1 of 2

Materials Research at Selected Japanese Laboratories

Based on a 1992 Visit

- Overview
- Summary of Highlights
- Notes on Laboratories and Topics

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FOREWORD

This report summarizes discussions and information gathered during a visit to selected Japanese laboratories during July 1992 to obtain a first-hand view of materials research in Japan. Materials research in Japan is carried on in too many laboratories for a single visitor to view and comprehend in the short span of a month; consequently, the following report is biased by the present traveller's interest in ceramic and intermetallic materials. However, the report is not limited to those two classes of materials as I took the opportunity to explore other subjects whenever possible.

The information reported here was generously provided by my many Japanese hosts. I am very grateful to those many Japanese scientists who met with me and who provided an informative and pleasant visit to their country. The section on Principal Contacts provides a chronological list of those whom I visited and their laboratories. The information which my hosts provided in many instances was current and frequently unpublished information. Discussions and first-hand observation often conveyed information not available in published reports and professional articles.

As I prepared this report, I was especially aware of the gracious hospitality of my Japanese hosts, of the lunches and dinners together and visits to beautiful sites, in addition to the many stimulating conversations. This report cannot adequately convey the pleasure of experiencing Japan, the Japanese people and their culture. It was indeed a pleasure for me to visit Japan again after five years, to renew old friendships and to make many new friends. The hospitality extended to me by many individuals did much to relieve the fatigue of visiting over 25 facilities in a month's time and to make by visit a memorable one.

The U.S. Department of Energy supported this trip. I especially want to thank Robert J. Gottschall of DOE's Division of Material Sciences for his encouragement to undertake this trip and for the advice and information which he provided both before and after my time in Japan. Dr. C.T. Liu of Oak Ridge National Laboratory provided several invaluable introductions to scientists investigating intermetallic alloys. I was also assisted with by Mr. Milton Eaton of the Department of Energy Liaison Office in Japan with several contacts. Professor Kozo Ishizaki, of Nagaoka University of Technology, whom I have known since my days in graduate school, assisted me in reaching several individuals and arranged my visit to Nagaoka University of Technology. I also indebted to Dr. Masaya Miyake of the National Research Institute for Metals, Dr. Yoichiro Sato of the National Institute for Research on Inorganic Materials, Dr. Nobuo Kamiya of the Toyota Central Research and Development Laboratory, Professor Kenji Suzuki and Professor S. Handa of the Institute of Materials Research at Tohoku University, Dr. Tatsuo Shikama of the IMR Oarai Facility, Dr. Tatsuki Ohji of the Government Industrial Research Institute in Nagoya, Professor Masaharu Yamaguchi of Kyoto University, Dr. Hisayoshi Yoshida of the Government Industrial Research Institute in Kyushu, Professors Koichi Niihara and

Yoshinari Miyamoto of Osaka University, and Dr. Takako Takahashi of Government Industrial Research Institute in Osaka for their assistance in making local arrangements for my visits. There are undoubtedly others who have contributed in significant ways to the success of this trip and who deserve mention but whom I have unwittingly overlooked. To each and everyone of them, I extend a heartfelt thank-you. ありがとうございます。

Finally, I want to thank Mary E. Stowers who very capably provided the word processing support for this report and assembled it.

Alan L. Dragoo
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EXECUTIVE SUMMARY

I visited Japan from June 29 to August 1, 1992. The purpose of this visit was to assess the status of materials science research at selected governmental, university and industrial laboratories and to establish acquaintances with Japanese researchers. The areas of research covered by these visits included ceramics, oxide superconductors, intermetallics alloys, superhard materials and diamond films, high-temperature materials and properties, mechanical properties, fracture, creep, fatigue, defects, materials for nuclear reactor applications and irradiation effects, high pressure synthesis, self-propagating high temperature synthesis, microanalysis, magnetic properties and magnetic facilities, and surface science.

On this trip I visited over 25 laboratories and talked to over 100 researchers and managers. I gave seminars at the Hitachi Research Laboratory, Nagaoka University of Technology, ISTE, JFCC, NGK Spark Plug/NTK Technical Ceramics, GIRIN, Kyoto University and Osaka University. These seminars generally presented an overview of the DOE Materials Sciences program although an attempt was made in each presentation to adapt some of the specific topics to the interests of the audience. A copy of the abstract for these seminars and a seminar announcement can be found in Appendix I.

I found strong competences in the areas of materials synthesis and processing of ceramics, alloys and oxide superconductors; single crystal growth; high pressure research and hot isostatic pressing (HIP); film growth; magnetic materials and magnets; electron microscopy; and materials for nuclear reactors.

Laboratories and facilities which served major programmatic thrusts of the Science and Technology Agency (STA) or of Agency of Industrial Science and Technology (AIST) of MITI were well supported, often having new equipment, if not a new laboratory. Industrial laboratories also generally appeared to be well-housed and equipped. In contrast, the facilities of older government and university laboratories were often crowded and in need of maintenance. Such conditions were evident to me at the older national universities which I visited - notably Tokyo University, Kyoto University and Osaka University; however, the Japanese government is reported to have begun to remedy this situation; cf. Science, 258, 23 October 1992. In contrast, the recently opened science campus of Ryukoku University, a private university, provided very modern, spacious facilities.

Although research facilities at the older governmental laboratories and national universities often appeared to be inadequate and overcrowded, these institutions maintained high-quality research, with a higher priority placed on equipment than on the condition of the building. Also, often when the general condition was one of overcrowding and need of renovation, high-priority programs were notably well-equipped, often with state-of-the-art instrumentation.

In areas such as high T_c superconductivity, high-temperature research and nuclear energy on which considerable technological emphasis has been placed, government funding agencies and industry have both individually and jointly established laboratories with state-of-the-art equipment. These laboratories often appeared to be focused on materials processing, testing and device development and were less well-equipped for a multifaceted materials research program. University laboratories and the older governmental institutes, on the other hand, appeared to be carrying out more diversified materials research.

High-quality high resolution electron microscopy (HREM) studies were evident at several laboratories, with a substantial emphasis given to imaging but little emphasis to elemental analysis. Analytical equipment on electron microscopes appeared to be limited primarily to x-ray analysis with energy-dispersive spectroscopy (EDS). I noted the availability of electron energy loss spectroscopy (EELS) in only one or two instances. I also was surprised to learn that electron microscopists are frequently considered to be technicians rather than scientists so that there is little professional scientific motivation to advance in this field of research.

Theoretical modeling and simulation of electronic and atomic structure did not appear to as widely practiced in Japan as in the U.S. However, this observation may be partly a consequence of the particular projects which I had the opportunity to visit. With the exception of work at the Government Industrial Research Institute at Osaka on grain boundaries in SiC and transition metal- Al_2O_3 interfaces using the tight-binding approximation and a program at the Institute for Materials Research at Tohoku University on materials design by computer simulation of which I was aware, modeling and simulation activities were not brought to my attention.

The **Summary of Highlights** section summarizes the major observations of my visit. This section is followed by a section which describes the laboratories and programs I visited. Finally, many of my observations are elaborated in a series of topical sections. The topics include Ceramics; Metals, Alloys and Intermetallics; Superconductors; and Magnetic Materials and Magnet Facilities.

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OVERVIEW

Japan's Scientific Competence

Japan's continued success in the application of scientific discoveries to new products is evident in any electronic store in the U.S. In recent years, partly in response to western criticism, Japan has begun to place increasing emphasis on basic science.

This new emphasis builds on many past successes in both basic and applied research. Japanese scientists have contributed significantly both in theoretical and experimental research to the discovery of new high T_c superconducting phases and the understanding of superconducting-related phenomena. They have contributed significantly to developing and understanding the behavior and properties of semiconductors, advanced ceramics, intermetallics, metals and alloys, nanophase particles, irradiation effects, magnetic materials, etc. Japanese companies are among the leaders in the construction and application of high voltage electron microscopes, and Japan operates and is constructing major research centers and facilities for synchrotron radiation, fission and fusion research, surface science, magnetism and magnetic materials, high-temperature research, and superconductivity. Its scientists and engineers contribute a significant number of articles to U.S. scientific journals, participate in scientific meetings in the U.S. and in jointly sponsored symposia, and work alongside U.S. colleagues as guestworkers in U.S. laboratories.

Since in scientific research and development, and for materials in particular, Japan is both an important competitor but also an equally important collaborator, it is important to maintain a continual awareness of Japanese research and acquaintance with Japanese scientists.

Research Funding

To understand government-supported materials research in Japan, it is helpful to know that research support is provided principally through three government organizations: the Science and Technology Agency (STA), in the Ministry of State for Science and Technology; the Agency for Industrial Science and Technology (AIST), in the Ministry for International Trade and Industry (MITI); and the Ministry of Education, Science and Culture ("Monbusho"). Total agency funding for FY 1991 is given in the accompanying table. The amounts listed are totals for "general" and "special" accounts, and hence include salaries and institutional costs in addition to amounts used for direct support of research programs.

Government support for research in natural sciences has climbed from ¥14.9 trillion in 1984 to ¥18.7 trillion in 1989, according to the STA. While an increase in absolute numbers, it has decreased from 0.49% to 0.46% of the GNP. Total R&D expenditures have increased from ¥71.7 trillion in 1984 to ¥109.1 trillion in 1989, due largely to an increase in private expenditures which increased to 2.7% of the GNP.

Basic scientific and technological research and large scale projects are carried out under the Science and Technology Agency. In addition, STA plans, formulates and implements basic science and technology policy and coordinates policies developed by other administrative bodies. The large-scale projects under its aegis include nuclear energy, space and ocean development and various pioneering fields, including earth sciences, disaster prevention, special materials, life sciences and aeronautical technology. STA administers six institutes, of which I visited the National Research Institute for Metals (NRIM) and the National Institute for Research in Inorganic Materials (NIRIM). In addition, seven public corporations are under STA, which promote research and development in important areas of nuclear energy, oceanography, space and technology. Of its total budget of ¥522.6 billion for FY1991, ¥120 billion was for material science and technology.

The Agency for Industrial Science and Technology promotes industrially related R&D through support of work on basic concepts, stimulation of technological creativity, distribution and transfer of results, and improvement and expansion of the infrastructure for the development of science and technology. AIST administers 16 research institutes, of which I visited the Electrotechnical Laboratory and three of the Government Industrial Research Institutes (Kyushu, Nagoya and Osaka). Though the New Energy Development Organization (NEDO), AIST is engaged with the private sector in the construction and operation of a number of technology related research centers, including the new Japan Ultrahigh Temperature Research Institute (JUTEM) with centers at Yamaguchi and Gifu. The total FY 1991 budget (draft) for the AIST was ¥255.9 billion. This included ¥27.7 billion for the New Energy Technology Project (Sunshine Project), ¥10.4 billion for the Energy Conservation Technology Project (Moonlight Project), ¥4.8 billion for the Project on Basic Technologies for Future Industries, and ¥28.8 billion for ordinary R&D (personnel and ordinary expenditures of laboratories). In contrast to the United States where project costs include research expenses, personnel costs and overhead, project allocations in Japan such as those for the Moonlight Project and Sunshine Project are solely for research expenses. AIST also earmarked ¥18.2 billion for R&D expenses incurred by laboratories for major project work, laboratory expansion, and expenditures incurred in operating joint Tsukuba facilities; expenses roughly approximate to capital costs in the U.S.

Principal support for research at national universities is provided by the Ministry of Education, Science and Culture. In 1992 the research grant budget of the Ministry of Education was ¥64.6 billion (about \$516 million) [Science, 23 Oct. 1992], an amount appreciably less than the total agency funding cited in the table below since the purview of the Ministry of Education extends to all levels of education and not only university research. Of this amount about \$177 million is distributed in many small peer-reviewed grants, and about \$133 million is distributed to team projects and group grants.

FY1991 Support for Science and Technology by the Japanese Government

Agency	Total Support, M¥	Growth Rate, %
Ministry of Education	936,324	4.7
STA	522,561	5.6
MITI	255,913	1.7
Defense Agency	115,045	10.3
Ministry of Agriculture	73,557	4.9
Ministry of Health and Welfare	56,144	9.6
Ministry of Posts and Telecomm.	33,904	10.6
Ministry of Transport	20,514	17.9
Environmental Affairs	10,900	18.3
Ministry of Foreign Affairs	8,160	15.0
Other	18,209	1.0
Total	2,051,231	

Source: AIST

Summary of Findings

My visit to Japan was an attempt to gain a partial overview of materials research in Japan since a similar visit by Robert Gottschall of DOE's Division of Materials Sciences in 1988. I am very appreciative of the advice, notes and information he made available to me before my trip. His report, Basic Research in Superconductor, Ceramic and Semiconductor Sciences at Selected Japanese Laboratories [DOE/ER-040], remains a useful reference for anyone seeking a guide to materials research in Japan.

On this trip I visited over 25 laboratories or facilities and talked to over 100 researchers and managers. I revisited three laboratories - the Government Industrial Research Institute at Nagoya, the National Institute for Research on Inorganic Materials at Tsukuba, and Nagaoka University of Technology - which I had visited briefly in 1987 and renewed acquaintances which I made on that visit. I gave seminars at several of the laboratories I visited in which I presented an overview of the DOE Materials Sciences program. A copy of the abstract for these seminars and a seminar announcement are included in Appendix I.

In my discussions and laboratory visits I focused on materials and materials issues with the greatest relevance to energy. These included high T_c superconductors, structural ceramics, intermetallic alloys, materials for nuclear reactor applications and irradiation effects, superhard materials and diamond films, high-temperature materials and properties, magnetic properties, surface science, self-propagating high-temperature synthesis, and materials processing. I gave little attention to electronic materials which, with the exception of photovoltaics and some sensor applications, have less application to energy issues. Furthermore, these materials due to their large commercial importance have probably been given more attention by most other visitors to Japan.

I found strong competences in the areas of materials synthesis and processing of ceramics, alloys and oxide superconductors; single crystal growth; high pressure research and hot isostatic pressing (HIP); film growth; magnetic materials and magnets; electron microscopy; and materials for nuclear reactors. Laboratories and facilities which served major programmatic thrusts of the Science and Technology Agency (STA) or of Agency of Industrial Science and Technology (AIST) of MITI were well supported, often having new equipment, if not a new laboratory. However, the facilities of older government and national university laboratories were often crowded and in need of maintenance. The contrast between these older facilities and new facilities, often established by a joint government-industrial collaboration, such as the Japan Ultrahigh Temperature Research (JUTEM) Facility at Gifu was striking.

In areas such as high T_c superconductivity, high-temperature research and nuclear energy on which considerable technological emphasis has been placed, government funding agencies and industry have both individually and jointly established laboratories with state-of-the-art equipment. These laboratories often appeared to be focused on materials processing, testing and device development and were less well-equipped for a multifaceted materials research program. University laboratories and the older governmental institutes, on the other hand, appeared to be carrying out more diversified materials research.

High-quality high resolution electron microscopy (HREM) studies were evident at several laboratories - indeed, the observation of oxygen atoms in superconductors by S. Horiuchi at NIRIM is a notable accomplishment. In contrast to the great emphasis given to imaging, I was surprised at the small amount of effort in analytical electron microscopy and the limited analytical capabilities on many electron microscopes. Analytical equipment appeared to be limited primarily to x-ray analysis with energy-dispersive spectroscopy (EDS). I noted the availability of electron energy loss spectroscopy (EELS) in only one or two instances. I also was surprised to learn that electron microscopists are frequently considered to be technicians rather than scientists so that there is little professional scientific motivation to advance in this field of research.

I found few examples of modeling and simulation of electronic and atomic structure. The tight-binding modeling of grain boundaries in SiC and transition metal- Al_2O_3 interfaces by M. Kohyama et al. at the Government Industrial Research Institute at Osaka is one exception. Also, I did not talk with Professor Kawazoe at the Institute for Materials Research at Tohoku University who is doing materials design by computer simulation. As a consequence of my limited contact with these activities, it appeared that there is considerably less effort in modeling and simulation of materials in Japan than in the U.S.

Visits to the research facilities provided first-hand impressions which are not easily gained from research reports and published research budgets. The lack of funding for building upkeep and crowded, poorly lighted laboratory facilities with old general purpose equipment is common at the older government and national university laboratories. Nevertheless, even at these older institutions, research laboratories supported by high-priority programs are well-equipped with often state-of-the-art instrumentation. In general, a higher priority appeared to be placed on equipment than on the condition of the building. In contrast to these older institutions, new joint government-industrially funded research institutes such as Superconductivity Research Laboratory of ISTEK and the Japan Ultrahigh Temperature Research Institute have modern facility and the latest in instrumentation. Industrial laboratories also generally appeared to be better housed and equipped than the government and university laboratories.

The **Principal Contacts** section below can be quickly scanned for a list of the laboratories and scientists visited. Following that, the **Summary of Highlights** section presents a brief description of important observations broken down first by topic and, within each topic, by laboratory. Following this section, the laboratories and programs are described in the **Laboratories** section. Research highlights are elaborated upon in the topical sections which include **Ceramics; Metals, Alloys and Intermetallics; Superconductors; and Magnetic Materials and Magnet Facilities.**

Japanese Hospitality

If the Japanese succeed in anything, it is gracious hospitality. The researchers, engineers and managers whom I visited were very interested in describing their work and results and in showing me their laboratories. In addition to many discussions and lab tours, I was provided several interesting side trips to the countryside and visits to restaurants that I never would have found on my own. Maso Takeyama (NRIM) and Yoichiro Sato (NIRIM) went out their way to help me with bus and train connections. Yoshio Bando and Kazuhiro Otsuka provided an evening at a sushi restaurant. Tatsuo Shikama (IMR-Oarai) provided a very enjoyable visit to the coastal region at Oarai, a visit to a fishermen's shrine, and a memorable restaurant in Mito. A pleasant dinner in the home of Kenji Suzuki (IMR-Sendai) remains as one of the high points of my trip.

Shotaro Morozumi (Emeritus of the IMR and now of the Ciba Institute of Technology) provided an opportunity to visit the Mt. Zoa area. I had several interesting sidetrips with Kozo Ishizaki and his students, including to Kashiwazaki Nuclear Power Facility, a casting company and a maker of traditional Japanese swords. Tatsuki Ohji (GIRIN) and Nobuo Kamiya (Toyota CRDL) generously hosted my visit to Nagoya and handled many of my arrangements for visits to laboratories in the Nagoya area. Masaharu Yamaguchi (Kyoto University) provided a memorable evening in Kyoto. Manshi Ohyangi (Ryukoku University) took me to visit the Shiga Art Museum which had excellent exhibits of early 20th Century Japanese art and contemporary western art, including an Andy Warhol soup can. Yoshinari Miyamoto (Osaka University) provided a pleasant evening during my stay in Suita-Osaka.

International Workshop on Superconductivity

Enroute to Japan I attended the International Workshop on Superconductivity which was held in Honolulu, Hawaii, from June 23-26. The workshop was co-sponsored by the International Superconductivity Technology Center (ISTEC) and the Materials Research Society. Since three DOE Superconductivity Pilot Centers had provided financial support for the workshop, I was asked as the only representative of DOE in attendance to say a few words of welcome at the beginning of the workshop. The workshop lectures and discussions focused on status of growth and processing of single crystal and ceramic oxide superconductors, the preparation of superconducting wires and tapes, and the formation and properties of pinning centers. The siting of this workshop at a location intermediate between Japan and mainland United States and the joint sponsorship by ISTEC and MRS were effective in bringing together a sizeable group of scientists from the two countries.

PRINCIPAL CONTACTS

Sites Visited:	6/29 National Research Institute for Metals (NRIM), Tokyo	Dr. K. Nii, Dir. General Dr. M. Takeyama Dr. M. Nakamura Dr. I. Nakatani Dr. H. Aoki Dr. N. Nagata Dr. C. Tanaka
	6/30 Tohoku University, Institute for Materials Research (IMR), Oarai Research Facility	Dr. T. Shikama
	7/1 National Institute for Research on Inorganic Materials (NIRIM), Tsukuba	Dr. Y. Sato Dr. S. Horiuchi Dr. S. Ikegami Dr. N. Ishii Dr. M. Mitomo Dr. K. Takahashi Dr. N. Yamaoka Dr. Y. Bando
	7/2 NRIM, Tsukuba	Dr. K. Inoue Dr. H. Shiraishi Dr. T. Hirano
	7/2 Electrotechnical Laboratory (ETL), Tsukuba	Dr. K. Endo Dr. K. Kajimura
	7/2 University of Tsukuba	Dr. K. Otsuka
	7/3 Hitachi Research Laboratory (HRL), Hitachi City	Dr. T. Miyoshi Dr. K. Maeda Dr. T. Aoyama Dr. S-P. Matsuda
	7/6 Tohoku University, Institute for Materials Research (IMR), Sendai	Dr. T. Masumoto, Director Dr. K. Aoki Dr. K. Sumino Dr. H. Matsui Dr. S. Hanada Dr. T. Sakurai Dr. K. Suzuki Dr. H. Komatsu

7/7	Tohoku University, Sendai	Dr. M. Shimada Dr. R. Watanabe Dr. J-F. Li Dr. M. Sasaki
7/7	Tohoku University, IMR	Dr. K. Watanabe Dr. T. Hirai Dr. M. Omori Dr. H. Yamane Dr. M. Sasaki Dr. T. Goto Dr. S. Morozumi Ciba Institute
7/8	Nagaoka University of Technology, Nagaoka	Dr. Y. Uchida, President Dr. K. Ishizaki
7/9	Kashiwazaki Nuclear Power Facility, Kashiwazaki	
7/10	Nagaoka University of Technology	Dr. K. Matusita Dr. T. Komatsu Dr. K. Kamata Dr. K. Uematsu Dr. Y. Ichinose Dr. T. Umemura Dr. H. Okino Dr. Y. Inoue Dr. Y. Hirotsu
7/13	AFOSR-Far East Office, Tokyo	Dr. I. Ahmad
7/13	International Supercon- ductivity Technology Center, Superconductivity Research Laboratory, Tokyo	Dr. S. Tanaka, Director Dr. N. Koshizuka Dr. Y. Shiohara Mr. T. Kobayashi Mr. K. Shibasaki Mr. S. Hosaka
7/14	University of Tokyo, Institute of Industrial Science	Dr. Y. Kagawa Dr. M. Maeda
7/15	University of Tokyo	Dr. H. Yanagida
7/16	Toyota Central Research and Development Laboratory (CRDL), Nagakute, Aichi	Dr. N. Kamiya Dr. T. Hioki Dr. M. Ohkubo Dr. H. Takahashi Dr. A. Danno

7/17	Japan Fine Ceramic Center (JFCC)	Dr. M. Isotani Mr. N. Kosuge Mr. Y. Yamaguchi
7/17	ISTEC Nagoya Division	Dr. I. Hirabayashi Mr. T. Nakamoto
7/18	NGK Spark Plug/NTK Technical Ceramics, Iwasaki, Komaki-shi	Mr. H. Banno, Dir., R&D Dr. Y. Tajima Mr. T. Shimamori Mr. M. Okuyama Mr. K. Urashima Mr. M. Watanabe
7/18	Japan Ultrahigh Temperature Research Center (JUTEM), Tajimi-City, Gifu	Dr. K. Itoh, Director
7/21	Government Industrial Research Institute, Nagoya (GIRIN)	Dr. S. Tomiyama, Dir. General Dr. T. Ohji Dr. H. Tabata Dr. S. Tomura Dr. K. Nakano Dr. K. Watari Dr. F. Wakai Dr. Y. Kuwahara Dr. M. E. Brito Mr. M. Awano Mr. M. Yasuoka Mr. M. Mabuchi
7/22	Kyoto University	Dr. M. Yamaguchi Dr. Y. Shirai Dr. H. Inui
7/24	Ryukoku University, Shiga Campus, Seta	Dr. M. Koizumi Dr. M. Ohyanagi
7/29	Government Industrial Research Institute, Kyushu (GIRIK)	Dr. H. Yoshida Dr. E. Tani Dr. T. Watanabe Dr. Y. Inukai

7/30	Government Industrial Research Institute, Osaka (GIRIO)	Dr. T. Komiyama, Dir. General Dr. T. Takahashi Dr. M. Kinoshita Dr. H. Yamashita Dr. K. Kadono Dr. I. Matsubara Mr. R. Funahashi Dr. S. Higuchi Dr. S. Tanase Mr. Y. Miyazaki
7/31	Osaka University, Institute of Scientific and Industrial Research, Osaka	Dr. Y. Miyamoto Dr. K. Niihara Dr. Y. Umakoshi Dr. N. Furushiro Dr. T. Shibata
8/1	Sumitomo Electric Industries Itami Research Laboratories, Itami	Dr. M. Miyake, Gen. Manager

SUMMARY OF HIGHLIGHTS

Advanced Processing Methods

National Research Institute for Metals

Floating zone unidirectional solidification in an image furnace has been used to grow stoichiometric Ni_3Al with improved room temperature ductility, polysynthetically twinned TiAl , a variety of transition metal disilicide single crystals and CaSi_2 single crystals. [32,78]*

Nagaoka University of Technology

Various chemical vapor deposition methods are being investigated for the growth of amorphous $\text{SiC-Si}_3\text{N}_4$, diamond-like carbon, and oxide films such as TiO_2 and ZnO . [41]

International Superconductivity Technology Center

An Automated Ceramic Processing System is operation which a means for automatically batching large numbers of similar samples or series of compositions where standard powder mixing, grinding and sintering operations can be performed. [44]

University of Tokyo

In the Institute of Industrial Science studies are being conducted on the in situ formation of Al_2O_3 -matrix/ Si,Mg composites by controlled oxidation of Al-Si-Mg melts. [45,65]

Ryukoku University, Shiga Campus

A high-density titanium carbide material has been obtained from a combustion synthesis process (self-propagating high-temperature synthesis, SHS) using Ti-C fuel and an ignition pellet of a pressed Ti-C powder mixture. [56]

An SHS technique has been used to bond diamond to a metal substrate. [56]

* Page numbers in the square brackets refer to pages on which further details are given.

