



Institute for Materials Research, Tohoku University



KINKEN Research Highlights 2012



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KINKEN Research Highlights 2012 Contents

Research Highlights

1. Infrastructural Materials

Microstructure Design of Structural Metallic Materials Division	3
Chemical Physics of Non-Crystalline Materials Division	5
Bio-Materials Science Division	7
Multi-Functional Materials Science Division	9
Deformation Processing Division1	1
Advanced Materials Development and Integration of	
Novel Structured Metallic and Inorganic Materials 1	3

2. Energy-related Materials

Crystal Physics Division	. 15
Surface and Interface Research Division	. 17
Metal Physics with Quantum Beam Spectroscopy Division	. 19
Materials Design by Computer Simulation Division	. 21
Irradiation Research on Nuclear Materials Division	. 23
Nuclear Materials Science Division	. 25
Nuclear Materials Engineering Division	. 27
Non-Equilibrium Materials Division	. 29
Crystal Chemistry Division	. 31
Hydrogen Functional Materials Division	. 33
Advanced Analysis of Materials Division	. 35
NEDO Laboratory for Metallic Glass Research Collaboration and Promotion	. 37

3. Electronic Materials

Theory of Solid State Physics Division	39
Magnetism Division	41
Low Temperature Condensed State Physics Division	43
Physics of Crystal Defects Division	45
Physics of Electronic Materials Division	47
Magnetic Materials Division	49
Radiochemistry of Metals Division	51
Analytical Science Division	53
Materials Processing and Characterization Division	55
Advanced Crystal Engineering Laboratory	57

Research Centers

	Center for Computational Materials Science	. 67
	International Collaboration Center (ICC-IMR)	. 69
	Integrated Materials Research Center for a Low-Carbon Society (LC-IMR)	. 71
	Center of Neutron Science for Advanced Materials	. 73
	Laboratory of Low Temperature Materials Science	. 75
	Laboratory of alpha-Ray Emitters	. 77
	Analytical Research Core for Advanced Materials	. 79
A	Author Index	. 82
k	Keyword Index	. 83



Preface

Dear colleagues,

Around one and half years have passed since the Great East Japan Earthquake happened on 11 March 2011. The Institute for Materials Research, Tohoku University (KINKEN) has already recovered and the people at KINKEN are working under ordinary conditions. We would like to express our sincere thanks to you for helping us to come back to ordinary working conditions after the horrible disaster.

We are pleased to bring out *KINKEN Research Highlights 2012*, which is the sixth annual report with a collection of research output during the past year from the Institute for Materials Research (IMR), Tohoku University. KINKEN (short Japanese name of IMR, which is familiar to the materials community, particularly in Japan) determined in 2007 to launch this report annually so that our colleagues around the world can recognize our research activities. In this report, the research activities of individual research laboratories and research centers, as well as joint projects with other academic institutions, are provided, especially for the following three key research fields: (1) Infrastructural Materials, (2) Energy-related Materials, and (3) Electronic Materials.

The Institute was established at Tohoku Imperial University in 1916 by Professor Kotaro Honda as a steel research organization known officially as the 2nd Division of the Provisional Institute of Physical and Chemical Research. In 1987, the Institute was reorganized into its present form as a national collaborative research institute attached to Tohoku University. The name of the institute was consequently changed to the Institute for Materials Research (IMR). Since its establishment, IMR has become known for its excellence in both basic and applied research on metals and a wide range of new materials. A variety of functional materials have been studied and developed at the Institute, including the KS magnet steel, new KS magnet steel, SiC fiber, compound alloys, metallic glasses, and others.



* Dimomi

Director

IMR has greatly contributed to the advancement of materials science. As one example, our study of magnetism resulted in the invention of the strongest permanent magnet, the KS magnet, which dramatically improves the performance of electrical machines. IMR has been paying great attention to basic research that opens up the most advanced areas of applications. More recently, IMR has created a wide array of new materials, including high-performance, high-quality, and multifunctional materials such as amorphous alloys; bulk metallic glasses; intermetallic compounds; quasicrystals; oxides; ceramics; nanostructured metals; Si; Ge; III-V, II-VI, and oxide semiconductors; optical and electronic materials; solar cell crystals; biomaterials; organic materials; hydrogen storage alloys; and shaped crystals.

Now, we are facing the serious issues of the deteriorating global environment and the depletion of worldwide natural resources and energy sources. IMR will further promote materials research to address the problems associated with the global environment and energy resources, aiming at sustaining human development and ensuring a high standard of living for all people. In this way, we will offer a brighter future for the next generation.

We earnestly hope that *KINKEN Research Highlights* will help you recognize and support our research activities and will serve as a medium to promote worldwide collaborations in materials research with our institute. We sincerely ask for your continuing support and welcome any suggestions.

Sincerely yours

Strengthening of Low-Alloy Hot-Forging Steel with Nanosized Precipitation

In a recent national research project on high-performance steels, the strengthening of medium-carbon lowalloy steel for automobile parts was extensively studied. The key technology for strengthening is the use of fine dispersions of alloy carbides several nanometers in size. Here, we describe briefly the microstructure-property relationships from our research conducted in this project.

To reduce the fuel consumption by automobiles, medium carbon steels for forging parts, such as shafts and connecting rods, must be further strengthened. When carbide-forming elements such as Ti, Nb, and V, are alloyed with carbon steels, a fine dispersion of alloy carbides and large precipitation hardening can be achieved. Continuous cooling after austenitization has been frequently reported to produce repeated nucleation of alloy carbides at ferrite/austenite interphase boundaries during the growth of ferrite or pearlite, leading to formation of precipitates in regularly spaced rows. This peculiar precipitation phenomenon is known as interphase precipitation [1].

In medium- and high-carbon steels containing vanadium, interphase precipitation of VC is used for strengthening. However, there are few studies on interphase precipitation in medium- and highcarbon steels, and the precipitates formed through interphase precipitation in those steels have not been characterized quantitatively. In this study [2],



Fig. 1 Effects of V content on the maximum hardness of the specimens isothermally transformed at various temperatures.



Fig. 2 Dark-field TEM of VC dispersion formed via interphase precipitation in low alloy 0.4% C steels containing 0.5% V (transformed at 923 K).

the variations in hardness and microstructure, including the size and number density of VC with V addition, have been investigated.

Fig. 1 shows the variations in peak hardness at various temperatures as a function of V content. Peak hardness increases linearly with V content at all three temperatures, while the slope at 973 K is smaller than those at 873 K and 923 K. As the temperatureatwhichtheferrite/pearlitetransformation occurs decreases, greater hardening is observed. Fig. 2 is a dark-field TEM micrograph of the interphase precipitation of VC in the 0.4% C alloy containing 0.5% V. It is clearly seen that fine VC particles (imaged as bright particles) is aligned in rows parallel to the interphase boundary. Such VC precipitation was also observed in low-alloy eutectoid steel containing vanadium.

Precipitation/dispersion strengthening can be classified into the following two categories: a cutting mechanism and a by-pass (Orowan) mechanism. A larger particle size leads to higher strength in the former case and vice-versa in the latter case. The



Fig. 3 Comparison of the increase in strength by precipitates between calculation based on the Ashby–Orowan model and experiments: (a) original Ashby–Orowan model where $\lambda = x$ and (b) modified Ashby–Orowan model assuming λ to be 3x.

increase in yield strength in low-carbon ferritic steel containing fine alloy carbide particles is well explained by the Orowan-type dispersion hardening model modified by Ashby [3].

$$\Delta \tau_{\rm calc} = 0.84 \left(\frac{1.2 {\rm Gb}}{2 \pi {\rm L}}\right) \ln \left(\frac{\lambda}{2 {\rm b}}\right)$$

Here, L is the average spacing between particles in the slip plane, G is the shear modulus, b is the magnitude of Burgers vector, and λ is the outer cut-off distance.

Fig. 3 shows the relationship between the estimated and observed values. The original Ashby– Orowan model underestimates the strength significantly, as shown in Fig. 3(a). After some modification of the cut-off distance, a more reasonable agreement between observation and estimation was obtained (Fig. 3(b)). These findings were used in the first systematic, physically based model proposed to predict the microstructure and yield strength of vanadium-microalloyed medium-carbon steels [4].

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Structural Analysis of Amorphous Zr50Ni50

The structure of Zr50Ni50 amorphous alloy was analyzed by anomalous X-ray scattering (AXS) coupled with reverse Monte-Carlo (RMC) simulation. Topological features in the nearest-neighbor region suggest that the strong chemical interaction between Ni and Zr pairs breaks the icosahedral-like local ordering units commonly realized in the dense random packing of hard sphere (DRPHS) model [1].

Zr-based amorphous alloys have attracted many researchers' interests because of their characteristic physico-chemical properties [2-3]. Among them, Zr-Cu and Zr-Ni amorphous alloys have been extensively studied to elucidate the relationship between thermal stability and atomic scale structure. In the case of Zr-Ni amorphous alloy, the short distance of the Zr-Ni pair in the nearest-neighbor region was demonstrated to be a consequence of a strong chemical interaction, and this suggests crystal-like chemical short-range ordering (CSRO) around Ni [4]. Nevertheless, the available structural information is insufficient to examine and clarify the possible CSRO around Ni. This prompted us to perform AXS-RMC analysis of the Zr-Ni amorphous alloy sample. AXS-RMC analysis is suggested to be one of the most powerful methods for elucidating stereoscopic atomic configurations.

The detailed procedure of AXS-RMC analysis has been discussed previously [5,6]. For the convenience of discussion, only the important points are given below. AXS measurements at the Ni K absorption edge and the Zr K absorption edge were carried out at beam line stations 7C and NW10A of the Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Japan. Pairs of incident energies corresponding to 25 eV and 300 eV below each of the Ni and Zr K absorption edges were employed in the present AXS measurements. The RMC modeling started with an initial model of 2,000 atoms (Zr: 1,000 and Ni: 1,000) with a body-centered cubic (BCC) arrangement in a cubic hyper-cell (density = 7.36 Mg/m³).

Fig. 1 shows the ordinary RDF measured at E = 17.699 keV (Zr Kedge-300 eV) and the environmental RDFs around Ni and Zr obtained by AXS measurements. The vertical dashed lines indicate the distances for the Ni–Ni, Ni–Zr, and Zr–Zr pairs estimated from Goldschmidt radii. The ordinary RDF suggests three kinds of correlations in the 0.2–0.4 nm range. The hump at around 0.27 nm is a harmony of the Ni–Ni and Zr–Ni pairs, and the remaining peak at 0.32 nm corresponds to the Zr–Zr pair. On

the other hand, the environmental RDF around Ni showed only the harmony of the Ni–Ni and Zr–Ni pairs; the Zr–Zr correlation in the ordinary RDF was not observed here. A similar discussion is possible for the case of AXS analysis for Zr, where the structural information on the Zr–Ni and Zr–Zr pairs is included. It should be noted that the first-neighbor Zr–Ni correlation in the ordinary RDF is obviously shorter than that for the Zr–Zr correlation. This feature could be considered as an indication of the strong chemical interaction between Zr and Ni.



Fig. 1 Ordinary and environmental RDFs for Zr50Ni50 amorphous alloy. Vertical dashed lines indicate atomic distances estimated from the Goldschmidt radii.

The AXS-RMC analysis reproduces three independent interference functions $Q\Delta i_{Ni}(Q)$, $Q\Delta i_{Zr}(Q)$, and Qi(Q), and we can discuss the three $g_{ij}(r)$ functions for Zr50Ni50 amorphous alloy, as shown in Fig. 2. Nevertheless, it should be noted that the partial structure factors and corresponding $g_{ij}(r)$ functions estimated from AXS-RMC analysis are necessary conditions at best, not sufficient conditions. The maximum peak positions for Ni–Ni and Zr–Zr like-atom pairs indicate almost equal distance, respectively, in comparison with those estimated by Goldschmidt radii. On the other hand, the distance of the unlike-atom Ni–Zr pair is shorter than the estimated value. This feature again suggests the strong bonding between the unlike atomic pair. The calculated coordination numbers in the nearest-neighbor region indicate no strong preference for the correlation of unlike-atom pairs, as suggested in the previous report.



Fig. 2 Three partial *g*_{ij}(*r*) functions of Zr₅₀Ni₅₀ amorphous alloy.

Fig. 3 shows the preferred Voronoi index around Ni found in Zr₅₀Ni₅₀ amorphous alloy. The ideal icosahedron with a Voronoi index (0 0 12 0 0) was found as one of the typical environments around Ni, with a 4.1 % rate of occurrence. This fraction is much larger than that around Zr (0.3 %). This result is readily explained by considering the atomic size ratio R^* : the value of R^* for Ni was much closer to that for an ideal icosahedron ($R^* = 0.90$) than that of Zr. It may be worthwhile to note that, in Zr–Ni alloys, the fraction of icosahedral structure around Ni is much smaller than that around Cu, although R^*



Fig. 3 Preferred Voronoi indices around Ni and Cu found in amorphous alloys. Filled and hatched bars correspond to those for Zr50Cu50 [5] and Zr50Ni50, respectively.

values for Cu and Ni show no significant difference [5]. This suggests that the strong chemical interaction between Zr and Ni breaks the icosahedral-like local ordering structure common in the DRPHS model.

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Characteristics of Biomedical β-type Titanium Alloy Subjected to High-Pressure Torsion

 β -type titanium alloy, T–29Nb–13Ta–4.6Zr (TNTZ), developed for use in biomedical applications, exhibits nontoxicity and a low Young's modulus similar to that of bone. Severe plastic deformation, such as high-pressure torsion (HPT), is effective for grain refinement and dislocation strengthening. In this study, the effect of HPT on the microstructure and hardness of TNTZ was systematically investigated to improve its mechanical strength while maintaining the low Young's modulus. In the cross sections of TNTZ subjected to HPT, a heterogeneous microstructure consisting of a matrix and an unetched band not corroded by an etching solution were observed. Both the matrix and the unetched band comprise a single β phase. Furthermore, submicron-sized grains or subgrains were formed by HPT, and grain misorientation increased with the number of HPT rotations. The hardness distribution in the cross section of TNTZ subjected to HPT was also heterogeneous; the hardness was higher in the matrix than in the unetched band when the number of HPT rotations was small. However, with increasing number of HPT rotations, the hardness of the unetched band became comparable to that of the matrix.

Stress transfer between a metallic implant and bone is non-homogeneous when the Young's modulus of the metallic implant and that of the bone are different. The Young's moduli of the metals and alloys used for fabricating metallic implants are much higher than that of bone; therefore, stress stimulation to the bone is reduced (stress shielding effect), with the result of inducing bone atrophy and then loosening of the metallic implant and refracturing of the bone. Thus, to mitigate the stress shielding effect, metals and alloys with Young's moduli equal to that of bone (10-30 GPa) are believed to be ideal for fabricating metallic implants [1]. Consequently, extensive efforts have been made to develop β -type titanium alloys with Young's moduli nearly equal to that of bone. One such alloy, Ti-29Nb-13Ta-4.6Zr (TNTZ), has been developed by the authors [2]. This alloy has a low Young's modulus of around 60 GPa under a solutionized condition. However, the mechanical strength of this alloy under the solutionized condition is less than that of the conventional titanium alloy, Ti-6AI-4V ELI, used for fabricating metallic implants. Thus, various thermomechanical treatments have been examined to improve the mechanical strength of TNTZ [3]. These treatments improve the mechanical strength, but they also increase the Young's modulus because a large amount of precipitates is formed. Therefore, a method that affords TNTZ with both low Young's modulus and high mechanical strength is required.

Grain refinement is generally an effective method for strengthening metals and alloys. As a method for obtaining submicron-sized grains, severe plastic deformation has attracted considerable attention. In comparison with other strengthening methods, grain refinement is expected to achieve high mechanical strength while maintaining a low Young's modulus for TNTZ because it retains the β phase, which ensures the desired low Young's

modulus. Therefore, by employing high-pressure torsion (HPT) as a representative severe plastic deformation technique, we recently attempted to improve the mechanical strength of TNTZ while keeping its Young's modulus low [4, 5].

A hot-forged bar of TNTZ was used in this study. The bar was subjected to solution treatment, cold rolling, and high-pressure torsion under an applied pressure of around 1.25 GPa with a rotation speed of 0.2 rpm for 1, 5, 10, or 20 rotations (*N*) at room temperature. The microstructures were evaluated by optical microscopy, transmission electron microscopy (TEM), and X-ray diffraction (XRD). The hardness was measured by subjecting the specimens to the Vickers hardness test.

Fig. 1 shows optical micrographs of the TNTZ cross section subjected to HPT at N = 10, as a representative result. The white band (unetched band), which was not corroded by the etching solution, is observed horizontally in the middle of this TNTZ cross section. The unetched band is expected to have higher corrosion resistance than





Fig. 1 Optical micrographs of cross section of TNTZ subjected to HPT at N = 10.



Fig. 2 Results of TEM observation at a plan view from the center of the thickness direction of TNTZ subjected to (a) cold rolling and (b) subsequent HPT at N = 5.

the other regions (matrix). Such unetched bands were observed in the other TNTZ cross sections subjected to HPT under all specified rotations, but they did not form after cold rolling. Furthermore, the thickness of the unetched band increased with the number of rotations and the center-to-edge distance. The equivalent strain increased with the number of rotations and the radius of the specimen. Therefore, this result indicates that the unetched band was formed in the region where a large strain was imposed.

The XRD profiles of the TNTZ surfaces subjected to cold rolling and subsequent HPT at each rotation showed only the β phase for every TNTZ specimen; the matrix in TNTZ subjected to HPT for any number of rotations is probably composed of a single β phase.

Fig. 2 shows the TEM results obtained from a plan view from the center of the thickness direction TNTZ subjected to cold rolling and subsequent HPT at N = 5. These regions correspond to the unetched bands observed in the TNTZ cross sections subjected to HPT. In the selected area electron diffraction patterns, spots derived from the β phase are observed in TNTZ subjected to cold rolling, whereas Debye rings appear for TNTZ subjected to HPT at N = 5. This result indicates that the unetched band comprises a single β phase as well as the matrix. Furthermore, small grains or subgrains are formed by HPT, and grain misorientation increases with the number of HPT rotations. In other words, the number of high-angle grain or subgrain boundaries increases with strain.

Fig. 3 shows the hardness distributions in cross sections of TNTZ subjected to HPT at N = 1 and 20. Overall, the hardness values tend to increase with the number of rotations. Furthermore, the hardness



subjected to HPT at N = (a) 1 and (b) 20.

values increase gradually with the center-to-edge distance. These results indicate that the hardness increases with the equivalent strain. However, the hardness at the center of the TNTZ cross section subjected to HPT at N = 1 is lower than that near its surface, whereas the hardness of the TNTZ specimen subjected to HPT at N = 20 is almost uniform throughout the thickness direction. Unetched bands were formed by HPT at the middle of the cross sections of every TNTZ. Therefore, the hardness of the unetched band is found to be less than that of the matrix in TNTZ subjected to HPT at N = 1 but comparable to that of the matrix in TNTZ subjected to HPT at N = 20. The misorientation of grains or subgrains in the unetched band increased with the number of rotations, as shown in Fig. 2. Thus, it is considered that the hardness increases with the number of high-angle grain or subgrain boundaries.

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Transparent Lutetium-based Oxides Prepared by Spark Plasma Sintering

Transparent polycrystalline ceramics are promising optical materials exhibiting excellent properties that surpass single crystals. Spark plasma sintering is a versatile technique to obtain fully dense ceramics with fine grains and high transparency because of its fast densification. We demonstrated the preparations of transparent, practical, and novel Lu-based oxides by spark plasma sintering.

Rapid progress in the development of optical devices, such as lasers and scintillators, requires novel materials and processing techniques. Optical materials are commonly used in a single crystal form grown from melt. Therefore, a high melting point of a potential compound often prevents a new optical material design.

Lutetium (Lu)-based oxides, Lu₂O₃ and Lu₃Al₅O₁₂ (LuAG), have recently attracted much attention for their potential applications in lasers, scintillators, and phosphors because of lutetium's small ionic radius and high atomic number (Z = 71) among rare earth elements. Conversely, Lu-based complex oxides, such as Lu₂Ti₂O₇ and Lu₃NbO₇, have rarely been studied in either single crystal or polycrystalline form, due to their high melting points (over 2300 K).

Transparent polycrystalline ceramics are an alternative to single crystals because of their short production time, feasibility to produce large and complicated shapes, and high-concentration, uniform doping of active ions. The main issue in conventional sintering techniques is the requirement of homemade nanopowders. Moveover, the high temperature and prolonged time causes grain coarsening, which results in low transmittance and low mechanical properties.

Spark plasma sintering (SPS) is a versatile technique to prepare transparent polycrystalline ceramics because of its fast densification by the combination of pulsed current and uniaxial pressure (Fig. 1a). A short holding time (several minutes) and a low sintering temperature prevent grain coarsening and favor the fabrication of fine-grained ceramics with high transparencies.

Lutetium sesquioxide: Lu2O3

Lu₂O₃ exhibits high thermal conductivity among rare-earth sesquioxides, which makes it a promising optical medium for high power lasers. We proposed a two-step pressure sintering combined with a low heating rate to prepare transparent Lu₂O₃ ceramics (Fig. 1b) [1–3]. The preload pressure affected the intermediate relative density, and the transmittance in the visible range was more sensitive to preload pressure than that in the infrared range. A high heating rate resulted in a significant increase in density but a large grain size and porosity, which degraded transparency. The combination of a low heating rate and the two-step pressure profile resulted in a high transparency by inhibiting defect formation and eliminating pores. High transmittances





of 60% at 550 nm and 79% at 2000 nm were obtained under a preload pressure of 30 MPa at a heating rate of 0.17 K s⁻¹ (Fig. 1c). Transparent Y₂O₃ ceramics can also be prepared by SPS using a moderate temperature and pressure profile [4].

Lutetium aluminum garnet: Lu3Al5O12

Lutetium aluminum garnet (Lu3Al5O12, LuAG) is a promising host medium for scintillation materials owing to its high density (6.7 Mg m⁻³) and high effective atomic number (Zeff = 63). LuAG can be an efficient and fast-response scintillator when doped with rare-earth ions such as Ce³⁺ and Pr³⁺. Singlephase LuAG bodies with high densities (>99.5%) were obtained at sintering temperatures of 1573-1923 K. The average grain size of the LuAG bodies was 0.18-0.52 µm at 1573-1773 K and the optimal sintering temperature was 1773 K, which showed a transmittance of 77.8% at 2000 nm after annealing at 1423 K in air for 43.2 ks (Fig. 2a). Grain growth became significant at 1823 K and pores were observed at the triple junctions of the grain boundaries at high sintering temperatures, which decreased transparency [5].

Lutetium fluorite-related oxides: Lu2Ti2O7, Lu2Hf2O7, and Lu3NbO7

Lutetium titanate (Lu2Ti2O7) has a pyrochlore structure, consisting of two interpenetrating networks of corner-sharing Ti₂O₆ octahedra and Lu₂O chains, which provides unique properties. Therefore, transparent Lu2Ti2O7 is an interesting multifunctional material that combines optical and other properties, such as ion conduction, dielectric behavior, catalytic activity, and radiation resistance. Single-phase pyrochlore Lu2Ti2O7 ceramics were prepared at sintering temperatures above 1273 Κ. А homogeneous microstructure was observed at 1573-1723 K, and grain coarsening occurred at 1823 K. The transmittance showed the highest values, 57% and 74% at wavelengths of 550 and 2000 nm, at a sintering temperature of 1723 K, which might be related to the homogeneous microstructure (Fig. 2b) [6,7]. The effect of calcination of the starting powder was also investigated [8].

Lutetium niobate (Lu₃NbO₇) has a cubic defectfluorite structure, where Lu and Nb cations randomly occupy the 4*a* site, and 1/8 of the 8*c* sites for the O anion are statistically defective. Such disordering of

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cations and O defects make Lu₃NbO₇ an interesting multifunctional material. We demonstrated the preparation of transparent Lu₃NbO₇ ceramics for the first time. The transparent Lu₃NbO₇ body had a uniform microstructure with an average grain size of 0.77 µm. The transmittance at 550 nm reached 68% (Fig. 2c) [9].

Lu₂Hf₂O₇ is a promising scintillation material, as it has the highest density (9.95 Mg m⁻³) and high effective atomic number ($Z_{eff} = 68.9$) among rareearth hafnates; however only the powder synthesis has been reported because of its high melting point (2700 K). A transparent Lu₂Hf₂O₇ body was prepared by reactive SPS using Lu₂O₃ and HfO₂ powders. The transmittance reached 78% at 2000 nm after annealing at 1123 K for 21.6 ks [10].

