Bi–Mn Binary Phase Diagram in High Magnetic Fields

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To examine magnetic field effects on the Bi–Mn equilibrium phase, a high-magnetic fields differential thermal analysis (HF-DTA) was performed for fields up to 18 T and temperatures ranging from 300 to 753 K. For zero field, the peritectic temperatures \( T_{p1} \) (BiMn\(_{0.08}\) + Bi-rich liquid \( \rightarrow \) BiMn) and \( T_{p2} \) (aMn + Bi-rich liquid \( \rightarrow \) BiMn\(_{1.08}\)), and the eutectic temperature \( T_e \) (the Bi-rich liquid \( \rightarrow \) Bi solid + BiMn) were determined to be 632, 721 and 538 K, respectively. The Bi–Mn phase diagram at 18 T was obtained, which showed that \( T_{p1} \) increases with increasing magnetic fields at the rate of 2 K T\(^{-1}\). Furthermore, the liquidus boundary temperature \( T_{liq} \) between BiMn\(_{1.08}\) + liquid and Bi-rich liquid was found to increase nonlinearly with increasing magnetic field. [doi:10.2320/matertrans.M2012310]

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1. Introduction

Bi–Mn alloys have attracted attention for their basic physical properties and applications.\(^1\)–\(^3\) At low temperatures, the intermetallic compound BiMn with a NiAs-type hexagonal structure (LTP: low temperature phase) is a ferromagnet (FM).\(^4\)\(^,\)\(^5\) The magnetic moment \( m \) of LTP is 3.9 \( \mu_B \) at 0 K.\(^6\)\(^,\)\(^7\) LTP-BiMn is known to have a strong uniaxial anisotropy at room temperature\(^5\)\(^,\)\(^7\),\(^8\) and a high coercivity even at 500 K.\(^6\),\(^9\) The mean field calculation for LTP indicated that the Curie temperature \( T_C \) reaches \( \sim 720 \) K.\(^10\) However, with increasing temperature \( T \), LTP undergoes a first order magnetic phase transition from the FM state to the paramagnetic (PM) state at \( T_{p1} \sim 630 \) K, accompanied by a structural transformation from the NiAs-type to a disordered Ni\(_2\)In type hexagonal structure (HTP: high temperature phase).\(^7\)\(^,\)\(^9\) HTP has \( m \) of 1.7 \( \mu_B \) at room temperature and \( T_C \) is \( \sim 473 \) K.\(^10\) Chen reported that the composition of HTP was BiMn\(_{1.08}\), different from LTP and produced a Bi–Mn phase diagram (Fig. 1) in zero magnetic field.\(^11\) According to the diagram, this transition temperature \( T_{p1} \) corresponds to the peritectic temperature of BiMn from BiMn\(_{1.08}\) + Bi-rich liquid.

Using Bi-rich Bi–Mn alloys, some researchers synthesized the anisotropic microstructure of ferromagnetic BiMn in the nonmagnetic Bi-matrix by means of heat treatment under high magnetic field (B).\(^12\)–\(^15\) From the magnetic measurements, Liu et al.\(^16\) reported that the magnetic transition from LTP to HTP increases with increasing \( B \) up to 10 T at a rate of \( \sim 2 \) K T\(^{-1}\). Differential thermal analysis (DTA) performed by Koyama et al. also showed that \( T_{p1} \) increased with increasing \( B \) up to 14 T at a rate of 2 K T\(^{-1}\).\(^17\),\(^18\) They also suggested that \( T_{p1} \) reaches the peritectic temperature \( T_{p2} (= 719 \) K) of BiMn\(_{1.08}\) from aMn + Bi-rich liquid.\(^17\),\(^18\) However, recent DTA results reported by Koyama et al. showed that \( T_{p1} \) increases from 632 K (at a zero field) to 714 K by applying \( B = 45 \) T, but \( T_{p2} \) does not reach \( T_{p2} \).\(^1\) Furthermore, their results clearly showed that \( T_{p2} \) rises by \( \sim 5 \) K by applying a field of 45 T.\(^1\) These results suggest that the form of Bi–Mn binary phase diagram is controlled effectively by magnetic field, and new high quality materials of the Bi–Mn alloy can be synthesized by high magnetic fields.

A Bi–Mn phase diagram for different magnetic fields is thus important in developing the materials by in-field heat treatments, but at present no phase diagram exists. In this work, to clarify the effect of magnetic fields on the Bi–Mn binary phase diagram for various alloy compositions, we performed DTA experiments under high magnetic fields (HF-DTA) for \( B \leq 18 \) T over 300 \( \leq T \leq 753 \) K.