Osaka University

A combination of combustion synthesis, or self-propagating high-temperature synthesis, and hot-isostatic pressing has been used to simultaneously synthesize and densify $\text{Si}_3\text{N}_4/\text{SiC}$ ceramics. [61,65]

Amorphous Materials

Nagaoka University of Technology

The crystallization and viscosity of $\text{BaF}_2\text{-ZrF}_4$ glasses are being studied to develop improved control of the high-temperature processing of these glasses. These glasses have potential use as IR transparent optical fibers, and their viscosity is a strong function of temperature. [42,73]

TeO_2 glasses are being investigated which are capable of containing high concentrations of functional oxides such as LiNbO_3 and BaTiO_3 , with little change in refractive index and high transparency. [42]

Organic molecules with special functional groups are being encapsulated in low-melting oxyfluoride glasses in the system, Sn-P-Pb-O-F , where O and F are present in approximately equimolar amounts. The goal is to produce glasses with nonlinear optical properties. [42,73]

Reprocessing of waste Al silicate filtration materials is being studied as a means to produce glass compositions for use as aggregate in building materials. [42,73]

Rapid solidification is being studied as a method to prepare metallic Co-Ni-Fe-Si-B glasses. [42,73]

Government Industrial Research Institute, Osaka

Improvements in the glass transition temperature and stability are being sought for glasses in the $\text{ZnBr}_2\text{-BaBr}_2\text{-KBr}$ system which are potential IR transmitting material with possible application in windows and optical fibers for CO_2 laser radiation. Some improvement in the glass transition temperature have been realized by the addition of high melting point compounds. [58,73]

Analyses of the infrared absorption bands of cadmium halide glasses and molten salts have suggested that cadmium is tetrahedrally coordinated in Cd-Cl and Cd-Br glasses but has 5 and 6 coordination in the molten salt. Cd-I appeared to have the same coordination in both the glass and the molten salt. [58,73]

The ionic conductivity has been determined by ac impedance for lithium halide glasses. Li-I glasses were found to have the highest conductivity. The glass-forming region was determined for the pseudoternaries LiX-KX-CsX-BaX_2 , where X was Cl, Br or I, and where the KX/CsX ratio was fixed. [58,73]

The ionic conductivity has been determined as function of composition for copper (I) halide based glasses with alkaline and alkaline earth halide glass modifiers and with a single halide species. The composition $30\text{CuCl}-30\text{CuBr}-30\text{RbCl}-5\text{CaCl}_2-5\text{BaCl}_2$ exhibited the highest room temperature conductivity. [58,74]

The third-order nonlinear susceptibility of silica glass has been increased by ion-implanting Au followed by annealing to grow colloidal Au particles. [58,74]

A composite porous glass gas-separation membrane has been prepared by hydrolyzing a mixture of Si and Zr alkoxides in a porous alumina tube. [59,74]

Ceramics

National Institute for Research on Inorganic Materials

The effect of yttrium dopant concentration of the structural phase transformation of ZrO_2 is being investigated by means of the heat of solution and bend strength measurements. This structural transformation may provide the basis for the "intelligent" self-healing of cracks in the ceramic bearings. [31,66]

Conditions for forming duplex structure silicon nitride ceramics are being studied by the 5th Research Group. [32,67]

Indenter introduced crack tips in SiC and Si and cracks in sialon induced by crushing have been imaged by high-resolution electron microscopy. The cracks were found to be atomically sharp with no evidence of yielding. [32,69]

Institute for Materials Research, Tohoku University

Trichloro-phenylsilane is being used as a precursor for the synthesis of SiC/C composites. The organic precursor is polymerized into a three-dimensional network which can be dissolved and casted as a film. [39,64]

The oxidation of chemically vapor-deposited SiC has been investigated in Ar-O_2 and CO-CO_2 atmospheres for a temperature range from 1567°C to 1650°C , and the oxygen partial pressure for the transition from active to passive oxidation was determined. [39,70]

Tohoku University, Other Programs

The unsymmetric, isoelectronic ternary chalcogenides ZnGeP_2 , ZnGeN_2 and ZnSiN_2 have been synthesized by a high pressure technique, and their crystallographic structures have been determined. [40,74]

A wet spray combination process has been developed which yields functionally gradient materials with more thinly graded compositions. [40]

High strength ZrO_2 -SiC composites and SiC-AlN ceramics with lower sintering temperatures are being developed. [40]

Nagaoka University of Technology

A technique has been developed using a neutral optical density effect to study the interior of features of spray-dried particles. Observed features were shown to leave artifacts in green ceramic bodies even after isostatic compaction at pressures of 600 atm. [43,68]

A thermal program desorption (TPD) apparatus was developed and used to study the effect of washing on the removal of absorbed gases from silicon nitride powders and on the effect of washing on powder fluidity. [41,64]

Low-temperature specific heat measurements are being used to determine the amount of amorphous phase in ceramic powders. This technique was previously used in a quantitative evaluation of amorphous content of the grain boundary phase of Si_3N_4 . [42,68]

Carbothermal reactions during sintering have been investigated to convert $\text{AlN/Y}_2\text{O}_3$ to AlN/YN and to prepare $\text{Si}_3\text{N}_4/\text{SiC}$ composites from Si_3N_4 , containing a native layer of oxide and coated with a layer of graphite. [41,64]

The preparation of porous ceramics by hot-isostatic pressing was demonstrated by preparing porous titanium dioxide ceramics with controlled porosity between 28% and 40% of total sample volume. [41,65]

University of Tokyo

A load cell and fixture have been developed for microscopic observation of crack propagation transparent brittle solids. A laser technique ("laser caustics") also is being developed to measure the stress-intensity factor at a crack tip. [45,69]

Crack growth and fracture of fiber-reinforced composites are being studied using laser techniques and a transparent matrix, consisting of lithium aluminosilicate glass, and containing transparent fibers, silicon oxynitride. [45,69]

Microscopic studies of crack fronts in transparent, brittle solids have been conducted using indenter induced cracks and from notched cantilever beam. [45,69]

Diphasic materials are being studied as potential humidity and chemical sensors. A p-Si/n-Si junction has been shown to recognize various types of alcohols. [46]

Toyota Central Research and Development Laboratory

Research on injection molding of ceramic rotors has been discontinued, and work is now focused on development of a slip casting method. Monolithic ceramics such as silicon nitride remain the materials of choice, as composites are considered to be too expensive to produce. [47,75]

Japan Fine Ceramics Center

A reference alumina (REFROCERAM) has been developed and will be proposed to the International Standards Organization as an international standard. [48]

NGK Spark Plug, NTK Technical Ceramics

A desk-top cyclic fatigue tester equipped with a high power piezoelectric bimorph has been developed to test small test pieces. [50,68]

Since monolithic Si_3N_4 forms a duplex, two-phase structure, and since Si_3N_4 -matrix composites have only marginally better toughness values and are more expensive to produce, monolithic Si_3N_4 is considered to be more attractive for automotive applications. [75]

Government Industrial Research Institute at Nagoya

A process for the synthetic preparation of kaolinite is being developed since local sources of natural kaolinite are dwindling. Spherical kaolinite has been developed as an intermediate product and is useful in reducing hysteresis effects in forming. [53,63]

Carbon-fiber/ceramic composites with Si_3N_4 and Si_3N_4 -sialon have been fabricated and mechanically tested with respect to room and high-temperature flexural and dynamic fatigue to establish a basis for design standards and life prediction. Fracture surfaces from high-temperature tests suggested that shearing of the softened interface occurred between fiber and matrix. [53,67]

Room temperature and high-temperature flexural strengths have been studied for SiC/carbon fiber composites which were prepared by infiltrating carbon prepreps with slurries of SiC and AlB_2 powders and polystyrene, pyrolyzing the postform and hot-pressing. [53,67]

Tensile fatigue, tensile strength and long-term (100,000 hours) tensile creep are being determined for monolithic Si_3N_4 , $\text{Si}_3\text{N}_4/\text{SiC}$ -whisker composites and SiC . The tensile strength of hot-pressed Si_3N_4 containing 5 wt% Y_2O_3 and 3 wt% Al_2O_3 showed a drastic decrease at temperatures above 1000°C due to softening of the grain boundary glassy phase and some plasticity at temperatures above 1300°C some plasticity with a lower yielding point appearing at low displacement rates. Creep and creep rupture behavior were investigated for Si_3N_4 with and without SiC whiskers from 1200°C to 1400°C . Slow steady-state creep was observed under low stresses at 1200°C . Evidence of accelerated creep was observed toward the ends of the creep tests at 1300°C and above. [53,70]

Government Industrial Research Institute of Kyushu

Process conditions and properties of hot-pressed carbon/carbon composites from calcined coke or phenol resins have been studied for various carbide additives. Physical properties and other characteristics investigated included bend strength, lattice constant, electrical resistivity, apparent crystallite size, loss of bend strength due to thermal shock, and reactivity with oxygen and with strong oxidizing acid. [57,68]

Government Industrial Research Institute of Osaka

Gas-pressure sintered Si_3N_4 with Y_2O_3 or La_2O_3 sintering aids showed bend strengths higher than 900 Mpa at 1300°C , whereas composites with Pr_6O_{11} - Y_2O_3 or Pr_6O_{11} - Al_2O_3 yielded strengths on the order of 800 Mpa. [60]

Preparation of SiC whisker/ SiC composites from whiskers and polycarbosilane precursor has been investigated by ball-milling whiskers with polycarbosilane prior to forming and decomposition to obtain SiC , and by infiltrating whisker preforms with polycarbosilane. Low densities and bend strengths were obtained in both cases. [60]

Various precursors and process conditions have been studied for the preparation of $\text{Si}_3\text{N}_4/\text{SiC}$ composites with SiC whiskers or chemically vapor deposited SiC fiber and of SiC /carbon composites with carbon black as the source of carbon. The materials were characterized with respect to bend strength and fracture toughness. [60,67]

Al_2O_3 or TiO_2 coated SiC powders have been developed for low-pressure plasma spraying of SiC -based coatings on to normal carbon steel substrates. The SiC - Al_2O_3 coating had a coating with a coarse grained structure and poor bonding. The SiC - TiO_2 reacted to form TiC and SiO_2 which melted in the torch and formed an adherent coating. [68]

In tests of hardening of (10 $\bar{1}$ 0) and (0001) surfaces of sapphire, 3 MeV Ni^{+2} ions at high fluence had greater penetration and hardening effect than did 3 MeV Au^{+2} ions. [60]

Ceramic materials are being studied for molten carbonate fuel cell (MCFC) and solid oxide electrolyte fuel cell applications. Alkali and alkaline earth carbonate systems are being investigated with respect to conductivity and corrosion resistance in simulated MCFC tests. $(\text{CeO}_2)_{0.8}(\text{SmO}_{1.5})_{0.2}$ -based solid oxide electrolytes with additional oxide dopants are being studied to develop materials with improved ionic conductivity and reduced parasitic losses by electronic conduction. [59]

A self-consistent tight-binding method with the supercell technique has been used to calculate the interfacial energies for the possible polar and nonpolar constructions of a $\{122\}$ ± 9 grain boundary in β -SiC (zincblende structure). The N-type, C-terminated interface was found to be the most stable for a C-rich atmosphere, and either type of polar interface to be more stable than the nonpolar interface. [60,72]

The bonding between an (0001) surface of sapphire and a series of 4d transition metals was investigated using the tight-binding method and for various degrees of metal deposition over the surface oxygen plane. Modeling of the Nb- Al_2O_3 interface showed that a direct chemical bond of both covalent and ionic character can be established between the surface O atoms and the deposited Nb atoms. [60]

Osaka University

Nanocomposites of coarse grain matrices of Al_2O_3 , Si_3N_4 , B_4C , or MgO with a dispersoid of ultrafine SiC, ZrO_2 , and TB_2 grains have been prepared and characterized with respect to bend strength and toughness. [61,66]

Sumitomo Electric, Itami Works

Silicon nitride ceramics with reportedly the world's greatest strength and reliability twice that of existing materials have been developed by precise control of grain size. A continuous production process free of impurity contamination, to approximately double product reliability has been established with the goal of supplying test samples to manufacturers by April 1993. The new ceramics will be marketed primarily for automotive engine components such as valves and piston pins. [62,76]

Electronic and Optical Materials

National Research Institute for Metals

FeSi_2 and Bi_2Te_3 - Sb_2Te_3 , among other materials, are being studied as possible thermoelectric materials. [27]

National Institute for Research on Inorganic Materials

Seventeen new sulfide phases have been synthesized and their structures have been determined. [32]

Electrotechnical Laboratory

Research includes epitaxial growth methods for wide band-gap semiconductors, development of semiconductor devices, and fundamentals of semiconductor heterostructures. [34]

Institute for Materials Research, Tohoku University

The nature, formation, dynamics and interactions of defects and dislocations are being studied in semiconductors such as Si and GaAs. Electronic properties of semiconductors with defects formed by electron or neutron irradiation have been studied using measurements of deformation and electrical properties. [37]

Tohoku University, Other Programs

The preparation of FeSi_2 -based thermoelectric materials with improved thermal stability and power factor is being studied by the selected additions of first, second and third row transition metal silicides. [40]

Government Industrial Research Institute, Osaka

A "3-D Ion Microscope" has been developed for surface analysis, measurement of elemental depth distribution and investigation of electronic states. Gold pad patterns on Si have been analyzed. [59]

Hard Materials and Films

National Institute for Research on Inorganic Materials

Growth conditions and properties are being studied for diamond and boron-doped diamond films grown by microwave plasma CVD. [31]

The high-pressure synthesis of diamond has been demonstrated to occur in the presence of a number of sulphate, carbonates, and hydroxides of alkali and alkaline earth metals. [32]

Magnetic Materials and Magnet Facilities

National Research Institute for Metals

In-situ formation of magnetic particles in organic fluids has been accomplished by two techniques: (1) condensation of metal vapors on a fluid coated surface, and (2) decomposition of a metal carbonyl in kerosene in the presence of ammonia gas. [27,89]

The High-Field Magnetic Laboratory operates a variety of high-resolution magnetic systems, hybrid magnets, long pulse magnets and large bore magnets for studies of high T_c superconductors, highly correlated electronic materials, heavy Fermion materials, organic superconductors and magnetic resonance studies. [27,90]

An extremely high-field research center is under construction for characterization of the high-field performance of oxide superconductors. This center will include a 40 T hybrid magnet, a 20 T class superconducting magnet with large bore, a 80 T class long-pulse magnet, and several kinds of small superconducting magnets. [33,90]

Institute for Materials Research, Tohoku University

The microstructural evolution of $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ to yield a ferromagnetic α -FeSi phase has been studied by atomic probe field ion microscopy and high-resolution electron microscopy. [37,89]

The High Field Laboratory for Superconducting Materials provides high field magnets and instrumentation for measuring superconducting, magnetic, optical and other properties of test samples in a program to develop superconducting materials for superconducting magnets for plasma confinement fusion reactors. [39,91]

Nagaoka University of Technology

The interface region between soft magnetic thin films of Fe-Al-Si produced by rapid solidification and the substrate is being studied by Mossbauer spectroscopy. [42]

Materials for Radiation Environments

National Research Institute for Metals

Corrosion fatigue of low alloy steels has been studied in environments simulating that of coolant waters, and low-cycle lifetime tensile tests were conducted on ASTM A533B steel under simulated boiling water reactor conditions. [28]

SiC-based coatings and composites are being investigated for low-activation materials for nuclear applications. SiC coatings have been prepared by laser deposition. SiC composites have been prepared by chemical vapor infiltration. [33,71]

Creep and creep rupture of high-temperature metals are being investigated for the possible use of these metals in fusion reactor first wall applications. [33,82]

Structural changes in real time for graphite and molybdenum subjected to ion irradiation are being studied by Raman spectroscopy. [33,82]

Institute for Materials Research, Tohoku University

The Oarai Irradiation Experimental Facility provides a means for university researchers in Japan to carry out irradiation research at the Oarai Research Establishment which is operated by the Japan Atomic Energy Research Institute. [29]

The effects of neutron and gamma irradiation on the conductivity of insulating ceramics are being studied at the Japan Materials Testing Reactor by in-situ AC impedance measurements. [29,71]

Anomalous swelling of vanadium alloys under high-energy helium (^3He) particle irradiation is being studied with a new experimental approach. Vanadium alloys are of interest for first wall applications in fusion reactors. [37,82]

NGK Spark Plug/NTK Technical Ceramics

Spinel ceramics are being developed for in-core hermetic seals for neutron sensors. [50]

Metals, Alloys and Intermetallics

National Research Institute for Metals

Small amounts of Mn additions were found to improve the room temperature ductility of TiAl-based alloys. [27,80]

Cr-modified TiAl was found to have a ductility in vacuum of over 4%, but its ductility in hydrogen and air was reduced to about 1%. Cast TiAl without the Ti_3Al (α_2 -phase) was found to be unaffected by hydrogen. [80]

Oxygen was found to have little effect on the removal of the TiAl γ -phase. Si additions were found to remove the oxidation resistance of TiAl-alloys. [80]

TiAl-alloys with a grain size of 5 μm were found to be superplastic. [27,81]

Long-term creep rates for steels at high temperatures and low stresses have shown convergence of creep rupture strengths, suggesting that the inherent creep strength is controlled by the ferritic matrix. [28,82]

University of Tsukuba

Type II lattice invariant shear twinning identified for the cubic to orthorhombic martensitic transition of a Cu-Al-Ni shape memory alloy. Only a Type I shear twinning has been commonly known. [35,81]

Institute for Materials Research, Tohoku University

An improved system for performing powder metallurgy under inert conditions has been put into operation. Metal powders are prepared by atomization and rapid solidification under vacuum, then consolidated and sintered under inert conditions without exposing them to air. [36]

Research on Ti alloys and TiAl and Nb₃Al include floating zone growth and deformation studies. [36]

State-of-the-art field ion-scanning tunneling microscopes with the capability of internal tip exchange have been used for studies of adsorption on Si and Ag. [38,83]

X-ray and neutron small-angle scattering are being used to study nanocrystallization by mechanical grinding. [38]

Tohoku University

A modified small punch technique has been used to measure yield strength at high temperatures and to determine the brittle to ductile transition temperature in alloys composited with AlN. [41,81]

Nagaoka University of Technology

The synthesis and structure of the high-temperature structural silicides, Ti₂Zr₃Si₃ and Zr₅Si₃, have been reported. These silicides have the 16H crystal structure. [41,78]

Toyota Central Research and Development Laboratory

Powder processing of TiAl, casting of Al alloys, and high-strength, heat resistant Ti alloys are being studied to make high-quality parts by controlling material composition and processing technique and reducing weight. [47]

The use of a fluidized bed technique is being studied to improve a Toyota-developed thermal deposition process for refractory hard coatings. Development of a hard coating also is in progress for aluminum. [47,83]

Government Industrial Research Institute, Nagoya

Aluminum alloys composited with submicron sized silicon nitride or silicon carbide particulates have been developed which are capable of undergoing high very tensile deformations at high strain rates during hot extrusions. [53,81]

Kyoto University

The twinning behavior of polysynthetically twinned (PST) crystals of TiAl has been characterized, and deformation behavior of PST crystals has been determined with respect to tensile and compressive stresses. [54,77,79]

Vacancies, anti-site atoms and dislocations in Ti-rich, near-stoichiometric and Al-rich TiAl have been investigated with positron annihilation spectrometry. [54,78]

The success of cold-rolling of PST TiAl has been shown to depend on the orientation of the lamellae with respect to the rolling plane and direction, with as much as 50% reduction being attained if the operative shear deformation is parallel to the lamellar planes. [54]

Although CoSi_2 is cubic, and hence is expected to have a sufficient number of slip systems to exhibit significant plastic deformation, in an initial study it was found to only to have 2-4% deformation before undergoing catastrophic failure. [55,80]

Osaka University

The deformation mechanisms of Ti-rich PST TiAl crystals have been determined with respect to shear parallel to lamellar boundaries (easy shear) and to shear across lamellar boundaries (hard shear). The plastic behavior of PST TiAl also has been found to depend strongly on the lamellar spacing. [61,79]

Alloying of CrSi_2 with MoSi_2 to possibility activate additional slip systems at low temperatures was shown to yield little improvement in ductility. [61,80]

Superconductors

National Research Institute for Metals

A cold-working process has been developed for the preparation of Nb_3Al multifilimentary wire for high-field magnets which circumvents previous barriers to the formation of Nb_3Al by reactive diffusion. [33,87]

National Institute for Research on Inorganic Materials

The syntheses of Y-Ba-Ca-O and Bi-Pb-Sr-Ca-Cu-O superconductors are being investigated using the devitrification of vitreous precursor approach. [32,86]

The oxygen columns in $\text{YBa}_2\text{Cu}_3\text{O}_{7.7}$, prepared by high pressure oxidation, have been imaged for the first time using a high voltage electron microscope. [31,87]

Electrotechnical Laboratory

Superconducting research includes organic superconductors, Langmuir-Blodgett films, film deposition by molecular beam epitaxy and chemical vapor deposition, physical properties of oxide superconductors, and development of new superconductors. [34]

Institute for Materials Research, Tohoku University

A very elegant high-temperature microscope system has been developed for in-situ observation of phase equilibria and flux growth of oxide superconductors. Phenomena and phases observed during flux growth in the $\text{Bi}_2(\text{Sr,Ca})_{1+x}\text{Cu}_x\text{O}_y$ system have been reported. [39,85]

Two growth mechanisms have been observed for the growth of $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$ from the melt: tiling type growth and spiral growth. [39,85]

The effect of amorphous structure on electron correlation is being studied for heavy fermion Ce and Yb alloys. [38]

Tohoku University, Other Programs

An effort is in progress to grow an infinite layer $(\text{Ba,Sr})\text{CuO}_3$ structure using a high pressure technique. [40]

Nagaoka University of Technology

An oxygen hot isostatic pressure has been used to prepare the $\text{YBa}_2\text{Cu}_4\text{O}_8$ and the $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ phases with much shorter process times than are typically required without the application of an isostatic load.

[41,86]

Work is in progress to improve the synthesis of high T_c superconductors using the devitrification of amorphous precursors and to understand the source of normal conductivity that occurs at the grain boundaries of superconducting materials prepared by this method.

[42,86]

International Superconductivity Technology Center

A small single crystal of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ * has been grown by the Czechawalski method. A single crystal of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ ** has been grown by the float zone method.

[44]

The 35th organic superconductor, $x\text{-(BEDT-TTF)}_2\text{Ag(CN)}_2$, has been discovered by Division III of ISTE's Superconductivity Research Laboratory.

[44]

Low temperature growth of ultrafine Y-123 and Y-124 have been developed by Division IV using a sol-gel method.

[44]

Platinum doping of melts was found to reduce the size of Y_2BaCuO_5 precipitates in Y-123. Rhodium doping of Y-123 has been observed to behave similarly to platinum doping.

[84]

Rapid thick film painting techniques have been investigated for the application of thick Y-123 films on to flexible polycrystalline yttria-stabilized zirconia substrates.

[85]

A strong interaction has been found between the electrons and the lattice vibrations in CuO_2 planes in many Cu oxides with layered structures.

[87]

Toyota Central Research and Development Laboratory

Vacancy ordering in Y-123 has been modeled using a Monte Carlo method.

[48,87]

* In this report the less cumbersome designations Y-123, Y-124 and Y-247 will be used for the yttrium-barium-copper oxide superconducting phases $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{YBa}_2\text{Cu}_4\text{O}_8$ and $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$, respectively. The Y-Ba-Cu-O materials are commonly referred to as YBCO, "yib-co."

** Similarly, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ will be designated by Bi-2212 and Bi-2223, respectively. The Bi-Sr-Ca-Cu-O materials are commonly referred to as BSCCO, "bisc-co."

Government Industrial Research Institute, Nagoya

Mist pyrolysis, spray-drying and sol-gel methods are being investigated as methods for preparing submicron sized homogeneous powders which will enhance formability and critical currents in Y-123 and Bi-Pb-Sr-Ca-Cu-O superconductors. [54,86]

Government Industrial Research Institute, Osaka

Whiskers of the Bi-2223 high T_c superconducting phase have been prepared by annealing whiskers of Bi-2212 whiskers in a $\text{Bi}_2\text{Sr}_2\text{Ca}_4\text{Cu}_6\text{Pb}_{0.5}\text{O}_x$ powder. Single crystals of Bi-2212 were converted by the same method into Bi-2223 sheets. [59,85]

LABORATORIES

NATIONAL RESEARCH INSTITUTE FOR METALS (NRIM), TOKYO

The National Research Institute for Metals is a part of the Science and Technology Agency (STA) and serves as a general research institute on metals. NRIM carries out the following work:

1. Fundamental and applied research on advanced materials such as high-performance heat-resistant alloys, workable intermetallic compounds and new superconductors;
2. Research on reliability materials to ensure safety of structural components and facilities.

NRIM has two locations: an older site in Meguro District of Tokyo and a newer site in Tsukuba Science City, 80 km northeast of Tokyo. The Tokyo laboratory will be closed soon.

I visited the NRIM-Tokyo on June 29 and NRIM-Tsukuba on July 2. My visit to NRIM-Tokyo was graciously hosted by Maso Takeyama of the 3rd Research Group (Intermetallic Materials). Takeyama had worked for three years at ORNL with C. T. Liu.

Kazuyoshi Nii, Director General of NRIM, welcomed me to NRIM. Despite the fact that he was involved in an emergency budget meeting, Nii took a generous amount of time to learn about DOE and to discuss science in Japan and the United States. He was very interested the future of scientific funding in the United States, explaining that a cut in U.S. funding for research has a significant impact on funding for research in Japan. His immediate concerns was that these cuts might make it more difficult for him to obtain the increased budget needed to move the remainder of the laboratory to Tsukuba. In addition, since the STA is placing greater emphasis on fundamental work, NRIM is encountering greater difficulty in obtaining full support for its applied programs.

The 3rd Research Group (Intermetallics) which is led by M. Nakamura, has 15 members and 4 subgroups. Most of the research of the group is concerned with TiAl-based alloys. These materials are of interest for possible use in Japan's aerospace plane and its developing aircraft industry. Research on TiAl-based alloys at NRIM dates from 1978. At that time, the U.S. Air Force had already conducted secret research on these alloys for a number of years but by 1980 had lost interest in these materials because they were believed to be too brittle at ambient temperatures and too difficult for hot working. By 1980 work at NRIM had shown that TiAl with a low Al content, about 48 at% Al being optimum, was not so brittle at room temperature. By 1982 the NRIM research had shown the first evidence of the ability to hot work TiAl alloys by demonstrating hot extrusion with lateral pressure.

Research in the 3rd Research Group includes environmental effects on the ductility of TiAl-alloys (1st Subgroup), effects of alloying and processing on microstructure and ductility, hot workability to improve high-temperature yield strength, coating of TiAl alloys and Ni-TiC for corrosion resistance (2nd Subgroup), fabrication of TiAl and NiTi by self-propagating high-temperature synthesis (3rd Subgroup), and control of microstructure during radiofrequency melting (4th Subgroup).

