Magnetic Manipulation of Polymeric Nanostructures

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Polymersomes are bilayer vesicles self-assembled from amphiphilic block copolymers. They are ideal and versatile nano-objects since they have many adjustable properties such as their flexibility, permeability and functionality, which can be used as nano-containers and nanomotors for nanochemistry and drug delivery [1, 2]. We have recently developed a polymersome system using poly(ethylene glycol)-polystyrene (PEG-PS) block copolymers. PEG-PS polymersomes have the advantage that their flexibility can be controlled by the contents of organic solvents like THF and dioxane, which act as a plasticizer on the polystyrene membrane. It also allows flexible polymersomes to be fixed by adding an excess of water.

For many applications, the shape of a polymersome is very important since shape and functionality are closely related. In this talk an overview will be given of our efforts to control the shape of polymersomes by application of osmotic and/or magnetic forces. It will be shown that high magnetic fields can be used in two different ways: either to probe the polymersome shape using magnetic alignment or to modify the shape by magnetic deformation.

We have investigated two different methods in which an osmotic pressure is used to change the polymersome shape. The first method involves dialysis of spherical polymersomes in water against a mixture of water, THF and dioxane [3]. The second method involves equilibration of spherical polymersomes which are prepared by out-of-equilibrium self-assembly [4]. The shape changes that occurred were probed \textit{in situ} using a magnetic birefringence setup that measures magnetic orientation of polymersomes in solution [3-5]. For both methods the magnetic birefringence measured at relatively low magnetic fields (2 T) is sufficient to discriminate between the different polymersome shapes as determined by electron microscopy. It was observed that the spherical polymersomes first deflate into discs, which subsequently fold into bowl-shapes vesicles (so-called stomatocytes), which then started to inflate again while maintaining a stomatocyte shape (Fig. 1b). Our experiments demonstrate that osmotic pressure determines the final reduced volume after deflation, whereas the bending energy of the polymersome membrane determines the shape at each volume.

Although a field of 2 T is enough to probe shape changes in polymersomes, the magnetic alignment at this field is still far from saturation. Therefore, we also performed magnetic alignment experiments on \textit{rigid} polymersomes of several different shapes in high magnetic fields up to 29 tesla. We observed saturation of disc-shaped polymersomes, partial alignment of stomatocytes and no alignment of spherical-shaped...
polymersomes. These detailed experiments provide a means to accurately determine the anisotropy in the magnetic susceptibility of the PEG-PS polymer chains in the bilayer membrane.

High magnetic field experiments on flexible polymersomes demonstrate the possibility to deform polymersomes, since not only the polymersomes themselves but also the polymers within the polymersome align [5]. This method enables to reversibly open and close the mouth of stomatocyte by applying a magnetic field, allowing to capture and release cargo at will, which paves the way to a novel magnetically controlled drug delivery concept.

Birefringence of Nanocomposite Gels polymerized in a Magnetic Field

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Nanocomposite gel (NC gel) is obtained by adding clay in the polymerization process of poly(N-isopropylacrylamide) (PNIPA) [1],[2]. Clay in NC gel is uniformly dispersed and work as closslinking points. This NC gel is one of the gels which shows the excellent mechanical properties. Generally, clay in an aqueous dispersion is randomly oriented by Brownian motion, resulting in formation of isotropic NC gel. We have reported at previously workshop [3] that anisotropy can be given in NC gel when the NC gel is polymerized in a magnetic field. However the origin of the birefringence of NC gel is not clarified yet. In this study, we carried out in-situ observation of the birefringence of clay dispersion containing monomer of PNIPA in a magnetic field in order to clarify the origin of birefringence of NC-gel.

We manufactured the equipment for in-situ measurement of birefringence in a magnetic field. This equipment shows us change of birefringence as change of interference color. The interference color is captured by personal computer as a movie in this equipment.

The interference color of the clay dispersion showed slightly blue shit in the magnetic field. This means the clay dispersion in the magnetic field shows positive birefringence. This result strongly suggests that clay was aligned by magnetic torque under the magnetic field. Previous paper reported that magnetization easy axis of clay is perpendicular direction of c-axis of clay [4]. This is consistent with our birefringence result for the clay dispersion.

While the interference color of the clay dispersion containing the monomer of PNIPA showed yellow shit in the magnetic field. This means the clay dispersion containing the monomer in the magnetic field shows negative birefringence. This is consistent with our birefringence of NC gel polymerized in the magnetic field. Therefore, the birefringence of NC gel polymerized in the magnetic field could originate in PNIPA adsorbed at clay surface oriented by a magnetic torque.

【References】
Molecular self-assembly of block copolymers and small molecule surfactants gives rise to a rich phase behavior as a function of temperature, composition, and other variables. The ability to precisely control their chemical functionality combined with the readily tunable characteristic length scales (~1-100 nm) of their self-assembled mesophases identifies these systems as a versatile and attractive class of materials for compelling applications ranging from selective transport to lithography. A longstanding problem in this area is the inability to reliably and rapidly generate well-ordered structures with specified orientations in, and over, application-relevant geometries, and dimensions, respectively, i.e. to direct their self-assembly in useful ways. In this presentation I will discuss recent advances in scalable approaches for directing the assembly of soft nanostructured materials, and novel routes for generating highly ordered soft heterostructures.

We consider the directed self-assembly of such soft mesophases using magnetic fields, principally through the use of in situ x-ray scattering studies. Field alignment is predicated on a sufficiently large product of magnetic anisotropy and grain size to produce magnetostatic interactions which are substantial relative to thermal forces. We examine the role of field strength on the phase behavior and alignment dynamics of a series of soft mesophases. Directed self-assembly in the block copolymers considered proceeds by nucleation of randomly aligned grains which thereafter rotate into registry with the field, rather than by selective nucleation of aligned grains. This is consistent with estimates which show that magnetic fields as large as 10 T have little discernable impact on the phase behavior of systems considered, with shifts in order-disorder transition temperatures of 5 mK or smaller. We highlight the tradeoff between decreasing mobility and increasing anisotropic field interaction that dictates alignment kinetics while transiting from a high temperature disordered state to an ordered system at lower temperatures. We demonstrate that simple tuning of mesophase composition enables field alignment at sub-1T field strengths, opening up new possibilities for low cost field processing and local morphology control by field screening using magnetic nanoparticles. The ability to produce highly ordered functional materials over macroscopic length scales is demonstrated and we explore the role of alignment and connectivity in controlling anisotropic ionic transport in nanostructured systems.
Tailored microstructure in ceramics is important for improving their properties. Especially, crystallographic orientation is expected to be effective way to utilize the anisotropic properties and to understand their properties as well, such as electric conductivity. In general, the textured ceramics can be produced by the templated grain growth, hot forge. In this decade, we have reported that the crystalline orientation can be controlled even in diamagnetic ceramics by slip casting and electrophoretic deposition in a high magnetic field.

