Journal of Alloys and Compounds 509 (2011) L78–L80

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Letter

Change of the equilibrium state of ferromagnetic MnBi by high magnetic fields

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ARTICLE INFO

Article history:
Received 18 August 2010
Accepted 11 November 2010
Available online 19 November 2010

Keywords:
MnBi
High magnetic fields
Differential thermal analysis
Phase transition
Magnetocaloric effect

ABSTRACT

Differential thermal analysis was carried out for ferromagnetic material MnBi in the temperature range 300–773 K in magnetic fields up to 45 T to investigate the effect of high magnetic fields on its decomposition process and corresponding phase diagram. The decomposition temperature T_t (MnBi → $Mn_{1.08}Bi$ + liquid Bi) increases from 632 K (at a zero field) to 714 K by applying a magnetic field of 45 T. Furthermore, the magnetocaloric effect of MnBi is observed in 11.5–45 T in the vicinity of 689 K, showing that a field-induced composition process occurs. The obtained results show that the equilibrium state of MnBi can be controlled by a high magnetic field.

1. Introduction

Ferromagnetic compound MnBi has an NiAs-type hexagonal structure (low-temperature phase: LTP) [1]. The magnetic moment (m) of LTP can be extrapolated to a value of 3.9 μ_B at 0 K [2,3]. The mean field calculation for LTP-MnBi indicated that the Curie temperature (T_C) reaches up to 717 K [4]. However, with increasing temperature from room temperature, LTP-MnBi undergoes a first-order magnetic phase transition from the ferromagnetic (FM) state to the paramagnetic (PM) state at $T_t \sim 630$ K, accompanied by a structural transformation from the NiAs-type to a distorted Ni_2In-type hexagonal structure (high-temperature phase: HTP) [3]. Chen reported that HTP is a separate compound with a chemical formula of $Mn_{1.08}Bi$ [5]. According to the equilibrium diagram of the Mn–Bi system [5], the phase transition of MnBi at T_t upon heating is associated with the periectic decomposition of MnBi (LTP) into $Mn_{1.08}Bi$ (HTP) and liquid Bi. HTP has a magnetic moment of 1.7 μ_B at room temperature and T_C is ∼ 473 K [2].

Recently, on the basis of magnetic measurements for MnBi, Liu et al. [6] reported that T_t increases with increasing magnetic fields (B) up to 10 T at a rate of ∼2 K T^{-1}. Differential thermal analysis (DTA) performed by Koyama et al. [7,8] also showed an increase in T_t with increasing B up to 14 T at a rate of 2 K T^{-1}. They suggested that T_t reaches the peritectic temperature of HTP ($T_m^{HTP} = 719$ K) upon applying a magnetic field of ∼45 T [7,8]. This suggests that HTP vanishes and the equilibrium state can be controlled by high magnetic fields. In order to study the effect of magnetic fields on phase transitions and equilibrium states, thermal analysis under high magnetic fields is one of the most important experiments [7,8]. In addition, a high magnetic field of 45 T is realized by the 45-T hybrid magnet (the world's highest steady magnet field) of the National High Magnetic Field Laboratory (NHMFL), USA [9]. However, there is no instrument for thermal analysis under magnetic fields over 20 T in the world. In this work, we performed high-field DTA (HF-DTA) experiments for ferromagnetic MnBi in magnetic fields up to 45 T for the first time by combining a newly developed DTA instrument and the hybrid magnet of the NHMFL to clarify the effect of high magnetic fields on the decomposition process and a corresponding phase diagram of MnBi under high magnetic fields.

