc. The measurement of the electric potential distribution on the back of a thin plate anode was carried out by using an experimental setup as shown in Fig. 1. The current density distribution was derived by comparing the measured potential distribution with calculated results from the expected current density distributions on the molten pool. It was verified for the first time that the current density distribution on the molten pool is not a Gaussian distribution but a flat-top (equi-current density) distribution resembling a frustum of a cone.

The temperature distribution of the arc near the molten pool surface influences the temperature distribution on the pool surface and the consequent

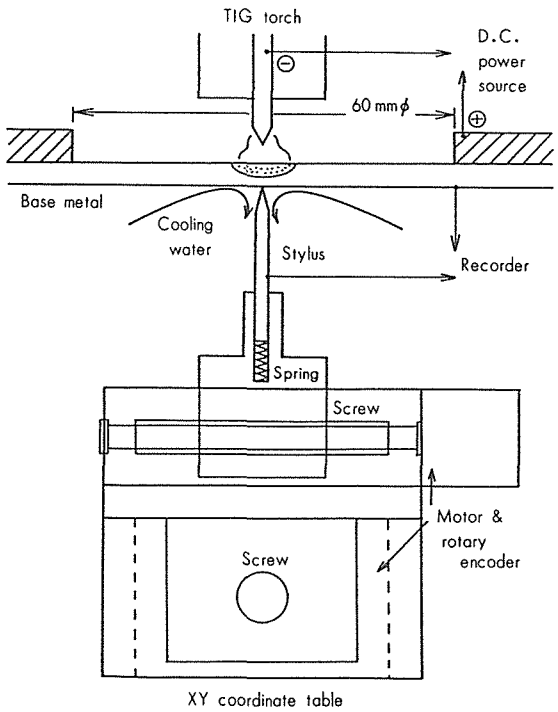


Fig. 1 Schematic diagram of the experimental set up for measurement of the electric potential distribution on the back of a thin plate in stationary TIG arc welding.

vaporization area. Figure 2 shows that result of the current density distribution under the condition of a strong plasma jet stream (45° cone electrode) and a high arc length (5mm), which contribute to expansion of a high temperature region of the arc near the surface. In contrast, Fig. 3 shows the result under the condition of a weak plasma stream (truncated electrode) and a small arc length (2mm) which reduce the high temperature region. Thus, it is possible to control the anode area on the molten pool by varying the temperature of the arc near the molten pool.

The vaporization area is influenced by surface active trace elements. Elements such as sulfur and oxygen suppress the vaporization from the molten pool surface and constrict the anode area. It was tried to reduce the influence of a change in anode area due to the trace elements on melting phenomena by controlling the shape of the high temperature region of the arc near the molten pool.

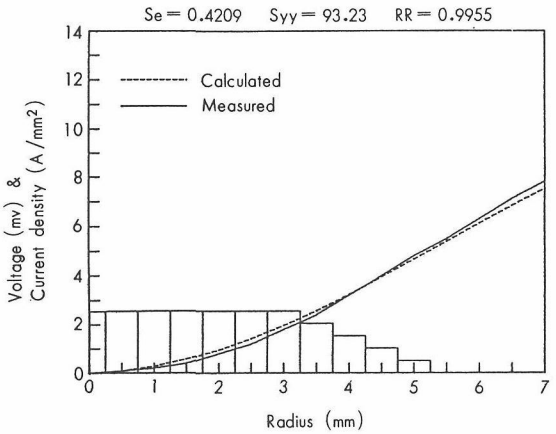


Fig. 2 Current density distribution and comparison between measured and calculated potential distribution (arc length: 5mm, electrode tip: 45 cone).

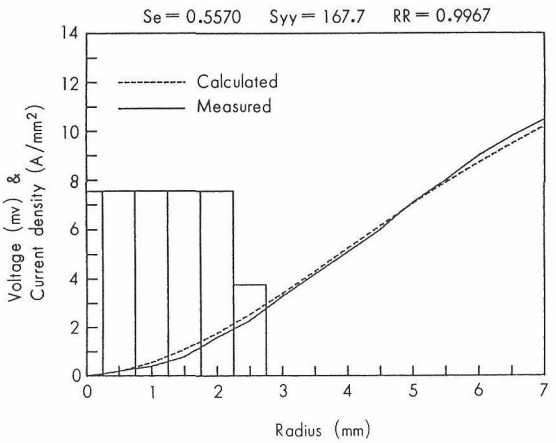


Fig. 3 Current density distribution and comparison between measured and calculated potential distribution (arc length: 2mm, electrode tip: frustum of cone)

Pool Shapes in Stationary Arc with Wedge Shaped Electrode

Figure 4 shows the molten pool shapes produced by generating a stationary TIG arc for 25 seconds on the steels S and X, with a wedge shaped electrode as shown in Fig. 5. The plate designated steel S had a low sulphur and oxygen and the steel X had a somewhat higher level. Heat input on the pool surface is unsymmetrical and the shape of the pools in steels S and X is distinctly different.

The result may be explained as follows. Concerning the temperature distribution of the arc near the pool surface, the shape of the highest temperature isotherms corresponds to the shape of the electrode tip but the shape of the lower temperature isotherms becomes elliptical with the major axis at a right angle to the electrode edge because of the increase in plasma jet stream along the major axis. In steel X

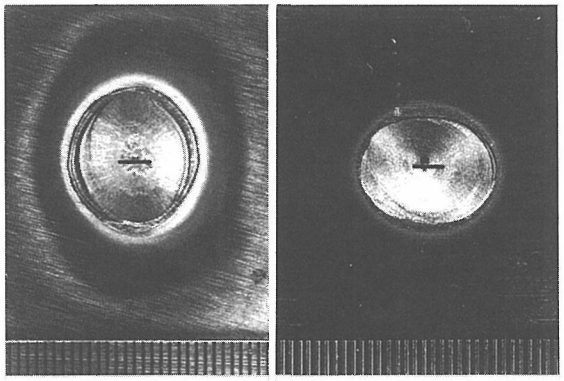


Fig. 4 Pool shapes in stationary arc with wedge shaped electrode as in Fig. 5 (Line in pool shows electrode tip position. Scale unit is 0.5mm).

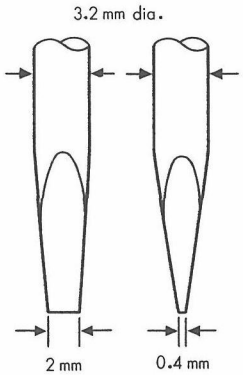


Fig. 5 Schematic representation of the wedge shaped tip of the tungsten electrode.

which tends to suppress vaporization, the anode area is influenced by the shape of the higher temperature region of the arc. On the other hand, the anode area in steel S is influenced by the shape of the periphery of the arc.

Control of Trace Elements Effect

The influence of anode area on melting phenomena can be estimated from measured results of the current density distribution. The influence of a difference in anode area on the width of the back bead is effectively weakened by reducing the difference in the expansion of the anode area at a right angle to the weld line. If the welding is done with the electrode edge at a right angle to the weld line using the wedge shaped electrode, it is expected that the trace elements effect on the weld characteristics is reduced.

The results of the welding tests have been reported as the results of the round robin tests in VAMAS project "Weld Characteristics". It was possible to form a uniform bead indepent of the different contents of sulphur.

Research of Laser-Ultrasonic Technique and Its Application for Materials Evaluation

Yamawaki, H. : Failure Physics Division

Key words: Laser, Ultrasonic, Nondestructive testing, Materials evaluation

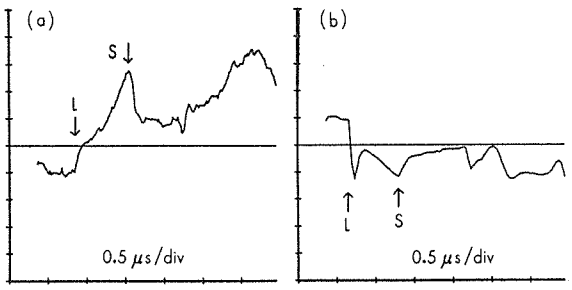
The laser-ultrasonic technique is a measurement technique in which completely non-contact ultrasonic generation and detection on a solid are realized by means of pulsed laser irradiation and laser interferometry. The generation and detection methods are based on the optical means that enable remote and non-contact ultrasonic measurements. The laser-ultrasonic technique is expected to be a useful non-destructive evaluation (NDE) method for materials at high temperature or objects of complex shapes. NDE of new materials such as ceramics and composites are also the target of the research.

Generation of Ultrasound by Laser Irradiation

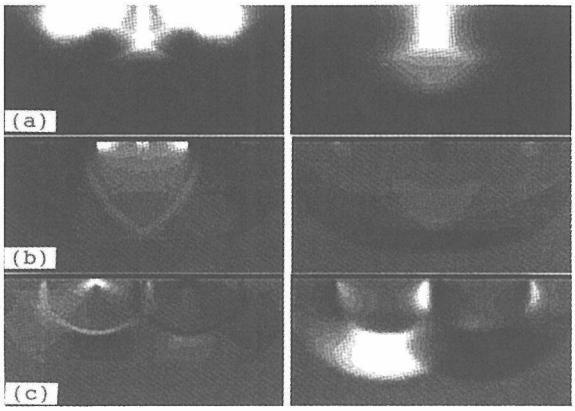
Ultrasonic waves generated by the pulsed laser irradiation are different from the waves generated by ordinary ultrasonic transducers used in general contact ultrasonic testing, since the waves change according to the laser pulse energy. In case of low energy pulses, the major mechanism of ultrasonic generation is due to the thermal stresses induced by the absorption of laser light. With an increase in the pulse energy, the major mechanism changes to become dependent on the vaporization pressure of the irradiated materials. These two modes that are called the thermal stress mode and the ablation mode have a difference in the direction of the force vector. Both modes reveal complex ufltrasonic wave forms as shown in Fig. 1. The wave forms in Fig. 1 are the surface displacement of ultrasonic waves propagating in a solid and detected by a homodyne interferometry. For engineering applications of laser generated waves to NDE, behavior of ultrasound in a solid must be made clear.
Figure 2 shows distribution patterns of propagating laser-generated ultrasonic waves that are calculated using 2-dimensional finite difference method for elastic waves. From the Figures some important facts are recognized. In thermal stress mode, ultrasonic waves originate at the edge of the laser irradiated area where the thermal gradient is most signficant. In ablation mode, however, longitudinal plain waves are generated from the whole of the laser irradiated area. In this simulation, it is also possible to obtain ultrasonic wave forms in a solid. The calculated results are believed to be useful for future analysis of laser-ultrasonic experimental results.

Detection of Ultrasound by Laser Interferometry

Ultrasound detections by optical methods are classified into interferometric methods and non-interferometric ones. Non-interferometic methods are well-known with a knife edge technique that detects surface ripples caused by ultrasonic waves propagating with angles, but such a technique is only applicable for flat surfaces. So, major techniques of optical detection of ultrasound are by interferometric ones.
The homodyne technique is a popular technique for the analytical study of laser generated ultrasound as shown in Fig. 1, because it can detect surface displacement directly due to its broadband frequency response. Heterodyne technique is useful for the quantitative measurement of ultrasonic amplitude, because it uses frequency detection of the laser beam that is reflected at the vibrating surface and affected by the Doppler effect of optical frequency. Figure 3 shows a schematic diagram of a heterodyne interferometer system built in our laboratory. This system has an optical setup that is commonly used as the Michelson interferometer. A new feature of the system, which makes it better than the existing system, is the frequency detection mechanism which works as a demodulater. The frequency detection system in Fig. 3 has the advantage that the frequency of the ultrasound to be demodulated can be easily increased by changing the delayed time of the delay line, and the sensitivity at the



(a) Thermal stress mode
(b) Ablation mode
Fig. 1 Displacement wave forms generated by pulsed laser irradiation



(a) Magnitude of displacement. (b) Volumetric strain (c) Shear strain. Left figures are for thermal stress mode and right ones are for ablation mode. Longitudinal and shear waves are obviously seen in figures (b) and (c), respectively.

Fig. 2 Two-dimensional distributions of laser-induced ultrasonic waves in a solid

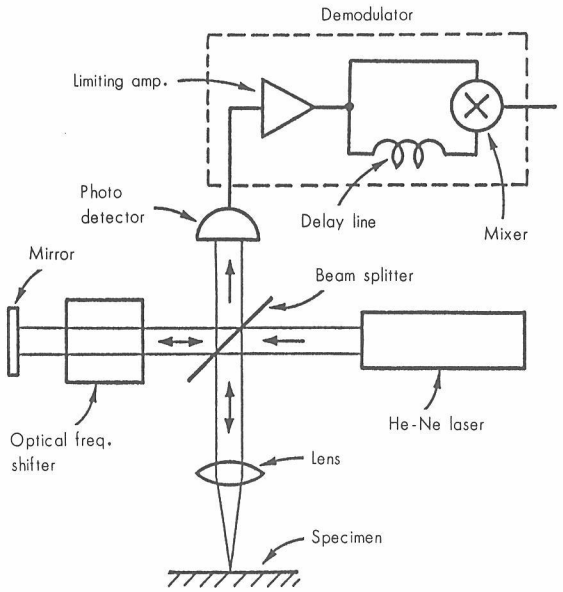


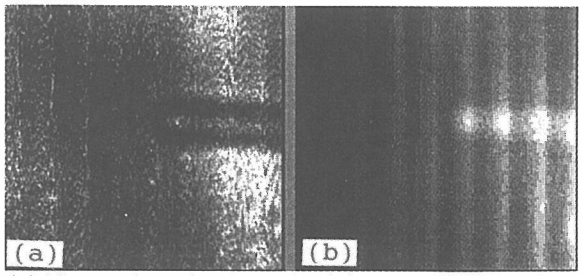
Fig. 3 A schematic diagram of an optical heterodyne system for non-contact ultrasonic detection.

center frequency to be detected is better than that of other demodulation systems. Therefore, this system is expected for the ultrasonic detection technique of quantitative NDE using high frequency ultrasound.

Ultrasonic Imaging by Laser Interferometry

Recently, microscopic techniques using ultrasound such as a scanning acoustic microscope (SAM) are applied for the flaw detection or materials characteriation on small regions. The laser ultrasonic technique may be also used for the detection of small flaws.

Figure 4 shows the ultrasonic images of a copper wire that is included in a bonding layer between a thin steel plate and an acrylic resin plate. The diameter of the wire is 0.1mm and the thickness of the front steel plate is also 0.1mm. Ultrasonic pulse waves with a frequency of 10MHz are transmitted by a piezoelectric transducer that is attached on the rear acrylic resin plate. The ultrasound vibration due to the ultrasonic pulse wave is detected at the surface of the steel plate by the heterodyne interferometer in Fig. 3. The specimen is scanned by a XY-stage, and the detected signals of the ultrasonic pulse are plotted synchronously on the computer display with gray scale. The amplitude and traveling time of the pulse are measured simultaneously, and plotted as shown in (a) and (b) of Fig. 4. The ultrasonic waves are diffracted by the wire and the fringe pattern that indicates the shape of the wire appeares in Fig. 4(a). The pattern of the traveling times represents a simple figure which indicates that diffracted waves take longer time for arrival at the surface.



(a) Ultrasonic pulse intensity (b) Traveling time. Size of pictures is 2.5mm by 2.5mm

Fig. 4 Ultrasonic images of a copper wire in bonding layer between a thin steel and an acrylic resin plates.

Laser-ultrasonic techniques still include several problems for practical use. The detection techniques are sensitive to the surface roughness of specimens. The generation phenomena are different from those of the traditional methods, and it is therefore hard to treat the waves as in traditional methods. But the capability of laser-ultrasonic techniques for the new materials NDE has been proved by the experimental applications for materials in high temperature, flaw detection on curved surfaces, microscopic imaging, and etc.

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R&D of Structural Intermetallic Compound TiAl

Tsujimoto, T. : 3rd Research Group

Key words: Intermetallic compound, Light heat-resisting material, Deformation twin, Isothermal forging, Superplasticity, Microstructure control

The intermetallic compound TiAl has a specific gravity of 3.6, and excellent oxidation resistance and high strength at elevated temperature, which suggests that TiAl is promising as a light, heat-resisting material. This compound had been studied extensively and exclusively by the Air Force of the USA as a material for military use under strict secrecy of the research contents. At present we know that this study lost its strong activity in the middle of the 1980's. There is no other full-scale study than that by the Air Force of the USA. The reason is considered that TiAl was believed to be too brittle at ambient temperature and too difficult for hot working. Thus, any investment for study of TiAl was too risky for private enterprises.

Research on TiAl in NRIM was begun in 1978 and has been continued up to date without any interruption. During the first half of this period where NRIM was only a main participant, NRIM brought out various excellent characteristics of TiAl in mechanical properties and in processing. It became clear that the possibility of TiAl-base alloys being used on a large scale as an industrial material in future technology was increased. At present, R&D of TiAl has become very active world-widely not only in the academic field but also in the industrial field. As a result, the role of NRIM in R&D of TiAl is changing now from a trigger to a technological pioneer based on the abundant experience and inherent challenging spirit.

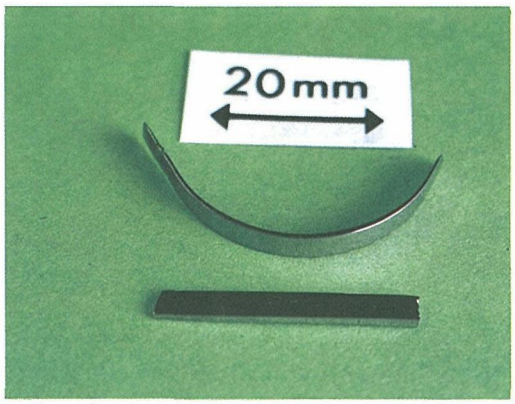
Table shows the chronicle of the results reported by NRIM. The first item was the most important finding and the starting point for a full-scale study on TiAl-base alloys in NRIM, because TiAl had been believed to be too brittle for use as a structural material in those days. However, tensile ductility of the binary TiAl compound at room temperature was not enough, because a metallic structural material is required to have at least elongation of 3% at room temperature.

TiAl has a crystal structure of $L1_0$ with an axial ratio of 1.02. The prolonged distance between the nearest pair of a Ti-atom and a Al-atom comes from a covalent-like bonding of the p-d hybrid, for which the 3p-electrons of Al atoms are responsible. This means that addition of the third elements which replace Al-atom will change the axial ratio and the plastic behavior of TiAl. The fifth item in the table was the first work in the world displaying that the room temperature ductility was improved by alloying. An example of bending for the alloys containing Mn is shown in Fig. 1. On the polished tension-side surface of the bent specimen numerous deformation twins were observed, showing that the deformation mechanism is plural in the alloy. The finding of the sixth item attracted attention of materials scientist as a new concept of deformation mode design to improve the poor ductility of intermetallic compounds.

Hot working of TiAl had been believed to be far more difficult than we know it to be today. The third item was the first work in Japan which showed that hot working of TiAl was possible. In this case, a rather special method was used in anticipation of the severe difficulty for deformation. Later, isothermal forging was developed as a more general method as cited in the seventh item. Using a slow deformation rate was inevitable for hot working of

Table Chronological results for TiAl-base alloys done by NRIM

1. Finding the fact that TiAl of low Al content is not so brittle at room temperature. (1980): The best composition is an alloy with about 48 at% Al.
2. Reporting feasibility for machining. (1981)
3. Reporting a success in hot extrusion with lateral pressure. (1982)
4. Reporting on melting by vacuum high frequency furnace with CaO crucible. (1983)
5. Finding room-temperature ductility of about 5% by bend test in Ti-48at% Al-1at% Mn alloy (containing Ti_3Al). (1984)
6. Reporting on active twin deformation at room-temperature in the above alloy. (1985)
7. Establishing an isothermal forging technique. (1986)
8. Improving oxidation property by addition of Si. (1987)
9. Confirming a positive temperature dependence of fatigue strength. (1988)
10. Finding fine grain superplasticity and dynamic superplasticity. (1989)
11. Establishing thermomechanical processing techniques for structure control to get fine equiaxed $TiAl+Ti_3Al$ alloys. (1990)



The alloy platelet of 0.8mm thickness wound around a cylinder with a radius of 10mm at room temperature.

Fig. 1 Addition of 1.0 at %Mn enables bend work.

TiAl, because the flow stress of TiAl increases rapidly with strain rate, and this reflects strongly upon the attainable fracture strain.

Superplasticity is a very useful phenomenon which can be used for secondary forming. Figure. 2, which is taken from the first work in NRIM, represents fine grain superplasticity obtained for a material with microstructure of Fig. 3. We can also see dynamic superplasticity, when temperature is changed during deformation. A merit of dynamic superplasticity is in a point that super-plastic working is applicable even for as-cast TiAl-base alloys.

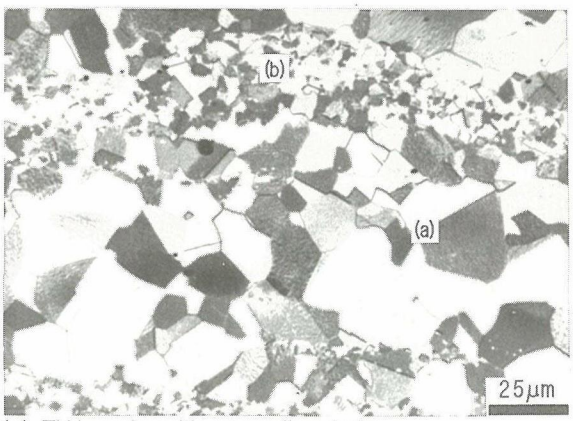
Molten TiAl is not so active as molten Ti-alloys, because the titanium content in TiAl is only half that of Ti-alloys. Utilizing this difference, melting using a Ca0 crucible was studied as given in the fourth item. As a vacuum high frequency melting furance is conventional equipment, this fabrication method is very economical and easily applicable. It was found finally that inclusion of oxygen of 0.13 wt.% is inevitable with a Ca0 crucible, which is the equilibrium value of molten TiAl to Ca0. It was also found that oxygen is concentrated in Ti_3Al when TiAl+Ti_3Al 2-phase alloys are annealed. For TiAl-base alloys melted with a Ca0 crucible, ductilization at room temperature is being studied by means of a combination of addition of a third element and heat treatment.

It is becoming clear that the microstructure in TiAl-base alloys changes considerably with heat-treatment or thermomechanical processing, and that the mechanical properties of the alloys change remarkably with microstructure. We can see prospects in this technical field. It may be stated that the front work of development for the alloys is changing from composition control to microstructure control. A strong endeavor is being made now for the establishment of structure control techniques of TiAl-base alloys in NRIM.

(a) Before test

(b) After test (at 1200K, $1\times10^{-4}s^{-1}$, elongation exceeds 200%)

Fig. 2 Tensile specimens.



(a) TiAl grain with annealing twins

(b) Fine Ti_3Al particles and TiAl grains

Fig. 3 Microstructure of isothermally forged TiAl intermetallic compound.

As shown in the eleventh item, we succeeded in obtaining TiAl-base alloys with a special configuration and distribution of Ti_3Al by thermomechanical treatment. This structure is especially effective for obtaining superplasticity at high temperatures, and has a positive effect on room temperature ductility. Furthermore, we are developing a sophisticated heat treatment which uses the strong temperature dependence of compositions of the TiAl/Ti_3Al (or α-Ti) phase boundary in the equilibrium phase diagram. We are getting various microstructures: structures with excellent creep resistance, structures with toughness to impact, structures with good ductility at room temperature, and so on.

This research has been done mainly by the 3rd Research Group as a part of Designated Research "Production and character evaluation of functional intermetallic compounds". Part of the research is financed by the Agency of Industrial Science and Technology belonging to MITI of Japan as "High performance materials for severe environments".

Design and Development of Nickel-Base Superalloys and Titamium Alloys

Yamazaki, M. : Materials Design Division

Key words: Alloy design, Nickel-base superalloy, Titanium alloy, ODS nickel-base alloy, Superplasticity

Two National Projects and Alloy Design

We had two national projects in which alloys were developed. The first one was "Advanced Gas Turbine"; in this project we treated conventionally cast nickel-base superalloys and directionally solidfied columnar nickel-base superalloys. The second one was "Advanced Alloys with Controlled Crystalline Structures"; single crystal nickel-base superalloys, superplastically workable nickel-base P/M alloys, and oxide dispersion strengthened nickel-base superalloys were treated. In the second project Ti alloys were also treated. We developed a computer-aided alloy design method for gamma/gamma-prime type nickel-base alloys. The essential part of these alloy design programs is made up of giving pairs of gamma and gamma-prime phase compositions in multi-component systems. Many pairs of analysed compositions of gamma and gamma-prime phase compositions were used to express phase relations. From the calculated phase compositions, by giving arbitrary phase volume fractions, one can obtain an alloy composition together with some other factors for the alloy such as lattice parameters of the phases, lattice mismatch, density, creep rupture life, hot corrosion resistance, solution window, etc.

Single Crystal Ni-Base Superalloys

The target for single crystal alloys (SC alloys) was as follows: Rupture life at 1313 K and 137.3 MPa; more than 1000 h. Repture elongation at the same conditions as above; more than 10%.
We modified our alloy design program described above, to be applied to SC alloys. Various factors such as gamma-prime volume fraction, lattice mismatch of gamma and gamma-rime phases, W/Ta ratio in gamma-prime, solid solutioning degree of gamma-prime (according to our therminology, SI), and solution treatment temperature allowance (window).
Many of the developed alloys satisfied the target values described above.
Near the end of the project, the second version of alloy design program for Ni-base alloys was developed. In this version the lattice mismatch played an important role and by running this program some high Mo alloys were indicated to have long creep rupture strengths. The most probable high Mo light alloy is TMS-62, and its composition is as follows.
TMS-62 (High Mo SC alloy)
7.9Cr, 6.9Mo, 5.8Al, 0.9Ti, 2.4Nb (in Mass %)

Superplastic Ni-Base Superalloys

The target for superplastically workable Ni-base superalloys in the project was as follows. The UTS at 1033 K is more than 1569 MPa, tensile elongation at that temperature is more than 20%, and the alloy must be superplastically forged at around 1300 K. After the project started it was found that this target, except superplasticity, was too high to be achieved. Preforms for superplastic forging were made through HIP-processing of powders without extrusion.
For the alloy design, the above described alloy design program for Ni-base alloys was applied to calculate gamma and gamma-prime compositions to be present in a P/M Ni-base superalloy, RENE 95, and a series of alloys, including the original alloy, RENE 95, with various gamma-prime contents but with the calculated compositions of the two phases. An alloy, TMP-3 designed to have a gamma-prime content a little higher than the one in the original alloy showed better superplasticity than that of the original.
NRIM continued research works to get alloys with higher strength and elongation values through composition modifications as well as heat treatments and some doping. Stronger alloys were developed. An improved version of alloy design program was then developed, which showed that there existed still better alloys, althouchg they could not reach the target values.

Oxide Dispersion-Strengthened Ni-Base Superalloys

Oxide dispersion strengthened (ODS) alloys, made up of gamma, gamma-prime and yttria particles, are stronger than SC alloys and are expected to be used as materials for gas turbines. Mechanical alloying in an attritor, extrusion, forging, zone annealing, and bonding are usually considered to be applied to make ODS blades.

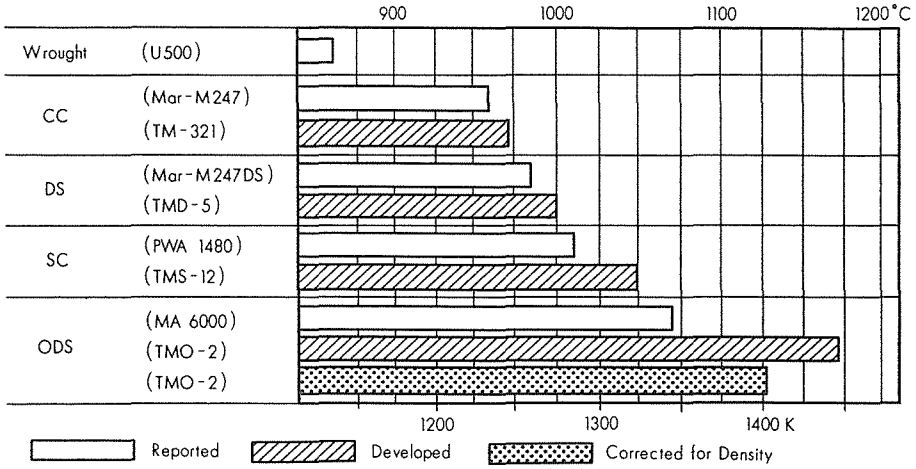


Fig. 1 Temperature capability to give a 1000 h rupture life at 137.3 MPa for Ni-base superalloys. CC: Conventionally cast alloy, DS: Directionally solidified alloy, SC: Single crystal alloy, and ODS: Oxide dispersion strengthened alloy.

NRIM again proposed a candidate alloy; this was named TMO-2. This alloy, comared to MA 6000, a famous INCO alloy, is higher in W and gamma prime contents.

The target for the ODS alloy was as follows:

Rupture life at 1373 K and 137.3 MPa; more than 1000h.

Rupture elongation at that condition; more than 5%.

Alloy TMO-2 gave a rupture life much longer than the target value and hence than that of alloy MA 6000, but the elongation value was about 4% or less, being probably similar to that of alloy MA 6000.

NRIM improved the intermediate temperature strength of this type alloy by further increasing gamma-prime content of TMO-2, to get, for instance, TMO-20 which was designed to have a gamma-prime content of 75%.

Figure 1 shows temperature capabilities of developed Ni-base superalloys and representative commercial ones.

Superplastic High-Strength Ti Alloys

Ti alloys were developed to be applied to gas turbine compressor discs. Superplastic forging was used for this purpose with preforms made from HIP. The extrusion process was not applied to make preforms to avoid installation of a big extrusion machine.

The target of the project was as follows:

Specific strength at 573 K; more than 27.46 × 10 Nm/kg,

Elongation at the same condition; more than 10%, and Superplasticity; superplastically forged to disc shapes with preform made by HIP

Three types of alloy design methdos, Methods A, B, and C were tried. In principle, in all the methods, alpha and beta phase compositions at superplastic forging temperatures (1020 to 1170 K) are calculated, and alloys with phase volume frction ratio of 1:1 were designed. Some properties, such as m values for superplasticity, were estimated by equations developed.

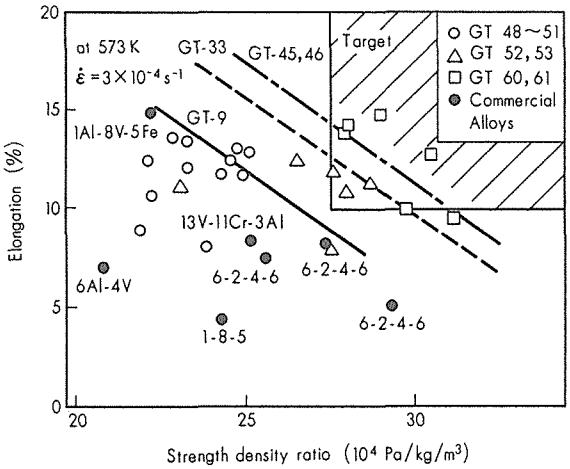


Fig. 2 Tensile properties of developed alloys and commercial alloys at 573 K with a strain rate of $3\times10^{-4}s^{-1}$.

Three methods, A, B, and C were used to calculate alpha and beta phase compositions in multicomponent Ti systems. Method A depends on the syntheses of related Ti-X phase diagrams and Method B utilizes compositions of the two phases measured by EPMA. Method C, a thermodynamical one, depends on Hillert's surbregular solution model. Recently, we are trying sublattice model calculations to incorporate the effect of oxygen and also to treat alpha-2 phase.

Alloys GT-33, GT-60, and GT-61 attained the target of the project. All the alloys developed have fairly good superplastic properties.

Figure 2 shows the properties of representative Ti alloys developed by us and some commercial Ti alloys.

Progress in High-T_c Superconducting Tapes Development

Kumakura, H., Togano, K. and Maeda, H. : 1st Research Group

Key words: $Bi_2Sr_2Ca_1Cu_2O_x$, Doctor blade method, Ag sheath method, Microstructure, Critical current density

Construction of superconducting magnets using high-T_c oxide superconductors is expected in various technological fields. However, the application of superconducting materials to magnets requires the winding of tape or wire conductors with sufficient flexibility and sufficiently high transport critical current desnity J_c into a solenoid. Since oxide superconductors are intrinsically brittle, the development of special techniques is essential for tape or wire fabrication. Recently, we have succeeded in fabricating flexible $Bi_2Sr_2Ca_1Cu_2O_x$/Ag composite tapes with a textured microstructure and excellent J_c values applying a doctor blade casting method and a Ag sheath method.

Figure 1 shows schematic illustration of the doctor blade method[1]. Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO powders were mixed in the molecular ratio of 2:2:1:2, calcined at 820°C and milled into a fine powder. The obtained $Bi_2Sr_2Ca_1Cu_2O_x$(2212) powder was mixed with an organic formulation consisting of solvent, binder and dispersant and again mixed together. The resulting slurry was cast under a doctor-blade into green tapes 30–200μm in thickness. The green tapes were mounted on 50 μm-thick Ag tapes and preheat-treated at 500°C for 2h to remove the organic formulation. The subsequent high temperature heat treatment had a strong effect on the microstructure and superconducting properties of the oxide[2]. The heat treatment condition which gave the largest J_c was 890°C for 10 min., slow cooling to 870°C at a rate of 5–10°C/h, and finally cooling to room temperature at a rate of 30–100°C/h. During heat treatment the thickness of the oxide layer decreases from 1/3 to 1/5 of the green tape thickness. The oxide layer also sticks well to the Ag substrate providing good electrical and thermal contact. This suggests that Ag would be a good stabilizing material.

The Ag sheath tapes were prepared as follows. A 2212 powder was put into an Ag tube of 10mm and 6mm in outer and inner diameter, respectively. The tube was cold rolled into tape of 2mm in width and 100 μm in thickness, and then heat treated. The optimum heat treatment condition for the Ag sheath tape is almost equal to that of the doctor blade tape.

Figure 2 shows the fractured cross-section of the composite tape prepared by the doctor blade method and heat treated at optimum condition. A well-aligned microstructure with plate-like grains is observed. Most of the peaks observed in X-ray diffraction patterns of the surface of the tape can be

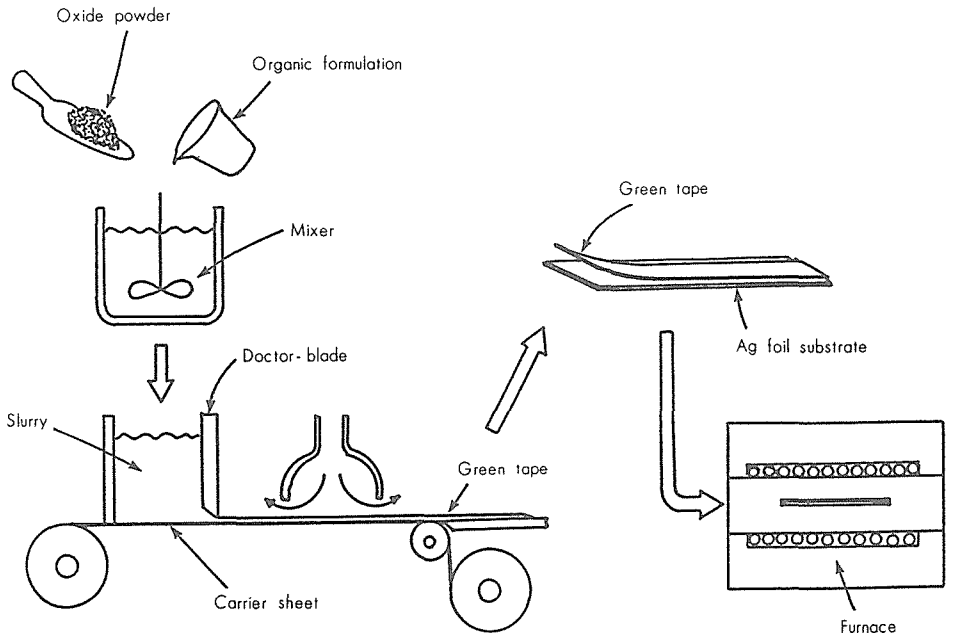


Fig. 1 Schematic illustration of the $Bi_2Sr_2Ca_1Cu_2O_x$/Ag tape preparation by the doctor blade method.

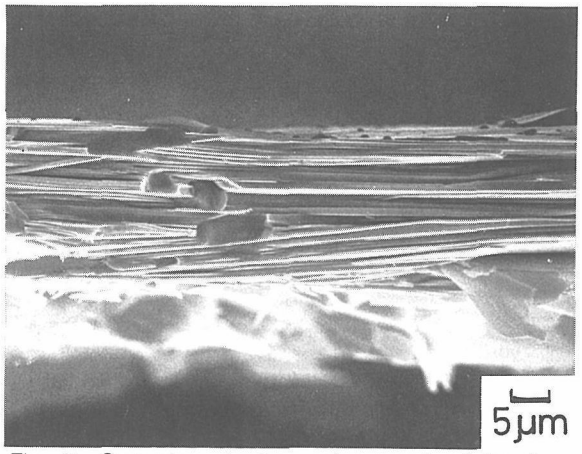


Fig. 2 Scanning electron micrograph of the fractured cross section of the $Bi_2Sr_2Ca_1Cu_2O_x$ tape prepared by the doctor blade method.

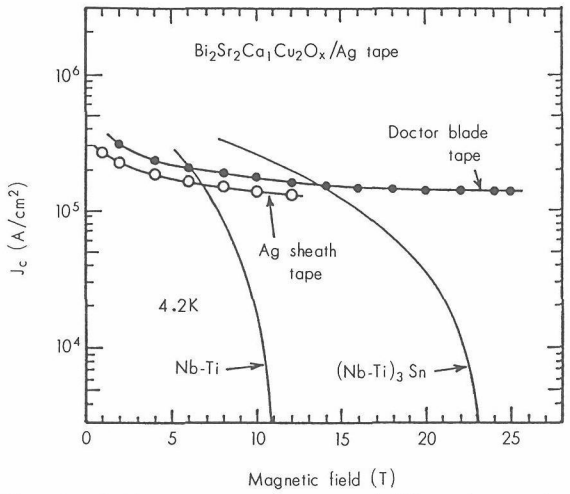


Fig. 3 J_c-B curves at 4.2K for the $Bi_2Sr_2Ca_1Cu_2O_2O_x$/Ag composite tapes and conventional metallic superconductors Nb-Ti and $(Nb, Ti)_3Sn$.

indexed as (00l) reflections of the 2212 phase, indicating a strong preferential orientation with the c-axes aligned perpendicular to the tape surface. This textured microstructure was obtaiend by solidifying from the partially molten state during slow cooling from 890°C to 870°C[2].

Some portion of the Ag substrate dissolves into the liquid oxide during the heat treatment, thereby lowering the melting point of the oxide[3]. Furthermore, the Ag substrate seems to play an important role in texturing. Preliminary observations show that highly textured 2212 microstructures are not produced when Pt or Au are used as substrate materials.

A similar textured microstructure was obtained for the Ag sheath tape when heat treated at optimum condition.

The transport critical current density J_c was measured by the standard four-probe resistive method in the temperature range 4.2K to 77K in magnetic fields up to 25T. Measurements at 4.2K and 18–27T were carried out at the High Field Laboratory for Superconducting Materials at Tohoku University. The textured tapes have a much higher J_c (at least 10 times greater) than non-textured tapes due to better coupling between grains. At 77K, J_c values greater than 10^4A/cm^2 were easily obtained in zero magnetic field. However, this high J_c was substantially reduced by magnetic fields as weak as 0.01–0.1T, with the sharpest decrease in J_c occuring for fields applied perpendicular to the tape surface (parallel to the c-axes)[4]. This large magnetic field dependence of J_c values were obtained even in high magnetic fields.

Figure 3 shows typical J_c-B curves of the doctor blade tape and Ag sheath tape at 4.2K in magnetic fields parallel to the tape surface. These tapes have excellent J_c values, higher than 10^5A/cm^2 in fields up to 25T. Due to the extraordinarily high B_{c2} value at 4.2K, the magnetic field dependence of J_c for the 2212 tapes is much smaller than that of the conventional metallic superconductors such as (Nb, Ti)$_3$Sn. These results indicate that textured 2212 tapes are very promising for high magnetic field application above 20T for which no practical superconducting tape or wire is currently available.

Acknowledgement

This research was performed in collaboration with Asahi Glass Co. and Hitachi Cable Co. The authors are indebted to J. Kase of Asahi Glass Co. and K. Momura of Hitachi Cable Co. for their contribution. The authors are also grateful to Prof. K. Watanabe of Tohoku University for providing them the opportunity to use the high field testing facilities.

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Corrosion Fatigue-Stress Corrosion Cracking Interaction of Structural Materials for Light Water Reactor

Nagata, N. : 5th Research Group

Key words: Corrosion fatigue, Stress corrosion cracking, da/dN, △K, Fractrographic feature, Striation

Environmentally Assisted Cracking in LWR's Component Materials

One of the major concerns about the safety of nuclear power reactors may be the integrity of the pressure boundary components which work as the enclosure of radioactive substances during the plant life. History has so far shown many component malfunctions which are considered to be due to degradation of materials in reactor coolant environments such as stress corrosion cracking or corrosion fatigue.

For decades, NRIM has been making an effort to acquire materials properties of these components in high temperature pressurized water simulating reactor coolants in order to accumulate scientific knowledge for regulation of nuclear power plants and to clarify the degradation mechanism of the materials, especially of environmentally assisted cracking under high temperature water environments. The present research program has been undertaken to clarify the effect of actual loading modes on the ultimate growth rate in environmentally assisted cracking of primary component materials in addition to the acceleration mechanism of crack growth in high temperature water.

Interactions of Corrosion Fatigue and Stress Corrosion Cracking

In the structural materials of light water reactors, damage is caused by corrosion fatigue and stress corrosion cracking under dynamic stress conditions by thermal stress at the time of mixing cold water and hot water, stress fluctuation by temperature and internal pressure which accompany the start-up of nuclear power plant and occurrence of low cycle stress by temperature differences.

Research regarding CF and SCC has been carried out for many years. However, their interaction has not clarified yet, and it seems that many problems, from studying cracking mechanisms to the prevention of cracking still remain to be solved.

A New Machine for Corrosion Fatigue-SCC Combination Tests

Superposition of corrosion fatigue and stress corrosion cracking was postulated to simulate material response to actual loading conditions which might bring about the maximum rate of environmentally assisted cracking. A new machine which was capable of superpositioning cyclic loadling and slow strain rate loading for a compact tension specimen was designed and constructed by modifying an existed SSRT machine by installing an electro-servo hydraulic actuator (Fig. 1 and Fig. 2). An autoclave and a water-feed unit were also installed for high temperature environments. The material tested was ASTM A533B cl.1 low alloy steel and the environment was high temperature pressurized water at 563K simulating BWR water coolants with enhanced dissolved oxygen concentration of 2ppm. Tests were carried out under conditions of pure fatigue loading mode with various stress ratios, pure SSRT loading mode with various strain rates and their superimposed loading mode. A schematic

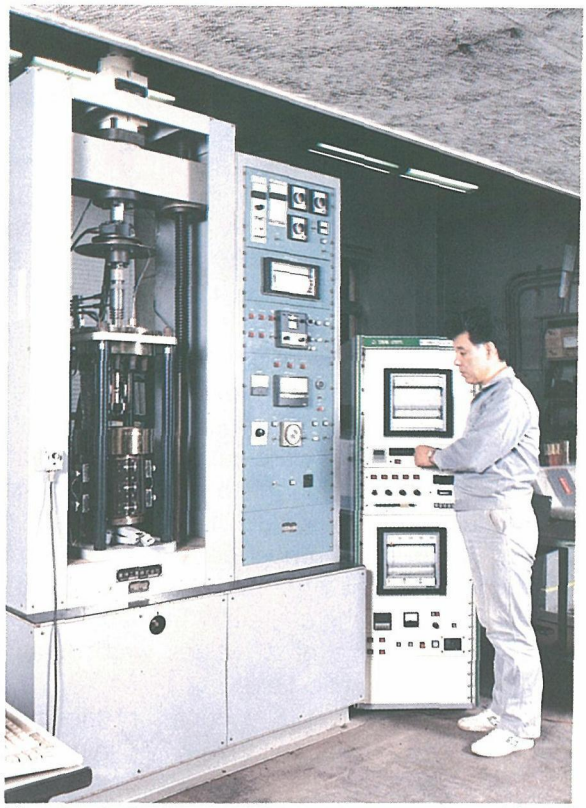


Fig. 1 A testing machine which is capable of superposition of cyclic loading and slow strain rate loading

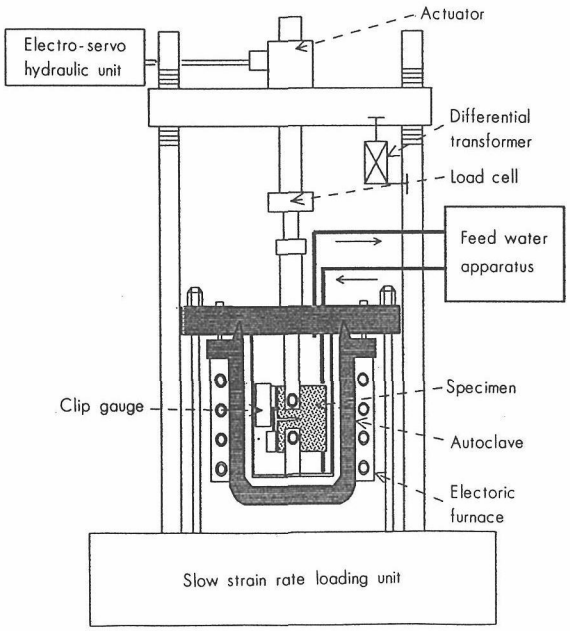


Fig. 2 Block diagram of the combined mode loading system

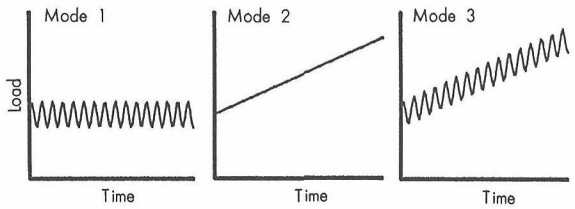


Fig. 3 Schematic illustration of loading modes

illustration of the loading modes tested is shown in Fig. 3. Monitoring of crack length of the specimen is a key technology in EAC, for which a compliance method using an encapsuled linear variable differential transformer (LVDT) was applied. The LVDT was mounted on the compact tension specimen in the autoclave.