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Origin of Metastability and Strain-induced Martensitic Transformation in Biomedical-grade Co–Cr–Mo Alloys with Negative Stacking Fault Energy

Biomedical-grade Co–Cr–Mo alloys are used as artificial hip or knee joints, which need significantly high wear resistance as well as good biocompatibility and mechanical properties. The phase stability of the alloys is affected by a small amount of nitrogen doping. The metastable γ -fcc phase exhibits negative stacking fault energy at room temperature. We have revealed the mechanism of meta-stability for the γ phase, which is thermodynamically stable at temperatures higher than approximately 1223 K. The strain-induced martensitic transformation has been investigated to elucidate the plastic deformation of Co–Cr–Mo alloys at room temperature.

The Co–29Cr–6Mo (CCM) alloy has two phases: a γ phase (face-centered cubic (FCC) structure) and a ε phase (hexagonal close packing (HCP) structure), which are stable at high and low temperatures, respectively. Recent research indicates that a small amount of N addition (0.1–0.16 mass%) to CCM alloy leads to the Co–Cr–Mo–N (CCMN) alloy, and full γ phase microstructure is obtained after even a moderate rate cooling from high temperature. Nevertheless, the γ phase in CCMN alloy is still metastable even at room temperature.

In our study [1], the distribution of the N atoms with respect to those of the other three elements in the alloy was observed using a 3D atom probe, as shown in Fig. 1 a, for Cr and N atoms. The N atoms (red circles) were randomly distributed about the Co and Mo, indicating that there was no obvious affinity between the N atoms and the Co or Mo atoms. However, each N atom was surrounded by Cr atoms, implying that the N atoms selectively existed in the vicinity of the Cr atoms. The density distributions of the Cr and Mo atoms are shown as functions of the distance from a N atom in Fig. 1 b. The normalized Cr atom density was markedly higher than the Mo atom density in the vicinity of the N atoms, implying that the N atoms were closer to the Cr atoms. Thus, it is apparent that the Cr atoms interact more strongly with the N atoms than do the Mo and Co atoms, which form an inert matrix in this alloy. The atomic radius of N (0.80 Å) is slightly larger than one-half of the atomic radii of Co, Cr, and Mo (1.26, 1.27, and 1.40 Å, respectively). The N dissolved in the CCMN alloy is speculated to occupy the octahedral interstitial sites of the matrix. Since an additional driving force is considered necessary to destroy or alter the existing Cr–N cluster during the $\gamma \rightarrow \varepsilon$ phase transformation, the γ phase is indirectly stabilized. In other words, the formation of Cr-N clusters increases the energy barrier for the $\gamma \rightarrow \epsilon$ phase transition, although this transition remains a G-decreasing process.

On the basis of the abovementioned results, we propose a schematic model of the positioning of the elements in the CCMN alloy (Fig. 1 c). The Cr and Mo atoms are thought to be randomly distributed in



Fig. 1 (a) 3-D atom probe tomography for Cr–N. (b) Atomic density of Cr and Mo atoms as a function of distance from the N atom; the inset graph is a schematic model of the positioning of N atoms in matrix, in which N atoms selectively occupy the octahedral interstitial sites where at least one Cr atom is present in the vicinity. (c) Schematic representation of γ-phase stabilization by N addition in CCMN alloy.

the Co matrix, while the N atoms selectively occupy the octahedral interstitial sites where at least one Cr atom is present in the vicinity. In CCMN alloy, N addition accelerates the $\gamma \rightarrow \varepsilon$ phase transition by making *G* of the ε phase higher than that of the γ phase, but it also increases the energy barrier for the $\gamma \rightarrow \epsilon$ phase transition by the formation of Cr–N clusters. Therefore, the stability of the γ phase is controlled by these two opposite and competitive processes, and the energy barrier resulting from the Cr–N cluster formation appears to have a greater effect on the phase transition since the γ phase is effectively stabilized by N addition in CCMN alloy.

Biomedical Co–Cr–Mo (CCM) alloys have been commonly used for artificial hip and knee joint prostheses, but the need to improve their biomedical inertness and wear resistance has become widely recognized. The mechanical behaviors of CCM alloys are dominated by strain-induced martensitic transformation (SIMT), which causes crack initiation during plastic deformation but enhances the wear resistance dramatically in practical use. To develop more reliable CCM alloys, it is essential to clarify the factors affecting the occurrence of SIMT. In the present study, we investigated the effect of annealing twin boundaries (ATBs) on SIMT behavior.

We analyzed in detail the substructures near a parallel pair of ATBs after deformation under a stress that was preferential towards a slip parallel to the ATBs. Preferential formation of the ε phase at the ATBs was found by both SEM-EBSD analysis and TEM observation. A phase-field simulation was conducted by utilizing our original code developed for studying Suzuki segregation [2]. HRTEM images indicated that the thickening of the ε phase does not proceed irregularly, leaving a high-density of stacking faults. In addition, the thickness of the $\boldsymbol{\epsilon}$ phase was found to be different even at ATBs on both sides of the twin. This difference was attributed to the internal stress due to strain incompatibility at the ATBs on the basis of a residual stress analysis by the EBSD-Wilkinson method. Fig. 2 shows the result of the EBSD-Wilkinson analysis. Fig. 2 a, b, c, and e are an image quality (IQ) map, kernel average misorientation (KAM) map, phase map, and inverse pole figure (IPF) map. SIMTed ε phase is clearly observed on the upper ATB. IQ and KAM are measures of plastic strain, and their maps indicate that plastic strain is relatively high in the region immediately above the SIMTed ε-phase. Fig. 2 e shows the distribution of internal shear stress for Shockley partial dislocation slips. The thickest ϵ -phase plate ($d_t \sim 1.5 \mu m$) is formed in the region where both the external applied stress and internal stress promote the SIMT, and thinner ε plates ($d_t \sim$



Fig. 2. SEM-EBSD micrographs of the twin-containing Co–Cr–Mo alloy. (a) Image quality (IQ) map, (b) kernel average misorientation (KAM) map, (c) phase map, (d) inverse pole figure (IPF) map, and (e) shear residual stress for (1-1-1)[-11-2] M leading partial slip.

0.5 µm) were formed in the region where the external applied stress promotes the SIMT but the internal stress suppresses it. Interestingly, very thin ε plates ($d_t < 0.1 \mu$ m) were formed even in the region within the twin, near the boundary, despite the suppressive external stress for the SIMT and the absence of a slip trace parallel to the ATB. This is attributed to the internal stress. Thus, the effects of ATBs on SIMT have been clarified. Based on this result, more reliable biomedical CCM alloys will be developed.

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Development of Ni-free Ti-based Metallic Glasses and Composites with Potential for Biomedical Applications

The effects of minor additions on the glass-forming ability (GFA), thermal stability, and mechanical and corrosion properties of Ni-free Ti-based (Ti-Zr-Cu-Pd) metallic glasses were investigated. The substitution of Cu by 2% Sn significantly improved the GFA. Minor additions of Nb, Ta, and noble metal elements improved the plasticity and corrosion resistance. Using a spark plasma sintering process, large-size Ti-based bulk metallic glasses, composites, and porous glassy alloys having the approximate Young's modulus of bone were developed.

Ti-based bulk metallic glasses (BMGs) are promising materials for functional applications such as biomedical materials due to their high corrosion resistance, excellent mechanical properties, and good biocompatibility. Many Ti-based BMGs have been developed in the framework of the Ti-Ni-Cu and Ti-Zr-Cu-Ni alloy systems. However, these Tibased BMGs contain Ni, Be, etc., which are not suitable for contact with the human body because of cellular toxicity, limiting their applications in medical fields. Recently, we developed Ni-free Ti-Zr-Cu-Pd BMGs with high strength and good corrosion resistance that make it possible to create novel Ti-based BMG implants [1]. However, a relatively low glass-forming ability (GFA) (with critical diameter of 7 mm) restricted the biomedical applications. A large critical diameter and excellent mechanical properties of BMGs are the fundamental requirements for these applications. Minor additions are fundamental to controlling the formation, manufacture, and properties of metallic materials by controlling nucleation during solidification. In this study, we investigated the effect of minor additions on GFA, thermal stability, and the mechanical and corrosion properties of the Ti-Zr-Cu-Pd glassy alloy system [2,3].

The substitution of Cu by 2% Sn significantly improved the GFA. A Ti40Zr10Cu34Pd14Sn2 bulk

glassy alloy rod with a diameter of 12 mm has been fabricated by a copper mold casting technique (Fig. 1). The addition of 2-4% Sn enlarged the supercooled liquid region, indicating good thermal stability. TiZrCuPdSn bulk glassy alloys exhibited high compressive strengths of about 2000-2050 MPa [2]. We also implanted the Ti-based (Ti40Zr10Cu34Pd14Sn2) BMG bars under the skin and in the bone of rats. The Ti-based BMG bars exhibited excellent biocompatibility in both soft and hard tissue. They also showed nice osteoconductivity when implanted in bone tissue, and no metal ion diffusion was found up to one month after implantation.

High strength and distinct plastic strain were observed in the stress–strain curves for Nb-added Ti–Zr–Cu–Pd alloys. A yield strength exceeding 2050 MPa, low Young's modulus of about 80 GPa, and distinct plastic strains of 6.5% and 8.5% corresponding to serrated flow sections were obtained for the 1% (Fig. 2) and 3% Nb-added alloys, respectively. These minor additions of Nb or Ta also exhibit higher corrosion resistance, as shown in Fig. 3. The minor addition of noble metal elements (Au, Pt) can significantly improve the plastic stain of the Ti–Zr–Cu–Pd glassy alloys (Fig. 2) due to nanoparticles dispersed in the glassy matrix blocking the propagation of shear bands [3].



Fig. 1 XRD patterns of TiZrCuPdSn alloys.







Fig. 3 Potentiodynamic polarization curves of the (Ti40Zr10Cu36Pd14)99M1 alloys at 310 K. The curves of pure Ti and Ti-6AI-4V alloy are also shown for comparison.

It is known that BMGs are commonly produced using solidification techniques such as copper mold casting or water quenching. However, when using a solidification technique, a rather high cooling rate is required to suppress the formation of more thermodynamically stable crystalline phases. The sample size and shape are seriously limited, thereby limiting the range of applications. On the other hand, by using a consolidation technique, it is possible to produce larger metallic glassy alloy parts in a greater variety of shapes than by using a solidification technique. Spark plasma sintering (SPS), developed as a rapid consolidation technique, has great potential for producing large-size glassy samples in a short sintering time [4,5].

We prepared Ti-based metallic glassy powders using a high-pressure argon gas atomization method. Using the glassy alloy powders, or their mixed powders blended with hydroxyapatite (HA) powder, we produced Ti-based BMGs and composites with diameters over 15 mm by the SPS process [6,7]. The HA particles were uniformly distributed in the glassy matrix. No crystallization of the glassy matrix was observed. The thermal stability was almost independent of the addition of the HA particles. The produced composites exhibited lower Young's moduli than those of the as-cast Ti-based bulk glassy alloys.

Furthermore, we also produced porous Tibased BMGs (Fig. 4) with diameters over 15 mm by spark plasma sintering a mixture of gas-atomized Ti-based glassy alloy powders and solid salt (NaCl) powders, followed by a leaching treatment into water to eliminate the salt phase. Pores were homogeneously distributed in all of the sintered samples. The porosity can be controlled by controlling the volume fraction of the added salt phase. In this way, high-strength porous Ti-based BMGs with low Young's modulus, equal to that of bone, can be obtained.



Fig. 4 SEM images of sintered porous Ti-based (TiZrCuPdSn) samples, after leaching NaCl, with various porosities produced by the spark plasma sintering process at 643 K, 600 MPa, 10 min.

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Control of Domain Size and Doping of Barium Disilicide Epitaxial Thin Films for Earth-abundant High-efficiency Solar Cells

Barium disilicide (BaSi₂) is regarded as a promising candidate for a novel earth-abundant material for highefficiency thin-film solar cells owing to its large absorption coefficient and ideal bandgap. We attempted to realize high-quality BaSi₂ epitaxial thin film crystals with large crystal domains and controlled doping. Intentional introduction of a miscut to the Si(111) substrate selectively enlarged one of the three equivalent epitaxial variants by modifying the nucleation sites; this led to extraordinarily large crystal domains. Ion-implantation of BF₂ and subsequent annealing were found to be useful to obtain p-type BaSi₂ with a carrier concentration of around 10¹⁸ cm⁻³.

Orthorhombic barium disilicide (BaSi₂) has been proposed as a promising, novel candidate for high-efficiency thin-film solar cells owing to its large absorption coefficient of 10^5 cm⁻¹ at 1.5 eV [1] and bandgap that is tunable to 1.4 eV by substituting half of the Ba sites with isoelectronic Sr atoms [2]. A base layer only 1 µm thick is considered sufficient to absorb all the photons with energies higher than the bandgap. Importantly, all the constituent atoms are earth-abundant and suitable for the global deployment of photovoltaic technology.

To fabricate a solar cell based on BaSi₂, it is of crucial importance to realize high-quality thin film crystals with controlled doping. So far, epitaxial BaSi₂ thin films with (100) orientations have been grown on Si(111) substrates. However, the epitaxial relationship allows formation of three epitaxial variants that are equivalent in terms of 60° in-plane rotations. As a consequence, many crystal domains and lattice defects exist in the films. A possible route toward realization of high-quality BaSi₂ with large crystal domains is to reduce the symmetry of the surface to selectively grow one of the epitaxial variants.

For this purpose, we investigated the impact of a miscut given to the Si(111) substrate on the microstructures of epitaxially grown BaSi₂ thin films [3]. BaSi₂ epitaxial films were prepared by reactive deposition epitaxy followed by molecular beam epitaxy. First, Ba atoms were deposited on the Si(111) substrate at a deposition rate of 0.9–1.0 nm/ min for 5 min, thereby producing a thin template BaSi2 layer. An *a*-axis-oriented BaSi2 epitaxial film with a thickness of 80–90 nm was formed subsequently by depositing Ba and Si atoms on the template layer. On-axis and vicinal (with a 2° miscut towards the [112] direction) Si(111) substrates were used.

Fig. 1 compares the electron backscatter diffraction (EBSD) orientation maps of the BaSi2 films on (a) on-axis and (b) vicinal Si(111) substrates. In Fig. 1(a), it is seen that three epitaxial variants randomly appear and that the domain shape is complicated. The size of most domains is less than several micrometers. On the other hand, one of the three epitaxial variants was dominant when the BaSi2 film was grown on the 2°-inclined substrate, as shown in Fig. 1(b). In the dominant variant, the *b* axis was found to be parallel to the miscut direction.

Atomic force microscopy clarified that, on the 2°-inclined substrate, barium silicide platelets are found next to the step-bunched regions and the proportion of one epitaxial variant is increased. This result suggests that lattice matching with the step edge is an important factor for orientation selection.



Fig. 1 EBSD crystal orientation maps of BaSi2 epitaxial films grown on (a) on-axis and (b) 2°-inclined substrates.

Assuming that the steps are strictly straightforward, the step edge is parallel to the Si<110> direction. The BaSi₂[001] is accordingly parallel to Si<110>. The repeating-unit length of BaSi2[001] is 0.12% smaller than three Si<110> repeating-unit lengths. The other two orientations differ by 60° around the BaSi2 a axis from the large-domain orientation. In such orientations, the BaSi2[031] direction is almost parallel to Si<110>; the angle between these directions is 0.25°. The repeating-unit length of BaSi2[031] is 0.88% smaller than six Si<110> repeating-unit lengths. Thus, the lattice mismatch to the step edge for the small-domain orientations is larger than that for the large domain. The orientation of the large domain is, therefore, energetically more favorable than the orientations of the small domains. This would explain why the large domain is produced when the 2°-inclined Si(111) substrate is used.

In regards to doping, both n-type and p-type BaSi2 thin films have been obtained by in-situ doping during molecular beam epitaxy. The electron concentration of n-type BaSi2 has been widely controlled in the range of 10¹⁶–10²⁰ cm⁻³. On the other hand, the carrier concentration in p-type BaSi2 is still limited to the order of 10¹⁶–10¹⁷ cm⁻³. It is therefore desired to discover a p-type dopant that brings about a high carrier concentration of around 10¹⁸ cm⁻³ or more.

Boron is expected to be a p-type dopant, as is the case for the other group-III atoms AI and In. We adopted BF₂ ion implantation and subsequent annealing [4], since it is time-proven to produce p-type Si. In general, to recover the damaged layer, annealing at $(2/3)T_m$ is necessary, where T_m is the melting point. Since the melting point of BaSi₂ is 1180 °C, annealing at 696 °C is necessary.

Fig. 2 shows the Raman spectra of 120 nm BaSi2 films implanted with BF2 ions at doses of (a) 1.5×10^{12} cm⁻², (b) 1.5×10^{13} cm⁻², and (c) 1.5×10^{14} cm⁻². The spectra of the as-implanted samples and those after rapid thermal annealing (RTA) at 800 °C for 30 s are shown in solid and dotted lines, respectively. The spectrum of the as-implanted film agrees with that reported for BaSi2 [5]. According to the previous report, the vibrations with wave numbers above 250 cm⁻¹ can be interpreted based on the *T*_d symmetry of the discrete [Si4]⁴⁻ anion. The full width at half maximum (FWHM) of the Raman peak at 485–490 cm⁻¹ increased with increasing dose,



Fig. 2 Raman spectra of BaSi₂ films with BF₂ implantation doses of (a) 1.5×10¹², (b) 1.5×10¹³, and (c) 1.5×10¹⁴, cm⁻². Solid and dotted lines show the spectra of the as-implanted and annealed samples, respectively.

indicating that the as-implanted samples contain damage. After RTA, a Si peak at 520 cm⁻¹ is observed that originates from the oxidation of BaSi₂, which must be somehow suppressed. Importantly, the FWHM value decreases to the as-grown level, indicating that the implantation damage is removed almost completely by RTA. Furthermore, Hall measurement revealed that the majority carriers in the B-doped BaSi₂ films are holes and that their concentration reaches 2×10^{18} cm⁻³ at the highest implantation dose of 1.5×10^{14} cm⁻². This is, so far, the highest observed carrier concentration in p-type BaSi₂. We have thus revealed that B is a promising acceptor dopant for BaSi₂.

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Dynamical Generation of Spin Currents

Generating spin currents in nonmagnetic materials is crucial for exploring spin physics in condensed matter. We demonstrate that dynamical spin current generation driven by magnetization precession offers an easy and versatile pathway for spin injection into semiconductors. This dynamical spin injection method enables efficient spin injection into high resistivity materials, opening a route for accessing spin–charge conversions in a wide range of materials.

Spintronics is a promising technology in which the spin states of electrons are utilized as an additional degree of freedom for device operation [1]. There has been significant progress in recent years in spin injection into semiconductors, which uses tunnel barriers to circumvent the impedancemismatch problem; the impedance mismatch between ferromagnetic metals and high-resistivity materials drastically limits the spin-injection efficiency [2,3]. However, because of this problem,



Fig. 1 Spin pumping in a NiFe/GaAs junction. *I* and *V* are the microwave absorption intensity and electromotive force, respectively. *H* is the external field.

there is no route for spin injection into semiconductors through low resistivity interfaces, i.e., ohmic contacts, even though it promises an easy and versatile pathway for spin injection into high-resistivity materials.

The impedance-mismatch problem arises from the fact that spins are injected by carrier transport across а ferromagnetic metal/semiconductor interface. Thus, it seems natural to consider that this problem disappears when spins are injected directly into the semiconductor layer without using charge transport across the interface; the driving force for the spin flow is expected to offer a way for versatile spin injection free from the impedance-mismatch problem. In this work, we experimentally demonstrate efficient spin injection into semiconductors through ohmic contacts using dynamical spin injection: spin pumping. Spin pumping, the generation of pure spin currents from magnetization precession [4], provides a powerful way for direct spin injection. The spin angular momentum of the precessing magnetization in a ferromagnetic metal layer is transferred to the carriers in the semiconductor layer via dynamical exchange interactions at the ferromagnetic metal/ semiconductor interface, inducing a pure spin voltage (the potential acts on spins, not on charges) in the semiconductor layer. This enables spin injection into both p- and n-type GaAs from NiFe through both ohmic and Schottky contacts in a NiFe/ GaAs interface even at room temperature (see Fig. 1). Furthermore, as shown in Fig. 2, we demonstrate that the spin exchange interaction can be controlled electrically by applying a bias voltage across the NiFe/GaAs interface, enabling electric tuning of the spin pumping [5].

Dynamical spin injection is a powerful method for exploring the physics of spin currents in high resistivity materials. A spin current is coupled with a charge current through the spin–orbit interaction in



Fig. 2 Electric tuning of spin exchange and spin pumping at a Schottky NiFe/GaAs interface.

solids. This coupling gives rise to the conversion of spin currents into charge currents (the inverse spin Hall effect) providing a route for electric detection of spin currents [6]. However, so far, the inverse spin Hall effect has only been accessible in a limited number of materials, excluding a wide range of indirect-bandgap semiconductors and precluding further development. Notable in this group is Si, currently the most fundamental material in electronic chips. Accessing the inverse spin Hall effect in Si has been believed to be difficult because of the very weak spin-orbit interaction. Here, we show that dynamical spin injection allows access to the inverse spin Hall effect in Si at room temperature thanks to the ability to generate giant spin currents in a macroscopic area. In spite of the small spin-orbit interaction in Si, we found a clear electric voltage due to the inverse spin Hall effect in a p-type Si film, as shown in Fig. 3 [7], demonstrating that Si can be



Fig. 3 Observation of the inverse spin Hall effect in Si.

used as a spin current detector.

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Novel Material Science Using Neutron Scattering

MR is a unique institute, even worldwide, that has a neutron facility based on a strong background in advanced material science. The IMR neutron scattering group is investigating issues in materials science, such as ferroelectric materials, high-Tc superconductivity, hydrides, and application materials, as well as developing high-performance devices in neutron science. In particular, our group is aiming to construct an originative neutron spectrometer with next-generation technologies in J-PARC, which will be a flagship instrument of material science in IMR.

1) Anomalous Spin Response in Metallic Antiferromagnets

Recent inelastic neutron-scattering experiments performed on Fe-based superconductors [1] give a close-up view of the spin dynamics of spin-density waves (SDW) in metallic antiferromagnets, which would be relevant to high- T_c pairing formation. Mn3Si and Mn2.8Fe0.2Si are antiferromagnetic (AF) metals with T_N of about 20 K. The AF magnetic fluctuations show a steeply dispersive relation (or a continuum) [2]. These behaviors appear similar to those in the SDW state of the AF metal Cr [3].

We succeeded in observing magnetic excitations at a wide $\mathbf{Q} - \omega$ phase using a large single crystal of Mn2.8Fe0.2Si on a time-of-flight chopper spectrometer (SEQUOIA) at the SNS of Oak Ridge National Laboratory in the U.S.A. Salient data are shown in Fig. 1. While AF low-energy spin-wave excitations are located around L positions [Fig. 1(b)], the magnetic symmetry in **Q** space is different above 50 meV and the cross section concentrates at some (not all) zone-center Γ positions [Fig. 1(a)], i.e., at (2,2,2) and (2,0,0) but not at (0,2,2) or (4,0,0). Moreover, as shown in Fig. 1(c), such a dynamical response at Γ points persists vertically to more than 100 meV in the magnetic dispersion.

(H, -2, -2)
Fig. 1 Neutron intensity contours using a single crystal of Mn2.8Feo.2Si measured by a chopper-type time-of-flight spectrometer. (a, b) **Q**-slices and (c) ω-Q slice.

0

E.

excitations is distinct, but no reasonable explanation has been established yet. Further studies on these complicated spin dynamics are now in progress to reveal the spin correlations in magnetic metals, where localized spins and itinerant-electron spins coexist.

(H. Hiraka)

2) Impurity Effect in High Tc Superconductors

The role of magnetism in high transition temperature (T_c) superconductors has been argued, since the parent compounds of high-T_c cuprates are antiferromagnetic (AF) Mott insulators. Studying the effect of impurities in Cu sites is an effective way to assess the correlation between magnetism and superconductivity, because small amounts of impurities can induce remarkable changes in both superconductivity and magnetic properties without major changes to the bulk lattice framework. It is known that a non-magnetic Zn impurity suppresses superconductivity more severely than a magnetic Ni impurity, which is in contrast to the impurity effects on BCS superconductors. Studies on µSR have elucidated the microscopic picture for Zn doping; Zn locally kills superconductivity and T_c is suppressed by the reduction in superconducting carriers. However, there exists no microscopic



Fig. 2 A plot of *E*_{comme} versus *T*_c upon Ni-doping. The horizontal error bars represent broad superconducting transition, which is characteristic to Ni-doped high-*T*_c cuprates [ref 2-1]

10 - 7 mel

(L, ZB)

explanation for the weak suppression by Ni doping. To solve this issue, we have performed inelastic neutron scattering (INS) measurements on single crystals of La_{1.85}Sr_{0.15}Cu_{1-y}Ni_yO₄ over a wide doping range from y = 0.009 to 0.04.