2. Experimental procedure

Polycrystalline MnBi was prepared by arc-melting a mixture of stoichiometric amounts of pure elements (Mn, 3N; Bi, 5N) in an argon atmosphere. The obtained button ingot was turn over and remelted several times. After that, the ingot was annealed at 573 K for 5 h in a quartz tube with an argon atmosphere and then quenched in water. X-ray powder diffraction measurements were carried out using CuKα radiation at room temperature. The sample was confirmed to be LTP-MnBi with a small amount of Bi and Mn, and we did not observe the reflection peaks of HTP-$Mn_{1.08}Bi$. HF-DTA was carried out for $11.5 \leq B \leq 45$ T using the 45-T hybrid magnet at the NHMFL. In addition, the DTA signal was also measured for $B \leq 18$ T using cryogen-free superconducting magnets and $B \leq 26$ T using the 28-T hybrid magnet of the High Field Laboratory for Superconducting Materials (HFLSM), Tohoku University, Japan. For $300 \leq T \leq 773$ K, the DTA data were obtained during the heating at a rate of 6–7 K min^{-1} under a vacuum (∼10^{-1} Pa). In the HF-DTA measurements, we used non-magnetic Pt–PtRh thermocouples, and powder Al_2O_3 was utilized as a reference sample.

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doi:10.1016/j.jallcom.2010.11.082

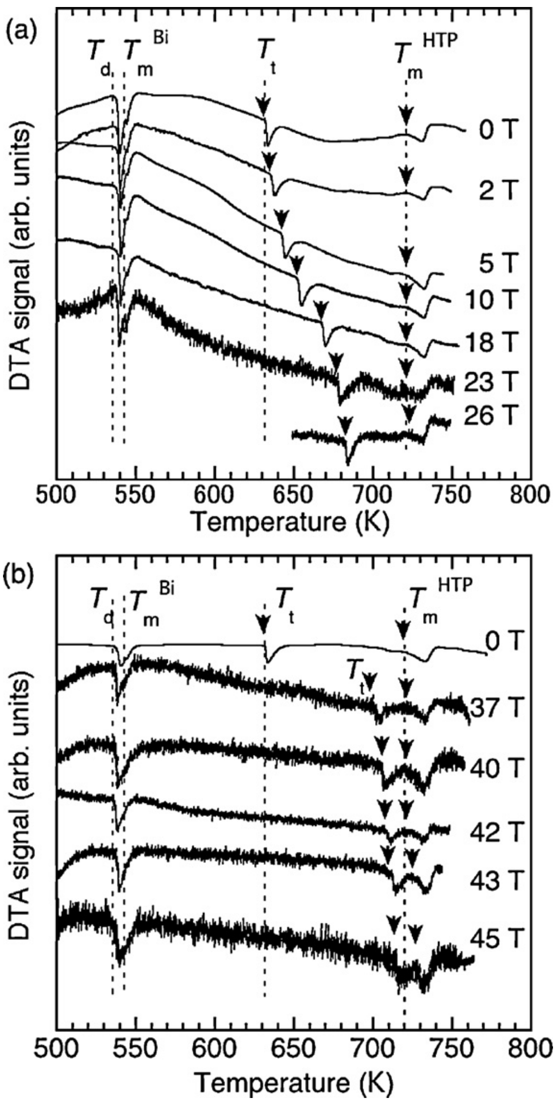

Fig. 1. DTA curves for MnBi in various magnetic fields up to 45 T, which are measured at the HFLSM, Japan (a) and the NHMFL, USA (b). The vertical arrows indicate the determined decomposition temperature T_t and the peritectic temperature T_m^{HTP}.

3. Results and discussions

Fig. 1(a) and (b) show typical results for the DTA curves of MnBi, which are obtained at the HFLSM and the NHMFL facilities, respectively. Here, the noise of the DTA signals for $B \geq 23$ T is due to the vibration of the water-cooled coils in the hybrid magnets. For $B = 0$ T, four endothermic peaks were observed at $T_d = 536$ K (the peritectic temperature), ($T_m^{Bi} = 544$ K) (the melting temperature of Bi), $T_t = 632$ K (the decomposition temperature: MnBi → $Mn_{1.08}Bi$ + liquid Bi), and $T_m^{HTP} = 722$ K (the peritectic temperature: $Mn_{1.08}Bi$ → Mn + liquid Bi). Here, these transition temperatures were determined by the onset of the endothermic peaks. These temperatures are consistent with the reported equilibrium diagram for $B = 0$ T [5]. As seen in these figures, the endothermic peaks at T_d and T_m^{Bi} are independent of B. On the other hand, the endothermic peak at T_t shifts to a higher temperature with increasing B, and no extra peak was observed in the vicinity of T_t. This means that the phase transition at T_t is strongly affected by applying magnetic fields. Furthermore, the endothermic peak at T_m^{HTP} slightly shifts to a higher temperature by applying high magnetic fields.