Concluding Remarks

The results obtained showed no distinct acceleration of crack growth rate due to corrosion fatigue-stress corrosion cracking interaction except at a region of high $\triangle K$ values where a trend of acceleration was slightly observed. This might be due to the fact that ferritic steels behave less susceptible to stress corrosion cracking in high temperature water compared with austenitic stainless steels. On the other hand, the fracture path under the interaction of corrosion fatigue and stress corrosion cracking is thought to have a complicated course as the stress intensity factor changes according to crack growth. At present, the fractographic features which may indicate the crack growth mechanism in the corrosion fatigue-stress corrosion cracking interaction process have not been clarified. Figure 4 represents an example of a fracture surface which occurred under the loading mode 3 of the stress ratio range of 0.4–0.6. The fracture surface indicates quasi-brittle fracture facets together with striation due to fatigue fracture. It is conjectured that such a fracture pattern occurred as a result of the interaction of corrosion fatigue and stress corrosion cracking, different from the striation observed in the corrosion fatigue under the loading condition of mode 1. In conclusion acceleration of crack growth rate due to corrosion fatigue-stress corrosion cracking interaction for ferritic steels is so small that is thought to be negligible.

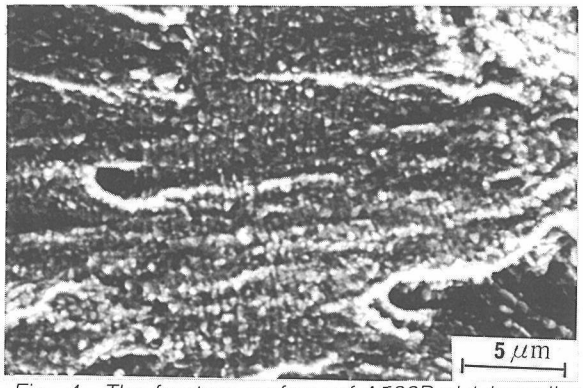


Fig. 4 The fracture surface of A533B.cl.1 low alloy steel tested in high temperature water.
Note: Quasi-brittle fracture facet with striation

Material Chemistry in Extreme Conditions under Irradiation

—Dynamic Aspects of Surface Reaction and Damage Process Induced by Irradiation—

Kitajima, M.: 2nd Research Group

Key words: Real-time measurement, Ion irradiation, Dynamic processes, Disorder induced Raman scattering, graphite

Materials are subject to both chemical and physical attacks by particle bombardment in irratiation field, which leads to modfication in various physical and chemical properties in surface region. Our research subjects are on the elucidation of the mechanism of surface reaction processes activated by irradiation and on the development of new analytical methods with emphasis of real-time observation of this kind of phenomenon. Kinetic or phenomenological modeling on the surface reaction and damage process is also our main target. The analytical methods we are employing and will employ for the above purpose are Raman spectroscopy[1~3], photoemission spectros-copy, mass spectroscopy (QMS and TOF), ellipsometry, emission spectroscopy, reactive scattering using pulse beam techniques etc. This report describes very recent results on *in situ* real time Raman mesurements of graphite under ion irradiation.

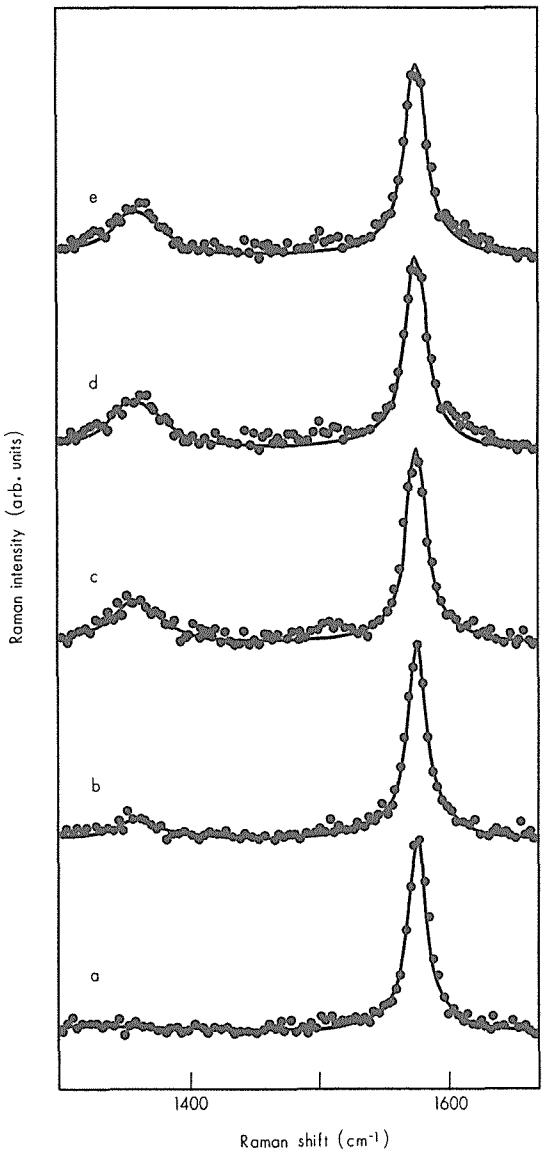
Ion beam irradiation causes ion implantation and the kinetic energy of the implanted ions introduces lattice disorder and radiation damage. The Raman spectroscopy is a sensitive tool for monitoring the ion irradiation processes. It is of great interest to look at the lattice disorder induced by irradiation from a dynamic aspects point of view, because this kind of process is intrinsically rapid. No research exists on direct observations of the time dependence of Raman spectra. We therefore develped an experimental apparatus for real-time irradiation, and here present the first results on the time-resolved Raman measurements of graphite under argon ion irradiation.

The sample used was highly oriented graphite (HOPG), and was cleaved using the adhesive tape technique for each measurement. Argon ion irradiation was performed in an ultrahigh vacuum chamber (UHV) (base pressure $<10^{-8}$ Pa) with an energy of 3 keV and a flux of 2×10^{11} ions/cm^{2}s. The incident angle of the ion beam was 45 degrees normal to the c-face. Incident radiation of 514.5 nm and 500 mW was provided by a cw argon-ion laser. The scattered radiation was collected through the sapphire window of the UHV chamber in the back scattering configuration, analyzed by a double-grating monochromator, and detected by a spectrometric multichannel analyzer. The minimum exposure time was 33 ms, and the exposure time used in this experiment was about 6 sec to get a sufficiently intense signal. The Raman spectra were analyzed by curve fitting assuming a Lorentzian line shape for the peaks. More details on the experimental procedure are described elsewhere[1].

Figure 1(a) shows a typical example of a first-order Raman spectrum of HOPG before Ar^+ irradiation. The peak observed at around 1580 cm^{-1} (G) is a Raman-active E_{2g} mode vibration peak. Ion irradiation induced a peak at around 1360 cm^{-1} (D) as shown in Figs. 1 (b-e) which were measured during ion irradiation at 18, 48, 78, and 108 sec after the beginning of irradiation. The peak height of the D peak increases and that of G peak decreases as the irradiation time increases. The linewidth of both the D and G peaks increases due to irradiation. A broad asymmetric Raman line near 1500 cm^{-1}, characteristic of the amorphous regime, was not observed. The in-plane phonon correlation length and/or crystal domain size (La nm) can be deduced from the peak intensity ratio (R) of the D peak with respect to the G peak. R is then a measure of disorder caused by the lattice damage, and plotted as a function of irradiation time in Fig. 2. The results show that the observed relative intensity increases steeply immediately after starting irradiation. This means that the graphite crystal is damaged greatly in the early stages of ion irradiation.

In the case of 3 keV Ar^+ irradiation with an incident angle of 45 degrees normal to the c-face, the penetration depth was 3 nm. Since the optical skin depth of an argon-ion laser (514.5 nm) is about 40 nm, Raman spectroscopy probes both the damaged and non-damaged layers, and the Raman spectrum observed is made up by the superposition of the scattering for both layers. The actual damage introduced by irradiation is, then, larger than that estimated from the appearance of the observed one. The size, La, at the initial slope of the rise in the relative intensity ratio, R, were corrected to be about 4.8×10^{-2}s^{-1} by considering the depth dependence of the Raman scattering intensity[1].

Our previous studies of the Raman scattering on the



(a) Before ion irradiation, and obtained during irradiation after (b) 18, (c) 48, (d) 78, and (e) 108 sec. from the beginning of irradiation.

Fig. 1 Raman spectra of HOPG

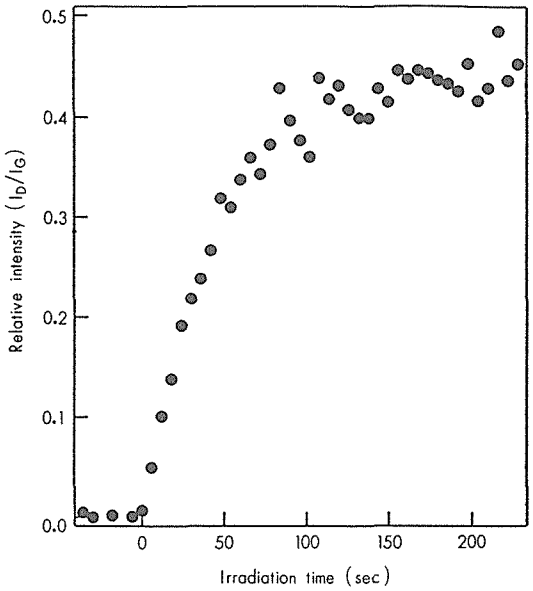


Fig. 2 Time dependence of the relative intensity ratio of peak D (1360 cm^{-1}) to peak G (1580 cm^{-1}) as a function of irradiation time.

electron beam irradiated graphite showed that La derived from the Raman spectrum corresponds to the phonon correlation length[2,3]. The change in La in graphite caused by ion irradiation may be explained in terms of the reduction of long-range-ordering by the creation of defects. A mean distance between ion impacts of 30 nm is equivalent to a dose of 10^{11} ions/cm^2, which may correspond to La after 1s of irradiation. The phonon correlation length could correspond to the mean distance between defects. We think that the steep increase of R corresponds to the creation of single defects, and the slower increase after about 100 sec corresponds to the creation of defect clusters because the formation of defect clusters should make the mean distance between defects longer. A theoretical modeling is now in progress to explain the time dependence of R.

Through our research, we developed an experimental apparatus for *in situ* real-time Raman measurements and first observed the time dependence of graphite lattice damage caused by Ar^+ irradiation. Our preliminary results apparently showed an initial steep rise and successive slow increase in the relative intensity of the Raman peaks, which implies strong lattice damage in the early stages of ion irradiation. We are now forwarding further experiments on the effects of ion energy, ion mass, ion flux, and the substrate temperature on the initial time dependence. The chemical effects are also within our scope and will be examined in the near future.

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High Purification of Rare Earth Metals by Physical Methods

Furubayashi, E., Hasegawa, R., Ozaki, T., Goto, K., Ogawa, Y., Honda, K, Kamihira, K. and Yoshimatsu, S*: Chemical Processing Division

Key words: Rare earth metals, Physical refining method, Mutual separation, Laser excitation method, Interstitial impurity elements, Solid state electro-transport

Separation of Rare Earth Elements by Laser Excitation

Mutual separation of the rare earth elements is commonly carried out by solvent extraction, but the separation coefficient of two adjacent elements is very small because the extraction is based upon a slight difference in chemical equilibrium. In the laser excitation purification process, an impurity is separated from a raw metal by using highly selective photo-excitation of atoms. The atoms have their own discrete excited states which differ from one element to another. Laser beams with proper wavelengths are directed at the raw metal in vapor form in order to excite only the atoms of target element. The atoms are selectively excited and finally converted into ions which can be extracted with an electric field. In this way, a high level of purity in the desired rare earth element can be attained (Fig. 1). Under ideal conditions, therefore, the selectivity is infinite. This process is called a Laser Materials Purification (LMP) process. The LMP technique can be used for either the recovery of the pure matrix metal or the removal of a specific impurity element. The former option has been chosen in this study. Each process has its own advantages and drawbacks.

The equipment used for those experiments consist of (1) a high-vacuum reaction chamber in which the raw metal is vaporized by an electron gun to form the atomic beam which is then irradiated with a laser, (2) a high-resolution tunable CW laser system for measuring spectroscopical performances, and (3) a high-output tunable pulsed laser system for separation and recovery. Systematic measurements were made of the factors fundamental to the laser excitation process, including the electronic energy levels, hyperfine structures and excitation lifetimes of neodymium atoms. Also, quantitative analysis was made of the isotope shift and lifetime, etc. of the first excited state. Furthermore, it was confirmed by mass spectrometry that two-step selective ionization could be achieved by resonance excitation to neodymium's first excited level and by non-resonance ionization from the level. In addition, a new method to ionize neodymium was found out. The efficiency was extremely high and the mass spectrometry revealed that a material in vapor phase could be purified by more than thousand-fold.

This method was applied to selective ionization of neodymium atoms in vapor stream containing 1% of praseodymium as a main impurity. The ions generated were collected on an electrode. A film of refined neodymium (thickness: 1000 nm) deposited on the electrode was analyzed by SIMS and the composition was compared with that before refining. It was found that the concentration of praseodymium decreased by an order magnitude. This is the first demonstration of a refining process using lasers, and marks a significant step towards the realization of an extremely efficient purification process. Further development of the LMP technology may be expected in the extension of its applicability not only to the production of ultra-pure metals, but also to the manufacturing of ultra-pure films and powders.

This study was a joint work of the Chemical Processing Division of NRIM and the R&D Laboratories-I of Nippon Steel Corporation. Participants in this study intend to further pursure this refining process, and to search for a selective ionization process which attains an even greater ionization efficiency. We also intend to raise the efficiency of

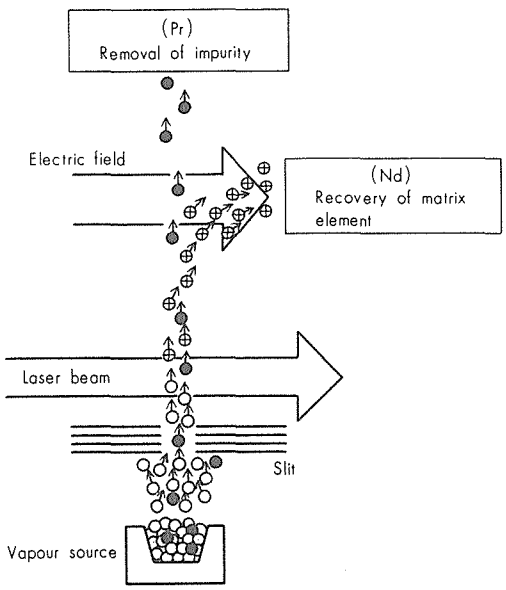

Fig. 1 Laser materials purification process

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ion separation and recovery. By these means, we hope to identify the maximum degree of purity of rare metals which can be attained by this process.

Removal of the Interstitial Impurity Elements by Solid State Electrotransport

In contrast to laser excitation purification process which is a future technology, solid state electrotransport is an already known process as a laboratory-scale high purification method for preparing ultra-high purity rare earth metals. However, the previous studies have been carried out at the institutes such as the Ames Laboratory in USA and the Birmingham University in UK, since the interest in high purity rare earth metals was not so high as it is today. Moreover, attention was mainly focused on yttrium and gadolinium metals which are relatively easy to be prepared without contamination from the environment. In this study, solid state electrotransport was carried out to grasp salient features of the behavior of the interstitial impurity elements in the above-mentioned four kinds of rare earth metals. Winning of metals with low interstitial impurities was also carried out and a high purity gadolinium (0:49 ppm, N:32 ppm) could be obtained from an electron beam melted starting material (0:1050 ppm, N: 105 ppm).

The principle of solid state electrotransport purification is the migration of impurity ions under the field of a large direct current. The driving force for the migration is generally considered to be both an electrostatic force between the impurity ions and the electrodes and the collisions of flowing electrons with the ions. Moreover, it is empirically known that interstitial impurity ions migrate much faster than substitutional ones and also faster than lattice ions. This fact is utilized to remove the interstitials which are quantitatively the main impurity in rare earth metals. Usually, the commercial-grade metals contain more than a thousand ppm of oxygen and other gaseous elements.

The apparatus used for the experiment is a stainless steel vacuum chamber equipped with a direct current source (max. 10 V, 700 A), an dthe basal pressure of the chamber was 7×10^{-8} Pa after baking. Starting materials were thin rods which were mounted between the two electrodes installed in the chamber. In the usual experiments described in previous literature, a sample rod is placed vertically or horizontally, heated to an appropriate temperature and kept at this temperature for several days to one month. In this experiment, vertically held rod, 1.6 mm id diameter and 100 mm long, was heated to a temperature corresponding to about 80% of the melting point of the sample metal and kept four days. After the experiment the rod was cut into small pieces, which were analyzed with the aid of the

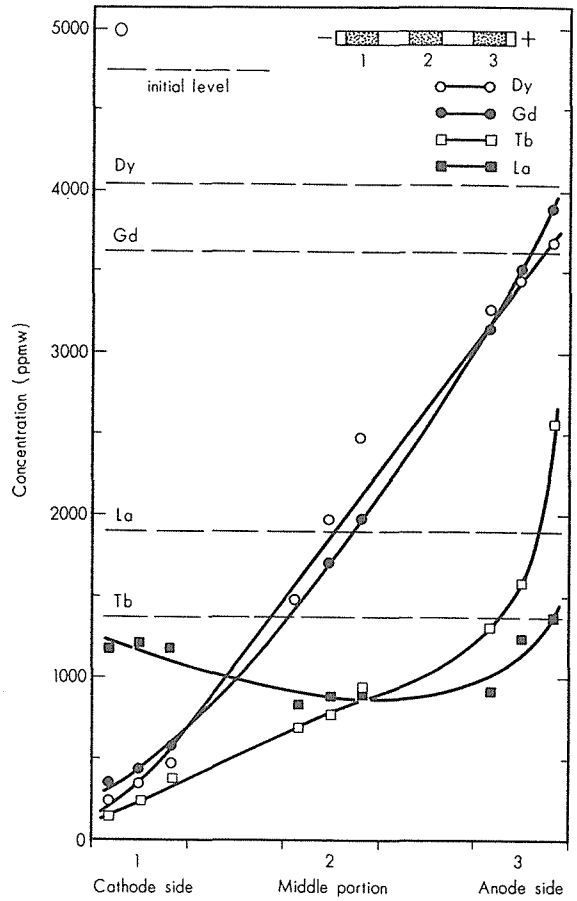

Fig. 2 Concentration profile of oxygen after solid state electrotransport.

LECO gas-analysis equipment. Microscopic observation of the structure and measurement of RRR values were also carried out. In most cases many fine particles of the oxide inclusion were found in the starting materials.

Only oxgen showed a significant electrotransport in gaseous elements. This is demonstrated in Fig. 2. Mean while, evidence of the migration of carbon was hardly discernible. From these facts, it may be concluded that the movement of oxygen ions is accelerated and that of carbon ions is retarded by a stream of electrons under the experimental conditions. Moreover, it was found that the behavior of the interstitials in lanthanum metal is quite diffent from that in the other three metals. This may be due to the difference in crystal structure and electrical conductivity. Solid state electrotransport is an interesting phenomenon from the view point of the diffusion of solute ions. Limiting our attention to refining, "the purer the starting metal, the purer it becomes". This is evident not only from experimental results but also from the theoretical equations of mass transport. Additional interest in solid state electrotransport refining is the removal of substitutional impurity elements by the combination of zone refining. However, we could not confirm the effects because of the technical difficulties we encountered in high frequency heating in the high vacuum chamber.

Research in Progress 1990–91

List of Research Subjects

Numbers with circle indicate subjects newly started from Apr. 1991.
Numbers with square indicate subjects ended by Mar. 1991.

Characterization/Properties

Electronic and nuclear properties

[1] Synthesis and Properties of Dense Kondo Compounds
[2] Physical Properties and Electronic Structures of Highly Correlated Electron Systems in High Magnetic Field
3 Electronic Structure and Superconducting Mechanism in High Temperature Superconductors
4 Theory of Structure and Electronic States in Systems with Randomness
5 Studies on Electronic and Magnetic Properties at high Pressure
6 Structures and Electronic Properties of Low-Dimensional Compounds
7 Relaxation Phenomena in Magnetic and Superconducting materials

Atomistic arrangement

[8] A Study of Solid State Amorphization process by Computer Simulation
9 High Resolution Transmission Electron Microscopic Study for Interfaces of Materials

Phase transformation and micro structures

10 Interfacial Phenomena of Microstructure Formation in Iron Alloys
(11) A Molecular-Dynamics Study of Nucleation Process at Liquid-Solid Interfaces
12 Mobilities of Austenite/Martensite Interface in Fe-Based Shape Memory Alloys
13 Mechanism of Variant Selection in Stress Induced Transformation
[14] Phase Transformation by Deformation at Cryogenic Temperature under High Magnetic Field

Surface and interface properties

[15] Diffusion Behavior of Structure Controlled Thin Film
(16) Effect of Oxidation on Mechanical Degradation of metallic Materials at High Temperature
17 Compatibility of High Temperature Materials in Liquid Metals
[18] Fabrication and Characterization of Semiconductor Quantum Well Wires
(19) Fabrication of Quantum Well Box Systems by Droplet Epitaxy for Advanced Optoelectronics Devices

Mechanical properties

20 Crystal Growth on the Surface of Intermetallic Compounds
21 NRIM Fatigue Data Sheet Project (IV)
[22] Life Extension of Heat Resisting Steels by Control of High Temperature Damage
(23) Controlling and Recovering High Temperature Damage
24 Tensile Fracture Mechanism for Long Ceramic Fibers
[25] NRIM Creep Data Sheets (III)
(26) NRIM Creep Data Sheets (IV)
[27] Evaluation of Effect of a Surface Film on Environmental Fatigue Crack Initiation
(28) Effect of a Material Surface Film on Deformation of Bulk Matrix
[29] Evaluation of Material Performance of Pressure Vessel Steels in Sulfied Solution
[30] Evaluation of Creep Crack Initiation and Growth under Static and Cyclic Loading Condition
(31) Evaluation of Crack Initiation and Growth of Superalloys under Creep and Creep-Fatigue Conditions
[32] Fatigue Crack Propagation under Random Loading in Corrosion Environment
(33) Real Time Evaluation of Fatigue Damage during Crack Propagation under Random Loadings
34 Mechanism of Mechanical Damage Accumulation in Brittle Materials
[35] Improvement of Fretting Fatigue Properties
(36) Mechanism of Fretting Fatigue Failure in Composite and Surface Modified Materials
(37) Fatigue Crack Initiation Process in Corrosive Environment

Measurement and evaluation

38 Vaporization and Ionization by Arc Plasma
39 Investigation on Non-Contact Materials Evaluation Using Laser Beam
40 Characterization of Metals and Alloys Using Synchrotron Radiation
(41) Sensitive Instrumental-Analysis of Metallic Materials by Direct Methods and Separation Methods
42 'In-Situ' Analysis/Evaluation of Radiation Damage in Materials
43 Characterization and Control of Elementary Functions of Materials in the Localized Fine Area
44 Measurements of Transient Phenomena Due to Beam-Solid Interaction
45 Development of Fundamental Technologies for X-Ray Microtomography
[46] Advanced Methods on Physical Analyses for Metals
(47) Advanced Techniques for Physical Analysis of Metals
[48] Study on Development of Chemical Instrumentation Using Plasmas
(49) Study on Mechanism of Ion Products in Low Temperature Plasma
50 Image Analysis of Metallurgical Structures with a Computer Network System
[51] Damage Measurement by Electron Lithography and Mechanism of Damage Formation
(52) Sensing and Analysis of Material Damage Formation Processes
[53] Fundamental Study on Quantitative Non-Destructive Evaluation of Small Defects in Materials
[54] Nondestractive Evaluation of Fracture Process for Metal Matrix Composites by X-Ray Computed Tomography Using Synchrotron Radiation
55 In-Situ Observation of Fatigue Damage
[56] In-Situ Scanning Tunneling Microscopy of Metal/Liquid Interfaces
57 Quantitative Evaluation of Fracture at High Strain Rate and Low Temperature in Ferritic Steels
[58] Application of AC-Impedance Technique for Environmentally Assisted Cracking of Low Alloy Steels in High Temperature Water
59 International Joint Research on Evaluation and Standardization of Advanced Materials
[60] Elemental Analysis in Response to the Development of New Metallic Materials
(61) Chemical Analysis of Organotin in Marine Environmental Samples
62 Database Development in Assistance of New Superconducting Materials Research
63 Database Systems for R&D of Superconducting Materials

Simulation and theory

[64] Research on a Knowledge Base System for Computer-Aided Chemical Substance Design
[65] Study on the Acquisition and Systematization of Knowledge for Materials Design
(66) Study on the Computer Aided Design Tools for the Development of Materials
67 Development of Knowledge Based System for Materials Life Prediction
68 Prediction of Materials Strength and Endurance under Irradiation Using Ion Beam

Materials

Non-ferrous materials

(69) Study on Changing the Properties of Metallic-Oxide Films for Increasing the Hydrogen Permeabilities
70 Basic Research to Establish Design Techniques for Advanced Materials

Intermetallic compounds

71 Advanced Intermetallic Compounds for Nuclear Reactors
[72] Development of SO_x and NO_x Sensor Using Solid Electrolyte
73 Preparation of Spontaneous Exothermic Metals and Its Application
[74] Effect of Slip Modes on Fatigue Damage in TiAl Intermetallic Compounds
(75) Fatigue Fracture Mechanisms for TiAl Intermetallic Compounds at high Temperature
76 Production and Character Evaluation of Functional Intermetallic Compounds
See also No. 138

Composites

77 Thermal Effects on the Material with Heterogeneous Phase

Materials for mechanical application

78 Development of High Vibration Damping Materials
(79) Intelligent Structural Materials
[80] Mechanism for Strengthening and Toughening and Improvement of Mechanical Properties in Titanium Alloys
(81) Microstructural Refinement and Mechanical

Properties of Titanium Alloys
(82) Development of Metal Matrix Composites for High Temperature Use through Combination of Advanced Powder Metallurgy Processes

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Research Programme

Characterization/Properties

Electronic and nuclear properties

1 Synthesis and Properties of Dense Kondo Compounds

Apr. 1988~Mar. 1991
Aoki, H.
Materials Physics Division

The purpose of the present project is to study (1) the physical properties and electronic structures of **dense Kondo compounds** and (2) those of their **thin films**. Particular effort has been made to elucidate the peculiar physical properties arising from the confined geometry of the thin films.
A study of the de Haas-van Alphen effect in the dense Kondo system of CeSb has been performed and a new high frequency branch has been found. (3) Thin epitaxial films of **$CeSi_2$** (001)/Si(001) and **CeSb**(001)/Saphire (0001) with thicknesses ranging from a few tens of nm down to a few unit cell layers were successfully grown by the MBE method. The magnetic scattering by the Kondo effect, the coherence, electron-electron interaction and localization of the heavy electrons, and magnetic properties have been studied as a function of the film thickness. It has been shown that the localization occurs for films with thicknesses less than 4 nm and the cohercy is maintained for thicker films. The magnetic scattering and electron-electron interaction are increased with decrasing film thickness. These properties are interpreted in terms of the quasi-two dimensional nature of the thin films.

Related papers

" *New High Frequency dHvA Branch of CeSb* ", Aoki, H., Crabtree, G. W., Joss, W. and Hulliger, F. J. Magn. Magn. Mat. **96** (1991) 100–103.
" *MBE Growth of $CeSi_2$ Thin Films and Their Electrical Transport Properties* ", Aoki, H., Yata, M., isoda, Y., and Uji, S.: submitted to J. Magn. Magn. Mat.
" *Fermi Surface of NbO* ", Aoki, H., Asada, Y., Hatano, T., Ogawa K., Yanase, Y. and Koiwa, Y.: J. Low Temp. Phys. **81** (1990) 19–29.

2 Physical Properties and Electronic Structures of Highly Correlated Electron Systems in High Magnetic Field

Apr. 1990~Mar. 1991
Aoki, H.
Materials Physics Divison

Collaborations with the High Field Magnet Laboratory of CRNS/MPS in Grenoble and other French Laboratories have been made on the development of high magnetic field facilities of NRIM, and on the improvement of experimental techniques under **high magnetic field** *and low temperatures, and on their applications* particularly to the **highly correlated electron systems**. An exchange of scientists between France and Japan has been also made for this purpose. Experiments on the highly correlated electron systems have been performed using facilities in both the NRIM and French laboratories. (1) An anomalous increase of the magnetoconductivity in the quantrum limit was discovered for InSb in the High Field Magnet laboratory in Genoble. A more detailed study on the transverse and longitudenal magnetconductivity and on the Hall effect has been made in our laboratory and has confirmed the anomalous behaviour of the electrical tansport properties in the quantum limit. (2) Transport properties of electron-doped high Tc oxide $Gd_{2-x}Ce_xCuO_4$ single crystals have been studied in our laboratory and jumps in the electrical conductivity due to successive magnetic transitions have been found. Magnetic properties of the single crystals are now being studied by using a high sensitive SQUID magnetometer in collaboration with the Louis Neel laboratory.
The pulse magnet systems and the experimental techniques for the high resolution magnet systems have been also improved through this collaboration.

3 Electronic Structure and Superconducting Mechanism in High Temperature Superconductors

Apr. 1988~Mar. 1994
Oguchi, T.
Materials Physics Division

The **high-temperature superconductor** (HTSC) is a potential material for a variety of applications. Despite of much effort basic research on the **electronic structure** and properties of HTSC, the superconducting mechanism has not been clarified yet. In this work, we have studied the electronic structure of HTSC based on band-structure calculations with the local-density approximation (LDA).
The electronic structure of La_2CuO_4 has been investigated for two different crystal structures, K_2NiF_4 and Nd_2CuO_4. The calculated band struc-

ture shows the importance of the position of oxygen atoms outside CuO_2 planes in realizing the two-dimensional character of the electronic structure near the Fermi energy (E_F). The high density of states just below E_F obtained for the Nd_2CuO_4 structure implies a relative instability when doping holes, which in consistent with the observed fact that no hole-doping is possible in Nd_2CuO_4.
LDA band calculations have been performed for $YBa_2Cu_3O_y$ (y=6 or 7) (abbreviated as Y123). Several characteristic aspects have been derived by comoparing other HTSCs. The importance of the energy separation between Cu-*d* and O-*p* states was pointed out in connection to poto-emission experiemnts. Signifcance of the *p*-*p* hopping between the nearest oxygen atoms was also discussed.
Quit recently, the electronic structure of $YBa_2Cu_4O_8$ (Y124) has been calculated. Overall characteristics of the electronic structure are quite similar to those of Y123. A large energy-level lowering of oxygen *p*-states at chain sites was found. This result may explain the relative stability of the oxygen ions in Y124. Some differences in the Fermi surfaces between Y123 and Y124 were also suggested.

Related papers
" *Electronic Property of La_2CuO_4 with Two different Layered Structures* " Oguchi, T.: Jpn. J. Appl. Phys. **26** (1987), L417–419.
" *Implications of Band-Structure Calculations for High-T Related Oxides* " Park, K. T., Terakura, K., Oguchi, T., Yanase, A. and Ikeda, M.: J. Phys. Soc. Jpn. **57** (1988), 3445–3456.
" *Electronic Band Structure of $YBa_2Cu_4O_8$* ", Oguchi, T., Sasaki, T. and Terakura, K.: Physica C **172** (1990), 277–281.

molecules. It was demonstrated that the method enables us to carry out first-principle MD simulations and has several great advantages over the conventional methods for **electronic-structure** calculations. Some new concepts which are necessary to extend to metallic systems were also discussed.
Formation energies for stacking faults of Al have been evaluated with the DF-MD method. In the present work, we considered twin and intrinsic stacking faults. To model these faults, a supercell geomertry which contains repeated fault planes was used. The formation energies calculated by taking full atomic relaxation into account are in fairly good agreement with the experimental values. It was found that only small atomic relaxations occur, which is consistent with the close-packed structure of the faults.
It is well known that highly-conductive ZnSe promises realization of new devices such as blue LED's. However, no stable *p*-type ZnSe smaple has been obtained so far. Here, the origin of the instability of *p*-type ZnSe has been studied with the DF-MD method. Based on the total energies calculated for Li-doped ZnSe and host ZnSe, we have proposed a new compensation mechanism for a Li acceptor in ZnSe and have shown that Li is not suitable as the *p*-type dopant of ZnSe.

Related papers
" *Li Impurity in ZnSe: Electronic Structure and the Stability of the Acceptor* " Sasaki, T., Oguchi, T. and Katayama-Yoshida, H.: Phys. Rev. **B43** (1991), 9362–9364.
" *Density-Functional Molecular-Dynamics Method* ", Oguchi, T., and Sasaki, T.: Prog. Theor. Phys. Suppl. No. 103 (1991), 93.

4 Theory of Structure and Electronic States in Systems with Randomness

Apr. 1990~Mar. 1993
Oguchi, T.
Materials Physics Divison

We investigated theoretically the structure and electronic states of bulk materials which contain imperfections such as point defects, stacking faults of phase boundaries. The analysis is based on the density-functional (DF) electronic theory combined with the molecular-dynamics (MD) method (abbreviated as DF-MD method). This DF-MD method provides and useful tool to determine the optimum atomic arrangement affected by the imperfections as well as the electronic states.
First of all, physical backgrounds and concepts of the DF-MD method have been studied intensively. Numerical techniques and algorithms involved in the method have been examined in detail by performing small-scale calculations for silicon mole-

5 Studies on Electronic and Magnetic Properties at High Pressure

Apr. 1990~Mar. 1993
Matsumoto, T.,
Materials Physics Division

We are interested in the change of physical properties which are induced by high pressures. One of the important purposes of this research program is to clarify the quantitative changes of physical properties under pressure. Thus we have developed the original apparatuses in order to measure the magnetization and specific heat under pressure with a high accurcy. Our recent studies have been focused on oxides with low carrier densities and rare earth compounds with valence instability and abnormal electron mass.
One of our typical results if the **pressure effect** on the **oxide superconductor** $YBa_2Cu_4O_8$. In this research, the pressure dependence of T_c and the crystal structure have been investigated by the experiments of electrical resistivity and neutron

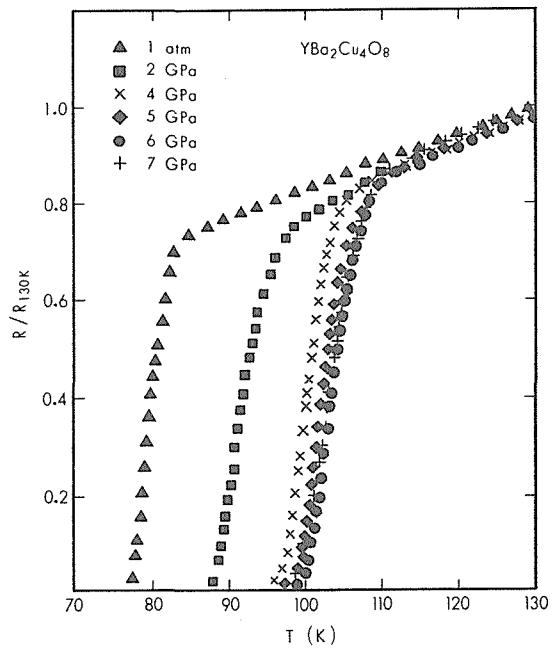

Fig. 1 Pressure dependence of electrical resistance in $YBa_2Cu_4O_8$.

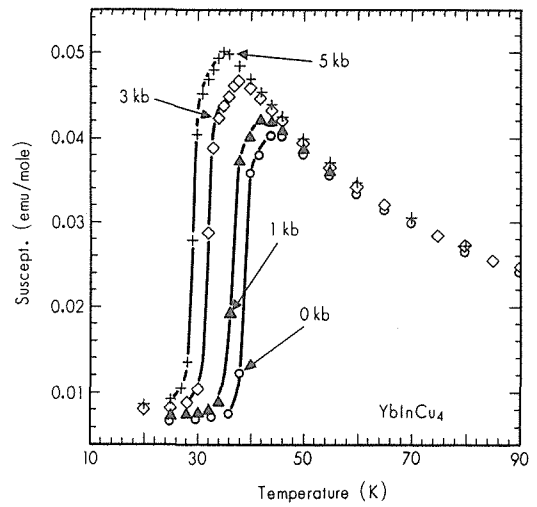

Fig. 2 Change in magnetic susceptibility of $YbInCu_4$ as a function of pressure.

diffraction. Figure 1 shows the change in electrical resistance as a function of pressure. It is very interesting to note that T_c easily exceeds 100K above a pressure of 5GPa. From the analysis of the results of neutron diffraction under pressure, the increment of T_c is concluded to be caused by the **carrier redistribution** from CuO chains to CuO_2 planes at high pressure.

The pressure effect on the valence phase transition, T_v of Yb intermetallic compound shas been studied by magnetic measurements. Magnetic susceptibilities are shown in Fig. 2 which indicates a decrease in T_v with increasing pressure. From the results, the Yb^{3+} magnetic state at higher temperatures is explained to be stabilized by pressure.

Related papers

" *Structure Changes of Superconducting $YBa_2Cu_4O_8$ under High Pressure* ", Yamada, Y., Jorgensen, J. D., Pei, S., Lightfoot, P., Kodama, Y., Matsumoto, T., and Izumi, F.: Phsyica **C173** (1991), 185–194.

" *Electrical Resistivity and Specific Heat of La_{2-x} $Sr_xNiO_{4+\delta}$* ", Matsushita, A., Matsumoto, T., Takayanagi, S. and Môri, N.: Physica **B165&166** (1990) 1351–1352.

" *Pressure Effects on the Yb Valence State in $YbIn_{1-x}$ Ag_xCu_4* ", Matsumoto, T., Shimizu, T., Yamada, Y. and Yoshimura, K.: (submitted to '91 International Conference on Magnetism)

6 Structures and Electronic Properties of Low-Dimensional Compounds

Apr. 1989~Mar. 1992
Okochi, M.
Materials Physics Division

Low-dimensional transition metals **compounds**, which are characterized by anisotropic electrical conductivities, are expected to have other useful unfamiliar anisotropic properties. Single crystals of non-stoichiometric molybdenum oxides have been investigated in the third lab. of Materials Physics Div. and have shown new anisotropic **color properties**, that is, different reflected colors in different crystallographic planes: Under natural light the single crystal of Mo_4O_{11} shows purple color with metallic luster in the cleavage plane, while gold color in the plane perpendicular to the cleavage plane. Furthermore, the golden color changes into purple in polarized light parallel to the cleavage plane.

Polarized reflectance spectra of **Mo_4O_{11}** have been observed in the wave range 200 to 900 nm and have shown a strong dependence on crystal orientations relative to the direction of the polarized incident light. It is concluded from the measurements of polarized reflectance spectra that the anisotropic color properties are caused by selective interband transitions mainly from electrons around the Fermi level.

The color anisotropies are principally related to the crystal structures of low-dimensionality which invariably give rise to the anisotropic electronic structures. The structure of Mo_4O_{11} is composed of three layers of octahedra, which are formed from oxgyen atoms surrounding one molybdenum atom, separated by one layer of tetrahedra. From the coordination number the charges of molybdenum are considered to the +6 and +4 in the octahedron and tetrahedron, respectively. X-ray photoemission observed spectra have brought out the unexpected result that the charges of molybdenum are evaluated to be below+6 for the octahedra, and to be nearly +6 for the tetrahedra, whose facts, however, are in agreement with prediction from bond length-bond strength relationships. Other studies in the

laboratory are connected with the interaction strength between transition metals and oxygen atoms, and searching of new materials by data analysis of structural characteristics.

7 Relaxation Phenomena in Magnetic and Superconducting Materials

Apr. 1990~Mar. 1993
Uehara, M.
Surface and Interface Division

Recently much attention has been given to dynamical nature in magnetic and superconducting systems such as spin glasses, amorphous magnets and **high-T_c superconductors**. We study the **magnetic relaxation** phenomena in which a macroscopic system in a **metastable state** undergoes a transition to a lower state via thermal excitation or quantum fluctuations through the barrier.
It was shown that the thermal activation mechanism responsible for the diffusion of ferromagnetic **domain walls** in a $SmCo_{3.5}Cu_{1.5}$ single crystal shows a strong anomaly below a temperature of 50K. This effect, initially attributed to quantum fluctuations, has been studied in more detail. In particular it was shown that the evolution of the magnetic after effect at low temperature fits a simple model where an effective temperature T^*~10 K accounts for energy fluctuations of domain walls at zero Kelvin. This temperature coincides with the characteristic frequency, $\omega_o \sim 10^{12}$ sec^{-1} of domain wall vibrations in metastable equilibrium. At lower temperature, collective jumps of magnetization in a metastable state were observed in a reversed magnetic field. Such behavior strongly suggests the existence of simultaneous wall motion on the scale of the sample, due to thermal "avalanche effect", associated with dissipation, and initiated by wall tunneling events on a microscopic scale. The studies on magnetic relaxation in superconducting $Bi(Pb)_2Sr_2Ca_2Cu_3O_y$ and $YBa_2Cu_3O_{7-\delta}$ ceramics and in high-quality single crystalline $Bi_2Sr_2CaCu_2O_8$ are currently in progress.

Related papers

" *Noncoherent Quantum Effects in the Magnetization Reversal of a Chemically Disordered Magnet* ", Uehara, M. and Barbara, B.: J. PHysique **47** (1986), 235–238.

" *Staircase Behavior in the Magnetization Reversal of a Chemically Disordered Magnet at Low Temperature* ", Uehara, M., Barbara, B., Dieny, B. and Stamp, P. C. E.: Phys. Lett. **A114** (1986), 23–26.

" *Anomalous Demagnetization Process at Low Temperature in Nd-Fe-B Magnets* ", Otani, Y., Coey, J.M.D., Barbara, B., Miyajima, H., Chikazumi, S. and Uehara, M.: J. Appl. Phys. **67** (1990), 4619–4621.

Atomistic arrangement

8 A Study of Solid State Amorphization Process by Computer Simulation

Apr. 1988~Mar. 1991
Kusunoki, K.
Materials Physics Division

Molecular-dynamics (MD) simulations have been performed to study the relaxation process of materials which have several types of crystal configurations. **Lennard-Jones type 4–8 potentials** were used for the calculation of forces between atoms. Firstly, we have investigated the relaxation process of the **single crystals**, to which relatively large numbers (about 2 to 10%) of **vacancies** were introduced. The results have shown that the amorphization did not occur for the monoatomic systems but occurred for the binary alloy systems which are composed of atoms with large size difference between unlike atoms. Furthermore we have investigated the relaxation process of initially crystalline **binary diffusion couples**. In this case, the occurrence of grain boundary amorphization was observed only for the systems which generate large negative **excess volume of mixing** between unlike crystals. These results were not changed by calculations which used a more shallow or deep potential-well between unlike atoms compared to those between like atoms.
From the viewpoint of thermodynamics, the above results suggest that the **solid-state amorphization** (SSA) of crystals can be brought forth by decreasing the **free energy** of the systems, which is caused essentially by the increase in the **configurational entropy** during the SSA reactions, and that both the large size difference between the unlike atoms and the excess volume around the atoms stabilize the amorphous phase. The occurrence of this SSA reaction will be also supported by the large negative **heat of mixing**, between unlike atoms. To verify this idea, another type of MD calculations, the volume expansion of single crystals, was carried out. The results confirmed that the amorphization can occur only for alloy systems composed of atoms with large size differences between unlike atoms.

Related paper

" *Molecular-dynamics Study of Grain Boundary Amorphization* ", Kusunoki, K.: Proceedings of the International Workshop on Computational Materials Science, Tsukuba Science City, August (1990), 219–222.

9 High Resolution Transmission Electron Microscopic Study for Interfaces of Materials

Apr. 1990~Mar. 1993
Ikeda, S.
Surface and Interface Division

Images of atomic structures of **interfaces** of materials are studied by means of a **high resolution transmission electron microscope** (HREM).

A high resolution electron microscopic study of **iodine** intercalated **Bi-type superconducting oxides** has been performed to determine the location of the iodine atoms between the Bi-O layers and also to investigate the nature of the state of the iodine atoms (molecular or atomic). Thin plates of iodine intercalated and non-intercalated **single crystals** of 2212 phase were cut into flakes or ionmilled after being sandwiched by silicon plates, cut by a wire saw and by a dimple grainder. Samples thus prepared were examined by a 400kV high resolution electron microscope. It was found that the **intercalation** increased the cell parameter c by 20%; the mode of the **modulation** was kept in the type I, the wavelength of the modulation to the b direction increased from 2.75 to about 3.7 nm and the wave length became slightly diffuse. The I atoms appear to be located between the Bi-O planes. The relative distributions of iodine and bismuth atoms are closely related, since alternating I concentrated and I deficient regions can be distinguished in the image of the intercalated plane. The HREM images of the (100) plane show that the resulting contraction and expansion of the lattice planes induce more fluctuations of the periodicity of the structure along the b direction compared with the nonintercalated compound.

