Magnetic Field Effects on Colloids and Surface Phenomena

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Magnetic property is one of universal properties of materials, which arises from angular momentum of an electron and nucleus. Diamagnetism and paramagnetism result in orbital motion and spinning of electrons. Therefore, any material will interact with magnetic fields. If the structures and properties of materials are controlled by magnetic fields, we may be available for a general method of materials processing.

Magnetic fields affect chemical reactions,[1,2] chemical equilibria,[3-5] structures and physical properties of materials[6-7] via both the direct effects such as quantum mechanical, thermodynamic, and mechanical effects and the indirect effects such as convection, concentration changes, and temperature changes. However, since the magnetic energy of diamagnetic and paramagnetic materials is much smaller than the thermal energy at moderate temperature, it was believed to be insufficient to overcome the activation energy associated with chemical and physical processes. The magnetic energy (12.5 mJ mol^{-1}) of an electron spin in a field of 1 T corresponds to the thermal energy of 0.67 K or electric energy of 58 μV, and is about only 10^{-5} of the thermal energy of 205 kJ mol^{-1} at 300 K.[8] Therefore, thermal energy disturbs magnetic effects in feeble magnetic systems. Consequently, it does not seem that magnetic field effects appear even at moderate temperatures at which materials are processed. However, a variety of magnetic field effects were found in fact using high magnetic fields in appropriate systems and sophisticated techniques.

Magneto-Science,[8-10] a new science of materials using magnetic fields, is recently developed all over the world. Magneto-Science covers mainly the subjects on feeble magnetic materials such as soft matters, carbons, ceramics, organometals. Colloidal and interfacial systems under magnetic fields are very attractive and important because the dimension is very much sensitive to magnetic fields. In this review we introduce several examples in colloid and interface chemistry under magnetic fields. Molecular assembles such as micelles, bimolecular membranes, and vesicles were changed in shape and, in some cases, size by magnetic fields. Since mesophases are sensitive to relatively low magnetic fields, magnetic fields controlled not only its own structures and functions but also cooperatively other magnetically-insensitive materials. Moreover, a few interesting magnetic response in hydrogels are summarized.

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Chiral surface formation by magnetoelectrolysis

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1. Introduction

Chiral surfaces of catalysts are responsible for asymmetric synthesis of organic materials. Particular concern is that surfaces of minerals could play chiral catalytic roles for prebiotic synthesis of amino acids in molecular evolution. A study of chiral surface formation is thus of great significance from wide viewpoints of chiral catalysts, pharmaceutical industry and the origin of life on the early earth.

When a magnetic field is imposed to an electrochemical cell, the Lorentz force acting on the faradaic currents causes convections around the electrodes in the electrolytic solutions. This is well known as the MHD (magnetohydrodynamic) effect. There exists two kinds of MHD flow in the magnetic fields perpendicular to the electrode surface; micro-MHD vortices on a fluctuated surface of the electrodeposits and a macroscopic flow around the electrode edge (the vertical MHD flow). The micro-MHD vortices could produce chiral defects such as screw dislocations on the electrodeposit surfaces, and the vertical MHD flow breaks the symmetry in the micro-MHD vortices, leading to the induction of surface chirality. Our previous papers[1,2] reported that the magnetoelectrodeposition (MED) induces surface chirality of Ag and Cu films. Here we show two new methods for the chiral surface formation; magnetoelectrochemical etching (MEE) and rotational MED.

2. Magnetoelectrochemical etching

The symmetry breaking mechanism in the coupling of micro-MHD and vertical MHD flows would be applicable to magnetoelectrochemical etching, thus we have tried to explore chiral surface formation in MEE processes. The MEE experiment was a galvanostatic dissolution of a copper film in a 50 mM $CuSO_4$ + 0.5 M H_2SO_4 aqueous solution under a magnetic field of 5 T perpendicular to the film surfaces. The MEE copper films were used as an electrode, and the chirality of such electrodes was examined by voltammetric measurements of enantiomers of alanine (an amino acid). The MEE film electrodes exhibited the difference in oxidation currents between the enantiomers, and such a chiral behavior depended on the magnetic field direction and the etching current. The former result shows that the MEE process could induce chirality on the etching film surfaces, and the latter suggests that the chirality induction is responsible for the combination of the micro-MHD vortices and the vertical MHD flows, as proposed in the MED processes.