A crystal with an anisotropic magnetic susceptibility will rotate to an angle minimizing the system energy when placed in a magnetic field. The reduction of the magnetic energy on the rotation is

\[
\Delta E = \frac{\Delta \chi V B^2}{2 \mu_0}
\]

where \(\Delta \chi\) is the difference of the magnetic susceptibility between each axis in the crystal, \(V\) is the volume of each particle, \(\mu_0\) is the permeability in a vacuum and \(B\) is the applied magnetic field. This is the driving force for magnetic alignment.

It is for this purpose that dispersion of powders in a suspension is necessary to effective work of a magnetic field, because large interaction between the agglomerated particles restrains the powder in a suspension from rotating by a magnetic field. Colloidal processing for particle dispersion was used in this study for developing for consolidating fine particles to avoid heterogeneous agglomerates by electrostatic repulsion due to surface charge.

In the case of \(\text{Al}_2\text{O}_3\), SiC and \(\text{LiCoO}_2\), the \(c\)-axis of hexagonal crystal structure aligned parallel to the magnetic field. The bending strength for the crack-growth direction parallel to the \(c\)-axis was higher than that perpendicular to the \(c\)-axis in both textured \(\text{Al}_2\text{O}_3\) and SiC. The thermal conductivity parallel to the \(c\)-axis was higher than that perpendicular to the \(c\)-axis in textured SiC.

In the case of AlN, ZnO and Si\(_3\)N\(_4\), we confirmed that the \(a\)-axis aligned parallel to the magnetic field. The rotating magnetic field was used to control the development of the \(c\)-axis orientation in order to improve the thermal conductivity. Figure 1 shows the \{0001\} pole figure in textured AlN prepared by the static magnetic field and the rotating magnetic field. The ring of high intensity was at its periphery in the specimen prepared by the static magnetic field, it indicated that the \(c\)-axis is radially symmetric on the in-plane perpendicular to the magnetic field. In contrast, a strong distribution of the \{0001\} only near the centre indicated that the
basal plane was oriented on RT plane, that is, the $c$-axis was aligned perpendicular to the rotating plane in the specimen prepared using the rotating magnetic field. Thermal conductivity of the $c$-axis oriented AlN was higher than that of the $a$-axis oriented AlN and the random AlN.

Fig. 1 0001 pole figure on VT plane perpendicular to the magnetic field and RT parallel to the rotating plane of magnetic field, respectively.

Fig. 2 Pole figure on T plane perpendicular to the slip casting direction in Bi$_4$Ti$_3$O$_{12}$ prepared by slip casting in a magnetic field with platelet particles.

If the orientation axes of platelet particles aligned due to a geometrical effect and a magnetic field are different, the multi-dimensional orientation can be controlled by simultaneous use of both the effects, and control of the elaborate microstructure will be expected. The {001} pole figure shows a very strong spot at the center, which indicates that the $c$-axis was aligned parallel to the casting direction. The {100} pole figure exhibits a couple of strong spots at the points of 90° from the center along the latitude line. The $<$100$>$ texture was aligned parallel to the magnetic field. Since the $c$-axis and the $<$100$>$ axis orientation can be simultaneously controlled.

Effect of Amorphous Region on Magnetic Orientation of Poly(lactic acid) Blend Films with Different Molecular Weight

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In a previous study, crystalline poly (L-lactide) (PLLA) / amorphous poly (DL-lactide) (PDLLA) blend films (PLLA/PDLLA films) were prepared in order to rotated PLLA crystals in magnetic field and thermal process. It was shown that amorphous regions play an important role in preparation of PLLA oriented films in an applied magnetic field [1].

In this study, the molecular weight dependence of PDLLA on magnetic orientation in blend films was studied by wide-angle X-ray diffraction (WAXD).

PLLA/PDLLA films were prepared as follows. PLLA \((M_w=1.0\times10^5): PLLa10\) and PDLLA \((M_w=1.0\times10^4): PDLa1, 1.0\times10^5: PDLa10\) chloroform solutions of conc.1.0wt% were prepared, respectively. These were mixed and stirred for 2hrs, and the solution was put in petri dish and was stood for 24hrs. PLLA/PDLLA films were dried at 70°C for 2hrs in vacuum oven. Preparation of PLLA/PDLLA oriented films in magnetic field carried out at Institute for Materials Research, Tohoku University. The PLLA/PDLLA films were annealed according to the following procedure. The films prepared were kept at 185°C for 10min. After that, the films were kept for 0, 2, 15hrs at 140°C, and then these were cooled down to room temperature. The magnetic field induced was started at heating of the film. The heating and cooling rate was 3°C/min. At this time, crystal melting temperature is 185°C and crystal growth temperature of PLLA is 140°C [2].

The crystalline orientation of the films was evaluated by WAXD measurement which the film was rotated by 360° at intervals of 30°. The degree of orientation \(f_0\) was defined as the azimuthal angle in \((200)/(110)\) reflection [3]. From a result of WAXD measurement, the c-axis of PLLA crystals had a tendency to orient the parallel to the magnetic field. In the case of PLLA10/PDLLA1 films, the \(f_0\) decreased because spherulites were formed when the isothermal crystallization time \(t_c\) was 15hrs. On the other hand, the case of PLLA10/PDLLA10 films, \(f_0\) increased with increasing \(t_c\) in thermal process. The maximum value of \(f_0\) was 65% when \(t_c\) was 15hrs. Therefore, PLLA10 inhibited the forming spherulites in thermal process.

It is suggest that the high molecular weight of PDLLA was effective for preparation of PLLA oriented films under magnetic field.

Selective Crystallization in Mn-based Alloys by In-field Heat Treatment

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In-field heat treatment for magnetic material realizes the improvement of their functions. The diffusion coefficient, phase equilibrium, crystal orientation and morphology can be control by the magnetic field application [1-3].

On the other hand, Mn-based ferromagnetic magnetic materials are known to have a large magnetic moment. In particular, MnBi and L10-Mn-Al have a large uniaxial magnetic anisotropy. However, it is difficult for both alloys to obtain a single ferromagnetic phase. Thus, many preparation methods have been performed for improving their magnetic properties so far. In-field heat treatment is suitable method for improving the magnetization of Mn-based ferromagnetic phase because ferromagnetic phase stabilizes in magnetic field. In this paper, the recent results of the in-field heat treatment effect for MnBi [4-6] and Mn-Al alloys are presented.

