Magnetic-Field-Induced Acceleration of Phase Formation in $\tau$-Mn-Al

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The phase formation of ferromagnetic L1$_0$-MnAl ($\tau$-phase) was accelerated by annealing in magnetic field. With in-field annealing at 623 K, the magnetization of the $\tau$-phase annealed at 15 T was a maximum of 72.2 A·m$^{-2}$/kg at 1.5 T, which is over 4 times larger than that annealed without an external magnetic field for the same annealing time. On the other hand, the transformation from $\tau$-phase to $\beta$-phase was suppressed under magnetic field. The obtained bulk sample did not show magnetic anisotropy because of the $\epsilon$- $\tau$ solid-state transformation. Obtained results suggested that magnetic field induced acceleration of transformation was due to the gain of Zeeman energy, which increases the driving force of the $\epsilon$-$\tau$ transformation. [doi:10.2320/matertrans.MAW201709]

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1. Introduction

Mn-based ferromagnetic alloys have received attention as magnetic functional materials because they exhibit a high Curie temperature $T_C$, large magnetic moment $m$, and uniaxial magnetic anisotropy $K_u$. To date, there have been many reports of Mn-based ferromagnetic materials, including MnBi and MnAlGe compound, Mn-Ga and Mn-Al alloys. Since Kono found that Mn-Al alloy exhibit ferromagnetism, there have been a lot of reports for improving the magnetic properties of ferromagnetic Mn-Al phase ($\tau$-phase). Koch found that the deformation increased the coercivity field $H_C$ of the $\tau$-phase and was accompanied by a decrease in magnetization. The magnetic properties, such as $T_C$, $m$, $K_u$, and anisotropy field $H_K$ of $\tau$-phase were reported to be $T_C$ = 653 K, $m$ = 2.4 $\mu_B$/f.u., $K_u$ = 1.5 J/m$^3$, and $H_K$ = 5 T, respectively. The $\tau$-phase with a tetragonal CuAu-type (L1$_0$) structure is commonly formed by isothermal annealing from a quenched $\epsilon$-phase with hcp structure or cooling from the high temperature $\epsilon$-phase. The $\epsilon$-phase was reported to show antiferromagnetism with Néel temperature $T_N$ ~ 90 K. According to the Al-Mn phase diagram, the $\tau$-phase is not the equilibrium phase. Thus, the single $\tau$-phase is difficult to obtain because of the co-existence of equilibrium non-ferromagnetic $\beta$- and $\gamma$-phases.

To improve the magnetic properties of Mn-Al, various preparation methods have been performed, such as spark plasma sintering, melt spinning, and mechanical milling. As it is known that the addition of carbon stabilizes the $\tau$-phase, the magnetic properties of MnAlC magnet have been evaluated. However, the addition of carbon decreased the Curie temperature of the $\tau$-phase from 653 to 558 K. On the other hand, a magnetic field $H$ stabilizes the ferromagnetic phase because of the gain of large Zeeman energy. For example, the equilibrium phase diagrams of Fe-C and Bi-Mn systems were drastically changed by the application of $H$. The large difference in Zeeman energies between the ferromagnetic phase and non-ferromagnetic phase was largely responsible for the change in phase equilibrium. In addition, the solidification, crystallization, and the reaction process for the materials were influenced by the application of a magnetic field. In-field heat treatment (IFHT) effects on the magnetic materials have been studied for the coercivity field $H_C$ of a Nd-Fe-B permanent magnet, magnetostriiction of a TbFe$_2$-based alloy, segregation of Sn in iron, etc. In particular, to control the phase fraction and morphology, IFHT is effective for Mn-based ferromagnetic alloys because of the large magnetic moment of Mn and the large uniaxial magnetic anisotropy of the ferromagnetic phase. In addition, constituent elements of ferromagnetic Mn-based alloys are not ferromagnetic state, so a large difference in Zeeman energy is expected between the synthesized ferromagnetic phase and the raw materials. Previously, we found that the reaction from Mn and Bi to ferromagnetic MnBi was drastically enhanced by in-magnetic-field reactive sintering. Furthermore, the synthesized bulk MnBi exhibits an almost completely uniaxial crystal orientation. On the other hand, IFHT for Mn-Al film also has been carried out by Fischer et al. The magnetization for the sample annealed at 1.5 T was 4 times larger than that annealed at 0 T. In addition, in our previous study, magnetic field effects (MFE) on the $\epsilon$-$\tau$ transformation of bulk Mn-Al alloys were examined with a short annealing time of 4 h. It was found that the magnetic field also influenced the $\epsilon$-$\tau$ transformation when the annealing temperature was just below $T_C$. For further understanding of MFE on the phase transformation in Mn-Al alloys, it is required to investigate the influence of in-field annealing on the phase formations of Mn-Al in detail.