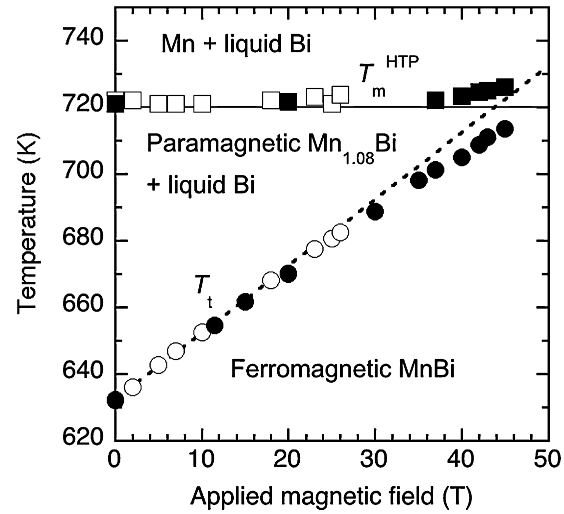

Fig. 2. Phase diagram of MnBi in magnetic fields up to 45 T. The open and solid symbols indicate the data taken at the HFLSM and the NHMFL, respectively. The circles and squares indicate the decomposition temperature T_t and the peritectic temperature T_m^{HTP}, respectively. The broken line indicates the extrapolation calculated by the least-squares method for T_t using the data for $B \leq 14$ T. The solid horizontal line at 720 K is a guide to the eyes.

Fig. 2 shows the magnetic field dependence of T_t and T_m^{HTP} of the Mn–Bi compound. In this figure, the open and solid symbols indicate the data obtained at the HFLSM and the NHMFL facilities, respectively. The decomposition temperature T_t increases almost linearly with increasing B up to ~20 T at a rate of ~2 K T^{-1}, as shown by the broken line in Fig. 2. However, we can see that the data over ~20 T deviate from the broken line (~2 K T^{-1}) and T_t cannot reach T_m^{HTP} (~720 K) even for $B = 45$ T. In addition, we found that the peritectic temperature T_m^{HTP} increases with increasing B, which is clearly observed over 40 T.

Fig. 3(a) and (b) show typical results for the magnetic field dependence of the DTA signals and the sample temperature of MnBi in the vicinity of 689 K, respectively. In this measurement, the sam-

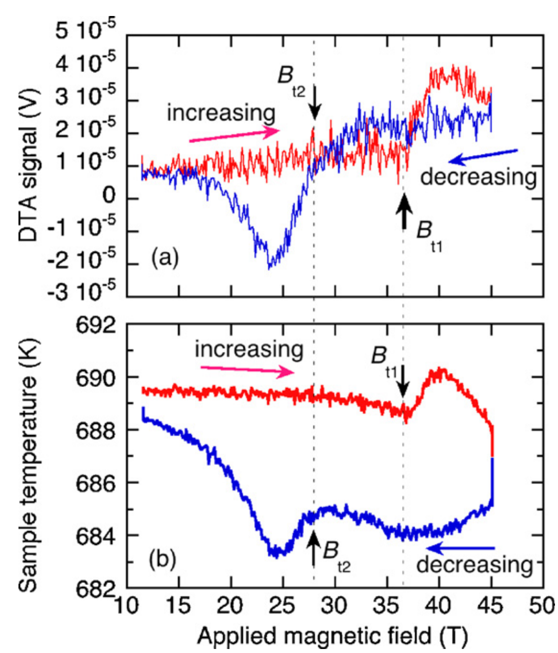

Fig. 3. Magnetic field dependence of the DTA signals (a) and the sample temperature (b). The vertical arrows indicate the determined phase transition fields B_{t1} and B_{t2} for increasing and decreasing magnetic fields, respectively.