3. Rotational magnetoelectrodeposition

Another method for the symmetry breaking in the micro-MHD vortices is Rotational MED,[3] in which the electrochemical cell was rotated in a magnetic field of 5 T during the electrodeposition with a frequency of 2 Hz in a clockwise or anticlockwise direction. The MED copper film electrodes exhibited chiral behavior for the electrochemical reaction of alanine enantiomers, and the direction of rotation allowed control of the chiral sign.[4] This chiral induction arises from the asymmetric influence of the system rotation on the cyclonic and anticyclonic micro-MHD vortices around the electrode surfaces.

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Diamagnetic responses in biogenic micro crystals and possible application for micromirror device

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Living creatures such as fish and algae are utilizing micro crystals which are genetically produced in cellular tissue. In case of fishes, guanine crystals are generated in chromatephore on the surface of fish body, and control the structural colors for the purpose of utilizing solar light reflection. Some of alga carry out photosynthesis and fix the carbon dioxide. Coccolithophore is one of the alga that forms calcium carbonate crystal by biomineralization. Coccolith is a dish shaped assemble of calcium carbonate crystals whose physiological functions unrevealed at present.

In this report, we observe quick responses of the biogenic crystals of both fish and algae under magnetic fields. At first, we found a drastic change of light scattering in goldfish scale guanine crystals under magnetic fields of 5 T ~10 T. A structural color in guanine crystal array was changed during the magnetic field sweeps. A determination of threshold of the magnetic field effect revealed that the minimum magnetic fields for the light scattering inhibition was around 200 mT for the case of the biogenic guanine crystal plate. The crystals caused a diamagnetic orientation at several hundreds of mT and changed the light reflection direction. The same kind of measurements were carried out on the coccolth discs of coccolithophore, *E. huxleyi*. We observed a change in structural colors in an aggregation of coccolith discs during magnetic field changing between 0 T and 2 T. However in the same manner with guanine crystals suspension, a homogeneously isolated coccolith discs showed a magnetic orientation at 400 mT. We obtained a light scattering changes which depended on the combination of the directions of light, magnetic field and the observation.

The employed micro crystals were floated in an aqueous solution with a Brownian motion. The magnetic response at 200 mT suggested that their diamagnetic energy exceed the thermal energy kT. A simple calculation of the energy supported this hypothesis. It is expected that the magnetic control of the floating micro crystals can be applied for the micro-mirrors in wet MEMS that will provide a new micro-fluidic device for biomedical systems.

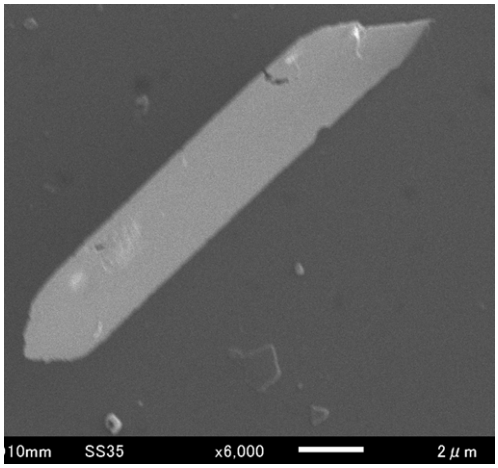

Fig. 1. SEM image of a guanine crystal Plate from goldfish scale.