Related paper

" *HREM Study of Iodine Intercalated* $IBi_2Sr_2CaCu_2O_8$ ", Chenevier, B., Ikeda, S. and Kadowaki, K.: Proceedings of H^2S-HTSC III, special volume of Physcia C. (in press)

Phase transformation and micro structures

10 Interfacial Phenomena of Microstructure Formation in Iron Alloys

Apr. 1990~Mar. 1993

Enomoto, M.

Physical Properties Division

*Effects of **Microalloying** Elements on the Kinetics of Austenite to Ferrite Transformation*

The nucleation Kinetics of proeutectoid ferrite at austenite grain boundaries and the subsequent growth will be measured in Fe-C-Nb, and V alloys etc. The causes of retarding or enhancing the transformation kinetics by the addition of these elements will be considered in terms of nucleation and diffusion growth theories currently utilized in analyzing the transformation kinetics in iron alloys.

Grain Growth of Single Phase Materials Having an Anisotropic Grain Boundary Energy

The **grain growth** behavior of single phase materials (ferrite and austenite), which may be characterized by a strongly anisotropic grain boundary energy will be investigated by **computer simulation** . The simulation techniques will include the 3-D Monte Carlo method and/or the vertex models. The influence of various metallurgical factors (pinning effect, annealing temperature etc.) on the grain growth, the mechanism for texture formation and the relationship thereof with the magnitude of the anisotropy of grain boundary energy will be investigated.

(11) A Molecular-Dynamics Study of the Nucleation Process at Liquid-Solid Interfaces

Apr. 1991~Mar. 1994

Kusunoki, K.

Materials Physics Division

Almost every metallic material is composed of grains whose size distribution and form have great effect on both the physical and the mechanical properties of the material. The feature of the grains in the metallic materials is directed to their final state at the very early stage of solidification which is triggered by **heterogeneous nucleation** occurring in an atomistic scale. Unfortunately, at present there are no tools for the observation of the above stage nor theories to describe it. This study is aimed at the clarification of the solidification mechanisms at **solid-liquid interfaces** from the standpoint of atomistic simulation. A **molecular-dyanmics calculation** has been applied to this study, which use more realistic interatomic potentials based on the **tight-binding model** and the **embedded atom model** for the calculation of forces between atoms. The empirical potentials such as **Lennard-Jones type 4–8 potentials** will also be tested for time saving in the calculation of forces.

One of the main purposes of this study is to investigate the relation between the interface structures and the **critical nucleus size** as well as the **growth rate of the nucleus**. Whether the **classical nucleation theory**, which has been constructed on the basis of the continum model, can be applied to this problem or not will be examined as well.

12 Mobilities of Austenite/Martensite Interface in Fe-Based Shape Memory Alloys

Apr. 1989~Mar. 1992

Kajiwara, S

Physical Properties Division

NiTi is the most widely used shape memory alloy and has many excellent properties. This alloy, however, is very expensive, and hence, Fe-based shape memory alloys are recently being investigated instead. The most promising Fe-based shape memory alloy is an Fe-Mn-Si alloy and its modification, Fe-Mn-Si-Cr-Ni alloys, which has excellent corrosion-resistance. On the other hand, we recently found that even high nickel steels containing carbon have a good shape memory effect if the austenite/martensite interface moves reversibly and the strengh of the austenite is high enough to prevent plastic deformation at the time of shape change of a specimen by an external force.
In the present work we have studied the velocity of the austenite/martensite interface on heating by opticl microsocpy, because the high mobility of the interface is one of the important parameters to obtain a good shape memory effect.
The composition of the alloys used is Ni: 26–33 wt.%, C: 0.1–0.8 wt.%, Fe: bal., where the Ni content was adjusted to keep the Ms temperature near liquid nitrogen temperature, namely the Ni content was increased with decreasing C content. It is surprising that the reversible interface movement was observed even in an alloy containing 0.8 %C. During heating (heating rate: 50–1000 K/min) above room temperature, carbides (cementite) had precipitated in the martensite phase before the austenite/martensite interface passed by, that is, the interface moved across the carbide precipitates. This fact encourages us to use carbon as a component of shape memory alloys.
The measured velocity of the austenite/martensite interface was 2–25 nm/s for joule per mol. In the near future, a similar study on the velocity of the austenite/martensite interface will be done on other Fe-based shape memory alloys, such as Fe-Mn-Si, Fe-Mn-Si-Cr-Ni and Fe-Ni-Co-Ti.

Related papers

" *Nearly Perfect Shape Memory Effect in Fe-Ni-C Alloys* ", Kajiwara, S.: Trans. Jpn. Inst. Met. **26** (1985), 595–596.
" *Shape Memory Effect and Related Transformation Behavior in Fe-Ni-C Alloys* ", Kajiwara, S. and Kikuchi, T.: Acta Metall. Mater. **38** (1990), 847–855.
" *In Situ Observation of the Interface Movement in Reverse Martensitic Transformation in Fe-Ni-C Alloys* ", Kajiwara, S. and Ohtsuka, H.: Proc. 6th Intern. Conf. on Martensitic Transformation, Sydney, Australia, 1989, Material Science Forum, **Vol. 56–58** (1990) pp. 673–678. Pt II. Trans Tech Publications.

13 Mechanism of Variant Selection in Stress Induced Transformation

Apr. 1989~Mar. 1992
Miyaji, H.
Advanced Materials Processing Division

Thermomechanical processing has the potential of controlling the texture as well as the microstructure of steels. In the present work attention has been payed to find artificial controlling methods of **transformation textures** which are developed by **martensitic transformation** occurring in rolling.
Variant selection problem is one of the most important subjects in understanding the texture transition from austenite (γ) to martensite (α). This is because 3, 12 or 24 different α orientations (called variants) can be formed from only one γ crystal in the case of the Bain, Nishiyama or K-S relation, respectively. But in many cases not all of them are actually observed. In view of the fact that martensitic transformation is a kind of shear deformation, certain stresses associated with rolling deformation are considered to affect the selection of variants. The present study was undertaken to clarify the basic mechanism of variant selection by means of computer simulation, as well as experimental determination, of textures of rolled Fe-Ni alloys before and after transformation.
A variant selection model was proposed in which the criterion for selection was based on the strength of the mechanical work done by triaxial stresses in the material and the hypothetical Bain strain of the martensitic transformation. With this model, experimental textures and their difference between transformation after and during rolling could be exlained satisfactorily in terms of acceptable stress state in rolled materials.

Related papers

" *Effect of Specimen Size on the Variant Selection in Martensitic Transformation* ", Miyaji, H. and Furubayashi, E. : Texture Microstruct., **12** (1990), 189–197.
" *Effect of Stress on the Variant Selection in Martensitic Transformation* ", Miyaji, H. and Furubayashi, E.: (to be published in Proceedings of 9th International Conference on Textures of Materials (1990, 9 France)).

14 Phase Transformation by Deformation at Cryogenic Temperature under High Magnetic Field

Apr. 1990~Mar. 1991
Nagai, K.
First Research Group

Metastable **austenitic stainless steels** like 304L (-LN) and 316 L (-LN) are practically used for superconducting applications. Metastable austenite transforms into b.c.c. martensite at lower temperature and the transformation is accelerated by plastic deformation and/or a magnetic field. The b.c.c. martensite increases the magnetization because of its ferromagnetism. Furthermore,

the phase is believed to be more brittle than the matrix. Thus the **martensitic transformation** is thought to be unfavorable for **cryogenic structural materials**. However, we have few data on the martensitic transformation of engineering materials under **high magnetic fields**. The present study aims at quantitative evaluation of the martensitic transformation introduced by plastic deformation under magnetic fields.

Conventional superconducting magnets do not have enough core space for full-size mechanical tests. In our institute, a 10 Tesla grade solenoid magnet with a 50 mm ϕ bore is available for this purpose. A loading equipment of 20 kN capacity was constructed for deforming a subsize specimen under a high magnetic field in the superconducting solenoid bore. The load is generated by a servohydraulic power supply and the loading system is controlled using a personal computer. Both monotonic loading and cyclic loading can be applied. The specimen is deformed up to given load values in liquid helium under a magnetic field between 0 and about 10 Tesla. The load cell is shielded by Permalloy plate to eliminate the magnetic field effect on the output. The actuator displacement is monitored with a linear gage. Wire-leads are set for the direct measurement of specimens's deformation using strain gages, of which the output should be calibrated under magnetic field.

Magnetization curves were obtained for SUS304L and SUS316LN. Undeformed samples did not transform in liquid helium up to 8 Tesla. However, plastic deformation under 0 Tesla brought about transformation and some additional effect of the magnetic field was observed for the SUS304L.

Surface and interface properties

15 Diffusion Behavior of Structure Controlled Thin Film

Apr. 1988~Mar. 1991
Ikeda, Y.
Failure Physics Division

Ceramic film—Suppression of spalling and diffusion

Our previous work showed that the excellent high-temperature oxidation resistance conferred through REM addition is attributed to the suppression of **surface segregation** of S with REM. This study was performed to extend the above REM effect model to Al_2O_3 coating layer/alloy systems. Surface segregation of S was measured by the AES technique on alloys doped with REM or Y_2O_3. These alloys were subsequently coated with Al_2O_3 and oxidized cyclically.

It was found that addition of REM or dispersion of Y_2O_3 in alloys considerably suppresses the surface segregation of S, and accordingly the spalling of Al_2O_3 coating layer, and the diffusion of Mn and Cr into the Al_2O_3 layer. These results offer corroborating evidence for the REM effect model proposed previously and will serve as a guide to the development of ceramic coating technology.

Metal film—Unique diffusion behavior

Thin metal film is expected to have a different energy state compared with the bulk metal and to show unique characteristics. Six kinds of film/substrate couples Nb/Ti, Ti/Nb, Ti/Cu, Cu/Ti, Cu/Nb and Nb/Cu, were used to investigate diffusion behavior of the substrate element through films by AES and XPS. The **rapid diffusion** behavior of the substrate element to the film surface was observed in the following couples: Nb/Ti, Ti/Cu, Cu/Ti and Cu/Nb. The activation energies of the rapid diffusion were about 60% of those in bulk metal. These low activation energies correspond to surface diffusion or grain boundary diffusion. The order of these diffusion coefficients was 10^5 times or more above that in bulk metals. The diffusing element concentrated on the film surface and it saturated at a certain concentration. These results did not depend on the deposition method. The **surface free energy** is a necessary parameter in order to explain the above results thermodynamically.

Related papers

" *High Temperature Oxidation and Surface Segregation of Sulfur* ", Ikeda, Y., Nii, K. and Yoshihara, K.: Proc. 3rd JIM Int. Symp. on High Temperature Corrosion of Metals and Alloys", Suppl. to Trans. Jpn. Inst. Met., **24** (1983), 207–214.

" *Detrimental Effect of S Segregation to Adherence of Al_2O_3 Coating Layer on Stainless Steels and Superalloys* ", Ikeda, Y., Tosa, M., Yoshihara, K. and Nii, K.: ISIJ Int., **29** (1989), 966–972.

" *Diffusion Behavior in the Films of Nb-Ti Systems* ", Yoshitake, M. and Ysohihara, K.: J. Jpn. Inst. Metals, **54** (1990), 1013–1017 (in Japanese).

16 Effect of Oxidation on Mechanical Degradation of Metallic Material at High Temperature

Apr. 1991~Mar. 1994
Ikeda, Y.
Failure Physics Division

Previous studies showed that surface segregation of S is detrimental to the high temperature oxidation resistance, and that dispersed Y_2O_3 improved the oxidation resistance through suppressing surface segregation of S. Mechanical properties at high temperature, such as creep and fatigue strength, are considered to be lowered through cracking, spalling and local penetration of oxide. Thus Y_2O_3 dispersed alloys are expected to have excellent mechanical prop-

erties at high temperature because of their high oxidation resistance and the dispersion strengthening effect.
This work consists of three parts.
(1) How do dispersed Y_2O_3 particles suppress the surface segregation of S and the oxide spalling? TEM, analytical electron spectroscopy, AES and STM techniques will be used.
(2) How is the high temperature fatigue strength improved by **Y_2O_3 dispersion**? High temperature fatigue tests will be performed with Y_2O_3 dispersed alloys and the fractured surface will be examined with SEM, EDX and STM.
(3) How does oxidation, especially internal oxidation, deteriorate mechanical properties? Examination with optical microscope, SEM and EDX will be made on the cross-section of specimens which were subjected to fatigue or creep.

Related papers

" *High Temperature Oxidation and Surface Segregation of S* ", Ikeda, Y., Nii, K. and Yoshihara, K.: Proc. 3rd JIM Int. Symp. on High Temperature Corrosion of Metals and Alloys", Suppl. to Trans. Jpn. Inst. Met., **24** (1983), 207–214.

" *Detrimental Effect of S Segregation to Adherence of Al_2O_3 Coating Layer on Stainless Steels and Superalloys* " Ikeda, Y., Tosa, M., Yoshihara, K. and Nii, K.: ISIJ Int., **29** (1989), 966–972.

17 Compatibility of High Temperature Materials in Liquid Metals

Apr. 1987~Mar. 1992

Suzuki, T.

Mechanical properties Division

The quasi-equilibrium of **stainless steel** in **sodium** at 600–700°C with a 1–2 wppm in oxygen level, and 4.0 m/s in velocity at maximum isothermal region in a non-isothermal sodium loop constructed of Type 316 stainless steel has been examined using specimens of martensitic/ferritic steels. The compositions of the stainless steel samples in quasi-equilibrium were approximately identical to Fe-5Cr-<1Ni at 700°C, Fe-6Cr-<1Ni at 650°C and Fe- 7Cr-<1Ni at 600°C. From the results, it appears that the formation free energy change of the Na-Cr-O complex from Cr is larger than that of the Na-Fe-O complex from Fe in the sodium. Also, the buffering action of Cr for oxygen in sodium, which would lower the **corrosion** of steel in sodium, was confirmed.
As part of the "Compact Fusion Advanced Rankine Cycle" conceptual design experiments, corrosion of a Type 304 stainless steel and a Mo-base TZM alloy (Mo-0.5Ti -0.084Zr-0.025C-0.025 oxygen in wt%) in refluxing mercury with and without 0.004 mol fraction of potassium has been studied using small capsules at 600 and 700°C. The capsule wall of the 304 stainless steel was severely corroded due to selective dissolution of Ni and Cr to form a ferritic layer on the surface, which is more stable than the austenitic phase. In contrast, the TZM alloy showed no noticeable changes except for carburization of the surface after heating for 2000 h, probably due to the low solubility of Mo in mercury.

Related papers

" *Quasi-Equilibrium of Stainless Steel in a Non-Isothermal Sodium Loop Constructed of Type 316 Stainless Steel* ", Suzuki, T. and Mutoh, I.: J. Nucl. Mater. **186** (1991) 20.

" *Corrosion of a Type 304 Stainless Steel and a Mo-Base TZM Alloy in Refluxing Mercury with a small amount of Potassium* ", Suzuki, T. and Mutoh, I.: J. Nucl. Mater. **184** (1991) 81.

18 Fabrication and Characterization of Semiconductor Quantum Well Wires

Apr. 1989~Mar. 1991

Koguchi, N.

Surface and Interface Division

Semicoductor **quantum well wires** or boxes are promising structures for high electron mobility devices or advanced laser diodes. In spite of the fundamental interest in making quantum well wires or boxes, progress in their fabrication has been slow. Although the electron beam lithography and subsequent argon ion milling have been used for the fabrication of these microstructures, the dimensions are quite difficult to control and radiation damage in the microstructure is inevitable. The fractional epitaxy method to fabricate the quantum well wires is proposed, but it is difficult to make wires having a sectional area with an accuracy of mono-atomic scale. It is highly desirable to look for alternative method to fabricate these microstructures.
In this laboratory, we proposed a new **molecular beam epitaxial growth method** for InSb quantum well wires or boxes surrounded by CdTe which has a lattice constant equal to that of InSb. We term this method as "Droplet Epitaxy" which is based on Sb atom incorporation into In droplets deposited on a CdTe single crystal substrate in the molecular beam epitaxial growth chamber. Indium droplets formed lines having a sectional area of about 150 nm × 150 nm along the CdTe bunching steps. By supplying Sb atoms to these In droplet lines, these droplet lines changed into InSb microcrystal lines. The quantum well wires may be fabricated by growing the CdTe epitaxial layer over the InSb lines.

19 Fabrication of Quantum Well Box Systems by Droplet Epitaxy for Advanced Optoelectronic Devices

Apr. 1991~Mar. 1996

Koguchi, N.

Surface and Interface Division

The **quantum well box system** is a promising structure for high electron mobility devices or advanced laser diodes as mentioned in the Research Topics of this brochure. In spite of the fundamental interest in making quantum well boxes, progress in their fabrocation has been slow.
In this laboratory, we proposed a new **molecular beam epitaxial growth method** for InSb quantum well boxes surrounded by CdTe which has a nearly equal lattice constant to InSb. This method is based on the Sb incorporation into In droplets.
At first, In was deposited on the CdTe epitaxial layer at 473 K in the molecular beam epitaxial chamber. Then an Sb flux was supplied at the same temprature. The reflection high energy electron diffraction pattern and the high resolution scanning electron microscope observations revealed that the In droplets deposited on the CdTe epitaxial layer changed to InSb pyramidal shape epitaxial microcrystals truncated by (111) and (100) facets after the Sb molecular beam supply. The base size of the pyramidal microcrystals is 50 nm × 200 nm and the height is about 70 nm.
GaAs microcrystals with the size of 10 nm × 10 nm × 10 nm were grown by the same procedure on a ZnSe epitaxial layer which has a lattice constant nearly equal to that of GaAs. The quantum well box system may be fabricated by growing the CdTe or ZnSe epitaxial layer over the InSb or GaAs microcrystals.

Mechanical properties

20 Crystal Growth on the Surface of Intermetallic Compounds

Apr. 1990~Mar. 1992
Hirano, T.
Chemical Processing Division

The goal of this study is to develop new interface materials. Layered intermetallic compounds exhibit clean and ordered surfaces by cleaving. We focus on the **crystal growth** and chemical reaction of metal overlayers on the clean cleaved single-crystal surfaces on intermetallic compounds. We directed our efforts towards **surface science** of the single crystals $CoSi_2$ and $CaSi_2$, since these **disilicides** provide a characteristic surface. The experimental techniques in use are floating zone method with infrared heating, X-ray photoemission spectroscopy, and Auger spectroscopy.
We have grown single crystals of many metal disilicides from IIa group through VIII group metals in the periodic table. It is found that $CoSi_2$ and $CaSi_2$ exhibit a different surface atomistic termination by cleaving. It is considered that the surface termination affects the chemical reaction of metal overlayers with the surface. We presently examine the crystal growth and chemical reactions by surface-sensitive analysis.

Related papers
" *Single-Crystal Growth and Electronic Properties of $CaSi_2$* ", Hirano, T.: J. Less-Common Metals. **167** (1991), 329–337.
" *Surface Analysis of Cleaved Single-Crystalline $CaSi_2$ by Auger Electron Spectroscopy* ", Hirano, T. and Fujiwara, J.: Phys. Rev. B, **43** (1991), 7442–7447.

21 NRIM Fatigue Data Sheet Project (IV)

Apr. 1991~Mar. 1995
Nishijima, S.
Failure Physics Division

It is well known that **fatigue** of metallic materials could be a cause of hazardous accidents in machines and structures suffering fluctuating loads during work. This project is aimed at the establishment of **standard reference data** on the basic fatigue properties of Japanese engineering materials commonly used for those machines and structures.
The work has been conducted since 1975 under successive five-year-term programs for ease of periodical reviews. In the present term IV, the accent is put on the ambient temperature properties of **high strength steels** and **aluminum alloys**, intermediate temperature properties of **steels for pressure vessels**, and high-temperature time-dependent properties of **heat-resisting alloys**. Table gives a brief summary of **NRIM Fatigue Data Sheets**.
In parallel with this program, series of more basic research projects have been performed to understand materials behavior and mechanisms of degradation under fatigue. Some of the latest concerns related to fatigue are: mode I-II transition of fracture in aluminum alloys, quantitative evaluation of the effect of non metallic inclusions in hard materials, effect of surface oxidation layers on crack initiation, interaction of strain aging at intermediate temperatures, prediction of long-term creep-fatigue life, and so forth.
The output data thus validated by the basic research projects have been published and exchanged worldwide with scientific and technical organizations. An **on-line data service** has become available from the Japan Information Center of Science and Technology since 1990. It is anticipated that the NRIM Fatigue Data Sheet Project contributes to the safe and effective use of en-

Table Summary of NRIM Fatigue Data Sheets

Subthemes and Items Investigated	No. Issued
<Machine Structural Materials> High/Low Cycle Properties on: Carbon and Low Alloy Steels, Stainless Steels, Carburizing Steels, Spring Steels, Tool Steels, and Aluminum alloys	29
<Welded Joints> High/Low Cycle and Crack Growth Properties Looking at the Effect of: Specimen Size, Welding Procedure, Stress Ratio, Weld/HAZ Materials, and Welding in Aluminum Alloys	20
<Elevated Temperature> Properties of Carbon and Low Alloy Steels, Stainless Steels and Heat Resisting Alloys in: High/Low Cycle and Time Dependent Low Cycle Ranges, Frequency Dependence at Intermediate Temperatures	17

gineering materials, not only becuase of its comprehensive nature, but also by the enrichment of knowledge on materials behavior.

Related papers

" *Effect of Humidity on Fatigue Properties of 5083–O Aluminum Alloy* ", Matsuoka, S., Nishijima, S. and Hirukawa, H.: Proc. 4th Int. Conf. on Aluminum Weldments, Tokyo, April 1988, (1988), 3/15–26.

" *Fatigue Strength and Fatigue Crack Initiation and Propagation of High Strength Steels* ", Abe, T. and Kanazawa, K.: J. Materials Science, Japan, **40** (1991), 1447–1452 (in Japanese).

" *Fatigue Strength Evaluation of Butt Welded Al-Mg Alloy: Test with Maximum Stress at Yield Strength* ", Ohta, A. and Mawari, T. Fatigue and Fract. of Engng Materials and Structures, **13** (1990), 53–58.

" *Creep-Fatigue of 1Cr-Mo-V Steels under Simulated Cyclic Thermal Stresses* ", Yamaguchi, K., Ijima, K., Kobayashi, K. and Nishijima, S.: Iron and Steel Inst., Japan, International, **31** (1991), 1001–1006.

" *Environmentally Affected Fatigue Crack Growth* ", Nishijima, S., Matsuoka, S. and Takeuchi, E.: Fatigue 90, Proc. 4th Int. Conf. on Fatigue and Fatigue Thresholds, Hawaii, July 1990. **3** (1990), 1761–1770.

22 Life Extension of Heat Resisting Steels by Controll of High Temperature Damage

Apr. 1988~Mar. 1991

Shinya, N.

Failure Physics Division

Mateials used for high temperature components are subject to long term deterioration of integrity due to the accumulation of **creep cavities** on grain boundaries. The nucleation and growth of such cavities is a significant life-limiting parameter in many components. If the cavities could be removed by rejuvenation treatments during service, overall life of high temperature components would be extended remarkably. Hence, attempts have been made to remove the cavities concerned with a low alloy steel and an austenitic stainless steel. The following conclusions were obtained.

(1) **Sintering heat treatments** have been carried out in air, in hot isostatic pressing and under longitudinal compressive stresses to remove grain boundary cavities in a 1.3Mn-0.5Mo-0.5Ni steel and a 316 stainless steel following creep tests up to the

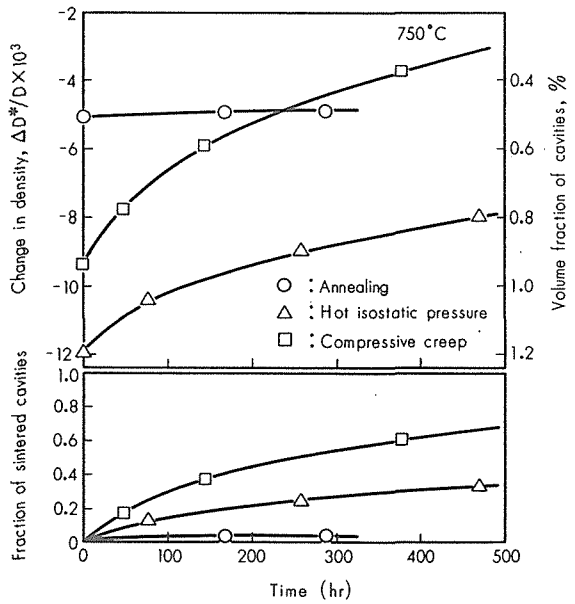

Figure Comparison of annealing, hot isostatic pressure and compressive creep for sintering effect of cavities.

tertiary stage. Figure shows the comparison of the three treatments for the 316 stainless steel. The amount of cavities was measured using a high sensitive density measurement technique. It is indicated that annealing under compressive stress is very effective in **removing cavities**.
(2) Crack-like cavities (>2 μm) still remained after long plain annealing, whereas small cavities (<2 μm) were removed easily. The sintering rates calculated by the existing grain boundary diffusion models were much higher than the experimental data of the plain annealing. THis suggests that the sintering rate is controlled not by the grain boundary diffusion, but by an other process such as volume diffusion. These results mean that early plain annealing before the tertiary stage is necessary for a considerable prolongation of the life.
(3) Annealing under compressive stress quickly removed not only small cavities but also large crack-like ones (> 10 μm). The sintering rates calculated by a modified model using the constrained growth theory is consistent with experimental data. The consistency indicates that the constraint at grain boundaries accompanied with sintering of cavities is relaxed by the compressive stress.

Related papers

" *Sintering of Creep-Induced Grain Boundary Cavities in 316 Stainles Steel* ", Murata, M., Tanaka, H., Shinya, N. and Horiuchi, R.: J. Soc. Mat. Sci. Japan. **39** (1990), 485–495 (in Japanese).

(23) Controlling and Recovering High Temperature Damage

Apr. 1991~Mar. 1994
Shinya, N.
Failure Physics Division

Low ductile fracture of metals after long term high temperature creep results from the progressive accumulation of **grain boundary cavities** throughout the creep process. Therefore, technologies for controlling and recovering the cavities are important for the development of reliable heat resisting alloys and also for the maintenance of high temperature components. In this work a self-recovering mechanisim of the cavities will be studied, and a life extending system, based on control of the cavities, will be proposed.

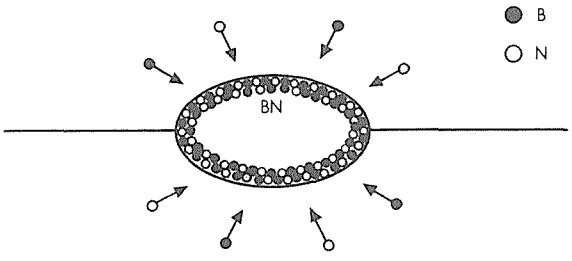

Figure Precipitation of BN at cavity surface during creep.

Self-recovering of grain boundary cavities
The growth rate of the cavities is controlled by the slower process of the grain boundary diffusion or the surface diffusion. If the surface diffusion could be suppressed markedly, the cavity growth would be restrained. In a previous work it was confirmed that a BN compound is formed at the cavity surface during creep in austenitic stainless steels. Shielding by a stable compound like BN at the cavity surface may suppress the surface diffusion and the cavity growth remarkably. Accordingly the precipitation of BN at the cavity surface may provide a kind of self-recovering functon to heat ressting alloys. The precipitation process is shown in Figure.
Extension of creep life
A rejuvenation investigation for providing a prolonged creep life is being aimed at eliminating grain boundary cavities. Effective sintering treatments were proposed and also a metallurgical technique for the prevention of surface cracks, which can not be recovered, was developed in previous works. Using these techniques, a life extending system for high temperature components will be developed.

24 Tensile Fracture Mechanism for Long Ceramic Fibers

Apr. 1990~Mar. 1992
Masuda, C.
Failure Physics Division

Several kinds of long ceramic fibers are used for reinforced materials in several composites such as plastic matrix, metal matrix or ceramic matrix composites. The **tensile strengths** of those composites are strongly influenced by the strength of the reinforcement fibers. In order to obtain basic data of the strength for mono-filament, tensile tests were performed with **boron fibers** in relation to the probability and the **fracture mechanism**. In the Weibull probability graph of the tensile strength for boron fibers three regions were found, the lower, the higher and the middle region. On the fracture surface in the middle and lower regions of the tensile strength the initial origin and mirror, mist and hackle zones were observed. In this case, the size of initial origin for the lower region was larger than that for the middle region. For the higher region the initial origin was hardly seen on the fracture surface. The depth of the mirror zone which originated at the specimen surface was linearly related to the fracture strengths on log-log coordinates, that is, the fracture toughness of boron fiber was nearly 10 $MPam^{1/2}$. On the other hand, the fracture toughness at voids near the

Table NRIM Creep Data Sheets which contain 10^5h creep rupture data

Year of Issue	No.	Material
1986	3B	2.25Cr-1Mo (tube), STBA 24
	4B	18Cr-8Ni (tube), SUS 304 HTB
1987	5B	18Cr-10Ni-Ti (tube), SUS 321 HTB
	18B	1.3Mn-0.5Mo-0.5Ni (plate), SBV2
1988	14B	18Cr-12Ni-Mo (plate), SUS316-HP
	15B	18Cr-12Ni-Mo (bar), SUS316-B
	30B	Co base 25Cr-10Ni-7.5W-B (casting)
1989	23B	Fe base 20Cr-20Ni-20Co-W-Mo-(Nb+Ta) (bar)
	24B	Ni base 15Cr-28Co-Mo-Ti-Al (bar)
1990	9B	1Cr-1Mo-0.25V (forging), ASTM A470–8
	16B	25Cr-20Ni-0.4 C (cast tube), SCH 22-CF
	29B	Ni base 13Cr-4.5Mo-0.75Ti-6Al-2.3 (Nb+Ta)-Zr-B (casting)

core fiber was about 5 MPam$^{1/2}$. The difference in fracture toughness between these two types could be due to the difference in the residual stresses near the specimen surface and the core, respectively. The effect of crosshead speed on the formation of mirror zone was discussed for boron fiber. The size of the mirror zone decreases with increasing crosshead speeds over 250 mm/min. It is suggested that the mirror zone is formed by a slow crack growth mechanism.

[25] NRIM Creep Data Sheets (III)

Apr. 1986~Mar. 1991

Tanaka, C.

Environmental Performance Division

In this program, **long-term creep rupture tests**, **creep tests** and **stress relaxation tests** are systematically conducted on domestic heat-resistant steels and alloys which are used for components of high temperature plants. The data obtained are evaluated statistically and metallurgically, and distributed as the **NRIM Creep Data Sheets** in order to contribute to the safety, the improvement of reliability of the plants and to the development of materials.

The data of 41 kinds of materials have been already published in the NRIM Creep Data Sheets up to this year. 12 data sheets among them which contain 10^5h creep rupture data, designated as version B, are shown in Table.

Investigations concerning the following subjects have been made in connection with the NRIM Creep Data Sheets program:

(1) **long-term creep curves** of 1Cr-Mo-V and 2.25Cr-1Mo steels could be described well by a constitutive equation which was deduced from the modified θ projection concept, and using this method the rupture life could also be predicted accurately,

(2) **long-term stress relaxation**, tests were carried out on low alloy steels, and a procedure by which the residual stress was predicted simply from the creep rupture properties was proposed,

(3) the decrease of electromotive force in the calibration of PR thermocouples used for long-time creep tesing was investigated, and a procedure to achieve a complete recovery of the electromotive force was recommended, and

(4) the **long-term creep rupture strength** of heat-resistant steels and alloys was investigated in relation to microstructural changes and fracture mechanisms.

(26) NRIM Creep Data Sheets (IV)

Apr. 1991~Mar. 1995

Tanaka, C.

Environmental Performance Division

The objective of this program is to obtain 10^5h data of heat-resistant metallic materials in creep and rupture tests, to publish the data obtained as **NRIM Creep Data Sheets** which contribute to fundamentals of ensuring safety and reliability of structural components in high temperature plants, to investigate **long-term creep deformation behaviour** and creep rupture prop-

erties, and to develop an evaluation method of **long-term creep and rupture strength** at high temperature.
This program has been carried out since 1966 and is still being continued in order to obtain further long-time creep testing data of domestic steels and alloys. In the new program IV which has been started this year, tubes and plates of mod. 9Cr-1Mo and 9Cr-2Mo steels are added to 41 kinds of testing materials on which the creep tests have already been conducted. The publication of Technical Documents is also planned. The testing results and analyses of data which can not be shown in Creep Data Sheets will be reported in the Technical Documents. The contents of the 1st Technical Document for creep will consist of the plan of NRIM Creep Data Sheets, the procedures and techniques for obtaining accurate data in long-term creep and rupture tests, the evaluation method of long-term creep rupture strength, and so on.
Long-term creep deformation behaviour and rupture strength of steels and alloys at high temperature are investigated using the data and ruptured specimens which are obtained from the NRIM Creep Data Sheets program. The subjects investigated are as follows;
(1) to evaluate the creep deformation behaviour for low alloy steels based on the modified θ projection concept,
(2) to clarify the fundamental properties of long-term creep strength for ferritic steels,
(3) to evaluate the long-term creep strength for heat-resistant steels and alloys in relation to microstructure and damage mechanism, and so on.

27 Evaluation of Effect of a Surface Film on Environmental Fatigue Crack Initiation

Apr. 1988~Mar. 1991
Kanazawa, K.
Environmental Performance Division

Fatigue cracks generally initiates at the surface of metallic materials, as the fatigue damage concentrates at the surface under cyclic stressing. When a suitable surface film is formed at metallic materials, it is believed that the film can suppress the formation of fatigue cracks from the surface.
This phenomenon can be recognized experimentally for high-temperature, high-cycle fatigue of engineering materials in air environment. A surface crack is not easy to initiate under low stress levels, as oxide at the specimen surface prevents dislocations from slipping off from the surface. During this period, fatigue life increases but another type of **fatigue crack initiation** process occurs, that is, the fish-eye fracture occurs from an inclusion in the interior of the specimen.
The effect of a surface film on the deformation of bulk matrix materials must be clarified to evaluate the resistance of surface films to fatigue crack initiation.

Related papers
"*Effect of Oxidation on Fatigue Crack Initiation and Propagation*", Kanazawa, K., Sato, M. and Kimura, M.: Proc. 5th Int. Conf. Fatigue and Fatigue Threshold, vol. **3** (1990), 1577–1582.

28 Effect of a Surface Film on Deformation of Bulk Matrix Material

Apr. 1991~Mar. 1994
Kanazawa, K.
Environmental Performance Division

This project aims at studying the effect of surface film on deformation of bulk matrix material for the evaluation of the resistance of a surface film to **fatigue crack initiation** from the surface.
In the first stage, the method of strength evaluation of the surface film is studied by using a dynamic ultra micro hardness tester.

29 Evaluation of Material Performance of Pressure Vessel Steels in Sulfide Solution

Apr. 1989~Mar. 1991
Aoki, T.
Environmental Performance Division

Tensile fracture behavior of **pressure vessel steels** in an acid solution containing **sodium thiosulfate** has been investigated with the **slow strain rate technique.** The purpose of this study was to develop a method to evaluate the susceptibility of steels to sulfide stress corrosion cracking.
The results showed a marked decrease in ductility at strain rates less than 10^{-6}/s, and the maximum ductility loss was observed at a sodium thiosulfate concentration of about 10^{-3} mol/l. In hydrogen absorption tests, the maximum hydrogen concentration was also observed at a sodium thiosulfate concentration of about 10^{-2} - 10^{-3} mol/l.
In comparison with the other types of sulfide **stress corrosion cracking** test solutions, the susceptibility to stress corrosion cracking in the solution containing sodium thiosulfate was less severe than that in NACE solution (H_2S saturated acid salt water), but was nearly equivalent to that in BP solution (H_2S saturated artificial seawater).

[30] Evaluation of Creep Crack Initiation and Growth under Static and Cyclic Loading Condition

Apr. 1989~Mar. 1991

Yagi, K.

Environmental Performance Division

In order to improve the reliability of high temperature engineering components and to develop accurate life prediction methods, the evaluation method of crack initiation and growth under creep and creep-fatigue conditions must be investigated. In this study, the correlation between ceep crack growth rate and microscopical fracture mechanism under high temperature creep condition and the relationship between creep damage mode and **creep-fatigue interaction** were investigated. The following results were obtained.

(1) **Creep crack growth tests** were conducted using CT specimens on 316 stainless steel and NCF 800H alloy at various temperatures and loads. Creep crack growth rate vs. **C^* parameter** relations were dependent on the microscopical creep **fracture mechanism**. Creep crack growth rate for wedge and cavity-type intergranular fracture was about five times higher than that for transgranular fracture. The faster creep crack growth rate for wedge-type fracture was due to the low creep ductility. The faster crack growth rate for cavity-type fracture was considered to be related to the comparatively low creep ductility and wide creep-damaged region ahead of the crack tip.

(2) Combined **creep-fatigue loading tests** were conducted on NCF 800H alloy and fine- and coarse-grained 321 stainless steels. The creep damage ϕ_c and the fatigue damage ϕ_f which were accumulated during the combined creep-fatigue loading tests were calculated using a **linear life fraction damage rule**. The ϕ_c vs. ϕ_f relation obtained was related to relevant **microscopical creep damage mode** and was found to be independent of the materials used. In the case of transgranular creep fracture, the value of ϕ_c was related to softening or hardening of the matrix under fatigue loading.

Related papers

" *Characterization of Creep Crack Growth Behaviour of 316 Stainless Steel in Terms of Microscopical Fracture Mechanism* ", Tabuchi, M., Ohba, T. and Yagi, K.: ISIJ International, **30** (1990), 847–853.

" *Relationship between Creep Damage Modes and Creep-fatigue Interaction* " Yagi, K., Kubo, K., Kanemaru, O., Tanaka, C. and Masuda, H.: Advanced in Fracture Research, ed. by K. Salama et al., Pergamon Press, New York, (1989), 1715–1722.

[31] Evaluation of Crack Initiation and Growth of Superalloys under Creep and Creep-Fatigue Conditions

Apr. 1991~Mar. 1993

Yagi, K.

Environmental Performance Division

An understanding of crack initiation and growth behaviour under creep and creep-fatigue loading conditions is one of the most important factors in ensuring the reliability of high temperature structural components. We have been studying the relationship between **creep damage mode** and **creep-fatigue interaction**. The results indicate that the creep-fatigue life is affected by the change in creep damage mode. We have also clarified that the relationship between the creep crack growth rate and the C^* parameter is dependent on the microscopical fracture mechanism. Therefore, it is considred that th evaluation of crack growth rate under creep-fatigue loading conditions will become more acurrate by taking the micro fracture mechanism into account. In order to develop the evaluation method of crack initiation and growth under creep and creep-fatigue loading conditions, we will investigate the following two subthemes in this study.

(1) **Creep crack growth** behaviour of **Ni-base superalloys**

Complicated metallographic changes were observed during long-term creep loading on Ni-base superalloy. Long-term creep crack growth tests will be conducted at 900 and 1000°C and the creep crack growth behaviour will be investigated in detail from the viewpoint of change of microstructure and fracture mode.

(2) **Creep-fatigue crack growth** behaviour of Fe-base superalloy

The rupture life of NCF 800H alloy was strongly affected by creep-fatigue interaction under wedge-type cracking conditions. It is thought that under these conditions, creep crack growth rate will also be high. The study of creep-fatigue crack growth under wedge-type cracking conditions will lead to a better understanding of cree-fatigue interaction.

(32) Fatigue Crack Propagation under Random Loadings in Corrosive Environment

Apr. 1988~Mar. 1991

Ohta, A.

Environmental Performance Division

Fatigue crack propagation properties of **welded joints** in which high tensile residual stresses exist were investigated under **random loading** in synthetic sea water.

Fatigue crack closure was prevented by the high stress ratio condition formed around the crack tip due to residual tensile stresses. The fatigue crack propagation rate, $\overline{da/dn}$, under random loading was well predicted from results obtained from constant amplitude loading, assuming a linear cumulative damage law, that is, $\overline{da/dn}=C\{\Delta K_{eq}{}^{m} - \Delta K_{th}{}^{m}\}$ where the equivalent stress intensity factor, $\Delta K_{eq}=\{\sum n_i \cdot \Delta K_i{}^{m}/\sum n_i\}^{1/m}$, where $n_i=0$ for $\Delta K_i \leqq \Delta K_{th}$, or $n_i=n_i$ for $\Delta K_i>\Delta K_{th}$.

Related papers

" *Fatigue Crack Propagation Curve for Design of Welded Structures* ", Ohta, A., Maeda, Y., Machida, S. and Yoshinari, H.: Trans. JWS, **20** (1989) 17–23.

" *Fatigue Crack Propagation in Welded Joints under Variable Amplitude Loading in Synthetic Sea Water*", Ohta, A., Maeda, Y., Machida, S. and Yoshinari, H.: Int. J. Fatigue, **12** (1990) 475–480.

" *Evaluation of Fatigue Crack Propagation Properties under Random Loading Avoiding Crack Closure* ", Suzuki, N., Takeda, H., Ohta, A. and Ohuchida, H.: Fatigue & Fracture Engng. Mater, Struct., **14** (1991) 815–821.

(33) Real Time Evaluation of Fatigue Damage during Crack Propagation under Random Loadings

Apr. 1991~Mar. 1994

Ohta, A.

Environmental Performance Division

Fatigue crack propagation properties of several metals are investigated under crack closure free conditions by holding the maximum load during cycling. The relationship between da/dn and $\Delta K/E$ is investigated, where da/dn is the fatigue crack propagation rate, ΔK is the range of stress intensity factor and E is the Young's modulus. The crack opening displacement, δ, is monitored during the whole period of **random loading** blocks by means of an optical type displacement gage and personal computers. The equivalent value of the crack opening displacement is also calculated as $(\sum n_i \cdot \delta_i{}^{m})^{1/m}$, ignoring the cycling below the threshold.

34 Mechanism of Mechanical Damage Accumulation in Brittle Materials

Apr. 1989~Mar. 1992

Horibe, S.

Mechanical Properties Division

Recently much attention is being paid to mechanical properties of brittle non-metallic bonded materials such as **ceramics**, because they are very promising as structural components for engineering applications at high temperatures where metallic bonded materials are not applicable. The mechanical properties of ceramics however have not yet been studied in sufficient detail. In particular, fundamentals of **cyclic fatigue** phenomena are poorly understood, although cyclic stressing is condsidered to be inevitable for the structural components put into practical use.

In this study, the cyclic fatigue properties of various kinds of non-transforming ceramics (silicon carbide, silicon nitride, sialon and alumina) produced by using different processes were evaluated and the basic fatigue mechanism of brittle ceramic materials, which should be inherently different from that of metallic materials because of the absence of plastic deformation in ceramics, is discussed from the microstructural point of view. (The details are described in Research Topics "Fatigue Fracture in Ceramic Materials").

Related papers

" *Fatigue of Silicon Nitride Ceramics under Cyclic Loading* ", Horibe, S.: J. Eur. Ceram. Soc., **6** (1990), 89–95.

" *Indentation Fatigue of Silicon Carbide and Silicon Nitride* ", Takakura, E. and Horibe, S.: Mater. Trans., **32** (1991), 495–500.

" *Cyclic Fatigue of Ceramic Materials: Influence of Crack Path and Fatigue Mechanisms* ", Horibe, S. and Hirahara, R.: Acta Metall., **39** (1991), 1309–1317.

[35] Improvement of Fretting Fatigue Properties

Apr. 1989~Mar. 1991

Sumita, M.

Mechanical Properties Division

Fretting fatigue properties were investigated in air and in seawater under freely corroding or cathodically protected conditions using high strength steels having ultimate tensile strengths of 490, 690 and 880 MPa and a Ti-6Al-4V alloy.

A normal contact load was applied to the pads on both flats of the fretting specimen. When the cyclic load was applied to the specimen, a small relative slip occurred between the specimen and the pads, and fretting damage was introduced at the contact area.

With increasing normal **contact pressure**, fretting fatigue lives of the steels and the Ti-6Al-4V alloy decreased monotonously at high stress amplitudes, and showed a minimum and then a maximum at low stress amplitudes as shown in Figure. The latter was explained by the stress concentration which depends on the ratio of the stick area to the slip area in the contact area.

Fretting fatigue life increased under the condition where microcracks initiated at the contact areas were pared off due to abrasive wear before one of them grew into a large crack which caused failure.

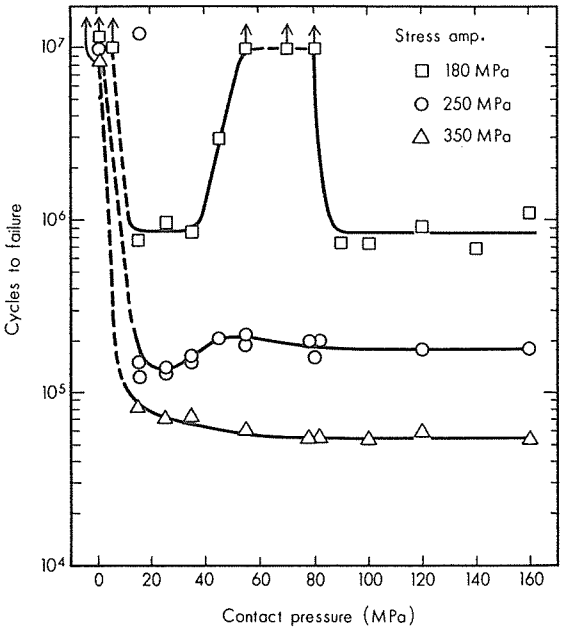

Figure Cycles to Failure as a Function of Contact Pressure for a 880 MPa Grade Steel in Air with R=0.1.