I. Nishida and M. Okamoto (2nd Subgroup) are investigating FeSi_2 , Bi_2Te_3 - Sb_2Te_3 , etc. as possible thermoelectric materials. FeSi_2 is of interest for possible high temperature applications. M. Nobuki (4th Subgroup) is investigating hot workability of TiAl-alloys to improve their yield strength at temperatures above 1000°C and is studying the effect of Ti, Hf, W etc. on the microstructure. He has discovered how to make an equiaxed material, with a $5\text{ }\mu\text{m}$ grain size, which is superplastic at high temperatures, having an elongation of greater than 300%.

A program on mesoscopic materials and magnetic fluid materials was presented to me by Isao Nakatani, leader of the Physical Properties Division. He described two innovative in-situ methods for preparing magnetic fluids. The general approach was to surround ultrafine magnetic particles of iron, cobalt or nickel as they were formed with an amine surfactant so that the particles could be dispersed at high concentration in an organic fluid. In the first approach fine magnetic particles were formed by evaporative condensation on to the surface of a horizontally rotating cylinder which was coated with a film of an oil (alkylnaphthalene). The particles were immediately coated with a surfactant and were recovered in the pool of oil. In the second approach iron nitride was formed by heating to 185°C a stirred solution of iron-carbonyl, $\text{Fe}(\text{CO})_5$, in kerosene containing an amine surfactant in the presence of ammonia gas. Particle size was uniform and could be closely controlled by controlling the $\text{Fe}(\text{CO})_5$ concentration. Magnetization curves exhibited no hysteresis and high saturation magnetic flux density which ranged up to 2330 G.

Materials studied in the High-Field Magnetic Laboratory in the Metal Physics Division, under H. Aoki, currently include highly correlated electronic materials, high T_c oxide superconductors, heavy Fermion materials and organic superconductors such as ET_2KHgSCN . The laboratory operates and develops a variety of magnetic instruments, including hybrid magnets, long pulse magnets, large bore magnets and high resolution magnetic systems. One high-resolution system can produce fields up to 16 T with a homogeneity of $10^{-4}/10\text{mmdsv}$ and is equipped with a top-loading dilution refrigerator. This system is used for studies of quantum oscillations (de Haas-van Alfen and Shrebnikov-van Alfen effects) and for ordinary transport and magnetic measurements. Broad band nmr and other magnetic resonance experiments are carried out on a second high-resolution system which can produce a field of 15.5 T with a homogeneity of $10^{-5}/10\text{mmdsv}$ and a stability of $10^{-5}/\text{hr}$ in a 50 mm diameter sample space. NMR probes from 1.5 K to 800 K and an eprobe have been developed for this system. Magnetic resonance studies of ^3He in a 15.5 T field were carried out recently. A third instrument is a 500 MHz high resolution solid state nmr system with a room temperature bore of 89 mm.

Magic-angle spinning frequencies up to 10 kHz for this system and the temperature between -100°C and 100°C are available on this system. Pulsed systems include a 80 T magnet with a rise time of 10 ms, a hybrid magnet (20 T at 40 mm diameter; 15.3 T at 314 mm diameter) which is used for engineering purposes, and a hybrid magnet (40 T at 30 mm diameter). A large bore system permits the installation of experimental chambers such as a pressure cell.

Corrosion fatigue and stress corrosion cracking in steels for light water reactors and pressure vessels are studied in the 5th Research Group, under N. Nagata. He was very familiar with DOE and EPRI programs in these areas and was previously a member of the International Group on Cyclic Crack Growth Rate. Corrosion fatigue of low alloy steels has been studied in environments simulating that of coolant waters, and low-cycle lifetime tensile tests were conducted on ASTM A533B steel under simulated boiling water reactor conditions.

The Environmental Performance Division, led by C. Tanaka, determines long term creep and creep rupture data for heat-resistant steels and alloys and published creep data sheets. This program has provided neutral baseline data for the development of Japan's materials processing industry and, more recently, for development of nuclear energy. Creep and creep rupture tests are performed for as long as 11.5 years (100,000 hr). 878 creep machines, 144 multiple-type creep testing machines and 30 special-type creep testing machines are operated for this purpose.

INSTITUTE FOR MATERIALS RESEARCH (IMR), OARAI

The Institute for Materials Research (IMR), called "Kinken," at Tohoku University was reorganized in 1987 as a collaborative research institute for material science. The Institute, which prior to 1987 was known as the Research Institute for Iron, Steel and Other Metals, was established in 1922 by Professor Kotaro Honda. Honda is noted for the development of KS magnetic steel which produced the strongest permanent magnet of its time.

The main laboratory of the IMR is at the Katahira Campus of Tohoku University in Sendai. In 1969, an Irradiation Experimental Facility was built at the Oarai Reactor Research Establishment in Ibaraki Prefecture. I visited Oarai facility on June 30 and the main facility on July 6 and 7.

Tatsuo Shikama whom I had met in 1986 at a workshop sponsored by DOE's Division of Materials Sciences hosted my visit to Oarai. Shikama not only provided me with an opportunity to tour the facility and the Japan Materials Testing Reactor (JMTR), but he also provided a memorable tour of the rugged, pine-covered coastal area, along which at the Oarai Research Establishment is located.

The Oarai Irradiation Experimental Facility provides a means for university researchers in Japan to carry out irradiation research at the Oarai Research Establishment. The Oarai Research Establishment is operated by the Japan Atomic Energy Research Institute (JAERI) which is under the Science and Technology Agency (STA), while Tohoku University is under the Ministry of Education. JAERI carries out fundamental research on reactors, reactor materials and reactor safety and operates the Japan Materials Testing Reactor (JMTR). The Power Reactor and Nuclear Fuel Development Corporation (PNC), a partially government owned corporation, also carries out research at the site and is developing heavy-water breeder reactors.

The IMR facility which is operated by four scientists and seven technicians provides hot cells, glove boxes and a variety of characterization equipment for visiting university scientists. Equipment included three JEOL electron microscopes: a 400 KV HREM instrument with EELS; a conventional TEM with EDX; and an older microscope. Other equipment included a DTA/TGA instrument; a surface analysis instrument; FTIR spectrometer; and a small SEM. A Rigaku x-ray diffraction facility was equipped with a rotating anode, a microdiffractometer and a powder diffractometer. An imaging furnace with a single halogen lamp was used for float-zone growth of single crystals. All of these instruments appeared to be new (i.e., manufactured within the last 2 to 3 years). Gloveboxes are available for handling radioactive materials.

Considerable effort is made to scrub and monitor the gases from all the rooms. Solid waste from the IMR laboratory is processed by JAERI, but the laboratory must store its liquid waste. The laboratory has four large stainless steel vessels for this purpose.

At the JMTR I toured the instrument floor surrounding the reactor, viewed the gloveboxes and hot cells, and discussed Shikama's research with him. The JMTR is a 50 MW reactor with a high neutron flux (4×10^{14} n/cm²s max.) for irradiation studies. About 100 experimental holes are provided to accommodate a wide variety of experiments. Two rows of monitoring instruments ring the periphery of the reactor vessel.

Shikama who has collaborated in his work with E. Farnum, LANL, and Y. Chen, ORNL, is carrying out in-situ measurements of irradiation effects on the conductivity of insulating ceramics. Samples are inserted into the reactor core by means of a shroud facility which isolates the sample from the primary coolant and allows the environment around the sample to be controlled. Electrical leads extend from the specimen to the impedance analyzer which is located at the periphery of the reactor vessel. AC impedance measurements are made using a three-point technique. He is also conducting studies using the gamma radiation from spent fuel rods which are retained in the water-filled canal between the reactor and a storage building where spent fuel assemblies are stored after they have cooled.

NATIONAL INSTITUTE FOR RESEARCH ON INORGANIC MATERIALS (NIRIM)

The National Institute for Research on Inorganic Materials is an institute of the Science and Technology Agency (STA). NIRIM conducts research on inorganic materials having ultrahigh purity and specific properties required by advanced science and technology. My visit to NIRIM was arranged by S. Ogura, Y. Bando and Y. Sato.

The research activities at NIRIM are carried out in 15 Research Groups, the High Pressure Research Station, the High-Temperature Research Station, and the Research Center for Creating New Materials. There are about 120 researchers and 20 technicians; these numbers have been nearly constant for several years. In addition to the permanent staff there are about 30 guest scientist and 30 visiting scientist from industry and universities. There are about 5 or 6 post-doctoral research associates at NIRIM; under a new program of the STA they come for a period of 3 years. The government has a policy of 1 to 2% automatic reduction in program support every year to make room for new activities so that agencies must propose new programs to maintain a constant number of staff.

During my visit I saw several international caliber programs in materials science, with high scientific productivity. Nevertheless, two problem areas were apparent. One was the general aging of its scientific staff. The rate of attrition of staff is extremely low since permanent staff enjoy job security until the retirement age of 60 and the total number of supportable positions is at best constant. Thus, younger staff members with new ideas are added at a very low rate. The second problem is the limited pool of talent to draw from in making up new research teams.

There are two multicore research programs - Research and Development of New Oxide Superconductors, and Promotion of the Research of Intelligent Materials - which are located in several research groups and the research stations. A research group exists for a period of 5 years, after which time it is dissolved and a new group is formed. Any researcher at NIRIM can propose a project. If the project is funded, the principal investigator can assemble a new research team. Mid-term reviews of the research group projects after the third year were recently instituted by the Director-General.

The STA has recently instituted special research projects, described to me as center of excellence programs, at the national laboratories. One of these areas is "super diamond," materials such as cubic boron nitride (c-BN) and diamond films, for which STA has approved a project at NIRIM since my return from Japan.

The growth and properties of diamond and boron-doped diamond films are investigated in the 8th Research Group, under Y. Sato. Film growth is carried out primarily by microwave plasma CVD. In addition to several microwave CVD units, a UHV chamber for a molecular or ion beam growth unit is under construction. This system will be equipped with a quadrupole mass spectrometer and two Ar lasers to study the chemistry of the beam in the near surface region during film growth.

Sato has found that UV radiation enhances the growth of diamond by plasma-assisted CVD at 500°C. Although some enhancement is obtained at lower temperatures, the quality of the crystallites obtained under UV radiation is deteriorated. Spectroscopic studies of the optical centers in diamond grown by plasma-assisted CVD have indicated that the principal defect may be associated with sp^2 -bonded carbon.

He has found that during diamond growth on Ni films at 800°C that carbon tends to diffuse through the Ni to form graphite on the backside. Most Ni substrates used in studies were polycrystalline due to expense of single crystal Ni substrates; however, he has found that diamond grows epitaxially on Ni, and he is investigating growth on (110) and (001) Ni surfaces.

The 4th Research Group, under S. Horiuchi, has succeeded in imaging oxygen atoms in oxide ceramics, especially in oxide superconductors, using NIRIM'S new high voltage electron microscope (HVEM). The HVEM has a resolving power of 1 Å at an accelerating voltage of 1.3 MV.

The oxygen atoms were first imaged in ZrO_2 with the electron beam incident along the [010] direction. More recently weak contrast regions were observed at the expected positions between Cu atoms in Y-123. Contrasts at the expected oxygen positions for crystal structure along the [001] and [100] directions were clearly observed in $YBa_2Cu_3O_{7.7}$ which was prepared by oxidation at high pressure. Work is in progress to image the O-atoms in Bi-oxide superconductors.

A new program to develop ZrO_2 -based structural materials as an intelligent material having an ability to self-repair cracks was recently begun under S. Ikegami, Senior Researcher of the 1st Research Group. ZrO_2 , partially stabilized with Y_2O_3 , CaO, MgO or other additives, is being studied. The heat of mixing and three-point bend strength as functions of composition are being investigated as possible indications of clustering of oxygen vacancies at high concentrations of aliovalent dopants, such as Y. Clustering of vacancies is thought to inhibit the phase transition which toughens the ceramic.

The synthesis and determination of structure for ternary sulfides are being carried out by the 2nd Research Group, under M. Ishii. The group has synthesized 17 new sulfide phases, including Ba_3TiS_5 , Ba_2TiS_4 , BaTiS_3 , BaNbS_3 , Ba_2ZrS_4 , $\text{Ba}_3\text{Zr}_2\text{S}_7$, $\text{Ba}_9\text{Ta}_4\text{S}_{20}$, $\text{Ba}_3\text{Ta}_2\text{S}_8$, BaTa_2S_5 , $\text{Ba}_{16.5}\text{Ta}_9\text{S}_{39}$, Ba_2TaS_5 , BaCu_2S_2 , AgTaS_3 , Ag_7TaS_6 , and $(\text{PbS})_{1.12}\text{VS}_2$, an incommensurate compound. Structural determinations are carried out by x-ray diffraction. Other characterization includes electrical conductivity, thermal conductivity, and vibrational spectra.

Improved SiC and Si_3N_4 ceramics for engineering purposes such as gas turbines for electrical power generation are being developed in the 5th Research Group, under M. Mitomo. To control fracture toughness by controlling microstructure, conditions are being investigated for the formation Si_3N_4 ceramics with a duplex structure of equiaxed α - Si_3N_4 and larger, acicular β - Si_3N_4 grains. A collaboration with Nissan is in progress to test improved silicon nitride ceramics in engine components. Directionally alignment of SiC whiskers by slip casting is being studied as a means to improve the sintering of SiAlON matrix composites.

Examination of crack tips in 6H- SiC , Si and 15R-sialon by high resolution electron microscopy (HREM) has shown the crack tips to be atomically sharp with no evidence of a yielding zone. Cleavage cracks in Si were found to always propagated in the (111) plane.

Preparation of oxide superconductors by devitrification of glassy precursors is being investigated by K. Takahashi. Rapidly quenched melts of Ba-Y-Cu-O with the 123 composition resulted in a material with an amorphous outer layer and an interior containing a fine crystalline Y_2O_3 phase. Heat treatment at 950°C yielded a material with blocky Y-123 grains and fine whiskers. The thin film yielded a zero resistivity at 87 K with a critical current of 1.3 A/cm^2 .

Thick film Bi-Sr-Ca-Cu-O samples also have been rapidly quenched and then heat-treated to crystallize them. Thick films with the composition $\text{Bi}_{1.73}\text{Pb}_{0.43}\text{Sr}_{1.63}\text{Ca}_{2.03}\text{Cu}_3\text{O}_y$ yielded a crystalline material with a T_c of 104 K after annealing for 300 h and J_c of 200 A/cm^2 at 77 K.

The high-pressure synthesis of diamond at the High Pressure Research Station, under N. Yamaoka, has been demonstrated to occur in the presence of a number of sulphate, carbonates, and hydroxides of alkali and alkaline earth metals. Diamond crystals synthesized in the presence of CaCO_3 had rather rounded surfaces; whereas those synthesized in the presence of MgSO_4 were octahedral with well-developed {111} surfaces. The diamonds synthesized using these nonmetallic catalysts were colorless and transparent with sizes up to $100\mu\text{m}$.

NATIONAL RESEARCH INSTITUTE FOR METALS, TSUKUBA

At the Tsukuba facility fabrication of low and high- T_c superconductors and the development of high field magnets is carried out in the 1st Research Group, under Hiroshi Maeda. Development of Nb_3Al multifilamentary superconductor wire for use in windings for high-field magnets was described by Kiyoshi Inoue. Nb_3Al wire shows less stress distortion of the critical current than does Nb_3Sn wire. Since Nb_3Al cannot be formed by customary solid state reactions, NRIM has developed a cold-drawing process for the formation of multifilament Nb_3Al wire.

An extremely high-field research center is under construction for characterization of the high-field performance of oxide superconductors. This center will include a 40 T hybrid magnet, a 20 T class superconducting magnet with large bore, a 80 T class long-pulse magnet, and several kinds of small superconducting magnets. The 40 T hybrid magnet will consist of an outer superconducting magnet inducing a central magnetic field of 15 T for a room-temperature clear bore of 400 mm, in which a polyhelix-type water-cooled magnet is energized. Two kinds of inner resistive magnets will be used: a 30 mm clear bore for 40 T and a 50 mm clear bore for 35 T. A capacitor bank with rating of 16 MJ at 5 KV and consisting of 160 units of oil-immersed 128 mF capacitors has been developed for the 80 T pulsed magnet.

The 1st Research Group also carries out research on fabrication of high- T_c superconductors, including vapor deposition processes, chemical reactions, and wire fabrication by solid state and liquid phase reactions.

Research and development on materials for advanced reactors such as fusion, fast-breeder and high-temperature gas reactors is carried out in the 2nd Research Group, under H. Shiraishi. Surface reaction processes activated by radiation are studied by M. Kitajima who uses real-time Raman spectroscopy. He has observed disorder induced spectra changes in graphite and molybdenum under ion irradiation. Johsei Nagakawa is investigating the effects of radiation damage on creep and creep rupture in high-temperature metals for fusion reactor first wall applications. Present emphasis is on developing prediction techniques for material strength and life under irradiation and on conducting in-situ analysis and evaluation of radiation damage. SiC-based composites are being developed as low activation materials for nuclear energy applications. Tetsuji Noda discussed development of carbon fiber/SiC composites prepared by chemical vapor infiltration (CVI).

In the Mechanical Properties Division Toshiyuki Hirano is using floating zone unidirectional solidification to grow stoichiometric Ni_3Al with improved room temperature ductility, polysynthetically twinned TiAl, and a variety of silicide single crystals.

ELECTROTECHNICAL LABORATORY (ETL)

I visited the Electrotechnical Laboratory on July 2. ETL is a laboratory under the Agency for Industrial Science and Technology (AIST) of the Ministry of International Trade and Industry (MITI); K. Endo of the Quantum Materials Section was my host. Koji Kajimura, head of the Physical Science Division, provided an overview of ETL. Kajimura was formerly with IBM in the U.S.

ETL was established in 1891 as an electrical testing laboratory under the Ministry of Communication. It has played a key role in the development of Japan's electronic and telecommunication industries. In 1956, it succeeded in developing the world's first transistorized electronic computer with a built-in program. Today the mission of ETL is to contribute to the development of electronics and related technologies in close cooperation with other organizations.

Research on alloy superconductors at ETL dates from the mid-1950s when work began on superconducting magnets for electrical power applications. Today superconductivity research at ETL includes organic superconductors, Langmuir-Blodgett films as a means for designing ultrathin organic superconductors, physical properties of oxide superconductors, development of new superconducting materials such as oxide superconductors with multiple CuO_2 layers, establishment of growth conditions for oxide superconductors by MBE under atomic scale control, development of metal organic CVD and MBE growth of superconductor films, and development of devices such as Josephson junctions. The Quantum Materials Section, under Sadafumi Yoshida, has grown Y-Ba-Cu-O superconducting films on MgO substrates by metal-organic molecular beam epitaxy (MOMBE) using fluorine-free diketonates of Y, Ba and Cu. The Y-Ba-Cu-O films had a T_c of 45 K. Bi-2223 films with a c-axis orientation have been grown on MgO substrates by in-situ metal-organic CVD. These films had a T_c of 97 K and a J_c of $3.8 \times 10^5 \text{ A/cm}^2$ at 77 K and zero magnetic field.

In addition to oxide superconductors, the Quantum Materials Section investigates methods of molecular beam epitaxy (MBE) and chemical vapor deposition (CVD) of semiconducting materials and magnetic materials. Research on semiconducting materials includes epitaxial growth of wide band-gap semiconductors such as SiC, GaN and AlN; development of hardened semiconductor devices; and fundamentals of semiconductor heterostructures. GaAs and GaN were grown on GaAs(001) and GaAs(111) by gas-source MBE using dimethylhydrazine. Cubic GaN was grown on GaAs(001), and hexagonal GaN on GaAs(111).

Magnetic superlattices and multilayers have been grown by MBE and sputtering. Research on this program is concerned with enhancement of magnetic anisotropy, Kerr effect, surface magneto optical Kerr effect, and RHEED intensity oscillations.

UNIVERSITY OF TSUKUBA

I met with K. Otsuka of the Institute of Materials Science at the University of Tsukuba on the afternoon of July 2. The University of Tsukuba was established in Tsukuba in 1973, although its antecedents go back to the Tokyo Normal School, founded in 1872. Today, it is multiprogram university with an enrollment of about 12,000.

Professor Otsuka's work is on high-efficiency shape memory alloys and martensitic transformations. High-efficiency shape memory alloys have possible application in energy storing springs to recover kinetic energy of a decelerating vehicle for reuse upon acceleration.

He has identified a second type of lattice invariant shear twinning in the α_1 to γ'_1 phase transition of Cu-Al-Ni alloys. Type II twinning is characterized by a second invariant plane and a symmetry operation of 180° rotation about the twinning shear direction.

HITACHI RESEARCH LABORATORY (HRL)

I visited Hitachi Research Laboratory on July 3 as the guest of Tadahiko Miyoshi and Kunihiro Maeda. Hitachi Research Laboratory is a comprehensive corporate research laboratory located near Hitachi City, in Ibaraki Prefecture, about 180 km northeast of Tokyo. The laboratory carries out research and development in energy and environmental control systems; urban, transportation and industrial systems; electronics for information control systems and information peripherals; computational science; superconductivity; new functional devices; and materials for energy systems, electronics and devices.

I was shown the Materials Characterization Research (MCR) Center by Takashi Aoyama. The MCR develops new analytical machines, techniques and new applications. Aoyama discussed three research studies using the HF-2000 FE (field-emission gun) transmission electron microscope: phosphorus at grain boundaries in steel, dislocations in Si in the neighborhood of a Si/SiO₂ interface, and dislocation loops in Si induced at the edge of a W contact. The laboratory is also equipped with a high-resolution scanning electron microscope with a field emission gun (FE-SEM); a step-scannable FTIR with polarization modulation to reduce background; and a high-pressure calorimeter which was developed to analyze small samples (50 mg) for liquid crystal research. Software is being developed for a Rigaku x-ray diffractometer used for the determination of the interfacial and multilayer thickness.

Shin-Pei Matsuda provided a tour of the Superconductor Center at the Rinkai Branch Laboratory. The Superconductor Center is engaged in research on superconductors and in development of superconducting magnets.

Maeda hosted my visit to the 6th Department (Ceramics), of which he is the manager, at the Hitachi Branch Laboratory. I gave a seminar about the DOE materials sciences program to staff members of 6th Department and toured the ceramics processing facility.

INSTITUTE FOR MATERIALS RESEARCH, SENDAI

My visit to the IMR at Sendai was arranged by Professor Kenji Suzuki. Following a brief visit with Professor Tsuyoshi Masumoto, Director of the Institute, Takashi Goto of Professor Hirai's group escorted me to my various interviews and devoted considerable time to resolving my scheduling conflicts.

Research groups are organized according to the model established by the Ministry of Education (Monbusho). Each group is led by a professor. There may be one or more associate professors and Ph.D. research associates under him. Students belong to the group and not to a particular professor.

Professor Masumoto is also head of the Non-equilibrium Materials Research Laboratory. Kiyoshi Aoki described the program on non-equilibrium materials. Aoki is known in the United States for his work with O. Izumi on the ductilization of Ni_3Al with boron. His present work is in the areas of rapid solidification, mechanical alloying, quasicrystals, and hydrogen embrittlement. At the time of my visit, a second generation apparatus for preparation of amorphous metal powder by atomization of liquid metals had recently been completed. This unit permits a powder to be prepared by atomization, collected, sieved, transferred to a metal mold, compacted and sintered entirely under inert conditions, thus avoiding oxygen contamination, or worse, a pyrophoric reaction.

In other work in the group, Ti alloys are prepared using a floating zone technique in an image furnace with a xenon lamp heat source. Mechanical alloying (MA) is carried out with control of temperature and ambient gas. The effects of pressure on the textured growth of oxide superconductors during rapid solidification has been investigated.

Shuji Hanada and his group are studying deformation processes in high-temperature intermetallic compounds such as TiAl and Nb_3Al , fabrication of wires of superconducting oxides and A15 compounds, improvement of the deformability of titanium and its alloys, and deformation and fracture of SiC/Al composites. Hanada commented that Japan sees aerospace as a driver for technological growth and is placing an increased emphasis on high-temperature intermetallics compounds as advanced aerospace materials.

The group on Physics of Crystal Defects which is led by Professor Koji Sumino is studying the nature, dynamics and interactions of defects and dislocations in semiconductors such as Si and GaAs. He has studied dislocation velocities as a function of applied stress, temperature and impurity interactions. Generation of dislocation at surface irregularities has been studied by indentation or scratching of the surface, followed by careful removal of the damaged layer. In the case of Si, amorphous Si has been found to be formed at the site of the damage.

Electronic properties of semiconductors with defects formed by electron or neutron irradiation have been studied using measurements of deformation and electrical properties, including resistivity, Hall effect and the electronic structure of the defect. This work has focused not just on recombinative centers but also on donors. Sumino is also investigating the correlation between microscopic properties of dislocations and the electrical and optical properties of a semiconductor. In the case of GaAs, dislocations have been found to behave as non-radiative centers. Zinc impurities were found to make dislocations more radiative. Silicon in GaAs forms a complex or cluster, heating changes the radiative properties of these centers.

Instrumentation used by Sumino's group include a JEOL 2000 electron microscope equipped for cathodoluminescence measurements, FTIR (JEOL JIR 100), EPR spectrometer, and photoluminescence spectrometer. EPR is used for studies of "low drag" defects, one-dimensional agglomerates and ionic impurities and dopants in Si. Deep-level energies of irradiated dislocations have been determined from liquid-helium temperature to room temperature by photoluminescence.

Research in the Nuclear Materials Engineering Laboratory which is led by Professor Hideki Matsui is concerned with materials for fusion and fusion reactors. He is involved with the ITER program and with light water and fast breeder reactors. At the time of my visit he had been unable to recover a sample which was in the Fast Flux Test Facility (FFTF) at Hanford when it was shut down.

Matsui's research program is directed toward developing materials which maintain strength and integrity after long exposure to displacement radiation. The anomalous swelling behavior of V alloys is of particular interest. V is preferred to stainless steel because it exhibits less He embrittlement which is a major concern in fusion reactors.

He noted that JAERI plans to use TiAl as the first wall material in its second Steady-State Tokamak Reactor (SSTR2). Less activation is expected because Ti has small cross section above 14 MeV.