The INS studies elucidate the anomalous energy and Ni dependences of the broadening of low-energy incommensurate peaks, which is evidenced by the appearance of a commensurate peak at the AF zone center (π,π) and finite energy Ecomme. Fig 2 shows a plot of Ecomme vs Tc upon Ni doping. With increasing Ni content, Tc decreases from 36.8 K (y = 0) to 22.9 K (y = 0.015), 11.6 K (y = 0.029), and 0 K (y = 0.04). The horizontal bars represent the transition width of ΔT_c determined from the shielding signal of the magnetic susceptibility measurement. We have clarified that Ecomme decreases in proportion to $T_{\rm c}$. The linear relationship between Ecomme and Tc explains the weak suppression of $T_{\rm c}$ for Ni doping by reduction in the characteristic energy of spin fluctuations.

(M. Matsuura)

3) Vibrational Properties of Hydrogen Storage <u>Materials</u>

Hydrogen has been identified as an alternative clean energy carrier for mobile applications. For instance, hydrogen storage technologies are one necessity for the widespread use of hydrogen. Since the discovery of the reversible hydrogen storage properties of Ti-doped NaAlH₄ [4], Al-based hydrides have been extensively studied both experimentally and theoretically [5]. In order to gain further insight into their hydrogen storage properties, it is important to investigate the vibrational properties of a series of Al-based hydrides. Inelastic neutron scattering (INS) can be a powerful technique because hydrogen has a large inelastic neutron scattering cross-section (82.02×10-24 cm²) that is approximately 10 times as large as those of most other elements.

Using first-principles calculations, we elucidated the vibrational properties of Al-based hydrides with different AlH₆ networks: Na₃AlH₆ with isolated AlH₆ units, CaAlH₅ with a one-dimensional AlH₆ network, and α -AlH₃ with a three-dimensional AlH₆ network (Fig. 3) [6]. The INS spectrum of Na₃AlH₆ was mainly divided into four regions: (i) the translational modes at < 218 cm⁻¹, (ii) the librational modes of the AlH₆





units at 339–515 cm⁻¹, (iii) the H–Al–H bond-bending modes at 715–994 cm⁻¹, and (iv) the Al–H bondstretching modes at 1166–1534 cm⁻¹. However, the spectra of both CaAlH₅ and α -AlH₃ were mainly divided into three regions because there were no gaps between regions (ii) (the external motions) and (iii) (the intramolecular motions) due to the networked nature of the AlH₆ units. Although both CaAlH₅ and α -AlH₃ showed qualitatively similar INS spectra, the librational modes of AlH₆ on α -AlH₃ exhibited higher frequencies than CaAlH₅ because of tighter bonding between the AlH₆ units.

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Atomistic Level Description of Phase Diagram of Clathrate Hydrates

In order to accurately estimate the thermodynamic properties of hydrogen clathrate hydrates, we developed a method that allows one to take into account multiple cage occupancy, host lattice relaxation, and the description of the quantum nature of guest behavior. Starting from first-principles estimation of the guest-host interaction with a TOMBO approach, the thermodynamic properties of clathrate hydrates and the hydrogen concentration at various pressures can be evaluated without recourse to any empirical parameter fitting. Thus, the present methodology can support the experimental exploration of novel storage materials.

The reduction of the use of fossil fuels and their replacement with alternative and sustainable energy sources is one of the present grand energy challenges. Hydrogen is an ideal candidate for this substitution and, therefore, the technology of using hydrogen as an environmentally clean and efficient fuel is an active research area worldwide. However, it is important to overcome the many scientific and technological hurdles that exist between the present state of hydrogen production, utilization, and storage capabilities and those required for a competitive and sustainable hydrogen economy.

Clathrate hydrate is one potential candidate for hydrogen storage. This is a guest-host, or inclusion, compound in which water molecules form a threedimensional host structure where the molecules (quests) can be encaged in the empty voids. Recently, it has been reported that the clathrate hydrate structure II (see Fig. 1) can store around 4.96 wt% hydrogen at 220 MPa and 234 K. Following this work, many studies of hydrogen hydrates using different methods have been conducted. Much of this work focused on the formation of hydrogen hydrates at lower pressures since the high-pressure conditions for pure hydrogen hydrate formation place a limiting constraint on its practical application. A reduction by nearly two orders of magnitude in the hydrate formation pressure was found in the tetrahydrofuran (THF) - hydrogen - water system. Thus, the possible formation of hydrogen hydrates with different structures by adding various guest molecules suggests the practical feasibility of a binary hydrate as a hydrogen storage candidate. Therefore, it is important to study the phase diagrams of multicomponent clathrate hydrates in detail, which is still a challenging experimental task due to their complexity.

There are several types of gas hydrate structures with different cage shapes, and some of these hydrate structures can hypothetically store more hydrogen than the hydrate of structure CS-II. Taking into account the same cage occupancy as in the case of CS-II hydrate, larger values of hydrogen mass (6.33 wt%) can be achieved with the CS-I structure than with the proposed hydrogen mass (4.96 wt%) for the CS-II structure.



Fig. 1 Hydrogen CS-II clathrate hydrate. (Inset) Fragment of CS-II hydrate structure in which the two fundamental cages (5¹² and 5¹²6⁴) are connected directly.

From these points of view, theoretical approaches can be useful for understanding the physical and chemical properties of the binary hydrates, and they can support the experimental exploration of novel hydrogen storage materials based on clathrate hydrates. Therefore, a novel approach based on the solid solution theory of van der Waals and Platteeuw has been developed. This model allows one to take into account the influence of guest molecules on the host lattice and guestguest interactions, especially when more than one guest molecule occupies a cage. We used the guasiharmonic lattice dynamics (QLD) method to estimate the free energies, equations of state, and chemical potentials [1]. The QLD approach includes the quantum effects in the energy and entropy calculations. These effects are significant in water ice at low temperatures and no procedure has been established to correct these effects within molecular dynamic calculations. The short-range repulsion part of the H₂-H₂ interaction was estimated using the all-electron mixed-basis method (TOMBO code), which allowed us to better describe the interactions between hydrogen molecules in water cavities.

Using this approach, the phase diagrams of pure hydrogen and mixed $H_2 + C_3H_8$ [2], $H_2 + CH_4$ [3] and $H_2 + C_2H_6$ [4] with multiple cage filling by hydrogen were constructed. The obtained results were in agreement with known experimental data.

Moreover, a structural transformation in propane hydrate was propose to explain the formation of CS-IV hydrates with greater storage capacities than those observed in CS-II hydrate [5].

At low temperature, the mass percentage of hydrogen in pure CS-II hydrogen hydrate can reach up to 3.8 wt% for pressures of 16–18 MPa. At higher pressure, the hydrogen storage capacity can increase to 4 wt%. Increasing the temperature to 260 K reduces the amount of stored hydrogen. The maximum amount of hydrogen stored at this temperature and high pressure is about 3.5 wt%. The introduction of propane as a second guest component in the binary hydrogen hydrate not only reduces the formation pressure but also reproduces the hydrogen storage ability of the pure clathrate hydrate [2].



Fig. 2 Pressure dependence of hydrogen storage capacity of pure CS-I and CS-II hydrates at T = 250 K.

Fig. 2 shows the hydrogen storage capacity of hydrogen hydrates with CS-I and CS-II structures as a function of pressure at T = 250 K. The calculation results confirmed that, for pure hydrogen hydrate, the CS-I structure can store more hydrogen than the CS-II structure. It can be seen that in low pressure regions the CS-I structure can store up to 3.1 wt% at T = 250 K. However, it has been found that the CS-I structure is thermodynamically unstable compared to CS-II [4]. This result can explain the experimental realization of the hydrogen CS-II hydrate only.

In order to stabilize the CS-I structure, a second guest component was selected according to the following conditions. In pure form, this guest is able to form both the CS-I and CS-II hydrates, and the CS-I hydrate with this guest is more stable than the CS-II structure. Based on these conditions, the mixed H_2 + CH₄ and H_2 + C₂H₆ hydrates with CS-I and CS-II structures have been studied with different gas concentrations.

The stabilization of the CS-I hydrate can be realized for both the H₂–CH₄–H₂O and H₂–C₂H₆–H₂O systems with a small concentration of methane and ethane, respectively, as shown in Fig. 3.



Fig. 3 Pressure p(T) of monovariant equilibrium: gas phase of CH₄+H₂ – ice I_h – CH₄+H₂ CS-I (squares) and CS-II (circles) hydrates at 6% methane concentrations in the gas phase.

The amount of hydrogen storage depends on the concentration of the second component in the gas phase. Thus, at a low concentration of ethane, 2.5 wt% hydrogen storage can be achieved in the CS-I hydrate at T = 250 K. However, for hydrogen storage applications, realization of ethane– hydrogen hydrate with the CS-II structure is preferable because, based on the recent experimental analysis, 3.5 wt% of hydrogen storage can be achieved by this structure [4].

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Study of Microstructural Changes in Thermally Aged Stainless Steel Weld Overlay Cladding of Nuclear Reactor Pressure Vessels by Atom Probe Tomography

The effect of thermal aging on microstructural changes in stainless steel weld overlay cladding of nuclear reactor pressure vessels composed of austenite and δ -ferrite phases was investigated using atom probe tomography. We found that thermal aging at 400 °C for 10,000 h caused a large fluctuation in the Cr concentration due to spinodal decomposition as well as the precipitation of G phases in the ferrite phase. It was suggested that the hardening by thermal aging was mainly caused by the spinodal decomposition of Cr.

Stainless steel weld overlay cladding is used as a protective barrier against corrosion on the inner surface of commercial water-cooled reactor pressure vessels (RPVs). The cladding materials are subjected to neutron irradiation and prolonged thermal aging at a service temperature of about 300 °C. These thermal and irradiation environments may cause microstructural changes, resulting in the degradation of mechanical properties and corrosion behavior. Thus, a detailed analysis of the microstructural evolution of the cladding is necessary to assure the integrity of RPVs.

The cladding material is composed of about 90% austenite phase and 10% δ -ferrite phase with net-like structures [1]. The mixed ferrite and austenitic phases bring about enhanced corrosion resistance of the claddings [2]. On the other hand, it is known that the ferrite phase is significantly hardened during thermal aging, giving rise to a toughness loss [3]. As reported for duplex stainless steels (DSSs) [4], the spinodal decomposition of the ferrite phase into Ferich α and Cr-rich α ' phases, together with the formation of Ni-rich G phase and Cr-rich M23C6-type carbide, are considered to play a key role in the hardening. However, the detailed mechanisms of these changes in the weld overlay cladding and DSS have yet to be understood because advanced experimental tools have not yet been applied to reveal the fluctuation of chemical compositions with nanometer- scale spatial resolution.

In this work, we applied atom probe tomography (APT), a unique method of mapping the alloying elements in three-dimensional real space with nearly atomic scale resolution [5], to investigate the spinodal decomposition of Cr and the formation of the G phase in the δ -ferrite in weld overlay claddings subjected to thermal aging [6,7].

The material studied was stainless-steel overlay cladding made by electroslag welding on A553B steels. The as-received material was subjected to post-welding heat treatments (PWHT) at 615 °C for 7 h. The microstructure was composed of net-like δ ferrite phases formed along some grain boundaries of the austenite matrix, as shown in Fig. 1. The

material was thermally aged at 400 °C for 10,000 h as an accelerated aging for practical conditions.



Fig. 1 Microstructure of the overlay cladding with net-like δ -ferrite phases observed by optical microscope.

The microstructural analysis was carried out with a laser-pulse APT (LEAP 3000X-HR by CAMECA) equipped with an energy- compensating reflectron lens. The samples for the APT analysis were first electrochemically polished, and finally sharpened by a dual-beam FIB/SEM ion milling system in order to select the ferrite phase at the tip of the needle specimens.

Fig. 2 shows a comparison of several atom maps of the as-received and thermally aged ferrite phases. The atom maps were constructed from slices 8 nm in thickness to clearly illustrate detailed chemical composition fluctuations. Larger fluctuations in the Cr and Fe concentrations over nano-scale areas were observed in the aged ferrite phase than in the as-received one. In the aged ferrite phase, Si, Mn, P, Ni, and Cu-concentrated precipitates (G precipitates) were also observed.

The Cr concentration fluctuated between about 20% and 35%, and the wavelength of the fluctuation was estimated to be about 8–10 nm for the asreceived phase. The fluctuation in the Cr concentration was magnified by the aging to between about 10% and 45%, while the wavelength of the fluctuation, estimated to be around 10 nm,

remained almost unchanged. These findings indicate that the fluctuation in the Cr concentration is caused by spinodal decomposition in both the ferrite phases subjected to the cooling process after the PWHT and prolonged thermal ageing.



Fig. 2 Solute atom maps of the ferrite phase in the asreceived material (a) and in the aged material (b).

Fig. 3 shows the 1D concentration profiles at and near the G precipitates in the aged ferrite phase. The chemical composition at the central part of the large precipitate was 53% Ni, 23% Si, 20% Mn, 1% Fe, Cr, P, and slight Cu and Mo. The ratios of Ni, Si, and Mn were Ni:Si:Mn = 16:7:6. This type of precipitate is called a G phase [4]. Although the small precipitates contained more Fe and Cr than the large one, the ratios of atoms were almost Ni:Si:Mn = 16:7:6 as well.



Fig. 3 1D concentration profiles penetrating the G precipitates at the ferrite phase in the aged material.

Finally, we found a linear relation between the ferrite hardening and a scalar parameter representing the spinodal decomposition for the as-received and aged ferrite phases. It was suggested that the hardening by thermal aging was mainly caused by the spinodal decomposition of Cr.

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Behaviors of Hydrogen Isotopes in Silicon Carbide for Evaluation of Hydrogen Permeability and Retention in Nuclear Fusion Systems

The behaviors of hydrogen isotopes in silicon carbide were studied after hydrogen isotopes were injected into the silicon carbide (SiC) by exposure to a hydrogen plasma from the fusion plasma machine of GAMMA-10, irradiation in the high flux fission reactor of HFIR with lithium containing oxides (tritium injection through (n, α) nuclear reaction of lithium), and ion accelerator irradiation with hydrogen and deuterium.

The behaviors of hydrogen isotopes in silicon carbide (SiC) were studied after hydrogen isotopes were injected into the SiC by exposure it to a hydrogen plasma from the fusion plasma machine of GAMMA-10, irradiation in the high flux fission reactor of HFIR with lithium containing oxides (tritium injection through (n, α) nuclear reaction of lithium), and ion accelerator irradiation with hydrogen and deuterium. The GAMMA-10 exposure showed a high retention of tritium in the SiC of about 5×10²⁰ H/m² even after a short exposure period of about 30 seconds. The HFIR irradiation revealed that the retention of tritium in the SiC is substantial and the

mobility of tritium is limited even at 800 °C [12,3], while the accelerator irradiation with 10 keV deuterium showed that deuterium has a good mobility at about 800 °C [4]. The comparison among the data obtained shows the importance of the trapping of hydrogen isotopes by radiation-induced defects. Silicon carbide has some attractive material properties, such as a low Z, low induced radioactivity, high strength, good radiation resistance, and refractoriness. It is a strong candidate for nuclear fusion materials in several applications, such as thermal and tritium barriers, and as a plasma facing material. There, the mobility and the retention



Fig. 1 Hydrogen concentration in the SiC exposed to the plasma from GAMMA-10. (Exposure to 28 shots of 0.39 second duration with average ion energy of 150 eV.) Recoiled hydrogen by 2.8 MeV helium was detected as a function of its energy (ERD). The horizontal axis corresponds to the depth of the hydrogen in the SiC.



Fig. 2 Tritium profile in the SiC irradiated in the HFIR at 800 °C. The cross section of a 1 mm SiC disk was exposed to the imaging plate (IP) after the HFIR irradiation. LTO: Lithium titanate (Li2TiO3); LAO: Lithium aluminate (LiAIO2)

behavior of the hydrogen isotopes injected into SiC are very important engineering factors. The SiC will not work as a tritium barrier if the mobility is high, and the tritium inventory will be seriously high if the retention is high.

Fig. 1 shows the hydrogen retention in single crystal SiC exposed to the GAMMA-10 edge plasma for 29 shots of 0.29 second pulse. [5] The average ion energy was about 150 eV, with a total fluence of 1×10²² H/m². The elastic recoil detection (ERD) analysis by 2.8 MeV helium revealed that the hydrogen retention is about 5×10²⁰ H/m². Exposure up to (3-6)×10²³ H/m² did not increase the amount of retention, indicating that the retention was efficient in the early stage but it saturated soon. Fig. 2 shows the tritium concentration profile in single crystal SiC that was irradiated in the HFIR [1]. Tritium was injected into the SiC from the oxide through the nuclear reaction of Li6(n, α)T during the reactor irradiation. Thus, the whole of the SiC was irradiated by high-flux neutrons during the tritium injection, but the radiation damage in the tritium-trapped area was dominated by the damage caused by the energetic tritium. The irradiation temperature was about 800 °C. The retention of the tritium was measured by the image plating (IP) technique and was found to be substantial. It was estimated that the whole of the tritium injected into the SiC was trapped and that it did not move along the SiC matrix during heavy irradiation in the HFIR at 800 °C extending for more than three months.

lon acceleration studies up to now have shown that the injected hydrogen isotopes will start to move at just below 800 °C, as shown in Fig. 3 [4], which is contradictory to the results obtained in the HFIR mentioned above. These results imply that the radiation-induced microstructures in the SiC are acting as strong trapping sites but saturate easily. Thus, the saturation amount of the retention will be strongly dependent upon the defect concentration introduced by radiation damage. SiC is a covalent material and its radiation damage structures and

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Fig. 3 Release of deuterium from SiC after accelerator injection. Deuterium concentration was measured by the elastic recoil detection (ERD) method.

tritium trapping defects will be different from those in metallic and ionic materials. The tritium trapped by the defects in the SiC, probably Si–T and C–T, are strong candidates for the trapped hydrogen isotopes observed in the present study, which are strongly bound and easily saturate the concentration.

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Effects of Displacive Radiation, Hydrogenation, and Creep in Zr-Based Alloys and FCC Metals

To develop materials for advanced fission and fusion reactors, we investigated Zr- and Fe- based alloys by means of a TEM interfaced with an ion accelerator, an HVEM, and mechanical testing techniques. Irradiationinduced hardening in Zr-Nb alloys was evident at a dose of less than 1 dpa (displacement per atom). Microstructural evolutions under hydrogenation were clarified by in-situ observations. Creep in Zircaloy-4 was investigated to modify the deformation mechanism map, and a new low-temperature creep behavior without the assistance of diffusion processes was found. In fcc metals, the microstructural configuration of subcascades in extremely high-energy cascades were characterized.

The mechanical degradations of nuclear materials strongly depend on their environments. For instance, Zr alloys for cladding in LWRs are affected by the distribution of hydrides as well as radiation defects, and Fe alloys for fusion blankets are affected by both radiation and helium accumulation. Therefore, it is indispensable to understand the microstructural evolutions and resulting mechanical degradations and to clarify their correlations. We investigate hardening induced by ion irradiation and/or He/H implantation in Zr- and Fe-based alloys by nano-hardness testing and electron microscopy, as well as fundamental study on the stability of defect clusters under electron irradiation in an HVEM.

(1) Effects of hydrogenation in Zr alloys [1,2]

Three kinds of tubular-shaped alloys, namely Zr-1.8Nb, Zr-1.6Nb-0.1Cr, and Zr-2.5Nb (wt. %), were employed in this work. The samples were to corrosion and hydrogenation subiected experiments. The corrosion experiments were performed in PWR primary water conditions, and the hydrogenation was done in a hydrogen-gas-flow chamber. The disk-shaped samples were irradiated at 570 K with 4 MeV Ni or Zr ions up to 10 dpa at a

depth range from the surface to 500 nm. Conventional measurements of hydrogen absorption and corrosion as well as SEM, TEM, EBSD, and XRD were performed.

The characteristics of hydrogenation in Zr-Nb alloys are summarized as follows: a linear increase in hydrogen absorption to the duration of exposure to hydrogen gas, the formation of hydride mostly parallel to the clad surface, and the formation of highdensity hydride at the rim of the specimen at hydrogen absorption above 500 ppm. In-situ observations under 20 keV H2+ ion implantations at room temperature in the TEM-accelerator facility at JAEA revealed that the microstructural evolution in Zr-Nb alloys was dominated by hydride nucleation, especially at the beginning of the implantation, while the growth of hydride dominated in zircaloy over the whole period of irradiation. Crystallographic information on the hydrides was clarified by TEM, EBSD, and XRD. In the corrosive environment, the difference between the Zr-Nb alloys and zircaloy was evident. In the Zr-Nb alloys, the weight gain curve did not show a transition within the experiments, and indeed, a trivial absorption of hydrogen was observed. This suggests a higher sustainability of the alloys under in-reactor environments.



0 ions/m²

Fig. 1 Microstructural evolutions in Zr-1.8Nb under irradiation with 20 keV H₂+ ions at room temperature.

(2) Creep behavior in Zircaloy-4

Creep tests have been performed in Zircaloy-4 to revise the deformation mechanism map at low temperature, because the alloy has shown a new creep mechanism with an apparent activation energy (Q) of about 20 kJ/mol at less than 373 K. As shown in Fig. 2, after the creep test, the dislocations were straightly aligned and were merely tangled. This indicates that the dislocations are mobile without evident trapping and tangling sites, that dislocation-core diffusion is inactivated in grain interiors, and that dislocations pile up at grain boundaries. Due to the extra-low Q values, rather than the conventional diffusion processes, slipinduced grain boundary sliding (GBS) works as a rate-controlling process by absorbing the piled-up dislocations. The GBS can be activated through dislocation shuffling, which requires a shorter length of atomic jump and does not assist the diffusion process. This is a new creep mechanism in Zircaloy-4 at low temperature.

(3) Defect clusters in fcc metals irradiated with spallation neutrons

Correlation of defect structural development under high-energy neutron irradiation among different energy spectra is a key issue for research and development of future nuclear materials. To examine the defect reactions involved in extremely large collision cascades, we inspected defect clusters in fcc pure metals irradiated with spallation neutrons (energies up to 500 MeV) at room temperature at KENS, High Energy Accelerator Research Organization (KEK).

In gold, large defect groups included more than 10 clusters, and the damage region extended over 50 nm, which was larger than that induced by 14 MeV D–T fusion neutron irradiation (<20 nm) [3]. Although small stacking fault tetrahedra (SFTs) were formed at subcascades by fission and fusion neutron irradiation [3], dislocation loops were also observed in the present experiments, as shown in Fig. 3. Large dislocation loops (>10 nm) were identified as vacancy type by the conventional inside–outside contrast method. Large vacancy loops are formed through cooperative reactions among subcascades in a single collision cascade with a large recoil energy.



Fig. 2 Dislocations were straightly aligned after creep test at 294 K.



Fig. 3 TEM images of defect cluster groups in Au irradiated with (a)–(f) spallation neutrons 1×10^{18} n m⁻², (g) fission neutrons 4×10^{21} n m⁻², and (h) fusion neutrons 2×10^{20} n m⁻².

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Keywords: hydrogen implantation, neutron irradiation, electron microscopy

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Preparation of Nanoporous Metals by Dealloying With Metallic Melts

Dealloying, which commonly involves corrosion processes in aqueous solutions, is a promising technique for preparing functional nanoporous metals. While this technique is ideal for preparing nanoporous noble metals such as of Au, it is not readily applicable to less-noble metals. Here, we propose a novel dealloying method employing a metallic melt, instead of an aqueous solution, as the dealloying liquid for the preparation of nanoporous base metals.

Nanoporous metals have attracted considerable attention for their excellent functional properties, including high catalytic activity, sensing capabilities, and surface-enhanced Raman scattering, which differ significantly from those of their dense, bulky counterparts. Such nanoporous metals have mainly been prepared by dealloying in aqueous solution. Dealloying is a selective corrosion phenomenon wherein the base metal in an alloy is selectively etched by corrosion to form a three-dimensional porous structure within. However, this technique is only applicable to the noble metals such as Au. The less-noble metals cannot form nanoporous structures because they are easily oxidized in the aqueous solution. To overcome this, we have recently developed an alternative dealloying method using a metallic melt instead of an aqueous solution[1]. The origin of the dealloying phenomenon in the metallic melt is not corrosion but the attractive/ repulsive forces among the atoms. The heat of mixing is the quantitative indicator of the atomic interactive force. A positive heat of mixing indicates a repulsive force between atoms and a negative one indicates an attractive force. To confirm the feasibility of this new dealloying method, the preparation of nanoporous Ti was performed based on the above strategy. Ti is a typical base metal with a very low standard electrode potential, and it has never formed nanoporous structures by the conventional dealloying technique with aqueous solution.

A Cu–Ti alloy and pure Mg were employed as the precursor and metallic melt, respectively. From the aspect of the atomic interaction, the positive heat of mixing between Mg–Ti and negative one for Mg–Cu should result in the selective dissolution of Cu from the precursor to the metallic melt, namely, the dealloying of Cu by the Mg melt.