In seawater under freely corroding condition, the number of fretting cycles beyond which fretting damage saturated depended heavily on the kind of steel used and on the stress frequency. Using cathodic protection, the fretting fatigue life in seawater was significantly increased, and became longer than that in air.

Related papers

" *Effect of Contact Pressure on Fretting Fatigue of High Strength Steel and Titanium Alloy* " Nakazawa, K., Sumita, M., and Maruyama, N.: ASTM STP, to be published.

" *Effect of Testing Environments on Fretting Fatigue Strength of a Ti-6Al-4V alloy* ", Maruyama, N., Sumita, M., and Nakazawa, K.: J. Iron and Seel Inst. Jpn., **77** (1991), 290–297 (in Japanese).

" *Fretting Fatigue of High Strength Steels in Seawater* ", Nakazawa, K, Sumita, M, and Maruyama, N.: Proc. Int. Conf. on Evaluation of Materials Performance in Severe Environments, ISIJ, Kobe (1990), 151–158.

(36) Mechanism of Fretting Fatigue Failure in Composite Materials and Surface Modified Materials

Apr. 1991~Mar. 1994

Sumita, M.
Mechanical Properties Division

The aim of this research was to obtain a fundamental understanding of the mechanism of **fretting fatigue failure** from a microstructural viewpoint using metal matrix composites and surface modified metallic materials. The most important factors which influence fretting fatigue strength are the friction coefficient and the behaviour of the stick region on the contact area between the specimen and the pad. According to the hypothesis on the adhesive force on the contact area, the friction coefficient is expressed as the ratio of the shearing force on the contact area to the hardness. If this hypothesis is not denied, the friction coefficient is micro-structually controllable and is can be decreased.

On the other hand, cracks are initiated at the boundary between the stick region and the slip region on the contact area. The behaviour of the stick region also seems to be microstructurally controllable.

In order to improve fretting fatigue strength according to the above idea, the structure of the material used has to consist of hard phases and soft phases or of hard layers and soft layers. Moreover, the design of the volume fraction, the size and the shape of each phase, and the thickness and the number of layers are of important.

Using those materials, the friction coefficient, the size of stick region, the roughness of the contact area, the number of fretting cycles to cause the saturation of damage, and fretting fatigue life are measured.

(37) Fatigue Crack Initiation Process in Corrosive Environment

Apr. 1991~Mar. 1994

Hamano, R.
Mechanical Properties Division

In many structural components, failure by **corrosion fatigue** tends to increase with increasing strength when they are exposed in corrosive environments under cyclic loading. In order to improve the resistance to corrosion fatigue cracking, it is important to clarify what kinds of metallurgical factors control the resistance to fatigue cracking. The aim of the present study is to determine microstructure—environment influence on the fatigue crack initiation process in corrosive environment, and to control the performance of new alloys.

We investigated the effects of slip character and slip length on corrosion fatigue cracking and fracture path as a function of the cathodic potential in a NaCl aqueous solution. It was observed that the environmental susceptibility to fatigue cracking of precipitation hardened high strength steel is dependent both on the aging condition and on the strength of the material. For example, the underaged materials showed less resistance to corrosion cracking at the same yield strength compared to the overaged materials. The fatigue fracture surfaces of the materials consisted of prior-austenite grain boundaries due to hydrogen embrittlement. There-

fore, environmental enhancement of atigue cracking is dependent on the easiness of cracking through prior-austenite boundaries caused by hydrogen. To clarify the intrinsic role of microstructure and the extrinsic role of environment on the fatigue cracking behaviour, we observed the slip deformation mode and the crack path arising from a combination of microstructural and environmental contributions. As a result, it was shown that **slip planarity** of disllocations decreases the resistance to corrosion fatigue cracking, which was contributed to increase hydrogen embrittlement.
Despite these significant results, some important problems are still unresolved. Environmental effects on **pre-crack deformation** and **early fatigue crack growth** must be investigated for **high strength materials**. These are now in progress.

Related papers

" *Roles of Precipitates on Corrosion Fatigue Crack Growth of High-Strength Steels in Corrosive Environments* ", Hamano, R.: J. Materials Science, **24** (1989), 693–697.

Measurement and evaluation

38 Vaporization and Ionization by Arc Plasma

Apr. 1990~Mar. 1993

Okada, A.
Advanced Materials Processing Division

The electric current distribution on the molten pool in a GTA weld is expected to depend on the **vaporization** area on the pool because the **ionization** potentials of metal vapors are much lower than those of argon and helium gases. The **current density distribution** on the molten pool was estimated by measurement of the electric potential distribution on the back of a thin plate (3.5 mm, Ti-6Al-4V). This plate is one of the base metals in which it is expected that the anode distributes over the wide range on the molten pool. The measurement was carried out in a stationary GTA with an arc current of 150A and arc length of 3mm, and in the stationary state of the heat flow (molten pool diameter: 9.5mm) which is obtained by water-cooling at the back of the plate. The results show that it the current density distribution is not a Gaussian distribution but a flat-top (equi-current density) distribution like frustum of cone (OD:7–8mm).
Ionized and excited state densities of plasma components in a Ar-He **mixed gas** arc plasma have been studied by measuring line spectrum intensities of Ar I and Ar II using light spectroscopy. The line spectrum intensity depends on density and temperature of each of the plasma components in a mixed gas arc. However, both the gas densities and temperatures are unknown in an Ar-He mixed arc, becuase demixing of plasma components in a mixed gas arc was expected from the measurement of the concentration distriution at the anode surface using mass sepectroscopy. A new method was developed to estimate the density and temperature of each of the plasma components in a mixed gas arc from measurement of the intensity ratio of the lines Ar I and Ar II. The results show that He gas is concentrated at the axis of the arc column and that the temperature near the axis does not change upon introduction of He gas into the Ar arc.
He-H_2 mixtures were found to be very effective in evaporating anode material. It is thought that the formation of a highly constricted anode spot is a main contributor to anode vaporization. The vaporization mechanism in a mixed gas arc was investigated using light spectroscopy and calorimetry during arcing, and SEM analysis of the condensed powders produced.

Related papers

" *Current Distribution on Molten Pool in Stationary TIG Arc Welds of Ti Alloy—Study on Behaviour of Anode on Molten Pool in TIG Arc Welds (1st Report)—* ", Okada, A. and Nakamura, H.: Quarterly J. Japan Weld. Soc., **9** (1991), 216 (in Japanese.)
" *Local Plasma Compositions at Anode Surface in Mixed Gas Shielding GTA* ", Hiraoka, K.: Quarterly J. Japan Weld. Soc. (in Japanese). To be published.

39 Investigation on Non-Contact Materials Evaluation Using Laser Beam

Apr. 1987~Mar. 1992

Saito, T.
Materials Characterization Division

Non-contact ultrasonic generation and detection using **Laser** beams, which constitute the so-called laser-ultrasonic technique, allow materials evaluation at high temperatures, and inspection of small specimens and areas. In this study, laser-ultrasonic techniques, which may induce many advantages in materials evaluation, are investigated for the development of a new materials evaluation technique. This study has three sub-themes, which are: exploration of ultrasonic generation phenomena, technical development of ultrasonic detection techiques, and their experimental application to materials. Major outcomes were as follows.
A method for the computer simulation for laser generated **ultrasound** was developed. The simulation model was based on finite difference methods, and consisted of typical laser induced effects of thermal stress and vaporizing pressure. It calculated wave forms and the state of the ultrasonic propagation in the solid, which is difficult to be observed experimentally, and calculated wave

forms are in good agreement with those detected by a laser interferometer.
Optical heterodyne interferometry was investigated for non-contact quantitative ultrasonic detection. Its basic system for the detection of high frequency ultrasound was developed using a new phase detection technique which enabled the demodulation of ultrasonic signals with frequencyies up tp to 50MHz.
The current work is on the development of a non-contact microscopic ultrasonic imaging system using the laser-ultrasonic technique. Up to now, imaging of a specimen that includes small model flaws was examined with a combination of optical detection and a contact ultrasonic probe, and ultrasonic images of copper wire of 0.1mm diameter in layered thin plates were obtained. The next aim is the imaging in a perfect non-contact state at high temperature. At present, a system for its application is under construction.

40 Characterization of Metals and Alloys Using Synchrotron Radiation

Apr. 1990~Mar. 1992
Saito, T.
Materials Characterization Division

Use of **synchrotron radiation** (SR) as a powerful research tool in materials characterization has grown tremendously in recent years. In the present program, from a view point of materials characterization, new analytical techniques and apparatuses as well as their practical applications have been extensively studied.
*Near-**surface analysis*** using *grazing incidence X-ray fluorescence*
The grazing incidence X-ray fluorescence technique is suitable for the analysis of thin film and of the near-surface of materials because of the shallow penetration of X-rays around the critical angle. During the present study, some new techniques have been developed for chemical state analysis, depth analysis and the evaluation of layered thin filmes.
EXAFS
(1) Application of EXAFS to structural studies of **amorphous alloys**; EXAFS has been one of the most popular experimental techniques using SR. In this study, the possibility of solid state amorphization during mechanical alloying was examined by EXAFS. The amorphrization process of immiscible Cu-Ta system was first observed.
(2) Development of a new labo-EXAFS facility; The labo-EXAFS is considered to be complementary with EXAFS experiments using SR. In our institute, a new facility has been developed, and limitations of the conventional laboratory spectrometer have been diminished by the use of a fast rotating anode X-ray source and the improvement of the optical system.
*Evaluation of structure and defects by **X-ray computed tomography***
In order to analyze the structure, defects and fracture process of **metal matrix composites** during the tensile test, the nondestructive evaluation was discussed by X-ray computed tomography using SR. Threee-dimensional images have been constructued on the basis of cross sectional CT images. The debonding parts between fiber and matrix, and fractured fibers have been clearly observed. The resolution of this scanner was about 10 μm.
Evaluation of composition and microstructure for heat resistant alloys
The lattice misfits between **Nickel base** single crystal **superalloys** were evaluated by SR **parallel beam diffractometry**. Profile fitting with a pseudo-Voigt function was used to determine the 2 θ angle to a 0.001 degree accuracy for the synchrotron power data. The lattice parameters of γ' phases in γ matrix and those extracted from γ matrix were significantly different.

(41) Sensitive Instrumental-Analysis of Metallic Materials by Direct Methods and Separation Methods

Apr. 1991~Mar. 1994
Hasegawa, R.
Materials Characterization Division

The study comprises the following three themes. This investigation aims at the development of fundamental techniques including direct methods and separation methods for the sensitive instrumental-analysis of metals, alloys and related materials.
Study on direct analysis of solid samples
(1) Analysis of Ti metal and its alloys for traces of elements including C, N and O and alloying elements by **glow discharge mass spectrometry**
(2) Determination of H in steel by the high frequency furance hot extraction-thermal conductivity method
(3) Determination of O in low-melting metals by the inert gas fusion method using the impulse heating technique
Study on direct analysis of liquid samples
(1) Determination of traces of elements having a vapor pressure different from that of the matrix in Ti and Ta by **graphite furnance atomic absorption spectrometry**
(2) End-on and side-on observation of inductively coupled plasmas using electrothermal vaporization and time-resolved measurement
Study on separation analysis of liquid samples

(1) Determination of traces of impurities in molybdenum disilicide by co-precipitation and inductively coupled plasma-atomic emission spectroscopy (**ICP-AES**)
(2) Determination of traces of carbide-forming elements in Fe using flow injection and ICP-AES
(3) Determination of Hf in W by ICP-AES after ion exchange chromatography
The investigation also includes the improvement of analytical techniques available for the chemical analysis of various samples which are provided by other divisions of our Institute.

42 'In-Situ' Analysis/Evaluation of Radiation Damage in Materials

Apr. 1988~Mar. 1994
Furuya, K.
Materials Characterization Division

Radiation damage of metallic materials is characterized by atomic displacements in the crystalline structure by the irradiation of energetic particles. Many types of defects and defect clusters are supposed to be produced by this atomic process and the resultant microstructure generally becomes complicated with the formation of dislocation loops, voids, precipitates and so on. For the basic understanding of **radiation damage**, in-situ irradiation of materials during the observation in the transmission electron microscope (TEM) is one of the fascinating ways to investigate the structural evolution induced by particle bombardments and implantations.
The purpose of this research is to develop a new facility for the **"in-situ" analysis** of the microstructure of materials under dual-beam ion irradiation. The so-called **"SUBNANOTRON"** facility (as illustrated in Figure) consists of a **1 MV TEM** with **two ion accelerators**. The 1 MV TEM results in a resolution >0.15 nm, while it allows for a specimen thickness and a sample volume at the testing location involving thermomechanical treatment which satisfy the analytical purpose pursued. Analytical tools such as MAD, EDS and EELS are essential to characterize the complicated structural changes of irradiated materials. The construction of the SUBNANOTRON is in progress and will be completed at the end of 1993, and the details of the specifications can be improved during this period if so required.
A special effort for SUBNANOTRON has been made by using a standared 200 kV TEM incorporating two types of small ion accelerators which can produce 100 keV heavy ions and 30 keV inert gas ions such as H and He. The ion fluxes from both systems were about 6×10^{17} ions $m^{-2}s^{-1}$ at the specimen position. Several specimens of Al, Ni and Si have been

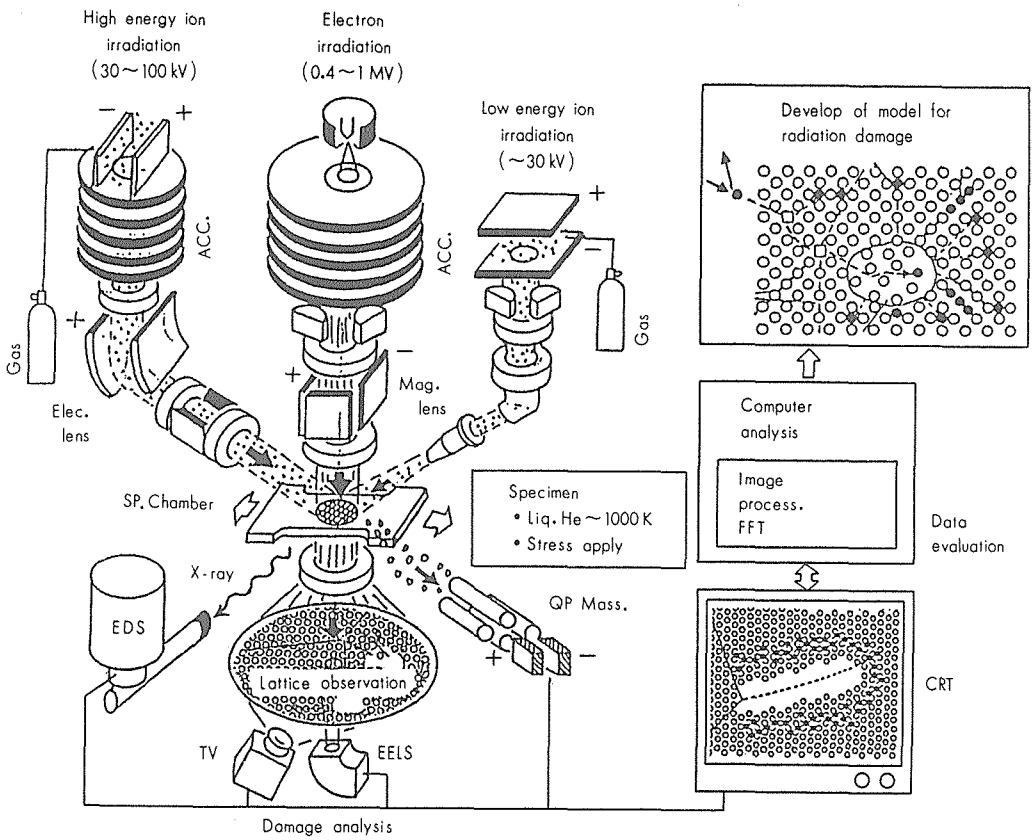

Figure Schematic drawing of the SUBNANOTRON which is based on a 1 MV transmission electron microscope incorporated with two ion accelerators and with several state-of-art analytical tools.

irradiated in this system and the dynamic behavior of defect clusters was observed in the images taken by a fiber optically coupled TV camera, and recorded with a VTR through a real time image processor. Currently critical technical problems are pointed out for SUBNANOTRON to improve beam control and the data analysis system.

Related paper

" *Dual Ion Beam Irradiation of Fusion Materials in the Electron Microscope—on the "SUBNANOTRON" Project* " Furuya K., Kimoto T., Noda T., Shiraishi H. and Okada M.: submitted to J. Nucl. Mater.

43 Characterization and Control of Elementary Functions of Materials in the Localized Fine Area

Apr. 1989~Mar. 1993

Furuya, K.

Materials Characterization Division

Bulk functions of materials are controlled by the physical and chemical properties in localized fine ares ranging from 10^{-6} to 10^{-9} m. Especially, the electronic and magnetic properties of metals and semiconductors are considered to originate from the heterogeneity in the materials such as surfaces, grain boundaries and domains. Focused ion beam (**FIB**) has gained in applicability for creating artificial heterogenetity by ion implantation, etching and lithography with submicron dimensions. However, the microstructural aspects and elementary functions of the prduced areas by FIB could not be analyzed in the conventional experiments. The purpose of this research is to develop new equipment for **in-situ observation** of materials during the **micro-lithographies** by FIB in the transmission electron microscope (**TEM**).

The equipment called "FIB/TEM" (as illustrated in Figure) consists of a 200 kV standard TEM with 25 kV Ga^+ FIB. The FIB system is mounted in the specimen column of TEM and the working distance for FIB reduces to 100 mm for a ion beam spot smaller than 200 nm diameter. In addition to TEM observation of micro-fabricated area produced by FIB, analytical tools such as cathodeluminescence spectroscopy (CL), energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) are used to characterize the basic physical properties of the localized fine area. The FIB/TEM will be completed at the end of 1992, and improvements will be carried out on the heating and/or cooling devices of specimens.

The preliminary work was planned to obtain information with SEM and TEM on the microstructural changes of Si (100) locally milled by 8 keV Ga^+ FIB. A Ga^+ beam which focused on a thin section of TEM specimens made a hole of about 0.01 mm at room temperature and the observations were carried out in the region adjacent to a hole. The results of SEM and TEM indicated that a beam affected zone

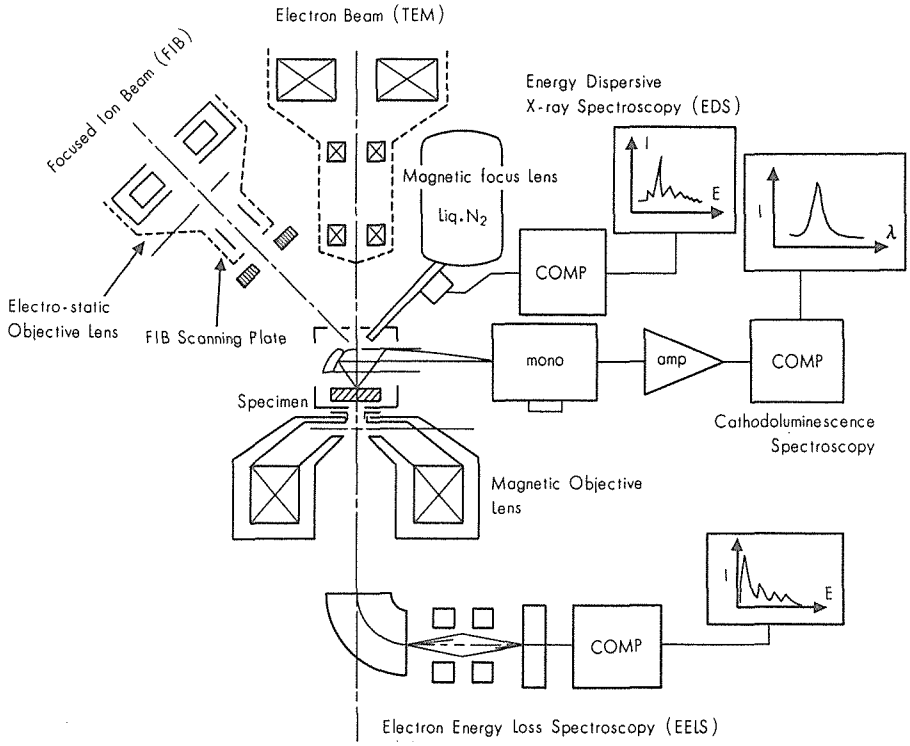

Figure Schematic drawing of the FIB/TEM which is based on a 200 kV transmission electron microscope incorporated with 25 kV Ga^+ focused ion beam system and with several analytical tools such as CL, EDS and EELS.

formed around a hole, where Ga was detected by EDS. TEM photographs also showed the flakes of Ga-related film having a orientation relationship with the Si (100) matrix spread in this regime. Analysis of electron diffraction patterns and the phase relationship of Si-Ga system indicated the possibility of these flakes to be a **metastable Ga phase** which had a interplanar spacing larger than 0.3 nm.

Related papers

" *Microscopic Observation of Si (100) TEM Film Locally Milled by Ga^+ Focused Ion Beam* ", Furuya K. and Ishikawa N.: submitted to Radiation Effects and Defects in Solids.

44 Measurements of Transient Phenomena Due to Beam-Solid Interaction

Apr. 1990~Mar. 1992
Kishimito, N.
Materials Characterization Division

Microstructural evolution in irradiated materials results from a dynamical balance between generation and relaxation of point defects. Rate equations of point defects are often used to describe the damage phenomena. The relaxation time of each elementary process is expressed by microstructural parameters, such as diffusivity of vacancies, interstitial/solutes, caputre efficiencies of defect sinks etc. A transient response of a material to a pulsed-beam perturbation conveys kinetic information and may present a direct technique to measure the microstructural parameters. The purpose of this research subject is to explore a new detection technique based on **transient phenomena** due to **pulsed irradiation** and to determine the microstructural parameters from the macroscopic responses.

Strain measurement has so far been conducted with a high strain resolution of about 10^{-5}, keeping the specimen resistance constant by DC heating. A square-wave beam of high-energy light ion (2 msec or 1200 s; 11 MeV deuteron) is irradiated onto a foil specimen of Fe-Ni-Cr alloy, with a damage production rate of 10^{-6} dpa/s.

An **anomalous contraction** of the specimen is caused by the pulsed beam irradiation, under uniaxial loading, whereas positive normal creep is usually observed for continuous beam irradiation. The contraction takes place both for the slow and fast pulsed-beams. While the positive creep is basically caused by stress-induced preferential-absorption of point defects, the negative creep seems to be due to a kind of hardening effects. The pulsed irradiation alters the population balance of point defects favorably with regard to vacancies and increases chances to form agglomerates. The observation of the transient anomaly indicates that the relevant reaction proceeds within 2 ms. Further analyses may give the information of vacancy diffusion or reaction rate.

Up to now, the strain and electrical conductivity have been measured for the microstructural probes. Their frequency and temperature denpendences are under investigation. Optical devices for photoconduction are also being installed into the accelerator system.

45 Development of Fundamental Technologies for X-ray Microtomography

Apr. 1989~Mar. 1992
Yamauchi, Y.
Materials Characterization Division

Since, in the conventional microscopy, observation is done on a certain cross-section, there always remains some ambiguity as to whether the sample is cut at the right plane containing the inherent information. On the other hand a **three-dimensional** image provides us overall information of an object. The nondestructive characteristics of x-ray tomography provide a unique feature, i.e., three-demensional image which consists of multi-sliced tomographs taken in a fine pitch along the rotational axis.

However, techniques of **X-ray computerized tomography** have so far been applied to relatively large objects, such as in medical diagnostics of human bodies or in industrial inspection of manufactured components. In those applications the required spatial resolution is usually in the order of 1 mm or 0.1 mm at most. These values are rather poor for microscopical application. The spatial resolution is circumscribed by the dynamic range of detected x-ray signal or the steepness of x-ray absorption. Further, mass data storage and computational power has to be considered for the three-dimensional imaging. The constraints above would be alleviated if it is allowed to restrict the size of objects. In such a case the limited number of pixels may not affect the pixel size nor the resolution of image. Based on this idea, we have been developing the x-ray **microtomography** device.

Previously, high resolution tomographies of a small object were obtained with the parallel beam projection using a conventional point x-ray source. A resolution of about 10 μm was achieved for a ceramics sample of 1 mm in diameter.

Currently, the function of the device is being extended to fully three-diensional. The development of fluorescent screens for x-ray image detection in higher resolution is also in progress.

Related papers

" *X-Ray Microtomography Using Super High Power Rotating Anode Generator* " Yamauchi, Y., Ikuta, T.: to be published in Nondestructive Characterization IV (Plenum Press).

[46] Advanced Methods on Physical Analyses for Metals

Apr. 1988~Mar. 1991
Tamura, Y.
Materials Characterization Division

The purpose of this investigation was to develop physical analysis methods applicable to advanced metallic materials. The main results obtained so far are the following;
(1) Physical analysis by **EPMA** A microcomputer system was developed, with which a speedy EPMA data analysis can be successfully carried out. This new system is now being applied for the quantitative analysis of a very small content of Ga in mineral ores.
(2) Physical analysis by **SEM** It was found that the superposition of a secondary electron image and a back-scatter electron one could be used for evaluating the surface composition of metal powders.
(3) Physical analysis by **TEM** The structural analysis of lattice images was performed on metal/ceramic interfaces by means of a high resolution TEM.
(4) Physical analysis by **XRD**. The conventional X-ray diffraction method was improved and a new method was proposed, by which the site occupancy of the third element in binary alloys could be determined. The method is now being used with Ti-Al alloys in order to examine its applicability.

(47) Advanced Techniques Physical Analyses for Metals

Apr. 1991~Mar. 1994
Tamura, Y.
Materials Characterization Division

The purpose of this investigation is to develop higher performance techniques of physical analyses for advanced materials with the help of data processing by microcomputers. Physical analyses include X-ray diffraction, electron probe micro-analysis, transmission electron microscopy, scanning electron microscopy and optical microscopy.
The scope of the investigation is as the follows;
(1) Techniques of crystal **structure analyses**
1) Study on new X-ray analysis A preliminary investigaion is carried out to develop a sophisticaed X-ray diffractomtry method applicable in place of the so-called ALCHEMI-method.
2) Sudy on quantitative analysis A computer software development is intended, by which the crystal structure of an unknown substance can be identified on the basis of its X-ray diffraction data.
3) Study on **surface structure analysis** An application technique is studied of X-ray total reflection method in order to obtain the information of crystal surface structures.
(2) Techniques of materials **composition analyses**
1) Study on compuer processing of EPMA data Computer software is developed for the purpose of highly accurate on-line microanalysis.
(3) Application On request, physical analyses and consultantive functions are performed.

[48] Study on Development of Chemical Instrumentation Using Plasmas

Apr. 1988~Mar. 1991
Saito, M.
Materials Characterization Division

The glow discharge mass spectrometry (**GDMS**) is a simple, rapid and sensitive method for the determinaion of target composition and a convenional method for investigating reactive sputtering processes. However, this method is unable to accurately determine impurities in materials without a reference material because the mechanism of ionization in a glow discharge is still not completely elucidated.
Thus, we studied the mechanism of ion poductions in a glow discharge by using high resolution mass spectrometry, and clarified parameters which influenced the ion intensity signals of metals. In order to minimize matrix effects, the solution sample technique was also examined. The method by which the solution was deposited on the end of a graphite electrode (rod) was developed for GDMS. In addition, by using Kr, Xe and Ne, whose metastable energy levels in the exited state are different from those of an Ar discharge gas, the main mechanism of ion production of metals was studied. The results showed the ratio of **Penning ionization** of sputteing species to be 60–80% and the other mechanism of ion production seems to be correlated to electron impacts. The factors which governed the ion intensity signals for a metal were found to depend on its ionization potential, ion cross section and molecular ion products.

(49) Study on Mechanism of Ion Products in Low Temperature Plasma

Apr. 1991~Mar. 1994
Saito, M.
Materials Characterization Division

Low temperature plasmas (**glow discharge**, plasma CVD) are widely used fo the production of new materials, and in view of the expansion of the application of the low

temperature plasma for the production of new materials, it has become of particular importance necessary to elucidate the reaction mechanisms in the plasma. However, the **mechanism of the ionization** and reaction of sputtering species in the plasma is still not completely understood. Thus, we will study on the ion eaction mechanism of a low temperature plasma and carry out the following subjects;

(1) Mechanism of molecular ion production projects in glow discharges.

When Ar, Kr/CO_2 or a CH_4 mixture gas is used as the discharge gas, the molecular ion products are examined in detail with a high-resolution and sensitive mass spectrometry.

(2) Mechanism of ion production during laser irradiation.

The laser used is pulse ruby laser (wavelength: 0.69 μm, power: 1×10^9 W/cm^2). The metal and molecular ions produced when the laser beam irradiates the samples in an atmosphere of Ar, Kr/CO_2 or N_2 mixture gas, are examined in detail with sensitive mass spectrometry.

The results obtained are expected to be very valuable for the development of new chemical instrumentation.

50 Image Analysis of Metallurgical Structures with a Computer Network System

Apr. 1989~Mar. 1992

Fukamachi, M.

Materials Characterization Division

In order to carry out an accurate and rapid computer **image analysis** of metallurgical structures observed with the X-ray maps of **EPMA**, the feasibility of a local area **network system** of small computers has been studied. In the system, 5 computers are connected to share application programs, X-ray map data and data files among computers. X-ray maps data are processed to reduce the image noise, to correct the image distortion and to extract the factors necessary to evaluate the metallurgical structure. After the measurement and evaluation of X-ray map data, results are stored as a reference data file for future analysis.

The investigation has been carried out to find a suitable method for the utilization of the proposed system.

51 Damage Measurement by Electron Lithography and Mechanism of Damage Formation

Apr. 1988~Mar. 1991

Shinya, N.

Failure Physics Division

New electron lithographic techniques for micro-deformation measurements and a finite element computational model for creep deformation in polycrystalline solids have been developed.

In micro-deformation measurements, many kinds of orthogonal fiducial micro-grids with ion etched grooves or deposited metals were prepared on the creep specimens by **electron lithography**. Using these grids, grain boundary sliding and local strain distribution during creep in a pure coppper and a 321 stainless steel were measured. The grain boundary sliding in the copper has been found to give rise to textured regions of compressive longitudinal strain as well as strain concentrations in uniaxial tensile creep tests. Furthermore the surface crack formation in 321 stainless steel is controlled mainly by the direction and amount of the grain boundary sliding. The multi-grained finite element model, which can allow for variations in the grain boundary viscosity, explains these complexities of the strain distribution.

In an **electron Moiré method**, an application of lithographic technique to **micro-deformation** measurements, a fine microgrid prepared by electron lithography is used as a model grid and a exposure of an electron beam as a master grid of Moiré method. The scanning exposure of electron beam on the specimen with a model grid produces Moiré fringes of bright and dark lines formed by the different amounts of secondary electrons. The Moiré fringe pattern makes it possible to determine the distribution of strain and grain boundary displacement in a small area with high accuracy.

Related papers

" *Measurement of Grain Boundary Sliding and Observation of Surface Cracking Process during Creep by Microgrids for High Temperature Use* ", Kishimoto, S., Egashira, M. and Shinya, N.: J. Soc. Mater. Sci. Jpn., **39** (1990), 770–775 (in Japanese).

" *Effect of Grain Boundary Sliding on the Creep Micro-Deformation of Copper* ", Carolan, R. A., Egashira, M., Kishimoto, S. and Shinya, N.: Materials Trans. JIM, **32** (1991), 67–73.

" *Observation of Micro Deformation by a Moiré Method Using a Scanning Electron Microscope* ", Kishimoto, S., Egashira, M. and Shinya, N.: J. Soc. Mater. Sci. Jpn., **40** (1991), 637–641 (in Japanese).

52 Sensing and Analysis of Material Damage Formation Processes

Apr. 1991~Mar. 1994

Shinya, N.

Failure Physics Division

In this work, a sensing system for continuous damage monitoring and advanced analytic techniques of damage formation processes will be developed. The main

research programme is as follows.
(1) A surface treatment for the detection of local strain and micro cracks is being developed. For the detection a **piezo polymer film** will be deposited on the metal surface. The principle of this method is shown in Fig. 1.
(2) An **electron Moiré method** for measurement of micro-deformation, which has already been developed using an electron lithography and an electron beam scan, will be advanced to a highly sensitive technique with finer Moiré fringes by application of ion beam lithography. This method will make it possible to observe the micro-deformation, construct a strain contour map and to analyze the damage formation process.

53 Fundamental Study on Quantitative Non-Destructive Evaluation of Small Defects in Materials

Apr. 1989~Mar. 1991
Masuda, C.
Failure Physics Division

It is important of know the **reliability** of **advanced materials** to be applied for practical use. In particular, the detection and evaluation of **damage** or small **defects** in the materials is a key problem, which is highly demanded for the reliability. The main object in this study is to get fundamental information to develop a **non-destructive evaluation** method to detect and characterize small defects in the material with high accuracy.
Two types of approaches have been investigated in this work, which are ultrasonic and electro-magnetic non-destructive evaluation methods.
As for the study by ultrasonics, the major concern is the detection and evaluation of inner defects in metals and advanced materials such as ceramics and composites. The **ultrasonic non-destructive testing** approach has been theoretically examined by the **numerical simulation** method developed by ourselves, looking at the fundamental problems in the effect of the beam displacement affecting the detection precision and in the echo response from defect or damage produced in the material. An **acoustic microscopic approach** has also been attempted using SAM to study he mechanism of failure in composite materials.
As for the study by electro-magnetics, efforts have been made to detect and evaluate surface defects of the materials with high acculacy. **Magnetic flux leakage testing** method has been studied theoretically by using a dipole model, in one hand, and experimentally by using Hall element sensors for quantifying the dimension of defects, on the other hand. Material evaluation by **incremental permeability techniques** has also been studied successfully showing a possibility for steel classification.

Related papers
" *Numerical Simulation of Beam Displacement and Beam Path Distance Variation in Total Reflection in Ultrasonic Angle Beam Examination* ", Fukuhara, H.: Journal of JSNDI, **49** (1991), 13–19 (in Japanese).
" *Effect of Sensor Size on Results of Magnetic Flux Leakage Testing* ", Uetake, I., Ito, H and Saito, T.: to be published in Journal of JSNDI, **40** (1991), (in Japanese).
" *Effect of Several Factors on Evaluation of Damage for Metal-Matrix Composites Using SAM* , Tanaka, Y and Masuda, C.: to be published in Journal of SMSJ, (in Japanese).

54 Nondestructive Evaluation of Fracture Process for Metal Matrix Composites by X-Ray Computed Tomography Using Synchrotron Radiation

Arp. 1990~1991
Masuda, C.
Failure Physics Division

There are many tensile fracture mechanisms for long fiber reinforced composites. The fracture process is very important to analyze the strength of those composites during the tensile test. To analyze the fracture process of **metal matrix composites**, it is necessary to observe the **inner fibers, debonding** or cracks. There are some nondestructive testing mehtods to observe the inner defects, **inner cracks** of damage in the material such as computed tomography using ultrasonic or commercial X-ray scanners. However, the resolution power of these conventional methods is lower than the size of the defects and fractured inner fibers in composites. The **computer tomography** using **synchrotron radiation** has a high resolution making it possible to analyze the fracture of inner fibers or debondings between matrix and fibers in composites.
In this study, the fundamental observation conditions were discussed in order to detect the inner fiber or debonding parts in metal matrix composites. The inner reinforcement fibers, core carbon fibers or debonding parts could be clearly observed for B/Al, SiC/Al, SiC/AA6061 and SiC/Ti-6Al-4V alloy matrix composites and the resolution was about 10 μm in the energy range of X-rays of 20–30 keV. The specimen size was discussed in relation to the energy and monochrometers **3-dimensional images** for B/Al and SiC/Al composites. The size of the debonding parts could be quantitatively evaluated from the 3-dimensional image. Moreover, inner cracks could be detected in the SiC particual reinforced aluminium matrix composite after a fati-

gue test and inclusions containing C/C composites have also been observed.
In order to investigate the fracture process of the metal matrix composites during the tensile test, the tensile machine used in the computed tomography was fabricated.

55 In-Situ Observation of Fatigue Damage

Apr. 1989~Mar. 1992
Matsuoka S.
Environmental Performance Division

In order to clarify the **fatigue mechanism** of **metallic materials,** observation of slip markings, and fatigue and brittle fracture surfaces with the **scanning tunneling microscope** (STM), and the measurement of **exso-electrons** emission from the bare surface are being carried out.
The STM observation was done with a tunnel current of 1 nA and a tunnel bias of 25 mV in air. It was apparent from STM images of slip markings for seven pure metals: Au, Ag, Cu, Fe, Zn and Al and three kinds of engineering materials such as SB42 carbon steel, SUS304 stainless steel and Ti-6Al-4V titanium alloy that the slip interval and step were 2 and 0.2 μm, respectively. STM images of the fatigue fracture surface for Ti-6Al-4V titanium alloy and the brittle fracture surface for chromium and molybdenum had a fractal character (i.e. self-similarity) up to very high magnification where the scanning ranges of 40 nm in X and Y directions corresponded to about 150 atoms for the three metals mentioned. However, the fractal character is expected to break down when scanning range is below 20 nm.
The exso-electron emission from the bare surface, which is very sensitive to the material and its oxidation rate, was measured for eleven pure metals: Au, Pt, Ag, Cu, Ni, Fe, Cr, Ti, Al, Pb and Zn, and two ceramics of SiC and Si_3N_4 in air and vacuum (10^{-4} ~ 10^{-6} Torr). The amount of exso-electron decreased with decreasing water vapour pressure. This result explained the dependence of the fatigue life on the water vapour pressure.

56 In-Situ Scanning Tunneling Microscopy of Metal/Liquid Interfaces

Apr. 1990~Mar. 1991
Matsuoka, S.
Environmental Performance Division

The **scanning tunneling microscope** (STM) can be used not only in vacuum but also in air and in aqueous solutions. So far, there has been no device which can detect nano-meter size surface morphology changes by **electrochemical reactions**. Therefore, study on electrochemical reactions with STM has become popular. However, few studies using STM have been carried out on the corrosion behavior of **metallic materials**.
In this study, the corrosion behavior of pure iron, SNCM439 low alloy steel and SUS304 stainless steel in 1% NaCl and 0.1% HNO_3 aqueous solutions was studied with STM. In-Situ STM observation for all steels used was possible at anodic and cathodic potentials in two kinds of aqueous solution. In addition, the local and average corrosion rates for the pure iron and the low alloy steel could be obtained by the subtraction of two STM images. The average corrosion rate obtained was corresponded with the corrosion rate calculated from Faraday's conversion of the anode current density, while the local corrosion rate was more than 3 times higher than the local calculated one. From these results, it is concluded that the local corrosion behavior can be studied accurately with STM.

57 Quantitative Evaluation of Fracture at High Strain Rate and Low Temperature in Ferritic Steels

Apr. 1989~Mar. 1992
Yasunaka, T.
Environmental Performance Division

Ferritic steels are embrittled at low temperature. At higher strain rates the embrittlement occurs at higher temperatures. For the integrity of structures such as containers of nuclear spent fuel, it is important to evaluate fracture quantitatively on the basis of fracture mechanics. The objective of this study is to clarify the effect of temperature and strain rate on fracture toughness and to attempt to predict the onset of embrittlement from the fundamental viewpoint of plastic deformation.
For the measurement of **dynamic elastic-plastic fracture toughness**, a drop-weight type tensile testing machine has been designed and built. Using 25mm-thick compact tension specimens, a measuring method of fracture toughness has been established. An ultrasonic method is applied for detecting the onset of crack propagation. The materials used are **carbon steel** and **nodular cast iron**.
In the ductile fracture region, it has been found that the dynamic and static fracture toughness of nodular cast iron increases with decreasing temperature. However, in this region a fracture toughness parameter can be proposed as a material constant, and the material can be evaluated by using of this parameter. In view of plastic deformation, the onset of embrittlement is responsible for the change in the behavior of plastic deformation. The occurrence of

deformation twins in the microscopic region is noticed. The **low temperature embrittlement** of the materials is expected to be evaluated quantitatively.

Related paper

" *Determination of Dynamic Elastic-Plastic Fracture Toughness by a Drop-Weight Impact Testing Machine* ", Yasunaka T., Nakano K. and Saito T.: ISIJ International, **31** (1991), 298–303.

58 Application of AC-Impedance Technique for Environmentally Assisted Cracking of Low Alloy Steels in High Temperature Water

Apr. 1990~Mar. 1991

Katada, Y.

5th Research Group

A study on the mechanism of **environmentally assisted cracking** (EAC) of low alloy pressure vessel steels in high temperature water is in progress by applying an **AC-impedance technique**.

Materials used are two kinds of low alloy pressure vessel steels (A533B cl.1): low sulfur material (S=0.004wt%) and medium sulfur material (S=0.014 wt%). The specimen used in this work is a WOL (Wedge Opening Loading) type specimen of 35 mm width and 6.25 mm thickness. Tests are conducted under constant displacement conditions by using a wedge mounted into the notch of the specimen. The specimen is installed in an autoclave filled with high temperature water simulating a light water reactor environment of 561K and 8MPa in pressure. An external reference electrode of Ag/AgCl is used, of which the capillary tube is mounted in the center hole machined in the specimen in order to measure the corrosion potential in the crack tip. The frequency range of the FRA (Frequency Response Analyzer) is 0.1 mHz—100 kHz. Equivalent electric circuits of the relevant cell obtained from Bode-diagrams and Nyquist-diagrams are discussed to determine the **corrosion rate** during crack growth. Crack length is monitored intermittently in ambient air.

The corrosion rates of the two materials, as determined from the electrochemical measurements by using the AC-Impedance method, are indispensable for modeling of EAC of the materials in high temperature water.

59 International Joint Research on Evaluation and Standardization of Advanced Materials

Apr. 1989~Mar. 1992

Maeda, H.

1st Research Group

NRIM has participated in the studies on the establishment of standard measurement methods in several technical working areas (TWA) of **VAMAS**, such as **superconducting materials, cryogenic structural materials, surface chemical analysis, mechanical properties at high temperature** and inter-operability between **materials databases**, and has been acting as the central laboratory in the TWA of superconducting and cryogenic structural materials. When these programs are completed, useful recommendations for standard measurement methods will be presented.

For superconducting materials, the 1st round robin tests were carried out to identify problems in the measurements of **critical current** (I_c) using Nb_3Sn multifiamentary wires and ac losses using NbTi multifilamentary wires. The 2nd round robin tests, which are so designed as to specify the measuring conditions as detailed as possible, are currently in progress. Preliminary results of the 2nd tests concerning the I_c have shown that the scatter in data among laboratories is substantially reduced, revealing the importance of the strain related measuring conditions.

Highly reliable and precise evaluation of mechanical properties at liquid He temperature is a key to develop and provide high quality engineering materials used for superconducting and cryogenic systems. The 2nd round robin tests concerning **tensile properties** and **fracture toughness** are being undertaken using SUS316LN steel and Ti-5Al-2.5Sn alloy. In this program, the tests are done in accordance with the drafts for cryogenic test standards (submitted to the ASTM) which contains the reseults of the 1st round robin tests. Strain gauge calibration tests at cryogenic temperatures are also performed concurrently.

To improve the reliability of surface analytical techniques, we have carried out **AES** and **XPS** round robin tests using Au-Cu alloys and Co-Ni alloys. The errors in the measured surface concentrations of these alloys were examined. In the case of AES, the error lies between 3% and 10%, while in the case of XPS, it lies between 2% and 6%. From these experiments, we have also recognized that the reproducibility of the intensity of simple spectra among laboratories is abysmally poor. To increase the reliability of these surface analytical techniques, and also to use the spectrum data mutually, we have started to construct a system, in which spectra taken by different machines are interpreted.

For mechanical properties at high temperature, the 2nd round robin tests of **creep crack growth** were carried out on IN100 superalloy, brittle material, at 1005K. The creep crack growth rate for IN100 superalloy, which was evaluated using the non-linear fracture mechanics parameter C^*, was higher

than that of 1Cr-Mo-V steel, ductile material, which was examined in the 1st round robin tests.
Although demands for building and use of computerized materials databases are rapidly growing, the sharing of materials data in the global community is very limited because of the difference in languages, computer systems, implementation techniques, etc. Specifically, we work on issues related to the pre-standardization aspects of such topics as metadata, data evaluation models and data exchange of materials properties via international communication networks. So far we constructed inter-laboratory comparison of data evaluation methods commonly used in computerized materials systems. Also interesting is to establish the concept of MDIF (Mateials Data Interchange Format) which can be used as an inter-laboratory data exchange system.

Related papers

" *VAMAS Intercomparison of ac Loss Measurement: Japanese Results* ", Itoh, H., Wada, H., Ando, T., Yoneda, E., Ito, D., Iwakuma, M., Yamafuji, K., Nagata, A., Watanabe, K., Kubota, Y., Ogasawara, T., Akita, S., Umeda, M., Kimura, Y., and Tachikawa, K.: Advances in Cryog. Engineer. Mater., **36** (1990), 199–206.
" *VAMAS Interlaboratory Fracture Toughness Test at Liquid Helium Temperature* ", Ogata, T., Nagai, K., Ishikawa, K., Shibata, K. and Fukushima, E.: Advaces in Cryog. Engineer. Mater. **36** (1990), 1053–1060.
" *The Reliability of Quantitative Analysis with AES* ", Yoshiwara, K. and Shimizu, R.: Surf. Interf. Anal., **16** (1990), 140–143.
" *VAMAS International Joint Researcvh on Testing Method and Evaluation of Creep Crack Growth* ", Yokobori, T., Tanaka, C., Yagi, K., Kitagawa, M., Fuji, A., Tabuchi, M. and Yokobori, T., J. Iron and Steel Inst. Jpn., **76** (1990), 503–514 (in Japanese).
" *Significance of Data Evaluation Models in Materials Databases* ", Nishijima, S., Monma, Y., Kanazawa, K.: VAMAS Technical Report No. 6, Oct. 1990.