MnBi was prepared by in-field reaction sintering. Fig.1 shows the X-ray bulk diffraction pattern of the sample sintered at 523 K and 553 K in 15 T, which was solid- and liquid-phase reaction, respectively [6]. 00l diffraction was strongly detected in both patterns, resulting the uniaxial orientation. The obtained MnBi phases in the both samples were over 70wt.% [6], which indicated that the in-field reactive sintering was suitable method for obtaining high fraction and uniaxial-oriented MnBi phase.

The results of the magnetic field effects for the Mn-Al alloys will be shown in the presentation.

References:
In-Magnetic-Field Synthesis for Ferromagnetic Mn-Al Alloys

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τ-phase Mn-Al with tetragonal L1₀ structure has been paid attentions as a permanent magnet. Because τ-phase is not the equilibrium state, appearance of the non-ferromagnetic equilibrium states decreases the magnetization. Many preparation methods have been performed for improving the magnetic properties.

On the other hand, ferromagnetic phase stabilizes under the magnetic fields due to the gain of Zeeman energy. In-field heat treatment for ferromagnetic alloys has been performed so far [1-2]. Among them, in-field heat treatment for Mn-Al film was also reported. The heat treatment in 1.5 T realized the increase of magnetization [3]. However, in-field heat treatment effects for bulk Mn-Al are not investigated. In this study, for obtaining high fraction of τ-phase, in-field synthesis for Mn-Al alloys was performed under high magnetic fields up to 15 T.

Mn-Al alloys were obtained by induction melting. Rod-shaped sample was cut into disks with 2 mm thick. The samples were annealed at 1373 K for 1 day and quenched. All samples were confirmed to be ε-phase with hcp structure by X-ray diffraction (XRD) measurements. In-field heat-treatments of samples were performed at 573 and 623 K in 0 T and 15 T.

Fig. 1 shows XRD patterns of Mn-Al alloys annealed at 573 K in 0 T (a) and 15 T (b). In 0 T, diffraction peaks of residual ε-phase and equilibrium β-phase were strongly detected. Meanwhile, although ε-phase remained, diffraction peaks of τ-phase were clearly observed for the sample annealed in 15 T. Thus, it was found that in-field heat treatment for Mn-Al alloys improved the synthesis of ferromagnetic τ-phase.

References:

Fig. 1. Bulk X-ray diffraction patterns of Mn-Al alloys.
Time-temperature-transformation diagram under magnetic field in a Ni$_45$Co$_5$Mn$_{36.5}$In$_{13.5}$ magnetic shape memory alloy

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Kinetics of martensitic transformations (MTs) is one of the essential subjects in materials science. It is related to the nucleation and growth process, and influences the microstructure formed through the transformation. From the point of view of kinetics, MTs are frequently classified into two categories: athermal MTs and isothermal MTs. In a typical athermal MT, the fraction of the martensite phase depends on intensive variables such as temperature and magnetic field but not on time. In isothermal MTs, the fraction of the martensite phase depends on both intensive variables and time. However, we suggested that there is no clear distinction between athermal MTs and isothermal MTs through our many studies on kinetics of martensitic transformations. Then, in order to confirm the propriety of the suggestion we have investigated a Heusler-type Ni-Mn-In alloy because the sign of isothermal nature was reported by Sharma et al [1] in a Ni$_{50}$Mn$_{34}$In$_{16}$ alloy, and by Ito et al [2] in Ni$_{50}$Co$_5$Mn$_{36.7}$In$_{13.3}$ alloy. In this study, we systematically investigated isothermal nature of MT in a Ni$_{50}$Co$_5$Mn$_{36.5}$In$_{13.5}$ alloy by applying magnetic fields.

The martensitic transformation start temperature $M_s$ of Ni$_{50}$Co$_5$Mn$_{36.5}$In$_{13.5}$ alloy is about 220K under zero magnetic field. It decreases gradually with increasing applied magnetic field up to 1.5 T, and $M_s$ vanishes under 2 T. Under this magnetic field, we found that the MT shows a clear C-curve in the TTT diagram as shown in Fig. 1 [3]. Using a thermal activation model for the nucleation of martensite [4], we calculated the TTT diagram for various magnetic field strengths and the calculated curve well reproduces the experimentally obtained one (dotted curves in Fig. 1). Through the analysis, we estimated the size of the thermally activated cluster, which may be regarded as the nuclei of martensite, to be (5 nm)$^3$. The size is the same order as those reported previously in other alloys such as Fe-Ni and Ti-Ni alloys.

Magnetic field effects on phase transformation of an ionic liquid, 
\(N,N,N\)-trimethylpropylammonium tetrasulfonylimide

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Ionic liquids (ILs) have melting point around room temperature because the interactions between their bulky and asymmetric ions will be weak. It is well known that ILs have unique phase behavior, such as premelting and excessive supercooling. We reported an electric potential generated between liquid and solid phases of one of ILs, \(N,N,N\)-trimethylpropylammonium tetrasulfonylimide (TMPA TFSI). Recently we also reported an electric potential induced by magnetic field \(H\) applied to liquid of TMPA TFSI at constant temperature. This phenomenon suggests that magnetic fields may induce a phase transformation of TMPA TFSI, interface formation in it, etc. In this paper we investigated other methods such as spectroscopic, thermal, and magnetic analyses in order to detect the phenomenon.

Raman spectra were measured in situ with an Ocean Optics QE65000 under various magnetic fields. An IL sample was poured into a quartz cell set in a cell-holder, which was held in a temperature-controlled bore in a JASTEC JMTD-6T150E1 superconducting magnet. Differential scanning calorimetry (DSC) was measured by a customized RIGAKU DSC8230 with a non-magnetic cell system under magnetic fields. Magnetization \(M\) of ILs was measured with VSM method as a function of \(H\) at constant temperature by a Quantum Design MPMS3 SQUID magnetometer. The IL sample was capsuled in a polycarbonate cell.

Applying magnetic fields changed Raman spectra of TMPA TFSI. A peak at around 700 cm\(^{-1}\) increased and another peak at around 3000 cm\(^{-1}\) decreased with increasing magnetic field. Though no significant DSC peaks appeared while scanning magnetic field, a faint difference in the slope of the \(M-H\) line was detected at around 3 T. The magnetic susceptibility change seems to be consistent with the appearance of the electric potential in the region of 3 T. These changes may arise from structural changes associated with magnetic as well as electrical properties.

![Fig.1 M-H plots of TMPA TFSI measured at each temperature.](image-url)
Characterization of liquid-liquid structure transition by in-situ magnetization measurement

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In the past few decades, the liquid-liquid structure transition (LLST) has aroused much attention and obtained many research products in the fields of physics, chemistry and material science, which enriches the phenomenology in liquid physics and has reference significance to explore the structure and property of liquid materials [1].