In the Surface Science Laboratory atom-probe field ion microscopy (APFIM) and high resolution electron microscopy (HREM) are used by Professor Toshio Sakurai and his colleagues to study the microstructure evolution of an $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ alloy. When the initially homogenous alloy is annealed at 550°C , phase separation begins with the nucleation of Cu-rich clusters, followed by fluctuations in the Fe concentration in the surrounding amorphous phase. These fluctuations are believed to nucleate formation of a ferromagnetic $\alpha\text{-FeSi}$ (bcc) phase. Other studies have included precipitates in aluminum alloys, the site preference of Cu in Ni_3Al , and compositional fluctuation in Co-Cr films.

The laboratory's present atom probe is equipped with a Poschenrieder lens elemental analysis. Two more units are under construction. An atomic beam diffraction unit is also under construction. A small MBE unit is available for preparation of films. The laboratory has a Philips 150 KeV CM12 TEM.

Field ion-scanning tunneling microscopy (FI-STM) is another major effort of Sakurai's group. Three field-ion systems are equipped with a Demuth-type STMs. A tip-exchange mechanism has been developed which permits a tip exchange to be carried out under UHV conditions. FI-STM studies have included alkali ion adsorption of (100) and (111) surfaces of Si, C_{60} on Si(100) and (111) surfaces, sulfur and chlorine adsorption on Cu(111), and oxygen on Ag(110).

The Noncrystalline, Nanocrystalline and Heavy Fermion Materials Research Laboratory, under Professor Kenji Suzuki, has four areas of research: (1) liquid and amorphous materials, (2) nanoscale materials, (3) small angle scattering (SAS), and (4) physical properties of heavy fermion systems. The structure of liquid and amorphous materials are determined by neutron scattering. Suzuki constructed one of the first pulsed neutron sources using an electron accelerator; the group now uses a spallation neutron source at the proton accelerator (KEK) at Tsukuba. Structural evolution of amorphous alloys produced by mechanically alloying (MA) mechanical grinding (MG) of alloys is carried out at the spallation neutron source.

Suzuki is collaborating with Hirai and Nishinada on a study of clusters derived from supersaturated vapor and plasmas. Small angle scattering, both x-ray and neutron, is being used for the study of sol-gel systems and of nanocrystallization by mechanical grinding.

The effect of amorphous structure on electron correlation is being studied for heavy fermion Ce and Yb alloys. Magnetism, Kondo effect and superconductivity are studied by measurements of low temperature specific heat, resistivity and magneto-resistance. Suzuki is collaborating with Karlsruhe on amorphous neptunium alloys which are expected to have strong electron correlations. This program is supported by the Japanese powder companies through the Central Research Institute for Electric Power (CRIEPI), the Japanese "EPRI."

Crystal growth in a variety of materials, including peritectic compounds and high T_c oxide superconductors is investigated in the Crystal Physics Research Laboratory, under Professor Hiroshi Komatsu. Growth of Nb_3Sn from Sn-rich flux was found to occur by a layer-by-layer mechanism. A coldfinger technique similar to that of Karpinski has been used for flux growth $La_4Sr_2Cu_2O_{10}$. The phase equilibria of Bi-Sr-Ca-Cu-O system has been studied in-situ using special high-temperature microscopy. An optical microscope was fitted with a heating stage consisting of a image heating chamber in which the radiation of a near-infrared lamp was focused on a sample suspended at the focal point of the imaged radiation.

Komatsu has studied mechanisms for growth of $EuBa_2Cu_3O_{7-x}$. Two mechanisms were observed: (1) tiling type growth from clusters of small crystallite, and (2) spiral growth with large Burgers vectors (b on the order of 1000 Å). When nucleation occurs in the flux there is a tendency for clusters to orient into coherent structures and not to develop atom-by-atom. Tiling occurs during early stages of growth, while spiraling occurs later. In SiC, many inclusions have been observed to provide loci for nucleating growth, resulting in "hollow tube" like structures. Dendrite growth has been studied in sodium chlorate with respect to concentration gradients characterized by interferograms.

In the High Temperature Materials Research Laboratory under Professor Toshio Hirai, Mamoru Omori is investigating the polymerization of dichloro-dimethylsilane which can polymerize into a three-dimensional networks, dissolved inorganic solvents for casting, and decomposed into SiC. Makoto Sasaki and Hirai are investigating SiC/C functional gradient films produced by CVD and AlN/Al_2O_3 composite films produced by microwave plasma CVD. The SiC/C were studied with respect to thermal barrier and thermal stress characteristics. Takashi Goto and Hirai have investigated the kinetics of passive and active oxidation of CVD-SiC. Recently, Goto collaborated with A. R. West of Aberdeen University (Scotland) in a characterization of the electrical conductivity of $Ba_6Ta_2O_{11}$ by ac impedance and thermal electric powder measurement. The critical current of high T_c superconducting oxide films was determined by Hisanori Yamane as a function of field direction for Ba deficient Y-Ba-Cu oxide films produced by CVD. Josephson junctions were prepared in films grown on MgO substrates with a grain size of about 1 μm by etching the grain boundaries.

The history of the Institute for Materials Research is closely tied to research on magnetic materials. Kotaro Honda who founded the Institute as the Iron and Steel Research Institute in 1919 developed KS magnetic steel which produced the strongest permanent magnet of its time. In 1981, the High Field Laboratory for Superconducting Materials was established to provide a research facility to develop superconducting materials which would be used for superconducting magnets for plasma confinement fusion reactors. The laboratory provides instruments for measuring superconducting, magnetic, optical and other properties of test samples. The laboratory has two hybrid magnets: the largest has a

maximum field of 31 T, and a conventional hybrid magnet with a maximum field of about 24 T. There are also four superconducting magnets with fields between 8 T and 15 T, and three water-cooled Bitter-type magnets with fields between 12 T and 15 T.

Shotaro Morozumi who has retired from the IMR and is now at the Ciba Institute of Technology discussed a method for growing FeSi layers on Fe surfaces.

TOHOKU UNIVERSITY

On July 7, I visited programs under Professor Masahiko Shimada and Professor Wakai, in the Faculty of Engineering, at the Aobayama campus of Tohoku University overlooking the Hirose River and Sendai Castle (Aobajo). Tohoku University was founded in 1907 as the third national university in Japan. The University has a number of scientific and engineering institutes, including the IMR described above, which accept students from the faculty of engineering.

Professor Masahiko Shimada, of the Department of Molecular Chemistry and Engineering, has three areas of research. The first area entails new phases of unsymmetric, isoelectronic binary and ternary oxide, nitride and phosphide compounds, such as ZnGeP_2 ceramic materials, at temperatures up to 1800°C and pressures up to 8 GPa. In the second area, Shimada and Hirotsugu Takizawa are attempting high-pressure growth of an infinite layer- CuO_2 structure of $(\text{Ba},\text{Sr})\text{CuO}_3$ in which BaO and SrO layers alternate indefinitely with CuO_2 planes. To date, the materials obtained have had a superconducting transition of about 40 K and have exhibit a small volume fraction of superconducting phase as determined by the Meissner effect. In his third area of interest, Shimada is developing improved thermoelectric materials based on FeSi_2 . For the system $\beta\text{-Fe}_{1-x-y}\text{Ru}_x\text{M}_y\text{Si}_2$ ($\text{M}=\text{Cr},\text{Co}$), he has found that a composition with 10% Ru and 3% Cr gave a power factor equal to greater than for $\beta\text{-FeSi}_2$ over the temperature range from 200°C to 1000°C .

The Functionally Gradient Materials (FGM) program, which is lead by Professor Wakai, was described to me by Ryuzo Watanabe. Watanabe described a new process, the wet powder spray combination process (WPSCP), which has allowed thinner graded composition layers to be laid down (on the order of $50\text{ }\mu\text{m}$) and nearly full density to be obtained. $\text{ZrO}_2\text{-SiC}$ composite layers are being developed in which the SiC will provide high strength at high temperatures and the ZrO_2 will provide high insulating properties. Jing-Feng Li, a research associate in this group, is investigating SiC-AlN ceramics to obtain materials with lower sintering temperature, high strength and low electrical conductivity for application on metals. When Si_3N_4 , Al_3C , graphite and CaO were cold isostatically pressed (CIPped) and pressureless sintered, $\alpha\text{-SiAlON}$ is formed as an intermediate phase, and if AlN is greater than 35%, an in-situ SiC-AlN composite is obtained. Makoto Sasaki is preparing SiC-carbon FGM with excellent thermal barrier characteristics by CVD as coatings for combustor nozzle.

Professor Wakai's group has adapted the small punch (MSP) technique, which was developed by Jan Kanada of DOE's Ames Laboratory, for the measurement of high temperature strength. A nearly linear relationship was demonstrated between yield strength obtained by MSP and that obtained in four-point bend measurements. The technique has been used to determine the temperature of brittle-to-ductile transitions (BDTT) and to study the effects of irradiation on mechanical strength of alloys in collaboration with Kanada.

NAGAOKA UNIVERSITY OF TECHNOLOGY

I visited Nagaoka University of Technology on July 9 and 10, to discuss research work with various faculty members and their students and to present a seminar. I had previously visited the university in March 1987. Professor Kozo Ishizaki arranged an enjoyable visit for me. In addition to discussions with several of the faculty, I attended a dinner meeting of the material science faculty, gave a seminar on DOE's Materials Sciences Program, and had an interesting side trip to the nuclear power facility at Kashiwazaki.

I had several discussions with Professor Ishizaki, of the Mechanical Engineering Department, and met with five of his Ph.D. students to hear brief reports of their research. Since my previous visit, the scope of his research has extended beyond on the development of phase diagrams for hot isostatic pressing (HIP).

Chemical reactions occurring during sintering have been studied to improve the thermal conductivity of AlN and to grow SiC as an in-situ grain boundary phase in Si_3N_4 . Carbothermal reduction of Y_2O_3 -additions to AlN was used to obtain an AlN-YN ceramic. Si_3N_4 powders were carbon coated to remove the oxide layer and produce graphite grains when hot-isostatically pressed. P. Celis and Ishizaki have reported the synthesis of the high-temperature structural silicide intermetallics $\text{Ti}_2\text{Zr}_3\text{Si}_3$ and Zr_5Si_3 .

Hot-isostatic pressing is being studied for the processing of a variety of materials, including TiO_2 ceramics with controlled pore size and the Y-124 and Y-247 phases. An oxygen-HIP was used for the oxide superconductors that permitted the total pressure and the oxygen partial pressure to be varied independently so that short process times were required.

An improved apparatus was developed by Kawamoto and Ishizaki for the determination of adsorbed gases on powders by temperature programmed desorption (TPD); and a procedure was developed for determination of the amount of amorphous phase in polycrystalline ceramics. The effect of aqueous washing of Si_3N_4 powders on adsorbed H_2 , H_2O , NH_3 , N_2 , CO and CO_2 was determined by TPD, and the results compared with the measured fluidity of the washed powders. Low-temperature specific heat measurements are being used for quantitative evaluation of amorphous grain boundary phase in Si_3N_4 ceramics.

Professor Kazumasa Matusita's group in the Chemistry Department was the first to report the synthesis of high temperature oxide superconductors using a glass processing method (1988). Since the J_c of the Bi-Ca-Sr-CuO ceramics, which obtained by recrystallizing the glass ceramics was about 150 A/cm^2 , work is in progress to understand the source of the normal conductivity that occurs at grain boundaries.

Matusita research also includes control of viscosity in $\text{BaF}_2\text{-ZrF}_4$ compositions for IR transparent optical fibers; low-melting Sn-P-Pb-O-F compositions, where O and F are present in approximately equimolar amounts, for the encapsulation of organic molecules with special functional groups; the reprocessing of waste Al silicate filtration materials as a means to make glass compositions for use as aggregate in building materials; and the rapid solidification and brittle fracture of metallic Co-Ni-Fe-Si-B glasses.

Professor Takayuki Komatsu, also in the Department of Chemistry, recently began an investigation of TeO_2 glasses containing functional oxides such as LiNbO_3 and BaTiO_3 , which are similar to TeO_2 in their refractive indices, so that the glasses appear transparent even with high concentrations of the oxide. He is also using Mossbauer spectroscopy to study the interface region between the film and the substrate for soft magnetic thin films of Fe-Al-Si produced by rapid solidification.

Professor Kiichiro Kamata, of the Department of Materials Science, is investigating vapor deposition processes for the formation of ceramic and diamond-like films. SiC and Si_3N_4 were found to be completely miscible in each other when deposited as amorphous SiC- Si_3N_4 films. SiC-rich films were found to increase the flexural strength of the substrate, whereas Si_3N_4 -rich films decreased the flexural strength.

The effects of process conditions on the growth on material properties were investigated for rf-CVD and by electron cyclotron resonance (ecr) deposition of diamond-like carbon (DLC) films. An application of a negative dc bias to the substrate was found to improve film density, deposition rate and film hardness. Application of a dc bias during film growth also decreased the ultraviolet threshold for photoemission in the film and increased the amount of CH_2 and CH_3 groups in the film.

Oxide films such as TiO_2 and ZnO have been grown by thermal CVD. Since a deposition rate of 100 nm/s has been achieved, Kamata and his students are now trying to improve the density of the film. In other work, BaTiO_3 has been grown by microwave CVD using Ba(DPM)_2 as a precursor, and ZrO_2 and SiC films have been grown by sputtering.

Professor Keizo Uematsu, of the Chemistry Department, has developed the use of neutral optical density fluids to study the microstructure of spray-dried particles. He has found that microstructural features, such

as hard surface layers and voids, observed in these particles persist through subsequent processing as density variations and stable pore structures. He is also interested in extending studies of properties such as viscosity of slurries to temperatures near the boiling point since much processing is carried out at elevated solution temperatures near the boiling point or the triple point.

Uematsu is participating in a program to develop International Standards Organization (ISO) standards for the evaluation of various stages of ceramic processing, from powder to sintered body.

KASHIWAZAKI-KARIWA NUCLEAR POWER FACILITY

Professor Ishizaki arranged a visit to the Kashiwazaki-Kariwa Nuclear Power Facility on July 9. This facility is located along the coast of the Sea of Japan in Niigata Prefecture. When this facility is completed it will produce 8,210,000 KW of power from seven reactors; almost doubling the present nuclear power generation capacity which amounts to 12,396,000 kW. Tokyo Electric Power Co. (TEPCO) which operates this facility will supply most of power to the Tokyo area.

At time of my visit three of the lightwater reactors had been completed and were operating, and a fourth was nearing completion. When completed, it will be the second largest nuclear power facility in the world. Two of the reactors at the site will be advanced boiling water reactors and will be constructed by a joint venture of General Electric, Hitachi, Ltd. and Toshiba Corp.

INTERNATIONAL SUPERCONDUCTIVITY TECHNOLOGY CENTER (ISTEC)

I visited ISTEC's Superconductivity Research Laboratory (SRL) on July 12. Professor Shoji Tanaka, Vice President and Director of SRL, was my host. I was given a background lecture on ISTEC by Naoki Koshizuka, Director of Division I.

ISTEC-SRL was organized in 1988 as a nonprofit foundation. The SRL provides a means by which companies can work together on basic research. Benefits are shared by low cost access to rights to license patented results. ISTEC has 101 member companies, 46 of which are identified as leading companies. Each company pays an initiation fee of ¥100,000,000 to join, plus annual dues of ¥12,000,000. ISTEC also receives support from the government of Japan through the National Energy Development Organization (NEDO) of MITI; this amount is approaching ¥2,000,000,000. These figures do not contain salary costs for the researchers which are paid by their member companies.

The SRL has seven research divisions at its site in Koto-ku, Tokyo, and one division in Nagoya. There are 78 researchers from member companies, 7 visiting researchers from universities and 10 foreign researchers. The total staff is little more than 100 persons.

The research divisions are as follows:

Division I (Characterization and Analysis of Fundamental Properties) is concerned with the growth and properties of single crystals. Recent successes include growth of a single crystal of Y-123 by the Czechawalski method and growth of a single crystal of Bi-2212 by float zone technique. Currently, they are devoting more effort now to Y-124 than to Y-123 due to the greater oxygen stability and the presence of two sets of Cu-O chains in Y-124.

Division II (High- T_c Superconducting Ceramics), under H. Yamauchi, is concerned with the design and synthesis of new superconducting materials. Research themes include novel crystallographic structures and/or compositions, materials with high critical temperatures, and mechanisms for "superconductor-ization" of materials. Projects have included development of high T_c Tl-based compounds, the mechanisms for inducement of superconductivity in $(Pb_{0.5}Cu_{0.5})Sr_2(Y,Ca)Cu_2O_z$ ($z \sim 7$) and $Pb_2Sr_2(Y,Ca)Cu_3O_8$ 1212-type phases, the effects of fluorite blocks on T_c and development of the Automated Ceramic Processing System (ACPS).

Division III (Organic and Other Superconductors), under S. Tanaka, investigates organic and other superconductors. Research themes include synthesis and characterization of new organic superconductors, theoretical studies of flux pinning, optical studies of high- T_c oxide superconductors, a tunneling study of oxide superconductors, the dynamics of flux lines, and a basic study for the application of Josephson effect in oxide superconductors. Division III has discovered the 35th organic superconductor, $x-(BEDT.TTF)_2Ag(CN)_2$.

Division IV (Chemical Processing), under Y. Shiohara, is conducting fundamental research on chemical processing of oxide superconductors. Techniques studied in this division include solid and melting/solidification processes, chemical solution processes (MOD), vapor phase deposition (MOCVD), and thermal plasma deposition. Low-temperature growth of ultra-fine Y-123 and Y-124 has been developed using the sol-gel method.

Division V (Physical Processing), under T. Morishita, is developing physical processes for thin film growth. Growth techniques which are being studied include reactive co-evaporation, ion-beam deposition and pulsed laser deposition. Multilayer structure and interfacial chemistry are topics for study.

Division VI (Fundamental Technology for Device Application), under Y. Enomoto, is investigating the fundamental technology for device application. The focus of this group is on demonstrating the application of a concept in a new device; development of the device is left to the member companies. Areas of research include nanometer fabrication, nanometer characterization, heteroepitaxial multilayer growth, surface and interface characterization, and evaluation of device properties.

Division VII (Data Base), under T. Maegawa, is concerned with storing the research results as a database.

Nagoya Division (High J_c Superconductors), under I. Hirabayashi, is concerned with processing oxide superconductors to obtain high critical current densities.

UNIVERSITY OF TOKYO

I visited Professor Yutaka Kagawa and Professor M. Maeda at the Institute of Industrial Science, at the Roppongi, Minato-ku, campus of the University of Tokyo on July 14, and Professor Hiroaki Yanagida, of the Graduate School of Advanced Interdisciplinary Engineering, at the main campus in Bunkyo-ku on July 15.

Professor Kagawa is carrying out research on the processing, microstructure and mechanical properties of ceramic and metal matrix composites. He has studied the in-situ formation of Al_2O_3 -matrix/Si, Mg composites by controlled oxidation of Al-Si-Mg melts. He is now interested in extending this work to in situ formation of AlN-matrix composites by a similar nitridation process. Other studies have included the effects of water vapor on the SiC-fiber/lithium aluminosilicate (LAS) composites; SiC/metal-matrix composites in which the metal matrix is Ti-15Mo-5Zr-3Al, and the influence of indenter induced microcracks on crack propagation in transparent ZrO_2 .

He is also investigating crack growth and fracture of LAS matrix composites containing silicon oxynitride fibers. Since the optical indices of matrix and fiber are matched, the matrix is transparent even with 40% fiber loading.

He has developed a small load fixture and technique for microscopic observations of stable crack growth in transparent, brittle solids. He is also developing a laser technique ("laser caustics") to measure the stress-intensity factor, K_{tip} , at a crack tip.

Interfacial frictional shear stress tests are conducted using both the pushout technique and the protrusion test. Mechanical properties and laser cutting of metal matrix composites also are being studied.

M. Maeda is investigating the processing of pure materials. Current work includes the preparation of pure Si by electron beam remelting of poly-Si particles with resulting volatilization of some impurities and segregation of less volatile impurities in a zone refining-type technique. He has also investigated the preparation of low-oxygen content TiAl by e-beam deposition.

H. Yanagida is Professor of Ceramic Materials and has directed the Environmental Science Center (ESC) since 1991. His principal interest is intelligent materials. He demonstrated a very simple intelligent material combination cut from a section of carbon-fiber, glass-fiber/polymer matrix reeve bar to illustrate the point that to achieve a self-diagnostic intelligent structural material, continuous fibers are required in which one fiber conducts electricity, light, heat or an acoustic signal and has a high modulus but limited elongation, and the second fiber has a lower modulus and provides elongation but has a much lower electrical, optical, thermal or acoustic conductivity.

Following on his discovery 13 or 14 years ago that the p-n junction properties of interphase boundaries in porous ZnO/CuO are sensitive to water vapor, he is investigating other diphasic materials as humidity and chemical sensors. He has found that p-Si/n-Si recognizes various types of alcohols. The reason for this behavior is not understood.

TOYOTA CENTRAL RESEARCH AND DEVELOPMENT LABORATORY

I visited Toyota Central Research and Development Laboratory (CRDL) on July 16. The very spacious, beautifully designed CRDL is located in Aichi near Nagoya. The Laboratory employs about 1000 people.

Nobuo Kamiya and Masataka Ohkuba were my hosts. Kamiya is known in the U.S. for his work with O. Kamigaito on the fatigue life of ceramic materials as well as other work on mechanical fracture. He is also involved in the testing and design of ceramic rotors.

After a general presentation and discussion about the range of research activities at CRDL, I gave a seminar about DOE's Materials Sciences program to a number of the staff members. Following the presentation, I toured the ceramics facility, the van der Graaff laboratory, the superconductivity laboratory and the creep laboratory.

Areas of R&D at the CRDL include combustion technology, gas turbine combustors, sound/noise reduction and modulation, high strength Si_3N_4 , polymers, metallic films, image analysis, automated process coordination, computer design of injection molding, development of bioassay techniques to determine the effects of exhaust gases on humans, and recombinant gene technology. The CRDL has developed the use of a transparent cylinder and Schlieren technique to study combustion process, Si_3N_4 with excellent strength to 1400°C , a polymer composite of nylon and clay which has muscle-like adjustable compliance and can be used for soft-gripping robots, and a three-fingered robot which can pick up varied shapes.

Toyota has been involved in ceramic research since 1967 when Kamigaito discovered SiAlON. Between 1981 and 1984, the Si_3N_4 swirl chamber was developed; between 1984 and 1990, Si_3N_4 turbocharger was developed and installation in Toyota automobiles began in 1990; and in 1987, work was begun on an automotive gas turbine engine. Recently the Laboratory selected the slip casting of Si_3N_4 turbocharger rotors for development over injection molding due to the long dewaxing times required by the injection molding process. Both hot pressing and "pressureless" sintering are used to sinter Si_3N_4 , both of the processes are carried out in atmospherically controlled furnaces.

Ceramic composites are presently considered to be too costly, due to the need to use expensive precursors and hot-pressing which does not lend itself to mass production. Nevertheless, although Toyota is conducting its principal ceramics research on materials such as silicon nitride, it is interested in such nanocomposites as the $\text{Si}_3\text{N}_4/\text{SiC}/\text{Y}_2\text{O}_3$ material developed by K. Niihara of Osaka University, they see limited opportunities of these materials in automotive applications at the present time.

Work on the gas turbine engine for small vehicles may be discontinued because this engine is thought to be inefficient for small vehicles. Friction and lubrication in ceramic engines is also considered to be a problem.

Powder processing of TiAl, casting of Al alloys, and high-strength, heat resistant Ti alloys are being studied to make high-quality parts by controlling material composition and processing technique and reducing weight.

Over 10 years ago Tohru Arai, of Toyota CRDL, developed a thermal deposition process (TD) for application of adherent refractory hard carbide coatings to high-carbon steel by adapting the boride bath process used to apply hard carbide coatings to high carbon steels. This process is less costly than CVD, lends itself to mass production techniques, and yields a strong coating. Vanadium carbide have been found to give the lowest wear rate. However, the atomic structure of the steel-carbide interface appears not to be clearly understood. The focus of Toyota's work is on further process development, including the use of a fluidized bed technique and the development of a similar process for aluminum.

The van der Graaff laboratory, under Tatsushi Hioki, contains three ion sources: a van der Graaff for light ions (H, D, He), a heavy ion accelerator (masses through Bi), and a low energy ion accelerator which is used for He backscattering characterization of surface structure. Projects are directed toward understanding the effects of ions on surface modification. The low energy surface analysis system uses a 90° electrostatic sector to measure the energy of backscattered He ions. This technique has a sensitive of about 0.5 nm.

Work in the superconductivity laboratory, under Masatake Ohkubo, is concerned with the use of high T_c superconductors for microwave applications. Ohkubo has used a Monte Carlo to model vacancy ordering in Y-123. His model structures appeared to be similar to model structures obtained by de Fontaine at LBL and Veal at ANL and to the ones observed by Horiuchi at NIRIM.

The creep laboratory contained four or five traditional deadweight creep machines and a new Instron 8500 series machine. The new instrument was equipped with a load fixture for four-point bending. Instead of a single pushed rod, there were 3 SiC pushed rods, each contacting a strain gauge; to better define both the displacement and the radius of curvature. This machine is fully automated. Kamiya stated that this technique is being proposed as a standard method in Japan.

JAPAN FINE CERAMIC CENTER (JFCC)

I visited the Japan Fine Ceramic Center in Nagoya on July 17. My hosts for this visit were Yoshimi Yamaguchi, Manager of the Structural Ceramics, Division II, and Noriyuke Kosuge, Chief Researcher. I gave a half-hour seminar on the work of DOE's Division of Materials Sciences, discussed a variety of programs and toured the laboratory.

The Japan Fine Ceramic Center was established in 1985 to carry out both industrial and government supported research. It has a staff of about 100. About 40 plus companies belong to JFCC and contribute researchers for a 3 year period.

Research activities include basic and applied research on fine ceramics, establishment of standards and testing methods, and development of a data base on fine ceramics. Areas of research include processing, microstructure, mechanical properties and fracture, friction and wear, NDT and ceramic thin films. As a rough estimate, about 20% of its activities are concerned with high- T_c oxide superconductors, 50% with structural ceramics and 30% with functional ceramics.

Recently, JFCC developed at reference an alumina (Al_2O_3) ceramic material, REFROCERAM, which is produced by Asahi Glass and certified by JFCC. This material will be proposed to International Standards Organization (ISO) as an international standard. Powder characteristics and processing method are fully disclosed. JFCC also is developing a reference Si_3N_4 material which is expected to be ready soon. The Center is also involved in international activities to develop ceramic powder characterization standards.