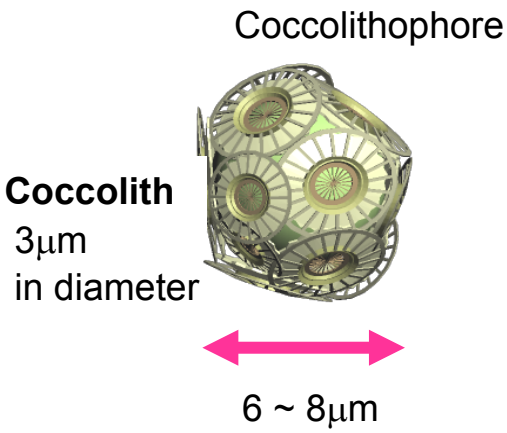

Fig. 2. Illustration of a coccolithophore cell with calcium carbonate crystals discs so called coccolith.

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Single Crystal Structure Analysis of Magnetically Oriented powder Crystal

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Introduction

We have been developed Magnetically Oriented Microcrystal Array (MOMA) method to make it possible to carry out single crystal X-ray diffraction analysis from microcrystalline powder. In the method, microcrystals suspended to the UV-curable monomer are there-dimensionally aligned by frequency-modulated rotating magnetic field. Then the obtained alignment is consolidated by the photopolymerization. From thus achieved MOMAs, we have been succeeded in crystal structure analysis for some substances [1] [2]. Though MOMA method is an effective technique, it has some following problems; in a MOMA, the alignment is deteriorated during the consolidation process. In addition, the sample microcrystals cannot be recovered from a MOMA. To overcome these problems, we performed an *in-situ* X-ray diffraction measurement using a 3D Magnetically Oriented Microcrystal Suspension (MOMS) of L-alanine.

Experiments

A measurement setting of the MOMS technique is schematically shown in **Fig 1**. L-alanine microcrystal suspension was poured into a glass capillary and placed on the rotating unit equipped with a pair of neodymium magnets. Rotating X-ray chopper with 10º-slits was placed between the collimator and the suspension. By using the chopper, it was possible to make specific direction of the rotating MOMS be exposed to the X-ray, realizing the same measurement situation as the 10 degree oscillation angle measurement for the usual single crystal measurement. A total of 22 XRD images of 10º increments from 0º to 220º were achieved.

Results & Discussion

The data set was processed in the same way as the single crystal measurement and the crystal and 3D Molecular structure of L-alanine was determined. They showed well agreements with the reported one determined from the single crystal (Fig. 2). *R*1 and *wR*2 were 6.53 and 17.4 %, respectively. RMSD value between the achieved 3D molecular structure and the reported one was 0.0042 Å. From the result, we concluded that this method can be effective and practical way to perform crystal structure analysis.

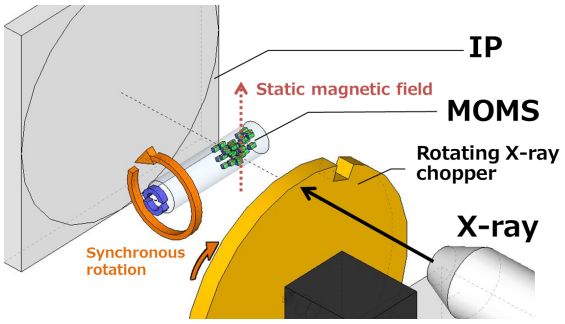

Fig. 1 Schematical image of the measurement setting.

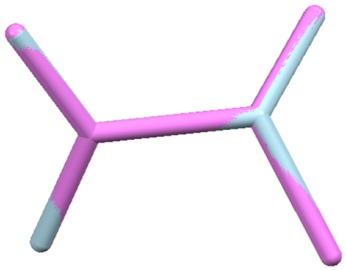

Fig. 2 Comparison of the structure determined in this study (blue) and reported one (pink).