In this study, the in-situ magnetization measurement is introduced as a powerful and convenient method to investigate the liquid-liquid structure transition in a wide temperature range from highly overheated state to deep supercooled state. The structure variation in the liquids is expressed by the slope variations in the in-situ measured magnetization or inversed magnetization curve. Within this method the structure transition inside Co-Sn and Co-B eutectic melt were studied. The time cumulative effect and reversibility of the structure transition were also analyzed.

KEY WORDS: Liquid-liquid structure transition; nucleation; magnetization

The effects of strong static magnetic fields on mammalian cells

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Magnetic resonance imaging (MRI) is used in many hospitals as a non-invasive diagnostic tool. A strong static magnetic field (SMF) is one of the key components of MRI. Since patients are directly exposed to the strong SMF during MRI diagnosis, the effects of exposure to a strong SMF on biological systems have been discussed. However, information on the effects of SMFs, especially strong SMFs, on biological systems is still lacking [1].

We would first introduce that a strong SMF or a high SMF gradient induced the orientation of myotubes formed from a mouse derived myoblast cell line, C2C12. The exact mechanism(s) underlying the SMF-induced myotube orientation have not yet been clarified. However, we speculated that the effects of SMF on cell migration were thought to be a key phenomenon underlying their orientation.

Next, we would show the results of the investigation of the effects of a SMF on cell migration. In our body, migration has close relation to malignant neoplasms, which are major causes of death in most developed countries. The majority of the mortality from malignancies is due to metastases. As the first step in the metastasis process, cancer cells digest the cellular matrix around the cells and invade into blood vessels. Based on these, we investigated the possibility that a strong SMF or a high SMF gradient may affect cancer cell migration, which means the ability of cells to migrate, and cell invasion, the ability of the cells to digest the cellular matrix and then migrate, using a human-derived malignant glioblastoma cell line, A172.

A superconducting magnet, JMTD-10C13E-NC (Japan Superconductor Technology, Inc., Kobe, Japan)-based exposure device, which was reported previously [2], was used in this study. The temperature was maintained at 37°C during exposure. The maximum magnetic flux density of the device was 13 T. The maximum value of the device of the product of the magnetic flux density and the magnetic gradient was 585 T²/m.

A unique extracting technique has been developed for recycling the Ni-bearing compound from the waste fluid of the electroless Ni-plating processes. The plating waste still contains the Ni ions with high concentration even after the several plating cycles. The magnetic separation experiments were conducted to collect the precipitates bearing Ni compounds. After forming the fine NiHPO$_4$ precipitate from the waste, the coarse NiSO$_4$ crystals were synthesized through the reaction with the concentrated sulfuric acid [1]. The open-gradient magnetic separation was employed to extract the NiSO$_4$ crystals from the mixed slurry composed of these compounds due to the difference between their magnetic properties. The experiments were practically conducted with use of the Gd123-based HTS bulk magnets with very steep gradient of magnetic field over 133 T/m, which were activated by the field cooling magnetization process operated at 35 K. The ratio of NiSO$_4$ content in the slurry attracted to the 3-T magnetic pole generating has reached up to 85.7%, as shown in the figure. This preferential collection suggests that one can complete the recycling system of Ni resource as a raw material in the plating processes.

Fig. Ratios of NiSO$_4$ content in the slurry which was attracted to the magnetic pole.

We are developing a magnetic separation system to remove scale from boiler feed water in thermal power plants with a superconducting magnet.

Reduction of CO$_2$ is an important issue to prevent global warming. Deposition of scale in plants degenerates energy conversion efficiency of thermal power plants and increase discharged CO$_2$. If we can reduce 20 $\mu$m of the thickness of scale on boiler wall, we may get a 1% improvement in heat exchange efficiency of boiler and reduce 4.5 million t CO$_2$/year in Japan.

Scale consists of iron oxides. Iron is transferred from walls of pipes and devices to boiler feed water at low temperature (~ room temperature) and flows to the boiler. When temperature of water $>$ 200$^\circ$C, most of irons form magnetite (Fe$_3$O$_4$) and deposits on walls of pipes. We expect to install the developing magnetic separation system near boiler.

We expect that the system is required to treat 2000 m$^3$/h of feed water (in case of 600 MW thermal power plants) and run in 200$^\circ$C and 20 atm. with low pressure loss. We adopt the high gradient magnetic separation that consists of a superconducting magnet and matrix. Feed water flows in a bore 1 m in diameter in the superconducting magnet and the matrix is located in the water. The matrix is constructed by metal wire sheets which are magnetized by the magnet and extract magnetite particles from feed water by the magnetic force.

We are studying optimum conditions of the system by numerical simulation and experiments. Both study show that the system can remove most of scale and is more effective at 200$^\circ$C than at room temperature. Because the kinematic viscosity of water at 200$^\circ$C is 1/8 of that at 20$^\circ$C, drag force, that interrupts magnetic particles to be attracted to magnetized wires, is weaker and capture efficiency is larger at 200$^\circ$C than 20$^\circ$C. Numerical analysis shows that the most upstream metal sheets or first sheets capture them, and downstream
sheets do not work in a matrix. This suggests that the flow is obstructed by accumulated scale on the first sheets in a short time and the cleanup cycle is short.

After inquiring the matrix structure and other conditions, we obtained some plans of suitable magnetic separation system to boiler feed water. In our paper we present them, including matrix structures, superconducting magnet, operating procedure.

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Using magnetic fields to decipher novel quantum states and manipulate spin in presence of strong spin-orbit coupling

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Study of the combined effects of strong electronic correlations with spin-orbit coupling (SOC) represents a central issue in quantum materials research. Predicting emergent properties represents a huge theoretical problem since the presence of SOC implies that the spin is not a good quantum number. Existing theories propose the emergence of a multitude of exotic quantum phases, distinguishable by either local point symmetry breaking or local spin expectation values, even in materials with simple cubic crystal structure such as Ba2NaOsO6. Experimental tests of such theories by local probes are highly sought for. In this talk, I will discussed our local measurements designed to concurrently probe spin and orbital/lattice degrees of freedom of Ba2NaOsO6. In particular, I will describe how strength and orientation of magnetic field are used to decipher role of spin and lattice in establishing novel magnetic quantum states in Mott insulators with strong spin-orbit interactions. Furthermore, unique ways to manipulate electronic spin in materials where spin is not a good quantum number due to strong coupling of spin and orbital degrees of freedom, will be presented.
Studies of spinning and charged droplets using diamagnetic levitation

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We review recent experiments, undertaken at the University of Nottingham, UK, to study the shapes and stability of cm-scale spinning liquid droplets, using diamagnetic levitation [1-3].