JFCC is investigation and intercomparing a number of powder characterization methods in order to develop powder characterization standards. JFCC carries out standards work based on orders from MITI which is responsible for the development of standards in Japan. Standards produced by JFCC become part of the Japanese Industrial Standards (JIS).

JFCC appeared to have a well-equipped characterization laboratory. Equipment included a Horiba EMGA-2800 C,N,O analyzer which was reported to be capable of providing an analysis within 2 to 3 minutes; a Horiba EMIA-110 for C analysis; two ICP units, one of which was equipped with a quadrupole mass analyzer; and an atomic absorption spectrometer.

A processing laboratory was equipped with factory size equipment for the development of industrial scale processes. Equipment included a spray dryer, a large injection molder (220 Ton rated max. pressure) and a small injection molder, a wet bag CIP unit (Kobelco, 5000 Kg/cm² rating), a HIP (Kobelco, 2000°C, 2000 Kg/cm² Ar or N₂), 2 hot-presses (1 for air, 1500 C; 1 enclosed for Ar, N₂ or vacuum, 2400 C), and a vacuum and gas sintering furnace (2400 C max., 2000 C normal operating pressure for Ar or N₂, 9.8 Kg/cm²).

An MBE facility, equipped for ion-assisted deposition, and a MOCVD facility are available for thin film work.

Creep studies are carried out on an Instron 1381 unit. Load fixtures are available for 3 and 4 point bend measurements. The 1381 provides for a single deflection measurement, at the center of the bend bar. Fatigue studies are carried out to study slow crack growth. A special cutting wheel has been developed to cut V-notches, both single and chevron, with a 3-6 μ m radius of curvature.

A magnetic properties laboratory is available for characterization of superconducting ceramics. Melting-solidification studies of oxide superconductors can be carried out in a remelting image furnace, with a single halogen lamp.

JFCC has a JEOL 4000 FX TEM, accelerating voltage up to 400 KeV, which is equipped with standard and low-mass EDX units. They expect to add EELS sometime in the future.

Under contract to an electric power company, ceramic materials for possible nuclear power reactor applications are being tested under hydrothermal conditions at 300°C and 200 atm water vapor. Under a second contract with an electric powder company, materials for oxide fuel cells, both electrodes and electrolytes, are being characterize in a thermoelectric facility (ETA-8410 H).

NGK SPARK PLUGS/NTK TECHNICAL CERAMICS

I visited NGK Spark Plugs/NTK Technical Ceramics at Komaki, near Nagoya, on July 20. Yo Tajima, Manager of Materials Research R&D Center at NGK Spark Plug Co., was my host. Tajima received his Ph.D. from MIT, having worked under Professor Kingery of MIT on a project funded by the Division of Materials Sciences. It was a pleasure to discover that we had some professional friends in common.

NGK which originally began as a division of the Noritake Ceramic Company became an independent company in 1936. Although it was originally established to produce spark plugs, it began to diversify its product line in 1949 with the establishment of NTK New Ceramics so that NGK/NTK now produces a variety of automotive ceramics, ceramic substrates, IC packages, sensors, seals, cutting tools, industrial parts, and prosthetic implants. NGK Spark Plugs is a separate company from NGK Insulators with which it shares a common Noritake origin.

After a general introduction to the company, I gave a presentation about the DOE's Materials Sciences program to members of the materials research staff. Following which, I toured the ceramic processing facilities and the spark plug production facility with Tagima.

NGK/NTK has facilities for static, cyclic and dynamic fatigue tests. Of particular interest was the small cyclic fatigue tester developed by the company (CFT-340-1) which is equipped with a high power piezoelectric bimorph and is designed to test small (3x4x36 to 41 mm) test pieces. The instrument has a frequency range of 100 to 400 Hz and a maximum stress of 1000 MPa.

NGK Spark Plugs has developed a variety of Si_3N_4 automotive parts, including turbocharger rotors, valves, rocker arms and bearings. Despite its considerable success to date in developing Si_3N_4 automotive ceramics, NGK Spark Plugs has found recently that the market for these materials has not developed as expected and that in many cases ceramics remain a too expensive alternative to metal parts.

Under a program through the Advanced Nuclear Equipment Research Institute (ANERI), NGK Spark Plug is developing spinel (MgAl_2O_4) ceramics for hermetic seals for in-core neutron sensors. Efforts are under way to improve the mechanical strength of these materials to avoid cracking during brazing to metals.

JAPAN ULTRAHIGH TEMPERATURE RESEARCH INSTITUTE (JUTEM), GIFU

I visited the Gifu Center of the Japan Ultrahigh Temperature Research (JUTEM), a 40 minute train ride from Nagoya, on July 20. Koji Itoh, Director of the Gifu Center, was my host.

JUTEM has two locations: one in Yamaguchi Prefecture near Ube City and the other in Gifu Prefecture near Tajimi City. The Gifu Research Center, which had been in operation less than a year at the time of my visit, is housed in a modern building with well-equipped laboratories containing state-of-the-art equipment for the measurement of mechanical and other properties at temperatures up to 2300°C. The Gifu facility is located part way up a ridge with a scenic view of the valley below.

JUTEM is incorporated as two separate entities: two Research Centers which own and manage the property and facilities, and two Research Institutes which use the Centers' facilities to perform research and carry out exchange programs. Both the Centers are capitalized through contributions from the national government, local governments and private enterprise. 50 companies are shareholders in the Centers and 45 in the Institutes. The largest contributor is MITI's National Energy and Technology Development Corporation (NEDO) which contributed one-third of the capitalization costs for the Centers and Institutes.

The purpose of JUTEM is to carry out high risk research and development on high-temperature materials for aerospace and energy applications. The Yamaguchi Center is devoted to materials development and processing research while the Gifu Center is devoted to high-temperature property measurement and material evaluation. The Centers carry out research, compile and analyze data, conduct conferences for information exchange, and provide training.

The Gifu Center has a skeleton staff of 3 researchers and 3 technical workers, plus support staff, to conduct contract research and to operate the facility. The member companies may assign personnel to carry out research. Results obtained by the industrial researchers may be retained exclusively by their companies. To facilitate confidentiality the Center has three data analysis rooms which are assigned for the exclusive use of the company personnel using the Center. In addition, experimental data is automatically transferred from measuring apparatus to computers located in the assigned rooms so that industrial researchers may privately monitor and obtain data. Sleeping facilities (Japanese style), a kitchenette and a small lavatory are provided for researchers who must stay overnight to monitor an experiment.

The facilities at JUTEM include laboratories for high-temperature tensile tests, creep, erosion, oxidation, heat shock and fatigue.

Tensile Test: There are two tensile test units a Shimadzu Autograph and a MTS machine. The Autograph has a 25 Ton maximum capacity and is equipped with three furnaces: a controlled atmosphere furnace with maximum temperature of 2300°C, a furnace for air operation with an upper limit of 1100°C. The MTS machine has a 20 T capacity. It can be used with a local zone heater to a maximum temperature of 1700°C, or in a controlled atmosphere furnace for temperatures to 2300°C.

Creep Tests: The Creep Test Laboratory has two Instron machines each with 25 Ton capacity which can be heated inductively, with a W-heater to 2300°C in a controlled atmosphere, and in air to 1600°C, using a furnace with MoSi₂-based heating elements. These two machines can be operated in either a compressive (three- and four-point bend) or a tensile mode (cantilever beam). This laboratory also has three compression type machines with either 800-2300°C operation in a controlled atmosphere or to 1600°C in air.

Environmental Tests: JUTEM-Gifu has two laboratories for environmental tests. The first laboratory provides facilities for heat shock tests and high-temperature oxidation studies. The second laboratory has a facility for high-velocity, high-temperature gas erosion tests. The apparatus for the high-temperature heat shock/heat cycle studies has a special hemispherical glass chamber in which the sample is located for heating by an imaged halogen lamp heating and for observation. The autohigh-temperature oxidation and sublimation machine has a similar design but the chamber is designed so that an oxidizing gas can be passed over the sample. The sample is also directly connected to a balance so that it can be weighed in-situ. The second laboratory contains an plasma arc wind tunnel which can generate velocities up to Mach 8 and temperatures to 2300°C.

Fatigue Tests: Two laboratories for high-temperature cyclic fatigue tests are equipped with an 8500 series Instron machine. Each machine has a maximum temperature of 2300°C in a controlled atmosphere.

GOVERNMENT INDUSTRIAL RESEARCH INSTITUTE (GIRIN), NAGOYA

I visited the Government Industrial Research Institute, Nagoya (GIRIN) on July 21. Tatsuki Ohji was my host for my visit to GIRIN and made many of the arrangements for my visit to Nagoya and other laboratories in the Nagoya area. This was my second visit to GIRIN; previously I had visited there in 1987.

GIRIN is a laboratory under the Agency for Industrial Science and Technology (AIST) of MITI. It has research activities in the fields of mechanical engineering, metallurgy, chemistry, radiation technology and ceramics. The focus of its activities is to create new materials and to develop new processing techniques for conventional and exotic materials, particularly in the field of ceramics. It works closely with a number of firms in the Chubu area, which includes Nagoya.

Research funding, although not plentiful, is available through several programs under AIST. The R&D Project of Basic Technologies for Future Industries, for which funds are obtained from a tax on utilities, has supported research on the ceramic gas turbine. Other AIST projects include the Sunshine Project for New Energy Technologies, the Moonlight Project for Energy Conservation, and the Fine Ceramics Project. The Ceramic Gas Turbine Project, which was initiated as part of the Moonlight Project in 1988 and which will conclude in 1996, has many companies participating in it. Ohji commented that there is a tendency to set unrealistically high project goals in these programs which researchers strive to meet but seldom attained. The Fine Ceramic Project which began in 1981 will conclude in 1992, and may be replaced by a project on advanced materials.

M. Mabuchi, T. Imai and K. Kubo have demonstrated superplastic deformation (elongation of 620%) at a strain rate of 2 s^{-1} at 560°C for 6061 aluminum alloy containing a dispersion of fine Si_3N_4 particulates. The microstructure obtained after annealing the as-extruded composite at 545°C for 1800 s showed grain sizes of less than $3 \mu\text{m}$ and subgrain structure. The subgrain structure is thought to have caused dynamic recrystallization during superplastic deformation.

A program under Shinji Tomura has developed a hydrothermal process for the preparation of synthetic kaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, from silica and alumina. Due to the depletion of high-purity, high-plasticity, natural clays in the Nagoya area which have supplied a major pottery, tableware and IC substrate industries in the region, a need has arisen to develop other sources. In response to this need, an artificial clay program was implemented by AIST in cooperation with eight prefectural institutes and the Research Association for Artificial Clays, composed of five private companies. A kaolinite synthesis process, including the chemistry of secondary ions, and the effect of kaolinite morphology on clay properties have been determined by Tomura. Spherical kaolinite, formed in the intermediate stage of a hydrothermal process, has been found to be useful in ceramic forming to reduce the hysteresis effect ("memory effect") caused by platy kaolinite during drying.

The development of structural ceramic composites and determination of strength and fracture characteristics are being carried out in a program under Kikuo Nakano as a basis for design standards and life predictions. Carbon-fiber/ceramic composites with Si_3N_4 and two Si_3N_4 -SiAlON compositions showed markedly different fracture behavior at room temperature and 1400°C . At room temperature the matrix peeled off the fibers leaving smooth surfaces; however at 1400°C wavy slip lines were evident on the fibers which may have been caused by shearing of the softened interface between fiber and matrix. SiC matrix/C fiber composites prepared by hot-pressing high modulus pitch-based carbon prepreps infiltrated with slurries consisting of SiC and AlB_2 powders and polystyrene and pyrolyzed. Increases in fracture toughness from $12 \text{ MPa}\cdot\sqrt{\text{m}}$ at room temperature to $19 \text{ MPa}\cdot\sqrt{\text{m}}$ at 1600°C were associated with softening of the matrix-fiber boundary layer at high temperature which facilitated fiber pullout.

The tensile strength, tensile fatigue and tensile creep of monolithic Si_3N_4 , Si_3N_4 /SiC-whisker composites and SiC are being determined by Tatsuki Ohji and co-workers. His laboratory has developed techniques for preparing tensile specimens with narrow gauge sections on a routine basis. Ohji has analyzed the high-temperature tensile strength behavior of hot-pressed Si_3N_4 containing 5 wt% Y_2O_3 and 3 wt% Al_2O_3 which showed primary and secondary yield points. The duplex nature of the yield curve was analyzed in terms cavitation followed by small microcracks driven to failure, and the lower yield point by the blocking of cavity spreading by a acicular large grains. Fracture resistance is measured using chevron-notched beam (CNB) specimens from room temperature to 1300°C .

Long-term creep tests, up to 100,000 hours duration, are carried out on eleven automated creep stations. Creep and creep rupture behavior have been investigated for Si_3N_4 with and without SiC whiskers at 1200°C to 1400°C. At 1300°C and above, evidence of accelerated creep was observed toward the ends of the creep tests.

Ultrafine, homogeneous powders of Y-123 and Bi-Pb-Sr-Ca-Cu-O are being developed by Masanobu Awano for enhanced formability and critical currents. Demonstration of superplasticity in these materials is one of the goals of this project. Mist pyrolysis, spray-drying and sol-gel methods are being investigated as methods for the preparation of submicron sized particles. Compacts of Y-123 powders which were densified by hot-isostatic pressing at 750°C for 4 hours, yielded ceramics with equiaxed grains with grain sizes less than 1 μm .

KYOTO UNIVERSITY

I visited Professor Masaharu Yamaguchi at Kyoto University on July 22. In addition to his own research on intermetallic compounds, Professor Yamaguchi is serving as coordinator for a three or four year study on the fundamentals of intermetallic compounds under the Ministry of Education (Monbusho). This program is one of 72 priority areas selected by Monbusho. It is funded at about $\text{¥}3 \times 10^8$ per year and involves 18 research teams at 7 or 8 universities.

In addition to discussions with Professor Yamaguchi and a tour of the laboratories, I gave a seminar entitled "Fundamental Material Science at the U.S. Department of Energy: The Program of the Division of Materials Sciences."

Professor Yamaguchi is studying Ti-rich and near stoichiometric TiAl which has a lamellar structure and higher strength as a material which may have high temperature structural applications and to understand the deformation behavior of lamellar structures. Although it has not been possible to grow single crystals of TiAl, he has developed a floating-zone technique for the growth of polysynthetically twinned (PST) crystals. These are crystals which have twins that belong to a specific twinning system. He has characterized the twinning behavior in TiAl using HRTEM and has studied the deformation of PST crystals with respect to compressive and tensile stresses applied at various angles to the lamellar boundaries. Cold-rolling of PST crystals at room temperature has shown that up to about 50% reduction in thickness can be obtained if the shear deformation is parallel to the lamellar planes.

Y. Shirai is using positron annihilation to study vacancies and dislocations in Ti-rich, near-stoichiometric and Al-rich TiAl. Deviations from stoichiometry were found to be compensated by anti-site atoms rather than vacancies on either side of the stoichiometric composition. The positron annihilation results suggested that dislocations in Ti-rich TiAl generally have smaller Burgers vectors than those in Al-rich single phase compounds.

Yamaguchi is investigating intermetallic silicides as an alternative to intermetallic aluminides which show a high reactivity to oxygen. Initial work has been on deformation mechanisms for CoSi_2 which has the cubic Cl (calcium fluoride) structure and is expected to possibly have a sufficient number of slip systems and to show high ductility even at room temperature. Although plastic deformation before fracture was observed, fracture strains were on the order of 2-4%, and all crystals fractured catastrophically.

High resolution electron microscopy is performed using a JEOL 4000FX electron microscope. Professor Yamaguchi expects to add a 200 KeV machine which will provide analytical capabilities.

Processing facilities included a two-lamp (halogen) image furnace used for floating zone crystal growth and a small IR furnace.

Two facilities exist for positron correlation and lifetime studies. One facility contains a small unit equipped with e-beam heating of the sample so that positron correlation measurements can be made up to the melting point of the sample. An older facility contains a linear correlation unit and a positron lifetime unit with two temperature stages: one operating down to liquid N_2 and the other to liquid He temperature.

RYUKOKU UNIVERSITY, SHIGA CAMPUS

I visited Professor Mitsue Koizumi at the new Shiga campus of Ryukoku University on the Friday afternoon, July 24. Professor Koizumi has established the Materials Chemistry Program at the Shiga campus. Since Professor Koizumi was involved in a conference for most of the afternoon, Manshi Ohyangi provided a tour of the laboratories, an extended discussion on self-propagating high-temperature synthesis (SHS) and a visit to the Shiga Art Museum.

Ryukoku University is one of the oldest universities in Japan, having been founded in 1639 to educate young men for the Buddhist priesthood. It has undergone several changes in the 20th C., expanding from a small college to a university, admitting women beginning in 1932, changing over to the American educational model in 1988, and opening a third campus at Seta in Shiga Prefecture in 1989. With the opening of the Shiga campus, the curriculum was expanded to include a Faculty of Science and Engineering in 1989. The Shiga campus is located in a designated Cultural Zone which also includes a medical university and the Shiga Art Center. The buildings are modern, spacious and tastefully designed. The laboratories which I visited appeared to be well-equipped.

The x-ray diffraction laboratory was one of the best equipped university laboratories that I saw during my time in Japan. It had three new Rigaku x-ray instruments: (1) a dual port instrument for standard powder patterns and rocking curve measurements; a theta-two theta high-temperature diffractometer; and small-angle x-ray scattering unit which was in use for polymer structure determinations.

As the high-temperature diffractometer was equipped with a standard type, narrow-angle detector and not a wide-angle (position-sensitive) detector, there were hopes of adding a position-sensitive detector to adapt the diffractometer for the study of SHS reactions.

A second laboratory contained a Bruker solid-state NMR spectrometer for ^{13}C , ^{29}Si and ^{31}P as well as ^1H resonance studies. A surface analysis laboratory provided micro-Raman, ESCA, FTIR and ESR. The electron microanalysis laboratory was equipped with a JEOL JEM-4000EX (400 KeV) instrument with 0.14 nm lattice resolution and 0.18 nm grain resolution, and a JEM-2000EX instrument. Both instruments were used for imaging work rather than microanalysis.

Ohyanagi has recently completed the construction of a new SHS chamber with both lateral and vertical video monitoring and thermal analysis by optical pyrometer, by light-pipe and by thermocouple. A sandpress is on order which will provide a quasi-hydrostatic pressure capability (7000 Kgf/cm₂).

By using an ignition pellet of a low-density Ti-C mixture instead of a hot filament, Koizumi, Ohyanagi and Masahiko Kano have succeeded in increasing the reaction temperature to between 2750 and 2760°C for the SHS reaction in Ti-C mixtures a high green density (up to 3.42 g/cm₃), thereby obtaining a high-density product and improved bend strength for samples with green densities greater than 2.7 g/cm³. Previously, other investigators have only reported the ability to ignite low green-density mixtures and obtained low-density products.

A SHS technique has been developed for instantaneous bonding of diamond grains to metal substrates, a process which is difficult to accomplish by normal heating due to the large difference in thermal expansion between the diamond and the substrate. This technique could be used, for example, to fabricate special material cutting tools. A Ti-C SHS reaction is used to rapidly heat the metal and a thin layer of Cu-Ag-Ti brazing metal on which a diamond grain is placed. The temperature rise during the reaction is about 1200°C; however, the cooling rate is extremely rapid, about 7000°C/min, and is believed to result in a large amount of undercooling. A joint project between Japan and Russia has been initiated to develop this process.

GOVERNMENT INDUSTRIAL RESEARCH INSTITUTE, KYUSHU

I visited the Government Industrial Research Institute, Kyushu (GIRIK) on July 29. Hisayoshi Yoshida, Director of the Department of Materials Science, was my host. GIRIK is located in Tosu, about 30 minutes from Fukuoka by train.

GIRIK carries out a number of research and development projects under major AIST programs such as the Sunshine Project, Basic Technologies for Future Industries, and International Research Cooperation, and also contributes toward the development of industrial technology and resources in Kyushu.

The program of the Materials Science Department is divided into carbon materials, ceramics and an overlap area of carbon fiber reinforced ceramic composites (CFRC). In each of these three areas both structural and functional properties are emphasized.

Ceramic materials of interest have been primarily nonoxide materials: Si_3N_4 , beta-SiAlON, SiC, borides, silicides and BN. Both bulk ceramics and ceramic films have been studied. Previous but recently concluded work has included boride-based ceramics having ductility at high temperatures, porous ceramic materials from rice husks and intelligent composite ceramics. The programs on hot-gas corrosion of ceramics and high-frequency vibration machining of ceramics are scheduled to conclude this year. It is anticipated that the high-temperature corrosion study will be replaced by a high-temperature erosion study of ceramics by fly-ash.

Work on structural carbon materials has emphasized homogeneous, high-density carbon materials. Present on-going work includes carbon/carbon (C/C) composites with oxidation resistance, sliding properties of carbon materials at high temperatures, carbon fiber reinforced ceramics and synthesis and functioning of inorganic polymers with layered structure. Carbon/carbon composites and carbon/carbide composites are being studied for high-temperature applications such as Japan's space shuttle program, metallurgical and glass processing, and other applications requiring light-weight, high-temperature materials. The preparation of C/C and C/carbide composites with additions of metal carbides such as NbC or TaC to modify properties have been investigated by hot-pressing and pressureless sintering. Accomplishments under this program have included the development of C/C composites in which both fiber and matrix were pitch-based and development of mechanical grinding technique to produce sinterable carbon, Si_3N_4 , and BN powders. Functional carbon materials have included carbon films, graphite electrodes and activated carbon.

Functional ceramics have included optical ceramics such as electrophotochromic materials, piezoelectric materials and photostrictive materials. A program on intelligent functional/structural ceramics has been proposed to MITI which would start next year.

In addition to studies of structural and functional applications, work on ceramic materials and ceramic-based composite materials has included hot-gas corrosion, welding of ceramic-to-ceramic and ceramic-to-metal, and FTIR and Raman characterization of structure and structural changes.

GOVERNMENT INDUSTRIAL RESEARCH INSTITUTE, OSAKA

My visit to Government Industrial Research Institute, Osaka (GIRIO) was arranged to by Takako Takahashi, Head of the International Research Cooperation Section. GIRIO is one of the 16 research institutes under the AIST. The program at GIRIO is directed toward energy-related materials; optical materials and functional surface materials.

Research on energy-related materials is funded through the AIST'S Sunshine and Moonlight Projects. Research under the Moonlight Project at GIRIO consists of work on lithium batteries, electric powered vehicles, fuel cells, superconducting oxides, plasma spraying, ceramic materials, water electrolysis, alloys for hydrogen storage, chemical heat pumps, photoresponsive materials, halide glasses for UV and IR transmission, glass melting under microgravity, functionally gradient materials, nonlinear optical materials, heterogeneous catalysis, functional surface materials, field-effect transistors, reaction injection molding of composites, fiber and whisker reinforced ceramics, mechanical properties of polymers and composites, and development of a 3-D ion microscope.

The Advanced Glass Section under H. Tanaka is conducting research on a variety of functional glasses for applications as phototransmitting materials, nonlinear optical materials, ion-conducting glasses and porous membranes. IR transmitting halide glasses, such as ZnBr_2 - BaBr_2 -KBr glass, which have applications as windows for CO_2 laser radiation are being studied to reduce their sensitivity to moisture. A group under K. Kadono has prepared Au-doped silica glasses by ion-implantation that have enhanced third-order nonlinear susceptibility. Tetrahedral coordination of Cd with Cl and Br and 5 or 6-coordination with I in ternary and quaternary cadmium chloride, bromide and iodide based glasses was inferred by the lowering of the Cd-Cl and Cd-Br stretching modes with respect to those of the molten salt; whereas, Cd-I showed similar stretching frequencies in both the glass and the molten salt.

Ionic conductivity in lithium ion-conducting halide glasses with 3 to 5 components was found to increase in the order chloride<bromide<iodide, reaching a value of 10^{-6} S/cm for iodide glasses at room temperature. The ionic conductivity of copper (I) halide based glasses with alkaline and alkaline earth halide glass modifiers and with chlorine, bromine or iodine as the single halogen species was determined as function of composition. The composition $30\text{CuCl}-30\text{CuBr}-30\text{RbCl}-5\text{CaCl}_2-5\text{BaCl}_2$ exhibited the highest room temperature conductivity, 0.001 S/cm.

A composite porous glass membrane containing 30 mol% ZrO_2 was prepared by soaking porous alumina tubing in a sol prepared by hydrolyzing $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) followed by addition of $\text{Zr}(\text{n-OC}_3\text{H}_7)_4$. The pore size distribution of the deposited membrane was determined, and separation of H_2 - N_2 mixtures, thermal resistance and water vapor resistance were measured.

The Functional Ceramics Section, under Hiroshi Yamashita, is studying the processing of superconducting ceramics. Ichiro Matsubara et al. have prepared whiskers and sheets of Bi-2223 by annealing Bi-2212 whiskers and sheets, respectively, in a $\text{Bi}_2\text{Sr}_2\text{Ca}_4\text{Cu}_6\text{Pb}_{0.5}\text{O}_{14.5}$ powder. However, an attempt to produce the 2223-phase from single crystals of $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (Bi-2201) resulted in only partially conversion of the 2201-phase to Bi-2223.

The Fuel Cell Section, under Y. Miyazaki, is conducting research on molten carbonate fuel cells (MCFC) and on solid oxide fuel cells (SOFC). New fuel cell materials and new electrolyte compositions are being tested by Miyazaki for the molten carbonate fuel cell program. Binary compositions of alkaline earth (Sr, Ca, Ba) carbonates and alkali (Li, K) carbonate are being investigated with respect to properties and phase diagrams. $(\text{CeO}_2)_{0.8}(\text{SmO}_{1.5})_{0.2}$ -based compositions are being investigated by S. Tanase for solid oxide fuel cells which would operate at 800°C . Tanase is investigating the effects of a third component oxide, such as Ta_2O_5 , ThO_2 and HfO_2 , to off-set the tendency of CeO_2 to reduce at low partial pressures of oxygen and of a fourth component oxide, such as BaO or SrO, to improve the ionic conductivity of the system.

In the Battery Section, under S. Higuchi, sodium-sulfur, zinc-chlorine, zinc-bromine and advanced lead-acid systems are being evaluated as part of a Moonlight Project to develop advanced battery systems for electric energy storage to facilitate load-leveling.