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Influences on the crystallization kinetics of iron-based amorphous alloys under high magnetic fields

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Introduction

Iron-based amorphous alloys are known as precursor materials of iron-based nano-crystalline alloys, which have excellent soft magnetic properties, such as low coercivity, high permeability and high saturation magnetization. These soft magnetic nano-crystalline alloys are produced by the crystallization of iron-based amorphous alloys, and have a unique texture, which consists of a nano-size bcc-Fe grain with a high volume fraction and an inter-granular amorphous layer. The characteristics of their texture dominate their soft magnetic properties. For instance, the coercivity highly depends on the grain size [1]. For improvement of the soft magnetic properties, therefore, the enhancement of a nucleation rate, the suppression of the grain growth and the stabilization of a residual amorphous phase on the crystallization of bcc-Fe are required. However, the nucleation and grain growth control by a simple thermal treatment and/or the adjustment of chemical composition are hardly to achieve homogeneous texture with ultra-fine grains. Thus, a new method is required for the accurate nano-crystallization control.

Recently, the material processing by applying magnetic fields has been investigated strenuously. A magnetic field is particularly important for the in-field processing of magnetic materials, because of the contribution of the magnetic energy to phase transformation and metallurgical effects. However, there are very few reports that dealt with the crystallization kinetics of amorphous alloys in high magnetic fields, although many studies for other magnetic materials such as steel, nickel and cobalt based alloys, have been reported. The detailed information about the crystallization kinetics in high magnetic fields is necessary for the development of the novel nano-crystallization process, which will achieve accurate control of the grain size and the precipitation of a crystal phase by applying a high magnetic field.

In this study, we have carried out differential thermal analysis (DTA) and magnetization measurements in high magnetic fields, in order to investigate the influence of a high magnetic field for the crystallization kinetics of iron-based amorphous alloys.

Experimental detail

$Fe_{83.3}Si_{4.2}B_{12.5}$ amorphous alloy, studied in this work, is the basic composition of $Fe_{83.3}Si_4B_8P_4Cu_{0.7}$ hetero-amorphous alloy, in which the nano-crystallization occurs by annealing. The sample ribbon was prepared by single-roll melt spinning with 3 mm in width and 27-29 μm in thickness. The DTA measurements in high magnetic fields were carried out at temperatures ranging from R.T. to 900 K in applied magnetic fields up to B = 20 T [2]. Magnetization measurements were carried out using a high field vibrating sample magnetometer (HF-VSM). The heating rate is 10 K/min for DTA and 5 K/min for magnetization measurements. The sample space was evacuated to ~ 10^{-3} Pa by a turbo-molecular pump system during the measurements. The structure of crystal phases was determined by X-ray diffraction.

Results and Discussion

Figure 1(a) shows the DTA curve at 0 T. Two exothermic peaks due to the crystallization reactions are observed. The first peak indicates the crystallization of bcc-Fe(Si) and the second peak the crystallization of iron-boron compounds such as Fe_2B and Fe_3B. The first and second crystallization temperatures, which are determined from the onset of the exothermic peaks, are T_{x1} = 706 K and T_{x2} = 795 K, respectively. Figure 1(b) shows the magnetic field dependence of the first crystallization peak up to B = 20 T. The crystallization peak of bcc-Fe(Si) shifts toward a lower temperature side under high magnetic fields, whereas the second crystallization peak shifts toward a higher side. The first

crystallization temperature is decreased by 10 K and the second one is increased by 4 K at 20 T, compared with those at 0 T.