The problem of the equilibrium shapes and stability of a spinning and charged droplet spans many fields of science. In physics, it unites the theory of nuclear fission, through Bohr and Wheeler’s liquid droplet model, with the theory of the shapes of celestial bodies determined by the competing influences of gravitation and rotation [4]. In chemistry, it is directly relevant to electrospray applications. In geology, it is at the heart of the study of tektites - stones formed in high-energy meteorite impacts. All these applications continue to spur experimental and theoretical research on this problem. Although the accuracy of numerical models of spinning droplets has improved with increases in computing power, experimental measurements are still necessary, and have produced some surprises. We present the results of experiments in manufacturing solid wax forms of the equilibrium shapes of a spinning liquid droplet, using diamagnetic levitation. These wax models imitate the curious shapes of tektites found in the field and can be used to validate numerical models of these objects. We also discuss recent experiments to study the shapes of spinning and charged droplets and, in particular, the effect of electric charge on the mode of fission of a spinning droplet.

Figure 1. a) Wax models of the equilibrium shapes of a spinning droplet, produced using magnetic levitation; from [1]. b) Three-lobed shape of a spinning levitating water droplet, from [3]. c) A charged and spinning levitated ethanol droplet undergoing fission.

Magnetic Levitation as a Portable Platform for Density-Based Analysis, Separations, and Self-Assembly

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This presentation will describe a portable system for magnetic levitation (MagLev) that enables density-based analysis, separations, and self-assembly of objects in 3D. The system comprises two permanent NdFeB magnets, and a container filled with a paramagnetic fluid positioned between the two magnets. Placement of objects into the container enables a simple approach towards MagLev. This presentation will discuss the application of MagLev towards monitoring of chemical reactions on solid supports, detection of protein-ligand interactions, separation of crystal polymorphs, forensic analysis of gun powders, and self-assembly of objects in 3D.
Bulk $\beta$-FeSi$_2$ crystal with three-dimensional alignment produced by an oscillating magnetic field

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Intermetallic compound $\beta$-FeSi$_2$ (orthorhombic structure) has received considerable attention because of its high potential as optoelectronic and thermoelectric materials. The single crystals are desired for evaluating intrinsic physical properties and for improving material performance. However, it is difficult to produce a single crystal, because $\beta$-FeSi$_2$ is produced through the peritectoid reaction (the solid state reaction). Thus, it is of interest to fabricate bulk $\beta$-FeSi$_2$ compound with the crystallographic alignment.

An application of high static magnetic fields is to fabricate crystallographically-aligned materials (materials with textured structure) using the magnetic anisotropy. Para- and diamagnetic materials with lower crystal symmetries (i.e. tetragonal, orthorhombic and so on) are candidates for the higher-order alignment due to the magnetic anisotropy. Especially, the three-dimensional alignment has paid much attention [1-3], because the alignment allows us to fabricate pseudo single crystals.

Figure 1 shows a proposed processing for the three-dimensional alignment. This study focuses the alignment, sintering and annealing for fabricating bulk crystals. As shown in Fig. 2, the three-dimensional alignment was obtained in the sintered specimens. The apparent density was as high as 96% for the specimen sintered for 160h. This paper demonstrates the processing and discuss problems for further development.

Fabrication of symmetrically graded microstructures by solidification under high magnetic field gradients

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It is important to control the distribution of the microstructure during solidification process, because it plays a key role in the final performances of materials. Recently, the application of high magnetic field to the preparation of materials has been paid much attention because of the possibility of in situ controlling the microstructure. It is believed that magnetic force can even drive alloying element enriched zones or particles towards the direction of the force if the value of the magnetic flux and its gradient, $B dB/dz$, is large enough. In previous studies, it was confirmed that Archimedes magnetic forces can drive the magnetic phase particles migration in the high temperature melt [1]. Thus, magnetic functionally graded materials that primary phase dendrites or particles gradient distributed along the magnetic field direction were fabricated directly in situ using solidification and semi-solid forming processes under high magnetic field gradient conditions [2,3]. While the above reported methods only applied unidirectional magnetic field gradient, and the performance of the functionally graded materials prepared by the above methods only monotonically increased or decreased in one direction. Therefore, rational design of the magnetic field distribution, it will be possible to realize the fine adjustment of the gradient structure, allowing prepare functionally graded materials with performance that varies more complex with location.

The present work describes a novel method for manufacturing symmetrically magnetic functionally graded materials by solidification and semi-solid forming processes in high magnetic field gradients. MnSb/Sb-MnSb composite materials, with a symmetrically graded structure in both morphology and composition, were fabricated directly in situ under symmetrically distributed high magnetic field gradient conditions. When a magnetic field was not applied, the primary MnSb phase of the alloy had a dendritic or granular morphology after the melt-out isothermal treatment or the semi-solid isothermal annealing treatment, respectively. The saturation magnetization of the samples was changed slightly along the top of the specimen to the bottom by the above processing methods, as shown in Fig.1. After applying a symmetric gradient high magnetic field, the generated positive and negative Archimedes magnetic forces caused the distribution of primary MnSb dendrites or particles of the alloy increases first and then decreases along the vertical axis of the sample. This is formed symmetrical gradient distribution along the middle of the sample. Therefore, the saturation magnetization of the Mn-89.7wt.%Sb alloy samples solidified and semi-solidly isothermally annealed under the symmetrical magnetic field gradient also increased and then decreased along the vertical axis of the sample, as shown in Fig.1. This symmetrically distributed saturation magnetization was caused by the Archimedes magnetic forces driving the Mn enriched zones or the MnSb particles towards the center of the specimen.
Fig. 1 The saturation magnetization distribution of Mn-89.7wt%Sb alloy: (a) solidified with and without a symmetrical distribution gradient magnetic field, (b) semi-solid treated with and without a symmetrical distribution gradient magnetic field.

Reference
Doping and Magnetic Field Effects on the Properties of Electrodeposited Metal Oxides

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While magnetoelectrodeposition has been an active area of research for twenty years, the study of magnetic effects on oxide deposition is more recent [1-2]. Despite the limited number of works on the electrodeposition of oxides under magnetic field, several papers emphasize the interest of magnetic field superimposition on the oxide properties [3-4]. In this work, an overview of such interest is given after a brief presentation of the different methods of electrochemical deposition of oxides, which include redox change, base or acid generation. Then, our recent results on doped oxide are presented in particular the challenge of tuning morphology. Deposits in the form of crystallites or films were synthesized on indium tin oxide (ITO) covered glass substrates. We focused on undoped and doped cuprous oxide and zinc oxide which have significant attracted interest due to their various potential applications in electronic devices by combining electronic and magnetic functionality. Defect ferromagnetism in dilute magnetic oxides can depend on preparation mode and magnetoelectrodeposition may offer new industrial opportunities. The influence of synthesis parameters has been investigated, in particular the composition and pH of the electrolyte, the electrochemical conditions and the magnetic field amplitude. The results revealed, for both oxides, interesting effects related to the type of dopant (Mn, Co), the doping level, as well as the magnetic field, especially in terms of morphology, crystallography, and therefore optical or magnetic properties.