The Ion Engineering Section, under K. Fujii carries out Rutherford Backscattering (RBS) characterization and ion implantation and analysis with a tandem generator. Ion beams focused to the order of a micron in diameter have been used as a "3-D ion microscope" for surface analysis, measurement of elemental depth distribution and investigation of electronic states by detecting backscattered ions, secondary electrons, and particle-induced x-ray emission (PIXIE). Gold pad patterns on Si substrates have been analyzed with C^+ and O^+ beams and secondary electron mapping.

The Engineering Ceramics Section, under M. Iwasa, is investigating the processing and properties of a variety of SiC-based and Si_3N_4 -based ceramics and ceramic composites as structural materials and coatings. SiC-based composite coatings with TiC and SiO_2 were successfully applied to carbon substrates by low-pressure plasma spraying of a mixture of SiC and TiO_2 . Kazuo Ueno has investigated the enhancement of bend strength of Si_3N_4 which was gas-pressure sintered with the use of Y_2O_3 , La_2O_3 , Pr_6O_{11} , $\text{Pr}_6\text{O}_{11}\text{-Y}_2\text{O}_3$, and $\text{Pr}_6\text{O}_{11}\text{-Al}_2\text{O}_3$ sintering aids. The processing of SiC-whisker/SiC composites by ball milling SiC whiskers with polycarbosilane (PCS) to form a pressable powder and by infiltrating a SiC whiskers into a preform with infiltrating with a solution of PCS in benzene were investigated by T. Tanaka and collaborators. The low densities of the resulting composites resulted in low bend strengths and indicated the need for further study of the sintering conditions.

K. Ueno, S. Sedeoka and J. Hirooka have studied the effect of sintering conditions on the bend strength and toughness for Si_3N_4 composites with either SiC whiskers or fibers. Strength and toughness were highest for SiC whisker/ Si_3N_4 composites sintered at temperatures above 1900°C where predominantly $\beta\text{-Si}_3\text{N}_4$ was formed and sintering times of less than 30 minutes. S. Sedeoka, K. Ueno, and Kazuhira have investigated the properties of SiC containing 5-15% graphite was fabricated by hot-pressing SiC and carbon black at $2000\text{-}2300^\circ\text{C}$.

Ion-implantation of the (1010) and (0001) surfaces of sapphire with 3 MeV Au^{2+} and 3 MeV Ni^{2+} was investigated to determine the effect of an expected compressive layer on the Knoop and Vickers hardness values and estimated residual stress. Implantation at fluence of 2×10^{16} ions/ cm^2 with either Au^{2+} or Ni^{2+} yielded a higher average compressive stress and a higher stress intensity factor than irradiations at lower fluences, with the (1010) surface showing greater enhancement than the (0001) surface.

Using a self-consistent tight-binding method with the supercell technique, M. Kohyama, S. Kose and R. Yamamoto analyzed the properties and relative stability for two polar and one nonpolar structure for the {122} $\Sigma=9$ grain boundary in $\beta\text{-SiC}$ (zincblende structure). The N-type interface which contains C-C wrong bonds was found to be the most stable for a C-rich atmosphere, whereas the P-type interface which contains Si-Si wrong bonds was most stable for a Si-rich atmosphere. The nonpolar interface was the least stable since it had somewhat larger bond distortions.

The bonding between an (0001) surface of sapphire and a series of 4d transition metals was investigated by M. Kohyama, S. Kose, M. Kinoshita and R. Yamamoto using the tight-binding method and with various degrees of metal deposition over the surface oxygen plane. The calculated local density of states (LDOS) for Nb- Al_2O_3 showed that a direct chemical bond of both covalent and ionic character can be established between the surface O atoms and the deposited Nb atoms, consistent with results from photoelectron spectroscopy. The model was extended to interfaces of Al_2O_3 with Zr, Mo, Ru and Pd.

OSAKA UNIVERSITY

I visited the Institute of Scientific and Industrial Research at Osaka University on Friday, July 31. Professor Yoshinari Miyamoto and Professor Koichi Niihara made the arrangements for my visit. In addition to the several discussions, I gave a seminar on DOE's program in material science and toured the inertial confinement project at the Institute of Laser Engineering.

At the Processing Research Center for High Performance Materials, Miyamoto has combined self-propagating high-temperature synthesis (SHS), also called combustion synthesis, with hot-isostatic pressing (HIP) into a technique called gas-pressurized combustion synthesis (GPCS). Using a N_2 ambients for simultaneous synthesis and densification, Si_3N_4/SiC ceramic composites were prepared from Si, C and Si_3N_4 reactants. The technique also has been used to prepare dense nitrides of Nb, Ti and Ta. The GPCS technique also has been used to densify and sinter of powder compacts encapsulated in a borosilicate glass, in which the combustion of surrounding powder bed of combustion agent provides the heat for the synthesis. Ti and C can be used as the combustion agent with Ar as the pressurizing gas, or Si powder in an over pressure of N_2 gas; a low-grade Si_3N_4 is obtained as a by-product in this latter case. Si_3N_4 powders have been sintered to 99.8% of theoretical density at $1950^\circ C$ and 170 MPa without additives. In addition, the following dense functionally gradient materials have been prepared: Ti+C, Ni reacted to form TiC/Ni; Mo+Si, SiC, TiAl to form $MoSi_2$, SiC/TiAl; Ti+B, Ni to form TiB_2/Ni ; and Cr+C, Ni to form Cr_3C_2/Ni .

Niihara is the head of the program on Synthetic Inorganic Materials and also leads the program at the Processing Research Center for High Performance Materials. Previously he worked at Tohoku University on high deposition rate CVD for the formation of functionally gradient materials. To acquire an understanding of fracture mechanics needed to develop a concept of structural materials, he then spent two years working with Professor Hasselman at Virginia Polytechnic Institute. Niihara sees composites as necessary to provide the breakthrough on the problem with monolithic ceramics - i.e., sensitivity to internal flaws. However, composites suffer from what he terms the Youngs modulus problem - i.e., the decrease in strength due to the mixed phases with weak interfaces. Composites are also sensitive to fabrication. His work on ceramic nanocomposites is widely recognized both in Japan and in the U.S.

Professor Yukichi Umakoshi of the Department of Materials Science and Engineering has studied plastic deformation of the titanium-aluminum intermetallic alloys and of transition metal silicides, including $MoSi_2$, $(Mo_{0.97}Cr_{0.03})Si_2$, and $CrSi_2$ single crystals and of polysynthetically twinned crystals of TiAl(γ) in the composition range 48.1-51.6 at.% Al. The results of the study indicated the possibility of improving the ductility of $MoSi_2$ by addition of Cr, but the improvement was not remarkable. The plastic behavior of polysynthetically twinned TiAl was found to depend strongly on the lamellar spacing and the angle between the loading axis and the lamellar planes; maximum elongation was obtained when the stress was applied at intermediate angles so that slip occurred on {111} planes parallel to the lamellae of the twinned material.

SUMITOMO ELECTRIC INDUSTRIES, ITAMI WORKS

On Saturday morning, August 1, I visited M. Miyake at Sumitomo Electric Industries at its Itami Works in Itami City, near Osaka. Sumitomo Electric has carried out research and development in ceramic materials, such as silicon nitride, cubic boron nitride (c-BN), metal carbides and nitrides, and diamond for a wide array of cutting tools. The company produces a sintered c-BN, a fine-grained AlN for high thermal conductivity substrates, and a functional gradient coatings of SiC on carbon/carbon composites. MgF₂ optical materials are produced for near IR applications. Diamond grains, about 1 cm in size, are produced by high-pressure synthesis, and diamond films by microwave plasma CVD.

At the time of my visit Sumitomo Electric had developed Si₃N₄ ceramics in which the size of the prismatic β -phase grains was precisely controlled at 0.5 μ m, which is about 10% of previously reported crystal sizes. Sumitomo Electric reported in Kagaku Kogyo Nippo, in February 1993, three-point bend strengths of the ceramics of 160 to 180 kg/mm², whereas typical commercial products are on the order of 80 kg/mm². The reliability of the material is evidenced by a Weibull modulus of more than 22, as compared to a value of 12 for commercial materials. By installing a model plant within its Itami Research Institute, the company established a continuous production process free of impurity contamination, to approximately double product reliability. Also in its February announcement, Sumitomo Electric announced plans to begin full-scale sample distribution to user industries, including major automobile manufacturers, in April 1993. The new ceramics will be marketed primarily for automotive engine components such as valves and piston pins.

CERAMICS AND GLASS

Apart from research on oxide superconductors which is described in the section on SUPERCONDUCTORS, most of the programs which I visited were concerned with structural ceramics, and of the possible materials systems, most were ceramic matrix composites. Even among the automobile companies which see little opportunity for composites materials at this time, there was a considerable amount of research on ceramic matrix composites. Silicon nitride appeared to predominate as the matrix material of choice, while SiC whiskers and fibers and graphite particles and fibers were employed as the reinforcing phase.

Much of the research appeared to be directed toward processing behavior and mechanical properties, including strength, toughness, creep and fracture mechanics. Processing knowledge and skills seemed to be very high both in the areas of powder preparation and ceramic densification. Process innovations appeared to be carried out with a considerable degree of imagination and development of precise control. However, I found very little effort directly toward modeling and simulation of structures and the investigation of microscopic, or atomic scale, mechanisms.

Hot-isostatic pressing, hot-pressing and pressured sintering are common densification techniques. Characterization techniques included a variety of powder characterization methods similar to those in use in the U.S., x-ray powder diffraction, various spectroscopies and electron microscopy. Electron microscopy appeared to be directed largely toward imaging and diffraction, with much less effort devoted to analytical microscopy.

Powders

At the Government Industrial Research Institute, Nagoya, a hydrothermal process has been developed by S. Tomura for the preparation of synthetic kaolinite, $\text{Al}_2\text{O}_2\text{O}_5(\text{OH})_4$, from silica and alumina to meet the needs of the ceramic industry in the Nagoya area. The effects of various starting materials and secondary cations and anions on the formation and crystallization of kaolinite were investigated. Spherical kaolinite which formed as an intermediate product was found to be useful in ceramic forming to reduce the hysteresis effect ("memory effect") caused by platy kaolinite during drying.

At Nagaoka University of Technology, K. Uematsu has investigated the influence of particle microstructure, such as that of spray-dried particles, on retained flaws in sintered bodies. By dispersing a small quantity of transparent particles in a neutral optical density fluid, he has been able to examine microscopically the interior structure of the particles. He has found that spray-dried particles typically contain some structure, such as large open pores, and higher density near the surface due the evaporative drying process during forming.

These structural inhomogeneities are often retained during further processing and appear as flaws in the fired ceramic body. Cold isostatic pressing even at pressures of 600 atm was found to be insufficient to remove particle surface features and pores from green bodies. To develop a better understanding of the dynamic processes occurring during evaporative drying of a particle such as during spray-drying, Uematsu is investigating the desorption of binder and water and diffusion in porous assemblies of particles.

Studies in K. Ishizaki's group at Nagaoka University of Technology have included powder analysis by temperature programmed desorption (TPD), the use of low-temperature specific heat to determine amorphous content, and theoretical analysis of the optimum particle size distribution for particle packing. M. Kawamoto and K. Ishizaki developed an improved TPD apparatus which was used to study the effects of washing of Si_3N_4 powders on adsorbed H_2 , H_2O , NH_3 , N_2 , CO and CO_2 . Powders characterized by TPD were used in a study of the effected improvements in fluidity resulting from aqueous washing of silicon nitride powders. Yasuhiro Konakawa and Ishizaki conducted an analysis of the optimum particle size distributions for obtaining the highest relative density in a compacted body. The size distributions were assumed to be log-normal with different geometrical standard deviations and to consist of a discrete Horsfield's distribution of five different sphere sizes.

The processing of powders for oxide superconductors is presented in the section, SUPERCONDUCTORS.

Polymeric Precursors

At the Institute for Materials Research (IMR), Tohoku University, M. Omori, in T. Hirai's group, has investigated the use of trichlorophenylsilane as a precursor of SiC/C composites. The precursor was polymerized over Na in toluene plus 18-Crown-6 catalyst to yield a network polyphenylsilane with phenyl side groups. This three-dimensional polymer can be dissolved in organic solvents and may be used to form a film. Degradation of the polymer at 1400°C yielded small SiC particles in a carbon matrix.

Sintering

K. Watari (now at GIRIN), M. Kawamoto and K. Ishizaki of Nagaoka University of Technology have investigated the use of a carbothermal reaction during sintering in a nitrogen atmosphere to convert $\text{AlN/Y}_2\text{O}_3$ to AlN/YN , with an improved thermal conductivity. T. Yanai and Ishizaki have used a carbothermal technique to prepare $\text{Si}_3\text{N}_4/\text{SiC}$ composites by coating Si_3N_4 particles with a layer of graphite (from decomposition of CH_4) to react with the oxide layer that commonly coats Si_3N_4 particles. Sample were compacted by cold-isostatic pressing and hot-isostatically pressed to produce a composite material of large Si_3N_4 grains with smaller SiC particles in the grain boundaries.

Ishizaki's group which has carried out extensive work on HIP stability diagrams, similar to Ellingham diagrams, recently has developed HIP techniques for the preparation of open pore ceramics with very little closed porosity and uniform pore sizes. Hot-isostatically pressing was demonstrated as a technique for preparing porous ceramics with improved control of the pore size and pore size distribution. Porous TiO_2 ceramics were prepared with an open porosity in the range of 20 to 40% of total sample volume.

K. Ueno at GIRIO has investigated the gas-pressure sintering of Si_3N_4 with Y_2O_3 , La_2O_3 , Pr_6O_{11} , $\text{Pr}_6\text{O}_{11}\text{-Y}_2\text{O}_3$, and $\text{Pr}_6\text{O}_{11}\text{-Al}_2\text{O}_3$ sintering aids. Samples were sintered at 1900-2050°C in nitrogen at 1 MPa pressure. Si_3N_4 sintered with Y_2O_3 or La_2O_3 showed bend strengths higher than 900 Mpa at 1300°C, whereas composites with $\text{Pr}_6\text{O}_{11}\text{-Y}_2\text{O}_3$ or $\text{Pr}_6\text{O}_{11}\text{-Al}_2\text{O}_3$ yielded strengths on the order of 800 Mpa.

T. Tanaka, N. Tamari, I. Kondoh and S. Kose at GIRIO have prepared SiC whisker/SiC composites by coating SiC whiskers with silane coating agent, then ball milling with polycarbosilane (PCS) and processing to obtain a composite, or processing the treated SiC whiskers into a preform, infiltrating with a solution of PCS in benzene, and then processing to obtain a composite. The PCS yielded a very fine α -SiC upon decomposition. Bend strength was found to depend upon method of preparation, but it was generally low due to the low density obtained in all cases.

Reactive Formation and Combustion Synthesis

Y. Kagawa of the Institute of Industrial Science of the University of Tokyo has studied the in situ formation of Al_2O_3 -matrix/Si, Mg composites by controlled oxidation of Al-Si-Mg melts. In the oxidation process, a pervious cap of Al_2O_3 develops above the surface of the melt, with a vapor region between the melt and the oxide dome due to a high Mg vapor pressure. However, the liquid metal creeps up the walls of the crucible and infiltrates the capillary channels in the oxide. A pool of liquid Mg forms on the exterior surface of the melt through which the oxygen is transferred to oxidize the Al metal underneath so that the cap grows from the exterior surface outward. The channels have been found to be Si-rich and Al-poor near the exterior side of the cap.

Y. Miyamoto of the Institute of Scientific and Industrial Research at Osaka University has used a combination of combustion synthesis, or self-propagating high-temperature synthesis (SHS), and hot-isostatic pressing (HIP) for simultaneous synthesis and densification of nitride and carbide materials. Dense Si_3N_4 /SiC ceramics have been formed from Si, C and Si_3N_4 reactants under an overpressure of 1 to 10 MPa of nitrogen. The SHS reaction is ignited by Ti-powder pre-ignitor. He also has applied the HIP-SHS technique to HIP sintering of compacted powders. Powder compacts, coated with BN and encapsulated in borosilicate glass, were surrounded by a Si fuel in a nitrogen pressurized reactor.

The temperature of the reactor was raised to 780°C to soften the glass prior to initiating the SHS reaction. Si_3N_4 powders were sintered to 99.8% of theoretical density at 1950°C and 170-MPa without additives. Si_3N_4 samples with two different levels of Al, Ca and Fe impurities were prepared by this method for a study of impurity-enhanced cavity formation.

Processing and Properties of Structural Ceramics

Crack closure resulting from the volume expansion associated with the tetragonal to monoclinic phase transformation of ZrO_2 is a property which T. Ikegami of NIRIM is attempting to exploit to develop a self-healing ("smart material") ceramic. Ikegami believes that the optimum yttrium dopant concentration needed to develop this self-healing property in yttrium partially stabilized ZrO_2 may occur at an Y concentration where defect clusters formed between Y ions and oxygen vacancies begin to become important. These defect clusters are expected to inhibit the phase transformation which is the source of the potential self-healing in Y-doped ZrO_2 . He is investigating the use of heat of solution measurements and bend strength measurements as indicators of the optimum Y concentration. The heat of mixing of Y_2O_3 and ZrO_2 were determined from measurements of heats of solution in sodium tungstate at 970 K. Bend strengths were measured in three-point bend tests for ZrO_2 containing between 2 and 4 mol% Y_2O_3 . ZrO_2 with 4 mol% Y_2O_3 was found to have the maximum heat of mixing, whereas the maximum bend strength occurred at little less than the 3 mol% composition.

To improve mechanical properties of structural ceramics K. Niihara, of the Institute of Scientific and Industrial Research at Osaka University, has pioneered the preparation and investigation of nanocomposites in which ultrafine grains are incorporated within grains and at grain boundaries of coarse-grained ceramics. His objective is to retain the strength of the matrix while increasing its toughness. He has examined Al_2O_3 , Si_3N_4 , B_4C , and MgO matrices with a dispersoid of ultrafine SiC grains, Al_2O_3 matrices with ZrO_2 grains, and B_4C matrices with TB_2 grains. In the case of MgO/SiC, strength and toughness improved relative to monolithic MgO, there was a reduction in number of flaws, and the brittle-to-ductile transition temperature (BDTT) reduced by 400-500°C. A dislocation network was observed to develop resulting in many subgrained boundaries which terminated at interior SiC grains and MgO grain junctions. Niihara is also investigating nanocomposites such as sialon/SiC in which the dispersoid SiC phase consists of microfibers. High temperature (1300°C) strength was found to improve from 623 to 1075 MPa, and room temperature toughness improved from 12 to 25 $\text{MPa}\cdot\sqrt{\text{m}}$.

At NIRIM processing conditions are being investigated by the 5th Research Group for the optimization of the duplex structure of Si_3N_4 ceramics. Microstructures of equiaxed α -type and larger, acicular β -type grains are correlated with observed fracture toughness. The addition of 5% β - Si_3N_4 powder as nuclei to the starting powder resulted in material with an improved K_{Ic} of 7.2 $\text{MPa}\cdot\sqrt{\text{m}}$. This group is collaborating with Nissan which is testing this material in engine components.

Carbon-fiber/ceramic composites with Si_3N_4 and Si_3N_4 -sialon were fabricated, characterized and mechanically tested by K. Nakano of GIRIN to establish a basis for design standards and life prediction. Flexural strength and dynamic fatigue were measured at room temperature and 1400°C. In fracture at room temperature the matrix peeled off the fibers leaving smooth surfaces; however at 1400°C wavy slip lines were evident on the fibers which could have been caused by shearing of the softened interface between fiber and matrix. The magnitude of the value of the dynamic fracture toughness of composite increased in the order: Si_3N_4 -sialon (3:7) < Si_3N_4 -Sialon (3:2) < Si_3N_4 . The load-deflection curve for Si_3N_4 -sialon (3:2) matrix composite indicated significant nonlinear behavior up to the maximum load point compared to the other two composites.

SiC matrix composites reinforced with C fibers also have been studied by Nakano's group. These were prepared by infiltrating high modulus pitch-based carbon prepreps with slurries consisting of SiC and AlB_2 powders and polystyrene. The pyrolyzed postforms were hot-pressed at 1850°C in Ar. Flexural strength was measured at room temperature, 1200, 1400 and 1600°C using 4-point bending with a single-edge notched beam. Fracture strength increased slightly with temperature from 420 MPa at room temperature to nearly 600 MPa at the high temperatures. Fracture toughness increased from 12 $\text{MPa}\cdot\sqrt{\text{m}}$ to 19 $\text{MPa}\cdot\sqrt{\text{m}}$. These increases in fracture strength and toughness were associated with softening of the matrix-fiber boundary layer at high temperature which facilitated fiber pullout.

K. Ueno, S. Sodeoka and J. Hirooka of GIRIO have investigated the effect of sintering conditions on the bend strength and toughness for Si_3N_4 with 20 wt% SiC whiskers. Strength and toughness were highest for sintering temperatures above 1900°C where predominantly β - Si_3N_4 , but they decreased for sintering times greater than 30 minutes due to increased bonding between the SiC whiskers and the Si_3N_4 grains. K. Ueno, S. Kose and M. Kinoshita hot pressed Si_3N_4 with 5 vol% chemically vapor deposited SiC fiber at 1400-1500°C using a MgO and MgF_2 mixture as sintering aid. The composite had maximum bend strength of 590 MPa and fracture toughness (SENB) of 15 $\text{MPa}\cdot\sqrt{\text{m}}$. S. Sodeoka, K. Ueno and K. Ueno fabricated SiC containing 5-15% graphite by hot-pressing at 2000-2300°C using carbon black as the source of carbon and 1 wt% of B_4C as sintering aid. The composite with 10% graphite had an average strength of 820 MPa and a fracture toughness of 4.5 $\text{MPa}\cdot\sqrt{\text{m}}$. Carbon black was observed to limit the growth of SiC grains.

K. Ueno, S. Sodeoka, S. Kose and M. Kinoshita of GIRIO deposited SiC-based coatings with either Al_2O_3 or TiO_2 as additive on normal carbon steel substrates by low-pressure plasma spraying. The SiC- Al_2O_3 coating showed a transformation of the alumina from α -type to γ -type, indicative of melting, and yielded a coating with a coarse grained structure and poor bonding. The SiC- TiO_2 reacted to form TiC and SiO_2 which melted in the torch and formed an adherent coating.

Quantitative evaluation of amorphous content of the grain boundary phase of Si_3N_4 were carried out by K. Ishizaki and Homasaki, of Nagaoka University of Technology, using low temperature specific heat measurement technique, previously reported in the Journal of the American Ceramic Society (1991). Specific heat measurements to below liquid nitrogen temperature (77 K) performed on samples with the composition $94\text{Si}_3\text{N}_4/3\text{Al}_2\text{O}_3/3\text{Y}_2\text{O}_3$. One sample with approximately 12% (wt.) amorphous phase and 1-2% crystalline grain boundary phase was annealed to crystallize the glass phase. After annealing the amount of glass phase was about 6%. The crystalline portion of the grain boundary phase was determined x-ray diffraction to be a yttrium nitrosilicate.

NGK/NTK has developed a small cyclic fatigue tester (CFT-340-1) which is equipped with a high power piezoelectric bimorph and is designed to test small (3x4x36 to 41 mm) test pieces. The instrument has a frequency range of 100 to 400 Hz and a maximum stress of 1000 MPa.

Hot-pressing of carbon powders from calcined coke or phenol resin and mixed with various ratios of boron carbide has been investigated in the Materials Science Department at GIRIK for the preparation of C/C and C/carbide composites. In some cases other carbides such as NbC or TaC were added in various ratios. Samples were hot-pressed at 200 Kg/cm² for 30 minutes at 1800, 2000 or 2200°C. Physical properties and other characteristics investigated included bend strength (three-point), lattice constant (d_{002}), electrical resistivity, apparent crystallite size, loss of bend strength due to thermal shock, and reactivity with oxygen and with strong oxidizing acid.

Fracture Mechanics and Crack Growth

Y. Kagawa of the Institute of Industrial Science at the University of Tokyo has pioneered microscopic techniques for the study of crack propagation in composites. In addition to using fiber pullout and protrusion tests which are widely used in the U.S., he has developed a load cell for microscopic observation of crack propagation. To observe stable crack growth in transparent, brittle solids, he has developed a small load fixture and technique for microscopic observations.

The technique utilizes a wedge shape (trapezoidal) specimen. A crack is initiated in at the narrow end of the wedge. The thin metal fingers (shims) are inserted at the outer end of the crack. Each shim is attached to one arm of a small tensile rig. A crack opening displacement is applied by turning a screw which is threaded through the two arms and causes them to separate. This apparatus is very compact and fits easily on to the stage of a microscope. He is also developing a laser technique ("laser caustics") to measure the stress-intensity factor, K_{tip} , at a crack tip.

Kagawa has investigated crack growth and fracture of lithium aluminosilicate glass (LAS) matrix composites containing silicon oxynitride fibers (Siemens) by taking advantage of the matched optical indices of matrix and fiber (1.7), which results in a matrix that is transparent even with 40% fiber loading. He has also studied the effect of water vapor to weaken the fiber bond in SiC fiber/LAS composites.

He has used microscopic techniques for crack propagation studies of indenter introduced cracks and for microscopically observing the behavior of the crack front during cantilever beam measurements of fracture toughness. Studies have included crack propagation in transparent ZrO_2 . A special cutting wheel has been developed to cut V-notches, both single and chevron, with a 3-6 μm radius of curvature.

M. Mitomo, of NIRIM's 5th Research Group, has studied crack tips in 6H-SiC, Si and 15R-sialon by HREM. The crack tips in SiC and Si were introduced with a Vickers indenter, whereas the those in sialon were introduced by crushing a hot-pressed sample. The crack tips were imaged in a high resolution electron microscope and were found to be atomically sharp with no evidence of a yielding zone. Cleavage cracks in Si always propagated in the (111) plane. Small dislocation segments were found around the crack and crack tip but were considered to result from the combined effect of the stress generated by the propagating crack and the successive ion-bombardment of the Si crystal.

