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.

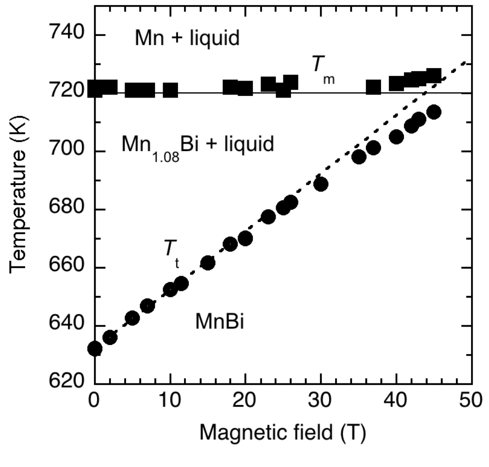

Fig.1. Phase diagram of MnBi [2,3]. The dashed line indicates the extrapolation calculated by using the least-squares method with data for $B \leq 14$ T. The solid horizontal line at 720 K is a guide to the eyes.

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.

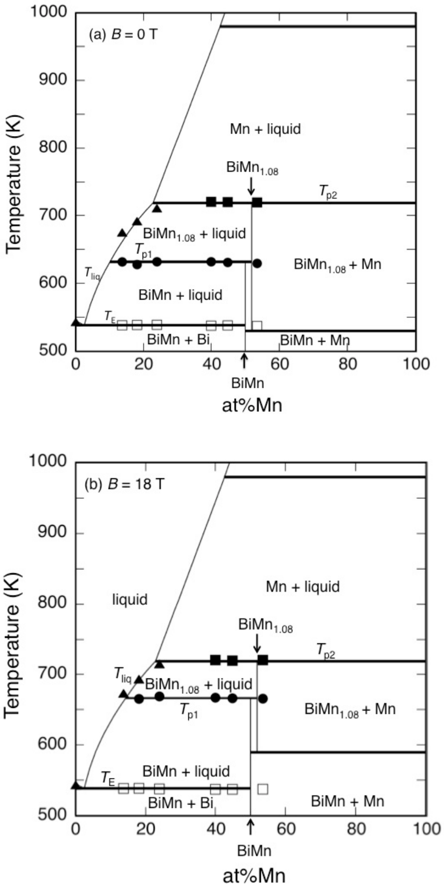

Fig.2. Equilibrium diagrams of Bi-Mn binary system at a zero field (a) and at 18 T (b). The symbols and lines indicate the experimental [4] and calculated results [5], respectively.

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