Fig. 1a shows the microstructure of the Cu–Ti precursor immersed in the Mg melt at 973 K for 5 s, followed by an etching treatment in 3 mol/l nitric acid aqueous solution for 30 min at room temperature. The figure shows that an open-cell nanoporous





Fig. 1 SEM images of the (a) surface and (b) cross section of the porous sample prepared by immersing Ti–Cu precursor into Mg melt at 973 K for 5 s followed by etching treatment[1]

b



Fig. 2 TEM image and SAED pattern for the porous sample prepared by immersing Ti–Cu precursor into Mg melt at 973 K for 5 s followed by etching treatment[1]

structure composed of three-dimensionally interconnected ~200 nm granules is present. The cross section of the porous sample in Fig. 1b indicates that the porous structure is uniformly spread throughout the entire section. The TEM image (Fig. 2) and corresponding selected-area electron diffraction (SAED) pattern confirm that the nanoporous sample has hcp structure, as no oxide or other compound phase was observed.

Based on the heat of mixing among the atoms in the precursor and the liquid metal, the detailed formation process of the nanoporous Ti can be explained as follows. The Mg-Cu and Ti-Cu bonds are attractive, whereas the Mg-Ti bond is repulsive. In the pure Mg melt, only the Cu atoms in the Ti-Cu alloy precursor are attracted by Mg atoms and, therefore, are eluted into the Mg melt. The Ti atoms left at the interface between the alloy precursor and the melt agglomerate and enrich to form fine solid granules, and finally, these granules spontaneously organize to yield a nanoporous structure. This process is essentially similar to dealloying in aqueous solution, in which the base metal in an alloy of noble and base metals is selectively etched by an electrolyte, and the noble metal atoms left at the surface form continuous islands due to surface

Keywords: foam, porosity, microstructure Hidemi Kato(Non-Equilibrium Materials Division) E-mail: hikato@imr.tohoku.ac.jp diffusion. By changing the temperature of the melt and immersion time in the melt, the diffusivity can be controlled and the characteristic lengths of the porous structure, such as pore size or ligament size, can be tailored over a wide range[2].

As demonstrated, dealloying with a metallic melt will be a breakthrough for the preparation of nanoporous structures of base metals for future functional materials.

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Control of Helmholtz Free Energy Relationship between Protein Polymorphs under an External AC Electric Field

The distribution of the bulk tetragonal phase and spherulitic crystals in hen-egg white lysozyme was controlled by applying an external alternating current electric field. The phase distribution differed depending on differences in the magnitude of the electrostatic energy contribution to the respective chemical potentials of the two solid phases. Consequently, the Helmholtz free energy relationship between the two solid phases could be controlled by varying the frequency of the applied external electric field. This method for controlling the Helmholtz free energy relationship among polymorphs is expected to be applicable to different types of proteins.

Structural crystallography is generally used to determine the 3D structures of protein molecules. However, since crystallography requires suitable crystals, much research has focused on preparing high-quality single crystals of proteins of interest. Despite significant efforts in this regard, crystallization of proteins remains a considerable



Fig. 1 (a) Optical micrograph of bulk and spherulitic crystals of HEWL coexisting in a droplet of solution. (b) Schematic illustration of the change in the stability relationship induced by applying an external electric field. With increasing magnitude of the electric field *E*, the line along which bulk and spherulitic crystals coexist shifts downward when the temperature and solute concentration are kept constant. Consequently, the stable phase changes from spherulite to the bulk crystal with increasing applied electric field *E*.

challenge, and it is still difficult or impossible to crystallize many proteins. Moreover, spherulitic crystals rather than bulk crystals are obtained under growth conditions that provide a high driving force for nucleation. Since spherulitic crystals are composed of thin needles that grow radially outward from a center (Fig. 1(a)), they are generally unsuitable for 3D structure analysis.

We have recently been able to increase or reduce the nucleation rate of hen-egg white lysozyme (HEWL) crystals by varying the frequency of an applied electrostatic field [1-4]. The ability to control the nucleation rate via an external electric field is attributed to the electrostatic energy contribution to the chemical potentials of both the liquid and solid phases. Whether the nucleation rate increases or decreases depends on the magnitude of the difference between the electrical permittivities of the liquid and solid phases [5]. A large dispersion in the electrical permittivity is observed in protein crystals when an electrical field with a frequency below 1 MHz is applied [6]. The magnitude of the difference in the electrical permittivities of the liquid and solid phases can be regulated by exploiting this large dispersion in the electrical permittivity, and thus the nucleation rate in HEWL crystals can be controlled by applying an external AC electric field [1]. This novel approach represents a breakthrough in controlling the nucleation of protein crystals.

Protein crystals contain large amounts of water, the amount of which varies among different crystal polymorphs. For protein crystals, it has been suggested that the frequency at which dispersion of the electrical permittivity occurs increases with increasing water content [7]. Furthermore, because different crystal polymorphs have different dielectric properties, it may be possible to control (or even reverse) the difference in the electrical permittivities of different crystal polymorphs. That is, as shown in Fig. 1(b), the phase stability relationship between the bulk and spherulitic crystals can be controlled by tailoring the relative contribution of the electrostatic energy to the respective chemical potentials of the two solid phases such that the phase stability is reversed. In the following, we demonstrate active


Fig. 2 Phase distributions in solution droplets with and without the application of an external electric field. (a) No electric field and applied fields at (b) 1 and (c) 3 MHz.

control of the phase distribution between the bulk tetragonal phase and spherulitic crystals of HEWL under the application of an external AC electric field [8].

Fig. 2 shows the phase distributions in droplets of the solution with and without an external electric field. They can be classified into four types: (i) no nucleation, (ii) bulk crystal, (iii) bulk crystal + spherulite, and (iv) spherulite. The number of droplets observed by optical microscopy is indicated in each figure. For a 1 MHz applied field, the proportion of bulk crystals formed in the solution droplet was larger than that without an applied field, whereas the proportion of spherulitic crystals decreased when a field was applied (Fig. 2(b)). This implies that the driving force for nucleation of the bulk crystal was larger than that of the spherulitic crystal when a 1 MHz external electric field was applied. In contrast, when a 3 MHz electric field was applied, the proportion of spherulitic crystals formed increased, whereas the proportion of bulk crystals decreased (Fig. 2(c)). This indicates that the driving force for the nucleation of bulk crystals is much smaller than that for spherulitic crystals when a 3 MHz external electric field is applied.

Such a large electrical dispersion is considered to be a common property of almost all protein crystals, and thus this method for controlling the Helmholtz free energy relationship among polymorphs should be applicable to many proteins.

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Complex Hydrides as Advanced Lithium Fast-Ionic Conductors

In this report, we briefly summarize the fast-ionic conduction in LiBH4, a typical complex hydride, and then we explain the conceptual development of complex hydrides as a new type of solid-state lithium fast-ionic conductor using LiBH4-based and LiNH2-based complex hydrides [1].

Complex hydrides exhibit various energyrelated functions, such as hydrogen storage, microwave absorption, and neutron shielding. Furthermore, we have reported another novel energy-related function: lithium fast-ionic conduction [2,3].

The conductivities of the low-temperature phase of (LT-)LiBH₄ are very low, between 10^{-8} and 10^{-6} S cm⁻¹, and they increase monotonically upon heating. Surprisingly, at approximately 390 K, i.e., the structural transition temperature, the conductivity jumps up drastically by three orders of magnitude. As a result, the high-temperature phase of (HT-) LiBH₄ exhibits high conductivity, on the order of 10^{-3} S cm⁻¹. The activation energies for conduction have been evaluated as 0.69 eV and 0.53 eV for the LT and HT phases, respectively.

The lithium fast-ionic conduction in LiBH4 could potentially contribute to the development of solid electrolytes in all-solid-state batteries. For related applications, however, it is highly desirable to enhance the conductivity at room temperature (RT). To achieve this, we now present our recent conceptual material developments of fast-ion conductors from LiBH4-based complex hydrides.

LiBH₄–LiX (X = Cl, Br and I) system [4,5]

Fig. 1 shows the electrical (here, simply ionic) conductivities of (1 - x)LiBH₄ + xLiI/xLiCI. The change in the activation energy due to the structural transition is observed at around 340 K for Lil with x = 0.13, whereas the conductivities for x = 0.25exhibit Arrhenius behavior throughout the measured temperature range because of the HT-LiBH4 stabilization. As expected, the conductivity at RT increases by three orders of magnitude without a decrease in the high conductivity of the HT-LiBH4. Furthermore, the activation energy decreases with increasing Lil content due to the faster mobility of Li+ ions caused by the high polarizability of the I- ions substituted for [BH4]- ions. The minimum value is obtained at x = 0.13 (0.39 eV). The replacement of [BH4]- ions with CI- or Br- ions enhances the conductivity.

LiBH4-LiNH2 system [6]

As shown in Fig. 2, Li₂(BH₄)(NH₂) exhibits a fast-ionic conductivity of 1 \times 10⁻⁴ S cm⁻¹ even at



Fig. 1 shows temperature dependence of the ionic conductivities of the LiBH₄–LiI/LiCI system.

RT, which is four and five orders of magnitude higher than those of the host hydrides LT-LiBH4 and LiNH₂, respectively. Moreover, the conductivity increases monotonically upon heating. The activation energy for conduction decreases significantly at around 368 K from 0.66 eV (303-348 K) to 0.24 eV (above 368 K) as a result of the melting of Li2(BH4)(NH2). The total ionic conductivity reaches $6 \times 10^{-2} \, \text{S cm}^{-1}$ after melting at the highest temperature measured, 378 K. This result suggests that Li2(BH4)(NH2) could be used as a new type of ionic liquid as well as a solid-state fast-ionic conductor. Li4(BH4)(NH2)3 also shows a high conductivity of 2×10^{-4} S cm⁻¹ at RT, and the value reaches 2 \times 10⁻¹ S cm⁻¹ at 513 K after melting. Furthermore, the activation energy for conduction before melting is determined to be 0.26 eV. It is noteworthy that this value is less than half the value of Li2(BH4)(NH2) before melting or LiBH4 (LT phase: 0.69 eV; HT-phase: 0.53 eV), indicating that Li4(BH4)(NH2)3 has higher Li⁺ ion mobility.

LiNH₂-Lil system [7]

Fig. 3 shows the ionic conductivities for x = 0.06, 0.13, and 0.25 of $(1 - x)LiNH_2 + xLiI$. For all values of x, the conductivities exhibit Arrhenius behavior throughout the measured temperature range. The maximum conductivity of 2×10^{-5} S cm⁻¹



Fig. 2 shows temperature dependence of the ionic conductivities of the LiBH₄–LiNH₂ system.

at 300 K, which is four and three orders of magnitude higher than those of the host materials LiNH₂ and Lil, respectively, is obtained at a composition of x =0.25. At this composition, the activation energy for conduction is determined to be 0.58 eV, comparable to that of HT-LiBH₄ (0.53 eV). The notable lithium fast-ionic conduction around x = 0.25 is probably caused by a specific crystal structure of the newly found single-phase Li₃(NH₂)₂I [7], as shown in Fig. 4; that is, many intrinsic interstitial sites appear at the center of clusters of six tetrahedral (T1, T2) and between the clusters. Li⁺ ions may migrate through these spaces.

Further research is expected to yield practical applications of the complex hydrides as solid-state lithium fast-ionic conductors (namely, solid electrolytes for batteries) and to demonstrate new phenomena that are characteristic of complex hydrides. This article was produced according to the review paper [1].

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Fig. 3 shows temperature dependence of the ionic conductivities of LiNH2–Lil system.

 $Li_3(NH_2)_2I$



Fig. 4 Crystal structure of L_{i3}(NH₂)₂l viewed along [600]. Please, see the details in Ref. [7]

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Electron Microscope Study of the Formation of Graphitic Nanostructures in Nickel-loaded Wood Char

Graphitization of carbonized larch wood chars impregnated with an aqueous solution of nickel acetate has been investigated by using scanning electron microscopy (SEM), both in secondary and transmission modes, and high-resolution transmission electron microscopy (HRTEM). Graphitization sporadically started at this temperature, and some of the Ni particles were aggregated. SEM observations on chars heat-treated at 900 °C suggested that graphitic nanoshells about 50–200 nm in diameter formed by the catalytic effects of the Ni particles.

Renewable carbon-neutral wood resources, or woody biomass, are promising sources for energy conversion in view of global warming and petroleum depletion; therefore, they are the subject of a number of research and development activities. For example, Suzuki et al. have reported an integrated refinery process for woody biomass, which accounts for about 90 % of the total biomass, by using nickeland/or iron-catalyzed carbonization [1, 2]. Their research started by recognizing the need for highly efficient but environmentally undemanding energy conversion and production techniques by employing low-cost wood resources and common chemicals as starting materials. One promising process is carbonization of nickel-acetated wood flakes, where impregnation of raw wood materials with a nickel acetate solution, followed by their carbonization at a high temperature, is the key treatment. The most distinctive feature of this method is the efficient production of high-quality wood charcoal or crystallized mesoporous carbon, which has the dual functionality of yielding high conductivity and a high molecular liquid-phase adsorption capacity. These functions make them potentially important candidates for electrode materials for lithium-ion batteries and electrical double layer capacitors.

These industrially important functions are closely related to the microstructure of the wood charcoals, and several studies have already been made. For example, Suzuki et al. used transmission electron microscopy (TEM) to show that nickelacetated wood charcoal carbonized at 900 °C consists of a crystal part, which looked like a ribbonshaped spiral, and of amorphous carbon. Their observation led them to develop a new wood charcoal, in which nickel catalysts and amorphous carbon are removed from Ni-catalyzed wood charcoals by acid treatment and oxidization. The new wood charcoal, which had improved conductivity, was not ribbon-shaped but consisted of shell-shaped particles covered with graphitic stacks, which they termed "graphitic shell chains" (GSCs). The purpose of this study was hence to follow the evolution of Ni atoms inside nickelacetated wood charcoal and to elucidate the underlying mechanisms of the formation of a threedimensionally extended GSC structure. We employed scanning electron microscopy (SEM), equipped with a scanning transmission electron microscopy (STEM) detector, to investigate



Fig. 1 Stereo pair of SEM image of wood carbon prepared with a metal catalyst, showing three-dimensionally entangled graphite shell units.



Fig. 2 (a) SE-SEM (30 kV); (b) BF-STEM; (c) DF-STEM images (150–380 mrad) of Ni-loaded wood char, heat-treated at 900 °C

morphological changes, and we used highresolution TEM for observations at the atomic scale. [3]

Fig. 1 is a stereo pair of SE-SEM images taken at 3 kV, showing that GSCs have grown outwards in a winding manner, giving rise to a three-dimensionally intertwined complex microstructure. These observations thus confirm that acid treatments and post-oxidization are effective means of removing metallic catalysts and residual amorphous carbon, leading to a drastic increase in surface areas, as reported previously.

Fig. 2 shows (a) SE-SEM (30 kV), (b) BF-STEM, and (c) DF-STEM images (150–380 mrad) taken from a thin area of 900 °C NiWC flake (all taken from



Fig. 3 HRTEM image (80 kV with a Cs value of -12 μ m) of graphitic layer structure and FFT of the region indicated by the arrow.

the same position). (a) The arrows show that the weakly contrasted areas are coincident with the strong contrasts in b and c. In the transmission mode (b and c), gray winding contrasts are also seen clearly. These contrasts originate from the graphitic shell chain structure. Most of the Ni particles are surrounded by GSCs, whereas the arrowed particle in (b) is "intact." The arrow in the upper left in (c) shows an aggregate of small Ni particles.

Finally, in Fig. 3, we show an HRTEM image of the GSC structure. Here, not only are the (0002) planes seen, but graphitic layers comprising an ABAB... stacking sequence can also be confirmed, even though the graphite atoms at the 2*b* and 2*c* positions, whose distance is 0.067 nm, are not resolved.

To summarize, we have demonstrated that a combination of low voltage SEM, both in conventional SE and transmission (STEM) modes, and HRTEM is a versatile technique to elucidate the mechanism of metal-catalyzed graphitization.

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Production of Ni-Based Amorphous Alloy-Coated Bipolar Plates for Proton Exchange Membrane Fuel Cells by Electrochemical Plating

In this study, Ni–P amorphous alloy-coated bipolar plates were produced by electroless plating, and Ni–Cr–P amorphous alloy-coated bipolar plates were produced by electroplating on metal plates with a flow field. Power generation tests were conducted at 353 K on single fuel cells with these bipolar plates. It was found that the single fuel cell with the Ni–Cr–P-coated bipolar plates showed better I–V performance than that with the Ni–P-coated bipolar plates. This is because the addition of Cr to the Ni–P amorphous alloy improves its corrosion resistance. The single fuel cell with the Ni–Cr–P bipolar plates showed excellent I–V performance, performing as well as a cell with carbon bipolar plates.

The bipolar plates are one of the most important components of proton exchange membrane fuel cells (PEMFC) [1]. In this study, we produced Ni–P [2] and Ni–Cr–P [3] amorphous alloy-coated bipolar plates by electrochemical plating and examined the I–V performance and long-time durability of a single fuel cell with these plates.

Production of Ni-based amorphous alloy-coated bipolar plates [2, 3]

Fig. 1 shows the outer view of the Ni-P



Fig. 1 Outer view of the Ni–P amorphous alloy-coated bipolar plate produced by electroless plating.



Fig. 2 XRD pattern of the electroless plated Ni–P alloy thin film deposited on an AI plate.

amorphous alloy-coated bipolar plate produced by electroless plating. Amorphous alloy thin films were deposited on both sides of Al substrates with a flow field.

Fig. 2 shows the XRD pattern of the Ni–P amorphous alloy thin film deposited on an Al plate. As clearly seen in the figure, the film showed a broad halo peak without any distinct peaks from crystalline phases. The P content of the film was 11.0 mass% P.

Fig. 3 shows the outer view of the Ni-Cr-P



Fig. 3 Outer view of the Ni–Cr–P amorphous alloy-coated bipolar plate produced by electroplating.



Fig. 4 XRD pattern of the electroplated Ni–Cr–P alloy thin film deposited on a Cu plate.

amorphous alloy-coated bipolar plate

produced by electrochemical plating. A Cu plate was covered with polymer film, exposing only the flow field area to the chemicals. So, the Ni–Cr–P alloy was deposited only around a flow field on both sides of the plate.

Fig. 4 shows the XRD pattern of the Ni–Cr–P amorphous alloy thin film deposited on a Cu plate. The broad halo peak comes from a single amorphous phase and the distinct peaks may come from the Cu plate outside the area around the flow field. According to the analysis, the alloy produced in this study was Ni₅₂Cr₂₅P₂₃ in at%.

Power generation tests [2, 3]

Fig. 5 shows the I–V curves of single fuel cells with the Ni–P and Ni–Cr–P bipolar plates. The I–V curve measured with carbon graphite is superimposed on the figure for comparison. As seen in the figure, the single fuel cell with the Ni–Cr–P bipolar plates shows excellent I–V performance, performing as well as that with the carbon bipolar plates. Furthermore, it was found that the single cell with the Ni–Cr–P bipolar plates showed better I–V performance than that with the Ni–P bipolar plates. This is because the former includes a high content of the corrosion resistant element Cr.

Fig. 6 indicates the results of the long-time power generation test conducted at a current density of 200 mA/cm² at 353 K for 440 h. The final product inside a fuel cell is water. Water should be removed from the fuel cell quickly so as not to degrade the cell performance, especially over a long operation time. Therefore, the gas flow rates of H2 and O2 were increased to 0.3 L/min for this test in order to drain off the water produced inside the fuel cell completely from the flow field of the fuel cell. As seen in the figure, the voltage decreased gradually with time from the beginning of the measurement until 300 h, and then the voltage was almost constant after 300 h. This may be because a protective passive film was formed on the surface of the Ni-Cr-P bipolar plates during the test, leading to fully passivated plate surfaces. Although some small microcracks were observed in the microstructure, they did not significantly affect the I-V performance shown in Fig. 5. The results of the long-time operation test in this work were not affected significantly by the microcracks. However, it is not clear whether the microcracks would degrade the cell performance



Fig. 5 I–V performance of single fuel cells with the Ni–P and Ni–Cr–P amorphous alloy-plated bipolar plates.



Fig. 6 The result of long-time power generation at a constant current density of 200 mA/cm² for 440 h.

after longer operation. We need to investigate further. It is also important to optimize the conditions to prepare electroplated amorphous alloy films with smooth surfaces and without microcracks.

At any rate, the Ni-based amorphous alloycoated bipolar plates were produced by electrochemical plating. The potential of amorphous alloy-coated bipolar plates produced by electroplating was successfully shown in this work.

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Electrically Activated Magnetic Insulators

We study the excitation of spin waves by the current-induced spin-transfer torque in a magnetic insulator. We predict the preferential excitation of surface spin waves induced by a perpendicular surface anisotropy, which strongly reduce the critical currents and enhance the excitation power of the current-induced magnetization dynamics.

By the discovery of electrical [1] and thermal [2] excitation of yttrium iron garnet (YIG) films, the Saitoh group established magnetic insulators as an important material class for spintronics and spin caloritronics [3]. The demonstration of the electrical generation of spin waves by the spin Hall effect (SHE) and their detection by the inverse SHE adds credibility to the spin-wave bus concept for low-dissipation interconnects between spintronics circuits [4]. Here, we discuss a theoretical treatment of spin wave generation by the spin Hall effect in Pt|YIG bilayers [5] (Fig. 1) and address the physics behind the observed low critical currents and complex power spectrum.

The magnetization dynamics of YIG are described by the Landau-Lifshitz-Gilbert (LLG) equation with boundary conditions that take into account injection of a spin current J_s at the x = 0interface and free boundary conditions at x = -d. The dynamics under excitation are governed by the magnetic anisotropy energy of the magnetization M as a function of its direction relative to the atomic lattice. The magnetic anisotropy can be very different at the surface, often favoring a ground state magnetization normal to the interface, which competes with the magnetostatic anisotropy that prefers in-plane magnetization. Both the spin current J_s and the surface anisotropy K_s can be parameterized in terms of the effective wave numbers $k_i = 2\gamma J_s / A_{ex} M_s$ and $k_s = 2\gamma K_s / A_{ex} M_s$ respectively, where Aex is the exchange constant or spin wave stiffness, Ms is the saturation magnetization, and γ is the gyromagnetic ratio.

We solve the above problem numerically after linearization for in-plane wave vectors **q**, leading to complex dispersions $\omega_n(\mathbf{q})$ of spin waves with mode index *n* as a function of k_j and k_s . The imaginary part of $\omega_n(\mathbf{q})$ is the effective damping, which is positive in the absence of a current and is governed by the Gilbert parameter α . The torque due to the absorbed spin current can either increase or decrease the damping, depending on its sign and polarization. At currents that render $\text{Im}\omega_n(\mathbf{q}) = 0$, the respective mode becomes instable, which defines the threshold for (mode-dependent) current-induced spin wave excitation [6]. In the following, we discuss the results obtained using established parameters for YIG and a magnetic film thickness of 0.61 µm. The magnitude of the surface anisotropy is not known and is treated as a parameter. The main results are shown in Fig. 2, in terms of the spin wave power spectrum approximated as



Fig. 1 The samples are bilayers of electrically insulating magnetic films (YIG) of thickness *d* with magnetization
M and normal metal (Pt). A spin current *Js* generated in the normal metal, *e.g.*, by the spin Hall effect in Ref. [1], excites spin waves in the ferromagnet by spin-transfer torque [6].

In Fig. 2, the power spectrum is plotted with and without magnetic surface anisotropy at various current levels. From these results, we can draw several conclusions:

- Perpendicular surface anisotropy induces a new type of surface spin wave that is excited more easily than bulk or magnetostatic surface spin waves.
- Multiple modes at various frequencies can be excited almost simultaneously. We explain the features of the experiments by Kajiwara *et al.* [1],



Fig. 2 Power spectrum (resolution $\delta\omega/\omega = 0.01$, where $\omega = \gamma \mu \sigma M_s$) at various current levels ($k_j = 0.2k_c$ at the top, decreasing by $\Delta k_j = 0.01k_c$), without (left: $k_s = 0$) and with (right: $k_s = 25.0/\mu$ m) surface anisotropy [5]. Inset: the integrated power versus k_j .

such as very small critical currents and a broadband spin wave power spectrum only in the presence of surface anisotropy, possibly induced by the Pt overlayer.

- Agreement with observed critical currents can be achieved by assuming highly efficient spincurrent-to-magnon conversion at YIG|Pt interfaces, as expressed by the spin-mixing conductance. This is consistent with predictions from first-principle calculations [7].
- 4) The easily excitable surface modes have significant group velocities.

We conclude from these studies that a magnetic surface anisotropy should be invoked to explain the experiments by Kajiwara *et al.* [1]. Our results indicate that YIG thin films are suitable materials to allow fast and efficient information transmission over large distances that can be applied as interconnects for power-saving future electronic devices.

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High Resolution of THz ESR Uncovers the Mystery of Spin Polyhedron

Mathematicians have investigated large and complex polyhedrons intensively for centuries because of their unique geometrical properties. Recently, coordination chemists found that the idea of an icosidodecahedron is realized in magnetic clusters. Today, the quantum truncated Keplerate {Mo75V20} is examined by the high-resolution ESR of the magnetism division. The origin of the residual magnetic moments and the exchange network are determined by the microscopic separation between the intrinsic and the extrinsic magnetic responses.