In this paper, the phase transformations from single $\epsilon$-phase to $\tau$-, $\beta$-, $\gamma$-phase under magnetic fields were evaluated. Furthermore, for investigating magnetic field effects on $\tau$-$\beta$, $\gamma$ transformation, IFHT for as-melt sample, which initially includes $\epsilon$-, $\tau$-, $\beta$- and $\gamma$-phase, are carried out.
2. Experimental

An Al-55at.%Mn rod with 10 mm in diameter was prepared by induction melting, following casting into a copper mold. The rod was cut into disks with 2 mm thick. Subsequently, the disks were sealed in a quartz tube with Ar gas. Heat treatment at 1373 K for 1 day was performed, and the samples were then quenched by breaking the quartz tube in ice water. Figure 1 shows the bulk X-ray diffraction pattern for the quenched sample (a) and the magnetization curves for the sample at room temperature (RT) (b). The obtained disks were confirmed to be single \( \varepsilon \)-phase with an hcp structure. The magnetization curve shows an almost linear relationship and small magnetization \( M / \text{uni} \leq 1.1 \text{ Am}^2\text{kg}^{-1} \) at 2 T, indicating the paramagnetism of the \( \varepsilon \)-phase. This result is consistent with the reported magnetic properties of the \( \varepsilon \)-phase\(^{10}\).

The obtained disks and as-melt samples were sealed in the quartz tube with Ar gas again, and IFHT was carried out at magnetic fields up to 15 T. The details of the electric furnace used at high magnetic fields are described in Refs. 17) and 31). A magnetic field \( H_\text{h} \) was applied parallel to the thickness of the disks. In order to prevent the ferromagnetic sample from moving in the quartz tube in magnetic field, the sample was held by quartz wool. The annealing temperature \( T_\text{a} \) of the single \( \varepsilon \)-phase samples was selected to be 573 K or 623 K, and \( T_\text{a} \) of the as-melt samples was selected to be 623 K. In order to evaluate the MFE on the phase formation of \( \tau \)-phase, \( T_\text{a} \) were selected to be below the \( T_\text{C} \) of the \( \tau \)-phase to obtain a large Zeeman energy. The annealing time \( t \) was up to 96 h for \( T_\text{a} = 573 \) K and 168 h for \( T_\text{a} = 623 \) K.

The obtained phases in the sample were characterized by bulk XRD measurements. The scattering vector of the X-ray was parallel to the thickness of the disks. The magnetic properties were obtained by using a vibrating sample magnetometer at magnetic fields up to 1.5 T at RT.

3. Results

Figure 2 presents the typical bulk XRD patterns for the samples annealed at 573 K (a) and 623 K (b). All diffraction peaks can be indexed by the \( \varepsilon \)-phase with hcp structure, \( \beta \)-phase with cubic structure, \( \gamma \)-phase with trigonal structure, and \( \tau \)-phase with tetragonal L1\text{0} structure, which indicated that there are no other intermediate phases. With increasing \( t \), the fraction of \( \varepsilon \)-phase decreased due to the formation of \( \tau \)-, \( \gamma \), and \( \beta \)-phase. At 623 K, it seemed that the appearance of \( \tau \)-phase was faster than \( T_\text{a} = 573 \) K. The coexistence of the \( \beta \)-phase was observed for all samples at 623 K. It should be noted that the diffraction peaks of the coexisting \( \beta \)-phase annealed at \( T_\text{a} = 623 \) K under a magnetic field were weaker than that in a zero field. These results suggest that the in-field heat treatment suppressed the co-formation of the equilibrium \( \beta \)-phase during the \( \varepsilon \)-\( \tau \) transformation.