ple is heated to 689.5 K in B = 11.5 T. As seen in Fig. 2, the sample contains PM-$Mn_{1.08}Bi$ and diamagnetic liquid Bi in this condition. After that, the magnetic field is generated from 11.5 T to 45 T at a rate of 7 T min^{-1}. After reaching 45 T, the magnetic field is decreased to 11.5 T at the same rate. As shown in Fig. 3(a), we observed the exothermic and the endothermic peaks at 36.5 T (=B_{t1}) for increasing B and at 28.8 T (=B_{t2}) for decreasing B, respectively. In other words, this is a magnetocaloric effect: the sample heating (+∼1.2 K) by applying B and sample cooling (−∼1.5 K) by removing the field, as shown in Fig. 3(b). Here, B_{t1} and B_{t2} were determined by the onset of the DTA peaks. Considering the phase diagram (Fig. 2), the exothermic and the endothermic peaks are due to the phase transitions from PM-$Mn_{1.08}Bi$ and liquid Bi to field-induced ferromagnetic (FIFM) MnBi for increasing B and from FIFM-MnBi to PM-$Mn_{1.08}Bi$ and liquid Bi for decreasing B, respectively. That is, the field-induced composition and decomposition processes occur in the Mn–Bi system.

The Zeeman energy part ($E_M = -mB$) in the free energy plays an important role in the effect of the magnetic field on the phase transition of magnetic materials [10]. For a zero field, m of MnBi is approximately 2.4 μ_B even at 600 K [7]. The mean field calculation suggested that the field-induced m of MnBi is approximately 2.0 μ_B in a magnetic field of 45 T at 720 K [7]. This m of MnBi is much larger than that of $Mn_{1.08}Bi$, because m of HTP-$Mn_{1.08}Bi$ is 1.7 μ_B at room temperature and T_C is about 473 K [2]. Therefore, we observe the increase in T_t by applying a magnetic field to MnBi. On the other hand, it is also expected that m of HTP-$Mn_{1.08}Bi$ in the vicinity of 720 K ($\sim T_m^{HTP}$) is induced by applying a high magnetic field. The gain of E_M of the $Mn_{1.08}Bi$ phase is larger than Mn and liquid Bi phases, because solid Mn and liquid Bi are an antiferromagnet and a diamagnet, respectively, in this temperature range. Therefore, it is possible that the peritectic temperature of $Mn_{1.08}Bi$ (T_m^{HTP}) slightly increases by applying a high magnetic field, as shown in Fig. 3.

Considering the equilibrium diagram of Mn–Bi [5] and the result of the neutron diffraction experiment [3], a small amount of the Bi atoms in the NiAs-type crystal structure of MnBi goes out over T_t, and MnBi decomposes to $Mn_{1.08}Bi$ and a small amount of liquid Bi. Therefore, the observed magnetocaloric effect indicates that the Bi atoms move between the crystal of MnBi and the liquid Bi by increasing and decreasing B. That is, the Bi atoms in the liquid will go into the crystal of $Mn_{1.08}Bi$ and MnBi is composed, when the free energy of the FIFM-MnBi state is lower than that of the PM-$Mn_{1.08}Bi$ and liquid Bi state by applying a magnetic field. From the point of view of materials science, the control of the chemical formula and the synthesis of the magnetic material under high magnetic fields are expected to be of considerable interest.

4. Conclusion

The high-field DTA experiment was performed in high magnetic fields up to 45 T in the temperature range of 300–773 K for the first time. The decomposition temperature T_t from ferromagnetic MnBi to paramagnetic $Mn_{1.08}Bi$ and liquid Bi increases from 632 K (at a zero magnetic field) to 714 K by applying a magnetic field of 45 T. Furthermore, the magnetocaloric effect of MnBi is observed in 11.5–45 T in the vicinity of 689 K. The obtained results show that we can control the composition and the decomposition temperatures and the equilibrium state of magnetic material MnBi by a high magnetic field.

Acknowledgments

This work was carried out at the HFLSM and the NHMFL. The NHMFL is supported by NSF Cooperative Agreement No. DMR-0654118, by the State of Florida, and by the DOM. This work was partly supported by the Iketani Science and Technology Foundation, and a Grant in-Aid for Scientific Research from the MEXT, Japan.

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