2. Experimental

Bi–Mn alloys were prepared by arc-melting an appropriate mixture of pure elements (Mn, 3N; Bi, 5N) in an argon atmosphere. The obtained button ingot was turned over and remelted several times. Next, the ingot was annealed at 523–573 K for 5 h in a argon-filled quartz tube and then quenched in water. The sample composition was determined by inductively coupled plasma-optical emission spectroscopy. The composition of each prepared sample for this study is listed in Table 1. X-ray powder diffraction measurements

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were performed using CuKα radiation at room temperature. The diffraction peaks, which depend on composition, were observed for BiMn, Mn and Bi.

The HF-DTA experiments were performed for Bi–Mn using cryogen-free superconducting magnets. The detailed experimental setup was described in the previous paper. In the HF-DTA measurements, we used non-magnetic Pt-PtRh thermocouples. A 50-mg Bi–Mn powder and a 20-mg Al2O3 powder were used for samples and reference, respectively. The DTA signals were measured during heating for temperatures 300–773 K at a rate of 6–7 K min⁻¹ under a vacuum (~10 Pa).

### Results and Discussion

Figure 2 shows the DTA curves for several Bi–Mn alloy compositions at zero field (a) and at 18 T (b). The vertical arrows indicate the eutectic temperature $T_E$, the peritectic temperatures $T_{p1}$ and $T_{p2}$, and the liquidus boundary temperature $T_{liq}$.

In zero field, two endothermic peaks at $T_E$ and $T_{p1}$, and the baseline change at $T_{liq}$ were observed for Bi–Mn. For $T > T_{p1}$, the volume of the liquid phase in the Bi-rich sample increases with increasing $T$. As a result, the baseline of the DTA curve changes gradually, because the thermal capacity of the sample changes with an increase in liquid phase. Furthermore, the baseline flattens with increasing $T$ when the coexisting state of the Mn₁₉Bi solid and the liquid phases change to a single liquid phase. Therefore, in this work, $T_{liq}$ (liquidus boundary) was determined from the baseline change.

In zero field, two endothermic peaks at $T_E$ and $T_{p1}$, and the baseline change at $T_{liq}$ were observed for Bi–Mn. Considering the phase diagram shown in Fig. 1, $T_E$ corresponds to the eutectic temperature of the Bi-rich liquid into Bi solid + BiMn, and $T_{p1} = 632$ K is the peritectic temperature of BiMn from BiMn₁₀₈ + Bi-rich liquid. A gentle change of the baseline of the DTA curve can be seen at $T_{liq} = 712$ K for Bi–Mn. From Fig. 1, this change at $T_{liq}$ corresponds to the liquidus boundary between BiMn₁₀₈ + liquid and Bi-rich liquid. For $T > T_{p1}$, the volume of the liquid phase in the Bi-rich sample increases with increasing $T$. As a result, the baseline of the DTA curve changes gradually, because the thermal capacity of the sample changes with an increase in liquid phase. Furthermore, the baseline flattens with increasing $T$ when the coexisting state of the Mn₁₉Bi solid and the liquid phases change to a single liquid phase. Therefore, in this work, $T_{liq}$ (liquidus boundary) was determined from the baseline change.

### Table 1 Bi–Mn sample compositions prepared for this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bi</th>
<th>Bi–14 at%Mn</th>
<th>Bi–18 at%Mn</th>
<th>Bi–24 at%Mn</th>
<th>Bi–40 at%Mn</th>
<th>Bi–45 at%Mn</th>
<th>Bi–53 at%Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi (at%)</td>
<td>100</td>
<td>86.4</td>
<td>82.0</td>
<td>76.2</td>
<td>55.4</td>
<td>55.4</td>
<td>46.7</td>
</tr>
<tr>
<td>Mn (at%)</td>
<td>0</td>
<td>13.6</td>
<td>18.0</td>
<td>23.8</td>
<td>39.8</td>
<td>44.6</td>
<td>53.3</td>
</tr>
</tbody>
</table>

The Bi–Mn phase diagram obtained from HF-DTA at zero field. The closed circles, the closed triangles, closed squares and the open squares indicate $T_E$, $T_{p1}$, $T_{p2}$ and $T_{liq}$, respectively.

Fig. 3 The Bi–Mn phase diagram obtained from HF-DTA at zero field. The closed circles, the closed triangles, closed squares and the open squares indicate $T_E$, $T_{p1}$, $T_{p2}$ and $T_{liq}$, respectively.
According to the powder X-ray diffraction experiments for Mn-rich compositions, this is due to the segregation of Bismuth.