Fig. 1 Bulk XRD pattern (a) and magnetization curve (b) at room temperature for the sample before IFHT.

Fig. 2 Bulk XRD patterns for the samples for \( T_\text{a} = 573 \) K (a) and 623 K (b). Diffraction intensity was normalized by the highest peaks in each pattern.
Figure 3 shows the magnetization curves for $T_a = 573$ K. For $t = 24$ h, although the magnetization curve shows a small magnetization and the difference between the IFHT sample and zero-field one was small, the IFHT sample shows ferromagnetism. At $t = 48$ h, the sample annealed in a zero field shows paramagnetism, indicating it consists almost of $\varepsilon$-phases. Meanwhile, the IFHT sample shows more noticeable magnetic properties, i.e., $M_s = 14.2$ A·m$^2$/kg at 1.5 T, which was about 5 times larger than the obtained magnetization of $M_s = 2.7$ A·m$^2$/kg in a zero field.

Figure 4 indicates the magnetization curves for $T_a = 623$ K. All samples, both IFHT and zero-field, show ferromagnetic properties because of the formation of the $\tau$-phase. The difference between the IFHT sample and that annealed in a zero field was observed more clearly than at $T_a = 573$ K. The maximum values of the magnetic properties were $M_s = 72.2$ A·m$^2$/kg and $H_c = 0.15$ T.

IFHT effects for the magnetic anisotropy of the bulk sample were evaluated. Figure 5 presents the typical magnetization curves for the sample annealed at 10 T. $H_{\perp}$ and $H_{\parallel}$ indicate the applied magnetic field direction perpendicular and parallel to $H$, respectively. The magnetization curves were almost the same for $H_{\perp}$ and $H_{\parallel}$, which indicated that a uniaxial oriented phase formation was not observed. This behavior was observed for all in-field samples. IFHT effects for the $\varepsilon$-$\tau$ transformation were not the same as that for the reaction of a Bi-Mn system$^{26}$.

Figure 6 indicates the annealing time $t$ dependence of the saturation magnetization $M_s$ at $T_a = 573$ K (a) and 623 K (b). In this study, $M_s$ was determined as the magnetization at the maximum magnetic fields. For the annealing time $t \geq 48$ h at 573 K, enhancement of $M_s$ by IFHT at 15 T was observed. However, it was found that the IFHT at 573 K in 10 T did not influence the magnetic properties. On the other hand, even at $\mu_0H = 10$ T, magnetization $M_s$ was drastically enhanced compared with that in a zero field at $T_a = 623$ K, which was different behavior from that at $T_a = 573$ K. Moreover, the magnetization of sample for $t = 168$ h in 15 T was slightly smaller than that for $t = 48$ h in 15 T. Because $\tau$-phase is only ferromagnetic phase in Mn-Al system alloy, decrease of $M_s$ is due to the transformation from ferromagnetic $\tau$-phase to other non-ferromagnetic equilibrium phase, such as $\beta$-phase. The obtained result indicated that $\tau$-phase did not become equilibrium phase even applying 15 T. On the other hand, $M_s$ still increased at $t = 168$ h in a zero field, and is as high as that for 48 h in 15 T, indicating the same fraction of $\tau$-phase for $t = 48$ h in 15 T, 168 h in 15 T, and 168 h in 0 T. Thus, it is indicated that the magnetic field accelerated $\varepsilon$-$\tau$ transformation. Figure 7 shows the XRD patterns for the IFHT sample at $t = 168$ h in 0 T and 15 T. Herein, it is noted that the phase fractions of the phases were difficult to determine in detail because the XRD measure-
ments were carried out using bulk samples. However, most diffraction peaks of ε-phase disappeared in both patterns, indicating small fraction of residual ε-phase. Therefore, the almost ε-phase transformed to τ− and β− phase for both patterns. Considering the slight decrease in $M_s$ for $48 \leq t \leq 168$ h at 15 T, phase formation of β-phase, including τ−β transformation, become dominantly as residual ε-phase vanished.