Figure 2 shows the magnetic field dependence of the growth curve of bcc-Fe(Si) at 660 K, which is obtained by isothermal magnetization measurements at 0.5 T and 10 T. The growth curve at 10 T shows abrupt time evolution, compared with that at 0.5 T. The magnetic field effect on the growth rate is discussed in terms of the elapsed time, $\tau_{0.5}$, which is defined as the time where the crystallization fraction, $x(\tau)$ attains $x = 0.5$. $\tau_{0.5}$ is decreased from 3.0 ksec at 0.5 T to 1.8 ksec at $B = 10$ T. This result suggests that the growth rate of the crystallization reaction increases under high magnetic fields. In this first crystallization reaction, ferromagnetic bcc-Fe crystallizes from paramagnetic amorphous matrix. Thus, the crystal phase gains lager magnetic energy, compared with the amorphous phase. Therefore, the gain of the magnetic energy decreases the activation energy required for the nucleation of the crystal phase. It is considered that the enhancement of the growth rate is caused by the increase of the nucleation rate due to decreasing of the activation energy by the magnetic field. We expect that the enhancement of the nucleation leads to the increase of the volume fraction of bcc-Fe(Si) with a small grain size, which results in the improvement of the saturation magnetization.

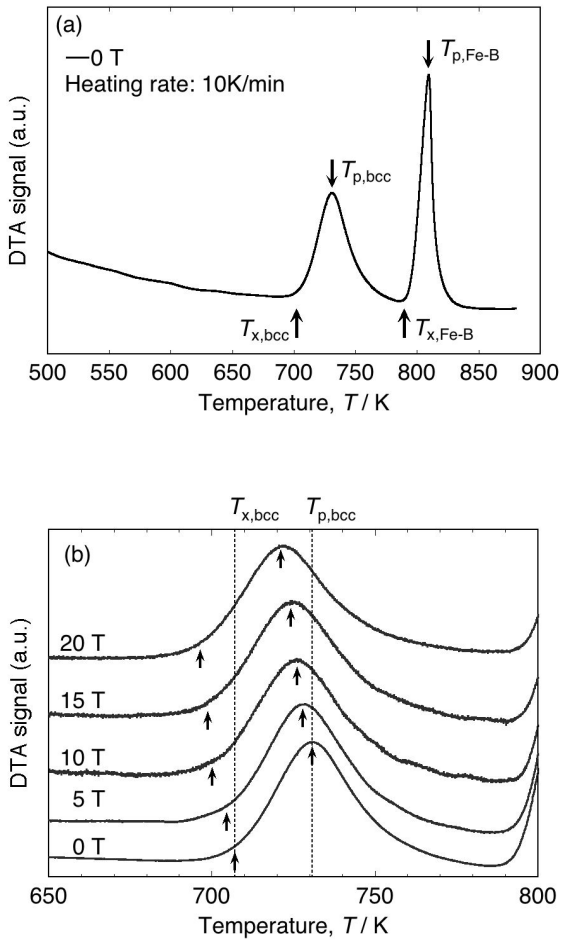

Fig.1 (a) DTA curve of $Fe_{83.3}Si_{4.2}B_{12.5}$ amorphous alloy at 0T. (b) Magnetic field dependence of the first crystallization peak in fields up to 20 T.

Conclusion

The crystallization kinetics of $Fe_{83.3}Si_{4.2}B_{12.5}$ amorphous alloy in high magnetic fields has been investigated by the DTA and magnetization measurements. In the DTA, the crystallization peak of bcc-Fe(Si) shifts toward a lower temperature side by applying magnetic fields. In the magnetization measurements, the growth curves of bcc-Fe(Si) were obtained by isothermal measurements. The growth curve at 10 T shows the acceleration of crystal growth, compared with that at 0.5 T. These magnetic field effects indicate that the nucleation of bcc-Fe(Si) is enhanced under high magnetic fields.