[60] Elemental Analysis in Response to Development of New Metallic Materials

Apr. 1988~Mar. 1991
Okochi, H.
Director of Special Research

A study on elemental analysis has been carried out. This study is connected with the study on the development and purification of new metallic materials. A part of the results is described.
In inductively coupled plasma-atomic emission spectrometry (**ICP-AES**), the following results were obtained; Hydride-forming elements in Mo were determined. Impurities in Mo and molybdenum trioxide were determined. Boron in iron disilicide and high-purity iron was determined after anion exchange chromatography. Rare earth elements (REEs) in Y, La, Gd and Yb were determined using an échelle spectrometer.
In graphite furnace atomic absorption spectrometry (**GFAAS**), the following results were obtained; Indium and Cd in Ni-base heat-resisting alloys were determined. Arsenic and Al in iron and steel were determined. Trace elements having a higher vapor pressure than iron and steel were determined using concentrated solutions. Lead, Mn and Co, which have different melting points and boiling points from those of Mo and Zr matrices, were determined. Sodium and K in Ta were determined. Trace elements in Mo, molybdenum disillicide, vanadium pentoxide and vanadium disilicide were determined after ion exchange separation.
In X-ray fluorescence analysis (**XRF**), Ti-alloys and Ni-base heat-resisting alloys were analyzed using the fundamental parameter method. Oxide superconductors and Ti-alloys were analyzed using the glass bead technique and the theoretical alpha coefficient method.
Ultra trace REEs in metallic La, Pr, Nd, Gd and Tb were determined by glow discharge mass spectrometry (**GDMS**).
Traces of Si in Nb, Ta, V and Zr were determined by spectrophotometry after distillation.
A method to decrease the background signal was applied to the determination of low ppm levels of O in high-purity iron.

Related papers

" *Simultaneous Determination of Arsenic, Bismuth, Antimony, Selenium and Tellurium in Molybdenum by Continuous Hydride Generation and Inductively Coupled Plasma-Atomic Emission Spectrometry* ", Kujirai, O., Kohri, M., Yamada, K. and Okochi, H.: Anal. Sci., **6** (1990), 379–383.
" *Determination of Rare Earth Elements in Y, La, Gd and Yb with an Échelle-type ICP Spectrometer* ", Nakamura, Y., Takahashi, K., Kujirai, O. and Okochi, H.: J. Anal. At. Spectrom., **5** (1990), 501–508.
" *Determination of Trace Amounts of Indium in Nickel-base Heat-resisting Alloys by Graphite Furnace Atomic Absorption Spectrometry* ", Kobayashi, T. and Okochi, H.: J. Japan Inst. Metals, **53** (1989), 1123–1128 (in Japanese).

(61) Chemical Analysis of Organotin in Marine Environmental Samples

Apr. 1991~Mar. 1996
Okochi, H.
Director of Special Research

In recent years, there has been growing interest in the analysis and speciation of tin derivatives in the environemnt. **Organotin** compounds have been widely used for a variety of commercial applications such as plastic stabilizers, biocides and fungicides. These compounds with short alkyl chains generally exhibit

considerable toxicity toward both aquatic organism and mammals.

The purpose of this study is to establish an ultra-trace determination method of organotin in marine environmental samples such as **sea water, sediment** and biological samples. In this method, an on-line flow system will be developed for high sensitive and precision determination of nanogram or subnanogram amounts of tin. The kinds of tin compounds under investigation are triphenyltin (TPT), diphenyltin (DPT), monophenyltin (MPT), tributyltin (TBT), dibutyltin (DBT), monobutyltin (MBT) and inorganic tin. At first, a comparative study will be performed in order to determine the total amount of tin as accurately and precisely as we can with atomic absorption spectrometry (AAS), inductively coupled plasm atomic emission spectrometry (ICP-AES) and ICP mass sepctrometry (CIP-MS). For sensitive determination, the hydride generation technique will be applied for these three determination methods and graphite furnace (GF)-AAS will also be studied. The optimum analytical conditions will be established for each determination method and then accuracy, sensitivity and detection limits will be compared among them. The established method will be applied for the determination of total tin in various marine environmental samples which will be obtained from the Tokyo bay and the deep see near Japan by (Sinkai 2000) or (Sinkai 6500) which belong to Japan Marine Science and Technology Center.

62 Database Development in Assistance of New Superconducting Materials Research

Apr. 1988~Mar. 1993

Nishijima, S.
Failure Physics Division

A flood of research information is appearing each month in journals related to new **high Tc superconducting materials**. It is generally thought that a numerical **database** on these superconductors is necessary especially for materials research and development. Pioneer work has already been done by Asada, Y. of NRIM, who collected data from published documents and constructed a compact database known today as SUPERCON. Although it is still ongoing, one of the outputs from this database is displayed below.

Looking for **empirical relations** between parameters for superconducting materials of type $YBa_2Cu_3O_z$, it was found that the lattice constants, L(a, b, c), the critical transition temperature, T_c, and the **oxygen content**, z, are to some extent related with some relations. A linear relation is existing between L and z with a high coefficient of correlaton, where the c-z relation is utmost significant. The orthorhombic distortion, p = b − a, is a good index for structural transformation which could be correlated to the variation of Tc with decrease of z. The values of z, where the phase transition takes place, are discussed in the refferred papers. These papers revealed that a drastic change of Tc is observed at z_1 = 6.75 and z_2 = 6.50 due to the **structural change**. It is proposed that Tc be related to p rather than to z.

Related papers

" *Dependence of Lattice Constants and T_c on the Oxygen Content z in $YBa_2Cu_3O_z$ from Database* ", Asada, Y., Nakada, E., Miyazaki, A., and Yokokawa, T.: J. Japan Inst. Metals, **5** (1991) 105–109 (in Japanese).

" *A Review of the Size of the Energy Gap in Superconducting Oxides* ", Hirata, T., and Asada, Y.: J. Superconductivity, **4** (1991) 171–177.

63 Database Systems for R&D of Superconducting Materials

Apr. 1989~Mar. 1992

Nishijima, S.
Failure Physics Division

As one of the coordinated research programs of the Science and Technology Agency, this project aims at the development of factual **database** systems on the **new oxide superconducting materials**, so as to assist researchers with more ordered information. It is however not simple to build a database for those superconductors which sometimes reveal high critical temperatures while the mechanism is so far not clear enough; there are still some problems to be solved such as poor reproducibility of samples, diverse definitions, and evaluation practices of properties.

This work attempts firstly to establish **common procedures for sample preparation** and **property evaluation** by comparing the data from multiple measurements at different laboratories for the same materials made in different factories. A prototype database is developed at the same time by using the acquired data as first inputs and taking consideration of the influencing parameters to be included in the data items to record (**metadata**). There are 33 participants from 28 industrial, university and national laboratories, where NRIM takes part in the development itself of the database and in the coordination of all the group tasks, as well.

The materials selected for the first runs were $YBa_2Cu_3O_z$ bulk, Ag-sheathed tapes, and thin films as well, prepared by ordinary processes with varying z as 6.9, 6.6 and 6.4. Various basic properties have been characterized in each laboratory, and the data have been collected, analyzed

and evaluated, so that the problems in experimental and analytical procedures are being reviewed and the metadata improved. All **primary experimental results** are compiled with detailed procedural descriptions, which will further be used for analyses and deduction of characteristic values and thus for editing a database useful in R&D of superconducting materials.

Simulation and theory

64 Research on a Knowledge Base for Computer-Aided Chemical Substance Design

Apr. 1986~Mar. 1991
Yamazaki M.
Materials Design Division

In recent years, **computer utilization** for developing new materials, including application of **artificial intelligence**, has advanced significantly. In the domain of metals and alloys one can never find two species of equal internal structure even if the chemical composition and outer shape are the same which means that one can not specify the object exactly in the database of materials properties. The problem which we should solve first is "What type of system is the most useful for the development of materials?" The answer which the system can offer inevitably contains fuzziness to some extent.
In the study, the following two systems have been developed so as to make clear the line of reasoning or the way of using knowledge in the development of alloys:
(1) **Consultation system** on **knowledge** of **Ni-base superalloys**
(2) Consultation system for alloy design of **Ti alloys**
Another line of study has been pursued in which knowledge included in the research articles is collected and stored in the computer, and responding to the queries of users, the system shows related knowledge.
Specifications of the system are briefly described in the following.
(1) Knowledge is composed of information obtained primarily from reports of experimental work on Ni-base superalloys. Stored data are as follows.
bibliography (title, author, affiliation, journal)
alloy being studied
experimental procedures
experimental results
conclusions
(2) Interactions between computer and human user are done in the **natural language** (Japanese).
(3) Queries which the computer accept can be classified into the following six types.
* Request for explanation or retrieval of a concept or a matter
* Request for the explanation of methods, procedures and conditions
* Questions on the cause of some effect
* Ask for the results of certain procedures
* Ask for the objects affected by specific procedures
* Ask if a certain proposition is true or not
(4) Experimental results, comments on observations or conclusions of the research are stored in a form of frame, in which each fact is expressed by a combination of four descriptions: object, attribute, value and condition. Text for interactions between man and machine is stored separately from the factual data above.
(5) In order to facilitate the future expansion of the system, editing tools for knowledge, technical terms and grammar have been prepared.
Figure shows schematically the construction of the system. The first version of the system was built on a personal computer using LISP. This system was too complex for a PC. Consequently, the system has been converted so as to work on EWS as well as to be implemented by expert shell to increase flexibility of inference.

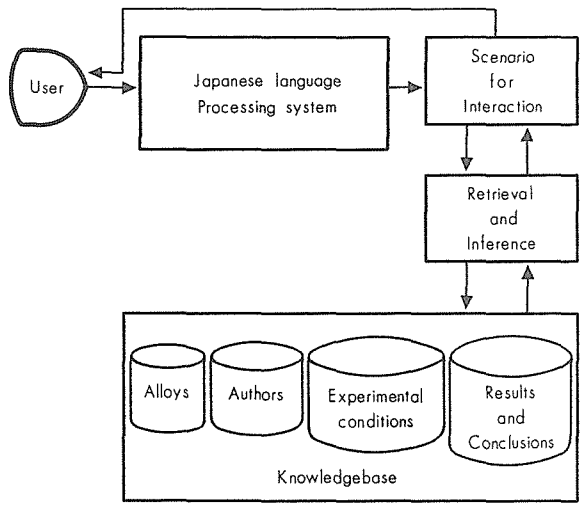

Figure Construction of the system.

65 Study on the Acquisition and Systematization of Knowledge for Materials Design

Apr. 1988~Mar. 1991
Hoshimoto, K.
Materials Design Division

The objective of the study is to investigate fundamental procedures to acquire knowledge from **factual data** of materials, as well as to establish the way to apply the **knowledge** to the field of **materials design**. The study has been performed principally on the application of **statistical methods** to acquire knowledge on alloy design. Methods of treating graphical data have also been

studied because the use of images and diagrams is very important in the expression of materials data. Experimental data on mechanical properties of **Ti alloys** which were obtained from handbooks or scientific reports were analyzed by means of the **multi-variate statistical analysis** method, with the aim of obtaining a quantitative relationship, which can be used for the alloy design. From the principal component analysis, it was found that the following three properties, namely the strength, the ductility and the toughness, are sufficiently representative for the seven mechanical properties. This reduction much simplifies the process of design. Multiple regression analysis was followed by the construction of a diagram showing the relation between the three representative mechanical properties and the factors dominating the properties of the alloys, and this clarified the direction in which the properties of the alloy should be improved.

Sensory tests followed by the analysis using a **multi-dimensional scaling method** have been adopted for the investigation of the relation between micrographic data of structure and fracture surface. The results have shown that the procedure should possibly be applied to the automatic recognition of microstructure by the computer.

As part of the scheme of optimization of the structure of the materials database, the most efficient way to computerize **binary phase diagrams** obtained from literature has been studied. A prototype system including graphical data files, attribute data files and physical properties data files together with the linkage files connecting all of the data files allows to obtain information such as solubility limit, ratio of quantities of existing phases, etc...., together with name of each phase and kind of reaction involved.

(66) Study on the Computer Aided Design Tools for the Development of Materials

Apr. 1991~Mar. 1994

Hoshimoto, K.

Materials Design Division

The objective of the study is to develop fundamental tools used for the **computer aided development of materials.** The following three subjects are studied:

(1) Development of **statistical tools** for **materials design**. Analysis of graphical data by the application of **multi-dimensional scaling procedures.** The results should be applied further to the automatic recognition of the **graphical data** in the materials design works.

(2) Optimization of the implementation of **materials data**

The optimum structure of a **database** for use in the work of materials design is investigated. A variety of media for the representation of materials data as well as the way of expression should be analyzed and optimized in order to establish the most effective linkage between them.

(3) Organization of **knowledge** on materials and its application to materials design

Investigation on the best way of expression and organization of knowledge on the materials and its application to materials design is under way.

67 Development of Knowledge Based System for Materials Life Prediction

Apr. 1988~Mar. 1993

Nagata, N.

5th Research Group

The safety and reliability of machinery and components are closely related to the technology of **materials life prediction**. We are planning to build an intergrated system for the advanced materials life prediction, by combining the factual **database** on materials strength data and the knowledge base on our scientific and empirical understanding of materials deformation and fracture processes.

This research program has been carried out firstly in the three separate fields of creep, fatigue and corrosion strength, respectively and the different factual databases for each field have been built by using the engineering workstations (EWS), which are connected with each other through a network communication system. Then, the advanced-integrated database management system, named as DIMS (Dialogical Integrated system for Material Strength database) was newly developed. This system can analyze the desired data set extracted from the database and find the combinations among characterized items of materials, not to mention the managing capability of the database. By using the DIMS, which works in a UNIX environment with the X-Windows system, many possible combinations among the characterized items of materials are being searched for and through these combinations the significant paths from the characterized properties to the materials life are also being found, which may result in the empirical mathematical models for materials life prediction. These empirical models will be added to the existing empirical knowledge and the **knowledge based system** for materials life prediction will be newly developed.

Related paper

" *Computer Simulation of High-temperature Deformation Behavior of Austenitic Stainless Steel* ", Takeuchi, T., Monma, Y. and Sakamoto, M.: J. Iron and Steel Inst. Jpn., **3** (1991), 140–147 (in Japanese).

68 Prediction of Materials Strength and Endurance under Irradiation Using Ion Beam

Apr. 1988~Mar. 1993
Nagakawa, J.
2nd Research Group

Irradiation creep is one of the most important radiation damage problems which **fusion reactor** materials must confront under high energy neutron flux and stress. Mechanisms for irradiation creep have been under active investigation for the last two decades and a number of theoretical models have been proposed. When a material is irradiated under stress, not a single but several kinds of irradiation creep mechanisms are competing for the freely migrating point defets and simulataneously contributing to the creep deformation, with or without a prevailing mechanism.
In the present study, four major mechanisms, i.e. SIPN, SIPA by dislocation loops, PA, and PAG, are taken into account and simultaneous rate equations are solved numerically to evaluate the creep deformation by each competing mechanism. This study is the first one to apply the rate theory directly to irradiation creep problems.
The major results obtained from the present simulation study for a stainless steel are as follows;
(1) Very significant transient deformation is expected at lower temperatures particularly in the annealed materials, in which grown-in network dislocations are low in density.
(2) Steady-state creep rates after the aforementioned transient shows excellent agreement with the reported experimental results, indicating that the loop nucleation process (SIPN) and the network dislocation climb (PA) are the prevailing mechanisms in the annealed and the cold-worked materials, respectivley.
The former result is of particular importance for the International Thermonuclear Experimental Reactor (ITER) in which the materials are bombarded at low temperature (60–300°C) to a rather low fluence (in other words, rather short duration).

Related papers
Nagakawa, J., yamamoto, N. and Shiraishi, H.: J. Nucl. Mater., **179–181** (1991) 986–989.

Materials

Non-ferrous material

(69) Study on Changing the Properties of Metallic-Oxide Films for Increasing the Hydrogen Permeabilities

Apr. 1991~ Mar. 1994
Amano, M.
Physical Properties Division

It is well known that **oxide films** on metals and alloys impede **hydrogen penetration**. However, a systematic investigation on the impediment mechanism of hydrogen penetration in oxide films has not been reported yet. The aim of this study is to change the properties of oxide films on the Va metals and alloys in order to increase the hydrogen permeability. We apply a reaction method for changing the composition and the structure of the oxide films. Various metal films are deposited on the membranes of the Va metals and alloys by using physical vapour deposition and the membranes are subsequently heat-treated in order to make the oxide films and deposited overlayers react with each other. The hydrogen permeability in the prepared membranes are determined by a gas permeation method. The characterization of the oxide films after the reaction method is performed by making use of AES, SEM and X-ray analysis.

70 Basic Research to Establish Design Techniques for Advanced Materials

Apr. 1989~Mar. 1994
Yamazaki, M.
Materials Design Division

Development of advanced materials is indispensable for progress of technology in 21st century. Advanced material design systems should be established to predict structures and properties, using stored knowledge on alloy design, materials physics on atomic and molecular level, and computer science. This research consists of three items. Their interrelationship is shown in Figure.
The structure design sub-system is used to predict structures from compositions and processes, and the property design sub-system is used to estimate properties from the compsitional and structural parameters. These two sub-systems are not mutulally independent. Therefore, establishment of these sub-systems is carried out for each material, such as Ni-base superalloy, titanium alloy, and C/C-composite. In Ni-base superalloys, the characteristics of the γ/γ' **phase equilibrium** were analyzed by the **cluster variation method** with the Lennard-Jones potential and the accuracy of phase calculation equation of the program was improved. In multi-component titanium alloys, α - β and α - α_2

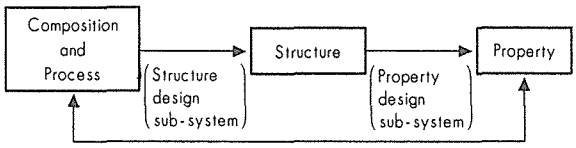

Figure Advanced materials design systems

phase equilibria were analyzed by **thermodynamic calculation methods**. This calculation also improved the accuracy of the estimation of the characteristics of phase equilibrium. Alloy design programs having these new phase equilibrium calculation equations are being successfully applied to the development of high specific-strength Ni-base single crystal superalloys and α - α_2 high temperature titanium alloys. In C/C-composites, high temperature oxidation behavior is investigated with a reaction rate theory in order to establish the properties design sub-system. In the expert system, we added an algorithm for rebuilding γ/γ' phase equilibrium calculation equations automatically when analyzed compositional data are added; this is based on some new information theory.

Related papers

" *Analysis of* γ/γ' Equilibrium in Ni-Al-X Alloys by the Cluster Variation Method with Lennard-Jones Potential ", Enomoto, M. and Harada. H.: Metall. Trans. A, **20A** (1989), 649–664.

" *A Thermodynamic Analysis of the* α *and* β Phases in the Ti-O system ", Onodera, H. and Yokokawa, T.: Scr. Metall., **24** (1990), 1119–1123.

Intermetallic compounds

71 Advanced Intermetallic Compounds for Nuclear Reactors

Apr. 1987~Mar. 1992

Hirano, T.

Chemical Processing Division

The objective of this study is to develop intermetallic compounds for advanced nuclear reactors, focusing on **transition metal silicides** and **aluminides**. These compounds are expected to have attractive high-temperature mechanical properties. However, these attractive properties are hard to obtain becuase it is very difficult to fabricate good samples. Our major efforts are in the field of **single-crystal growth**, characterization of crystal sturctures, and measurement of physical and **mechanical properties**, of these compounds. The effect of irradiation on the mechanical properties is also examined. The experimental equipment in use consists of a floating zone furnace with infrared heating, an X-ray diffractometer, a cyclotron irradiation facility, and mechanical testing equipment.

Single crystals of several transition metal disilicides, from group IVa through group VIII metal disilicides, have been successfully grown by a floating zone method. Temperature and crystallographic dependencies of their electrical properties have been investigated. Elastic constants of these compounds have also been measured. The high strength of $MoSi_2$ and WSi_2 at high temperatures revealed that these compounds have also been measured. The high strength of $MoSi_2$ and WSi_2 at high temperatures revealed that these compounds are attractive materials for high-temperature applications. Unidirectional solidification by a floating zone method brought a remarkable improvement in the room-temperature ductility of Ni_3Al without addition of ductility enhancing elements such as boron. The solidification structure was columnar along the growth direction, showing a large tensile elongation both parallel (more than 60%) and perpendicular to the growth direction (more than 20%).

Related papers

" *Electrical Resistivities of Single-Crystalline Transition-Metal Disilicides* ", Hirano, T. and Kaise, M.: J. Appl. Phys., **68** (1990), 627–633.

" *High Temperature Deformation Behavior of* $MoSi_2$ *and* WSi_2 *Single Crystals* ", Kimura, K., Nakamura, M., an dHirano, T.: J. Mater. Sci., **25** (1990), 2487–2492.

" *Tensile Ductility of Stoichiometric* Ni_3Al *Grown by Unidirectional Solidification* ", Hirano, T.: Scripta Metall. et Mater **25** (1991), 1747–1750

72 Developments of SOx and NOx Sensor Using Solid Electrolyte

Apr. 1988~Mar. 1991

Nakamura, H.

Chemical Processing Division

Detection of atmospheric pollutants SOx and NOx using the **solid electrolyte** sensor was studied. After investigations on candidate compounds and synthesis methods, amorphous materials consisting of oxides and sulfates (M_2O-B_2O_2-M_2SO_4, M=Li, Na, K) were synthesized by a rapid quenching mehtod. The matrials produced have high **electrical conductivities** (σ) of over 10^{-3} ($s \cdot cm^{-1}$), enough for the solid electrolyte, and were recognized to be ionic conductors by polarization measurements. It was found that the glass - forming composition range on ternaly phase diagram of the systems M_2O-B_2O_3-M_2SO_4 (M=Li, Na, K) increased in the order, K, Na Li.

The equilibrium electromotive force (E. M. F.) of the concentration-type **SOx sensor** constructed from K_2O-B_2O_3-K_2SO_4 and Li_2O-B_2O_3-Li_2SO_4 solid electrolytes was measured in the SO_2 concentration range of 0.2~1000 ppm (SO_2/O_2). The gradients of the obtained straight lines between measured E.M.F.s and temperature of the sensor for lower SOx

concentration were in agreement with those of the sensor for lower SOx concentration were in agreement with those of the theoretical ones calculated based on the thermodynamic values under the condition that the SO_2 content is over 0.5 ppm, and meausred values showed good reproducibility.
On the other hand, the measured E.M.F values of the sensor for higher SOx content were in good agreement with the theoretical ones in the SO_2 concentration range of 10~1000 ppm. It was confirmed from these results that the ionic transference number is unity. Furthermore the response to a rapid change in SO_2 content was good and the response time was within one minute.
These experimental results reveal that the materials used in this study are very appropriate solid electrolytes for the SOx sensor. For the **NOx sensor**, $CsNO_3$-$NaNO_3$ and $Ca(NO_3)_2$-$NaNO_3$ samples were synthesized under pressurized atmosphere. These two types of material show a high electrical conductivity of over 10^{-3} ($S \cdot cm^{-1}$), being also promising as solid electrolytes for the NOx sensor.

73 Preparation of Spontaneous Exothermic Metals and Its Application

Apr. 1990~Mar. 1993
Fujii, T.
Chemical Processing Division

Bulk materials showing spontaneous generation of heat under atmospheric conditions have been developed. The materials consist of intermetallic **compounds** of Al and/or Mg with transition metal atoms like Ni, and high densities of vacant sites of Al and/or Mg. We call these materaisl "Spontaneous **Exothermic Metals**".
In this study, Ni-Al alloys with a composition of 40–57.5 wt%Ni-Al were prepared by a self-propagating high-temperature synthesis (SHS) method under a vacuum of 1×10^{-3} Pa for the purpose of refinement of microstructure. These alloys are subsequently developed to dissolve Al in an alkaline aqueous solution kept at about 373K. The measurement of the exothermic behavior was conducted with a specially designed thermoblance. The results obtained at the present stage are summarized as follows:
(1) The alloys produced by SHS were almost all composed of two or three kinds of intermetallic compounds with $NiAl_3$, Ni_2Al_3 and Ni_xAl_y phases.
(2) After developed, X-ray diffraction patterns showed all intermetallic compounds with a large line broadining, indicating the **skelton structure**.
(3) The produced compounds exhibited a stable spontaneous exothermic reaction in air atmosphere and maximum spontaneous exothermic temperatures were 878K to 1013K depending on the amounts of Ni.
(4) On the developed surface of the Ni_2Al_3 phase, the particles consisting of NiO and Ni_2O_3 smaller than 10nm in diameter are presented much more frequently after spontaneous exothermic reaction.

74 Effect of Slip Modes on Fatigue Damage in TiAl Intermetallic Compounds

Apr. 1988~Mar. 1991
Yamaguchi, K.
Failure Physics Division

The **TiAl intermetallic compounds** has a potential for high temperature structural applications due to its low densiy, high strengh and good oxidation resisance. In this study its **fatigue properties** and **damage mechanism** were examined as a low ductility meterial and a high ductility material at room temperature and at 800°C, respectively.
One of the materials used is a fully-annealed Ti-34.7Al-1.74V (wt.%). The fatigue testing data are given in Figure. It shows a good fatigue resistance, especially at 800°C as compared with an engineering heat resistant material, NCF 800 (Alloy 800). The fracture surface examined at room temperature showed a mixture of three fracture modes: crystallographic fracture with linear steps, intergranular fracture with smooth facets of grain boundaries and transgranular cleavage fracture with river patterns. The fatigue cracks were found to be initiated by several mechanisms including slip-off steps or crackng under stress concentrations due to coarse slip and/or double **slip lines**.
The fracture mode at 800°C also consited of the same three types, but the initiation was found to be controlled by gran boundary cracking, with striped patterns on the facets, under stress concentrations due to large **twin-deformations** across the grains.

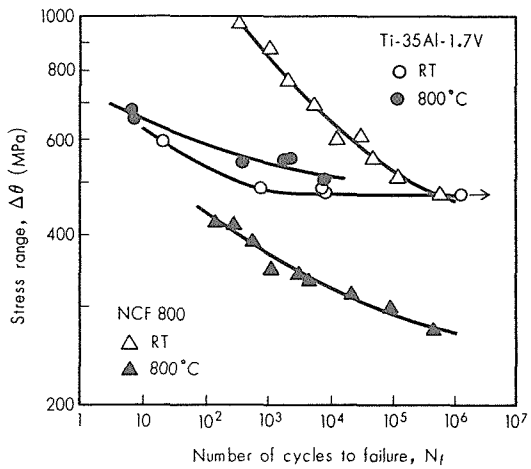

Figure Relationship between stress range and cycles to failure.

Related paper

" *Fatgue Properties and its Mechanisms of TiAl-V Intermetallic Compounds* ", Yamaguchi, K., Shimodaira, M. and Nishijima, S.: submitted to J. Iron and Steel Inst. Jpn, (in Japanese).

⑮ Fatigue Fracture Mechanisms for TiAl Intermetallic Compounds at High Temperatures

Apr. 1991~Mar. 1994
Yamaguchi, K.
Failure Physics Division

The properties of low fracture ductility **TiAl intermetallic compounds** at room temprature have been improved by addiition of third elements such as Mn or V, the composition control between Ti and Al, and thermal mechanical treatments to conrol the structure. The TiAl intermetallic compound, therefore, has been recognized as a new heat resistant material for applications in parts of aircraft or automobile engines, due to low density, high strength and good oxidation resistance. In order to promote the applications making a good use of the attractive and unique high temperature properties, it is necessary to know the dynamic behavior with regard to **fatigue crack growth, fracture toughness** and **thermal fatigue** as well as the static one. In this study it is planned to investigate the dynamic properties and the fracture mechanisms for next three years.

76 Production and Character Evaluation of Functional Intermetallic Compounds

Apr. 1988~Mar. 1993
Tsujimoto, T.
3rd Research Group

Contents of the research:
Characteristics of intermetallic compounds and controlling methods have been studied in order to develop new functional materials utilizing peculiar and excellent properties which conventional metals and alloys are not endowed with. Production, evaluation of characteristics and utilizing techniques of these materials have also been studied.
Sub-themes:
(1) Intermetallic Compound **Coatings** for High Temperature Corrosion Resistance
(2) Development of High Performance **Thermoelectric** Intermetallic Compound
(3) **Combustion Synthesis** of Intermetallic Compounds
(4) Development of **Light Heat-resisting Materials** Based on Intermetallic Compound TiAl

Related papers

" *Structure and Properties of Ni-TiC Cermet Films Formed by Ion Plating* ", Ishida, K., Ogawa, K., Kimura, T. and Takei, A.: Thin Solid Films, **191** (1990), 69–76.

" *Studies on the Holes of p-type* $Bi_2Te_{2.85}Se_{0.15}$ *Single Crystal* ", Kaibe, H. T., Sakata, M. and Nishida, I. A.: J. Phys. Chem. Solid, **51** (1990), 1083–1087.

" *Superplasticity of TiAl Intermetallics* ", Nobuki, M. and Tsujimoto, T.: "Advanced Structural Materials", Vol 2, ed. by Han, Y., Amsterdam, Elsevier Science Publishers B.V., (1991), 791–796.

Composites

77 Thermal Effects on the Material with Heterogeneous Phase

Apr. 1990~Mar. 1993
Shiota, I.
Physical Properties Division

Metal matrix composites (**MMC**s) consisting of **heterogeneous phases** are promising materials for applications in high temperature fields such as aerospace and atomic reactors, where materials of high specific strength, high specific modulus and high heat resistivity are required. MMCs are not thermodynamically stable, and the deterioration is often caused by chemical reaction at the interface between reinforcements and the matrix when they are exposed at elevated temperatures. The improvement of the **thermal stability** of MMCs is, therefore, the most essential for applications to high temperature field.
This work has been carried out to clarify the mechanism of the chemical reaction at the interface in MMCs. SiC/Ti (alloy) composites with 40%V_f were fabricated by hot-pressing. The reinforcement was continuous filament of SiC with C core which was produced by CVD. Some of the Ti matrices were modified by adding alloying elements. The MMCs with alloy matrix had a strength of more than 2 GPa and slightly lighter weight than Ti, which was two times stronger and nearly a half of weight of ordinary steel.
Relationship between the strength and reaction degree at the interface in the MMC was investigated after heat treatment of various periods. Several reaction products were formed, which showed a layer by layer structure. The strength of MMC decreased with increasing total thickness of the reaction products. The deterioration was very serious when the thickness reached values of 3 μm. The composition of the inner and outer layers could be expressed as TiC and Ti_5Si_3, respectively. Total thickness increased in proportion to the square root of heat treatment time. This means that the rate determining process of the reaction was controlled by the diffusion of Si or C.

We have found that adding some elements such as aluminum, vanadium and/or molybdenum, which restrain the diffusion in Ti, is effective in preventing the reaction at the interface. These elements also prevent the crack initiation, because they decrease the stress concentration which is considered to be caused by the uneven grain size of TiC.

Related papers

" *The Relationship Between Interfacial Reaction and Tensile Strength of SiC Filament Reinforced Ti Alloy Composites* ", Imai, Y., Shinohara, Y., Ikeno, S., Shiota, I.: Proc. 5th Japan-US Conf. Compos Mat. (1990), 347–354.

Materials for mechanical application

78 Development of High Vibration Damping Materials

Apr. 1989~Mar. 1992
Kawahara, K.
Physical Properties Division

Excellent **damping materials** made of laminated steel sheet have been developed recently. The laminated steel sheet, however, has restrictions in its usage because of the problem resulting from their layer structure. Development of damping materials without the lamination structure, therefore, is desired for engineering applications. We have examined the mechanical properties, the workability, and the corrosion resistance of **manganese-based alloys**, and found that some of these alloys, containing copper in the range of 20 to 30 atomic percent, showed a possibility of high damping characteristics. In order to improve the damping characteristics we have studied the effect of alloying elements such as zinc, tin, nickel, iron, cobalt, vanadium, chromium, and aluminum.
It has been found by the examination of cold rolled sheets that the important factor in controlling the damping capacity is associated with the morphology of second phases or impurities dispersed throughout the martensitic matrix. The change in casting micostructure remarkably affected the damping capacity. As for the logarithm damping capacity, a value of 0.5 sometimes was obtained in as-cast specimens, while a value of 0.2 was usually found in specimens that were cold rolled and then heat treated under the optimum condition. However, the scatter in the damping value of as-cast specimens was noticeably large. A scatter rangin from 0.006 to 0.5 was observed for the as-cast specimens, for example, cooled slowly from 1273K, even though specimens were heat treated under the same condition. We are investigating the cause of this large scatter.

Related papers

" *Workability of Manganese-Based Alloys* ", Kawahara, K., Sakuma, N. and Kimura, T.: J. Japan Inst. Metals, **53** (1989), 119–125 (in Japanese).

" *Mechanical Properties and Corrosion Resistance of Manganess-based Alloys* ", Nishizaki, Y. and Kawahara, K.: J. Japan Inst. Metals", **53** (1989), 792–798 (in Japanese).

79 Intelligent Structural Materials

Apr. 1991~Mar. 1996
Matsuoka S.
Environmental Performance Division

A new conception, namely the **intelligent material** is an original idea invented in Japan. Similarly to the living thing, the intelligent material has the ability to respond to environmental conditions intelligently, and manifest intellignet functions such as **sensing, processing** and **actuating**.
In this study, basic research is carried out in order to give intelligent functions to the **metallic engineering material** for structural use. In the structural materials, there are small cavities which do not detract the strength properties of the material. Therefore, putting sound-emitting material, phase-transformed material or others in the small cavities, an intellignent structural material with an ability such as self-sening or self-restoring of damage is developed. Furthermore, a nano-technology based on the scanning tunneling microscope and the atomic force microscope is developed in order to evaluate the intelligent functions of the materials on atomic scale.

80 Mechanism for Strengthening and Toughening and Improvement of Mechanical Properties in Titanium Alloys

Apr. 1988~ Mar. 1991
Kainuma, T.
Mechanical Properties Division

Effect of Beta Grain Size on Strength, Ductility and Toughness of the ***Beta-Type Titamium Alloys***

The effects of beta grain size on strength, ductility and toughness of three beta-type titanium alloys wiht different degrees of beta phase stability have been investigated. With increasing solution treatment temperature, the beta grain size changed from approximately 45 to 450 μm. In the solution treated and aged condition, 0.2% yield and tensile strengths exhibited approximately constant values irrespective of the grain size. Both the elongation and the reduction of the cross-section area decreased with increasing grain size. Notched tensile strength and fracture tough-

ness were independent of the grain size, and were found to depend on the strength level alone. The difference in grain size dependency between ductility and toughness could be explained by the change in fracture appearance.

Effect of Microstructure on the Fatigue Behavior of Blended Elemental P/M ***Ti-6Al-4V*** *Compacts*

Several different microstructural conditions were generated through combinations of processing and heat treatment to determine the optimum microstructure and also to investigate the effect of the alpha phase morphology on the high cycle fatigue strength. The best combination of high cycle fatigue strength and ductility was obtained by the new **blended elemental method**, in which sintered material was water quenched from the beta phase region prior to HIP' ing. The highest fatigue strength at 10^2 cycles, 72kg/mm^2, was obtained by the STA treatment.

Based on the fatigue crack initiation analysis, it is concluded that, irrespective of microstructural categories, the high cycle fatigue strength can be described as a function of the length of slip path in the alpha grain, with a colony considered as a single grain.

Related papers

" *Effects of Beta Grain Size on Strength, Ductility and Toughness of the Beta-Type Titanium Alloys* ", Muneki, S., Kawabe, Y., kainuma, T. and Takahashi,: Proc. 1st Japan Int. SAMPE Symp. (1989), 81–88.

" *The Effect of Yttrium, Erbium and Boron Additions on the Microstructure and Mechanical Properties of Ti-15V-3Cr-3Sn-3Al alloy* ",Kainuma, T. and Kawabe, Y.: 6th World Conf. on Titanium, France, (1988)), 849–854.

" *Effect of Microstructure on the Fatigue Behavior of Blended Elemental P/M Ti-6Al-4V Compacts* ", Hagiwara, M., Kaieda, Y., Kawabe, Y. and Miura, S.: J. Iron and Steel Inst. Jpn. **76** (1990), 2182–2189 (in Japanese).

" *Mechanical Properties and Age hardening Behavior of Electron Beam Welded Zone in Ti-15V-3Cr-3Sn-3Al Alloys* ", Fujita, M., Kainuma, T., Irie, H. and Kawabe, Y.: 6th World Conf. on Titanium, France (1988), 275–280.

(81) Microstructural Refinement and Mechanical Properties of Titanium Alloys

Apr. 1991~Mar. 1993

Kanuma. T.

Mechanical Properties Division

Recently, metastable beta-type titanium alloys have drown attention due to their excellent formability. However, it is well known that rapid grain growth occurs by high temperature annealing above the beta transition temperature. Ti-3Al-8V-6Cr-4Mo-4Zr (**Ti – 3 – 8 – 6 – 4 – 4**) alloy is a metastable beta-type alloy which was developed for applications where cold formability and strength are desirable features.

The aim of this work is to determine the refined effect of grain size, substructure and alpha precipitation phase in Ti – 3 – 8 – 6 – 4– 4 alloy by thermomechanical treatment and the hydrogen additioning treatment, and to determine the **mechanical properties** of the alloy with these refined microstructures.

Microstructural refinement *and mechanical properties*

The grain refinement treatments in Ti-3–8–6–4–4 alloy are mainly carried out by the hard cold-rolling and short time recrystalization method and the erbium additioning method. Also, the substructural refinement treatments in the alloy are carried out by various combinations of annealing conditions and reduction ratios in cold rolling. We would like to determine the relationship between the grain refinement and the alpha precipitate morphology.

Control of microstructural refinement by hydrogen addition

previous work has shown that hydrogen absorption and formation of induced dislocation structures occurs during the preparation of beta-type titanium alloy specimen, such as the cold rolling, the emery polishing, the diamond cutting and the water quenching.

In this work, both relationships between the amount of absorption of hydrogen and the composition of atmosphere, and between the amount of the hydrogen addition and the dislocation structure in Ti-3–8–6–4–4 alloy are clarified. In addition, the high dislocation density microstructure is made by using the pinning effect according to the introduced dislocation by the hydrogen addition and the thermechanical treatment. Fiurthermore, the possibility of the microstructure control such as the extra refinememnt of the grain size, the substructure and the alpha precipitation phase is examined.

(82) Development of Metal Matrix Composites for High Temperature Use Through Combination of Advanced Powder Metallurgy Processes

Apr. 1991~Mar. 1994

Hagiwara, M.

Mechanical Properties Division

Titanium alloys are ideally suited for airframe and gas turbine engine components because of their unique mechanical properties combinations. However, their service temperature is limited to 600°C due to a degradation of creep strength, metallurgical stability and environmental resistance. Much potential exists to expand the service temperature range of this class of alloys since their melting point is in excess of

1650°C. Development activities are currently centered around titanium aluminides but these alloys are intrinsically brittle, and success in improving low temperature ductility while maintaining high temperature mechanical properties has been limited.
However, for future aircraft design, there is still a demand for titanium alloys having superior combinations of high temperature strength, creep resistance, stiffness, corrosion resistance and thermal stability compared to their conventional counterparts in the temperature range between 600 and 1000°C.
The application of advanced **powder metallurgy** processes such as **rapid solidification** (RS) can be considered as one possible route to achieve this goal. RS offers potential for high temperature property improvement of conventional titanium alloys by the introduction of a fine distribution of insoluble dispersoid particles such as carbides, oxides and borides during post thermal exposure. Powder metallurgy also provides a flexible process for manufacturing composites reinforced with relatively large size (1–40 μm) ceramic particle.
Our research group is devoted to the production of RS titanium powders using the plasma rotating electrode process (PREP) and a melt spinning apparatus. We are also engaged in research work on the development of a new class of particle reinforced RS **titanium matrix composites** with emphasis on relating composition/microstructure to high temperature mechanical properties.

Materials for electronics application

83 Synthesis of New Functional Materials by the Application of Host-Guest Reactions

Apr. 1990~Mar. 1992
Amano, M.
Physical Properties Division

The aim of this project is to synthesize new functional materials by applying insertion/extraction reactions. We are trying to synthesize new ionic conductor materials by using ion exchange processes. Hydrous pentavalent oxides have been selected as the object materials, because they are known to possess interesting ion exchange properties and some **hydrous oxides** of Sn, Sb, Nb and Ta, e.g., $HSbO_3.xH_2O$ and $HNbO_3.xH_2O$, are known as inorganic conductors. These compounds can be prepared by acid treatment of the corresponding alkali metal compounds such as $KSbO_3$ and $LiNbO_3$. Different crystal structures of hydrous oxides can be obtained by changing the preparation process.
Proton conduction in the prepared samples is studied by measuring the complex ionic conductivity. The mechanism of the proton conduction in the prepared samples is investigated by means of NMR, TGM and FTIR. The applicability of the synthesized materials to fuel cells is also investigated.

84 High-Strength/High-Conductivity Materials and Their Application to High-Field Magnets

Apr. 1989~Mar. 1991
Maeda, H.
1st Research Group

The development of **high-strength/high-conductivity materials** is very important for improving a resistive **high-field magnet**, such as a water-cooled magnet and a pulsed magent. Therefore we have been studying on several Cu-based alloys, and recently have found that the heavily-cold worked **Cu-Ag** alloys show excellent properties as a conductor material. The Cu-Ag alloys, with a Ag content lower than 0.02 at %, are used commercially but do not exhibit enough strength for high-field generation. We have studied the mechanical strength and the electrical conductivity of Cu-(2–30) at%Ag alloy wires.
Only two phases, Cu-rich and Ag-rich solid solutions, exist in Cu-Ag alloy system. The heat treatment at 450°C forms Ag-rich fine precipitates in the Cu-rich matrix and improve the electrical conductivity of the wires. When cold-drawn, the fine Ag precipitates are deformed into ultra-fine filaments of several tens of nm in diameter, which act as barriers against dislocation movement and reinforce the mechanical strength of the wires. High tensile strengths above 100 kg/mm^2 and high electrical conductivities above 80% IACS have been obtained for the Cu-12at%Ag alloy wire. These values are far superior to those of conventional high-strength conductor materials (Cu-Al_2O_3, Cu-Cd, Cu-Cr, and Cu-Zr alloys), and similar to those of Cu-Nb alloys. Therefore, the Cu-Ag alloy wires are very interesting conductors for the water-cooled magnet and the pulsed magnet. Collaborating with the Francis Bitter National Magnet Laboratory (FBNML), USA, we have measured the resistivities of the Cu-Ag alloy wires in high fields, which are similar to those of the other Cu-based alloys. The application of the Cu-Ag alloy materials to high-field resistive magnets is also being discussed with the magnet designers of FBNML.

85 Development and Evaluation of Advanced Superconducting and Cryogenics Materials

Apr. 1990~Mar. 1993
Maeda, H.
1st Research Group

Three major materials have been studied to contribute to the development of advanced superconducting technologies.

Nb_3Al multifilamentary superconductors with a filament diamenter of 90 nm show a **critical current density** J_c superior to that of commercially available Nb_3Sn conductors in fields below 14T, when the Nb_3Al-formation temperature is lower than 1230K. In fields above 14T, however, the J_c of the Nb_3Al conductors decrease due to their relatively low **upper critical field** Hc_2. To improve the high-field properties of Nb_3Al conductors, we tried to heat-treat them at high temperatures for 0.1–1 sec by pulsed Joule heating. For the Nb_3Al conductors with relatively thick filaments of 3–4 μm, T_c and Hc_2 (4.2K) increase by 2K and 3T, respectively, but J_c-B (field) properties show a peak effect by the pulsed Joule heating. The peak J_c (4.2K) is about $10^4 A/cm^2$ at 19T. Furthermore, we have found that Ag addition increases the formation rate of Nb_3Al in the diffusion reaction between Nb and Al.

A highly efficient **magnetic refrigerator** to obtain temperatures below 2K has been developed. Large scale **rare earth garnet** single crystals of $(GdDy)_3(AlGa)_5O_{12}$ have been grown and tested as magnetic refrigerants. Specially designed components include a pulsed superconducting magnet, a Ti alloy heat pipe for the super-fluid helium production and a mechanical contact thermal switch for expelling the heat generated during magnetization. The system is operated with a static Carnot cycle with a cooling capacity of 100mW at 1.8K, and reached 1.35K without load. In the next stage, a compact and high capacitty system below 1K will be obtainable by using the garnets diluted with non-magnetic rare earth ions which may have low magnetic transition temperatures.

Cryogenic structure materials have to sustain strong forces, resist a catastrophic fracture, and undergo cyclic loading or deformation. Hence, the **strength, fracture toughness** and **fatigue** properties at very low temperatures have been evaluated for candidate materials like austenitic stainless steels, Ti alloys, and Al alloys with testing machines developed in our laboratory. We have found that the mechanical properties and the fracture mechanisms are closely related to the microstructure. Especially, the performance of the structural materials under high magnetic fields is quite unknown. We designed the facilities utilizing a superconducting magnet for measuring low temperature mechanical and physical properties under high magnetic fields.

