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 high-efficiency 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 $10^{18}$ 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 10^{16}–10^{20} cm^{-3}. On the other hand, the carrier concentration in p-type BaSi2 is still limited to the order of 10^{16}–10^{17} cm^{-3}. It is therefore desired to discover a p-type dopant that brings about a high carrier concentration of around 10^{18} cm^{-3} or more.

Boron is expected to be a p-type dopant, as is the case for the other group-III atoms Al 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, 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.

References

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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 impedance-mismatch problem; the impedance mismatch between ferromagnetic metals and high-resistivity materials drastically limits the spin-injection efficiency [2,3]. However, because of this problem, 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 a 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 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.

**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.**
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 used as a spin current detector.

References

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

Fig. 3 Observation of the inverse spin Hall effect in Si.
Novel Material Science Using Neutron Scattering

IMR 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 origative 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-Tc pairing formation. Mn3Si and Mn2.8Fe0.2Si are antiferromagnetic (AF) metals with TN 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 Q–ω 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.

The qualitative change upon ω in the magnetic 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 (Tc) superconductors has been argued, since the parent compounds of high-Tc 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 Tc is suppressed by the reduction in superconducting carriers. However, there exists no microscopic

![Fig. 1 Neutron intensity contours using a single crystal of Mn2.8Fe0.2Si measured by a chopper-type time-of-flight spectrometer. (a, b) Q-slices and (c) ω–Q slice.](image1)

![Fig. 2 A plot of E_comme versus Tc upon Ni-doping. The horizontal error bars represent broad superconducting transition, which is characteristic to Ni-doped high-Tc cuprates [ref 2-1].](image2)
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$_y$O$_4$ 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 ($\pi, \pi$) and finite energy $E_{\text{comm}}$. Fig 2 shows a plot of $E_{\text{comm}}$ vs $T_c$ upon Ni doping. With increasing Ni content, $T_c$ 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 $\Delta T_c$ determined from the shielding signal of the magnetic susceptibility measurement. We have clarified that $E_{\text{comm}}$ decreases in proportion to $T_c$. The linear relationship between $E_{\text{comm}}$ and $T_c$ explains the weak suppression of $T_c$ for Ni doping by reduction in the characteristic energy of spin fluctuations.

(M. Matsuura)

3) Vibrational Properties of Hydrogen Storage Materials

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 NaAlH$_4$ [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 ($82.02 \times 10^{-24} \text{ cm}^2$) 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 $\alpha$-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 bond-stretching modes at 1166–1534 cm$^{-1}$. However, the spectra of both CaAlH5 and $\alpha$-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 $\alpha$-AlH3 showed qualitatively similar INS spectra, the librational modes of AlH6 on $\alpha$-AlH3 exhibited higher frequencies than CaAlH5 because of tighter bonding between the AlH6 units.

(T. Sato)

References

Keywords: neutron scattering, spin lattice dynamics, novel magnetic materials
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Atomsitc 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 three-dimensional host structure where the molecules (guests) 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.

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 guest–guest interactions, especially when more than one guest molecule occupies a cage. We used the quasiharmonic 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 H2 + C3H8 [2], H2 + CH4 [3] and H2 + C2H6 [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 proposed 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].

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 + CH_4 and H_2 + C_2H_6 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 H_2–CH_4–H_2O and H_2–C_2H_6–H_2O systems with a small concentration of methane and ethane, respectively, as shown in Fig. 3.

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].

References

Keywords: clathrate hydrate, hydrogen storage, phase diagram
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Fig. 2 Pressure dependence of hydrogen storage capacity of pure CS-I and CS-II hydrates at T = 250 K.

Fig. 3 Pressure p(T) of monovariant equilibrium: gas phase of CH_4+H_2 – ice Ih – CH_4+H_2 CS-I (squares) and CS-II (circles) hydrates at 6% methane concentrations in the gas phase.
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 Fe-rich 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 the ferrite phase into Fe-rich 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.

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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.

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 as-received 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 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.

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.

References

Keywords: nuclear materials, steel, atom probe tomography
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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 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 \((n, \alpha)\) 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 \(5 \times 10^{20} \text{ H/m}^2\) 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](image1.png)

**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](image2.png)

**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 \((\text{Li}_2\text{TiO}_3)\); LAO: Lithium aluminate \((\text{LiAlO}_2)\)
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 $1 \times 10^{22}$ H/m$^2$. The elastic recoil detection (ERD) analysis by 2.8 MeV helium revealed that the hydrogen retention is about $5 \times 10^{20}$ H/m$^2$. Exposure up to $(3-6) \times 10^{23}$ H/m$^2$ 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, $\alpha$)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.

Ion 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 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.

References
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. Irradiation-induced 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 subjected to corrosion and hydrogenation 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 high-density hydride at the rim of the specimen at hydrogen absorption above 500 ppm. In-situ observations under 20 keV H\(^{+}\) 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.

Fig. 1 Microstructural evolutions in Zr–1.8Nb under irradiation with 20 keV H\(^{+}\) 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, slip-induced 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}.

References

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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 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. 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]
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 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.

References

Keywords: foam, porosity, microstructure
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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]
Control of Helmholtz Free Energy Relationship between Protein Polymorphs under an External AC Electric Field

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 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 control of the Helmholtz free energy relationship between protein polymorphs under an external AC electric field.

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 \( E \).
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 spherulite 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.

References
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 energy-related 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/xLiCl. The change in the activation energy due to the structural transition is observed at around 340 K for LiI with x = 0.13, whereas the conductivities for x = 0.25 exhibit 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 LiI 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 Cl⁻ or Br⁻ ions enhances the conductivity.

LiBH₄–LiNH₂ system [6]

As shown in Fig. 2, Li(BH₄)(NH₂) exhibits a fast-ionic conductivity of 1 × 10⁻⁴ S cm⁻¹ even at 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 × 10⁻² 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 × 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 Li₂(BH₄)(NH₂)₃ has higher Li⁺ ion mobility.

LiNH₂-LiI system [7]

Fig. 3 shows the ionic conductivities for x = 0.06, 0.13, and 0.25 of (1 - x)LiNH₂ + xLiI. For all values of x, the conductivities exhibit Arrhenius behavior throughout the measured temperature range. The maximum conductivity of 2 × 10⁻⁶ S cm⁻¹
at 300 K, which is four and three orders of magnitude higher than those of the host materials LiNH₂ and LiI, 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 \( \text{Li}_3(\text{NH}_2)_2\text{I} \) [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].

References

Keywords: hydride, ionic conductor, energy storage
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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 nickel- and/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 nickel-acetated wood charcoal carbonized at 900 °C consists of a crystal part, which looked like a ribbon-shaped 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 nickel-acetated wood charcoal and to elucidate the underlying mechanisms of the formation of a three-dimensionally extended GSC structure. We employed scanning electron microscopy (SEM), equipped with a scanning transmission electron microscopy (STEM) detector, to investigate 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.

![Fig. 1 Stereo pair of SEM image of wood carbon prepared with a metal catalyst, showing three-dimensionally entangled graphite shell units.](image-url)
morphological changes, and we used high-resolution TEM for observations at the atomic scale.

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 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 2b and 2c 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.

References
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 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 amorphous alloy-coated bipolar plate produced by electroplating. 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.

Fig. 4 shows the 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 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 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 alloy-coated bipolar plates were produced by electrochemical plating. The potential of amorphous alloy-coated bipolar plates produced by electroplating was successfully shown in this work.

**References**


Keywords: fuel cell, amorphous, plating
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