The Keplerate molecules {Mo72Fe30}, {Mo72Cr30} {M072V30} are state-of-the-art objects and synthesized by coordination chemists[1]. Each has 30 magnetic sites sitting on an icosidodecahedron, which is made up of pentagons and triangles. When magnetic couplings are antiferromagnetic, the system is strongly frustrated and the energy levels are highly degenerate. An S = 0 non-magnetic ground state is expected for the system because the number of magnetic sites is even. However, the number of states is huge for longer site spin such as Fe³⁺, and a proximity to the classical ground state might be realized with the recovery of the local moments[2].

On the other hand, the existence of an S = 0 singlet ground state is plausible when the site spin is short and is associated with a strong quantum fluctuation. The cluster of {Mor₂V₃₀} with S = 1/2, the V⁴⁺ spins is expected to be a "quantum Keplerate." When magnetic susceptibility is examined, however, a non-zero value is found at low temperatures. It is proposed that paramagnetic impurities remaining in the clusters are the origin of the residual magnetic components. Attempts have been made to separate the intrinsic and the extrinsic components of the magnetic susceptibilities, but it is difficult because of the very low density of magnetic moments and large diamagnetic backgrounds.

To overcome this difficulty, we use a microscopic probe of electron spin resonance (ESR) to separate the different components. The intensity of the ESR signal is proportional to the product of the population difference and the transition matrix element between multiplet levels. Thus, the temperature dependence of the intensity is useful to determine the energy levels of the clusters. For example, ESR of a paramagnetic impurity increases in intensity steadily toward lower temperatures. On the other hand, a Schottky-peak-like behavior is expected for the clusters with singlet ground states. The question is then how these two components can be separated. The answer is that the two components can be separated by their difference in line widths with the aid of the ultimate resolution of THz ESR.

Fig. 1 shows the schematic structure of a

Keplerate cluster. At the bottom, the equivalent magnetic model for a truncated Keplerate is shown [3]. This is the very rare realization of a saw-tooth chain with a periodic boundary condition. The ground state of the system is known to be singlet. There are excited triplets and other multiplets above the ground state, and those excited states contribute to the ESR transitions.



Fig. 1 The schematic structure of a Keplerate cluster {Mo72Fe30} is shown. In a quantum version, Fe³⁺ ion is replaced with V⁴⁺ ion. Further modification by truncating two pentagon rings at the top and bottom leads to a {Mo75V20} ring cluster. The system can be regarded as a saw-tooth chain with a periodic boundary condition.

Fig. 2 shows an example of the ESR spectrum at 190 GHz. The signal consists of two components with different line widths. When the temperature dependence is assessed, the two peaks show completely different behaviors. The sharp signal grows in intensity towards lower temperatures, while the intensity of the broad peak decreases rapidly when the temperature is lowered. With these temperature dependences, the origins of the two peaks can be assigned as follows: peak B is caused by a paramagnetic impurity and peak A is caused by a transition between thermally excited states of the {M075V20} cluster. One of the origins of the broad line width of the intrinsic signal is the strong exchange couplings among the magnetic ions. The frustration of the triangular network also causes broadening.

The present analysis verifies the idea of two magnetic components that was speculated upon from magnetic susceptibility measurements. The components can be separated easily by ESR from the difference in line width. It should be noted that the separation is possible because of the high resolution and high sensitivity of the THz ESR system.



Fig. 2 An example ESR spectrum of a {Mo75V20} cluster. The sharp and broad peaks are marked as B and A. B is assigned to a paramagnetic impurity signal. Signal A originates from the body of the cluster. The broad width of A is caused by the large exchange coupling and by the strong frustration.

The experimental and calculated temperature dependence of the intensity is plotted in Fig. 3. In this curve, there are several experimental fingerprints of the energy levels, such as the onset temperature, the peak position, and the peak intensity. These parameters are related to the singlet-triplet gap as well as the density of low energy levels and their absolute spacing. The structure of the energy levels depends on the exchange couplings of the triangular units. We found that the exchange coupling in the base of the triangular ring is half of those of the two legs. The absolute value was also determined to be 150 K. As shown here, ESR gives not only a qualitative view but also a quantitative understanding of the magnetic parameters of the system.



Fig. 3 Temperature dependence of the intensity of the intrinsic ESR signal A. The onset in the low temperature side is a measure of the singlet-triplet gap, and the absolute intensity and temperature of the broad peak are sensitive to the low-energy magnetic levels. These characteristics enable us to evaluate the exchange couplings.

In summary, we succeeded in separating the intrinsic ESR signal of the molecules from the signal of the magnetic impurities in the spin polyhedron cluster {Mo75V20}. The parameters of the underlying Heisenberg Hamiltonian were then deduced.

We would like to stress that ESR is a powerful tool to evaluate the low-energy spectrum of frustrated magnetic clusters. It is much more effective than other methods, such as specific heat.

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Electron Localization in Cooperation with Mott Insulator and Anderson Localization

The Mott–Anderson transition has been known as a metal–insulator transition due to both strong electron– electron interactions and the randomness of the electrons. Recently, we demonstrated the randomness effect of the strongly correlated electrons of BEDT-TTF molecule-based organic conductors. X-ray irradiation of the crystals introduces molecular defects, which cause random potential modulation for the correlated electrons. In combination with hydrostatic pressure, we are able to control the parameters of randomness and correlations for electrons approaching the Mott–Anderson transition.

The metal-insulator transition is an important research subject on electronic properties in solidstate physics. Among the various types of metalinsulator transitions, the Mott transition due to electron-electron interactions is one of the most attractive phenomena [1,2]. Another type of metalinsulator transition is caused by electron localization that originates from the interference of electron wave functions due to randomness. This results in an Anderson localization insulator, derived bv introducing disorder into the crystal [1,3]. For more than half a century, much active research has been conducted theoretically and experimentally since P. W. Anderson propounded the concept in 1958 [3]. Since randomness in the correlated electron system is essentially important in real materials, systematic studies of disorder and randomness effects are desired in systems near a Mott transition. A series of BEDT-TTF-based molecular conductors is a good candidate for studying the randomness effects in the correlated electrons. The Mott transition and superconductivity in the half filled dimer–Mott system κ -(BEDT-TTF)₂X have been investigated actively for a typical bandwidth-controlled metal–Mott insulator transition.

Randomness can be introduced by X-ray irradiation of the molecular crystals, which does not modulate the electronic states but only the scattering for conduction electrons [4] because the molecular defects are introduced mainly in the anion molecule layers. Random potential modulation in space for the conduction electrons in the BEDT-TTF molecule layers is induced by the anion molecules defects.

Fig. 1 shows the temperature dependence of the resistivity in κ -(BEDT-TTF)₂X with X = (a) Cu(NCS)₂, (b) Cu[N(CN)₂]Br, (c) Cu[N(CN)₂]Cl, and



Fig. 1 Temperature dependence of the dc resistivity of κ-(BEDT-TTF)2X irradiated by X-rays, (a) X = Cu(NCS)2, in which the residual resistivity increases with irradiation dose; (b) Cu[N(CN)2]Br, in which an Anderson localization insulating state appears from a strongly correlated metal state after a critical irradiation dose; (c) Cu[N(CN)2]Cl, in which the Mott insulating state changes to an Anderson localization insulating state; and (d) Cu2(CN)3, in which the Mott insulating state is robust to introduction of molecular defects. The time indicated in each panel is the total X-ray exposure time at room temperature. (e) Schematic phase diagram of κ-(BEDT-TTF)2X for Udim/W.

(d) Cu₂(CN)₃, which were irradiated by X-rays at room temperature. The series is arranged in order of the correlation strength U_{dim}/W , as shown in Fig. 1(e), where Udim is the onsite Coulomb interaction energy of a BEDT-TTF dimer and W is the bandwidth. The metal-Mott insulator transition occurs between $X = Cu[N(CN)_2]Br$ and $Cu[N(CN)_2]Cl$. X-ray irradiation of the samples changes the resistivity drastically. In the case of the superconductor X =Cu(NCS)₂, the characteristic hump structure around 100 K is suppressed. In contrast to $X = Cu(NCS)_2$, a rather low irradiation dose for the $X = Cu[N(CN)_2]Br$ sample induces a drastic change in the temperature dependence of the resistivity [5]. The resistivity hump at 100 K is completely suppressed, and then the resistivity curves show an insulating behavior at low temperature. The change in the resistivity clearly indicates that the observed metal-insulator transition is induced by disorder, i.e., an Anderson localization insulator by X-ray irradiation. On the other hand, in the Mott insulators $X = Cu[N(CN)_2]Cl$ and $Cu_2(CN)_3$, the resistivity decreases but shows an insulating behavior with X-ray irradiation. This change demonstrates a transition from Mott insulator to Anderson localization insulator. In this manner, the randomness from the molecular defects strongly affects the electronic states of κ -(BEDT-TTF)₂X. The effect becomes especially significant in X = Cu[N(CN)2]Br and Cu[N(CN)2]Cl, which are in the vicinity of the critical point for the Mott transition.

A schematic electronic phase diagram with the parameters of temperature, band width, and disorder is depicted in Fig. 2 [5,6]. The present $X = Cu[N(CN)_2]$ Y (Y = Br and Cl) samples are located near the Mott transition on the metallic and Mott insulator sides, respectively. The introduction of disorder changes a Fermi liquid (FL) metal to an Anderson-type localization insulator at a critical disorder value characterized by the resistivity value of $\rho_{\rm c}$. In the case of the superconductor $X = Cu(NCS)_2$, the electron correlation is not strong enough to cause localization of carriers at the same amount of disorder as in $X = Cu[N(CN)_2]Br$. In the Mott insulator $X = Cu[N(CN)_2]CI$, the randomness turns the Mott insulating state to an Anderson localization insulating state at a similar ρ_c value. The most important suggestion in the present phase diagram is the critical behavior at the Mott transition point for the disorder. A finite small value of disorder in the system



Fig. 2 Schematic electronic phase diagram of κ -(BEDT-TTF)₂X for temperature *T*, irradiation time *t*_{rrr} corresponding to disorder, and pressure *P* to bandwidth. The thick dashed red lines indicate the critical resistivity ρ_c between the metal (FL) and the localization insulator. The temperature dependence of the resistivity shows a metallic $\rho \sim T^2$ dependence in the FL metal. Note that a finite value of disorder suppresses the first order Mott transition.

modifies the pure Mott transition to Anderson localization. Several phase diagrams calculated on the basis of the disordered Hubbard model have been reported. For improved understanding of the correlated electronic states with disorder approaching the Mott critical point, theoretical suggestions in addition to experimental investigations are urgently needed in order to obtain a proper physical picture for the future.

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Detection of Misoriented Domains with a Preferential Orientation in Nonpolar GaN Layers

Controlling microstructure, including misorented domains, in nonpolar GaN layers is an important issue in realizing highly efficient optoelectronic devices. We investigated the microstructure of nonpolar GaN layers by transmission electron microscopy (TEM). Investigating the crystallographic orientation relationship between misoriented domains and the surrounding matrix, we efficiently distinguished misoriented domains distributed in nonpolar GaN layers.

GaN-based wide-bandgap semiconductors are favorable for short-wavelength light-emitting devices. In GaN layers grown along the [0001] polar



Fig. 1 (a) Bright-field TEM image of the GaN layers. (b) A diffraction pattern obtained from the area surrounded by a circle in (a), showing the orientation relationship between the misoriented domains and the surrounding matrix. (c) Dark-field TEM image of the same area as (a), exhibiting the distribution of misoriented domains. Arrows in (a) and (c) indicate the position of the interface between the GaN layers and sapphire substrate.

axis of the wurtzite (WZ) structure, electric fields are generated due to spontaneous and piezoelectric polarization, resulting in detrimental effects on device properties. In order to prevent or reduce such effects, the growth of nonpolar or semipolar layers has been developed. However, unlike (0001) c-plane GaN layers, nonpolar or semipolar GaN layers can easily contain domains with different orientations [1,2]. Although controlling the formation and evolution of misoriented domains is an important issue in the growth of nonpolar or semipolar GaN layers, such misoriented domains are often overlooked. Here, investigating by the crystallographic orientation relationship between misoriented domains and the surrounding matrix, we efficiently revealed misoriented domains distributed in nonpolar GaN layers.

GaN layers were grown by hydride vapor phase epitaxy. After the nitridation of *r*-plane sapphire substrates, 410 nm thick low-temperature (LT) GaN layers were grown at 550 °C. Then, the LT GaN layers were heated to 1040 °C. The annealed LT GaN layers were confirmed to be dominantly *a*-plane oriented by X-ray diffraction [1,2]. Cross-sectional specimens were investigated by TEM with various incident beam directions.

Fig. 1(a) shows bright-field TEM images of the GaN layers with a properly selected incident beam direction, the [$\overline{2}203$] direction of the *a*-plane oriented GaN layers. Fig. 1(b) shows a diffraction pattern obtained from the area surrounded by the circle in Fig. 1(a). In Fig. 1(b), the diffraction spots linked by white lines are from the *a*-plane oriented GaN layers. Besides those spots, an extra diffraction pattern was detected. The diffraction pattern indicated by triangles corresponds to that obtained with the incident beam parallel to the [$\overline{1}$ 120] direction (*a*-axis) of WZ GaN. Fig. 1(c) shows dark-field TEM images



Fig. 2 Schematic illustration of the experimentally observed preferential orientation relationship between the *a*-planeoriented layers and the misoriented domain. A green arrow parallel to the edge of a tetrahedron indicates the observation direction to efficiently distinguish the misoriented domains.

of the same area as Fig. 1(a) with the incident beam direction parallel to the $[\overline{2}203]$ direction of the *a*-plane oriented GaN layers. The dark-field images were taken using the $\overline{1}100$ diffraction spot shown in Fig. 1(b). As a result of the dark-field TEM observations with this incident beam direction, it was revealed that the misoriented grains were distributed in the vicinity of the interface between the GaN layers and the sapphire substrate.

Fig. 2 shows a schematic of the misoriented domain and the a-plane oriented layers. In WZ GaN, every atom is bonded to four neighboring atoms in the shape of a tetrahedron. In the tetrahedron, the *c*-plane is distinguished from the other three planes because the bond parallel to the c-axis (bc) and the other three bonds (ba) are not equivalent in the WZ structure. Considering the orientation relationship between the misoriented domains and the a-planeoriented layers by using the structure model, a possible formation mechanism for the misoriented domains can be suggested as follows: the *c*-planes of the misoriented domains are formed on a "pseudo c-plane" of the a-plane-oriented layers. Here, the "pseudo *c*-plane" is the atomic plane perpendicular to a ba bond. It has been indicated that the

inequivalence between bonds b_a and b_c can be negligible under a thermally unstable condition, which is the origin of the misoriented domains [3]. Based on the formation mechanism of the misoriented domains, we suggest a method to efficiently distinguish misoriented domains: observing along a direction parallel to an edge of the tetrahedron (one of the *a*-axes of the misoriented domains, green arrow in Fig. 2), we can find the misoriented domains with strong electron diffraction intensity from low index planes.

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Temperature Stability of Bandgap Energy of InN

Nitride semiconductors such as InN, GaN, AIN, and their alloys are very promising for fabricating devices with low power consumption, high power, and high frequency. InGaN-based blue light-emitting diodes (LEDs) and laser diodes (LDs) are already commercially available. New trends of nitride semiconductors that extend into the deep ultraviolet, green, and infrared wavelength regions will promote device applications that save energy and create new energy. Our research is related to these new technology trends, challenging the nitride semiconductor-based LDs for use in optical fiber communications systems, phosphor-free white LEDs, brilliant green LEDs, and high-efficiency solar cells.

InN is a difficult material to grow owing to the high equilibrium vapor pressure between the solid and vapor phases of nitrogen. Recently, we developed a pressurized-reactor Metalorganic vapor phase epitaxy (MOVPE) (PR-MOVPE). We found that the pressurized growth is beneficial for facet control of the InN growth and implementation of dense films at high growth temperature [1], which generally favors the formation of a stable crystalline structure. In this report, we investigate the temperature dependence of the bandgap energy of InN films grown by PR-MOVPE.

The InN film was grown on a polished (both sides) sapphire substrate at 625 °C under 800 Torr. The flow rates of NH₃ as a nitrogen source and trimethylindium as an indium source were 9 slm and 16 μ mol/min, respectively. The InN film thickness was about 300 nm. The carrier density was estimated to be about 1×10¹⁹ cm⁻³ from the plasmon frequency in the IR reflection spectra.

The absorption spectrum of the InN film is shown in Fig. 1. The squared absorption coefficient can be well fitted by a linear function of the incident photon energy in the region from 0.9 to 1.2 eV, based on a direct interband transition. This leads to an experimental value of the InN bandgap energy, 0.78 eV. In the inset of Fig. 1, it can be observed that a red shift of the bandgap energy occurs with increasing sample temperature. This shift is shown in detail in Fig. 2, with a relatively small temperature dependence compared with other semiconductors, such as InP, GaAs, and InAs [2].

The temperature dependence of bandgap energy is determined by the electron–lattice interaction, according to the Bose–Einstein model:



Fig. 1 Temperature dependence of the optical absorption spectra of the InN film.

$$E_{g}(T) = E_{g}(0) - 2\alpha / [\exp(\theta / T) - 1],$$

where α is the electron-phonon interaction strength and θ is the average phonon energy. By fitting the experimental data, these parameters were obtained and listed in Table 1. Compared with GaAs and InP, since α is smaller and θ is larger for InN, the value of $[E_g(T) - E_g(0)] / E_g(0)$ is smaller. The bandgap energy and its temperature stability in InN are very promising for fabricating laser diodes for optical fiber communications systems.

Table 1 Electron–phonon interaction strength and phonon energy of InN bandgap energy compared with other materials for infrared lasers.

	InN	GaAs	InP
α (meV)	12.8	57.0	35.0
θ (K)	266	240	209



Fig. 2 Temperature dependence of the InN bandgap energy compared with other materials.

The absorption edge increases with the residual electron density ne of an InN film by the Burstein-Moss effect [3]. The relationship between ne and the absorption edge energy was measured by optical transmission (open circles) and reflection (closed circles), as shown in Fig. 3 [4]. Measurements were made for InN films grown at different temperatures Tg. In the case of InN grown above 600 °C, ne values estimated by both transmission and reflection methods are in good agreement with each other. This result indicates that both the optical absorption edge measured by transmission and the plasmon frequency measured by reflection are directly connected to *ne* if the crystallographic phase is a wurtzite single phase. Moreover, ne is found to decrease as Tgincreases, indicating the improvement of the structural quality. However, in case of the InN films grown below 575 °C, a large discrepancy appeared between the ne values obtained from the two methods; this is probably explained by the



Fig. 3 Comparison between the residual electron density n_e dependence of the InN bandgap energy *E* from IR transmittance (open circles) and reflectance (closed circles) spectra, where n_e is a function of growth temperature.

incorporation of a zincblende phase and related defects at the boundary between the two phases [5,6].

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Magnetic Anisotropy and Chemical Order for L10-Ordered FeNi Films Grown by Alternate Monatomic Layer Deposition

L10-FeNi films with large uniaxial magnetic anisotropy energy (K_u) were prepared by alternate monatomic layer deposition, and K_u reached 7.0 × 10⁶ erg/cm³. Long-range order parameters (S) were evaluated by X-ray diffraction using synchrotron radiation, and the relation between K_u and S was investigated. It has been found that K_u is roughly proportional to S.

A perpendicularly magnetized film is used for the recording layer in a hard disk drive, and is also useful for spintronic devices such as magnetic random access memory. Large uniaxial magnetic anisotropy energy (K_u) is necessary for such a perpendicularly magnetized film to realize highdensity and stable recording. Fig 1 shows the relation between the uniaxial magnetic anisotropy energy ($K_{\rm u}$) and the saturation magnetization ($M_{\rm s}$) of typical materials for perpendicularly magnetized L1o-ordered CoPt and FePt alloys are films. attracting attention due to their very large Ku and adequate saturation magnetizations ($M_{\rm s}$). However, Pt is very expensive and deposits are restricted. L1o-FeNi consisting of only ubiquitous elements also has a large $K_{\rm u}$ of 1.3×10^6 erg/cm³, which was reported in the bulk form by Paulevé et al. [1]; thus, L1o-FeNi is a candidate for a noble-metal-free perpendicularly magnetized film. However, the preparation of L1o-FeNi is very difficult because atomic diffusion is quite slow below the orderdisorder transition temperature (320 °C). Therefore, L10-FeNi with a large $K_{\rm u}$ had been obtained only by annealing with neutron irradiation under magnetic fields in a nuclear reactor [1]. Recently, we have succeeded in fabricating L10-FeNi films by alternate monatomic layer deposition, because the L1o structure consists of alternate stacking of two different monatomic layers along the *c*-axis, which corresponds to the easy magnetization axis [2,3]. However, there were two major problems. One problem was a ferromagnetic buffer layer that hindered precise evaluation of the Ku of L10-FeNi. The other was the difficulty in evaluating of the longrange order parameter (S) of L10-FeNi by X-ray diffraction (XRD) because of very weak superlattice peaks due to the close atomic scattering factors of Fe and Ni.

A buffer layer should not only be nonferromagnetic but also have a flat surface and good lattice matching to L1o-FeNi (a \approx c=0.358 nm). We have found that the slight addition of Au for Cu growth leads to the formation of an atomically flat surface [4]. The lattice parameters of Au, Cu, and Ni are 0.408, 0.362, and 0.352 nm, respectively. Therefore, a non-ferromagnetic Au–Cu–Ni ternary alloy with a small Au composition is suitable for the buffer layer. The composition was preliminarily optimized to $Au_{0.06}Cu_{0.51}Ni_{0.43}$ by comparison of K_u for FeNi films on Au–Cu–Ni buffers with various compositions.

In order to obtain high intensities for the superlattice peaks of L1₀-FeNi in XRD, the use of synchrotron radiation is favorable, and grazing incidence geometry can exclude unnecessary diffracted X-rays from the substrate and buffers. Thus, grazing incidence XRD (GI-XRD) using synchrotron radiation was used to observe superlattice peaks and evaluate *S*. In this study [5,6], we prepared L1₀-FeNifilms on Au_{0.06}Cu_{0.51}Ni_{0.43} buffer layers at several substrate temperatures (*T*_s), and evaluate *S* by GI-XRD. The relation between $K_{\rm u}$ and *S* was examined by changing *T*_s.

Films were deposited by molecular beam epitaxy. An Fe seed layer (1 nm) and Au (20 nm) were deposited on a MgO(001) substrate at 80 °C, and Cu (50 nm) was grown at 500 °C. The Cu and Au layers alloyed into Cu₃Au [7]. Then the Au_{0.06}Cu_{0.51}Ni_{0.43} buffer (typically 50 nm) was grown at 100 °C by ternary co-deposition. Finally, Fe and Ni monolayers were alternately grown at $T_s = 40, 67, 100, 127, 157, 187, and 217$ °C. The Fe and Ni layering was repeated 50 times. Magnetic properties were investigated by magnetization measurements using a super-conducting quantum interference device (SQUID) magnetometer at room temperature. The GI-XRD measurements to estimate *S* were carried out at the BL46XU beamline in SPring-8.

Epitaxial growth for all the films was confirmed by reflection high-energy electron diffraction (RHEED) and GI-XRD. The (110) L10-FeNi superlattice peak was clearly observed by the in-plane GI-XRD. From the XRD patterns, *S* was evaluated by

$$S = \sqrt{\frac{\left(I_{sup} / I_{fund}\right)^{obs}}{\left(I_{sup} / I_{fund}\right)_{S=1}^{cal}}}$$
(1)

where I_{sup} and I_{fund} are integrated intensities for the superlattice peak and the fundamental peak, respectively. The denominator of eq. (1) is the calculated value when S = 1. The largest S of all the FeNi films prepared was found to be 0.48.

Magnetization curves were measured when the

magnetic field was applied in parallel and perpendicular to the film plane. Although the easy magnetization axis for all the films was the in-plane direction because of a large demagnetizing field due to the shape anisotropy of the film $(2\pi M_s^2 \cong 9 \times$ 10^6 erg/cm³), the $T_s = 187$ °C film showed large magnetic anisotropy in the perpendicular direction. From the magnetization curves, K_u was estimated by

$$K_{\rm u} = \left(\int H \mathrm{d}M\right)_{\rm in} - \left(\int H \mathrm{d}M\right)_{\rm perp} + 2\pi M_{\rm s}^{2} \qquad (2)$$

where *H* and *M* are the magnetic field and the magnetization, respectively. For the $T_s = 187 \text{ °C}$ film, the largest K_u obtained was $7 \times 10^6 \text{ erg/cm}^3$, which is larger than those of artificially synthesized FeNi films reported previously.