Related papers

" *Nb Tube Processed Nb_3Al Mutifilamentary Superconductors* ", Takeuchi, T., Kosuge, M., Ijima, Y., Hasegawa, A., Kiyoshi, T., Inoue, K.: IEEE Trans. Magnetics, MAG-**27** (1990), 2045–2048.

" *Analysis of a Magnetic Refrigerator Operating Temperature between 10K and 1.4K* ", Numazawa, T., Kimura, H., Sato, M., Maeda, H., Takahashi M., and Nakagome, H.: Proc. 6th Int. Cryocooler Conf. (1991) 44–57.

" *Subsurface Crack Initiation in High Cycle Fatigue of Ti-5Al-2.5Sn Extra-low Interstitial Alloy at Liuid Herium Temperature* ", Umezawa, O., Nagai, K. and Ishikawa, K.: Mater. Sci. Engineer. **A129** (1990), 217–221.

86 Fabrication of High-Tc Superconducting Wires

Apr. 1988~Mar. 1993
Maeda, H.
1st Research Group

The eventual goal of this study is to fabricate long **high-T_c oxide superconducting wires** and tapes with sufficient flexibility and a high transport **critical current density** J_c. As the oxide supercconductors are intrinsically brittle, we have been studying on various potential wire fabrication techniques based on vapour phase, solid phase and liquid phase processes, and the increase in J_c, espeically, in magnetic fields, for **Y-Ba-Cu-O** and **Bi-Sr-Ca-Cu-O** superconductors.

Using doctor-blade-casting and powder-in-tube techniques, highly textured $Bi_2Sr_2CaCu_2O_x$ (2212)/Ag composite tapes were prepared by applying a partial melting and slow cooling process. J_c of the tapes at 77K was higher than $10^4 A/cm^2$ in zero magnetic field, though it was found to be very sensitive to an applied field. The sensitivity is reduced at low temperatures. Jc's at 4.2K reach a practical level ($\sim 10^5$ A/cm^2) even in high fields above 25T, and more than $10^4 A/cm^2$ for Ag-sheathed multifilamentary wires with 56 filaments. Moreover, orther techniques such as plasma spraying, suspension-spinning and chemical coating combined with laser irradiation, glass crystallization, and internal oxidation have been studied to apply the fabrication of Bi-oxide superconductor tapes and sheets. To further improve J_c we have been studying on fundamental problems such as weak links between grains and flux creep appearing above 1T using Bi-2212 oxide single crystals and highly textured tapes.

For $YBa_2Cu_3O_y$ superconductors, on the other hand, vapour deposition techniques such as rf magnetron sputtering, laser ablation, and hot plasma flash evaporation were employed. Hastelloy (Ni-Cr-Mo alloy) tape was used as the metal substrate. A special emphasis was placed on the selection of buffer layer to avoid an adverse reaction between the film and the substrate. So far the best result was obtained by the KrF excimer laser ablation mehtod. The film deposited onto the Hastelloy with a YSZ/Pt buffer layer shows a T_c (R=0) of 90K and a J_c of 4.2×10^4 A/cm^2 at 77K and zero

field, which is the highest among the values reported to date on metallic substrates. Further improvements in the crystallinity and J_c by optimizing the deposition conditions are now in progress.

Related papers

" *J_c Characteristics of Textured Bi-Based Oxide Tapes* ", Kumakura, H., Togano, K., Dietderich, D. R., Maeda, H., Kase, J. and Morimoto, T.: IEEE Trans. Magnetics, MAG-**27** (1991), 1250–1253.

" *Comparison of Bi-System 2223 and 2212 Thick Superconducting Tapes: Grain Alignment, Current Density and Strain Effects* ", Sekine, H., J. Schwartz, J., Kuroda, T., Inoue, K., Maeda, H., Numata, K. and Yamamoto, H.: J. Appl. Phys., **70** (1991), 1596

" *Preparation of $YBa_2Cu_3O_y$ Superconducting Thin Films on Metallic Substrates by Excimer Laser Ablation* ", Saitoh, J., Fukutomi, M., Komori, K., Tanaka, Y., Asano, T., Maeda, H. and Takahara, H.: Jpn. J. Appl. Phys., **30** (1991), L898–900.

87 Study on Measurement and Evaluation Methods for Superconducting Properties

Apr. 1990~Mar. 1993

Wada, H.

1st Research Group

In accord with the rapid progress in development and use of superconducting materials, in a variety of scientific and technological fields a world wide demand for the **standardization** on these materials is developing. Thus, NRIM is working on the development and establishment of standard measurement and evaluation methods in collaboration with the National Institute of Standards and Technology (NIST). Based on the agreed program both institutes exchange researchers involved and cooperatively implement measurements and discussions at both locations. This study should develop and establish measurement and evaluation methods on;

(1) **stress effects on critical currents** in advanced superconducting materials

(2) **ac losses** in advanced superconducting materials

(3) critical currents in oxide superconductors.

Cooperative critical current measurements were carried out at NIST by both NIST and NRIM researchers using a normal direct current method as well as a pulse current method on the Bi-based superconductors prepared at NRIM. It has been confirmed that the pulse method is useful for samples with substantial contact resistivities; this is often the case for oxide superconductors. Moreover, it has been shown that the passive voltage-current simulator recently developed at NIST (Fig. 1) can successfully be used for the comparison of both measurement methods. A second simulator was developed and delivered to NRIM for the next cooperative measurements at NRIM.

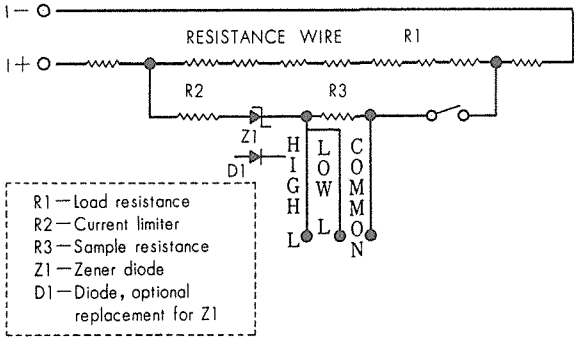

Fig. 1 Circuit diagram of the passive simulator (L.F.Goodrich, submitted to "CRYOGENICS").

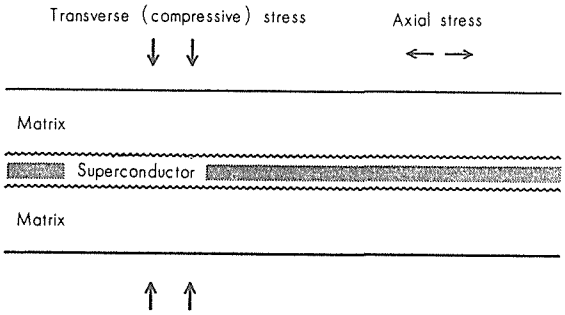

Fig. 2 Schematic illustration of axial and transverse stresses imposed on a superconductor wire.

Stresses imposed on a superconductor (Fig. 2) are known to seriously degrade its critical current. This is one of the most essential problems for superconductors when used for large-scale, high-field applications. Recently, it has been revealed that transverse stresses even more severely decrease the critical current than axial stresses. It has also been reported that the Nb_3Al superconductor has a higher mechanical stability than commercial Nb_3Sn. Thus, transverse stress effects were measured at NIST in cooperation with a NRIM visiting researcher using Nb_3Al multifilamentary superconducting wires fabricated at NRIM. The measurement results are being analyzed and will shortly be published.

88 Development and Characterization of Superconducting Materials for Fusion Reactor Magnet Use

Apr. 1989~Mar. 1994

Wada, H.

1st Research Group

This study aims at developing new, **high-field superconducting materials** appropriate for **fusion reactor magnet** use. For this purpose new, promising superconducting materials recently developed or under development are characterized and evaluated under those conditions that may be experienced by the superconducting magnet which should be

confining and controlling plasma in the reactor. Thus, effects of (1) strain, (2) **neutron irradiation** and (3) **time-varying applied field** on superconducting properties are being examined.

Strain effects have been studied in newly developed **Nb_3Al** and practical **Nb_3Sn** superconductors. It has been revealed that the superconducting properties, critical temperature and current, of Nb_3Al are more stable than those of Nb_3Sn with respect to axial tensile strains. Effects of transverse strains which are expected to be more serious are being examined.

Effects of neutron irradiation up to 10^{19} n/cm^2 on critical currents have been measured on Nb_3Al and Nb_3Sn superconductors, in cooperation with Osaka University and Kyoto University. It has been found that the change of critical current in Nb_3Al superconductors with irradiatiion is similar to that found for in-situ processed Nb_3Sn.

Effective diameters of Nb_3Al filaments have been measured with respect to ac losses; the filament diameters calculated from the initial volume ratio of the filaments to the whole conductor are in the submicron range. The effective diameter at 77 T is about 2 μm which is rather smaller than in Nb_3Sn, suggesting the Nb_3Al superconductors are stable in time-varying fields.

This study has been covering and supporting international collaborative programs, such as Japan-US work shop on high-field superconducting materials for fusion magnets as well as IAEA technical committee meeting on superconducting materials and magnets.

Related papers

" *Strain Effects on Superconducting Properties in Nb_3Al Multifilamentary Wires* ", Kuroda, T., Wada, H., Iijima, Y. and Inoue, K.: J. Appl. PHys., **65** (1989), 4445–4447..

" *Magnetization of Composite-Diffusion Processed Nb_3Al Superconductors Containing Ultra-Fine Filaments* ", Itoh, K., Yuyama, M., Kuroda, T., Takeuchi, T., Kosuge, M. and Wada, H.: Proc. 11th Int. COnfer. Magnet Technol. **2** (1990), 962–967.

Magnetic materials

89 Properties and Applications of Mesoscopic Scale Materials

Apr. 1989~Mar. 1992

Nakatani I.

Physical Properties Division

This project aims at developing preparation methods and investigating properties of materials of nanometer scale: **fine particles** and **thin whiskers**.

Magnetic fluids, composed of ferromagnetic fine particles of several nanometers colloidally dispersed in a suspending liquid, are liquids that can be strongly magnetized by applying magnetic field. In commercial use, magnetite (Fe_3O_4) or ferrite is used as ferromagnetic material. The purpose of this work is to develop magnetic fluids with higher magnetization than conventional ones by using metals, alloys and metal nitrides. We have developed the following three methods: (a) vacuum evaporation, (b) plasma chemical vapor deposition (CVD) and (c) chemical reaction in a liquid. The method (a) is used for preparing magnetic fluids from metals and alloys and the methods (b) and (c) are for iron-nitrides magnetic fluids. In the chemical reaction method (c), iron carbonyl ($Fe(CO)_5$) and ammonia gas react in a suspending liquid. The magnetic fluid obtained by this method has a saturation magnetization exceeding 0.2 T, which is remarkably higher than that of conventional magnetic fluids, typically 0.05 T. Magnetic properties of ultrafine particles in the magnetic fluids prepared by these methods were also examined. It was shown that the particles of iron, cobalt and nickel are ferromagnetic down to the size of 2 nm.

Titanium diboride (TiB_2) is a compound having high hardness and high electric conductivity. Whiskers of titanium diboride were prepared by chemical vapor deposition (CVD) from $TiCl_4$ and BBr_3. For obtaining whiskers it is essential to use fine particles of Ti-Ni alloy that work as a catalyst during the deposition. At present, whiskers with a diameter down to 10 nm have been obtianed. The whiskers are expected to be useful for heat resisting composite materials or electric conductive materials.

Related papers

" *Preparation and Magnetic Properties of Colloidal Ferromagnetic Metals* ", Nakatani, I., Furubayashi, T., Takahashi, T. and Hanaoka H.: J. Mag. Mag. Mater. **65** (1987), 261–264.

" *Iron-nitride Magnetic Fluids Prepared by Plasma CVD Technique and Their Magnetic Properties* ", Nakatani, I. and Furubayashi, T.: J. Mag. Mag. Mater. **85** (1990), 11–13.

" *Mössbauer Studies of Colloidal Ultrafine Particle of Iron* ", Furubayashi, T. and Nakatani, I.: IEEE Trans. Mag. **26** (1990), 1855–1857.

90 Fabrication and Properties of Novel Metallic Materials with Artificial Microstructures

Apr. 1989~Mar. 1992

Nakatani, I.

Physical Properties Division

Ferromagnetic fine particles are widely applied to recording media. Much interest has been attracted to their magnetic properties. An accurate description of the magnetic properties of **ferromagnetic single-domain particles**, however, remains an unsolved problem. If the microscopic status of the individual particles can be

specified in terms of magnetization, magnetic anisotropy and dynamic motion of magnetic spins, considerable progress of micromagnetics and their applications is foreseen. For clarifying these problems, suitable samples require the control of their particle size, shape, morphology, relative orientation and spacing. In this project, we apply **ultra-high-resolution electron-beam lithography** for fabricating ordered planar arrays of submicron particles of magnetic materials. Highly accurate magnetization measurements, ferromagnetic resonances and Lorentz transmission microscopy are employed to evaluate the particle arrays.

Opto-materials

91 Reversible Color Change Alloys

Apr. 1989~Mar. 1992
Sasano, H.
Physical Properties Division

An Ag-50mol%Cd alloy quenched from a temperature above 750K shows a pink color. The alloy exhibits a color change to pale gold on aging around 600K. The color change is reversible depending on the heat treatment. Such an alloy is called a **reversible color change alloy** and a candidate for **optical recording** material. The main objective of this program is looking for new alloys of this kind. There are many alloy systems which have 1.5 electron compound of B2 or DO_3 crystal structure. It is well known that compounds such as NiAl and Cu_3Al show a unique color. Therefore, our investigation has been focussed on the optical properties of these compounds. In our recent research, it was found that the Cu-Zn-Al, Ag-Zn and Ag-Cd alloys, having a specific composition, show a drastic color change with phase transformation, as shown in Fig. . It was also found that these alloys can be easily synthesized by the **vapor-solid diffusion couple method** which was invented by our group.

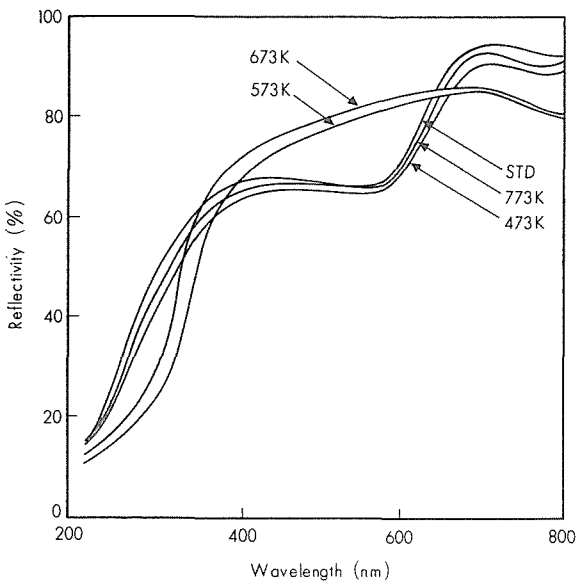

Figure Reflectivity change with heat treatment in Ag-55.5%Cd alloy.

92 Development of Intermetallic Compound Materials for Advanced Luminescent Devices

Apr. 1986~Mar. 1991
Koguchi, N.
Surface and Interface Division

The prospect of extremely low loss fluoride glass fibers has stimulated considerable interest in some III-V and IV-VI compound semiconductor heterojunction lasers for future mid-IR optical fiber communication systems. At present, the laser sources in this wavelength region are in a very early stage of development.
The IV-VI compound semiconductor **PbS**, which has an energy gap of 0.42 eV at 300 K, is a potentially useful material for such laser sources. Due to the lack of suitable materials lattice-matched to PbS for the confinement layers of double-heterostructure and/or quantum-well lasers, only p-n homojunction lasers have been fabricated, and the maximum pulse operating temperature was 120K. In our preliminary results, the lattice-matched double-heterostructure lasers consisting of $Pb_{1-x}Cd_xS_{1-y}Se_y$ confinement layers and a PbS active layer grown by **molecular beam epitaxy** operated up to 200 K at 3.27 μm. Improvement of the operating temperature by the application of latticle-matched heterostructures composed of new materials or quantum well structures is expected.
We have proposed a new quaternary material $Pb_{1-x-y}Cd_x\ Sr_y\ S$ for the confinement layers of the double heterostructure lasers with PbS active layers. The maximum operating temperature increases with decreasing lattice mismatch, and also increases by using a tilted substrate. The maximum operating temperature of the laser diode in this work is 240K. It is expected that the operating temperature can be further increased decreasing the lattice mismatches between active and confinement layers and/or using a tilted substrate.

Materials for energy application

93 Study on the Hydrogen Trapping in Palladium-Plated V-Ni Alloy Membranes

Apr. 1990~Mar. 1991
Amano, M.
Physical Properties Division

The **hydrogen permeation** characteristics of V-15at.%Ni based alloy membrane have been investigated in the temperature range 373–673 K. It has been found that palladium-coated V-15at.%Ni alloy membrane shows a good resistance to hydrogen embrittlement with hydrogen permeabilities larger than those of a palladium membrane. The **V-Ni alloy membrane** did not show any cracks even under an upstream hydrogen pressure of 0.2 MPa during the permeation test at 473 K. It showed a conspicuous **hydrogen trapping** phenomenon below 473 K. The hydrogen permeability of the V-Ni alloy membrane increased by adding 0.05 atomic percent of titanium, zirconium or yttrium, which was nearly equal to the amount of oxygen in the alloy. The hydrogen trapping phenomenon, however, could not be eliminated by adding such deoxidizers. The trapping phenoenon could be markedly improved by removing the deformed layer of the alloy membrane before plating with palladium

Related paper

" *Hydrogen Permeation Characteristics of Palladium-Plated V-Ni Alloy Membranes* ", Amano, M., Komaki, M. and Nishimura, C.: J. Less-Common Metals, 172–174 (1991), 727–731.

94 Study on Alloy Membranes for Hydrogen Separation

Apr. 1988~Mar. 1991

Amano, M.

Physical Properties Division

The aim of this study is to develop new **alloy membranes** having excellent **hydrogen-separation** characteristics. The main results obatined are as follows.

(1) The hydrogen permeability and diffusivity in a laminate sample consisting of a Pd overlayer, a sputter deposited $FeTi_{0.96}$ film and a Pd plate have been determined in the temperature range 473 to 773 K. The hydrogen diffusion coefficient in the $FeTi_{0.96}$ film was calculated using the proposed permeation theory for bilayer composites.

(2) The effects of a high concentration of CO and CO_2 (up to 50%) on the hydrogen permeation characteristics of the palladium membrane have been investigated in the temperature range 423 to 723 K and the pressure range 0.9 to 250 kPa. It was found that the deterioration of hydrogen permeability and diffusivity was observed in the case of using H_2-CO gases and showed a concentration dependence of CO below 473 K.

(3) It was found that the membranes of palladium plated V-15at.%Ni and V-15at.%Co alloys are promising candidates for the hydrogen-separation membranes. These alloy membranes shows good resistance to hydrogen embrittlement with hydrogen permeabilities larger than those of a palladium membrane.

Related papers

" *Hydrogen Diffusivity in Sputter-Deposited FeTi Film* ", Amano, M. and Nakamura, K.: Trans. JIM, **29** (1988), 308–313.

" *Effects of High Concentration CO and CO_2 on hydrogen Permeation through the Palladium Membrane* ", Amano, M. Nishimura, C. and Komaki, M.: Mat. Trans. JIM, **31** (1990), 404–408.

" *Hydrogen Permeation Characteristics of Vanadium-Nickel Alloys* ", Nishimura, C. Komaki, M and Amano, M.: Mat. Trans. JIM, **32** (1991), 488–494.

95 Research on Fundamental Techniques to Develop Functionally Gradient Materials for Relaxation of Thermal Stresses (II)

Apr. 1990~Mar. 1992

Shiota, I.

Physical Properties Research Division

A Functionally Gradient Material (**FGM**) is defined as a material of which the functionality changes continuously with space or time. Generally speaking, ceramics are heat resistive, and metals are tough structural components. Ceramics are often coated or sticked on the metal surface for thermal protection. However, in the case of the space shuttle, the ceramic tiles sometimes came off from the fuselage because of **thermal stresses** at the interface.

A space-plane (SP) is expected to fly at much higher speed than a shuttle. It is thus anticipated to be subjected to intense heat of 2000K, which may cause enormous thermal stresses in nose cones, turbines, combustion chambers and so on. At such elevated temperatures, no traditional heat protective system is reliable at a reasonable stress level. Relaxing the stresses is the most essential to construct the SP. FGM is the most hopeful candidate. It does not contain stress concentration parts, becuase functionality changes continuously as the internal composition varies gradually from ceramics on the face to metal on back side.

However, the FGM is a heterogeneous material and is thermodynamically in nonequilibrium. Therefore, thermal stability is the most important factor for its practical application. From this point of view, we are carrying out an investigation of **thermal stability** of metal-ceramics FGMs. The stability is influenced by its structure, which can be roughly classified into two types. One of them consists of sub-micron crystals, which are often found in FGMs produced by gaseous processes as PVD or CVD. The other type has larger crystals of over 1 μm, which are obtained by processes using powders as starting

materials such as PM, SHS and plasma spraying. We have found that fine size and random orientation of the crystals is mot essential to improve the stability of the first type of FGM, and low porosity is required for the second type. We have also found that a substrate metal without affinity for FGM is desirable. Now we are improving the FGMs on the bases of these results.

Related papers

" *Effect of Crystal Structure on Thermal Stability of Ti-TiC FGM* ", Shinohara, Y., Imai, Y., Ikeno, S., Shiota, I.: Proc. Int. Symp. FGM, (1990), 225–230.

" *Thermal Stability of Ti and TiC Related with Substrates* ", Shiota, I., Shinohara, Y., Imai, Y., Ikeno, S.: Proc. Int. Symp. FGM. (1990), 219–224.

96 The Improvement of Durability of Tungsten Fiber Reinforced Superalloys

Apr. 1987~Mar. 1991

Itagaki, T.

Materials Design Division

This research is aimed at developing a manufacturing procedure of high performance **tungsten fiber reinforced superalloy** (TFRS).

In the first part, a high performance cobalt-base TFRS was prepared to avoid deterioration due to **nickel induced recrystallization** of tungsten fibers. The TFRS was perpared using a vacuum casting method by using the doped tungsten and the cobalt-base superalloy. Its minimum creep rate at 1273K in air agreed well with that estimated by the rule of mixtures. This material did not show any deterioration of tungsten fiber after being heated at 1273K for 3.6Ms.

In the second part, a study was performed to gain knowledge on nickel-induced recrystallization. The nickel was plated on the surface of the doped tungsten wire. The recrystallization process was found to compose of two steps. In the extremely early stage of heating, the nickel diffused and infiltrated toward the center from the surface of the fiber. It caused the primary recrystallization. Most of the fibers were not deteriorated in this stage. After some time, the secondary recrystallization started. The ductile-brittle-transition-temperature of the fibre increased drastically in this stage. Sometimes it exceeded 1300K. This recrystallization did not decrease the high temperature tensile strength of the fibre. However, it remarkably decreased ductility at lower temperature. After the recrystallization, nickel was found to segregate at the grain boundaries of tungsten.

In the third part, a study was made to prevent the diffusion of nickel from the matrix to tungsten. Alumina was found to be the best material among the investigated candidates. The coatings were strongly bonded to tungsten.

97 Study on a Porous Gas-Diffusion Electrode

Apr. 1990~Mar. 1993

Kobayashi, M.

Chemical Processing Division

Fuel cells have many attractive features for power utilities desiring urban power generation, and are promising in the following decades. Pilot plants of phosphoric acid fuel cell have already been operated in several places in the world. They are operated at ca. 200°C, which poses severe problems for the constituent materials. Tough operating condition of an **alkaline fuel cell** is milder, the rate of oxygen reduction and hydrogen oxidation is slow. The aim of this study is to seek an effective **electrocatalyst** to promote the above electrode reactions.

There are many candidate materials for the electrocatalysts, therefore our experiments are divided two parts. One is rough screening using powder samples, and the other is the accurate measurement of the catalytic properties using sintered samples.

A simple test is considered to screen out the materials. A particular sample of the candidate material is charged in an alkaline solution. The catalytic properties are roughly evaluated from the cathodic polarization curve of the suspension under O_2 bubbling at 50°C. The latter experiments are conducted as follows. Disk samples (2 cm ϕ × 0.1 cm) are prepared by a hot press. The disk is installed the cell, one side of the disk is in contact with an alkaline solution and the opposite side is exposed to a pure oxygen atmosphere. Cathodic polarization is measured at 50°C.

The effectiveness of the above two step screening tests is confirmed by experiments using standard electrocatalysts, noble metals on the activated carbon. The next step of our study is to examine various materials by the two step screening.

98 Achievement, Measurement and Application of Extremely High Vacuum

Apr. 1988~Mar. 1991

Yoshihara, K.

4th Research Group

The demand for **extremely high vacuum** less than 10^{-10} Pa is increasing in the field of surface analyses and thin film preparations. The development of a material inert to gas adsorption is one of the most important issues in order to easily achieve this extra high vacuum.

We found that by annealing at more than 900K in a high vacuum, **boron nitride** precipitated on the surface of type 304 stainless steel doped with boron and nitrogen. The surface of precipitated boron nitride was inert to the adsorption of gases. This method, however, has the problem that high temperature annealing may deteriorate the mechanical properties of type 304 stainless steel.
We deposited a mixture of type 304 and boron nitride on the surface of type 304 substrate with a magnetron sputtering method. Scanning Auger electron microspectroscopy and X-ray photoelectron spectroscopy showed that boron nitride precipitated on the surface of the deposited film after annealing at more than 600K in a high vacuum. Precipitated boron nitride successfully covered the whole surface of the film. Only small amount of carbon and oxygen remained on the surface of the boron nitride after 3.6ks exposure in air. This result indicated that the precipitation temperature of boron nitride was lowered by 300K, and that the surface of boron nitride precipitated on the film was inert to gas adsorption.
We developed a cylindrical electrode for a magnetron sputtering method in order to deposit a boron nitride film on the inner wall of a vacuum chamber. Precipitated boron nitride successfully covered almost the whole surface of the inner wall of the vacuum chamber. Through-put measurements showed that the outgassing rate of a boron nitride covered vacuum chamber decreased by an order of ten compared to that of a usual vacuum chamber type 304 stainless steel.
The deposition of a film consisting of a mixture of stainless steel and boron nitride can be a promising candidate method for the surface modification of extra high vacuum vessels.

Related papers

" *Surface Precipitation of Boron Nitride on the Surface of Stainless Steel/Boron Nitride Film* ", Tosa, M. and Yoshihara, K.: Vacuum, **41** (1990), 1873–1875.

" *The Gas Deposition Behavior from BN Coated Vacuum Chamber* ", Tosa, M., Yoshitake, M. and Yoshihara, K.: J. Vac. Soc. Jap. **34** (1991), 62–64 (in Japanese).

99 Corrosion Fatigue—Stress Corrosion Cracking Interaction of Structural Materials for Light Water Reactor

Apr. 1987~Mar. 1991
Nagata, N.
5th Research Group

Corrosion fatigue—stress corrosion cracking interaction tests were conducted in order to search for important factors and to elucidate the maximum damage rate under combined loading of fatigue and SCC in high temperature water. This research program consists of 4 activities as folllows.
(1) Crack damage behaviour: Some representative results of crack damage behaviour under interactive conditions of CF and SCC are introduced in the Research Topics in this annual report.
(2) Influential factors: Factors correlated to corrosion fatigue and/or SCC have been investigated since 1980 in this laboratory. As the results, several important factors were revealed such as temperature, dissolved oxygen concentration (DO), flow rate, stress ratio, strain rate, sulfur content, microstructure of materials and so on.
(3) Electrochemical measurements: From the results of flow rate change test in high temperature water by using two kinds of **low alloy steels** with different sulfur contents, the increase of growth rate of fatigue crack of medium sulfur material was striking compared to that of low sulfur material, which was quite consistent with the fact that the corrosion potential of medium sulfur material showed a less-noble potential compared to that of the low sulfur material. Some other basic data associated with the electrochemical measurements such as a relation between corrosion potential and DO, effect of temperature on polarization curves were also obtained.
(4) Data evaluation: Data evaluation has been applied for the construction of the database related to the research programme titled "Knowledge based system for materials life prediction" in the designated researches.

Related paper

" *Fatigue Crack Growth Behaviour and Corrosion Potential of A533B Steels in High Temperature Water* ", Katada Y., Nagata N. and Sato. S: Proc. 4th Int. Conf. Fatigue and Fatigue Threshold" Fatigue 90, **3** (1990), 1819–1824.

100 Environmental Degradation of Structural Materials for Light Water Reactors

Apr. 1991~Mar. 1996
Nagata, N.
5th Research Group

This research was launched aiming at clarifying the initiation and growth mechanism of **environmentally assisted cracking** (EAC) in structural materials under high temperature pressurized water by applying electrochemical measurements and computer analysis. Elemental EAC processes of materials for primary pressure boundary components of **light water reactors** such as carbon steels, low alloy steels, austenitic stainless steels and nickel base alloys are analyzed for knowledge databases which can be

used for a materials life prediction.
For the evaluation of submicroscopic reactions such as dissolution of fresh surface in crack tips or corrosion pit formation, effort is being paid firstly to the development of a device of straining electrode analysis and electrochemical electrodes applicable to high temperature pressurized water. In this fiscal year applications for an Ag/AgCl external reference electrode and an AC impedance method for electrochemical measurements of local corrosion at cracks and pits in **high temperature water** are in progress. In addition, designing of a hydrogen electrode is underway. These measuring devices give us tools for quantitative information of the initiation and growth behaviour of environmentally assisted defects. Another program is the development of a straining electrode device for quantitative measurements of corrosion rate and repassivation rate of fresh metal surfaces disclosed in high temperature water. The transient behaviour of the electrochemical reactions will be analyzed by computer.

(101) Assessment of Strength and Structural Materials Database for Weldment in FBR Components

Apr. 1991~Mar. 1996
Monma, Y.
5th Research Group

Creep deformation and strength behavior of **weldments** are considered to be important in order to secure the structural integrity of large structures in **FBR** (fast breeder reactor) to be scaled up for practical applications. The goal of this theme is to establish the assessment procedure of strength characteristics of welded joints for FBR structural components at high temperatures.
The materials to be used are austenitic stainless (304, 316) and high Cr (Mod. 9Cr-1Mo) steels. Butt welded joints of GTAW (gas tungsten arc welding) are prepared using more than 50mm thick plates of base metal. In addition to the conventioal small specimens cut from the weldment, full-thickness specimens of welded joints will be used to obtain creep strain-time data at 500–600°C. Currently we are working to develop real-time measurement technique of the **strain distribution** by the CCD (charged couple device) Moiré interferometry and digital image processing.
We also are developing a computer simulation using FEM (finite element method) to calculate the stress-strain distribution of large weldment specimens subjected to creep. The experimental verification of the FEM computation is made by direct measurement of inelastic strain distributions in the large joint specimens. Attempts will be made to modify existing constitutive equations of creep on the basis of the damage mechanics concept so that a more realistic prediction of ceep behavior of weldment becomes possible.

(102) Fundamental Research on Application of New Functional Materials to Passive Components

Apr. 1990~Mar. 1994
Ishihara, T.
5th Research Group

In recent years **shape memory alloys** are being planned for an application as thermal actuator in the mobile louver of an air cooler, the shaft sealing of the reactor cooling pump and other devices in **nuclear power plants**. In the practical use of shape memory alloys, deterioration of the shape memory characteristics may occur as a result of interactions with reactor environments. Hence, evaluation of the shape memory characteristics under thermal and stress cycles in the environments are indispensable to ensure applicability and reliability of shape memory alloys in nuclear power reactors.
In this research, effects of cyclic transformation (parent phase ⇌ martensite) on the shape memory characteristics of a commercial **Fe-Mn-Si-Ni-Cr alloy** are studied. High temperature optical microscope with a tensile loading device was used to observe the structural change during tensile test or heating, and to measure shape memory characteristics such as **recovery stress**.
Results obtained indicate that the recovery stress increased during the first several transformation cycles but after that, decreased monotonically with increasing number of transformation cycles. Studies of shape memory characteristics of Ti-Ni alloys during tensile loading and in thermal cycling are in progress.

103 Development of the Fusion Reactor First Wall Materials Resisting to Plasma and Radiation Damage

Apr. 1987~Mar. 1992
Shiraishi, H.
2nd Research Group

High Heat Flux Material

In order to develop first wall and diverter plate materials for fusion reactor, **composite ceramics** consisting of carbon-boron-titanium were manufactured by hot pressing followed by sintering at 2000°C and the physical and thermo-mechanical properties of the products were studied. The produced specimens consisted

of graphite, TiC and TiB_2 and the graphite rich sample was tougher to mechanical fracture than the TiC+TiB_2 sample in **thermal shock** test.

Radiation damage resistance of microstructure controlled materials

For the further development of **high temperature structural alloys**, it is essential to reduce the susceptibility of materials to **helium embrittlement** due to grain boundary fracture. It was found that the long range creep strength and ductility of Fe-40-Ni-15Cr-3Nb-0.02C alloy was improved by helium trap mechanism to interfaces of Laves phase which was produced by transformation of gamma two prime $NiNb_3$ precipitates during the creep test. The other hopeful material is a ferritic steel. Only a small amount of embrittlement was found in the high temperature tensile test in the low activation 9Cr-2W and 9Cr-0.5V ferritic steels, which were helium implanted with 100 ppm at 673–873K by the NRIM cyclotron before tensile test.

Related papers

Fujitsuka, M, Shinno, H. Tanabe, T.: J. Nucl. Mater., **179**(1991) 189 ICFRM-4, Kyoto, Japan, Dec. 1989.

Yamamoto, N, Nagakawa, J. Shiraishi, H. Kamitsubo, H. Kohno, I. Shikata, T.: J. Nucl. Sci. Techn., **28** (1991) 1001.

Hasegawa, A. Shiraishi, H. J. Nucl. Mater., to be publsihed.

104 Material Chemistry in Extreme Conditions under Irradiation

Apr. 1989~ Mar. 1994

Kitajima, M.

2nd Research Group

Materials are subject to both chemical and physical attacks by particle bombardment, when they are in **irradiation** field. The main purpose of this research is to elucidate the mechanism of **surface reaction** processes activated by irradiation, and to develop new analytical methods for those processes with emphasis on real-time observation of these kinds of phenomena. Kinetic or phenomenological modelling of the **surface** reaction and **damage** process is also one of our targets. So far, disorder induced spectral changes in graphite and molybdenum have been observed under ion irradiation, using Raman spectroscopy and photoemission spectroscopy. We have succeeded in real-time *in situ* measurements of Raman spectra and ellipsometry for observations of **dynamic processes** induced by ion irradiation and plasma discharges. The *in situ* analyses of the activated chemical species in the plasma are also being studied. Finally, we plan to start studies on laser stimulated desorption and reactive scattering between particle beam and irradiated surfaces.

Related papers

"*Disorder Induced Line Broadening in First-Order Raman Scattering from Graphite*", Nakamura, Kazutaka. Fujitsuka, M., Kitajima, M.: Phys. Rev. **B41** (1990), 12260.

"*Electronic Structure in the Valence Band of Molybdenum Being Bombarded with Argon Ions*", Kitajima, M., Nakamura, Kazutaka, Fujitsuka, M., Shinno, H., Katoh, H., and Miyahara, T.: Phys. Rev. **B 44** (1991), 8338.

"*UPS Study of Mo (110) under Ar^+ Irradiation*", Nakamura, Kazutaka and Kitajima, M. : Proc. the 9th Int. Cong. Rad. Res. (ICRR), June 1991.

"*Real-Time Raman Measurements of Graphite under Ar^+ Irradiation*", Nakamura, Kazutaka and Kitajima, M.: Appl. Phys. Lett. **59** (1991), 1550;

"*Ion-Irradiation Effects on the Phonon Correlation Length of Graphite Studied by Raman Spectroscopy*", Phys. Rev. **44** (1991), Dec. 1 in press.

"*Time-Resolved Raman Study on Graphite under Ion irradiation*", Kitajima, M., and Nakamura, Kazutaka: Proc. the 9th ICRR, June 1991.

105 Development of Low Activation Materials

Apr. 1987~Mar. 1992

Noda, T.

2nd Research Group

Project Description

The use of **low activation materials** is one of key issues in fusion reactors from the viewpoint of reactor safety, waste management, and environmental aspects. The primary obectives of the program are (1) selection and design of low activation materials and (2) materials development including **iron-base alloys**, refractory alloys, and **ceramics composites**. The program contains the following main subjects.

(1) Selection and design of low activation materials
- development of the simulation code calculating **induced radioactivity** of materials
- evaluation of materials

(2) materials development
- development of reduced activation iron base austenitic and ferritic steels with high-temperature strength and toughness
- development of new processes for ceramics composites with a high purity and favorable mechanical properties

Major Products

The simulation code, IRAC, calculating transmutation and induced activity, and decay heat of elements and alloys under various neutron irradiation conditions covering thermal to 14MeV neutrons was developed. Based on the evaluation of induced activity, reduced activation iron base alloys such as **Fe-10Cr-30Mn** and **Fe-9Cr-1W-0.2V** which exceeded commercial heat-resisting steels in strength

and toughness were developed. The **CVI** method was applied to process ceramics composites and **carbon fiber/SiC composite** with a purity >99.99% and favorable mechanical properties could be obtained. Low temperature synthesis of SiC using **laser CVD** is being studied.

Related papers

" *Materials Selection for Reduced Activation of Fusion Reactors* ", Noda, T., Araki, H., Abe, F., and Okada, M.: J. Nucl. Mat., **155–157** (1988) 581–584.

" *Optimization of Reduced Activation Ferritic Steels* ", Abe, F., Noda, T., Araki, H., and Okada, M.: Reduced Activation Materials for Fusion Reactors, STP-1047, (1990) 130–139.

" *Carbon Fiber/SiC Composite for Reduced Activation* ", Noda, T., Araki, H., Abe, F., and Okada, M.: J. Nucl. Mat., **179–81** (1991) 379–382.

106 Research on Distributed Database for Advanced Nuclear Materials

Apr. 1990~Mar. 1996

Fujita, M.

2nd Research Group

Materials research on fundamental technologies, which could bring about technical breakthroughs in many areas of interest to nuclear industry, is being carried out at national laboratories. It is desirable to mutually utilize results of new and established research being done by are scientists and engineers to promote this project in a strategic way. Thus, a project named "Data-Free-Way" has been underway from April 1990 under the cooperation of National Research Institute for Metals (NRIM), Japan Atomic Energy Research Institute (JAERI) and Power Reactor and Nuclear Fuel Development Corporation (PNC. This project includesd the development and implementation of computerized and networked numeric/factual materials property data base easily accessible by engineers and scientists from their engineering workstations (EWS) with the minimum delay after each data acquisition. NRIM, JAERI and PNC have joined to perform this project and will construct the total system cooperatively. Each laboratory has already built a few materials data bases and will individually build additional material data bases of their specific fields to promote materials research fundamental technologies. In order to clarify real needs, the same type of software and hardware such as DBMS and EWS are used in all participating laboratories.
The schedule of the development of the Data-Free-Way System is as follows. The design of pilot system starts in 1990, a **network**, for transmission of the data in the pilot data bases was connected among NRIM, JAERI and PNC. In 1992, the national Research Laboratory of Metrology (NRLM) and Ship Research Institute (SRI) will join in the project and start to build the data base on fundamental materials. This system will be established within five years and utilized mutually by many engineers and scientists.
Many material research laboratories have joined to create the Data-Free-Way System. The main concern in developing this system is to share fresh and stimulating information for the development of new nuclear materials verified through matured materials technologies.

107 R & D of Advanced Heat-Resistant Structural Materials for Very High Temperature Gas-cooled Reactors

Apr. 1990~Mar. 1995

Tanabe, T.

2nd Research Group

R & D of **heat-resistant structural materials** for intermediate heat exchangers of **very high temperature gas-cooled reactors** is being carried out. The R & D has the following two aims.
(1) To develop new materials which have better high temperature mechanical properties including creep rupture properties than those of the existing materials (e.g. oxide dispersion strengthened superalloys) at very high temperatures (up to 1100°C) in the primary coolant environment of the very high temperature gas-cooled reactors (helium containing impurity gases such as H_2, CH_4, CO, etc.).
(2) To develop new methods and technologies of materials evaluation applicable up to 1100°C. These include test procedures at very high temperatures, analysis of static and dynamic **crack growth behaviour** from the view-point of **environemtnal effects** and/or **microstructures** of the materials, and **life prediction** and **residual life estimation** methods.

Materials for environmental performance

108 Study on Improvement of Metallic Biomaterials

Apr. 1989~Mar. 1992

Hoshino, A.

Physical Properties Division

Metallic biomaterials are susceptible to degradation in human bodies by biomechanical and biological factors, and the biodegradation appears as crevice corrosion, **fretting corrosion** or **corrosion fatigue**. In this

study, the fretting corrosion and corrosion fatigue tests of stainless steels and titanium alloys which are widely used for biomedical implant materials, are performed in a simulated body fluids environment in order to clarify the influence of materials factors on degradation.
A fretting corrosion testing apparatus of the Pin-on-Flat type was constructed for *in vitro* testing of the modified stainless steels whose repassivation potentials for crevice corrosion were evaluated previously in order to improve and replace the 316 type stainless steels.
The effects of addition of secondary components such as Si, Al, Nb and Fe on the corrosion fatigue behaviour of titanium are also tested by using tensile specimens in artificial physiological saline solution.
The purpose of this study is to develop the advanced biomedical titanium alloys which shows favorable fretting and fatigue resistance.

109 Fundamental Study of Microstructures and Properties to Develop High Performance Materials for Severe Environments

Apr. 1990~Mar. 1997
Yamazaki, M.
Materials Design Division

The research is a part of a national research project to develop various **heat-resisting materials** to withstand such severe environments as are encountered in space-planes, coal-gasifiers etc. This particular part of the research is aimed at establishing fundamentals required for developing materials based on intermetallic compounds or other materials. Current research is concerned with aluminides of titanium and niobium.

110 Development of Materials Design Techniques Concerned with Mechano-Chemical Attack of Light-Weight High-Temperature Materials

Apr. 1989~Mar. 1994
Tomizuka, I
Materials Design Division

The fesasibility of material design techniques is studied in the following four fields:
(1) Studies are made on the fesibility of the material design technique for environmental degradation of **nickel-base alloys** and **nickel-aluminide**-based intermetalloids which is based on the systematic analysis of the data obtained from dry oxidation, wet oxidation, hot corrosion and burner-rig tests.
(2) Studies are made on the feasibility of the **material design** techniques for stress/oxidation degradation of **C/C-composite** materials based on gravimetrical analysis of related materials in air and gas mixtures.
(3) Basic studies are carried out to develop a material design technique feasible for stress rupture of nickel-base ODS alloys.
(4) Basic studies are carried out to develop a material design technique feasible for fatigue rupture of nickel-base aluminide materials.

Related papers

"*Effects of Manufacturing Process in Hot-Corrosion Behaviour of a Ni-base Superalloy*", Numata H. et al.: Corros. Eng. **38** (1989), 293–301.
"*Modification of Ni-base ODS Superalloys*", Kawasaki Y. et al.: in E. Bachelet et al (ed.) High Temperature Materials for Power Engineering 1990.
"*High-temperature Creep-rupture Testing of a Carbon/Carbon Composite Material in Air*", Miyazaki A. et al.: Zairyo-Kagaku, **27** (1990), 329–336 (in Japanese).

111 Corrosion Resistance of Synthetic Barriers in Geological Disposal of Spent Nuclear Fuels

Apr. 1988~Mar. 1992
Kodama, T.
Environmental Performance Division

Objective

In the **nuclear fuel cycle** system proposed by Atomic Energy Commission of Japan, high level nuclear waste separated from spent fuels after reprocessing is molded into metallic containers in the form of solidified glass which is to be disposed of in deep geological repositories. In this system, radioactive waste must be isolated safely until radioactivity has been reduced to a nonhazardous level and a durability of 1000 years is expected for metallic containers. In advance of the proposed construction of a nuclear disposal and repository in the forthcoming century, it is desirable that sufficient data be prepared for the guarantee of nuclear safety. For this purpose we have studied corrosion and life prediction of metals for the use of nuclear waste disposal containers.
Progress in Research
(1) Corrosion monitoring in simulated geological environment
Several electrochemical techniques have been applied for the determination of the corrosion rate of mild steels and stainless steel in a simulated environment of a geological disposal site. Among tested techniques both electrochemical impedance and galvanostatic pulse methods showed good agreement between corrosion data determined by the electrochemical method any by mass loss. These methods eliminate ohmic drop caused during

electrochemical polarization.
(2) Water chemistry in geological environments
For the description of chemical environments of geological disposal sites, acidity in terms of pH and redox parameter in terms of Eh are thought to be the most fundamental variables which affect corrosion of metals, dissolution of glass, and adsorption of fission products to minerals and clays. For predicting these parameters in a geological environment, we have developed a new computer code for the automatic construction of chemical potential diagrams including Eh-pH diagram. In order to adopt this computer code to the nuclear waste disposal problem, it is necessary to prepare a database of thermochemistry for fission products and actinide elements.

Related papers

"*Automatic Construction of Chemical Potential Diagrams*", Kodama, T.: Proceedings of Fushoku-Boshoku '88 (1988)

"*Corrosion Resistance of Synthetic Barrier in Geologicalisposal of Spent Nuclear Fuels-I*", Kodama, T., Kurosawa, K.: Report on Atomic Energy Researches of Governmental Institutes, vol. 29, 18–1 (1990).