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Magnetic Field Effects on Crystallization of Dendrite Ice

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Magnetic field effects (MFEs) on crystallization have been studied in two decades since a superconducting magnet was used widely.[1] In general a crystal is made from its melt for a metal or the saturated solution for a molecular crystal. The driving force to crystallize is the supersaturation and supercooling. The liquid-liquid interfacial precipitation (LLIP) method is a crystallization technique from the solution. Where, two solvents were used to make an interface between them. The crystal was precipitated on the 2-dimensional interface. MFEs on the size and the morphology were found for the crystal of C60 fullerene, Taurine, Glycine etc.[2-4] The mechanism of the MFE was not fully understood at the moment, however, it was considered that the three mechanical forces were influenced to change the crystal size and the morphology: (1) a magnetic torque controlled the posture of the growing crystal in the 2-dimensional reaction field, (2) Faraday force (magnetic force) against the gravity controlled the precipitation speed and the reaction duration, and (3) Lorentz force controlled the diffusion and the degree of supersaturation. No papers were reported for ice so far although the same MFEs are expected for other materials, however. In the present work, an ice crystal was precipitated by the LLIP method and the MFE was studied for the dendrite ice under the influence of a magnetic field with/without gradient magnetic field.

In the experiment, the solute was water to make ice crystal. Toluene of 1.0 mL as a poor solvent was put into a glass made reactor with 10 mm diameter. The aqueous solution of 1.0 mL with 1-butanol (93 wt.%) was stacked gently on the poor solvent to make the liquid-liquid interface. The ice was crystallized for a few hours at −15°C under the influence and absence of the horizontal magnetic fields. The horizontal magnetic field of 7.0 T or the gradient magnetic field of 345 T²/m was applied. The behavior of the ice crystal growth was observed in situ by a CCD camera.

Fig. 1 (a) showed the ice crystal made by the LLIP in zero magnetic fields. The dendrite ice was observed at around the initial height of the interface. The trunks grew uniformly from the wall surface to the center of the reactor. The fractal growth was observed for many short branches, which grew not incline but horizontally. The random orientation of the trunks and branches were recognized. Fig. 1 (b) showed the dendrite ice made under the horizontal magnetic field with the gradient. The magnetic field was applied by the direction from the right hand to left hand, and the magnetic center situated to the left. The dendrites grew from only the wall of the right hand side. That is, the trunks tended to align to the magnetic flux. The mechanism of the magnetic alignment was considered as follows. The seed crystal of ice was born on all the wall, however the diamagnetic seed was moved toward the low magnetic field of the left hand direction by the magnetic force in gradient magnetic field. Consequently, the trunks of the
dendrite ice took root mainly on the right hand wall. Fig. 1 (c) showed the dendrite ice made under the horizontal homogeneous magnetic field at the center of the magnet bore. The direction of the magnetic field was the same to Fig. 1 (b). The dendrites grew from the right and left sides of the wall. The tendency of the alignment of the trunks was the same to the case of (b). Magnetic force was estimated to be weak at around the center of the magnet because the magnetic force was negligible small in this case. Therefore another mechanism to explain the growth pattern of the dendrite ice was considerable.

![Fig. 1. Dendrite crystals of ice prepared by LLIP method in the reactor with 10 mm diameter under the absence and the influence of the horizontal magnetic fields.](image)

(a) No magnetic fields  
\[ B = 0, \frac{dB}{dz} = 0 \]

(b) Horizontal gradient field  
\[ B = 7.0 \text{ T}, \frac{dB}{dx} = 345 \text{ T}^2/\text{m} \]

(c) Horizontal homogeneous field  
\[ B = 7.0 \text{ T}, \frac{dB}{dx} = 0 \]

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New Possibilities for Ultra-high Field Superconducting Magnets

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Two recent NRC reports, COHMAG (2004) [1] and MagSci (2013) [2] have described the scientific and technology rationales for many new types of ultra-high field (UHF) magnet: msec 150 T pulsed, pulsed 40 T for neutron or x-ray scattering, regional 32 T superconducting (SC), 40 T SC, 28 – 37 T high-resolution NMR, 25 – 40 T SC for x-rays and neutrons, 60 T DC, 20 T human MRI, as well as magnets for fusion, particle-accelerators, radiotherapy, axion and other particle detectors. The materials and magnet technology have now made sufficient progress that a few of these magnets are now feasible.

A vigorous materials, conductor and small magnet development program has occurred at the MagLab in the last 10 years and magnet applications of REBCO (REBa$_2$Cu$_3$O$_y$-$\delta$) coated conductors, Bi-2212 (Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$-$\delta$) and Bi-2223 ((Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$-$\delta$) are all underway. Small insert test coils (made by insertion into our 31 T, 50 mm bore resistive magnet) achieving 34 T with insulated round wire Bi-2212 [3], 35 T with insulated layer wound REBCO were achieved in 2011 and 2013 and most recently in April 2016, 40 T with a pancake-wound No Insulation (NI) REBCO coil. An all-superconducting magnet designed for 32 T (15 T Nb and 17 T REBCO) in a 32 mm cold bore designed is in final assembly and should be available for MagLab users by early fall [4]. I will describe this progress and the various pluses and minuses of the three present HTS conductor types and suggest some timelines under which high field coils beyond the capabilities of the Nb-Ti and Nb$_3$Sn magnets that many of you have might start to make it into commercial fabrication.

Work carried out with many collaborators at the MagLab, especially with programs led by Huub Weijers, Denis Markiewicz (32 T), Ulf Trociewitz (Bi-2212 coils), Seungyong Hahn (NI REBCO), Arno Godeke and Scott Marshall (Bi-2223), Eric Hellstrom, Jianyi Jiang, and Fumitake Kametani (Bi-2212), and Dmytro Abramov and Jan Jaroszynski REBCO


Carbon materials have been used for our lives, therefore, their properties have been improved. If we can control microscopic or macroscopic structures of carbons by external fields, it will give much more possibility for processing carbon materials. We expect that it lead special properties. Previously, we reported magnetic field effects on carbon materials prepared from coal tar pitch, which was explained by the magnetic orientation due to large benzene ring-derived conjugated domain. Orientation is caused by passage of the meso-phase, and appearance of this phenomena hugely depend on amount of hydrocarbons of low-molecular weight. In order to enhance this magnetic orientation, we prepared carbon materials from anthracene with changing the amount of low-molecular weight.