Fig. 2 shows the relation between $K_{\rm u}$ and *S*. $K_{\rm u}$ is roughly proportional to *S*. By extrapolation, it is considered that $K_{\rm u}$ would be beyond the shape anisotropy around *S* > 0.65, showing perpendicular magnetization.

In summary, we prepared L1o-FeNi films on Au0.06Cu0.51Ni0.43 buffer layers at substrate temperatures in the range from $T_s = 40$ to 217 °C. The largest K_u and S obtained were 7.0 × 10⁶ erg/



Fig. 1 The relation between the uniaxial magnetic anisotropy energy ($K_{\rm u}$) and saturation magnetization ($M_{\rm s}$) of typical materials for perpendicularly magnetized films. The inset shows the structure of L1o-FeNi. $K_{\rm u}$ of FeNi is strongly enhanced by ordering to L1o structure from fcc. L1o-FeNi has large $K_{\rm u}$ and $M_{\rm s}$ even without noble metals.

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Fig. 2 The relation between K_u and the long-range order parameter *S* for L10-FeNi films grown by alternate monatomic layer deposition. The shape anisotropy energy is $2\pi M_s^2 \approx 9 \times 10^6$ erg/cm³. Extrapolation indicates that K_u would be beyond the shape anisotropy around *S* > 0.65, showing perpendicular magnetization.

cm³ and 0.48, respectively. $K_{\rm u}$ was roughly proportional to *S*. Perpendicularly magnetized L10-FeNi films could be obtained with a further increase of *S*.

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Field-reinforced Superconductivity in Uranium Ferromagnets

Ferromagnetism and superconductivity have been thought to be mutually competitive phenomena, since the large internal field easily destroys the Cooper pair needed for conventional superconductivity. We discovered a new class of superconductivity in uranium compounds, such as URhGe, UCoGe, and UGe₂, which can microscopically coexist with ferromagnetism. The triplet-state of pairing allows superconductivity with a large upper critical field Hc₂. Surprisingly, superconductivity is reinforced by a magnetic field, in which both ferromagnetic fluctuations and Fermi surface instabilities are induced.

The discoveries of superconductivity in the ferromagnetic phases UGe2 [1], URhGe [2], and UCoGe [3] were spectacular events in the field of unconventional superconductivity, although the possibility of superconductivity near the ferromagnetic quantum critical point was theoretically predicted a long time ago. A spin-triplet pairing is presumably generated by the ferromagnetic fluctuation. It is established that in UGe2, URhGe, and UCoGe an equal spin pairing is realized. More surprisingly. field re-entrant (or reinforced) superconductivity was found in UCoGe [4] and URhGe [5]. When a magnetic field is applied to the sample, the superconductivity is easily destroyed, and this critical field is known as the upper critical field Hc2. Fig. 1 shows the temperature dependences of the upper critical fields Hc2 in UGe2, URhGe, and UCoGe. Although the superconducting transition temperature Tc is below 1 K, the value of Hc2 at 0 K is very large, and all curves show unusual S-shapes or even field-reentrant behaviors. In general, Hc2 is governed by two different effects. One is the socalled Pauli paramagnetic effect, which is related to the Zeeman spin splitting. The other is an orbital effect that is related to the cyclotron motion of the electrons. In conventional superconductors based on the spin-singlet state, Hc2 is usually limited by the Pauli paramagnetic effect, which suppresses Hc2 to a rather low value. However, in our ferromagnetic superconductors, Hc2 markedly exceeds the Pauli paramagnetic limit since the spin-triplet state is realized. Thus, only the orbital effect, which can be expressed by the Fermi velocity or the effective mass of the conduction electrons, governs Hc2 at 0 K. In this sense, a heavy fermion system, in which strong Coulomb interactions yield a large effective mass, is a goldmine for realizing a huge Hc2. In fact, all ferromagnetic superconductors in Fig. 1 reveal



Fig. 1 Temperature dependence of the superconducting upper critical field H_{c2} in the ferromagnetic superconductors, UGe₂, URhGe and UCoGe. All H_{c2} curves reveal very unusual behaviors, owing to the spin-triplet state, with ferromagnetic fluctuations at high fields [7]. "sc" represents the superconducting phase.



Fig. 2 History of the superconducting transition temperature T_c (a) and the upper critical field H_{c2} scaled by T_c (b) [8]. Ferromagnetic superconductors based on the spin-triplet state show huge H_{c2}. The large values of H_{c2}/T_c are realized by the strong mass enhancement of conduction electrons and the longitudinal magnetic fluctuations.

enhancements of their effective masses caused by ferromagnetic fluctuations under a magnetic field, which has been clarified by our precise experiments under extreme conditions using very high-quality single crystals. Interestingly, the ferromagnetic fluctuation is quite anisotropic with strong Ising behavior; thus, H_{c2} reveals a strong anisotropy as well [6,7].

Fig. 2 shows the history of H_{c2} scaled by T_c. Thanks to the discovery of the first heavy fermion superconductor almost 30 years ago, H_{c2} is dramatically increased because the superconducting Cooper pairs are mediated by magnetic fluctuations. Presently, a new stage of superconductivity with huge H_{c2} has just started with actinide ferromagnetic superconductors.

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Detection of Two-photon Transitions of Argon by Optogalvanic and Laser-induced Fluorescent Spectroscopy

By employing a simple experimental setup, two-photon excited optogalvanic and laser-induced fluorescence (LIF) spectra of argon were successfully observed in a Grimm-style glow discharge tube, which has been widely applied to depth profiling of the elemental composition of various film-like samples by emission spectrometry.

Optical excitation of nonmetallic atoms, such as O, N, and H, in the ground state is very difficult because the lowest resonance absorption of such elements is in the deep vacuum ultraviolet (VUV) region and the generation of tunable laser radiation in the VUV region is very difficult. However, nonlinear two-photon absorption occurs when an atom is exposed to high peak-power radiation generated from a conventional laser.

If two-photon excitation of atoms could be easily detected, conventional tunable lasers would be extensively applicable to spectrochemical analysis.

In this study, optogalvanic (OG) and two-photon laser-induced fluorescence (LIF) signals were used to detect the two-photon transition of argon atoms, as an example.

The optogalvanic (OG) effect originates from the change in impedance in a steady-state glow discharge when the discharge medium resonantly absorbs radiation. The radiation rearranges the excited-state population, which in turn alters the net ionization rate of the plasma. The change in the discharge impedance may be detected as a variation in the discharge current (i.e., a voltage change at the discharge electrode). This OG signal can be used to detect a two-photon transition. The fluorescence signal from the two-photon excited energy level can also be utilized in the detection of a two-photon transition.

After evacuating a discharge chamber to below $3 \text{ Pa} (2 \times 10^{-2} \text{ Torr})$, high purity argon was introduced to $4 \times 10^2 \text{ Pa} (3 \text{ Torr})$. The pressure of the chamber was measured with a Pirani gauge and a Baratron pressure gauge installed between an evacuation port and a rotary pump. The discharge current was adjusted to 3 mA using the constant current mode

of a DC power supply (the discharge potential ranged over 400-450 V). A pulsed Ti:sapphire laser was pumped by the second harmonic (532 nm) of a Nd:YAG laser. The line-width of the Ti:sapphire laser was about 0.1 nm and the oscillation wavelengths were between 735 and 850 nm. The output energy of the pulsed laser was between approximately 7 and 10 mJ, and the glow discharge plasma was directly illuminated by the laser beam. Resonant absorption of the laser beam in the argon plasma was confirmed by observing an optogalvanic (OG) signal. The OG signal was detected as a voltage drop through a register that was inserted in the discharge circuit. No focusing of the laser beam was needed to observe the two-photon excited optogalvanic (OG) and laser-induced fluorescence (LIF) spectra of argon. To detect two-photon LIF, firing of the laser pulse was monitored by a biased silicon photo detector, and the gate of an ICCD detector equipped with a spectrograph was opened to overlap the exciting laser pulse. A high-energy Ti:sapphire laser mirror reflecting between 740 and 860 nm was used to remove the strong backscattered Ti:sapphire laser radiation from the Cu cathode surface of the Grimm-style glow discharge tube.

<u>Two photon excited optogalvanic spectra of</u> <u>argon [1]</u>

About 29 two-photon optogalvanic peak lines were observed in the wavelength region of 735–850 nm. The two-photon OG spectra of argon were easily observed without focusing the pulsed laser irradiation to more than 1 mJ. The excitation mechanisms of the observed two-photon OG spectra could be classified into 2 types: two-photon direct transitions and two-photon stepwise transitions.

A partial energy-level diagram of several



Fig.1 Partial energy-level diagram of the two-photon transition optogalvanic spectra. J is total angular momentum.

observed strong two-photon OG peaks (two-photon direct transitions) is shown in Fig. 1.

Two photon laser-induced fluorescence spectra of argon [2]

The two-photon excited laser-induced fluorescence (LIF) of argon at 641.63 nm was observed with laser excitation at 753.39 or 795.66 nm. After the two-photon excitation, the optically allowed transition at 641.63 nm took place. A partial energy-level diagram related to the LIF peak at 641.63 nm is shown in Fig. 2.

Although many two-photon transitions of argon were observed in the optogalvanic study of the argon glow plasma [1], only the 641.63 nm LIF peak could be observed in this study. This is probably due to insufficient sensitivity of the present experimental setup to observe the other LIF spectra of argon.

In conclusion, two-photon transitions of argon



Fig.2 Partial energy-level diagram of the two-photon transition and optically allowed transition of the laserinduced fluorescence (LIF). J is total angular momentum.

atoms could be detected by optogalvanic (OG) and laser-induced fluorescence (LIF) spectroscopy. In this case, an ultraviolet (UV) transition could be detected when using near-infrared (near-IR) laser radiation.

By utilizing a two-photon excitation of an atom, conventional tunable lasers will be more applicable to spectrochemical analysis.

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Spin Degrees of Freedom in Carrier-Doped Antiferromagnetic Mott Insulator

Whether high-*T*_c superconductivity arises from a Mott insulator or a Fermi-liquid metal is a vital issue in strongly correlated electron systems. To clarify the nature of spin correlations in cuprate oxide superconductors, neutron scattering measurements give indispensable information. Our recent study on two single-layer systems, Bi_{2+x}Sr₂-xCuO_{6+y} and La_{2-x}Sr_xCuO₄, revealed the variation of two spin degrees of freedom with doping: localized spin and itinerant spin natures. Therefore, there exists a transition or crossover between the strong and weak couplings against doping, and the optimal superconductivity appears in the intermediate region.

Mechanisms of exotic superconductivity are a fascinating issue in modern physics research. In high-transition-temperature (high-Tc) cuprate oxide, the role of spin fluctuations in the emergence of superconductivity has been intensively discussed. Therefore, clarifying the nature of spin fluctuations in doped Mott insulators is important. [1] The concept of fluctuating spin and charge stripes, which is based on the localized spin picture, provides an appealing explanation of the magnetic fluctuations in the doped system. However, there is an alternative school of thought that the spin fluctuations are explained through Fermi-surface nesting. Although these pictures provide different ways to understand the physical properties in high-Tc superconductors, there has not yet been a successful experimental discrimination between them.

To gain a deep insight into the nature of spin fluctuations, we have performed neutron scattering measurements on a couple of new target systems. Here, we introduce the recent progress in our study of spin correlations in single-layer Bi_{2+x}Sr_xCuO_{6+y} (Bi2201) [2] and Fe-doped La_{2-x}Sr_xCuO₄ (LSCO) [3].

Universal doping-evolution of spin correlations in single-layer cuprate oxides

The doping evolutions of spin correlations in single-layer LSCO and double-layer YBa₂Cu₃O_{6+ δ} (YBCO) have been extensively studied, due to the availability of high-quality and sizable single crystals. However, there are only two systems for which the magnetic properties can be measured as a function of doping energy and temperature. Therefore, appropriate reference systems are highly required. Quite recently, we have succeeded in growing a large singe crystal of Bi_{2+x}Sr_{2-x}CuO_{6+y} (Bi₂201) and in observing the spin fluctuations in this system [2,4]. Figure 1 shows the constant energy spectra at 4–6 meV for four Bi₂201 samples with different hole



Fig. 1 Inelastic neutron scattering spectra at 4-6 meV in Bi2.2Sr1.8CuO_{6+y} with p = (a) 0.01, (b) 0.06, (c) 0.09, and (d) 0.12. Each spectrum was measured along the [1, -1,0] and [1,0,0] directions for (a,b) and (c,d), respectively.

concentrations (*p*). With increasing *p*, a single peak splits into two incommensurate (IC) peaks, and the distance between the peaks (2δ) increases while maintaining a linear relation between δ and *p*. Furthermore, the incommensurate modulation wave vector (\mathbf{Q}_{δ}) was found to change from tetragonal [1,1,0] to the [1,0,0]/[0,1,0] direction, and we confirmed that the rotation of \mathbf{Q}_{δ} occurs around the spin-glass and superconducting phases. These results are quantitatively consistent with the observations in LSCO. Therefore, we concluded that the doping evolution of IC spin correlation is

common over a wide hole–concentration range of single layer cuprate. These characteristic features of spin correlation for $x \le 0.12$ are well reproduced by the stripe and spin spiral models based on the localized spin picture [5,6].

<u>Cross over from localized spin picture to</u> <u>itinerant electron picture with hole doping</u>

The impurity effect on spin correlations has been extensively studied in connection with the mechanisms of suppression of superconductivity. It is known that by impurity doping the existing magnetic order in the underdoped (UD) LSCO (x < 0.16) can be enhanced with suppression of the superconductivity [7]. The simple explanation for this stability of magnetic order is that the stripe fluctuations are pinned statically by local defects. However, the existence of stripe fluctuations in the entire SC phase is still under debate.

Taking advantage of the remarkable effect on the stability of the magnetic order by Fe doping, we investigated the static spin correlation in Fe-doped LSCO (Fe-LSCO). In the heavily overdoped (OD) region, we clarified that only 1% Fe doping induces a static IC magnetic order with a relatively large δ below ~20 K. Figs. 2(a) and (b) show the holeconcentration dependence of δ and the magnetic ordering temperature in the LSCO family [8, 9]. Blue circles represent the results for Fe-LSCO. The overall δ -p relation exhibits a kink at p ~ 0.12, indicating a different nature of spin correlations separated by p at ~0.12. Our angle-resolved photoemission spectroscopy (ARPES) experiments on Fe-LSCO revealed that the doping dependence of δ in the OD region is well reproduced in term of Fermi-surface nesting [3]. This agreement between neutron scattering and ARPES results supports the itinerantspin picture, and spins of itinerant doped holes define the magnetic ordering ground state in the OD region.

Since the spin correlation in the UD region is well characterized by the localized spin picture, the evidence of itinerant-spin character in the OD region suggests a transition or crossover between the two



Fig. 2 (a) Hole concentration (*p*) dependence of (a) the incommensurability of magnetic order evaluated at low temperature and (b) the magnetic ordering temperature. The gray area represents the *p* region where CDW order was observed in the LSCO family. Results for La2- x(Sr,Ba)xCuO4 and La1.6-xNd0.4SrxCuO4 are taken from Refs. 8 and 9, respectively. In both figures, solid lines are guide to the eye.

spin degrees of freedom with increased hole doping.

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Development of Ce-doped Gd₃(Al,Ga)₅O₁₂ (GAGG) Scintillator and its Applications

GAGG crystals have been developed in our laboratory through collaboration with industry. This scintillator has a high light output of more than 60,000 photons/MeV, a decay time of approximately 80 ns, and no hygroscopic nature. This scintillator has been successfully applied to a dosimeter and it will be used in Compton cameras or other detectors and monitors.

Introduction

A radiation detector consists of a scintillator and photo-detector. The scintillator is the key material to determine the performance of the radiation detector; it works as an energy converter of keV or MeV radiation particles (alpha rays, gamma rays) into photons with energies of a few eV (UV, vis. light).

Radiation detectors are applied in X-ray computed tomography (CT), positron emission tomography (PET) and other medical imaging techniques, high energy and nuclear physics detectors, natural resource surveys, and so on. In order to obtain high detection sensitivity, high-light-output scintillators are required. Ce:LaBr₃ has recently been proposed and showed a high light output of ~60,000 ph./MeV; however, it is strongly hygroscopic [1]. A Ce:Lu2SiO₅ (Ce:LSO) scintillator also has a good light output of 30,000 ph./MeV, while Ce:LSO has an intrinsic background from Lu-176 (natural abundance of 2.59%) [2].

Crystal growth and its scintillation properties

We have investigated a novel scintillator with a high light output and no hygroscopic nature using a micro-pulling-down (μ -PD) method [3, 4] developed in our laboratory. This method enables the growth of one crystal within approximately 10 h, while conventional methods such as Czochralski (CZ) or Bridgeman techniques require much longer growth times of about one week or more. Optical properties (transmittance, emission, and excitation spectra), and scintillation properties (radio-luminescence, pulse height, decay time, etc.) were measured with our equipment [5, 6]. This prompt and complete cycle allows for quick material screening.

On the way to improve the light yield of Pr:LuAG, we found Ga substitution is effective. We have expected similar positive effect on Ce doped sample. Consequently, Ce:GAGG crystals achieving a high light output and no hygroscopic nature were developed. Additionally, the maximum emission wavelength of GAGG was 520 nm, which is in the high-detection efficiency region of Si detectors, such as avalanche photodiode (APD). This emission is ascribed to the 5d–4f transition of Ce³⁺, and the decay time was 80 ns [7].

After the study of GAAG prepared by the μ -PD

method, a floating zone method was applied to investigate the effect of the growth atmosphere [8]. A bulk crystal growth process was also developed. Until now, the CZ method was used to grow 2 inch size GAGG crystals (Fig 1, b), which showed a high light output of 60,000 photons/MeV and FWHM energy resolution of 5.4% at 662 keV, as measured by a Si-APD (S8664, Hamamatsu).

Applications

Using a GAGG scintillator, a novel dosimeter was developed as a product named "gamma spotter" by FURUKAWA Co., Ltd (Fig. 1, c). Since the GAGG scintillator has high sensitivity, this detector can measure a dose of less than 1 s. The gamma spotters are used by many consumers after the FUKUSHIMA accident.

The GAGG scintillator also could be applied in medical imaging or astronomy. The GAGG is especially advantageous for application in a Compton camera consisting of a Compton scatter part and a scattered gamma-ray absorber, because the angular resolution of a Compton camera depends on the energy resolution of the absorber. The scintillator could be used as the absorber due to its superior detection efficiency over semiconductors. Additionally, due to the lack of an intrinsic background, a Compton camera mounted with a GAGG scintillator would obtain high quality images. Recently, a national project supported by JST has been started with Univ. of Tokyo, JAEA and Furukawa Co.Ltd., in order to develop a GAGG Compton camera. Pollution mapping in the Fukushima area could be conducted by a GAGG Compton camera mounted on an unmanned helicopter.

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Fig. 1 Schematic view of the development cycle of the scintillator (a), picture of a GAGG scintillator with a 2 inch diameter (b), and gamma spotter (c).

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Advanced Evaluation of Radiation Effects on Fusion Materials

International Research Center for Nuclear Materials Science

A thermal desorption spectrometer with an ion-implantation gun and 15.5 T superconducting magnet system were installed in a radiation-controlled laboratory in IRCNMS. Samples irradiated by nuclear reactors are tested by these devices to study radiation effects on fusion materials. These devices are open for collaborative works not only with Japanese researchers but also with foreign researchers.

A new framework of bidirectional collaborative research program has been started in 2010 for the study of nuclear fusion reactor materials. By utilizing the environment of the research center at each university, joint research is conducted interactively between the centers and the National Institute of Fusion Science (NIFS). Two topics that were conducted in this framework are described in this paper.

The first topic is a study of a trapping mechanism of hydrogen Isotopes in neutron-irradiated plasmafacing materials [1]. One feature of fusion reactor environments is that helium and hydrogen are produced by nuclear transmutation, and the transport and retention of hydrogen isotopes and helium from the core plasma and tritium generated at the blanket occur under neutron irradiation. It is hence indispensable to clarify the effects of neutron irradiation on the behavior of hydrogen isotopes and helium in the candidate materials to assess the feasibility of their use in fusion reactors.

For this, in 2010 a thermal desorption spectrometer (TDS) apparatus (Fig. 1) was installed in a radiation-controlled laboratory at the International Research Center for Nuclear Materials Science (IRCNMS). This apparatus allows us to obtain thermal desorption spectra, thereby enabling the identification and quantification of hydrogen isotopes and helium contained in radioactive materials following reactor or accelerator irradiation. In 2011, the TDS apparatus was equipped with an ion gun to inject hydrogen isotopes or helium into neutronirradiated specimens.

By using this apparatus, the emission and retention behavior of D was measured in recrystallized tungsten (W) specimens that were first irradiated with 2.8 MeV Fe ions to 3 dpa (displacement per atom) and then exposed to D atoms with very low energy and low flux (fluence: 6.2×10^{22} Dm⁻²); the result is shown in Fig. 2. For comparison, the results for W specimens irradiated with neutrons or Fe ions



Fig. 1 Thermal desorption spectrometer (TDS) apparatus



Fig. 2 TDS results on D desorption rate in recrystallized pure W with different irradiation (Fe ions or neutrons) and D exposure (atoms or plasma (TPE))

and then exposed to TPE (tritium plasma experiment: high energy, high fluence 10²⁵ D m⁻²) are included.

In the case of TPE exposure, neutron irradiated specimens exhibit D desorption from relatively low temperatures to as high as above 1000 K, whereas Fe-ion-irradiated specimens exhibit the completion of D desorption at around 700 K. In the case of specimens with Fe-ion irradiation and D atom exposure, D desorption starts at around 500 K and continues even above 1000 K. The D desorption behavior suggests the existence of trapping sites for

hydrogen isotopes that are as strong as those in neutron irradiated specimens (de-trapping energy: ~2 eV). These results indicate that 2.8 MeV Fe-ion irradiation can induce strong trapping sites (detrapping energy: ~2 eV) for hydrogen isotopes and that such strong trapping sites survive under lowflux D exposure but disappear under high-flux D exposure. The de-trapping energy of ~2 eV corresponds to chemisorption entrapment of hydrogen isotope atoms at the inner surface of voids in W.

The second topic is the neutron-irradiation effect on the superconducting magnet systems of fusion devices [2]. A fusion reactor yields many high-energy neutrons, and some of them stream out of the plasma vacuum vessel, penetrate the blanket system, and reach the superconducting magnets that provide high magnetic fields to confine highenergy ionized particles. Under neutron irradiation, the magnet materials are activated and their properties may change.

Changes in the superconducting properties of the superconducting wires and degradation of the interlaminar shear strength (ILSS) of electric insulation materials are the most concerning possible irradiation effects. The superconducting magnet system (Fig. 3), which was installed in the radiation control area of IRCNMS, is a so-called dry magnet working without liquid helium. The magnet generates 15.5 T as the maximum field in a 52 mm RT bore, and it is equipped with Gifford–McMahon (GM) refrigeration with an air-cooled compressor . The magnet system requires only electric power.

A variable temperature insert (VTI) included in the system is a kind of sample holder that has a capacity of 500 A for a sample current. The sample holder is cooled down by thermal conduction with GM refrigeration, and the sample temperature can be controlled from 4.5 K to around 20 K at 500 A. The control system consists of amplifiers and a computer. The control computer is connected to another computer located in a non-radiation-control area by a dedicated internet line. Users are able to change the test conditions from the non-radiation room once an irradiated sample is set up. The 15.5



Fig. 3 15.5 T superconducting magnet (lower) and variable temperature insert (upper) in a magnetic field shield structure.

T superconducting magnet is placed and the VTI is set up on the magnet. Samples irradiated in nuclear reactors will be tested with the new facility, and very important data on the critical current, critical magnetic field, and critical temperature will be obtained.

The two experimental devices described above are open for collaborative works not only with Japanese researchers but also with foreign researchers.

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Materials for Highly Energy Efficient Electrical Devices/machines

Advanced Research Center of Metallic Glasses

We at the Advanced Research Center of Metallic glasses (ARCMG) are focusing on the development of new materials that have important functional properties, such as soft/hard magnetism, excellent mechanical properties, and easy fabrication abilities. The basic route to obtain these new materials is from the molten state to solidification in different forms, such as meta-stable glassy, nano-crystalline, and even single crystal form. The aim is to develop new materials that can benefit our society and environment. To do so, ARCMG is well equipped with advanced manufacturing and testing facilities for different materials. Researchers/students also have opportunities to understand their experimental results with simulations using a supercomputer. Additionally, ARCMG is open to various researchers working in the same or other universities/institutes, so the students have opportunities to widen their horizons.