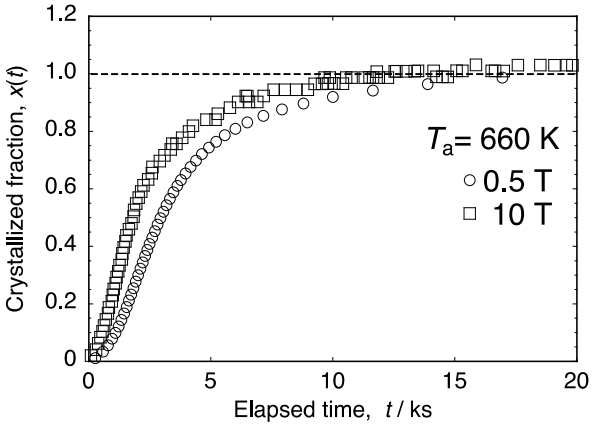

Fig.2 Magnetic field dependence of the growth curve of bcc-Fe(Si) at 660 K.

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Development of new in-field analytical system and synthesis of ferromagnetic materials under high magnetic fields

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Magnetic field is one of the key thermodynamic parameters such as temperature and pressure for controlling the equilibrium of condensed matters [1]. Therefore, in order to discover and develop a new material, magnetic field effects on the magnetic phase transition, chemical reaction, solidification, etc. have been studied using high field magnets all over the world. However, it is very difficult to observe these phenomena in high temperature and high magnetic fields over 20 T using commercial equipment. In general, magnetic energy is quite small compared to thermal energy. For example, the magnetic energy of an electron spin with one Bohr magneton (μ_B) under a magnetic field B of 1 T corresponds to the temperature T of 0.67 K [1]. This is a reason why high magnetic fields are needed for examining the magnetic field effects on materials over room temperature.

On the other hand, some magnetic materials have a large magnetic moment that interacts with one another by the exchange interaction. In this case, the phase transition of the magnetic materials can be observed by applying magnetic fields in the vicinity of room temperature. Indeed, some ferromagnetic materials show the large magnetocaloric effect or the magnetic field-induced strain, accompanied by a magnetic field-induced first-order phase transition at room temperature. These materials have been studied as a candidate of magnetic refrigerants or magnetic actuator materials, all over the world. One of the ferromagnetic materials that have a large magnetic moment m and show a first-order phase transition over room temperature is an MnBi compound.

In order to study magnetic field effects on equilibrium states of Bi-Mn binary system and other ferromagnetic materials, we have developed high-field differential thermal analysis (HF-DTA) equipment for utilization in a high field magnet with 30 mm bore [2]. We have reported magnetic field effects on the peritectic decomposition and composition states of a MnBi magnetic material in fields up to 45 T by using hybrid magnets [3].

Figure 1 shows phase diagram of MnBi [2,3]. The decomposition temperature (MnBi→$Mn_{1.08}$Bi + liquid phase: 632 K at zero field) T_t was found to increase linearly at a rate of 2 KT^{-1} in fields up to 18 T and to deviate from that linear increase above 20 T. In addition, the peritectic temperature ($Mn_{1.08}$Bi→Mn + liquid: 721 K at zero field) T_m was slightly increased by applying a magnetic field. At a magnetic field of 45 T, T_t and T_m reached 714 K and 726 K, respectively. Furthermore, the magnetocaloric effect of MnBi was observed in 11.5-45 T in the vicinity of 689 K, showing that a field-induced composition process occurs [3]. The behaviour of T_t and T_m for MnBi and $Mn_{1.08}$Bi under high magnetic fields could be discussed on the basis of mean field theory [2]. Obtained results indicate that we can generally control the equilibrium state of magnetic materials by steady magnetic fields.

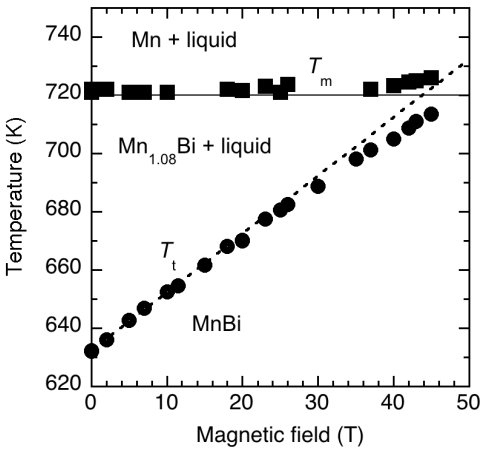

Fig.1. Phase diagram of MnBi [2,3]. The dashed line indicates the extrapolation calculated by using the least-squares method with data for $B \leq 14$ T. The solid horizontal line at 720 K is a guide to the eyes.