Samples were prepared with a self-constructed electric furnace system, which generates the high temperature of up to 1523 K in the bore of a superconducting magnet. Anthracene pitch, prepared from anthracene containing 5 % AlCl₃ under 503, 523, 543 K, was carbonized at 793 K in N₂ atmosphere. We refer to them as AnP503/793, AnP523/793, and AnP543/793, respectively. Coal tar pitch was also carbonized under same condition, which is called CP/793. Magnetic field of 10 T was applied only to carbonization process. Magnetic orientation of prepared carbon materials were measured by polarizing microscopy.

Fig. 1 shows polarizing microscopic images of AnP503/793, AnP523/793, AnP543/793, and CP/793. All of them prepared at 0 T had a marble pattern indicating an optical isotropic structure. 10 T samples had bright images suggesting optical anisotropic structure. Deflection angles written in each figure under 10 T were larger than those in 0 T. Since AnP543/793 had a maximum value of deflection angle, we will discuss about configured molecules in carbon materials.
Innovative low magnetic field orientation process using multilayered-graphene-coated $\beta$-Si$_3$N$_4$ seed particles to fabricate $c$-axis oriented Si$_3$N$_4$ ceramics

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Introduction

Silicon nitride (Si$_3$N$_4$) exhibits promising intrinsic thermal and mechanical properties. Si$_3$N$_4$ is expected to be applied as a substrate in silicon carbide (SiC) power devices. High thermal conductivity is desired in the thickness direction of the substrate. $\beta$-Si$_3$N$_4$ indicates a high thermal conductivity in the $c$-axis direction owing to its crystal anisotropy. In the previous studies, highly $c$-axis oriented Si$_3$N$_4$ ceramics have been fabricated by using a high magnetic field over 10 T [1-2]. The use of a superconducting magnet suppressed the industrial applications of this material because of small area of the magnet. In this work, we investigate the fabrication of $c$-axis oriented Si$_3$N$_4$ ceramics by molding in a low static magnetic field using multilayered-graphene-coated $\beta$-Si$_3$N$_4$ nanocomposite particles as seeds for developing the microstructure.

Experimental procedure

$\beta$-Si$_3$N$_4$ particles synthesized in our laboratory (80 vol%) and commercial multilayered-graphene (G-13L, EM Japan, Co., Ltd., Japan; 20 vol%) were used for preparing multilayered-graphene-coated $\beta$-Si$_3$N$_4$ particles. They were pre-mixed and mechanically treated at 600 W for 5 min in the chamber of a powder processing unit (Nobiluta mini, Hosokawa micron, Co., Ltd., Japan) with the large shear stress derived from high speed rotation. The total volume of the mixed raw powders was 60 cm$^3$. An aqueous slurry containing multilayered-graphene-coated $\beta$-Si$_3$N$_4$, $\alpha$-Si$_3$N$_4$ (E10, Ube Industries, Co., Ltd., Japan), Y$_2$O$_3$ (RU-P, Shin-Etsu Chemical, Co., Japan), HfO$_2$ (HF001PB, Kojundo Chemical Laboratory Co., Ltd., Japan), and SiO$_2$ (SO-C2, Admatechs Co., Ltd., Japan) powders were prepared using polyethylene imine ($M_w=10000$) as the dispersant. The starting composition was fixed at $\beta$-Si$_3$N$_4$: $\alpha$-Si$_3$N$_4$: Y$_2$O$_3$: HfO$_2$: SiO$_2$ = 10:82:2.5:5:0.5 by weight. The dispersion was achieved by mixing for 30 min using an ultrasonic homogenizer. The slurry with a concentration of 20 vol% was placed in plastic molds of 25 mm diameter followed by drying in a static magnetic field from 0.4 to 10 T to prepare particle-oriented green compacts. These compacts were calcined at 700 °C for 3 h in air to burn out the polymer dispersants followed by sintering at 1900 °C for 6 h in 0.9 MPa N$_2$ in order to densify and grow $\beta$-Si$_3$N$_4$ grains.
Results and discussion

Fig. 1 shows back scattered electron images of the graphene-coated β-Si₃N₄ seeds observed using a low acceleration voltage in field emission SEM (FE-SEM). Fig. 1 (a) and (b) correspond to the topographic images and (c) and (d) show the composition images. A contrast difference is observed on the surface of elongated β-Si₃N₄ seeds as shown in Fig. 1 (c) and (d). The brighter and darker regions should correspond to Si₃N₄ and carbon, respectively. Peeling could be observed in Fig. 1 (b); however, it is not evident from the contrast difference in Fig. 1 (d), indicating that a thin layer consisting of light elements is peeled off. From these results, it can be considered that the peeling was the edge of multilayered-graphene and it was coated on the β-Si₃N₄ particles. Fig. 2 shows XRD patterns of the c-axis oriented Si₃N₄ ceramics prepared by changing the magnetic field from 0.4 T to 10 T. The plane measured was normal to the applied magnetic field. The intensity of (002) peak increased markedly and the intensities of other peaks derived from (hk0) plane decreased definitely in the ceramics prepared with a magnetic field compared with Si₃N₄ ceramics prepared without a magnetic field. Especially, the c-axis oriented β-Si₃N₄ particles are obtained even at 0.4 T by using Nd magnets. If settling has effect on the orientation, although Si₃N₄ ceramics prepared without a magnetic field should in-plane orient, but the uniaxial axis orientation is impossible. In fact, orientation was not observed in the case of non-oriented Si₃N₄ ceramics, indicating that the superconducting magnet is not necessary for orientating β-Si₃N₄ particles after coating them with multilayered-graphene particles. However, the c-axis orientation lowered in the ceramics prepared with high magnetic field, especially at 10 T. The lower orientation at high magnetic field results from the orientation of small quantity (~5 wt% as the value included in a release book) of β-Si₃N₄ particles included in raw α-Si₃N₄ powder. The thermal conductivity obtained with the parallel direction is equal to 96 W m⁻¹ K⁻¹, which is higher than that with the normal direction (64 W m⁻¹ K⁻¹). In the case of non-oriented specimens, the thermal conductivity is equal to 77 W m⁻¹ K⁻¹. Such improvement in the thermal conductivity results from the c-axis orientation of Si₃N₄. Consequently, the low magnetic field molding technique using multilayered-graphene-coated Si₃N₄ particles are found to be useful for preparing high thermal conductive Si₃N₄ ceramics.