R. Nowak, Y. Horino, K. Ueno, M. Kinoshita, W. Ensinger and M. Satou of GIRIO investigated the anisotropy of indentation fracture of sapphire implanted with gold or nickel to determine the effect of surface modification on the mechanical properties of ceramic crystals. A (10 $\bar{1}$ 0) surface of sapphire was implanted with 3 MeV Au^{2+} and 3 MeV Ni^{2+} , nickel ions were expected to penetrate about twice the distance of gold ions. The ion-implanted samples generally showed increased Knoop hardness with respect to unimplanted samples, with the high density Ni^{2+} -implanted (fluence = 2×10^{16} ions/cm 2) showing the greatest anisotropy. Vickers hardness measurements were used to determine the residual stresses induced by ion-implantation in the (10 $\bar{1}$ 0) and (0001) surfaces of sapphire. Implantation at fluence of 2×10^{16} ions/cm 2 with 3 MeV Au^{2+} or Ni^{2+} yielded a higher average compressive stress and a higher stress intensity factor than irradiations at lower fluences, with the (10 $\bar{1}$ 0) surface showing greater enhancement than the (0001) surface.

High Temperature Properties

T. Ohji and co-workers at GIRIN are determining tensile strength, tensile fatigue and tensile creep of monolithic Si_3N_4 , $\text{Si}_3\text{N}_4/\text{SiC}$ -whisker composites and SiC . This laboratory has developed techniques for preparing tensile specimens with narrow gauge sections on a routine basis. Fracture resistance is also measured using chevron-notched beam (CNB) specimens from room temperature to 1300°C . Ohji has eleven automated creep stations in operation to carry out creep measurements for durations up to 100,000 hours.

The tensile strength of hot-pressed Si_3N_4 containing 5 wt% Y_2O_3 and 3 wt% Al_2O_3 showed a drastic decrease at temperatures above 1000°C due to softening of the grain boundary glassy phase. At temperatures above 1300°C some plasticity was evidenced in the stress-displacement curves with lower yielding point appearing at displacement rates less than $1.0 \text{ mm}\cdot\text{min}^{-1}$. Ohji analyzed the fracture mechanism in terms of Evans' mechanism of cavitation at glassy three grain junctions followed by cavity spreading along grain boundaries normal to the stress direction for the upper yielding point. Cavitation is assumed to form rapidly throughout the specimen. Failure near the upper yield point occurs when the driving force is high so that small microcracks are driven to failure. The lower yielding point is associated with the duplex nature of the Si_3N_4 structure. Cavitation is assumed to spread predominantly in the region of small equiaxed, α -type grains and to be blocked by the entangled large acicular, β -type grains. Further strain and energy are required to overcome these obstructions.

Creep and creep rupture behavior were investigated for Si_3N_4 with and without SiC whiskers from 1200°C to 1400°C . Slow steady-state creep was observed under low stresses at 1200°C . At 1300°C and above, evidence of accelerated creep was observed toward the ends of the creep tests. The appearance of accelerated creep at the higher temperatures was attributed to the formation of cracks throughout the specimen. Creep exponents of 3 to 5 which were obtained for the accelerated creep were associated with the formation of facet-sized cavities. Steady-state creep at 1200°C had an exponent of 1.7 consistent with a creep model enhanced by cavitation in which facet-sized cavities form, cavities coalesce to microcracks and microcracks coalesce to the critical-sized macrocrack.

T. Hirai's group at the IMR of Tohoku University has investigated the oxidation of CVD- SiC in Ar-O_2 and CO-CO_2 atmospheres in the temperature range from 1567°C to 1650°C . The oxygen partial pressure, $P^t(\text{O}_2)$, at which the transition from active to passive oxidation occurred increased with increasing temperature and with decreasing total gas flow rates. The values of $P^t(\text{O}_2)$ were almost in agreement with those calculated from Wigner's model.

Irradiation Effects

In the 2nd Research Group at NRIM (Tsukuba) SiC-based composites are being studied as low activation materials for nuclear energy applications. T. Noda has used an ArF excimer laser to deposit α -SiC on substrates of carbon, carbonized Mo and carbon-coated Cu by photo-CVD. Laser deposition resulted in a particle size of 5-50 nm. Carbon fiber/SiC composites also have been prepared by CVI. Bend strength depended strongly on the thickness of the SiC layer covering the composite; the maximum room temperature bend strength obtained was 800 MPa.

At the IMR facility at the Oarai Research Establishment, T. Shikama is determining the effect of neutron and gamma radiation on the electrical conductivity of insulating ceramics. In-situ ac-impedance measurements are carried out on samples placed in the reactor core and in a pool containing the spent fuel rods. AC impedance measurements are made using a three-point technique: high, low and guard electrodes. Samples are inserted into the reactor core by means of a shroud facility which isolates the sample from the primary coolant and allows the environment around the sample to be controlled. Electrical leads extend from the specimen to an impedance analyzer which is located at the periphery of the reactor vessel. Very precise and uniform temperature control at the sample is attained by regulating the pressure of He in the shroud, thus adjusting the thermal conductivity of the gas. With regard to the problem of the impedance effects of the long sample leads in the insertion tube, Shikama commented that each of the three leads is contained in a stainless steel tube and is surrounded with an epoxy resin. At some distance above the core the parallel leads are coupled into the coaxial leads which extend to the junction box at the impedance instrument. He has found that the junction impedance between the coaxial leads and the parallel leads has presented a greater problem than the long leads.

Shikama also is conducting studies using the gamma radiation from spent fuel rods which are retained for cooling in the water-filled canal between the reactor and the building where spent fuel assemblies are stored. The canal permits fuel assemblies to be moved from the reactor to storage without removal from the water. He said that it is difficult to obtain reproducible conditions for the gamma exposures due the nonuniformity of the radiation field.

Ionic Conductors

At the Government Industrial Research Institute in Osaka, new cell materials and new electrolyte compositions are being tested for programs on molten carbonate fuel cell (MCFC) and solid oxide fuel cells (SOFC) under Y. Miyazaki. As part of the MCFC program, several furnaces are in operation to test new cell materials and new electrolyte compositions under simulated conditions to develop materials resistant to the highly corrosive conditions present in these cells. Binary compositions of alkaline earth (Sr, Ca, Ba) carbonates and alkali (Li, K) carbonate are being investigated with respect to properties and phase diagrams.

Research on $(\text{CeO}_2)_{0.8}(\text{SmO}_{1.5})_{0.2}$ -based systems is being carried out by S. Tanase of GIRIO as solid oxide electrolytes for solid oxide fuel cells (SOFC) projected to operate at temperatures in the neighborhood of 800°C . To prevent the reduction to which CeO_2 is prone at low oxygen partial pressures and accompanying increase in losses by parasitic electronic conduction, a third component oxide such as Ta_2O_5 , ThO_2 and HfO_2 has been added to the electrolyte, but with the accompanying decrease of the ionic conductivity from $\sim 0.1 \text{ S/cm}$ to $\sim 0.05 \text{ S/cm}$. Tanase is trying to offset this decrease in conductivity by adding a fourth oxide such as BaO or SrO . Oxide samples are prepared by mixing of powders in a mechanical mortar, compaction and sintering.

Interfaces and Grain Boundaries

Using a self-consistent tight-binding method with the supercell technique, M. Kohyama, S. Kose and R. Yamamoto of GIRIO analyzed possible structures of $\{122\} \pm 9$ grain boundary in $\beta\text{-SiC}$ (zincblende structure). Two polar and one non-polar interfaces were constructed, each of which contains Si-Si and/or C-C wrong bonds. The N-type polar interface contains C-C wrong bonds and is characterized by a slight compression normal to the interface. The P-type interface contains Si-Si wrong bonds and is characterized by a slight dilatation normal to the interface. The results did not indicate any charge accumulation, macroscopic electric fields or existence of free carriers for the polar surfaces. The nonpolar surface was indicated to be characterized by translations in the $[411]$ direction and to have somewhat larger bond distortions. In both the polar and nonpolar interfaces the C-C wrong bonds introduce localized states at the bottom of the valence band and above the conduction band. The Si-Si wrong bonds introduce localized states at the bottom of the conduction band and the top of the valence band. In addition, there are states that are mainly localized at the 5-7 units at the band edges. The calculated thermodynamic potentials in the interfaces indicated that the N-type interface is the most stable for a C-rich atmosphere and that either type of polar interface is more stable than the nonpolar interface.

Glass

Glasses in the ZnBr_2 - BaBr_2 - KBr system are potential IR transmitting material with possible application in windows and optical fibers for CO_2 laser radiation since the transmittance of these glasses extends to 20 μm ; however, these glasses are moisture sensitive, their thermal stability is not good, and they have a phase transition at $\sim 100^\circ\text{C}$. Their transmittance range arises from the weak bond strength, but their thermal stability is controlled by ZnBr_2 which is the glass former component but is also moisture sensitive. At GIRIO the Advanced Glass Section has been able to increase the glass transition temperature, T_g , slightly by the addition of high melting point compounds. However, further work is in progress to find additives or compositions which increase the stability of the glass without sacrificing the transmittance of the glass at long wavelengths.

K. Matusita at the Nagaoka University of Technology is studying the crystallization and viscosity of BaF_2 - ZrF_4 glasses which have potential use as IR transparent optical fibers. These glasses show a much steeper rise of viscosity with temperature than do conventional silicate glasses, making control of high-temperature processing difficult. He is also investigating the oxyfluoride system, Sn-P-Pb-O-F , where O and F are present in approximately equimolar amounts, which has a glass transition temperature (T_g) of about 100°C . Due to their low T_g , organic molecules with special functional groups can be encapsulated in the matrix to produce glasses with nonlinear optical properties. He has begun a study of reprocessing of waste Al silicate filtration materials to make glass compositions which might be usable as aggregate in building materials. His group is also studying the preparation of metallic Co-Ni-Fe-Si-B glasses using rapid solidification. Although this glass is ductile at room temperature, it becomes brittle at 300°C , well below T_g .

K. Kadono and colleagues of the GIRIO Glass Section have examined glass formation and structure of glass in three and four component systems of cadmium chloride, bromide and iodide based glasses. From the observation that the infrared absorption bands associated with Cd-Cl and Cd-Br stretching modes in the glass were lower than those in the molten salt, it was inferred that Cd is tetrahedrally coordinated in the glass but 5 or 6-coordinated in the molten salt. Cd-I stretching frequencies in the glass and molten salt were the same, leading to the inference that the Cd coordination is the same in the glass and molten salt.

K. Kadono, T. Shimomura and H. Tanaka have also studied 3 to 5 component systems of lithium ion-conducting glasses. Ionic conductivity increased in the order chloride < bromide < iodide, reaching a value of 10^{-6} S/cm for iodide glasses at room temperature. Glass forming regions were identified in the pseudoternary phase fields $\text{LiX}-(\text{KX}+\text{CsX}, \text{KX}/\text{CsX} \text{ fixed})-\text{BaX}_2$ and were typically near the compositions 50:50 to 60:40 $\text{LiX}:(\text{KX}+\text{CsX})$, with $\text{BaX}_2 < 10\%$. The ionic conductivity was measured by means of complex ac impedance.

The ionic conductivity also was determined as a function of composition for copper (I) halide based glasses with alkaline and alkaline earth halide glass modifiers and with chlorine, bromine or iodine as the single halogen species by the GIRIO group and researchers from Kobe University. Fast ion conduction by Cu^+ ions was little affected by the halogen species but strongly influence by the type of alkaline and alkaline earth modifier. Alkali and alkaline earth ion with smaller ionic radii and larger electric charges were found to increase the ionic conductivity. The composition $30\text{CuCl}-30\text{CuBr}-30\text{RbCl}-5\text{CaCl}_2-5\text{BaCl}_2$ exhibited the highest room temperature conductivity, 0.001 S/cm.

Au-doping by ion-implantation, followed by heat treatment for several hours, has been used by K. Fukumi and others to modify the third-order nonlinear susceptibility, $\chi^{(3)}$, of silica glass. The heat treatment results in the growth of Au colloid particles. The third-order nonlinear susceptibility was found to increase with heat treatment to a maximum value of 1×10^{-7} esu, which was much larger than that obtained by a glass melting method.

The GIRIO researchers have prepared a composite porous glass gas-separation membrane containing 30 mol% ZrO_2 by soaking porous alumina tubing in a sol prepared by hydrolyzing $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) followed by addition of $\text{Zr}(\text{n-OC}_3\text{H}_7)_4$. The pore size distribution of the deposited membrane was determined, and separation of H_2 - N_2 mixtures, thermal resistance and water vapor resistance were measured.

New Ceramic Phases

M. Shimada in the Department of Molecular Chemistry and Engineering at Tohoku University is studying unsymmetrical isoelectronic compounds; for example, B_2O which forms a diamond-like structure at low pressures - B_2O is considered isoelectronic in the sense that both boron and oxygen are first row elements and oxygen has a two valence electron excess with respect to carbon while two boron atoms represents a two valence electron deficit with respect to carbon. He is using high pressure (belt technique) to prepare a series of unsymmetric, isoelectronic ternary chalcogenides such as ZnGeP_2 . At 800°C and 5 GPa, ZnGeP_2 forms an ordered chalcopyrite structure, but at 1200°C and 5.5 GPa it forms a disordered zincblende structure. ZnSiN_2 forms an orthorhombic, distorted wurtzite, structure between 5 to 7 GPa, whereas ZnGeN_2 forms an orthorhombic structure that is a distorted zincblende-type.

Industrial Research and Development

Toyota, NGK/NTK and Sumitomo Electric have a strong interest in Si_3N_4 . Sumitomo Electric's recent success in producing Si_3N_4 ceramics with controlled grain size and significantly improved strength and toughness, see section on LABORATORIES for further details, will very likely advance the use of Si_3N_4 ceramics even more. Due to its formation of a duplex crystalline structure, Si_3N_4 ceramics tend to form an in-situ composite during processing so that little benefit is derived by further reinforcing with additions of SiC whiskers or fibers, for example. Although Si_3N_4 ceramics generally require hot-isostatic pressing, hot-pressing or an overpressure of nitrogen during densification to avoid decomposition, research is in progress to develop powders which can pressureless sintered.

Toyota recently abandoned injection molding of Si_3N_4 rotors for turbochargers, which it began in 1980, due to problems with long dewaxing times and iron contamination. For example, following the molding operation, a 150 mm diameter rotor required two weeks for dewaxing to occur before the green ceramic part could be fired. In 1984, Toyota began investigation of slip casting which is currently the forming method of interest. Ceramic composites are presently considered to be too costly, since these generally require expensive precursors, and the use of hot-pressing or hot-isostatic pressing does not permit mass production techniques to be used. Toyota is interested in ceramics which can be pressureless sintered. Low pressure slip casting is being investigated.

NGK Spark Plug/NTK Technical Ceramics fabricates Si_3N_4 turbocharger rotors in two parts: the inner core is cold isostatically pressed and the blade section is injection molded. By fabricating these two parts separately, the dewaxing and burn out time is reduced and the probability of developing shrinkage cracks is reduced. The two sections of the rotor are cold-isostatically pressed together before firing. NGK Spark Plugs experimented with SiC whisker toughening of its Si_3N_4 ceramics but found that SiC whiskers added little to the overall toughness, since most of the toughness was derived from the acicular β - Si_3N_4 grains, and the SiC whiskers presented a health hazard in their use.

Despite its considerable success to date in developing Si_3N_4 automotive ceramics, NGK Spark Plugs has found recently that the market for these materials has not developed as expected and that in many cases ceramics remain a too expensive alternative. Revision of the tax structure for automobiles in Japan has made large automobiles more attractive than they were a few years ago and has reduced the demand for turbochargers to improve the performance of small engines. In addition, the present slowing of Japan's economy has reduced the overall market for automobiles. Although the market pressures for the use of Si_3N_4 have weakened, research interest in this material and further developments in the processing of Si_3N_4 components are to be expected.

Sumitomo Electric successfully developed silicon nitride ceramics with the world's greatest strength and reliability twice that of existing materials. In April 1993, Sumitomo Electric plans to begin full-scale sample distribution to user industries, including major automobile manufacturers, by installing a model plant within its Itami Research Institute (Itami City, Hyogo Prefecture). Using its own precision control technology for crystal grains, Sumitomo Electric was able to achieve a 3-point bending strength of 160 to 180 kg/mm². Sumitomo Electric also established a continuous production process free of impurity contamination, to approximately double product reliability. The new ceramics will be marketed primarily for automotive engine components such as valves and piston pins.

In the 1970s, Sumitomo Electric began its R&D on silicon nitride ceramics, and initially tried to develop applications primarily in super-hard tools to replace existing tool materials. Among its accomplishments thus far, metal plasticity machining tools, such as cast iron cutting, are already in the market.

Sumitomo Electric has developed the technology for precisely controlling the size of prismatic crystals (β -phase) at 0.5 μ m, which is about 10% of previous crystal sizes. Bending strengths of typical commercial products are on the order of 80 kg/mm² and of test-produced materials, 120 kg/mm². The improved reliability of the material is evidenced by a Weibull modulus of more than 22, as compared to a current value of 12.

METALS, ALLOYS AND INTERMETALLICS

Intermetallics

TiAl-based alloys are expected to have major applications in Japan's growing aircraft industry, and TiAl and Nb₃Al are the intermetallics on which interest has centered for Japan's aerospace plane. Nb₃Al also is a potential low-temperature superconductor material for high-field applications. Consequently, TiAl and Nb₃Al intermetallics and alloys have been selected by the Ministry of Education for its program on intermetallics and by the Ministry of International Trade and Industry (MITI) for its national program in intermetallics.

Present-day commercial TiAl-based alloys are fabricated to have a two-phase Ti-rich, equiaxed structure. These alloys have about a 2 to 3% elongation in air at room temperature. Yield strengths of both the Ti-rich and the Al-rich alloys begin to drop above 600°C, reaching a value of 200 MPa, or less, for a 0.2% yield at 1000°C.

M. Yamaguchi at Kyoto University has developed a floating-zone technique for growing polysynthetically twinned (PST) crystals of γ -phase TiAl since it is not possible to grow single crystals due to the ease at which TiAl forms a lamellar structure. Floating-zone growth of PST TiAl appeared to be used at several institutions which I visited in Japan. γ -TiAl possesses the L1₀-type crystal structure (tetragonal). Both Umakoshi's group at Osaka University and Yamaguchi's group at Kyoto University have investigated the twinning structure and deformation behavior of PST crystals of TiAl. PST crystals have twins that belong to a specific twinning system.

In addition to TiAl lamellae, Ti-rich γ -TiAl PST crystals have been found to contain Ti₃Al lamellae (α_2 -phase) as ordered domains. (0001) planes of Ti₃Al lamellae, which have the hexagonal DO₁₉ structure, were flat and parallel to (111) TiAl planes. The [110] variant of TiAl was found to be exactly parallel to the three equivalent $\langle 11\bar{2}0 \rangle$ directions of Ti₃Al; whereas the two $\langle 01\bar{1} \rangle$ directions were rotated by 0.2-0.3° with respect to the $\langle 11\bar{2}0 \rangle$ directions. These ordered relationships were found to exist not only across domain boundaries but within TiAl lamellae. The boundaries between two neighboring TiAl lamellae were observed to be flat and parallel to both (111) TiAl and (0001) Ti₃Al.

Processing

Image furnaces with halogen lamp sources were in use for metals processing and crystal growth by floating zone unidirectional solidification (FZ-UDS) at several laboratories that I visited in Japan. Versions with either single lamps or double, opposed lamps were in use. The mirrors in the double lamp units were sections of ellipsoids of revolution which shared a common focal point at which the specimen was located. The mirrors and all interior parts were gold coated to maximize reflection. At the NRIM, Tsukuba, laboratory T. Hirano, has used FZ-UDS to grow stoichiometric Ni_3Al with improved room temperature ductility, polysynthetically twinned TiAl , a variety of transition metal disilicide single crystals and CaSi_2 single crystals. The unidirectionally solidified Ni_3Al had columnar grains. A stoichiometric composition without a ductility enhancer such as B showed greater than 50% tensile elongation parallel to the growth direction and greater than 10% elongation perpendicular to the growth direction. The floating zone system facility at NRIM was among the largest that I observed and was thoroughly instrumented for control of the solidification process.

Synthesis of high temperature structural silicide intermetallics having a 16H crystal structure have been reported by P. B. Celis and K. Ishizaki of Nagaoka University of Technology. These intermetallics have the general formula M_5Si_3 , where M is a metal such as Ti, Zr or Mn. The stacking sequence in the $\langle 001 \rangle$ direction is ABACA, where the A-planes contain two atoms of the transition metal, and the B and C planes contain both transition metal and Si atoms; the B and C plane are rotated 180°C with respect to each other. In the case of the 23-Ti-Zr composition, the Ti atoms were found to occupy the basal planes. The melting point of these compounds is about 2500 K; density is 5370 and 5998 Kg/cm^3 for $\text{Ti}_2\text{Zr}_3\text{Si}_3$ and Zr_5Si_3 , respectively. Mechanical properties of these materials are being determined.

Self-propagating high-temperature synthesis (SHS) is being used by Y. Kaieda, M. Ohtaguchi and N. Oguro of the 3rd Subgroup of the 3rd Research Group at NRIM to fabricate TiAl and NiTi . The goal of this work is to develop commercially usable wire.

Point Defects and Dislocations

Y. Shirai at Kyoto University has studied vacancies and dislocations using positron annihilation in Ti-rich, near-stoichiometric and Al-rich TiAl . Deviations from stoichiometry were found to be compensated by anti-site atoms rather than vacancies on either side of the stoichiometric composition. The positron annihilation results suggested that dislocations in Ti-rich TiAl generally have smaller Burgers vectors than those in Al-rich single phase compounds.

Ductility

Y. Umakoshi, T. Nakano and T. Yamane have studied easy (shear parallel to the lamellar boundaries) and hard (shear across the lamellae) types of deformation in Ti-rich TiAl PST crystals. When a compressive yield stress is oriented at a 45° angle to the lamellar planes, the crystals deform easily, mostly by slip on $\{111\}$ planes of the γ -phase parallel to the lamellar planes. For loadings perpendicular to the lamellar planes, slip occurs on $\{111\}$ planes that cross the lamellae. In addition, deformation twins are formed due to blocking of dislocation motion by α_2/γ boundaries. Loadings parallel to the lamellae planes are similar to those at 90° but are not as effectively blocked by lamellae of the α_2 -phase. The highest strength and best ductility were found for samples with a fine, uniform distribution of lamellae.

Umakoshi and co-workers attributed the difference in strength between samples with loading parallel to the lamellae and perpendicular to the lamellae to the activation of two slip systems in thin ordered domains of α_2 -phase Ti_3Al . Slip was observed to occur on prismatic $\{10\bar{1}0\}$ planes, when the stress was parallel to the lamellae; whereas pyramidal slip occurred, when the stress was perpendicular to the lamellae. The difference was found to be due to the much higher critically resolved shear stress (CRSS) for pyramidal slip.

Yamaguchi also found a similar dependence of stress on orientation with respect to the orientation of the lamellar planes when the stress was applied parallel or perpendicular to the lamellar planes. In addition, he reported little significant difference in yield stress between tensile and compressive deformations. This similarity between tensile and compressive yield stress on deformation direction was explained by existence of six different types of TiAl domains in equal volume fractions in the lamellar structure and the switching of the deformation mode from twinning to slip and vice versa in each TiAl domain due to the change in loading mode. Deformation twins were determined to be of the $\{111\}\langle 11\bar{2} \rangle$ -type. The largest tensile elongation, as large as 20%, observed by Yamaguchi was for a specimen with an orientation of the lamellar planes at an angle of 31° to the deformation direction.

H. Inui, M.H. Oh, A. Nakamura and M. Yamaguchi reported that fracture under tensile load at room temperature occurred in a brittle manner, with two distinct modes depending on the tensile stress direction. When the tensile axis was parallel to the lamellar boundaries, a crack propagated in a zigzag path across the lamellar boundaries. When the tensile axis was perpendicular or inclined to the lamellar boundaries, fracture occurred in a cleavage-like mode with a habit plane parallel to the lamellar boundaries.

K. Hashimoto of the 1st Subgroup of the 3rd Research Group at NRIM has found that a small amount of Mn imparts room temperature ductility to TiAl-based alloys. In an effort to improve the high temperature strength above 1000°C, he is investigating the effect of additives such as Ti, Hf and Sb on the high temperature yield strength which typically decreases rapidly above 900°C.

Transition metal silicides are being investigated by Yamaguchi at Kyoto University and Umakoshi at Osaka University. K. Ito, H. Inui, T. Hirano and M. Yamaguchi have determined the basis for catastrophic failure of CoSi_2 , which has the cubic C1 (calcium fluoride) structure, when deformed at room temperature. They found that the primary slip systems under compressive deformation was $\{001\}\langle 100 \rangle$ and that the $\{001\}\langle 110 \rangle$ and $\{111\}\langle 1\bar{1}0 \rangle$ slip systems could not be activated. Appreciable fracture strains (2%-4%) were obtained in crystals deformed with $\{001\}\langle 100 \rangle$ -type slip; whereas, $[001]$ oriented crystals and all polycrystalline samples fractured catastrophically. Plastic deformation of CoSi_2 by $\langle 001 \rangle \{100\}$ slip was suggested to be controlled by the Peierls mechanism.

Y. Umakoshi, T. Hirano (NRIM), T. Sakagami and T. Yamane have studied the plastic deformation of MoSi_2 and $(\text{Mo}_{0.97}\text{Cr}_{0.03})\text{Si}_2$. MoSi_2 crystals were extremely brittle at low temperatures but became deformable at 900°C with activation of slip of $\{110\}\langle 3\bar{3}1 \rangle$ - and/or $\{013\}\langle 3\bar{3}1 \rangle$ -type. Above a maximum in the yield stress at 1000°C, the ductility of MoSi_2 and $(\text{Mo,Cr})\text{Si}_2$ increased rapidly with increasing temperature. Above 1200°C, ordinary $\langle 100 \rangle$ and $\langle 110 \rangle$ dislocations were activated. Pure stacking faults also were found in the deformed samples, these were much more prominent in the alloy than in the pure MoSi_2 samples. The increased occurrence of stacking fault formation in $(\text{Mo,Cr})\text{Si}_2$ was interpreted as due to the destabilization of the C1_b structure of MoSi_2 with respect to the C40 structure of CrSi_2 .

Environmental Effects

Environmental studies by M. Nakamura of the 1st Subgroup of the 3rd Research Group at NRIM have shown that Cr-modified TiAl has a ductility in vacuum of greater than 4%, but in hydrogen or air its ductility is reduced to about 1%. In hydrogen and air, fracture is along cleavage planes, whereas in vacuum fracture is along grain-boundary facets. The typical cast material consists of a mixture of γ phase and α_2 phase and has a lamellar structure. The 1st Subgroup also has found that TiAl with a large amount of α_2 -phase is not affected by hydrogen.