112 Corrosion Resistance of Coated Metals in Natural Environment

Apr. 1989~Mar. 1992

Kodama, T.

Environmental Performance Division

Objective

As a part of the Japan-ASEAN Cooperation on Science and Technology, which is in progress under the auspices of the Japan International Cooperation Agency (JICA), NRIM has been in charge of supporting projects on atmospheric corrosion carried out at national research institutes in Thailand and the Philippines by participating in the planning of experiments and technical discussion and by dispatching experts to these countries. In parallel with the overseas experiments on atmospheric corrosion, laboratory works on metal/polymer adhesion, mass transfer through paint films and surface treatment have been carried out at NRIM with participants from ASEAN countries.

Progress in Research

(1) Atmospheric Corrosion in Tropical Areas
In Thailand and the Philippines, atmospheric exposure tests are in progress for bare metals and steels with organic and inogranic coatings at several exposure sites selected from different atmospheric conditions. In parallel with the exposure tests, meteorological and pollution data are collected periodically. At NRIM, a new system of atmospheric corrosion monitoring has been developed. Monitoring data are compared with those of the corrosion rate at the tropical exposure sites.
(2) Chemical reaction at metal/coating interfaces
Using twin-compartment cells and new detecting system, ionic permeation through organic coatings has been measured using detached and attached films. The apparent diffusion coefficients of aggressive ions was compared with that of water and oxygen. The adhesion of paint films was measured before and after irradiation with ultraviolet light. Change in chemical bonding was also analyzed by FTIR.
(3) Corrosion resistance of surface treated aluminum alloys
Aluminum die-cast alloys were anodized in concentrated sulfuric acid followed by cathodic deposition of metals and alloys within pores of anodized oxide film. Microstructures of the newly developed surface layer have been investigated by surface analysis methods.

Related papers

"*Effect of pH of an Na_2MoO_4-H_3PO_4 Type Aqueous Solution on the Formation of Chemical Conversion Coating on Steels*", Kurosawa, K. and Fukushima, T.: Corro. Sci. **29** (1989) 1103–1114.

"*A Study on the Repassivation of Ions through Paint Films*", Kodama, T. and Habana, C. R.: 7th Asian Pacific Corrosion Control Conference (1991).

Processing

Separation and synthesis

113 Project Research on Purification Techniques of Rare Metals in View of Finding New Materials Properties (Phase II)

Apr. 1990~Mar. 1991

Furubayashi, E.

Chemical Processing Division

In succession to the previous study (Phase I: Apr. 1987-Mar. 1990) of the same title, the purification of rare metals, particularly **rare earth metals**, and the evaluation of their purity are being studied comprehensively in cooperation with some industrial laboratories and universities. The materials thus obtained are found to have much lower contents of oxygen or other interstitial elements, and such materials are used to study intrinsic physical properties of rare earth metals having higher purities than before.
(1) Superconducting Properties of Y-Oxides: Effects

of Ferromagnetic impurities like Fe, Ni, Co substituting Cu in Y-Oxides on the superconducting properties have been studied. From the measurements of the Mössbauer effect and magnetic susceptibities. The superconducting state has been found to coexist with the spin glass state.
(2) Reduction Behavior of Interstitial Impurities in Gd, Tb, Dy and La by **Electro-Transport** Method: Oxygen in these metals has been found to migrate intensively toward the anode by chemical analysis and microscope observation. But the migration of nitrogen or carbon are not well recognized.
(3) Mutual Separation of Chemically Similar Rare-Earth Metals by Laser Photo-Ionization (laser Materials Purification (LMP)) Method: A tunable Laser beam has been directed to the mixed atomic beam of Nd and Pr from a Nd-Pr alloy, and the method of selective ionization and extraction of Nd atoms has been studied. Multiple-step resonance excitation processes for Nd atoms have been clarified in collaboration with Nippon Steel Corporation. The method has been successfully applied to the efficient separation of Nd from Pr and to obtain purified Nd films.
A part of this article is presented in more detail at the Research Topics.

114 Development of Extraction Techniques of Gallium and Other Rare Metals

Apr. 1987~Mar. 1992

Fukuzawa, A.
Chemical Processing Division

Iron ore produced in the Panzhihua area in south-western China's Sichuan Province is famous for the typical vanadium bearing titaniferrous magnetite and in Panzhihua Iron and Steel Co. vanadium is recovered from the spray steelmaking method in the hot metal pretreatment stage as a byproduct. Besides, the ititanium rich part is separated during the dressing process. This ore also contains rare metals such as nickel, chromium, cobalt or gallium.
To recover these rare metals, especially for gallium, we, NRIM and the University of Science and Technology, Beijing, have started a joint research project in 1986, and this is the final year of this project. **Gallium** is one of the most important elements for semiconductors such as Ga-As, magnetic bubble memory and others.
Gallium, which content in **iron ore** is 40 to 50 ppm, is a little enriched in the blast furnace during reduction to values as high as 70 to 80 ppm in Panzhihua Iron and Steel Co. In the steelmaking stage gallium is partially oxidized when the hot metal is treated for vanadium extraction, but the most of gallium is retained in the molten steel. Therefore, our research work covered all of the **iron and steelmaking** processes from iron ore to molten steel to investigate the suitable points in the process line to recover gallium effectively. Then the following 3 targetss were selected and the results obtained by now are as follows.
Mineral processing: By EPMA observation gallium is scattered in the magnetite as an inclusion with alumina and magnesia, and not found in gangue and the titanium base matrix. As this inclusion is non magnetic, iron and gallium oxides were divided by a magnetic separator after fine grinding. If an economical dressing method can be applied, it may be possible to obtain gallium concentrate directly.
Extraction from vanadium slag: As gallium is also extracted from hot metal into the vanadium containing slag in concentrations as much as 150 t0 200 ppm, a wet extraction method has been applied after soda roasting. At first, gallium and vanadium were extracted from soda slag into a NaOH solution, then both elements were effectively separated by solvent extraction method.
Recovery by flux: Since from the preliminary tests, flux with CaO has shown a potential to retain gallium oxide in slag, simulataneous extraction of gallium and vanadium from hot metal is undertaken. THis process is more advantageous for vanadium recovery than the conventional process from the points of not to make spinel with high melting point and less soda pollution problem.

115 New Synthetic Methods of Metallophthalocyanine Complexes

Apr. 1988~Mar. 1991

Isago, H.
Chemical Processing Division

Phthalocyanine and its related compounds containing metal elements have been known as one of the most important organic pigments so far and have also been intensively studied as a group of new materials in recent years. In this laboratory, thin films of bis-(phthalocyaninato)praseodymium(III) complex, possessing a sandwich-type structure of phthalocyanine chromophore, has been found to be electrochromic. The purpose of this research work is mainly aimed at understanding the properties of a series of bis(phthalocyaninato)lanthanoid(III) complex, $Ln(pc)_2$·, as a molecular material.
Thin films of all the complexes initially showed a green color, and showed blue and red colors when electrochemically reduced and oxidized, respectively. Similar spectral changes were also observed in organic solvents by chemical reduction and oxidation. Therefore, the **electrochromic** properties

are intrinsic in the complex molecule and not due to integration of the molecules.
Similar blue-green color changes were observed also on some $Ln(pc)_2$· in organic solvents. These complexes showed green colors in solvents with a small donor number (benzene for example), and showed blue colors in solvents with a large donor number (triethylamine for example). These complexes becomes less **solvatochromic** with an increase in atomic number of the lanthanoid(III) ion (i.e., with a decrease in an ionic radius). Only $Ce(pc)_2$ was exceptional and showed a blue color in solvents with a small donor number.
The green species were ESR active in solid state and in organic solvents with a small donor number, showing the species to be stable as a neutral radical form. Therefore, a hole is created in the molecule. The electron deficiency makes the complex an electron acceptor and is considered to cause the solvatochromism mentioned above.

(116) Fundamental Study on Preparation and Characterization of the Metal Complexes Possessing a Peculiar Molecular Structure

Apr. 1991~Mar. 1994
Isago, H.
Chemical Processing Division

Phthalocyanine and its related compounds containing metal elements have been known as one of the most important organic pigments so far and have also been intensively studied as a group of new materials in recent years. Indeed, it has been found in this laboratory that bis(phthalocyaninato)lanthanoid(III) complexes exhibited remarkable electrochromic properties in organic solvents and in solid state as thin film. In these compounds, a hole is created in the complex molecule.
This research work consists of the following two subjects; 1) preparation and characterization of the bis(phthalocyaninator)cerium complex and its derivatives which show exceptional properties among a series of bis(phthanlocyaninato)lanthanoid(III) complexes and 2) an attempt to prepare the first **bismuth** complex ligating a phthalocyaninate or phthalocyaninates.
In the former subject, our interest is mainly directed towards the on behavior of the 4f electron of the **cerium** ion in the bis(phthalocyaninato)cerium complex. In this complex, the cerium is considered to be in mixed valence state between trivalent and tetravalent as suggested by electronic, infrared, ESR, and XPS spectra. It is likely that the 4f orbital of the cerium is largely hybridized with a phthalocyanine π orbital. In the latter subject, it is of interest whether the **bismuth-phthalocyanine** complex has a similar structure to those of the bis(phthalocyaninato)lanthanoid(III) complexes and whether the bismuth complex shows similar properties. It is because that a bismuth(III) ion has almost an identical ionic radius with those of lanthanoid(III) ions possessing the same coordination number. Moreover, coordination chemistry of the phthalocyanine complex of the other 5B elements in the periodic table as well as bismuth has been scarcely studied and hence a new field of chemistry and material science is expected to be developed.

[117] Rapid Solidification Process of Immiscible Alloys

Apr. 1988~Mar. 1991
Omori, G.
Advanced Materials Processing Division

For the purpose of obtaining basic information on the allying of **immiscible alloys**, experiments with **hypermonotectic Al-Pb alloys** have been performed by rapid cooling from the single liquid phase (above the **miscibility gap**).
In the present work, Al-Pb alloys were melted in alumina or graphite crucibles under argon atmosphere by a 10 kHz induction furnace. The temperature was measured directly by the use of a type R thermocouple and the melt was heated to a temperature above the maximum temperature of the miscibility gap and then chill cast into water-cooled copper or ferrite molds of the size of W: 150×H: 50–90×T: 5–20 mm.
The cooling rate and solidification process were measured by a thermal analysis apparatus for the cooling.
The L_1 phase (Al-rich phase) product spherically grew in volume. The dotted like L_2 phase (Pb-rich phase) which separated simultaneously with the formation of L_1 phase at the miscibility gap from the melt arrayed radiately from the center of the spherical L_1 phase. The lead particles of L_2 phase were homogeneously distributed in the aluminium rich matrix of L_1 phase and the gravity segregation could be prevented when cooling rate exceeded 8×10^2 K/s.
The shapes of the lead particles were approximately spherical. The rate of cooling through the temperature ranges of the single liquid phase and the two liquid phase decreased with increasing lead content; the distribution and size of the lead particles were quite sensitive to the rate of cooling.
It was found that the hypermonotectic Al-Pb alloys could be used for the beariing metal or superconductor.

(118) Alloying Method Using Decomposition of Metal Halides

Apr. 1991~Mar. 1994
Omori, G.
Advanced Materials Processing Division

In order to obtain basic information on an **alloying** method using **decomposition** phenomena of **metal halides**, an investigation is conducted on the merits of several **zirconium** containing materials for the alloying of this metal to **magnesium**.
Magnesium alloys containing zirconium metal have been used extensively in applications requiring high strength, because zirconium is an important grain refiner in magnesium. There are, however, many problems in the development of a practical alloying procedure. Elemental zirconium is not an efficient agent to use because of its high melting point and high oxidation tendency. So, prior to considering present procedures for the introducing zirconium into magnesium, it is necessary to examine the various possibile processes.
In the present investigation, an attempt is made to introduce zirconium into magnesium at high temperature by alloying with zirconium metal powder or at low temperature by a salt reduction process using various zirconium halides or complex halides.
The effort in this work is focused on the use of reducible zirconium salts; the mechanisms of the reaction between zirconium salts and magnesium are studied and thermoanalytical experiments are carried out as well.
The functional characteristics of the alloys are investigated by measurements of mechanical, physical and chemical properties.

Gaseous process

119 Fabrication of Oxide Superconductor Films by Means of Reactive Alternate Deposition Method

Apr. 1988~Mar. 1994
Nakamura, K.
Surface and Interface Division

Since the discovery of **high Tc oxide superconductors** extensive efforts have been made by a number of research groups to fabricate thin films of the oxides, especially Y and Bi Based superconductors, available for electronic deveices such as Josephson junctions. Our initial target in this project was to control the number of CuO layers, n, in a unit cell of $Bi_2Sr_2Ca_{n-1}Cu_nO_{2+4}$. An **Alternate deposition** method using a multitarget sputtering technique was applied successfully to obtain films with an n value ranging from 1 to 5. A High Tc phase with n=3 (Tc zero 10 K) can be also obtained by doping Pb into amorphous BiSrCaCuO film. The crystal quality of the films is characterized by means of X-ray diffraction, High resolution TEM and Rutherford backscattering (**RBS**) methods. In these methods, the RBS channeling measurement is extensively used to characterize the epitaxy of the films as well as the variation of composition with depth.
To investigate the growth mechanism of the oxide film during evaporation in the **reactive MBS** process, we have recently developed a system consisting of energy dispersive X-ray spectroscopy combined with reflective high energy electron diffraction. Using this system, we have succeed to detect the variation of surface cmposition and surface structure simultaneously during the evaporation process. To fabircate films with super/normal and super/insulator **superlattices** and to characerize them are two other important targets of our projejct.

Related papers
"*Formation of Thermally Stable Multilayered BSCCO Films with 2223, 2234 and 2245 Structures*", Nakamura, K., Sato, J., Ogawa, K.: Jpn. J. Appl. Phys., **29** (1990), L77–L80.
"*Growth of the 2223 Phase in BSCCO Oxide Films under a Controlled Pb Potential* ", Hayakawa, H., Kaise, M., Nakamura, K., and Ogawa, K.: Jpn. J. Appl. PHys., **28** (1989), L967–L969.
"*Cross-Sectional High-Resolution TEM Studies of Superconducting Oxide Films of the Bi System*", Ikeda, S., Sato, J., and Nakamura, K.: Material Transcations, Jim, **31** (1990), 602–607.

Liquid state process

120 Fundamental Study on the Fused Metal-Slag Reaction by Magnetic Leviation

Apr. 1990~Mar. 1991
Fukuzawa, A.
Chemical Processing Division

High temperature **equilibrium** measurements of **slag-metal reaction** always have a restriction as to the selection of container (crucible) material, and the obtained data are limited by the condition that the slag is saturated with the container material, such as alumina, magnesia or calcia. On the contrary, the actual slag in a furnace like LD converter is not saturated with the container material, and its composition is changing from time to time. Therefore, it has been strongly required to obtain the equilibrium data of the actual slag-metal reaction to estimate quantitatively whether it is in equilibrium or how far from the equilibrium.
To meet this demand, the cold crucible type **levitation process**, has recently been proposed to

melt metal of 100 gram order and NRIM is developing this technology with 3, 30 and 200kHz electric sources. The cold crucible method is a promising technology to melt refractory metals or reactive metals without interference from the surrounding material.
This research work has started to apply this technology for equilibrium measurement. However, to carry out this experiment heating equipment to melt slag, less conductive material, and to keep its temperature the same as that of the metal became necessary. After consideration, induction melting equipment with 4MHz has been installed and tested its potential to melt slag. The outline of this melter is as follows. Power: 7kW max. Oscillator: Vacuum tube type. COli: 4.5 cm ID, 7 cm L and 5 turns. After tests it became clear that not only semiconducting materials like silicon and FeO, but also slags with the resistance of Ωcm order can be melted in several minutes with this equipment. For further study, the coupling of this electric source with the above mentioned 200kHz source is considered to get simultaneous levitation of slag and metal for equilibrium experiments.
The cooperative research work with the Royal Institute of Technology, Sweden, has been performed in searching the appropriate slag system for the induction melting type equilibrium study by the use of THermo-Calc, a data base for metals and ceramics.

(121) Purification of Metals by Non-Contacting Melting Method

Apr. 1991~Mar. 1994
Fukuzawa, A.
Chemical Processing Division

The purpose of this study is to develop the **levitation melting** process of reactive metals and refractory metals using the **cold curcible** type non-contacting induction furnace. Up to now, the reaction between metal and crucible has made it difficult to purify the reactive metals and there has been no material for homogeneous melting of refractory metals. The cold crucible type melting method will solve these problems.
In these two years, we have made various kinds of trials on the cold crucible type non-contact induction furnace and many fundamental results concerning the cold crucible have been obtained.
In this term we are going to carry out further study by setting the cold crucible in an atmosphere controlling vessel for optimum levitating and purification of molten metals such as titanium and its alloys. The shape of the cold crucible, the high frequency coil and the electric output power will be examined in order to obtain the optimum levitating conditions in this vessel.
Next, we are going to develop the levitation technique concerning high-purification melting of reactive metals and refractory metals.

[122] Fundamental Study on the Levitation Technique for Melting and Solidification

Apr. 1990~Mar. 1991
Sakuraya, K.
Chemical Processing Division

The purpose of this study is to present the basic conditions for the **cold crucible** type non-contacting induction furnace. The fundamental condition for **levitation melting** was investigated concerning the shape of cold crucibles, the shape of the induction coils, the relative position between crucibles and coils and the output power of electricity. The measurement of the levitation force was carried out using a metal ball which was suspended in the cold crucible. The effect of the number of segments, the width of the slit, the number of the coil turns, the shape of the coil cross section, the relative position between crucibles and coils, and the material of the metal ball were investigated. The influence of frequency on the leviation force was also investigated.
After the measurement of the levitation force, aluminum and aluminum-copper alloy were melted in the cold crucible. The relation between levitating molten metal shapes and the cold crucible shapes was inquired. As the results showed, levitating molten metal shapes were influenced by the number of segments, the width of the slits and the hole diameter of the cold crucible.
The electromagnetic levitation melting by the cold crucible technique will make a contribution to melting refractory metals and reactive metals, which have the problem of crucible material, and to purification of the metals and alloys.

[123] Unidirectional Solidification Technology for Various Cross-Sectional Bars

Apr. 1988~Mar. 1991
Sato, A.
Advanced Materials Processing Division

Continuous casting processes are being studied and developed for the purpose of cost reduction of products by manufacturing **near-net shape cast materials**, directly from molten metals. The cost of near-net shape cast materials can be reduced by improving the efficiency of materials, energy and labor utilization and by increasing yeidls. Various processes of continuous

casting have been proposed and the downward and the horizontal continuous casting process are now widely used for both non-ferrous and ferrous alloys. Research on the **upward continuous casting** processes has been very scarce. After examining research on the upward continuous casting process reported up to the present, an attempt was made in this work to study, a **moldless upward continuous casting** process which has the following advantages: (a) Full **automation** can be realized by a program. (b) Small size cast materials can be easily manufactured. (c) Near-net shape materials, such as tapered rods, can be produced, (d) Cast materials composed of a grain/grains solidified completely unidirectionally, (e) Purification by solidification can be realized.
An apparatus for this process was constructed, and experiments using aluminum and its alloys were carried out. Round rods having tapers can be produced without formers on the surface of molten metals. Rods having various cross-sectional configurations and also having longitudinal tapers can be produced by this process using formers on the surface of molten metal. Solidification types of alloys have little effect on the production of rods, but their heat conductivity has a great effect on the size of cast strands.

Related papers

"*Trial production of aluminum rods by a moldless upward continuous casting process*", Sato, A., Osawa, Y., and Aragane, G.: Mater. Trans., JIM, **30** (1989), 55–83.

"*Production of Al-Cu and Al-Si alloy by a moldless upward continuous casting process*", Sato, A., Osawa, Y., and Aragane, G.: Mater. Trans., JIM, **32** (1991), 77–83.

(124) Solidification Processing for Fine-Grain Structure Materials

Apr. 1991~Mar. 1994

Sato, A.

Advanced Materials Processing Division

Many kinds of materials composed of various grain structures can be produced by **solidification processing**. Grain structures can be roughly divided into three groups. Firstly, there is the coarse-grain structure, or a single-crystal structure in the extreme case. Secondly, a **fine grain structure** can be found, or an amorphous structure in the extreme case. Lastly, a usual poly-crystal structure as found in conventional castings. The coarse-grain structure or the single-crystal structure can be obtained by a slow unidirectional solidification, while the fine-grain structure or the amorphous structure can be realized by a **rapid solidification**. The usual poly-crystal structure is acquired at a common solidification rate.
Rods, Composed of several grains solidified completely unidfirectionally from its one end to its other end, have been produced by the moldless upward continuous casting process studied so eagerly for the last several years. These rods, however, have not found any application, although they are expected to be used for various future purposes. On the other hand, materials composed of the fine-grain structures or the amorphous structure are now being used for diversified purposes. Therefore, it is concluded that research on production of materials composed of the fine-grain structure as well as those composed of the coarse-grain one should be performed.
The research on production of ingots composed of the fine-grain structure is being carried on by a rapid solidification process along with **vigorous agitation**. An apparatus for this process is being constructed, and experimetns using aluminum and its alloys be executed as soon as possible.

[125] Stirring Technology of Melts in Microgravity Environment

Apr. 1990~Mar. 1991

Sato, A.

Advanced Materials Processing Division

The discovery of **new functions of materials** is one of the most important aims of research and development in materials science. **Materials processing** on a micro scale is essential in the discovery of new functions of materials. A micro-gravity environment has the following special merits: (1) the liquid can be kept without containers. (2) There is no convection by the gravity. (3) There is no floating and no sedimentation by the density difference of mate-rials. (4) The surface tension becomes prominent due to the absence of static pressure. The research and development of materials processing in the **microgravity environment** can take advantage of those merits. Fundamental principles of materials processing can be clarified and new materials processings can be invented by experiments in the microgravity environment.
On the other hand, the homogenization of inhomogeneous melts in the microgravity environment is rather difficult because of the above mentioned special merits. In order to perform valuable experiments of materials processing in the microgravity environment, a **stirring technology** of melts and at the same time a **stopping technology** of fluid motion should be developed.
In this survey research, the stirring and the stopping technologies were divided into five subthemes according to their methods: (1) Mechanical/direct

stirring and stopping. (2) Stirring and stopping by sound/supersonic vibrations. (3) Electro-magnetic stirring and stopping. (4) Stirring and stopping by marangoni convection and other forces. (5) Stirring and stopping by an artificial gravity. Fifty copies of report were made and distributed to persons and organizations concerned.

126 Physical, Chemical and Biological Phenomena under Microgravity Environment

Apr. 1987~Mar. 1992
Yamazaki, M.
Materials Design Division

The discovery of materials having new functions is one of the most important objects of research and delopment in materials science. Materials processing on a micro scale is essential in the discovery of new functions of materials. A **microgravity environment** has some special merits and materials processings under these conditions can take advantages of its merits.
This research has many sub-themes and is being carried out by many researchers in government research institutes, universities and private companies. Three sub-themes are being performed in our institute and described briefly below.
(1) Effect of the fluid flow in melts and solutions on the crystal grown: Observation of an embryo in a melt or a solution just before its **solidification** or its crystallization is attempted using an ultramicroscope. At the same time, the crystallization of indium antimonide is observed dynamically using X-ray diffraction topography.
(2) Formation mechanisms of monotectic and eutectic composite structures: Binary **eutectic alloys** of Ag-Cu or multi-component alloys of Al-Cu with additions of Ba, Yb, Eu, etc. are crystallized by rapid or directional solidification on the earth and in the microgravity environment. Effects of gravity on structures obtained are examined and high T_c superconductors are expected to be composed using the above alloys.
(3) Homogeneous dispersion mechanism of particles in composite materials: Effect of the **mechanical alloying** time of particle **dispersion strengthened alloys** of Cu-W and Cu-Al_2O_3 on the refinement and the modification of the interface is examiend. The alloys are melted and solidified on the earth and samples for experiments in the microgravity environment will be prepared.

Solid state process

127 Materials Properties Induced by Transformation Superplasticity

Apr. 1990~Mar. 1993
Nakajima, H.
Advanced Materials Processing Division

Transformation superplasticity has two major features. The first is a large capacity for plastic flow which can be utilized in the forming process, as well as fine-grained superplasticity. The second is the effect on the various properties of materials. The main purpose of this investigation is to elucidate the change of the mechanical properties of carbon and alloy steels which have been subjected to deformation by transformation superplasticity. Specimens are heated and cooled over the transformation temperature range under constant tensile load, using a creep testing apparatus. The change of the length along the axis of the specimen during heating and cooling is measured with a dilatometer. After superplastic deforming, the **metallographical and mechanical properties** of the test specimens will be examined.

128 Metallurgical Analysis of Cutting Region

Apr. 1989~Mar. 1992
Yamamoto, S.
Advanced Materials Processing Division

The deformation behavior of the **chip shear region** in machining of various materials is being investigated from a metallurgical point of view, using the mciro-cutting device.
Figure shows the cutting region obtained by use of a quick stop device and the cutting direction in **micro-cutting**. When the cutting region was micro-cutted (depth of cut: about 10 μm) in the direction of the arrow, an increase in the **cutting force** was observed at the starting line of the shear region and

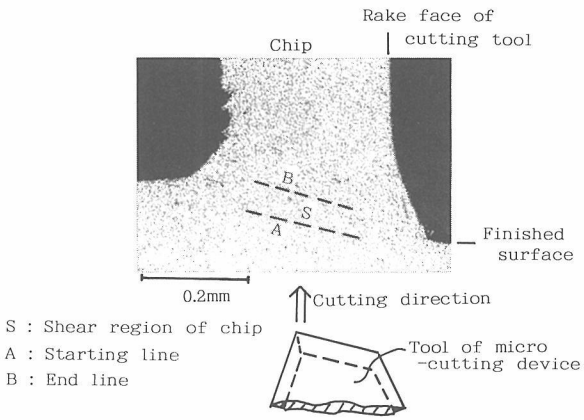

Figure Appearance of micro-cutting region.

it disappeared at the end line.
In micro-cutting of samples having various hardnesses, the end line of the shear region of harder samples coincided almost with the line of the shear angle (ϕ) geometrically calculated from the chip thickness. In softer samples, however, the starting line was located almost at the line of the shear angle (ϕ).
A very thin deformed layer was formed in micro-machining of test pieces for **fatigue test**. The effect of the **deformed layer** on the fatigue property of these test pieces is examined.

Powder processing

(129) Coating of Fine Powders by CVD Technique in Fluidized Bed

Apr. 1991~Mar. 1994
Itagaki, T.
Materials Design Division

This research is aimed at preparing various types of very fine powders coated with a very thin layer of a second substance. The fine coated powders have various advantages when they are used for sintering. For example, if the powder is coated with a sintering agent, the sintering will finish in much shorter time or will be performed at a lower temperature as compared with the case when the agent is added as a powder, because the agent is much more finely dispersed. When an alloying element is coated on powder of a refaractory metal, the alloying will be more homogeneous for the same reason.
A chemical vapour deposition technique in a **fluidized bed** is planned to be applied to make coating layers comprising ceramic materials.
The first experimnt will be concerned with coating **hafnium carbide** on **tungsten powder**. The particle size of the powder will be 1–10 microns, and the thickness of the coated layer will be several nanometers. Based on the research work performed until last year, we have been convinced that coating by **CVD** technique in fluidized bed is technically feasible. However, we have not yet succeeded in controlling the thickness of the coated layer. The obtained powder will be sintered at a high temperature to obtain tungsten alloy dispersed with hafnium carbide.
The next experiments will be concerned with coating of sintering agent on ceramics like silicon nitride or silicon carbide. This coating will be more difficult because the density of the powder is much smaller than that in the first experiments.

(130) Preparation of Superconducting Raw Materials Having Controlled Quality

Apr. 1988~Mar. 1994
Hasegawa, R.
Materials Characterization Division

Four studies are included in this item.
(1) **Purification** of Chemically Active Elements for Superconductors: Rare earth metals usually contain much impurities of similar elements. In this study, such impurities are intended to be reduced by vaporization under high vacuum or by chemical separation. The final objective is to prepare an effective method to prepare the target materials for thin foils.
(2) Physical Properties and Consolidation Behavior of **Powders** Used for High Pressure Forming of Superconductors: Hot isostatic pressing and sintering behavior of oxide powder superconductors has been studied in view of obtaining low porosity solids with high superconducting critical current densities (Jc).
(3) Preparation and Characterization of Ultrafine Particles used for making **Oxide Superconductors**: The 'Reactive Plasma-metals Methods' developed in this Institute has been successfully applied to prepare elemental fine particles for constructing Bi-Sr-Ca-Cu-O superconductors.
(4) Preparation and Characterization of Superconducting Oxide Powders by a Radpid-Solidification Method: The 'Centrifugal Atomization Method' developed in this Institute has been applied directly to form Bi-Sr-Ca-Cu-O superconductor powders.

(131) Coating Formation by Molten and Electrified Powders

Apr. 1991~Mar. 1994
Kuroda, S.
Advanced Materials Processing Division

This research aims to clarify the **deposition phenomena** of molten particles onto solid surfaces with a special interest for spray deposition of coatings in mind. The collision of a high velocity molten particle onto a solid surface and the subsequent solidification are very fast and complicated phenomena, on which various coating processes such as plasma spraying are based. How a particle spreads and looses heat to the underlying solid seems to be critically dependent on the temperature and velocity of the impinging particle as well as on the surface state of the substrate. With the aid of a technique developed to measure the velocity and temperature of flying particles, morphology of quenched splats will be related to those parameters. The mechanical prop-

erty as well as the microstructure of thus formed **coating/substrate interface** will be examined using various mechanical testing methods and microscopic techniques such as TEM. In addition, the feasibility of employing electrostatic force to control the motion of fine powders will be examined.

Related papers

"*Monitoring of Thermally Sprayed Pawrticles Using Thermal Radiation*", Kuroda, S., Fukushima, T., Kitahara, S., Fujimori, H., Tomita, Y. and T. Horiuchi,: Proc. ITSC'89., London, June 1989, P86–1–P86–6.

"*The Quenching Stress in Thermally Sprayed Coatings*", Kuroda, S. and Clyne, T. W.: Thin Solid Films **200** (1991) 49–66.

"*The Origin and Quantification of the Quenching Stress Associated with Splat Cooling during Sprya Deposition*", Kuroda, S. and Clyne, T. W.: Proc. 2nd Plasma-Technik Symp., Lucerne, Vol. 3, (1991) 273–283.

132 Study on Combustion Synthesis

Apr. 1990~Mar. 1991

Kaieda, Y.

3rd Research Group

Basic Research of making intermetallic compounds and composite materials by **combustion synthesis** and the characterization of the synthesized materials is conducted in a cooperative project between some institutes in the U.S.A. and N.R.I.M. This cooperative project has been enhancing the basic study of combustion synthesis. The method of cooperation consists of inviting U.S. researchers to NRIM and sending researchers of NRIM to U.S.A. to conduct experiments, to engage in discussion and to exchange information on combustion synthesis. Professor Z.A. Munir, associate dean of University of Calfironia, Davis, was invited to NRIM in 1991 to do cooperative experiments and discussion of combustion synthesis. The study of combustion synthesis of intermetallic compounds, NiAl and its foils were carried out in this cooperative study.

133 Comprehensive Research and Development of Special Structural Ceramics Using Colloid Processing

Apr. 1990~Mar. 1993

Kaieda, Y.

3rd Research Group

Development of composite materials which have some useful functions is desired because there are some limitations in properties of single component materials. To control the composition and structure in microscopic regions of a composite material is possible in the conventional manufacturing process. However, it is difficult to make complicated and large components of composite materials by a conventional method. In this research, the **combustion synthesis** which uses powders as raw materials, their heat of formation and its propagation to make compound materials is used to make special structural compound composite materials. The characterization of the synthesized material was carried out. In fiscal year 1990, a typical high melting point compound, **WC**, was selected as a matrix material. Left side of Fig. 1 shows the formed mixed powder of tungsten and carbon. Right side of Fig. 1 shows the combustion synthesized WC. Figure 2 shows the X-ray diffraction pattern of WC made by combustion synthesis. Almost all peaks observed are WC's, but a trace of W_2C is also observed.

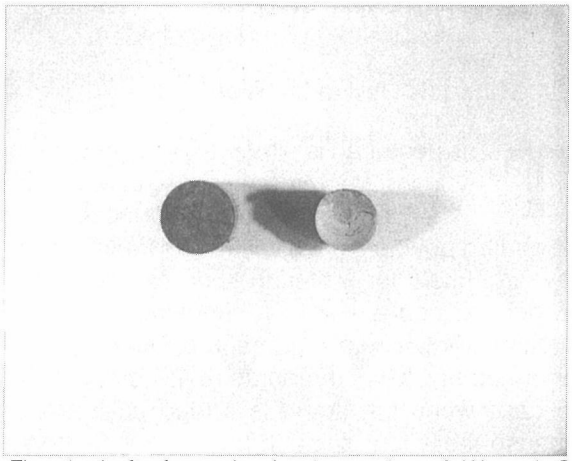

Fig. 1 Left: formed mixed powder of W and C. Right: WC synthesized by combustion synthesis.

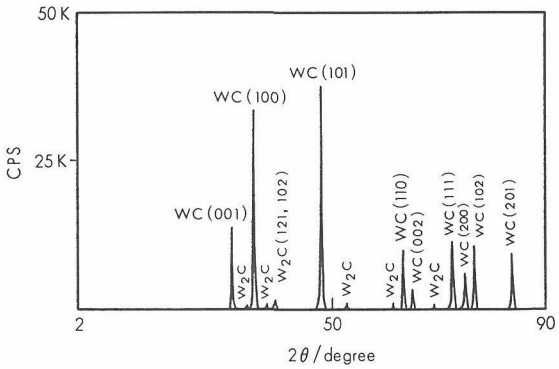

Fig. 2 X-ray diffraction pattern of WC synthesized by combustion synthesis.

134 Combustion Synthesis for Production of Intermetallic Compound

Apr. 1989~Mar. 1994

Kaieda, Y.

3rd Research Group

NiTi shape memory alloy is usually produced by a process including high frequency induction vacuum melting. The transformation temperature of the NiTi shape memory alloy is difficult to be controlled precisely because the martensitic transformation temperature changes by 10 K with a change of 0.1 mass % in Ni content. The NiTi intermetallic compound is synthesized by the **combustion synthesis** method, which is a newly developed manufacturing process, by controlling the content of Ni and Ti elemental powders. In the process, Ni and Ti powders are weighed and mixed to 50 atomic % of Ni by the dry ball mill. The mixed powder is filled in the graphite crucible and the top of the powder is ignited by heating with a tungsten heating coil in vacuum (10^{-4} Pa) or argon gas atmosphere. From then, the combustion synthesis of NiTi is self-propagating to the other end of the crucible. The synthesized NiTi is then sintered by a hot isostatic press (HIP). The HIP' ped NiTi is plastically worked to plate and wire. The ignition of the combustion synthesis is successful in high vacuum and argon gas atmosphere from room temperature to 873 K, and the chemical reaction is completely progpagated. 100% NiTi intermetallic compound is observed by the X-ray diffraction analysis in the combustion synthesized NiTi ignited at any temperature in the present experiment. As combustion-synthesized NiTi ingot is porous and the relative density is 50–60%, but after HIP'ping the relative density increased to 100%. The HIP'ped ingot is plastically worked with hot rolling, hot bar-rolling, hot and cold rotary-swaging and cold-drawing. When the oxygen content of the synthesized NiTi is about 0.5%, the 0.5 mm diameter wire can be obtained. However, when the oxygen content is under 0.07%, 0.09 mm diameter wire can be produced. The wire has a good **shape memory effect** and its shape memory temperature is about 370 K.

135 Production and Characterization of Advanced Powders

Apr. 1988~Mar. 1993

Yoshihara, K.

4th Research Group

This research consists of 6 sub-themes:
(1) Production of rapidly solidified alloy powders by **super high pressure liquid atomization**; Fine alloy powders of 5 micron average diameter are produced by high pressure water atomization. Their character and most suitable sintering conditions are investigated. These powders are expected to be used as raw material for metal injection molding.
(2) Synthesis and binding of **ultra fine composite particles**; Ni-TiN an Ni-TiO_2 ultra fine composite particles are synthesized by active-plasma-metal-reaction method or RF-plasma mehtod. Sintering characteristics, photo-catalytic characteristics and effects of synthesize conditions on their crystal structure are investigated. Hydroxyapatite powder produced by the sol-gel method is also investigated.
(3) Characterization of **ultra fine powders** and their sintered bodies; Surface chemistry, especially gas adsorption and desorption characteristics, are investigated by specially developed thermal desorption methods. Surface chemistry of ultra fine powders of Fe or Ni exposed in H_2O and/or 0 is clarified.
(4) Produciton of advanced powders by **centrifugal atomization**; Fundamentals of centrifugal atomization are investigated. The atomization mechanism and atomizing parameters are elucidated. The solidificated structure of atomized powders is also investigated. The importance of super-cooling is pointed out in the solidfication of centrfiugally atomized powders.
(5) Sintering of **metal-ceramics mixed powders**; Wettability and sintering characteristics of Cu-Al_2O_3, Cu-Y_2O_3 and Cu-W mixed powders are investigated. Physical properties of liquid-solid interfaces are measured from the vielw-point of controlling the liquid phase sintering.
(6) Reaction in metal thin film; Roll of surface free energy on the **rapid diffusion** and the formation of new phase in thin films is investigated by observing the reaction in Nb/Ti multi-thin-films in a vacuum.

Related papers

"*Slip Casting of Duplex Stainless Steel Fine Powders*", Takeda, T. and Minagawa, K.: J. Jpn Soc. Powder Powder Metall. *37* (1990), 198–202. (in Japanese).

"*Centrifugal Atomization of Iron-Rare Earth Alloys*", Halada, K., Suga, H. and Kiyama, T.: Materi. Trans. JIM, **31** (1990), 322–326.

"*Sintering and Gas Desorption Characteristics of Copper Ultrafine Powders*", Sakka, Y., Uchikoshi, T. and Ozawa, E.: Mater. Trans. JIM, **31** (1990), 802–809.

"*Solid-Liquid Interfacial Tension of the W-Cu System*", Muramatsu, Y., Halada, K., Dan, T. and Isoda, Y.: J. Jpn Inst. Met. **54** (1990), 79–684 (in Japanese).

Joining

136 Corrosion of Welds in Reactor Fuel Reprocessing Plants

Apr. 1986~Mar. 1991

Nakamura, H.

Advanced Materials Processing Division

Austenitic stainless steel welds are susceptible to **intergranular corrosion** in nitric acid with a high oxidizing potential.

This study aimed at achieving grain refinement of 25Cr-20Ni fully austenitic stainless steel welds by **pulsed TIG welding** and by electromagnetic stirring for the prevention of deep corrosion in the weld. Some surface modifications of welds with a CO_2 laser were executed to get more protection agains the corrosion. It was also evaluated the stability of the passive films on the valve metals in the highly oxidizing environment.

We were successful in obtaining very fine grains both in TIG weld metals and HAZs by a peculiar pulse current wave which had an extremely low average current and a large mark-space ratio (base current time / peak current time) though the peak current was sufficiently high to obtain a deep penetration. The intergranular corrosion rate was halved when using this peculiar pulse TIG welding procedure. Electromagnetic stirring and laser rapid solidification were also effective to increase corrosion resistance but not enough. On the contrary, electron beam welds showed excellent corrosion resistance even when the weld was exposed to severe conditions under heat flux.

The frequency response of the AC impedance for the valve metals generally showed a single semicircle of capacitive impedance, which corresponds well to the order of **stability of passivity**. The charge transfer resistance of the AC impedance diagram essentially agreed well with the polarization resistance of DC method.

Related papers

"*Grain Refinement by Pulse TIG Welding*", Watanabe, T., Nakamura, H. and Ei, K.: Trans. Nat. Res. Inst. Met., **29** (1987), 204–211.

"*Solidification Control and Relief of Intergranular Corrosion in TIG Welds*", Ei, K., Watanabe, T. an Nakamura, H.: Proc. 5th Internat. Symp. Jap. Weld. Soc. (1990) 947–952.

"*Improvement of Corrosion Property of TIG Welds in 25Cr-20Ni Stainless Steel by Laser Rapid Solidification*", Irie, H., Ei, K., Tsukamoto, S. and Nakamura, H.: ditto (1990) 952–958.

"*The Effect of Oxidizing Ions on the Passivity of the Valve Metals in Boiling Nitric Acid Solutions*", Fujii, T. and Baba, H.: Corrosion Science, **31** (1990) 275–280.

(137) Corrosion of Dissimilar Metals Joints in Reactor Fuel Reprocessing Plants

Apr. 1991~Mar. 1996

Nakamura, H.

Advanced Materials Processing Division

Dissimilar metals joints are to be used in a new reactor fuel reprocessing plant in Japan. The joints composed of austenitic stainless steels and valve metals are made by **solid state joining**. It is necessary for the safety of plant to assure sufficiently high **corrosion resistance** and also **corrosion fatigue strength** of the joints. The applicability of various methods of solid state joining to the purpose, optimization of process parameters in each process and evaluation of the quality of the joint in corrosive environment are investigated in this study. It would be ideal to get a solid state joint with a minimum input energy, where the residual stresses and the formation of intermetallic compounds are minimal.

(138) Joining of Intermetallic Compounds Utilizing Resistance Heating of the Compound to Be Joined

Apr. 1991~Mar. 1993

Fukushima, S.

Advanced Materials Processing Division

The aim of this study is to pursue the possiblity of the joining of intermetallic compounds which are to be used as structural materials. In this study, one of the titanium aluminides, **TiAl**, is used as a base material. The applied joining technique in the study consists of the **reaction sintering process** and **liquid-phase diffusion bonding process.** The two processes proceed simulataneously under a certain welding force and welding current.

Joining parameters to be examined are welding force, welding temperature, welding time, abutting surface condition, welding atmosphere and so forth. The microstructure of the joined parts will be mainly observed for the confirmation of the joined state.

[139] Research on the Fundamental Reaction at Joining Interface

Apr. 1988~Mar. 1991

Sasabe, K.

Advanced Materials Processing Division

Analysis of solid/liquid interface reaction

An attempt was made to clarify interface reactions for many combinations of solid and liquid alloy systems using AES. The most typical phenomena were observed by the analyses of interface reaction of solid copper with a liquid **Sn-Pb alloy** system. It was found that Sn in the liquid alloy segregated on the solid copper at the interface very rapidly and formed a very thin alloy layer, so called "halo", sorrounding a sessile drop of liquid alloy. The halo consisted of two layers: An Sn layer contacted with the base metal at the interface and a Pb layer on it. It was thought that the halo is not formed by diffusion or deposition of the elements vapoured from liquid but by spreading of liquid phase.

Joining of Amorphous Alloy Foils

Capacitor discharge spot welding was performed for Foil A of Fe-Co-Si-B alloy, Foil B of Fe-Ni-Mo-B alloy, Foil C of Co-Fe-Ni-Mo-Si-B alloy and Foil S of Fe-Si-B alloy.
Single spot-welded joints of Foil C had a sufficient tensile-shear strength and ductility. Weld nuggets of the foil did not crystallize by spot-welding. This fact was confirmed by the results of micro-X-ray diffraction analysis. Crystallization occurred within all of weld nuggets of the Foils A and B and some of Foil S.
The order of the ratio of crystallization temperature Tx to melting temperature Tm, Tx/Tm, fairly related to the order of spot-weldability of these foils.
Weld nuggets of the Foil C produced by irradiating with a defocused **Nd-YAG laser beam** pulse maintained the amorphous state, whereas weld nuggets of the other foils crystallized under the same joining condition.

Related papers
"*Spot Welding of Fe-Si-B Amorphous Metal Foil*", Fukushima, S. and Kasugai, T.: Q. J. Jpn. Weld. Soc., **7** (1989), 186–192. (in Japanese).
"*Spot Welding of Iron Based and Cobalt Based Amorphous Metal Foils*", Fukushima, S. and Kasugai, T.: Q. J. Jpn. Weld. Soc., **8** (1990), 343–349 (in Japanese).
"*Spot Welding of Iron-based and Cobalt-based Amorphous Alloy Foils (Report 2)*", Fukushima, S. and Kasugai, T.: Submitted to Q. J. Jpn. Weld. Soc.

(140) Effects of Temperature Distribution on Capillary Gap Penetration

Apr. 1991~Mar. 1993
Sasabe, K.
Advanced Materials Processing Division

The purpose of this study is to develop a computer simulation method of **capillary gap penetration** for brazing under a **micro gravitation**. The most important problem to be solved is the assesment of the change of tempertature distribution in the capillary gap during the penetration of the liquid, because the **capillary force** and the **marangoni flow**, depending on the surface tension gradient at the free surface of the liquid, disturb the regular penetration of liquid into the capillary gap.

Composite process

141 Material Processing for Making Layered Structures

Apr. 1989~Mar. 1991
Dendo, T.
Advanced Materials Processing Division

In this study, two different methods of material processing for making **layered structures** are attempted, and the feasibility of each process is explored through fundamental experiments.
Multi-layer crystal of refractory metals
The large-scale and multi-layer crystal have been developed from a hot rolled multi-laminated molybdenum sheet doped with CaO and/or MgO by means of **secondary recrystallization**. The crystallographic orientation relationships between primary and secondary recrystallized grains developed in multi-layer crystals was determined by X-ray conventional pole figures and micro-Laue techniques. The orientation of the secondary grain developed from each layer was closely related to the texture gradients in the thickness direction for primary recrystallized sheet. Most of the orientation of multi-layer crystal sheet corresponded to very weak components in the primary recrystallization textures and were related by a rotation of approximately 15°-30° about <100> and <110> axes relative to the strong primary {001} <110> and {111} <112> components.
Metal-ceramic composite material having layer structures
Some attempts are being made for manufacturing a metal-ceramic composite material with layer structure. Pressure **infiltration** of molten metal into porous ceramics is adopted as a basic method. Some experiments using molten Pb-Sn alloy and semi-sintered alumina have proved that a composite structure infiltrated with the alloy can be formed in the surface portion of ceramic compact. At present, the morphology of the layer structure formed is being examined in relation to process parameters such as the porosity of the ceramic and infiltration conditions.