The most important problem/issue in today's world is the creation and management of energy without affecting our environment. Electrical energy is the most important form of energy, and without it our society will collapse. Electrical energy is mostly obtained at the cost of our Earth's natural resources (coal, oil, etc.), and it sometimes involves dangerous methods of production (nuclear power plants). Therefore environmentally friendly methods of production and proper management of electrical power are very important. For example, in power applications such as transformers and motors, nonoriented silicon steel and oriented silicon steel are mainly used because of their high magnetic flux density (B), but the electrical power loss in the Sisteel cores is still high. Core loss (W) in silicon steels has been improved, but further improvement seems impossible. With the newly developed soft magnetic amorphous/glassy materials (in our and other laboratories), it is possible to further decrease the electrical power loss, but these materials have lower **B**. High **B** is important for reducing the size and weight of the electrical devices (which is necessary to make them energy efficient). Therefore, development and mass production (at low cost) of nano-crystalline soft magnetic alloys that can simultaneously exhibit high B similar to Si steel (~2.0 T) and low magnetic core loss (W) as amorphous metals is ideal.

We at ARCMG are close to the development of this dream material. The new Fe-rich nano-crystalline soft magnetic material Fe85-86Si1-2B8P4Cu1 is composed of ~95 mass% Fe without rare-earth metals [1]. This low-cost soft magnetic material exhibits high magnetic flux density (1.8–1.9 T) along with extremely low core losses (1/2–1/3 of ordinary materials). Fig. 1 shows the changes in magnetic core loss (**W**) at 50 Hz for the Fe85-86Si1-2B8P4Cu1 nanocrystalline alloys as a function of maximum magnetic induction (**B**_m). The data for amorphous Fe78Si9B13, highest-grade oriented Fe–3 mass% Si and Fe–6.5



Fig. 1 Magnetic core losses (₩) of nanocrystalline FeSiBPCu alloys as a function of maximum magnetic induction (𝔅m). The data for Fe78Si9B13 amorphous and Fe–Si crystalline alloys are also shown for comparison. mass% Si alloys are also shown for comparison.

These special nano-crystalline soft magnetic materials are produced by the careful crystallization of amorphous/hetero-amorphous metallic alloys. Amorphous/glassy alloys are attractive because of their unique random arrangements of atoms, which result in excellent properties such as soft magnetism, high mechanical strength, and corrosion resistance. Additionally, these metallic glasses have precision micro-/nano-machining capabilities, which make these materials very important for future nanotechnology applications [2]. We have been developing new Fe-based, Co-based, Cu-based, Ni- based, Ti-based, Zr-based, and Mg-based glassy/amorphous alloys for different required functionalities. In the development of these special materials for energy saving or precision machining, alloy design and processing condition optimization are very important. At ARCMG, we have state-ofthe-art facilities (automatic, semi-automatic, or manual) to develop such materials (Fig. 2)

Besides the reduction of power loss in electrical



Fig. 2 (a) Automatic arc-melting furnace at ARCMG and (b) typical shape of the Fe-rich Fe85-86Si1-2B8P4Cu1 alloy ribbon.

devices, storage of electrical power is also very important for the next generation of hybrid/electrical cars. Lithium-ion rechargeable batteries are very important. We at ARCMG are also focusing on the growth of single crystals for Li-ion batteries. Spineltype Li4Ti5O12 (m.p. 1288 K) single crystals for negative electrodes in lithium-ion rechargeable batteries were grown by a NaCl (m.p. 1074 K) flux growth method in air [3]. As shown in Fig. 3, the grown crystals had an octahedral shape with welldeveloped facets and a flat surface. The TEM image in Fig. 3 indicated that the Li4Ti5O12 crystals were of very high crystallinity without point defects or dislocations. Environmental damage and product costs are thought to be greatly reduced in the flux growth technique using NaCl flux.

In addition to experimental studies, it is also possible to gain a theoretical understanding of various amorphous and nanocrystalline alloys/ materials using computer simulations.

For example, a detailed study of the cooling process of Pd42.5Cu30Ni7.5P20 glassy alloy has been done using first-principles calculations, and the results were compared with the data obtained from



Fig. 3 (a) SEM and (b) TEM images of the Li4Ti5O12 single crystals grown from NaCl flux.

a synchrotron X-ray diffraction experiment. The calculated densities of states show noticeable structures changes in the electronic of Pd42.5Cu30Ni7.5P20 compositions during a cooling process. The detailed analysis of the atomic and electronic structure of the alloy in the liquid and glassy states reveals the formation of short-range chemical order in the temperature range corresponding to a non-Arrhenius temperature dependence of viscosity [4]. The theoretical group at ARCMG has a great deal of expertise in the application of modern theoretical methods for analyzing important properties of experimentally developed alloys or suggesting new alloys to experimentalists, based on their theoretical understanding.

ARCMG not only is engaged in new cuttingedge scientific research but also focuses on industry-related issues in the development of these new materials. The new Fe-based soft magnetic nano-crystalline alloy developed in ARCMG is an excellent example. Besides the excellent soft magnetic properties ($B_s \sim 1.8T$; Hc $\sim 3-5$ A/m), this alloy has low materials (only needs industry-grade materials, without expensive materials such as rare earths) and production costs (can be produced in air), which are extremely attractive for the commercialization of these alloys.

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In-field Heat-treatment Processing for New Materials Development Using the Cryogen-free Hybrid Magnet

High Field Laboratory for Superconducting Materials

In order to realize a hybrid magnet with no need of liquid helium for operation, we have developed a cryogenfree hybrid magnet, consisting of an outer cryogen-free superconducting magnet and an inner water-cooled resistive magnet. This easy-to-operate cryogen-free hybrid magnet is now operating for application-oriented research in high fields up to 27.5 T and at high temperatures up to 1400 K in combination with an electric furnace.

The High Field Laboratory for Superconducting Materials (HFLSM) has concentrated on the three key research fields of "High field magnet technology," "Materials science in high fields," and "Basic research under multiple extreme conditions" as cooperative research in the Institute for Materials Research, Tohoku University. The HFLSM has demonstrated the first instances of various kinds of cryogen-free superconducting magnets in the world [1]. A new research field that is called magneto-science has made great progress using a static high field generated by one such unique cryogen-free Magneto-science superconducting magnet. encompasses crystal growth, chemical reactions, biological reactions, and materials processing in high fields. It is especially important to focus on functional materials development from the melt in high fields.

In order to make an easy-to-operate hybrid magnet system, we have constructed a cryogen-free 27.5 T hybrid magnet (28T-CHM), consisting of an outer cryogen-free 8.5 T superconducting magnet and an inner traditional water-cooled 19 T resistive magnet. Fig. 1 shows 28T-CHM, which generated 27.5 T in a 32 mm room-temperature experimental bore [2], and this cryogen-free hybrid magnet surely demonstrates quite flexible machine time for use in long-term experiments.

We also installed a differential thermal analysis (DTA) combined with 28T-CHM. The DTA measurement furnace system consists of Pt crucibles and an alumina support equipped with two pairs of Pt–PtRh thermocouples allowing the temperature difference to be measured [3]. Sample powders and a reference sample of Al₂O₃ powders were investigated. The maximum temperature was assumed to be 1200°C when the temperature increased in the argon atmosphere.

The motor systems of evolving hybrid electric vehicles require a working potential at high temperatures above 200 °C. The coercivity decrease of a NdFeB magnet has been eased by the addition of Dy [4]. However, this rare-earth metal is now restricted as a strategic material, and in the future it will become quite difficult to obtain important rare-



Fig. 1 World's first cryogen-free 27.5 T hybrid magnet, composed of a 360 mm wide bore cryogen-free 8.5 T superconducting outsert magnet and a 32 mm roomtemperature experimental bore 8 MW-19 T water-cooled resistive insert magnet.

earth metals such as Dy. Therefore, the development of rare-earth-free bulk magnets at the temperature range of 500–600 K is needed as innovative materials science.

On the other hand, it is generally known that MnBi has a high coercivity even at 500 K [5]. However, since Bi and Mn usually remain as individual foreign phases, it is difficult to synthesize single-phase MnBi, and as a result, the development of a high-quality MnBi synthesis process is required. The first-order phase transition through the liquid phase in high fields and the magnetic anisotropy on the crystallographic axis for the MnBi system are expected to produce various functional compositions with in-field heat treatment. This means that the magnetic characteristics can be controlled by the in-field heat treatment. Therefore, it is necessary to make an equilibrium phase diagram for the efficient investigation of materials development in high fields.

Bi–Mn samples with different compositions were made by the method of arc-melting followed by heat treatment. The sample composition was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). Diffraction peaks from the low temperature phase of ferromagnetic MnBi and Bi were observed in the Bi-rich composition. On the other hand, diffraction peaks from MnBi, Mn, and unreacted Bi were observed in the Mn-rich composition.

The DTA curves for each composition were measured under a zero field. The endothermic peak $(T_{\rm Bi})$ from the appearance of the Bi–Mn liquid phase from the ferromagnetic MnBi phase and Bi was observed in all the compositions. This result corresponds to the diffraction peak from Bi observed the X-ray diffraction measurement. Since in unreacted Bi remained in the sample, the endothermic peak from Bi was also observed in the Mn-rich composition. Moreover, an endothermic peak (Tt) was observed due to a decomposition reaction accompanied by a magnetic transformation of ferromagnetic MnBi + Bi-Mn liquid phase to paramagnetic Mn1.08Bi + Bi-Mn liquid phase. In addition, an endothermic peak (Tm) due to the peritectic reaction of Mn1.08Bi + Bi-Mn liquid phase \rightarrow Mn + Bi–Mn liquid phase was observed.

The DTA curve measured when a magnetic field was applied to Bi–53at.% Mn is shown in Fig. 2. One notes that the endothermic peaks of T_{Bi} and T_{m} are unchanged in fields up to 18 T, while T_i increases with applied magnetic field. However, the T_i increase clearly deviates from linear behavior above 20 T, as shown in Fig. 3 [6]. We found that the magnetic energy of Mn1.08Bi at T_i increases nonlinearly in high fields above 20 T and becomes large, comparable to that of MnBi. These results show that we can generally control the composition, decomposition temperature, and the equilibrium state of ferromagnetic magnetic materials by a high magnetic field if the materials have a large magnetic moment.

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Fig. 2 DTA curves in magnetic fields up to 18 T for Bi– 53at.%Mn.



Fig. 3 The straight line is a fitting of *T*t by the minimum mean square method in magnetic fields up to 26 T. The dotted line is a fitting of *T*t in a magnetic field range below 18 T.

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Challenge for Metallic Material Innovation by Collaboration between IMR, Industry, and Government

Kansai Center for Industrial Materials Research

A collaboration project (Kansai Center) between IMR, Osaka Prefecture Government, and enterprises in the Kansai area, sponsored by the Ministry of Education, Culture, Sports, Science, and Technology, was established on April 2011. The Kansai Center strives to create a new value in manufacturing in the metallic material industry and to contribute to human resource development through collaborations with industry and government.

The Kansai Center was established in Osaka as a special unit of the Institute for Materials Research, Tohoku University in April 2011, based on an agreement with Osaka Prefecture Government. The center is sponsored by the government (Ministry of Education, Culture, Sports, Science, and Technology), and it took over the project of the Osaka Center, which was carried out from 2006 to 2011 aiming to support small and medium enterprises in the Osaka area. There are three primary scopes of the Kansai Center. First, we respond to technical problems in enterprises related to metallic materials and their process technologies, and we work with the industry to solve them. Second, the Center introduces academic research output to industry and strives to apply collaborative research with companies. Third, the Center educates nextgeneration materials scientists and researchers in universities and enterprise about material science applications. The project is conducted under various collaborations with other organizations in order to achieve efficient activities, especially with the Development Center for New Metallic Material at Osaka Prefecture University and the Research Center for Nano-Micro Structure Science and Engineering at the University of Hyogo. There are seven groups in the Center: Environmental Protection and Energy Conversion Materials, Functional Materials for Future Industries, Analytical Science and Technology, Structural Materials for a Low-Control Nanostructure Carbon Society, for Engineering Materials, Advanced Biomaterials, and Structure Design of Green Metallic Materials.

The Center has some unique features and activities. First, the Kansai Center has six full-time university academic staff members (four in Osaka and two in Hyogo) to achieve the work, which is different from other similar organizations at other universities. This enables us to concentrate on collaborative activities with industry and government. Second, the Center has various collaborations with other organizations and supporting industries, such as the Osaka Bay-area Consortium, Research Society for Global Materials Crisis, and General Production Companies, which enables efficient support of industries. Third, seven professors in the Center respond to technical inquiries from industries themselves, and this saves investigation and problem-solving time. Fig. 1 shows the number of inquiries from industries at Creation Core Higashi Osaka (a governmental body where sixteen universities and one college are located to respond to inquiries from industries). It is clear that the Kansai Center occupies the largest portion among the universities, and the number of inquiries to the Kansai Center increase each year.

The Kansai Center has opened technical seminars named "Monodukuri Kisokoza" on special topics to provide scientific knowledge to technicians and researchers in industry. The seminars are organized by the professors in the Center, and the topics were selected based on industrial needs. Since fall of 2011, the new seminar has started to provide fundamentals of individual metals, such as plasticity, corrosion, and characteristic functions, in addition to history and production. Furthermore, the Center professors provide lectures on materials design, technical skills, and related fundamentals of



Fig. 1 Fraction of inquiries from industries at Creation Core Higashi Osaka (where sixteen universities and one college are located); the red region corresponds to the Osaka Center. materials science to the students in Osaka Prefecture University and Hyogo Prefecture University to demonstrate the importance of material science contributions to industrial applications.

The Kansai Center developed structural and functional materials under collaboration with industries in the Kansai area. Last July, the first application using academic outputs was commercialized by an enterprise in Osaka: Ni-based two-phase intermetallic alloys composed of Ni₃Al and Ni₃V [1] were applied to the tool materials of friction stir welding (FSW) equipment (Fig. 2). This alloy exhibits extraordinarily high hardness above 700 °C compared to commercial WC hard materials, which is beneficial for heat-resistant materials.



Fig. 2 FSW (friction stir welding) equipment (left) and a non-consumable tool composed of Ni-based two-phase intermetallic alloys (right).

Fig. 3 shows a sink roll with a Ni–Mo–B amorphous spray coating film that exhibits anticorrosion behavior in hydrochloric acid [2]. The corrosion resistance of the developed Ni–Mo–B amorphous coating film is three times higher than that of Hastelloy C276 in concentrated hydrochloric acid, and its hardness is about the same as Cermet (WC-12Co). The Ni-based amorphous coating is expected to be applied to machine parts under heavy corrosive atmospheres.

Photocatalytic TiO₂ prepared by anodic oxidation [3] for water-purification is under development with an enterprise in Osaka. Fig. 4 shows a prototype device (left) and an incorporated Ti lath coated with anodic oxide (right), which could purify the contaminated water.

The Kansai Center strives to innovate in the metallic material industry through collaborations between industry, academia, and government and to promote material science.



Fig. 3 A sink roll with a Ni–Mo–B amorphous spray coating film (lower) and its hardness (upper).



Fig.4 Prototype device (left) and incorporated Ti lath coated with anodic oxide (right).

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Invention of New Materials by Supercomputer

Center for Computational Materials Science

Simulation is becoming more and more important as a third tool, along with experiment and theory. The research fields of materials design covered by computer simulations are expanding rapidly. The newly implemented supercomputer system HITACHI SUPER TECHNICAL SERVER SR16000 Model M1 has a 300 TFLOPS processing speed, 42.2 TB of memory, and 1.4 PB of disk storage capacity. We are planning to establish the basis to serve this large-scale supercomputer resource as one of the centers within a nationwide project headed by the K computer that form a network of researchers in materials design in Japan as well as worldwide.

The aim of computational materials science is to design and expedite the synthesis of new materials with novel or extreme properties. One of the advantages of computational materials science is that it can guide this exploration by providing efficient strategies. Mutual collaboration between experiments, theories, and computer simulations is important for materials science. Providing stimulating and useful computational environments is the key role of the Center for Computational Materials Science (CCMS). It includes high-performance supercomputers, the latest versions of software, and a high-speed network.

CCMS was developed from the Laboratory of Materials Information Science that was established

in February 1989. Its main tasks are as follows:

- 1. Administration and maintenance of the supercomputing system in this Institute and maintenance of the supercomputing system network.
- 2. Support the usage of the supercomputing system.
- 3. Support materials design by supercomputing simulation with parallelization.
- 4. Support HPCI (High-Performance Computing Infrastructure) and CMRI (Computational Materials Research Initiative). A brief introduction to CMRI is given in the last paragraph.



Fig. 1 System configuration.
The supercomputing system at CCMS aims to serve as a solution for researchers in materials design to realize a sustainable world by computer simulation. Fig. 1 shows the system configuration of the supercomputing system at CCMS, which was newly installed in April 2012. The details of each system are as follows:

- The supercomputer is the HITACHI SUPER TECHNICAL SERVER SR16000 Model M1, which is a shared-memory type parallel machine (watercooled system). It has a total processing power of 300 TFLOPS composed of 320 nodes each having 980.48 GFLOPS. This is a 40 times speed increase from the previous machine. It has 42.25 TB of main memory, which serves enough computational space for the large-scale computing required by the institute.
- 2. The application server is an IBM Blade Center HS22, which is a distributed memory parallel machine. It consists of 50 computing nodes and 4 GPFS servers. It is mainly used for software applications.
- 3. The file server is a HITACHI ENTERPRISE SERVER EP8000, which manages each user's home directory.
- 4. The disk storage system is a Hitachi Adaptable Modular Storage2500, which consists of a 1.4 PB storage area, sufficient for intermediate storage of large scratch files.

Fig. 2 shows an example of the results of largescale simulations for the theoretical design of new conductive oxides. Transparent conducting oxides (TCOs) are a unique class of materials that are optically transparent and electrically conducting with a wide variety of optoelectronic applications, such as transparent electrodes in flat panel photovoltaic cells, electrochromic displays, devices, and transparent semiconducting devices. One common TCO is tin-doped indium oxide (ITO), owing to its good conductivity and high optical transparency. At present, joint experimental and theoretical ab initio investigations are being performed to predict a new TCO with the prescribed characteristics of interest.^[1]

Finally, we introduce CMRI. CMRI was established in 2011 in IMR as a project-oriented section and is one of the three operating institutions of the Computational Materials Science Initiative



Fig. 2 Unit cell of indium oxide.

(CMSI), which was founded through a Grant for Field 2, "New Materials and Energy Creation," of the HPCI Scientific Program of the Ministry of Education, Culture, Sports, Science, and Technology.

The goal of CMRI is to use supercomputers, among which the K computer boasts the world's top performance, and the supercomputer system to innovate state-of-the-art computational materials research. Current research topics include firstprinciples calculations of mechanical properties, interface mechanical/functional relationships, and evolution of microstructure, etc. of various metallic alloy systems. CMRI researchers have been developing their own program codes for these projects, based on electronic structure and statistical mechanics theories.

In recognizing the importance of forming the basic infrastructure that will lead to the next generation of computational materials science, CMRI offers seminars and symposia on parallel computing and collaborative meetings with company researchers. CMRI also promotes training and education in computational materials science for students and researchers in universities and companies. ^[2]

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Growth and Characterization of Alloys of GaN, InN, and AIN for Optoelectronics by ICC-IMR Visiting Professorship

International Collaboration Center (ICC-IMR)

CC-IMR is a gateway to IMR from the worldwide community of material science. Those who want to perform collaboration with the groups in the institute can apply for a variety of programs. Here is an example of the achievement on the growth of nitride semiconductors conducted as a guest professorship.

ICC-IMR was founded in April 2008 to succeed the International Frontier Center for Advanced Materials (IFCAM). The mission of the center has extended from an international think-tank of materials science to the center for international research collaborations of the Institute for Materials Research. To achieve this purpose, the program of the center has expanded to include the research collaboration projects by international teams.

As one of the centers of excellence in material science, IMR holds 27 research groups and six research centers. ICC-IMR is working as the gateway for collaborations between international researchers and IMR. At present, the following seven different programs are carried out in ICC-IMR. 1: international project research, 2: visiting professorship, 3: short single research visits, 4: international workshops, 5: fellowship for young researchers, and 6: coordinaton of international research collaboration. 7: Material Transfer Program. We welcome applications for those international programs from all over the world.

Prof. Baskar, Crystal Growth Centre, Anna University worked at ICC-IMR as a guest professor in FY2011 at the Prof. Matsuoka laboratory. Here is a report of his activities, impressions about IMR, and message for future applicants.

Upon arrival to IMR, Prof. Baskar arranged to have detailed discussions about the facilities available for the growth of InGaN materials on sapphire substrates. The works here have been made very effective by using the two MOVPE systems of the laboratory. He has grown InN and InGaN materials. The epitaxial layers were analyzed by using high-resolution X-ray diffraction (HXRD), photoluminescence (PL), infrared reflectance spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), and a Hall measurement system. As such, the instruments at IMR are well prepared. The special growth conditions, such as temperature, high V/III ratio, and high reactor pressure, required for the growth of good quality indium-based nitrides have been easily achieved.

Furthermore, in-situ monitoring systems, such as the Laytech tool, required for understanding of the growth mechanisms of indium nitride in MOVPE, particularly the shape of the initial stage nucleation and the coalescences at higher temperature to obtain two-dimensional growth, have been discussed in detail. The possible use of InGaN for high-efficiency solar cells was also discussed, particularly the issues related to p-type doping, the advantages for concentrated solar cell applications due to strong bonding between nitrogen and indium, and small changes in the band gap with temperature. Those discussions with experts are very useful for progress studying the crystal growth of nitrides.

AIGaN samples with aluminum contents from 20 to 70% were prepared by MOVPE on a two-inch sapphire substrate and cut into 1 cm² and 1×2 cm² size samples using a diamond scriber. The samples were cleaned in acetone and isopropyl alcohol. Indium contacts were used to measure the carrier concentration and mobility by a probe method. Though the samples are un-doped, they exhibited n-type conduction with a carrier concentration on the order of 10¹⁷ cm⁻³ up to an aluminum content of 35%. The higher aluminum content samples, above 40%, were highly resistive and the conduction type was difficult to measure. The AlGaN/GaN samples with aluminum content of 22% and thickness of around 80 nm have shown a two-dimensional electron gas (2-DEG) with a mobility of 980 cm² V/ sec. The growth of high-aluminum-content samples on GaN surfaces without cracks and with good crystalline quality is challenging due to a 3% lattice mismatch between AIN and GaN. The samples were analyzed by scanning probe microscopy, and smooth atomic surface steps, pinholes, and microcracks were observed depending on the aluminium content. A typical microstructure of an AlyGa1-yN/ AlxGa1-xN/AlyGa1-yN double heterostructure (DH) on GaN/Al 2O3 observed by AFM is shown in Fig. 1.

Though the thicknesses of the GaN buffer layer and Al_yGa_{1-y}N barrier are the same, a small thickness variation of 5 nm resulted in micro-cracks, which terminate at pinholes. The micro-cracks are formed due to the relaxation of strain once the critical thickness of the active layer of Al_xGa_{1-x}N exceeds the limit. Attempts have to be made to grow highaluminum-content (Al > 40%) AlGaN with high crystalline quality and smooth morphology using an AlN buffer with a better lattice match. Once the conditions are optimized for the AlGaN layers, resolution of the doping issues, particularly p-type doping, will be undertaken to develop high-efficiency ultraviolet light-emitting diodes. Prof. Bakar has had much success in these crystal growth studies in the very short term of his visit due to the excellent research conditions of IMR.

During his stay, he visited Nagoya Institute of Technology, Hiroshima University, Kyushu University, and Hokkaido University over 14–20 October 2011. He found that all universities are eager to establish and strengthen the bilateral academic and research cooperation with Anna University, Chennai, India. As there are a large number of Japanese companies in Chennai and discussions are occurring between the government of Japan and Government of Tamil Nadu in Chennai, India, to establish a Japanese industrial park in Chennai, many institutions are looking for a trilateral cooperation between industry in Japan or India, academia in Japan, and Anna University.

Extensive discussions were made to strengthen the semiconductor research at the Crystal Growth Centre of Anna University. It has been proposed to have an India-Japan joint workshop on nitride semiconductors for electronics, photonics, and photovoltaic applications in the year 2012 so that researchers in Japan and India can join the workshop at Anna University to bring forth joint deliberations on future strategies to establish strong collaborations between Indian universities/institutions and Japanese universities. The deliberations will also be useful to strengthen the research on nitride semiconductors for the development of novel devices.

Prof. Baskar said that the ceremony for the declaration of international material science week on 11th October 2011 at IMR, Sendai was a wonderful opportunity to share some of his thoughts about the recent disaster at Fukushima, the collaborative research between IMR and Anna University, the new initiatives in the development of materials at Anna University, and other topics for a better and sustained future for mankind.

He has expressed thanks to IMR, particularly Prof. T. Matsuoka, and Anna University, India, for their support in establishing active collaboration.





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Activity of the Integrated Materials Research Center for a Low-Carbon Society

Integrated Materials Research Center for a Low-Carbon Society (LC-IMR)

he Integrated Materials Research Center for a Low-Carbon Society (LC-IMR) was founded to promote integrated research in materials science to contribute to achieving a low-carbon society. The main aim of LC-IMR is to promote outstanding projects in the field of materials research, which will contribute to making low-carbon emissions a reality through various perspectives, from energy saving to energy harvesting and storage. We are also making active collaborations with research groups outside our institution. Cooperation between industry, the general public, and the university will be sought through workshops and by actively making information available.