Also in the 1st Subgroup, T. Aritomi is conducting an SEM analysis of the effect of oxygen on TiAl-alloys. Electropolish of the alloys was found to preferentially dissolve the γ phase leaving an α_2 skeleton. However, oxygen appeared to show little effect on the removal of the γ phase. M. Kasahara has found that Si removed the oxidation resistance of TiAl-based alloys and that surface damage improved the oxidation resistance at 700°C.

Twinning, Phase Transitions and Shape Memory Alloys

K. Otsuka of the Institute of Materials Science, Tsukuba University, has identified a Type II lattice invariant shear twinning for the β_1 to γ'_1 transformation in a Cu-Al-Ni alloy. Type I deformation twinning is characterized by a symmetry operation of a mirror plane which is identical in all respects with the shear plane. Type I is commonly known. Type II twinning is characterized by a second invariant plane and a symmetry operation of rotation by π about the twinning shear direction.

Superplasticity

In an investigation of the hot workability of TiAl-based alloys to improve their yield strength above 1000°C, M. Nobuki, of the 4th Subgroup of the 3rd Research Group at NRIM, has found that material with a grain size of 5 μm are superplastic. The effect of Ti, Hf, W, etc. on the microstructure are being investigated as part of this work.

Very large tensile strains at high strain rates during hot extrusion has been demonstrated for aluminum alloys containing Si_3N_4 particulates at the GIRIN by M. Mabuchi, T. Imai and K. Kubo. For a 6061 aluminum alloy containing 20 w/o of 0.2 μm Si_3N_4 particulates an elongation of 620% elongation was achieved at a strain rate of 2 s^{-1} , with an m-value of 0.45, and a temperature of 833 K. A relatively high value m-value of more than 0.3 in a high strain rate range of 10^{-1} to 100 s^{-1} , but a low value of about 0.1 in a strain rate range below 10^{-2} s^{-1} . These strain rates and elongations are somewhat greater than those previously reported for whisker reinforced aluminum alloys. The microstructure obtained after annealing the as-extruded composite at 818 K for 1800 s showed grain sizes of less than 3 μm and subgrain structure. The subgrain structure is thought to have caused dynamic recrystallization during high strain rate deformation.

Metal Matrix Composites

Wakai's group at Tohoku University has adapted a modified small punch (MSP) technique for the measurement of high temperature strength. The small punch technique was developed originally by Jan Kanada, Ames Laboratory, who collaborates with Wakai's group. This technique requires an 8 mm diameter sample with about 0.5 mm thickness. A nearly linear relationship was demonstrated between yield strength obtained by MSP and that obtained in 4-point bend measurements. The technique has been used to determine the temperature of brittle-to-ductile transitions (BDTT) and to study the effects of irradiation on mechanical strength of alloys. Alloys with 70% AlN in-situ composite showed grain boundary sliding at temperatures greater than 1600°C. The material was found to contain large, AlN-rich, second phase grains. AlN-SiC with 50% alloy showed thermal conductivity of about $10 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$ compared to a SiC-AlN powder mixture with a thermal conductivity of about $50 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$.

Corrosion Fatigue, Stress-Corrosion Cracking (SCC), and Creep

Studies of corrosion fatigue (CF) and stress corrosion cracking (SCC) of ASTM A533B steel for light water reactors (LWR) and ASTM A508 steel for pressurized water reactors (PWR) by NRIM's 5th Research Group, lead by N. Nagata, have shown that both steels had good fatigue life, but the A533B steel showed a greater dependence of fatigue rate on strain rate. Low cycle lifetime tensile tests were performed under simulated conditions in a fatigue testing machine equipped with an autoclave. Fatigue cracks were observed to initiate at corrosion pits formed by the dissolution of MnS inclusions; fatigue life decreased with the increasing density of corrosion pits. Crack initiation was concluded to be more sensitive to S content of the steel than crack propagation.

The effects of radiation damage on creep and creep rupture in high-temperature metals are being investigated by J. Nagakawa of the 2nd Research Group at NRIM for fusion reactor first wall applications. The emphasis of program is on developing prediction techniques for material strength and life under irradiation and on conducting in-situ analysis and evaluation of radiation damage. H, D, ^3He and ^4He beams are used. TiC precipitates have been observed to trap helium.

Long-term (circa 100,000 hours) creep rates for steels at high-temperature and low stresses determined by the NRIM's Environmental Performance Division, lead by C. Tanaka, have shown convergence of creep rupture strength. This result has been interpreted as indicative of an inherent creep strength controlled by the ferritic matrix.

Irradiation Effects

M. Kitajima is using real time Raman spectroscopy to follow the surface reaction processes activated by radiation. Both ion-beam and molecular beam sources are used. Disorder induced spectra changes have been observed graphite and molybdenum under ion irradiation. In the case of graphite, the peak intensity ratio between an induced peak and that of the Raman active E_{2g} mode was correlated inversely with the average distance between defects (scattering distance).

At the Institute for Materials Research at Tohoku University, H. Matsui is carrying out research to develop materials for fission and fusion reactors which maintain strength and integrity after long exposure to displacement radiation. The anomalous swelling behavior of vanadium alloys is of particular interest. He noted that yttrium alloys last up to about 50 dpa; vanadium alloys become very spongy; but a material is needed which will last up to 500 dpa. Metals with fcc structure which are proposed for first wall structure materials are prone to void swelling. For example, Ti-modified 316 stainless steel exhibits about 5% swelling after about 100 dpa. Fe, Cr and Mo which are bcc metals exhibit better swelling existence so that the large amount of swelling in vanadium which is a bcc metal was unexpected. For example, V-5% Fe exhibits swelling of greater than 100%.

Swelling is more pronounced if the atomic size of alloying metal is smaller than that of vanadium. This is believed to arise because of the dumbbell configuration of interstitials in bcc metals, so called "split interstitial." Swelling is caused by an imbalance between the interstitials and vacancies due to preferential loss of interstitials to voids and dislocations. Interstitials have a larger strain field than vacancies, and small atoms have larger strain fields than do large atoms. Thus, small atoms will be more likely to be trapped by dislocations.

However, vanadium is preferred to stainless steel because it exhibits less helium embrittlement which is a major concern in fusion reactors because about 1000 times as much helium is produced as in a fission process. Helium goes to voids in a metal and forms bubbles; it also destabilizes grain boundaries resulting in helium embrittlement. Helium embrittlement sets the upper design limit for alloys. Four different experimental methods are used to study helium embrittlement:

1. Tritium trick: V can be doped with ^3H which converts to He;
2. Doping with ^{10}B which produces He by an (n,alpha) reaction;
3. Use of other alpha-emitters, for example, ORNL used ^{69}Ni in an austenitic stainless steel;
4. Alpha-injection by a cyclotron.

However, since the alpha/dpa ratio is different for these various methods, different results are obtained with different methods resulting in different microstructures.

Surface Science

Three field ion-scanning tunneling microscopes (FI-STM) are in use in T. Sakurai's group for the study of adsorption. These systems are equipped with Demuth-type STMs. A tip-exchange mechanism has been developed which permits a tip exchange to be carried out under UHV conditions. FI-STM studies have included alkali ion adsorption of (100) and (111) surfaces of Si, C_{60} on Si(100) and (111) surfaces, sulfur and chlorine adsorption on Cu(111), and oxygen on Ag(110).

Coatings

Toyota CRDL is investigating the use of a fluidized bed technique for thermal deposition (TD) of adherent refractory hard carbide coatings on high-carbon steel. Over 10 years ago, T. Arai of Toyota CRDL developed a TD process by adapting the borax bath previously used for boridization to the application of carbide coatings. Of the carbides of V, Nb, Cr and Ti, VC was found to have the lowest wear rate.

SUPERCONDUCTORS

Melt Growth and Single Crystal Growth

A small single crystal of Y-123 has been grown by the Czechawalski method by Division I of the Superconductivity Research Laboratory (SRL) of ISTE. Division I also has grown single crystal Bi-2212 by float zone technique, requiring 20 to 30 days. Division IV has improved grain alignment in melt-growth of Y-123 by increasing the temperature gradient to growth rate ratio which resulted in an increase of the critical current to 1900 A (77 K, 1 T).

The ISTE/SRL-Nagoya Division has found that Pt-doping reduces the size of the Y_2BaCuO_5 (Y-211) precipitates in Y-123. They also have found that stimulation of MOCVD with laser wavelengths of 193 nm or 250 nm results in a-axis rather than c-axis growth, whereas longer wavelengths result in c-axis or a mixed growth mode. Best a-axis growth results were obtained with substrate temperatures near the melting point. Small Y-211 particles which resulted from Pt-doping of melts were observed to improve flux pinning and J_c , whereas large Y-211 particles were found to have no effect. The effect of small Y-211 particles may be in part to decrease the formation of large cracks. Some stacking faults were observed around Y-211 particles, but the exact role of Y-211 particles in flux pinning is not understood. When Y-123 was formed as the peritectic phase by reactions of Y-211 particles with the $\text{Y}_2\text{O}_3\text{-CuO}$ melt, some Y-211 particles were incorporated into the growing Y-123 phase. Pt is believed to act upon Y-211 particles in melt near the surface of the Y-123 either to inhibit diffusion to the Y-211 particle and growth of the Y-211 particle or by blocking surface sites on Y-211 particles. Also, Pt was been observed to inhibit the Ostwald ripening of Y-211 grains. $\text{Ba}_4\text{CuPt}_2\text{O}_9$ (the 0412 phase) also is thought to possibly played a role in the process since its stability range agrees with that for typical melts. In the 0412 phase, Cu and Pt forms chains with O in which both the Cu and Pt are octahedrally coordinated.

Rh-doping of Y-123 has been observed to behave similarly to Pt-doping with an increased of J_c and a slight lowering of T_c . Doping with Ir, Ru or Re did not give any improvement of J_c as compared with an undoped sample and slightly lower T_c . Pd reduced J_c to 40 A/cm² and reduced T_c to 82 K. The XRD spectra of Ir, Ru and Re-doped Y-123 indicated some changed from that observed for undoped, Pt and Rh samples; and the Pd samples indicated a very different structure. All of the noble metal impurities, with the exception of Pd, tend to form quadrivalent ions; Pd tends to form divalent ions. Thus, it is expected that the site occupancy and coordination of these various noble metal dopants will differ.

H. Komatsu, of the IMR at Tohoku University, has developed a very elegant high-temperature microscope for in-situ observation phase equilibria and flux growth of oxide superconductors. An optical microscope was fitted with a heating stage consisting of a image heating chamber in which the radiation of a near-infrared lamp was focused on a sample suspended at the focal point of the imaged radiation. For compositions of $\text{Bi}_2(\text{Sr,Ca})_{1+x}\text{Cu}_x\text{O}_y$, for $3 > x > 1.2$, needles of $(\text{Sr,Ca})\text{CuO}_2$ were observed to react with the residual liquid at about 878°C to form thin crystals of the 2223-phase.

Komatsu in a study of mechanisms of growth of $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$ has observed two mechanisms: (1) tiling type growth from clusters of small crystallite, and (2) spiral growth with large Burgers vectors (b on the order of $1000 \text{ \AA}$). An explanation of the mechanism by which large Burgers vector growth occurs by the overlapping of crystallites was developed in earlier work which was reported in the 1981 Journal of Crystal Growth. When nucleation occurs in the flux there is a tendency for clusters to orient into coherent structures and not to develop atom-by-atom. Tiling occurs during early stages of growth, while spiraling occurs later.

Formation of Films

The Nagoya Division of ISTECH has investigated rapid thick film painting techniques using a metal mask and a squeeze for the application of thick Y-123 on to flexible polycrystalline yttria-stabilized zirconia substrates. The films were then sintered at $1000\text{--}1050^\circ\text{C}$ for 12 min. Additions of Ag and reduction of the sintering temperature resulted in improved grain orientation and some improvement of J_c to about 10^5 A/cm^2 (0 T, 77 K); the best value reported elsewhere is about $3 \times 10^6 \text{ A/cm}^2$.

Ceramic Processing

The high- T_c Bi-2223 phase has been prepared by I. Matsubara of GIRIO by annealing Bi-2212 whiskers in a $\text{Bi}_2\text{Sr}_2\text{Ca}_4\text{Cu}_6\text{Pb}_{0.5}\text{O}_x$ powder. Single crystals of Bi-2212 were converted by the same method into Bi-2223 sheets. The axial direction of the Bi-2212 whiskers was in the a -direction; the lattice misfit were evident in the b -direction. With $\text{Bi}_2\text{Sr}_2\text{CuO}_x$ (Bi-2201) single crystals as the starting material, Bi-2223 was partially formed after annealing in the $\text{Bi}_2\text{Sr}_2\text{Ca}_4\text{Cu}_6\text{Pb}_{0.5}\text{O}_x$ powder indicating that the rate of phase conversion was slower than that for the Bi-2212 phase. This difference was believed to be due to a favorable intercalation of Ca and one square planar CuO_4 unit between the CaO_5 units without Cu-O bond cleavage to convert Bi-2212 to Bi-2223, whereas for the conversion of Bi-2201 to Bi-2223 a more energetic Cu-O (apical) bond cleavage was required. Whiskers of the Bi-2212 phase were grown from glass containing additions of Al at $860\text{--}865^\circ\text{C}$. Several solid phases were present in the Al_2O_3 -containing melt, which provided a framework for the growth of the whiskers.

Mist pyrolysis, spray-drying and sol-gel have been investigated by

M. Awano as methods for preparation of submicron sized homogeneous powders of Y-123 and Bi-Pb-Sr-Ca-Cu-O to enhance formability and critical currents. Y-123 was densified by hot-isostatic pressing at 750°C for 4 hrs. while maintaining a equiaxed grains with sizes less than 1 μm . For samples hot-isostatically pressed between 775°C and 800°C less time was required for densification, but some grain growth occurred with the formation of elongated grains. The material densified at 775°C showed 35% compressive strain in a compressive test at 750°C and a stress of 30 MPa.

An oxygen hot-isostatic press (HIP) was used by K. Ishizaki and Sawai at Nagaoka University of Technology to prepare the Y-124 and Y-247 phases with short process times. While very long times are required to prepare the Y-124 phase in 1 atm of O_2 , at 2000 atm and 1000 C a very short time is required. The HIP apparatus permitted the total pressure and the oxygen partial pressure to be varied independently so that powder mixtures of Y_2O_3 , BaCO_3 and CuO could be processed at various T, P, and $\text{P}(\text{O}_2)$ conditions.

M. Shimada and H. Takizawa at Tohoku University are attempting high-pressure growth of an infinite layer- CuO_2 structure of $(\text{Ba},\text{Sr})\text{CuO}_3$ in which BaO and SrO layers alternate indefinitely with CuO_2 planes. To date, the materials obtained have had a superconducting transition of about 40 K and have exhibit a small volume fraction of superconducting phase as determined by the Meissner effect.

Devitrification of Amorphous Precursors

K. Matusita's group at Nagaoka University of Technology was the first to report the synthesis of high temperature oxide superconductors using a glass processing method (1988). BSCCO ceramics were prepared by recrystallizing a glass melt. Since the J_c for glass ceramics is very low, about 150 A/cm^2 was obtained after annealing for about 100 h, work has been in progress to understand the source of the normal conductivity that occurs at grain boundaries. The application of a glass melt to Ag ribbon, followed by recrystallization to obtain the superconducting phase, also is being studied.

The preparation of Y-Ba-Cu-O superconductors by means of a vitreous precursor route has been investigated by the 5th Research Group at NIRIM. Vitreous precursors for high- T_c superconductors have been prepared by rapid quenching of molten drops of oxide between two metal rollers. The quenched material had an amorphous outer layer and an interior containing a fine crystalline Y_2O_3 phase. Heat treatment at 950°C yielded a material with blocky Y-123 grains and fine whiskers. The thin film yielded a zero resistivity at 87 K with a critical current of 1.3 A/cm^2 .

Thick film BSCCO samples were prepared by rapid quenching and were heat treated at 850-880°C for 6-16 hr. The films heat treated at 880°C showed

zero resistance at 60 K, with critical current density of 220 A/cm² at 4.2 K. Thick films with the composition Bi_{1.73}Pb_{0.43}Sr_{1.63}Ca_{2.03}Cu₃O_y were prepared by rapid quenching. These yielded a T_c of 104 K after annealing for 300 h and J_c of 200 A/cm² at 77 K.

Structure

The oxygen columns in oxide superconductors have been imaged for the first time in a high-resolution electron microscope (HREM) by S. Horiuchi of NIRIM who used a new high voltage electron microscope (HVEM). This HVEM has a resolving power of 1 Å at an accelerating voltage of 1.3 MV. Horiuchi established the technique by first imaging the oxygen columns in ZrO₂. To improve the imaging of oxygen columns in Y-123 a high pressure form, YBa₂Cu₃O_{7.7} was prepared. With the beam incident along the [001] and [100] directions the oxygen columns were observed as the faint contrasts between darker Cu columns. A composite of many high resolution images indicated regional variations in contrast at expected oxygen positions suggesting locally homogeneous oxygen composition over the range of several unit cells but compositional variation over larger areas.

At Toyota CRDL M. Ohkuba has modeled vacancy ordering using a Monte Carlo method. The simulated structures resembled those obtained by modeling efforts at LBL and ANL, and seen with HREM by Horiuchi at NIRIM. The complex susceptibility was measured using a pulsed induction technique.

Properties of High T_c Oxides

ISTEC/SRL-Division III has discovered strong interaction between electrons and lattice vibrations in CuO₂ planes in many Cu oxides with layered structures. A model of electronic states in oxide superconductors has been proposed based on optical spectra measurements. The division has completed the first systematic measurement of tunnel spectra of Y-124.

Low T_c Wire

A metallurgical process for the preparation of Nb₃Al multifilamentary superconductor wire for high-field magnets has been developed in the 1st Research Group at NRIM-Tsukuba. A metallurgical process for fabrication of Nb₃Al wires had not existed previously, whereas Nb₃Sn wires are routinely made by a diffusion reaction between Nb and a Cu-Sn alloy ("bronze process"). A cold-drawing process was developed in which a Al-Mg alloy core was inserted in a Nb tube and cold worked to a reduced

diameter. 121 of these cold-worked wires were inserted in a second Nb tube, and the combination cold worked to a composite wire with a reduced

diameter. The process was repeated a third time to obtain a composite wire in which the Al alloy cores had about 0.1 μm diameter. The composite wire was heat treated at 850°C to obtain a wire with an optimum T_c of 15.6 K.

2 of 2

MAGNETIC MATERIALS AND MAGNET FACILITIES

Magnetic Metals and Alloys

Formation of the ferromagnetic α -FeSi (bcc) phase from an $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$ alloy and its stabilization were studied by T. Sakurai and colleagues at the IMR using an atom-probe field ion microscopy (APFIM) and high resolution electron microscopy (HREM) to study the microstructure evolution. Previous work had reported this alloy to develop its optimum magnetic properties when annealed at 550°C for 1 hr. Sakurai and coworkers found that when the initially homogenous alloy is annealed at 550°C, Cu-rich clusters containing lesser amounts of Nb, B and Si are nucleated. Fe is excluded, resulting in fluctuations in the Fe concentration in the surrounding amorphous phase. These fluctuations are believed to nucleate formation of an α -FeSi (bcc) phase. Nb and B are excluded from this phase to the remaining amorphous phase. The α -FeSi phase contains 25% Si and is metastable. Retention of this phase even after annealing may be due to the presence of dissolved B. Growth of the ferromagnetic α -FeSi phase is limited by the surrounding amorphous Nb-B-Si regions. The Cu-rich phase grows to about 5 nm in size which is less than the domain wall width so that the phase does not affect the magnetic properties of the material.

Magnetic Fluids

Two innovative in-situ methods for the preparation of magnetic fluids have been developed by I. Nakatani of the NRIM. His general approach was to surround ultrafine magnetic particles of iron, cobalt or nickel with a amine surfactant so that the particles could be dispersed at high concentration in an organic fluid.

The first approach consisted of evaporative condensation of magnetic particles in which the particles were condensed in a thin liquid film of alkylnaphthalene containing a surfactant of polybutenylsuccinpolyamine. The deposition was carried out in a continuously rotating, horizontally oriented, cylindrical vacuum chamber containing a pool of alkylnaphthalene. The evaporation source was located at the axis of the cylinder. Rotation of the cylinder constantly fed a fresh film of liquid on to the inner wall of the cylinder. Fine magnetic particles were formed by condensation in the liquid and are immediately coated with the surfactant and are removed in the pool of liquid. Particles were characterized by electron and x-ray diffraction, and the ferromagnetic resonance of the dispersions was measured as a function of particle concentration.

In the second approach particles were in a bath of kerosene containing iron-carbonyl, $\text{Fe}(\text{CO})_5$, and an amine surfactant. Iron nitride was formed by heating the stirred solution to 185°C in the presence of ammonia gas, NH_3 . The particles were shown to be $\epsilon\text{-Fe}_3\text{N}$ by electron diffraction. Particle size was uniform and could be closely controlled by regulating the $\text{Fe}(\text{CO})_5$ concentration. Magnetization curves exhibited no hysteresis and high saturation magnetic flux density which ranged up to 2330 Gauss.

Magnetic Field Research

The National Research Institute for Materials has developed a versatile facility under the leadership of H. Aoki for the high-resolution measurement of materials phenomena in magnetic fields. The magnetic instruments include hybrid magnets, long pulse magnets, large bore magnets and high resolution magnetic systems. One high resolution system can produce fields up to 16 T with a homogeneity of $10^{-4}/10\text{mmdsv}$ and is equipped with a top-loading dilution refrigerator. This system was used for studies of quantum oscillations (de Haas-van Alfen and Shubnikov-van Alfen effects) and for ordinary transport and magnetic measurements. Broad band nmr and other magnetic resonance experiments are carried out on a second high resolution system which can produce a field of 15.5 T with a homogeneity of $10^{-5}/10\text{ mmdsv}$ and a stability of $10^{-5}/\text{hr}$ in a 50 mm diameter sample space. NMR probes from 1.5 K to 800 K and an eprobe have been developed for this system. Magnetic resonance studies of ^3He in a 15.5 T field were carried out recently.

A third instrument is a 500 MHz high resolution solid state nmr system with a room temperature bore of 89 mm. The magic angle spinning frequency can be increased up to 10 kHz for this system and the temperature of the sample space can be varied from 100°C to -100°C . Pulsed systems include a 80 T magnet with a rise time of 10 ms, a hybrid magnet (20 T at 40 mm diameter; 15.3 T at 314 mm diameter) which is used for engineering purposes, and a hybrid magnet (40 T at 30 mm diameter). A large bore system permits the installation of several devices inside such as a pressure cell. Materials studied currently include highly correlated electronic materials, high- T_c oxide superconductors, heavy Fermion materials and organic superconductors such as ET_2KHgSCN . Flux creep in BSCCO and YBCO has been studied at 30 mK as a function of orientation.

High-Field Static and Pulsed Systems

The 1st Research Group of NRIM is constructing a new high-field research center which will include a 40 T hybrid magnet, a 20 T class superconducting magnet with large bore, a 80 T class long-pulse magnet, and several kinds of small superconducting magnets. The 40 T hybrid magnet will consist of a superconducting magnet inducing a central magnetic field of 15 T for a room temperature clear bore of 400 mm, in which a polyhelix-type water-cooled magnet is energized. Two kinds of resistive magnets will be used: a 30 mm clear bore for 40 T and a 50 mm clear bore for 35 T.

A capacitor bank consisting of 160 units of oil-immersed 128 mF capacitors has been developed for the 80 T pulsed magnet. The capacitor bank has a power rating of 16 MJ at 5 kV; maximum current is 70 kA and the ordinary current level is 35 kA. Difficulty was encountered in using Cu-Nb alloy wire for the coil since the need for very high strength requires heavily cold-worked Cu-Nb wire, which is difficult to fabricate. Recently, a process was developed for fabricating Cu-Ag alloy wires tensile strengths in excess of 1000 MPa after a 99.5% reduction by cold drawing and annealing at 450 C to precipitate the solute elements.

The IMR operates a high-field laboratory for superconductivity research. Two high field, hybrid systems with superconducting outer coils and resistive inner coils provide fields of 23 and 31 T. In addition, the laboratory operates four superconducting magnets and three resistive magnets. Recent research activities have included measurement of fractional quantum Hall effects of semiconductors, the Fermi surface of organic superconductors, the high-field spectroscopy of magnetic materials, field-induced magnetic transitions in materials, the chemical effects of high magnetic fields, and properties of materials for fusion reactor applications.

APPENDIX

Abstract

FUNDAMENTAL MATERIAL SCIENCE AT THE U.S. DEPARTMENT OF ENERGY:

THE PROGRAM OF THE DIVISION OF MATERIALS SCIENCES

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DOE's Division of Materials Sciences (DMS) supports theoretical and experimental research on fundamental properties and phenomena in wide variety of materials. The mission of DMS is to provide the underlying scientific support for the areas of energy technology in which the DOE has programs. The technology programs include electrical energy storage and distribution, heat engines, energy generation from fossil fuels, nuclear fission and fusion, and solar energy. In 1991, DMS-supported research was carried out 448 projects, at 15 DOE national laboratories, 88 universities, 13 companies, and 2 private research institutes. DMS also supports a number of national user centers at the DOE national laboratories. These user centers include 4 microanalytical and electron microscopy facilities, the National Synchrotron Light Source, the Stanford Synchrotron Radiation Laboratory, the Intense Pulsed Neutron Source, the Los Alamos Neutron Scattering Center, the High Flux Beam Reactor and the High Flux Isotope Reactor. An overview of the DMS program and examples of recent accomplishments will be given in this talk.

講演会のご案内

U. S. Department of Energy のDragoo博士
が来阪されます。この機会に、下記講演会を
開催致しますので多数の皆様の御来聴を歓迎
致します。

記

Fundamental Material Science at the
U. S. Department of Energy: The Program of
the Division of Materials Sciences

Dr. Alan L. Dragoo

Division of Materials Sciences, Office
of Basic Energy Sciences Washington, DC

日時：平成4年7月31日 午後2時～3時

場所：材料系3階会議室

産業科学研究所

宮本欽生

内線3461

工学部材料物性工学科

馬越佑吉

内線4410

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