142 Low Energy Joining with Controlled Surface Composition and Misorientation Angle

Apr. 1990~Mar. 1993
Ohashi, O.
Advanced Materials Processing Division

The aim of our research is to develop a technique of low energy **joining** with the use of controlled surface composition and misorientation angle. This technique is useful for the development of new functional materials. In the first fiscal year, we constructured the **diffusion bonding** device in ultra-high vacuum and have obtained the following results.
(1) With Mo single crystal of which the surface orientation to be joined is (121), it is found that the fracture strength depends on the **misorientation angle** and there are peaks in strength around the

coincidence boundaries. A more detailed study is to be performed in the following years.
(2) We have analyzed the **surface composition** of SUS304 stainless steel and Ti by AES under heating. Above 873K, impurities 0 and C disappear and solute impurity S segregates to the surface. The effect of impurities C, O and S on the strength of joints is to be investigated in the following years.
(3) We have studied the electronic properties at the interface theoretically. In our calculation, the binding energy is shown to become larger as the band width of the metal becomes narrower and the work function larger.
(4) The hydrogen permeability of the Pd-coated V-15at%Ni alloy membrane increases by adding Ti, Zr or Y in the temperature range 473–673K and the hydrogen trapping phenomenon is markedly improved by removing the defected layer before plating with Pd.

143 Fundamental Phenomena in Spray Deposition of Surface Coatings

Apr. 1988~Mar. 1991
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Advanced Materials Processing Division

Fundamental problems in the surface coating process called **plasma spraying** were studied by using specially developed diagnostic techniques. One of those was the heat and momentum transfer from a plasma jet to the injected powder particles. Even though the temperature and velocity of sprayed particles have been known to affect the properties of the spray deposited coating, no appropriate **monitoring techniques** were available. The developed technique is based on temporal and spectral analysis of **thermal radiation** emitted by flying particles and the instrument is compact. Effects of various process parameters and powder characteristics on the temperature and velocity of sprayed particles were systematically studied.
Another problem tackled was the generation mechanisms of **residual stresses** in spray deposited coatings, which are critical in various coating performances, such as adhesion strength and resistance to thermal shock. In-situ monitoring of stress generation in a coatin gduring deposition was made possible by continuously measureing the curvature of a substrate strip during deposition. Average stress due to quenching of individual splats was quantified for a wide range of spraying materials and substrate temperatures, and its significance for the final stress state of the coating was clarified.
By fully utilizing those techniques and the understandings obtained here, a much more systematic approach toward control of coating properties is now possible.

Related papers
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"*Generation Mechanisms of Residual Stresses in Plasma Sprayed Coatings*", Kuroda, S., Fukushima, T. and Kitahara, S.: Vacuum **41** (1990), 1297–1299.
"*The Quenching Stress in Thermally Sprayed Coatings*", Kuroda, S. and Clyne, T. W.: Thin Solid Films. **200** (1991) 49–66.

Process with aid of beam technology

144 Fundamental Study on Formation of Dissimilar Surface Layer by High Energy Density Beams

Apr. 1989~Mar. 1992
Irie, H.
Advanced Materials Processing Division

High energy density beams, such as **electron beam** and high power **laser** have been expected to have excellent characteristics as a tool for **surface modification**. When these heat sources are applied to **cladding** and **alloying**, they can form a surface layer with new or different properties without any significant damage to the base material and with long irradiation distance, not depending on configuration or properties of base material. In this research, fundamental study on formation processes for wide and uniform clad or alloyed surface is carried out, observing melting and flowing process of base metal and additional materials.
In laser surface modification using 5kW CO_2 laser by the multi-run melting process without beam oscillation, the alloying process is easily accomplished, but the cladding process has some difficulties. Powder supply is the easiest manner for addition of dissimilar materials and a multi-mode beam with as large a diameter as possible is adequate to form a uniform clad layer. A thin surface layer of base metal must be melt for a desirable clad layer. Melting, then cladding process depends strongly on properties of additional powder such as reflectivity of leaser beam, powder size and so on. The observation of molten metal flow will be carried out with a high-speed cine-camera in order to clarify the mixing process. A kaleidoscope will be used to obtain a more wide and uniform clad layer.
In electron beam surface modification, the wire supplying method is preferred for addition of dissimilar metals or elements. In this process, a magnetically mode-modified electron beam and beam scanning point (heating point) control by a

computer system have been studied to be applied, because the multi-mode beam is difficult to be obtained but precise and high speed control of irradiation point using a deflection system is easily accomplished.

Related papers

"*Formation Mechanism of Longitudinal Crack in Electron Beam Welding*", Irie H. and Tsukamoto, S.: Tran. Nat. Res. Inst. Met. **32** (1990), 208–216.

"*Formation Mechanism of Locally Delayed Solidification Pattern in Electron Beam Welding*", Tsukamoto, S. and Irie H.: Qu. J. Jpn. Weld. Soc., **8** (1990), 179–185 (in Japanese).

"*Fusion Property of A CO_2 Laser in Stainless Steels*", Irie H. and Tsukamoto S.: Doc. IIW Meeting in Montreal, IIW Doc. IV-547–90 (1990).

145 Fundamental Study on Control of Surface and Interface Microstructures and Modification of their Physical Properties by Ion Beam Techniques

Apr. 1989~Mar. 1991
Saito, K.
Surface and Interface Division

Ion implantation is a unique technique for creating nonequilibrium **surfaces, interfaces**, or **thin films**, since atomic injection or intermixing can be effectuated at low temperatures by ballistic processes involving defect production. In this study several metals, alloys and intermetallic compounds were implanted with various ions to control and modify their **microstructures** and **physical properties**, such as electrical, magnetic and optical properties. (a) The superconducting B1-MoN compound phase has firstly been synthesized by implantation of nitrogen ions into Mo thin films. The crystal and electronic structures of the specific phase were examined in detail by XRD and XPS. (b) The mangetic coercive force of Co-Ni alloy films was improved by nitrogen ion implantation followed by high temperature annealing. This was caused by the ion induced amorphization followed by the c-axis reorientation of the films. (c) The stress-corrosion resistance of intermetallic TiAl was significantly increased by nitrogen ion implantation which induced internal compressive stresses and a fine dispersion of Al- and Ti-nitrides in the surface layer. Furthermore, the surface color of ordered intermetallic NiAl was controlled from blue to pink or yellow color by the effect of Ar ion induced disordering of the near-surface region.

Related papers

"*Electronic Structure of Superconducting MoN Thin Films Produced by Ion Implantation*", Saito, K.: Nucl. Instrum. Methods in Phys. Res. **B39** (1989), 623–627.

"*Nitrogen Ion Implantation into Intermetallic Compund TiAl*", Saito, K. and Matsushima, T.: Mat. Sci. Eng. **A114** (1989), 355–359.

146 Study on the Synthesis of Special Compounds by a Combined Use of Ion Implantation and Ion Beam Deposition

Apr. 1991~Mar. 1993
Saito. K.
Surface and Interface Division

The combined use of **ion implantation** and **deposition** techniques is a promising method to synthesize novel **compound** with special atomic and electronic structures in a highly controlled manner. In this study we try to synthesize or modify thin film compounds with **layered** or intercalated **structures**, monolayered interfaces, etc. By the use of ion implantation technique we control the amount of atomic injection and displacement of chosen atoms, and create specially localized fields in a solid, subject to ultra-high temperature and ultra-high rate of quenching, e.g. ~ 10^{12} K/s in the thermal spike region. The deposition process under these ion induced nonequilibrium conditions is used for the synthesis of magnetic $Fe_{16}N_2$ compound with giant magnetization, superconducting BiSrCaCuO oxide films with high-T_c phase, and artificial **interface boundary** of the elements of the ordered intermetallic compounds, TiAl and NiAl.

Related papers

"*Thermal Spike and Displacement Effects of BiSrCaCuO Thin Films by Ar Ion Beams*", Saito, K. and Kaise, M.: to be published in Proc. 7th International of Metals by Ion Beams (Washington, July 1991)

"*Structural Changes and Aging behaviour of Ar ion irradiated BiSrCaCuO Thin Films*", Kaise, M. and Saito, K.: ibid.

Processing in special environment

147 Survey Reserch on the Usefulness of Extreme High Vacuum Environment

Apr. 1989~Mar. 1991
Yoshihara, K.
4th Research Group

The objective of this project is to investigate the usefulness of the **extreme high vacuum** environment for materials processing. We can obtain a very high potential to creating the materials by using **atomic scale manipulations**, if we can utilize this extreme high vacuum environment.

In this project, we could clarify the technical problems to create the extreme high vacuum

environment and to operate this system. We also investigated the possibilities of the creation of new materials using this environment. The investigation were carried out under the following categories: (1) Purification (2) Inter-metallic compounds (3) Quantum micro structures (4) Surface analysis (5) Nano-bonding (6) Ecology (7) Intelligent materials (8) Life science (9) Clean energy (10) Laser beam technology (11) Ion implantation (12) Electron beam technology (13) Scanning tunneling microscopy (14) Electron microscope (15) Ion beam technolgoy for analyses (16) Radiation damage.
By this survey research, we could point out the importance of the extreme high vacuum for the creation of new materials. Therefore, we are now planning to construct an extreme high vacuum factory, in which whole materials processing procedures (synthesize, processing, characterization) are carried out.

148 Development of Quantum Micro Structures in Ultra Clean Vacuum

Apr. 1990~Mar. 1995
Yoshihara, K.
4th Research Group

It is expected that materials with **quantum micro structures** will posess new and useful properties. However, to create these materials, it is necessary to handle the materials in extremely clean and high vacuum environment. Otherwise, impurities from the environment will deteriorate the material properties. This project is divided into two phases. In the first phase (Apr. 1990-Mar. 1993), we will construct the **ultra clean vacuum** system in which specimens are transferred by a magnetic flotation system. By using this system, we will transfer specimens from one station to the other station without any exposure to contaminating environments. In the second phase (Apr. 1993-Mar. 1995), we will create materials with quantum micro structures by using this ultra clean vacuum system.
Since April 1990, we have produced new vacuum pumps and special gate valves for extreme high vacuum. The inner surface of the vacuum vessel has been coated by boron nitride which is known not to adsorb air. The coating process of boron nitride was invented in National Research Institute for Metals. By using these parts, we have constructed an extreme high vacuum system. We are now planning to install a transportation system with magnetic flotation into this extreme high vacuum system. The whole system will be completed by the end of March 1993.

149 Development of Extremely High Field Magnets

Apr. 1988~Mar. 1993
Maeda, H.: 1st Research Group

For Evaluating the **high-field** properties of high-T_c oxide superconductors, we are developing several high-field facilites, such as a 80 T class long-**pulsed magnet**, a 40 T class **hybrid magnet**, a 20 T class large-bore **superconducting magnet**, and a **homogeneous-field magnet**.
In 1989, we constructed a capacitor bank of 1.6 MJ to be used as a power source for a long-pulsed magnet system. Using Cu-Nb wire, we made several small 50 T-class pulsed magnets. However we encountered difficulties in enlarging their size, due to the poor reproducibility of Cu-Nb alloy. Recently we found that Cu-(5–30)at%Ag alloys show excellent properties. Using the new Cu-Ag alloy wire, we are planning to make several high-field pulsed magnets.
The present design concept for the 40 T class hybrid magnet system refers to a superconducting magnet inducing 15 T for a clear bore of 400 mm, and a polyheilix-type water-cooled resistive magnet inducing an incremental field of 25 T for a clear bore of 30 mm. The detailed design of the superconducting magnet has been completed, and fabrication of the water-cooled magnet was started this year.
A 20 T class large bore superconducting magnet system is designed as a combination of four superconducting coils. Two outer coils are located in the outer chamber, and provide a back-up field of 15 T in the 314 mm diameter inner chamber. A middle coil is set into the inner chamber, and is expected to generate an incremental field of 3 T in a 160 mm free bore, where we will measure and evaluate the performance of various kinds of inner coils at about 20 T. The fabrications of two outer coils, middle coil, and the first inner coil have been almost completed in 1990.
We have almost completed the whole homogeneous-field magnet system in 1990, which includes three sub-systems for **NMR** measurement of solid matter at 1.5~800 K, for high-resolution NMR measurement up to 500 MHz at 173 ~ 373 K, and for measurement of many physical properties other than NMR above 0.03 K.

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Processing

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Gaseous process

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Liquid state process

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Solid state process

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Process with aid of beam technology

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Processing in special environment

(235) *"Unidirectional Solidification of Al-Pb-Bi Alloys under High and Low Gravitational Fields in KC135 Aircraft"*, Mohri, M. (NASDA), Curreri, P. (NASA MSFC), Smith, G. (Univ. of Alabama), Wu, M.K. (Columbia Univ.), Dietderich, D.R. and Togano, K.: Jpn. Soc. Microgravity Application, **7** (1990), 22–28 (in Japanese).

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NRIM Publications (Apr. 1990~Mar. 1991)

1. Bulletin of National Research Institute for Metals, in Japanese.
   No. 12 (Feb. 1991)
2. Annual Report of National Research Institute for Metals, in Japanese.
   For fiscal year of 1989 (Sep. 1990)
3. Kinzaiken News, in Japanese.
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4. Transactions of National Research Institute for Metals, in English.
   Vol. 32, No. 2 (Jun. 1990)
   Vol. 32, No. 3 (Sep. 1990)
   Vol. 32, No. 4 (Dec. 1990)
   Vol. 33, No. 1 (The last issue) (Mar. 1991)
5. Material Strength Data Sheet, in English.
   NRIM Creep Data Sheet,
   Nos. 16B and 35A (Sep. 1990)
   Nos. 36A and 41 (Mar. 1991)
   NRIM Fatigue Data Sheet,
   Nos. 63~66 (Dec. 1990)
6. Guide to National Research Institute for Metals, in Japanese and in English.
   For fiscal year of 1990 (May 1990)

International Exchange Apr. 1990~Mar. 1991

International Collaboration Research

Australia
1) Study on Surface Modification of Metals with Ultra-High Temperature Heat Sources. (CSIRO)

Brazil
1) Study on Ni-Base Superalloys. (Fundacao De Technologia Industrial)

Canada
1) Damage Evaluation and Residual Life Prediction of Structural Materials. (Energy Miles and Resources Physical Metallurgy Research Laboratory)
2) Basic Study for Design of Aerospace Materials. (National Aerospace Establishment)

China
1) Effective Utilization of Complex Ore for the Rare Metal Resources. (Beijing University of Science and Technology)
2) Production of Rapidly Solidified Alloy Powders by Super High Pressure Liquid Atomization. (General Research Institute of Non-Ferrous Metals)
3) Study on Preventing Methods of Welding Defects in Electron Beam Welding. (Chengdu Electrical Welding Machine Research Institute)
4) Investigation of High Temperature Titanium Alloy for Application over 600°C. (Northwest Institute for Non-Ferrous Metal Research)

Finland
1) Development of High-Tc Oxide Superconducting Thin Films. (Tampere University of Technology)

France
1) Superconducting and Cryogenic Materials (Service National des Champs Intenses, Centre National de la Recherche Scientifique Grenoble and Others).

Germany
1) Development of Superconducting Materials. (Kernforschungszentrum Karlsruhe)
2) Exchange of Creep and Fatigue Data Sheet. (5 Institutes)

Italy
1) Mechanism of Deformation, Fracture and Corrosion in Ni-Based Superalloys. (Istituto per la Tecnologia dei Materiali Metallicinon Tradizionali)

Korea
1) Application of Thermoelectric Materials to Energy Conversion. (Korea Advanced Institute of Science and Technology)
2) Processing Technology and the Characterization of Advanced Aluminum Alloys. (Korea Institute of Machinery and Metals)
3) On the Application of the Recrystallization Phenomena in Refractory Metals. (Korea Institute of Science and Technology)
4) Characterization of the Composite Film with Dispersion of Carbide Phase by PVD and CVD Process and the Establishment of the Process Parameters Leading to Fabrication Techniques. (Korea Institute of Machinery and Metals)
5) Fabrication Process for High-Tc Superconductors. (Korea Institute of Machinery and Metals)
6) Aluminide Intermetallic Compounds for High Temperature Structual Materials. (Korea Institute of Machinery and Metals)
7) Information Exchange on Materials Strength Data. (Korea Standards Research Institue).

Philippines
1) Evaluation of Corrosion Resistance of Metals by Atmospheric Exposure Test. (Materials Science Research Institute and Other Institutes)

Sweden
1) Application of Advanced Electromagnetic Technology to the Metallurgical Processing. (Royal Institute of Technology)

Thailand
1) Evaluation of Corrosion Resistance of Metals by Atmospheric Exposure Test. (Thailand Institute of Scientific and Technological Research, and Other Institutes)

U.K.
1) Development of Superconducting Materials and High-Field Magnets. (University of St. Andrews)
2) Prediction of the Life and Remaining Life of Huge Structure. (Welding Institute)

U.S.A.
1) Exchange of Creep and Fatigue Data Sheets. (National Institute of Standards and Technology)
2) US-Japan Fusion Cooperation Program. (Research Institute of Fusion in U.S.A.)
3) Extremely-High-Field Magnets. (Massachusetts

Institute of Technology)
4) Evaluation of Superconducting Materials. (National Institute of Standards and Technology)
5) Composition Synthesis for Production of Advanced Materials. (Lawrence Livermore National Laboratory)

EC
1) EC-Japan Fusion Cooperation Program. (Research Institute of Fusion in EC)

International
1) Versailles Project on Advanced Materials and Standards. (Summit Working Group on Technology)

List of Guest Researchers

*STA Fellowship

Nationality and Name	Affiliation	Term	Research subject
China			
Dr. Xing Zhao-jie*	General Research Institute for Non-Ferrous Metals	1990. 4. 2. ~ 1991. 4. 1.	Fablication and Properties of Novel Metallic Materials with Artificial Microstructures
Dr. Wang Xinhua*	University of Science and Technology, Bejiing	1990. 5. 9. ~ 1991. 5. 8.	Complex Ore for the Rare-Metal Resources
Mr. Wu Nian Zu	Shanghai 101 Factory	1990. 11. 13. 1991. 11. 12.	Study on Analysis and Control of Solid/Liquid Interface Reaction of metals
Mr. Jiang Chun Sheng	Institute of Metal Research, Academic Sinica	1990. 11. 27. 1991. 11. 26.	Synthesis and Characterization of the Composite Ultrafine particles by "Reactive Plasma-Metal" Reaction
France			
Dr. B. Chenevier*	Ecole Nationale Superieure de Physique de Grenoble	1990. 1. 11. ~ 1991. 7. 10.	High Resolution Electron Microscopic Study of Superconducting Oxide
Dr. A.G.M. Jansen	Grenoble High Field Magnet Laboratory	1991. 3. 16. ~ 1991. 3. 31.	Physical Properties and Electronic Structures of Highly Correlated Electron Systems in High Magnetic Field
India			
Dr. P. Mahajan*	Montana State University	1991. 1. 15. ~ 1992. 1. 14.	Characterization of Metals and Alloys Using Synchrotron Radiation
Dr. R. G. Sharma	National physical Laboratory	1991. 2. 25. ~ 1991. 3. 2.	Basic Study on Wire Fabrication of High-Tc Oxide Superconductors
Italy			
Dr. G. Maizza*	Politechnico di Torino	1989. 3. 25. ~ 1991. 3. 25.	Material Surface Chemistry in a Irradiation Environment
Dr. M. Maldini*	Institute for Non-Traditional Metallic Materials	1990. 4. 23. ~ 1991. 1. 23.	Microstructure and Mechanical Properties of Nickel-Base Superalloys
Korea			
Mr. Jae-Woong Ko	Korea Institute of Machinary and Metals	1991. 3. 1. ~ 1991. 3. 30.	Fabrication Process for High-Tc Superconductors
Dr. Koo Cho Yang	Korea Standard Research Institute	1991. 3. 25. ~ 1991. 3. 30.	Evaluation of Creep Crack Growth Behavior of Heat Resistant Materials at High Temperature
Netherlands			
Dr. J. P. Zijp*	Technisch Univeriteit Delft	1990. 11. 11. ~ 1992. 11. 11.	Vaporization Phenomena in Arc Plasmas
Philippines			
Ms. A.S. Viloria	Industrial Technology Development Institute	1990. 6. 18. ~ 1990. 11. 27.	Japan-Asean Cooperation Program on Materials Science and Technology Philippine Project on Atmospheric Corrosion (Inorganic Coating)

(Table continues on next page.)

List of Guest Researchers (Continued)

Nationality and Name	Affiliation	Term	Research subject
Ms. R.R. Corral	Metals Industry Research and Development Centre	1990. 6. 18. ~ 1990. 11. 27.	Japan-Asean Cooperation Program on Materials Science and Technology Philippine Project on Atmospheric Corrosion (Inorganic Coating)
Ms. N. A. Cruz	Industrial Technology Development Institute	1990. 6. 18. ~ 1990. 11. 27.	The same as above
Ms. C. R. Habana	Industrial Technology Development Institute	1989. 6. 19. ~ 1990. 6. 8.	The same as above
Sweden			
Mr. J. B. F. Shandell	Royal Institute of Technology	1991. 3. 10. ~ 1991. 3. 29.	Fundamental Study on the Fused Metal-Oxide Reaction by Magnetic Levitation
Thailand			
Mr. P. Buranawanich	Department of Mineral Resources	1990. 2. 26. ~ 1990. 2. 17.	Japan-Asean Cooperation Program on Materials Science and Technology Thai Project on Atmospheric Corrosion (Organic Coating)
Miss. M. Chaisoorayagan	Thailand Institute of Scientific and Technological Research	1990. 10. 22. 1991. 2. 15.	Study and Training of Scanning Electron Microscopy
Ms. S. Vangchan	Chulalongkorn University	1991. 1. 7. ~ 1991. 2. 27.	Japan-Asean Cooperation Program on Materials Science and Technology Thai Project on Atmospheric Corrosion (Organic Coating)
Mr. S. Kulkowit	Thailand Institute of Scientific and Technological Research	1991. 1. 14. ~ 1991. 4. 26.	The same as above
U.K.			
Dr. R.A. Carolan*	Cornell University	1989. 3. 27. ~ 1990. 11. 23.	Damage Measurement by Electron Lithography and Mechanism of Damage Formation
U.S.A.			
Dr. J. Schwarts*	Massachusetts Institute of Technology	1990. 2. 12. ~ 1990. 8. 11.	Improvements of Bi-System Oxide Superconducting Wires
Mr. B. I. Mary	Northwestern University	1990. 6. 21. ~ 1990. 8. 7.	In-Situ Analysis/Evaluation of Radiation Damage in Metals
Mr. W. A. Douglas	University of Florida	1990. 6. 21. ~ 1990. 8. 7.	Research on Development of Low Activation Materials for Fusion Reactors
Dr. J. L. McCarthy	Lawrence Berkley Laboratory, University of California	1990. 10. 1. ~ 1990. 10. 21.	Development of a Database on High Temperature Superconductor Materials
Prof. J. W. Morros, Jr.	University of California, Berkley	1990. 12. 8. ~ 1990. 12. 22.	Phase Transformation by Deformation at Cryogenic Temperature under High Magnetic Field
Prof. J. Weertman	Northwestern University	1990. 12. 10. ~ 1991. 1. 11.	In-Situ Scanning Tunneling Microscopy of Metal/Liquid Interface
Prof. Z. A. Munir	University of California, Davis	1991. 1. 3. ~ 1991. 2. 18.	Study on Combustion Synthesis
Dr. Y. Iwasa	Massachusetts Institute of Technology	1991. 3. 8. ~ 1991. 3. 28.	Extremely High Field Magnets

List of Visitors

*M: Meguro Main Site, T: Tsukuba Laboratories

Nationality and Name	Affiliation	*	Date
Australia			
Dr. J. Bear and her party	Division of Mineral Products, CSIRO	M, T	Jun. 1990
Mr. D. K. Judd	Crane Enfield Metals Pty. Ltd.	T	Jun. 1990
Prof. A.S. Moon and his party	Univ. of Technology Sydney	T	Dec. 1990
Dr. I.R. Sare and his party	Division of Manufacturing Technology, CSIRO	M	Feb. 1991
Austria			
Dr. M. Orange and his party	Fachverband der Metallindustrie Oesterreichs	T	Jun. 1990
Argentina			
Dr. I.F.Y. Nassiff and his party	National Technology Laboratory	T	May 1990
Mr. F.A. Actis and his party	Instituto Nacional de Technologia Industrial	T	Dec. 1990
Belgium			
Mr. Adrien	Boliden Cuivre et Zinc	T	Jun. 1990
Brazil			
Mr. R.C. Ibrahim	Department of Materials Engineering, Univ. of Campinas	T	Dec. 1990
Canada			
Mr. M.D. Everell and his party	Mineral and Energy Technology, Mines and Resources Canada	M	Feb. 1990
Dr. R. Thomason	Physical Metallurgy Research Laboratories, CANMET	M	Oct. 1990
Czecho Slovakia			
Dr. J. Polak	Czecho Slovakia Academy Science, Metal Physics Laboratory	T	Sep. 1990
China			
Mr. Jin Jinghon and his party	The Chinese Society of Rare Earth	M	May 1990
Mr. Bai En de and his party	State Administration of Import & Export Commodity Inspection of the People's Republic of China Inspection Control Division	M	Jun. 1990
Mrs. Zhang Fengxi and her party	China National Nonferrous Metals Industry Corp. Science & Technology Bureau	M	Jun. 1990
Mr. Guo Bo and his party	Shanghai Manicipal Institute of Civil Architectural Design	M	Jun. 1990
Prof. Yang Zhi-Au	Institute of Metal Research, Academia Sinica	T	Jul. 1990
Prof. Li Qingchun	Metallic Materials and Technology, Harbin Institute of Technology	M	Oct. 1990
Dr. Pan Wei and his party	Kobe Steel, Ltd., Iron and Steel Research Laboratory	T	Oct. 1990
Mr. Wang Xin-Ming and his party	Dalian Association for International exchange of Personnel	T	Oct. 1990
Prof. Guo Jing-Kun and his party	Shanghai Institute of Ceramics, Chinese Academy of Science	M	Nov. 1990
Cuba			
Dr. R.T. Antonio do Jesus and his party	Instituto Superior Politechnico Jose Antonio Echeverria	T	Jun. 1990
Egypt			
Mr. A.A. Younan	Central Metallurgical Research & Development Institute	T	Dec. 1990
Finland			
Dr. A.E. Valkonen	Helsinki Univ. of Technology	M	May 1990
Mr. I. Koppinen	Outokumpu Poricopper Oy	T	Jun. 1990
Formosa			
Mr. Lee Shih-Chie and his party	East Asia Association for Cooperation in Science and Technology	T	Apr. 1990

(Table continues on next page.)

List of Visitors (Continued)

Nationality and Name	Affiliation	*	Date
Mr. Lee Ying-Sheng	Institute of Nuclear Energy Research	T	Nov. 1990
France			
Mr. J.T. Cooper and his party	France Air Liquid Compary Mission	T	May 1990
Mr. G. Durand-Texte and his party	Ets Griset	T	Jun. 1990
Mr. C. Amzallag and his party	UNIREC-Center Commun de Researches	M	Jul. 1990
Prof. P. Vast and his party	Domaine Univ.	T	Nov. 1990
Prof. A. Vincent	INSA de Lyon	T	Jan. 1991
Dr. R. Capitini	Atomic Energy Agency	T	Mar 1991
Germany			
Prof. J. Richter	Aachen Technische Univ.	T	May 1990
Dr. A.W. Baukloh and his party	KM-kabelmetal AG	T	Jun. 1990
Mr. T. Rudolph and his party	Degussa AG	T	Aug. 1990
Dr. G. Effenberg	Max Planck Institut	M	Oct. 1990
Prof. H. Brodowsky	Univ. of Kiel	T	Oct. 1990
Dr. Gerbech	Central Institute for Nuclear Research Rossendorf	T	Oct. 1990
Dr. B. Pfalzgraf	Verein Deutscher Ingeneure	T	Nov. 1990
Dr. J.C. Spirlet	European Transuranium Elements Research Institute	M	Mar. 1991
Dr. G. Elssner	Max Planck Institut für Metalforschung	M	Mar. 1991
Greece			
Mr. T. Kassapoglou	Halcor Metal Works S.A.	T	Jun. 1990
India			
Dr. D. Sundararaman	Indira Gandhi Center for Atomic Research	T	Aug. 1990
Dr. R.K. Dayal and his party	Indira Gandhi Center for Atomic REsearch	MT	Sep. 1990
Mr. J.M. Sharma	Technical department, Udyong Bhavan	T	Dec. 1990
Indonesia			
Mr. Supomo	Ceramic REsearch & Development Institute	T	Dec. 1990
Italy			
Dr. M. Bovero and his party	Tubi-tubi Barre Italia S.R.L.	T	Jun. 1990
Dr. G. Ruggiero and his party	Tubi-tubi Barre Italia Sel Factory of Sarravaiie Scrivia	T	Jul. 1990
Dr. G. M. Babini	Research Institute for Ceramic Technology	T	Mar. 1991
Korea			
Mr. Jun Hae-Sung and his party	Energy & Resources Committee National Assembry	T	May 1990
Mr. C. H. Yang and his party	MBC-TV	T	May 1990
Dr. Chunghi Phee and his party	Korea Standards Research Institute	M	May 1990
Prof. Suh Chang-Min	Kyungpook National Univ.	T	Jul. 1990
Mr. Joo Dae Sik and his party	Sammi Steel Co. Ltd.	M	Nov. 1990
Mr. Tae Uk Hyun	Central Testing Laboratory	T	Dec. 1990
Prof. Kwuu Sook-In	Kourai Univ.	T	Feb. 1991
Malaysia			
Mr. N.A. Kamil	Standards and Industrial Research Institute of Malaysia	T	Dec. 1990
Netherlands			
Mr. H. Kröckel and his party	CEC Joint Research Center, Petten	M	Aug. 1990
Singapore			
Miss. T.C. Wan	Singapore Institute of Standard and Industrial Research	T	Oct. 1990
Spain			
Mr. P.L. Berti and his party	S.I.A. "Santa Barbara", S.A.	T	Jun. 1990
Thailand			
Ms. S. Chotipanich	Ceramic Research & development Center	T	Dec. 1990

(Table continues on next page.)

List of Visitors (Continued)

Nationality and Name	Affiliation	*	Date
U.K.			
Mr. B.G. Barker and his party	Policy REsearch in Engineering, Science and Technology, Univ. Manchester	T	Apr. 1990
Mr. T.C. Greaves and his party	Wednesburg Tube	T	Jun. 1990
Dr. K. Hossain and his party	The National Physical Laboratory	MT	Oct. 1990
Dr. M. J. Bennett and his party	AEA Industrial Technology, Harwell Laboratory	M	Dec. 1990
Dr. H.K.D.H. Bhadeshia	Univ. of Cambridge	M	Mar. 1991
U.S.A.			
Mr. D. Paul	The State Department Japanese Training Institute	T	May 1990
Mr. A. Dunn and his party	The Department of Commerce, Foundation Materials Office	T	May 1990
Dr. L.H. Schwartz	Materials Science and Engineering Laboratories, NIST	MT	May 1990
Dr. F.H. Froes and his party	Idaho Univ., Materials Processing Research Laboratory	T	Jun. 1990
Dr. I. Ahmad and his party	Office of Naval Research, Airforce Office of Scientific Research	M	Jun. 1990
Miss. T. Watanabe	Los Angeles Times	T	Jun. 1990
Dr. R.D. Shull	National Institute of Standards and Technology	T	Aug. 1990
Prof. T. Mura and his party	The Technology Institute, Northwestern Univ.	M	Aug. 1990
Dr. M. Suenaga	Brookhaven national Laboratory	T	Aug. 1990
Dr. R.B. Poeppel	Argonne National Laboratory	T	Oct. 1990
Dr. N. El-Kaddah	Univ. Alabama	T	Oct. 1990
Prof. J.R. Weertman	Department of Materials Science and Engineering, Northwestern Univ.	M	Dec. 1990
Dr. C.T. Liu	Metals and Ceramics Division, Oak Ridge National Laboraloty	M	Feb. 1991
Prof. J.W. McCauley and his party	New York State College of Ceramics at Alfred Univ.	M	Mar. 1991
USSR			
Dr. G. Paharenko	Institute of Metal Physics, Academy of Science	MT	Jun. 1990
Prof. F.A. Kuznetsov	Institute of Inorganic Chemistry	T	Oct. 1990
Dr. V. Moshnyaga	Institute of Physics, Latvian Academy of Science	T	Oct. 1990

Brief Introduction of STA Fellowship

The Science and Technology Agency (STA), an administrative organ of the Government of Japan, offers opportunities for promising young foreign researchers in the fields of science and technology to conduct research at Japan's national laboratories and public research corporations (exluding universities and university-affiliated institutes). The program is managed by the Research Development Corporation of Japan (JRDC), a statutory organization under the supervision of STA in cooperation with the Japan International Science and Technology Exchange Center (JISTEC).

Fellowship qualifications are as follows:

1) Possession of doctor's degree.
2) Less than 35 years of age, in principle.
3) Sufficient good health for research work and life in Japan.
4) Sufficient language ability in Japanese or English.

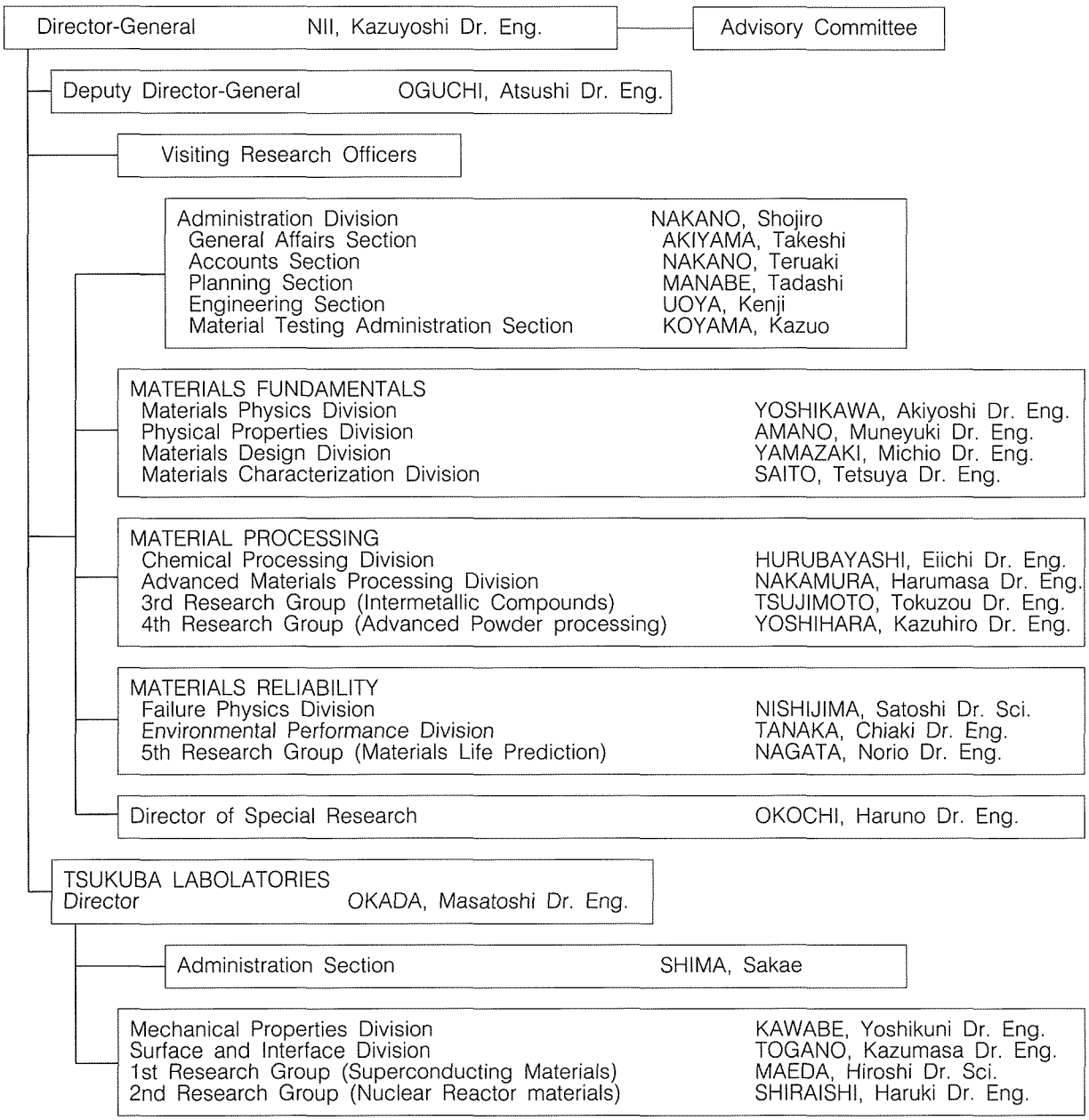
The tenure will be 6 months to 2 years. JRDC provides expenses for round-trip, monthly living with family, initial setting-in and travel in Japan. Research expenses will be paid for the host institute.

Further information can be obtained at:

Japan International Science and Technology Exchange Center (JISTEC)
Port One Building 6F, 1–7–6, Minato-machi, Tsuchiura City, Ibaraki Pref. 300, Japan
Phone +81–298–24–3355
Fax +81–298–24–3214

Organization of NRIM

☐ Organization



☐ Budget and Personnel in Fiscal Year of 1991

Budget		Personnel	
Research and facilities	2,891	Administrative staffs	98 (7)
Personnel expenses	3,319	Researchers	330 (99)
Total	6,210	Total	428 (106)

unit: million yen

Number in parenthesis: Tsukuba laboratories

How to get to NRIM

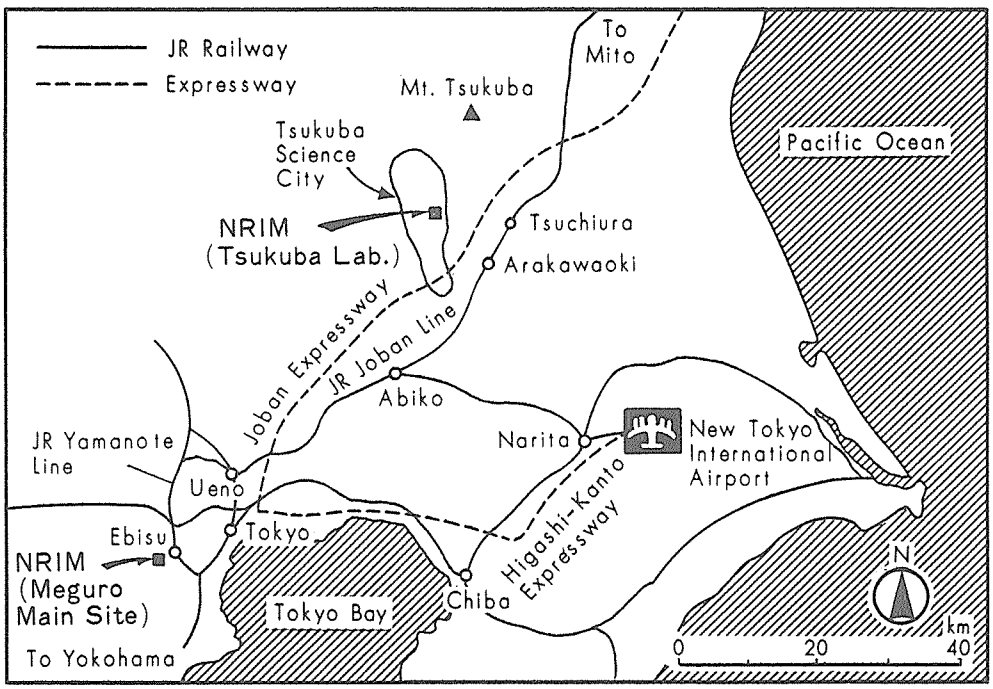
To NRIM Meguro Main Site（金属材料技術研究所 目黒本所）
2–3–12, Nakameguro, Meguro-ku, Tokyo 153（153 東京都目黒区中目黒 2 - 3 -12）
Phone +81−3−3719−2271　　Fax +81 −3−3792−3337

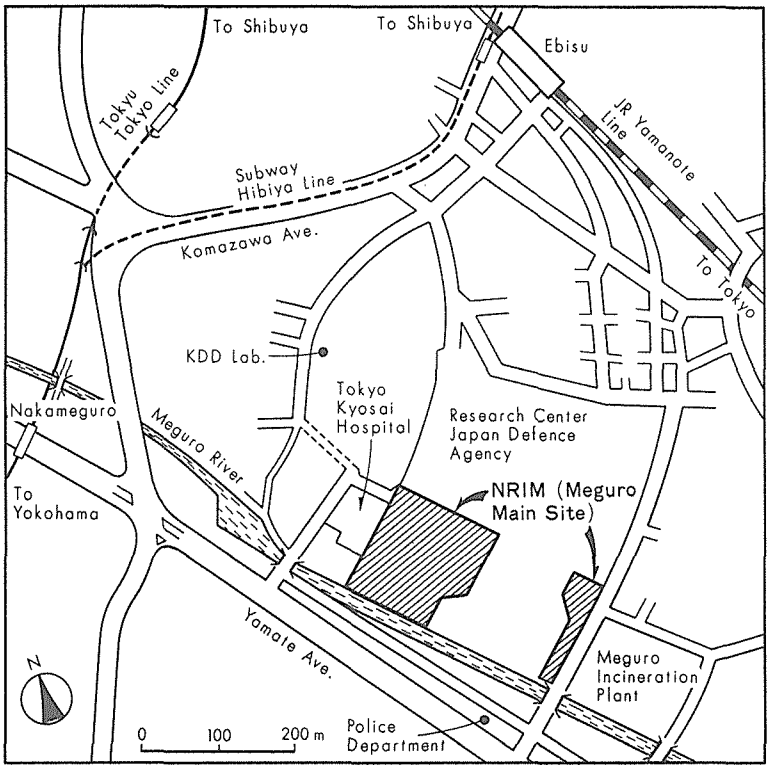
Narita Airport（成田空港）
↓　by train, JR Narita Express（成田エクスプレス）<60 min.>
Tokyo Station（東京駅）
↓　by train, JR Yamanote Line（山手線）<25 min.>
Ebisu Station（恵比寿駅）
↓　by taxi <5 min.> or on foot <15 min.>
NRIM（金属材料技術研究所）

To NRIM Tsukuba Laboratories（金属材料技術研究所 筑波支所）
1–2–1, Sengen, Tsukuba-shi, Ibaraki 305（305 茨城県つくば市千現 1–2–1）
Phone +81−298−51−6311　　Fax +81−298−51−4556

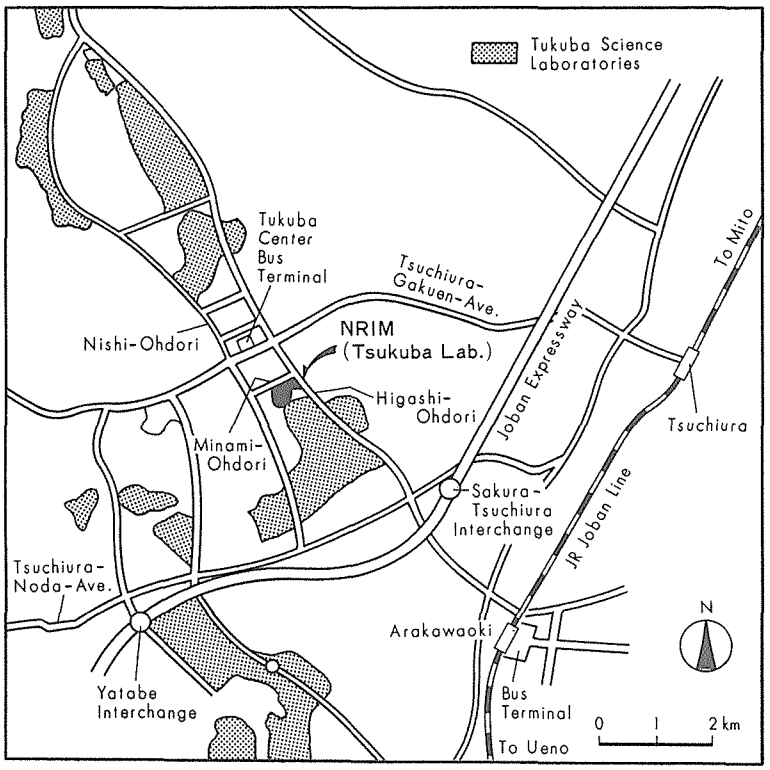
Narita Airport（成田空港）
↓　by train, JR Narita Express（成田エクスプレス）<60 min.>
Tokyo Station（東京駅）
Tokyo Station Yaesu-Minami-Guchi
（東京駅八重州南口）
↓　by bus, Joban Highway Bus for Tsukuba Center <70 min.>
（常磐ハイウエイバス，筑波センター行）
Tsukuba Center Bus Terminal（筑波センター）
↓　by taxi <5 min.> or on foot <15 min.>
NRIM（金属材料技術研究所）

JR: Japan Railway





Meguro Main Site



Tsukuba Laboratories

List of Keywords

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