It is important for the field of materials science to contribute to the achievement of low carbon emissions and a sustainable society. LC-IMR was founded in April of 2010 to promote integrated research in materials science towards the achievement of a low-carbon society. Individual members of LC-IMR belong to various materials research fields, such as structural materials, semiconductors, energy storage materials, electronics, and spintronics. We believe that integration of research in different fields is very important for making a breakthrough and thus seek collaborations both among our members and with outside centers/institutes/universities.

In the past two years, we have has been working on the following three subjects:





Fig. 2 One scene from the 1st LC-IMR workshop.

- 1. Conducting strategic research by individuals.
- 2. Supporting new research projects through management of internal research funding.
- 3. Having discussions with industry and government for a better understanding of the needs of our society.

Japanese funding agencies are determining that various strategic research programs in materials science are necessary for our future society. We are being funded and making good progress in those research programs.

LC-IMR is also managing an internal research program funded by IMR to support both promising and challenging research projects, particularly emphasizing on the center's mission. Examples of the projects selected so far include the strengthening of structural steels for automobiles and the development of new soft magnetic materials and sensor materials.

To publicize the work of our center, we organize an annual workshop and introduce our research activities. We also invite key persons from outside the university, such as industry or government, to discuss how to develop suitable systems for a sustainable society and the expected roles of materials science. Such collaborations are another important part of our activities. We will continue to make efforts to progress in our missions and ask support from everyone in the world.

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Neutrons for Advanced Material Science

Center of Neutron Science for Advanced Materials

The Center of Neutron Science for Advanced Materials (CNSAM) is a unique neutron facility that has a background of advanced material science at IMR. CNSAM operates two neutron spectrometers for material science in a reactor facility and is also the core of a project to construct a new neutron spectrometer in J-PARC/MLF, which is the world's brightest neutron source. Moreover, based on the crystal growth technology of IMR, CNSAM is developing novel neutron devices.

<u>Material science using IMR spectrometer and</u> <u>diffractometer in a reactor facility</u>

CNSAM operates a neutron spectrometer and neutron diffractometer for materials science in the JRR-3 reactor in the Japan Atomic Energy Agency (Ibaraki, Japan). The powder diffractometer, HERMES, (Fig. 1 upper panel) is an instrument to determine the structures of spins and nuclei in materials with high efficiency. HERMES is one of the most active diffractometers for material science in Japan because HERMES is a powerful tool for investigations of magnetic materials and environmentally applicable materials.

Using HEMRES, we have succeeded in observing the microscopic magnetic characteristics of a composite magnet, Fe52Pt30¹¹B18, based on a metallic glass, by polarized neutron diffraction (PND) experiments. PND is sensitive to small magnetic moments in magnetic materials. Fig. 2(a) shows the PND patterns of annealed Fe52Pt30¹¹B18; I⁺ (red) and I⁻ (blue) indicate the PND patterns for parallel and antiparallel neutron spins and sample magnetization,



Fig. 1 IMR neutron diffractometer, HERMES (upper), and spectrometer AKANE (bottom) installed in the JRR-3 reactor.



Fig. 2 PND patterns of I⁺ (parallel) and I[−] (antiparallel) for Fe₅₂Pt₃₀¹¹B₁₈ composite magnet for B=0.8T (a), and the difference patterns (b) for B=0.8T and B~5mT [1].

respectively. The small difference in peaks means that the peaks include weak ferromagnetic components. Fig. 2(b) shows the difference, I⁺ - I⁻, which is proportional to the ferromagnetic components, for different magnetic fields applied to the sample. Note that the ferromagnetic components of FePt remain even at 5 mT, while those of Fe2B disappear, meaning that the difference in soft and hard magnet characters can be directly distinguished by PND experiments.

The IMR neutron triple-axis spectrometer, AKANE, (Fig. 1, bottom panel) is an instrument to observe time and spatial fluctuations of spins and nuclei in materials with high accuracy. AKANE is indispensable for investigating the main issues of novel material science: high-Tc superconductors, metallic antiferromagnets, geometrical spin frustration systems, and so on. Note that observation of spin correlations under high pulsed magnetic fields, which is one of the characteristic technologies at IMR, has already been realized on AKANE.

Spin dynamics in quantum spin systems

Quantum spin systems have attracted much interest due to their non-trivial phenomena. Neutron



Fig. 3 Inelastic neutron scattering spectrum of the quasione-dimensional spin system CuGeO₃ measured in a wide energy-momentum space.

scattering experiments provide direct information, which connects experimental and theoretical studies. In the quasi-one-dimensional system CuGeO₃, frustration between antiferromagnetic exchange couplings within the spin-chain is reported to be responsible for the exotic physical properties. To elucidate the nature of the frustration in the spin system, we measured the full excitation spectrum of CuGeO₃ in collaboration with a group at J-PARC. Fig. 3 shows the inelastic neutron scattering intensity, which is directly related to the spin-spin correlation function. Clear continuum excitation exhibiting a quantum spin nature was observed. An intriguing feature was found in the form of a relatively strong intensity on the upper boundary of the continuum. This feature is not expected in a system without frustrated couplings, and the finding triggered a revisiting of the theoretical study of one-dimensional magnets. The observed spectrum was well reproduced by a recent model calculation that included frustrated couplings [2]. Further cooperative

study between experiment and theory on quantum magnets proceeds under an operation of J-PARC.

New projects in J-PARC

To make a jump in material science, CNSAM is trying to realize a new project: a second-generation spectrometer named POLANO at the world's brightest neutron beam facility at the Japan Proton Accelerator Research Complex (J-PARC), based on collaborations between Tohoku Univ. and KEK (project leader: K. Ohoyama) (Fig. 4). CNSAM is at the core of the POLANO project. The neutron spectrometer POLANO is characterized by polarized neutrons, which are very sensitive to pure magnetic correlations in magnets. Although we have already realized PND experiments on HERMES, the neutron flux for polarized neutron experiments is not sufficient for novel material science. To overcome this point and to make breakthroughs in material science using polarized neutrons, POLANO will be indispensable. From an applications viewpoint, POLANO will be important to develop rare-earthfree permanent magnet materials and for investigations of the fundamental physics in novel magnets. Since only a few polarized neutron spectrometers exist in the world, this spectrometer will be a key instrument to generate breakthroughs in novel material science in Japan.

In 2011, this project succeeded in gaining authorization by the J-PARC Center. With a goal of beginning construction in 2012FY, detailed engineering designs have already begun.

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Fig.4 A rendering view of the Tohoku Univ. spectrometer POLANO in J-PARC.

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Open Laboratory at Cryogenic Center for Wide Research Fields from Frontier Material Science to Low-Temperature Physics

Laboratory of Low Temperature Materials Science

he Laboratory of Low Temperature Materials Science supplies the platforms to perform basic research on materials though the measurement of transport and thermodynamic properties over a wide range of temperatures, from 350 K to 0.01 K. Using a variety of cryogenic equipment, a number of collaborative research projects with scientists from various research fields are ongoing under the technical and educational support of the staff in this laboratory.

Recently, cryogens, such as liquid helium, have been widely used by scientists not only in the fields of low-temperature condensed matter physics and applied physics but also in other fields that are not directly related to low-temperature matter. Most generic equipment for characterizing materials with automatic PC control (for example, SQUID magnetometers, NMR systems, etc.) is now available as commercial products, and one can easily operate it from room temperature down to 1 K without special techniques. However. low-temperature thev sometimes require the support of experts on lowtemperature science for maintenance, containing initial cooling, keeping the equipment cooled, and troubleshooting.

On the other hand, the special apparatuses for producing very low temperature environments below 1 K have also attracted many researchers working on low-temperature physics and frontier material science, since in many cases, novel quantum phenomena in new devices, materials, and compounds appear in the extreme absence of thermal effects. Experiments below 1 K usually require relatively large-scale facilities, particular techniques, expensive cryogens such as ³He, and a large amount of liquid helium (4He) for long-term cooling. Therefore, it is effective and convenient to keep such apparatuses together with the generic equipment at one division, which works as an open cryogenic center and consists of low-temperature experts.

On the basis of the concepts mentioned above, the Laboratory of Low Temperature Materials Science (LLTMS) possesses many kinds of cryogenic equipment (as listed below) that meet the demands of most researchers and enable them to measure the basic properties of materials as a function of temperature T and magnetic field H.

 (1) SQUID magnetometers (× 2 sets): for magnetization measurements at *T* = 1.8–350 K in *H* up to 7 (5.5) T.

- (2) VSM magnetometer (under reconstruction): for magnetization measurements at T = 4-300 K in *H* up to 14 T.
- (3) Superconducting magnet (SM) and variable temperature insert (VTI) system (× 2 sets): mainly for transport measurements at *T* = 1.2–320 K in *H* up to 11 (10) T.
- (4) SQUID microscope system: for observation of magnetic field distributions on sample surfaces at 2–100 K
- (5) Top Loading ³He cryostat and SM: for transport measurements at *T* = 0.26–300 K in *H* up to 8 T.
- (6) ³He cryostat and SM with field gradient coils: for magnetization measurements by Faraday methods at T = 0.3-2 K in *H* up to 8 T.
- (7) Dilution refrigerator and SM system: for transport and ultrasonic measurements at T = 0.02-1.4 K in *H* up to 10 T.
- (8) Superconducting vector magnet system with dilution refrigerator or VTI: for transport measurements as a function of magnetic field direction in *H* up to 7 T

Taking advantage of the plentiful liquid helium made in the Center for Low-Temperature Science (cryogenic center), much of the above equipment is always kept cooled and open to all scientists of Tohoku University. In addition to in-house research, a number of cooperative projects are now in progress under the careful technical and educational support of the staff of LLTMS. LLTMS contributes to the publication of more than 20 papers per year. The recent topics that the staff of LLTMS have deeply contributed to are:

<u>Discovery of superconductivity in KTaO₃ by</u> <u>electrostatic carrier doping [1]</u>

By employing an electric double layer transistor configuration for electrostatic carrier doping, superconductivity is successfully induced at the surface of KTaO₃, in which superconductivity has never before been observed (Fig.1).

Preparation of *n*-type metallic YBa₂Cu₃O_y using an electrochemical technique [2]

Realizing an ambipola cuprate superconductor is an important issue. Using an electrochemical technique, we succeeded in converting the sign of conduction carriers in YBa₂Cu₃O_y, which is known to be a typical *p*-type cuprate superconductor with $T_c = 90$ K, from holes to electrons (Fig. 2), to the extent that the new *n*-type YBa₂Cu₃O_y shows a metallic transport property.

Observation of field-induced anomalous magnetic states in a spin-gap material YbAI₃C₃ [3]

YbAl₃C₃ is known to be a rare 4*f*-electron compound that shows a spin-gap state, originating from dimerization of Yb³⁺ pairs. In the detailed measurement of magnetization curves below 1 K, the authors found that the 4*f*-electron dimer state in YbAl₃C₃ transfers to an unusual field-induced state (Fig. 3), which reveals different properties from that reported in *d*-electron dimer systems, through a crossover transition.



Fig. 1 Superconducting transition observed in the temperature dependence of resistance in KTaO₃ with an electric double layer transistor (EDLT) configuration at a gate voltage $V_G = 5$ V. The inset shows the concept of EDLT.



Fig. 2 Evolution of electrical resistivity with hole reduction and electron doping by an electrochemical reaction in YBa₂Cu₃O_y films. The horizontal axis is the carrier number per CuO₂ plane.



Fig. 3 Field dependence of magnetization of YbAl₃C₃ in units of μ _B per Yb atom. Two kinds of field-induced transition from the spin dimer state at low fields are observed around *H* = 4.5 T and 6.6 T at *T*= 0.47 K.

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Research Facility for Studying Physical and Chemical Properties of Radioactive and Nuclear Materials

Laboratory of alpha-Ray Emitters

More than 170 species of radioisotopes and nuclear materials can be used in the Laboratory of Alpha-Ray Emitters. This facility is one of the important centers in Japan for studying the physical and chemical properties of radioactive materials, especially for alpha-ray emitters such as actinide elements, as well as fission and fusion reactor materials. The facility has been used by many researchers from all over the country for preparation of samples and for chemical and physical measurements of a variety of radioactive materials.

In March 1960, a radioisotope (RI) handling facility was officially approved by the Science and Technology Agency (currently, Ministry of Education, Culture, Sports, Science, and Technology) as 'SHIDAI 337' and installed in the basement of Build. #1, IMR. The facility was relocated to the present building in 1978. The Laboratory of Alpha-Ray Emitters is currently approved for the use of more than 170 species of radioisotopes, including alpharay emitters such as actinide elements and nuclear materials (Fig. 1 shows the uranium metal stored in the facility). The number of such facilities is quite limited in Japan; the others are JAEA (Japan Atomic Energy Agency) and the International Research Center for Nuclear Materials Science (Oarai) of IMR. The Laboratory of Alpha-Ray Emitters has, therefore, an important role in the study of actinide elements in Japan, and this activity and capacity extends international research collaborations.

The facility is composed of two areas: the radiation-controlled area and the non-controlled area. The controlled area consists of three rooms for chemical experiments, three rooms for physical experiments, one room for radiation measurements, one contamination test room, and rooms for storage of RI and nuclear materials. Each chemical room has local exhaust ventilation systems for the treatment of various chemicals.

The radiation-detection equipment that can be used in this laboratory are two gamma-ray spectrometers (high-purity Ge semiconductor detector), a liquid scintillation counter, and an alpharay spectrometer (silicon detector). A mono-arc furnace, tetra-arc furnace, electrical discharge machine, X-ray diffractometer, and IP reader are used for the preparation and identification of nuclear material alloys, such as UCoGe. Two inert-gas glove boxes, a CHNS element analyzer, an ICP emission spectrophotometer, an FT-IR, a UV-visible spectrophotometer, a powder X-ray diffractometer, and an X-ray single crystal structure analysis system are used for the treatment of nuclear materials and other chemicals. A scanning electron microscope, automatic titration system, and electrochemical

measurement system are installed in the laboratory. A transmission electron microscope has been used to study the irradiation effects of nuclear materials. In recent years, a physical property measurement system (PPMS) was installed and used for the physical study of actinide compounds (Fig. 2).

In resent years, this laboratory has produced several outstanding achievements. The noted work introduced here includes (i) a study on the physical properties of uranium metallic compounds based on preparation of very fine single-crystals, and (ii)



Fig. 1 Uranium metal rods.



Fig. 2 Physical property measurement system (PPMS) installed in the radiation-controlled area. PPMS can be used to measure heat capacity as well as AC and DC susceptibilities.

the synthetic study of molecular-based magnets including f inner-transition elements, i.e., actinides and lanthanides.

interplay The of ferromagnetism and superconductivity has been a central topic of condensed matter physics. Recently, we presented the first example in which superconductivity is induced by ferromagnetic spin fluctuations in the ferromagnet UCoGe [1-2], and we further suggested the possibility that a spontaneous vortex state emerges as a compromise of the two competitive orders; a vortex induced by spontaneous magnetization can exist even at zero external magnetic field (right panel of Fig. 3), in contrast to a regular type-II superconductor (left panel of Fig. 3).



Fig. 3 Schematic illustration of superconducting phase diagrams.

Lanthanide and actinide complexes were widely investigated as candidates for quantum nano magnets, such as a single-molecule magnet (SMM) or a single-chain magnet (SCM), in which each molecule shows superparamagnetic behavior below T_c . We have synthesized the first example of a structurally designed Er(III) SMM (Fig. 4 and Fig. 5) [3].

The fission and fusion reactor materials intensively investigated are (1) Zr–Nb binary alloy development for advanced nuclear fuel rods, (2) irradiation behavior of ferritic–martensitic steels for fusion first walls, (3) vanadium-based alloy development for fusion (collaborating with NIFS), and (4) microstructural evolution and mechanical property change in steels irradiated with highenergyions, performed at the Cyclotron Radioisotope Center (collaborating with School of Engineering).

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Fig. 4 Molecular structure of the Er(III)Zn(II)₃ wheelshaped tetranuclear complex generated on the basis of X-ray data. Green and yellow spheres represent Er(III) and Zn(II) ions, respectively. Er(III) ion is located in a nine-fold coordination, of which six equatorial oxygen donor atoms are represented as red spheres. This type of anisotropic coordination geometry is essential for Ising-type magnetic anisotropy for Er(III) ion.



Fig. 5 Temperature dependence of the out-of-phase component of the AC magnetic susceptibility (χ M") measured for various frequencies. Below 4 K, slow relaxation of the magnetization occurs and frequency-and temperature-dependent χ M" signals were observed, which is typical for single-molecule magnets.

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Determination of Released Trace Elements in Static Immersion Test for Characterization of Metallic Biomaterials

Analytical Research Core for Advanced Materials

Our research group conducts elemental analysis of various materials to determine major, minor, and trace levels of metallic and non-metallic elements. This report introduces the analysis of metallic biomaterials, one of our recent activities. The amounts of metallic ions released from the materials using static immersion into simulated body fluids (SBF) were determined. Sensitive and accurate determination of trace metallic elements in SBFs could be performed by inductively coupled plasma optical emission spectrometry (ICP-OES). By using a H₂SO₄-fume pre-treatment method, it was possible to determine concentrations of elements in SBFs on a ppb order.

Metallic biomaterials have been widely employed by orthopedists or dentists in clinical practice. Each of the metallic biomaterials has been applied to appropriate parts of the human body. However, when the metallic biomaterials are implanted for a long time, metallic elements may be dissolved into the surrounding tissues. The resulting toxic influence of metals released from metallic implants has been demonstrated [1, 2]. It has been recently reported that not only allergies but also several medical disorders have been caused by these metallic elements. Allergy responses are especially sensitive to trace amounts of the metallic elements. Accordingly, metallic biomaterials that have high corrosion resistance (high safety for the human body and low metal release) are required; therefore, the evaluation of corrosion resistance is important for their development.

The corrosion resistance of metallic biomaterials is evaluated by using static immersion into a simulated body fluid (SBF) and then assessing the metallic ions in the SBFs. Therefore, trace metallic elements in the SBFs should be noted when investigating the properties of the metallic biomaterials. Moreover, in order to evaluate the trace elements released by the static immersion test, it is necessary to determine µg L⁻¹ (ppb) levels of trace metallic elements in the SBFs. The concentrations of various elements in SBF solution samples have been determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Fig. 1), inductively coupled plasma mass spectrometry (ICP-MS, Fig. 2) and atomic absorption spectrometry (AAS, Fig. 3) [3, 4].

ICP-OES has analytical advantages, such as the simultaneous determination of elements with a wide dynamic range. However, the operating conditions of the ICP are influenced by the matrix elements included in a sample solution [5, 6] or the viscosity of the solution. SBFs include a large amount of alkali metal salts (NaCl, KCl, etc.) and/or organic compounds (glucose, amino acids, etc.)



Fig. 1 Echelle-type inductively coupled plasma optical emission spectrometer.



Fig.2 Double focused inductively coupled plasma mass spectrometer.

and have a high viscosity. This could alter the signal intensities of the analytes, and thus it is difficult to obtain precise and accurate results in the analysis of elements in the SBFs. Accordingly, it is vital to select an optimal sample pre-treatment method before analysis of the elements using ICP-OES.

In order to develop a simple and easy procedure for high-sensitivity, precise, and accurate

determinations of trace metallic elements in the SBFs by ICP-OES, we investigated a H₂SO₄-fume pre-treatment method [7 - 9]. By using this method, the viscosity of a sample solution can be decreased and the solution can be stabilized in acidic condition. Moreover, the organic compounds contained in the SBFs can be removed. Thus, it is possible to determine the concentrations of elements in the SBFs to a ppb level

SBFs include high concentrations of salts, such as NaCl, KCl, and several alkali or alkaline earth metals. The authors investigated the influences of these matrix elements on measurements by ICP-OES. Solutions containing analytes (2 mg L⁻¹) and NaCl (8 g L-1) were prepared, and the emission intensities of the analyte elements were measured by ICP-OES. Their intensities and intensity ratios (elements/Y) are shown in Fig. 4. Both the intensities and the intensity ratios are normalized to unity when containing no NaCl. When containing NaCl, the intensities for AI and Pd were more than 1, but the intensities for the other elements investigated were less than 1. The intensity ratios for Au, Ca, Cr, Ti, V, and Zn were nearly 1. In this case, an internal standard correction method by using Y can be applied for these elements; however, it is not effective for the other elements such Al and Pd. Na has a serious influence on the measurement of such elements by ICP-OES, and therefore, it is necessary to prepare matrix-matched standard solutions for calibration to ensure accurate determination.

We determined the elements released from SUS 316 or Ti–6Al–4V alloys by static immersion tests. These materials were respectively immersed into lactic acid in a PFA bottle at 310 K for 20 days in ambient atmosphere. After removing the materials, the elements released into the lactic acid were determined by ICP-OES with the H₂SO₄-fume treatment. It was possible to determine concentrations of the released elements at a ppb level by using the H₂SO₄-fume treatment method.

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Fig.3 Continuous-light-source atomic absorption spectrometer



Fig. 4 Intensity and intensity ratio of analyte elements by ICP-OES in 8 g dm⁻³ NaCl solution. Both the intensities and intensity ratios are normalized to unity when containing no NaCl.

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KINKEN Research Highlights 2012



Author Index

Name	page
Α	
Abe, Hiroaki	28
Ando, Kazuya	18
An, Liqiong	10
Aoki, Dai	52
Ashino, Tetsuya	80
В	
Bauer, FW. Gerrit	40
C	
Chiba, Akihiko	12
F	
Fujita, Masaki	56
Furuhara, Tadashi	72
<u> </u>	
G Coto Takashi	10
	10
н	
Hiraka, Haruhiro	20
1	
Ito, Akihiko	10
ĸ	
K Kato Hidemi	30
Kawamata Toru	6
Kodama Yumiko	36
Koizumi Harubiko	32
Koizumi, Yuichiro	12
Konno, J. Tovohiko	36
L	
Li, Yunping	12
М	
Makino, Akihiro	62
Masahashi, Naoya	66
Matsumoto, Hiroaki	12
Matsunaga, Tetsuya	28
Matsuo, Motoaki	34
Matsuoka, Takashi	48
Matsuta, Hideyuki	54
Matsuura, Masato	20
Miyamoto, Goro	4
Mizuseki Hiroshi	22
Ν	
Nagai, Yasuyoshi	24

Name	page
Niinomi, Mitsuo	8
Nojima, Tsutomu	76
Nojiri, Hiroyuki	42, 70
0	
Ohoyama, Kenji	20, 74
Orimo, Shin-ichi	34
S	
Sahara, Ryoji	68
Saitoh, Eiji	18
Sasaki, Takahiko	44
Sato, Kazuhisa	36
Sato, Toyoto	20
Satoh, Yuhki	28
Shikama, Tatsuo	26, 60
Shirasaki, Kenji	78
Sugiyama, Kazumasa	6
т	
Takanashi, Koki	50
Tokumoto, Yuki	46
U	
Uda, Satoshi	32
Usami, Noritaka	16
W	
Watanabe, Kazuo	64
х	
Xiao, Jiang	40
Xie, Guoqiang	14
Y	
Yamada, Kazuyoshi	20
Yamaura, Shin-ichi	38
Yoshikawa, Akira	58

Keyword Index

Keyword	page
Α	
actinide	52
alloy	8
amorphous	6, 38
atom probe tomography	24
R	
biomedical	8, 14
С	
ceramics	10, 26
clathrate hydrate	22
Co-Cr-Mo alloy	12
crystal growth	32, 58
D	
defects	44
diffraction	6
E	
electrical spin injection	40
electron microscopy	28
electron spin resonance	42
electronic properties	44
electronic structure	54
energy gap	48
energy storage	34
F	
ferromagnetic	52
film	46
foam	30
frustration	42
fuel cell	38
G	
graphitization	36
н	
hydride	34
hydrogen implantation	28
hydrogen storage	22
I	
insulator	40
ionic conductor	34
ion implantation	16
L	
luminescence	58

Keyword	page
М	
magnetic	40
magnetic properties	50
mechanical properties	12
metallic glass	14
micro-pulling-down method	58
microstructure	8, 10, 30
N	
nanocluster	42
neutron irradiation	26, 28
neutron scattering	20, 56
neutron scattering measurement	56
nitride	46, 48
novel magnetic materials	20
nuclear materials	24. 26
nucleation and growth	32
 0	
optical absorption	54
optical properties	48
organic	44
P	
phase diagram	22
phase equilibria	32
phase transformation	4, 12
plating	38
porosity	30
powder metallurgy	14
S	
SEM	36
semiconducting	16
sintering	10
solar cells	16
spin correlation	56
spin current	18
spin lattice dynamics	20
spintronics	18, 50
steel	4, 24
structure	6
superconducting	52
т	
TEM	36, 46
thin film	50

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