As seen in Fig. 2(b), $T_{p1}$ increases from 632 K (at zero field) to 667 K by applying $B = 18$ T, whereas $T_E$ seems to be independent of $B$. From the DTA measurements under $B = 18$ T, the Bi–Mn phase diagram at a field of 18 T was determined (Fig. 4). By comparing this phase diagram with that at zero field (Fig. 3), we see that the area of the BiMn + Bi-rich liquid extends out, whereas the area for BiMn$_{1.08}$ + liquid narrows by applying higher $B$. This is because $T_{p1}$ is field enhanced, whereas $T_E$ is almost independent of $B$ and the field effect on $T_{p2}$ is very small.

Figure 5 shows the DTA curves of Bi–45 at.%Mn near $T_{p1}$ for several magnetic fields up to 18 T. The magnetic field dependence of $T_{p1}$ is shown in the inset of Fig. 5. $T_{p1}$ is found to increase linearly at a rate of 2 K T$^{-1}$ for $B \leq 20$ T. The $T_{p1}$-$B$ curve deviates from linearity for $B > 20$ T.1)

Figure 6 shows the DTA curves of Bi–24 at.%Mn near $T_{\text{liq}}$ for several magnetic fields up to 18 T. The baseline change according to the liquidus boundary at $T_{\text{liq}}$ is observed to shift to higher temperature by applying stronger fields. For $B = 18$ T, $T_{\text{liq}}$ is determined to be 715 K, which is 2 K higher than that in zero field. In addition, $T_{\text{liq}}$ increases parabolically with increasing $B$ (see inset of Fig. 6). Previous papers show that $T_{p2}$ for paramagnetic BiMn$_{1.08}$ also increases in a similar manner.1,19) Recently, we pointed out that the parabolic relationship for $T_{p2}$-$B$ is mainly dominated by the magnetic properties of HTP-BiMn$_{1.08}$.19)

The magnetic energy part of the Gibbs energy $G$ plays an important role in the effect of the magnetic field on the equilibrium state.21,22) Here, we briefly discuss the present results of the Bi–Mn phase diagram affected by magnetic fields based on the magnetic properties of LTP and HTP. The magnetization $M$ of solid $\alpha$Mn and liquid Bi are negligibly small, compared with $M$ of LTP and HTP, because solid $\alpha$Mn and liquid Bi are antiferromagnetic and diamagnetic, respectively. The magnetic energy $E_M$ is written$^{21)}$

$$E_M = \int_0^B M(T, B)dB.$$  

The magnetic field effect on $T_{\text{liq}}$ is mainly related with the gain of $E_M$ of HTP, because $T_{\text{liq}}$ corresponds to the liquidus boundary between HTP-BiMn$_{1.08}$ + liquid and Bi-rich liquid. Because $T_{\text{liq}}$ is much larger than $T_C$ ($\sim 473$ K) of
HTP, \( M(B) \) is expressible as \( M(B) = \chi B \), where \( \chi \) is the magnetic susceptibility. Indeed, the mean field calculation for HTP shows that \( M \) is proportional to \( B \).\(^{19} \) Then, \( E_M \) of HTP at \( ~T_{\text{liq}} \) becomes \( E_M = (1/2)\chi B^2 \). If the \( G-T \) relationship for HTP and liquid phase are almost linear each other in a zero magnetic field, \( T_{\text{liq}} \) is expected to be proportional to \( B^2 \) (see inset of Fig. 6).

In contrast, \( T_{p1} \) corresponds to the peritectic temperature of LTP-BiMn from HTP-BiMn\(_{1.08} \) + Bi-rich liquid. According to magnetization measurements obtained by Koyama et al., the field-induced \( M \) of LTP at \( T_{p1} \) is almost constant for \( B \leq 10 \, \text{T} \).\(^{17} \) In addition, this field-induced \( M \) of LTP is much larger than for paramagnetic HTP.\(^{19} \) Therefore, \( E_M \) is dominated by the magnetic property of LTP, and \( E_M \) is well represented by \( MB \) for \( B \leq 18 \, \text{T} \) about \( ~T_{p1} \). Consequently, \( T_{p1} \) increases linearly with \( B \).

4. Conclusion

The DTA experiments for various Bi–Mn compositions were performed in magnetic fields up to 18 T, to investigate the Bi–Mn phase diagram under high magnetic fields. This phase diagram, obtained for the first time with this study, clarifies field-dependent properties. The peritectic temperature \( T_{p1} \) of BiMn from BiMn\(_{1.08} \) + Bi-rich liquid increases with increasing field at a rate of 2 K T\(^{-1} \). Furthermore, \( T_{\text{liq}} \) of the liquidus boundary between BiMn\(_{1.08} \) + Bi-rich liquid and Bi-rich liquid increases nonlinearly with increasing field. As a result, the obtained Bi–Mn phase diagram at 18 T was quite different from that in zero field. The equilibrium diagram for the Bi–Mn binary system was found to be controllable with high magnetic fields.

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