On improvable upper bounds for confined polaron-type systems placed in external constant magnetic field

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A variational approach was developed which provides in a regular way a sequence of improvable upper bounds to the ground state energy of various polaron-type models confined in an external electrostatic potential. The approach holds for arbitrary strength of the electron-phonon interaction, allows for generalization to polaron-type systems placed in external constant magnetic field and may be of value for the studies of polaronic effects in quantum systems of reduced dimensions and dimensionality.

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**In-situ** observation of the behaviour of feeble magnetic materials under high magnetic fields

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**In-situ** observation of the behavior of materials under high magnetic fields sometimes brings us significant information to understand the mechanism of magnetic fields effects or to optimize the effects. In this stand point, we developed some optical devices utilizable under high magnetic fields and some *in-situ* observations of processes such as thermal convection of feeble magnetic fluids or magnetic separation of particles suspended in feeble magnetic fluids have been carried out using these devices.

Control of convection in a fluid is an important factor for many practical processes. Thermal convection behaviors of feeble magnetic fluids were observed using shadowgraph technique and schlieren device. With combining the evaluation of heat transfer across the fluid, we have experimentally confirmed that the flow of feeble magnetic electrolyte solutions remarkably suppressed due to the effect of the Lorentz force by using high magnetic fields. In addition, we also evaluated the effect when the sample was set under gradient magnetic fields and observed combined effect of the Lorentz force and the magnetic force. These observations give us useful information for the control of feeble magnetic fluids flow using superconducting magnets.

In High Gradient Magnetic Separation (HGMS), magnetic particles suspended in a fluid are separated based on the strong magnetic force due to the steep magnetic field gradient formed by the magnetization of ferromagnetic filter wires. Information about the way of particles deposition on the filter wire seems to contribute for the optimization of separation condition in practical processes. Therefore, *in-situ* observations of particles deposition process on the filter in HGMS were carried out in superconducting magnet bore. It was observed that the spike-like structure was formed toward the upper stream direction. As a results, the length of the spike structure tends to be long with higher applied magnetic field and lower flow velocity. These observations were qualitatively understood with considering the effects of flow and of the spatial magnetic field distriution.

Details of these observations will be reported in this presentation.
Analysis of Light Reflection from Biogenic Guanine Crystals by 3-Dimensional Diamagnetic Micromanipulations

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In nature, the “bio-reflectors” have a beautiful structural color and strong light reflection caused by periodic nanostructures of living creatures. There is a possibility that we can get a breakthrough for an optical device application if we discovery a new finding from these “bio-reflectors”. So, we focus on the biogenic guanine crystal derived from a fish. The periodic multi-layer structure consisted of these crystals and cells into their body surfaces have a strong light reflection of silver-white color and this reflection is caused by thin-film interference. In the previous study [1], the researchers focused on the clarification of the interaction between the multi-layer structure and light reflection. But, it’s non-existent method for measuring the light reflection from a plate of a biogenic guanine crystal by manipulating this single micro-crystal non-invasively.

So, in our study, we tried to control the biogenic micro-crystal without adding “magnetic micro-particle” by using diamagnetic property which all materials have under external magnetic fields. We succeeded in developing the method for manipulating the 3-dimensional rotation of the biogenic guanine crystal and analyzing the light reflection range from a plate of the biogenic guanine crystal, which have a molecular arrangement of the C=O and N–H bonds aligned along the long axis direction of this crystal [2].

We carried out the diamagnetic control for the twisting rotation of the biogenic guanine crystal by combining two kinds of magnetic field direction, vertical and horizontal direction. In results, it was completed successfully to develop and achieve the magnetic manipulation method for the 3-dimentional diamagnetic rotation [3]. In addition, it was clarified that the switching of light reflection was caused by tiny angle variation of the guanine crystal plane when we tried to carry out the characterization for analyzing the light reflection from a plate of biogenic guanine crystal by using the tiny diamagnetic anisotropy between the first and second easy axis of magnetization. This method may allow us to control the light reflection from a plate of a biogenic guanine crystal under magnetic field of a few hundred mT. In addition, it's hoped that this 3-dimensional manipulation contributes to clarifying the ethological function of the biogenic guanine crystal as a bio-reflector and is applied to the remote control of diamagnetic micro-mirrors in the fields of nano-biotechnology as a ripple effect.

High Magnetic Field Gradient-Controlled Migrations of solute and particles and Their Effects on Solidification Microstructure

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The quality of solid materials depends on the microstructure, which is affected by the distribution of solute elements or phases in the microstructure. The migration of precipitated phases or solute elements in alloy melts during solidification has a strong influence on their distribution in the microstructure and hence is important for the control of the properties of materials. In recent years, the effect of high magnetic fields on the solidification of alloys has attracted much attention for more precise control of microstructures [1]. In particular, if there is a magnetic field gradient, a magnetic force will be induced by the interaction of the magnetization of the material and the imposed magnetic field gradient. Thus, the magnetic force acting on the particle-like phases is necessary in controlling their migration in alloy melts. There arises then the possibility of a direct processing route in the in situ control of the migrations of solute and phases in alloy melt and thus their solidification microstructures by high magnetic field gradients.

Fig.1 Microstructures of the Mn-89.7wt.%Sb alloys after isothermal annealing in the semi-solid state for various times in high magnetic field gradients ($B=11.5 \text{ T}$). (a) 0 T, 30 min; (b) $dB/dz = -114 \text{ T}^2/\text{m}$, 30 min; (c) $dB/dz = -282 \text{ T}^2/\text{m}$, 30 min; (d) $dB/dz = -282 \text{ T}^2/\text{m}$, 60 min; (e) $dB/dz = 282 \text{ T}^2/\text{m}$, 30 min; (f) corresponding volume fraction distributions of the MnSb particles along the depth from the lower surface.

In this work, we applied high magnetic field gradients on the solidification process of some typical alloys to investigate their effects on the migration behaviors of solute and particle-like phases in the alloy melt. We also characterized the microstructural evolution of the alloys induced by the migrations of solute and...
particle-like phases. Results show that depending on the magnetic susceptibility and density of alloying elements, particle-like phases, and liquid matrix, the solutes and phases can be driven by the magnetic force to move along or opposite to the gravity direction in the alloy melt [2,3]. By in situ controlling such movement, we fabricated some bulk layered synthetic composites with a gradient structure in morphology or composition towards the surfaces by solidification from a semi-solid or liquid state in high magnetic field gradients (Fig. 1) [3,4]. The properties of these composites show a continuous change along the gradient direction of the microstructure (Fig. 2) [5,6].

![Fig.2](image-url)  
Fig.2 (a) Saturation magnetization and (b) maximum magnetostriction through the depths of Tb$_{0.25}$Dy$_{0.73}$Fe$_{1.95}$ alloys solidified in various high magnetic field gradients.