Figure 2 shows the equilibrium diagrams of Bi-Mn binary system at a zero field (a) and 18 T (b) [4, 5]. The symbols and lines were obtained by the HF-DTA [4] and calculations [5], respectively. Here, calculated Bi-Mn equilibrium diagrams in high magnetic

fields were numerically investigated by the Computer Coupling of Phase Diagram (CALPHAD) method with including a mean field calculation for magnetic energy. For a zero field (Fig.2 (a)), T_{p1} (T_t) T_{p2} (T_m) and T_E were determined to be 632 K, 721 K, and 538 K, respectively. When magnetic field of 18 T was applied, T_{p1} increases and reaches 667 K, whereas T_E seems to be independent of magnetic fields. Therefore, the area of MnBi + liquid extends out, whereas $Mn_{1.08}Bi$ + liquid becomes narrow with applying a magnetic field of 18 T. Recently, we pointed out that the parabolic relationship for T_{p2} T_{p2} (T_m)-B is mainly dominated by the magnetic properties of paramagnetic $Mn_{1.08}Bi$ [2]. The calculated results were good agreement with the experimental results.

The gain of the magnetic energy part (E_M = -mB) in the free energy plays an important role in the effect of magnetic field on phase transition and reaction of magnetic materials. Recently, we found that magnetic field enhanced a solid-solid reaction for form of ferromagnetic MnBi from nonmagnetic Bismuth and Manganese [6]. In addition, *c*-axis of the hexagonal structure of MnBi was oriented parallel to the magnetic field direction. Using this effect, we developed a new solid-state reaction sintering method under high magnetic fields for synthesizing permanent magnet [6].

Furthermore, recently, we have developed an in-situ observation system with DTA under high magnetic fields up to 10 T. We expect that the equipment will be one of the key analytical systems, in order to study magnetic field effect on the magnetic phase transition, chemical reaction, solidification, etc.

In this presentation, recent results of magnetic field effects for the ferromagnetic MnBi and Fe-C steel and our new analytical system utilized in high magnetic fields will be presented.

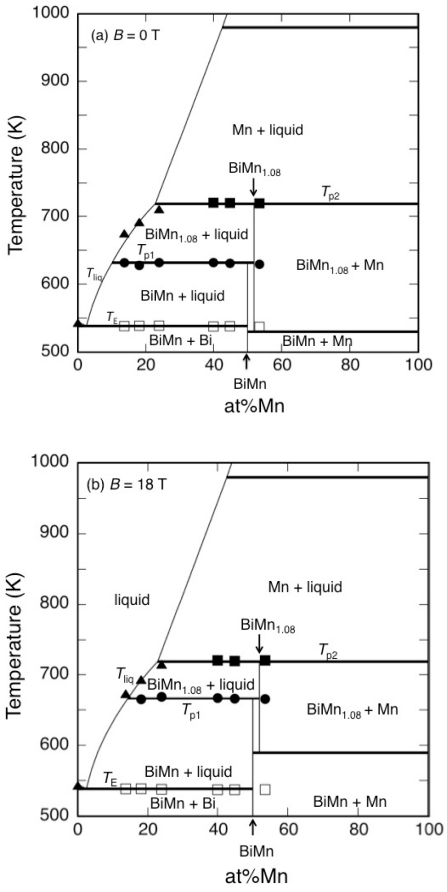

Fig.2. Equilibrium diagrams of Bi-Mn binary system at a zero field (a) and at 18 T (b). The symbols and lines indicate the experimental [4] and calculated results [5], respectively.

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