Figure 8 shows the coercivity field $H_c$ as a function of annealing time. With increasing $t$, $H_c$ increased for both $T_a = 573$ and 623 K. The increase in $H_c$ was related to the formation of the τ-phase. Thus, at $T_a = 623$ K, $\mu_0H_c$ saturated to be 0.15 T, regardless of IFHT or zero-field annealing. This value is as high as the previous report by ageing for a quenched strain-free ε-phase by Crew et al.9).

In order to investigate MFE on the τ−β, γ transformation, we performed IFHT for as-melt samples. As as-melt sample initially contained ε−, τ−, β−, and γ-phase, as-melt sample is suitable to observe the proceeds of τ−β or τ−γ transformation in shorter annealing time than that with single ε-phase.

Figure 9 shows the bulk XRD patterns of the as-melt samples. The diffraction peaks of the τ-phase in the sample annealed for 12 h in 15 T were same as that in 0 T. The peaks of the β-phase annealed in 15 T were smaller than that in 0 T for both annealing times, suggesting the suppression of the phase formation of β-phase by IFHT. Herein, it is difficult to determine whether the β-phase was formed by τ−β or ε−β transformation.

Figure 10 shows the annealing time $t$ dependence of the
magnetization of the as-melt samples. The $M_s$ for $t = 12$ h in 15 T was same as that in 0 T. With increasing $t$, the $M_s$ decreased for the sample annealed in a zero field, which was due to the transformation from $\tau$-phase to $\beta$-phase. This indicates that the IFHT suppressed the $\tau$-$\beta$ transformation. On the other hand, $M_s$ slightly increased for the IFHT sample with increasing $t$. Thus, it is also indicated the suppression of the $\tau$-$\beta$ transformation.

Fig. 6 The annealing time dependence of the magnetization of the samples at 1.5 T. The triangles, and circles indicated the $M_s$ of the sample annealed at each magnetic field, respectively.

Fig. 7 Bulk XRD patterns for the samples annealed at 623 K for 168 h in a zero field and 15 T. Diffraction intensity was normalized by the highest peaks of each patterns.

Fig. 8 The coercivity field $H_c$ as a function of annealing time at $T_a = 573$ K (a) and 623 K (b). The squares, triangles, and circles indicated the $\mu_0H_c$ of the sample annealed at each magnetic field, respectively.

Fig. 9 Bulk XRD patterns for as-melt samples for $T_a = 623$ K. Diffraction intensity was normalized by the highest peak of each patterns.

Fig. 10 The annealing time dependence of $M_s$ of the as-melt samples. The triangles, and circles indicated the $M_s$ of the sample annealed at each magnetic field, respectively.
4. Discussions

The magnetic field effects for phase transformation in Mn-Al are discussed with respect to the thermodynamics. The magnetic contribution for the free energy of $\varepsilon$-, $\beta$-, and $\tau$-phase Mn$_{55}$Al$_{15}$ under a magnetic field is expressed by

$$E_M = \int_0^B \mathcal{M}(T, H) \, dH,$$

where $M$ and $H$ indicate the magnetization of the phase, and external magnetic field, respectively. As $E_M$ for the ferromagnetic phase was much larger than that for the non-ferromagnetic phase, the metastable $\tau$-phase approached equilibrium. The gain in Zeeman energy $E_M$ for the $\tau$-phase at various annealing temperatures was evaluated. In this study, because the magnetic moment of the $\tau$-phase was reported to be $2.4 \mu_B$/f.u.$^8$ the thermomagnetization curve of the $\tau$-phase was calculated by mean-field theory using the following parameters: total angular momentum $S = 1$ and mean field constant $J = 979$ K ($T_C = 654$ K). The detail of the calculation method was described in Ref. 32.

Figure 11 shows the calculated thermomagnetization curves (a) and the temperature dependence of $E_M$ at 10 and 15 T (b). The $E_M$ values at 573 K and 623 K, evaluated from the curves, were 97 and 70 J/mol, respectively, at 15 T and 63 and 44 J/mol, respectively, at 10 T.

Figure 12 shows a schematic diagram of the energy states of the phases at annealing temperatures of 623 K (a) and 573 K (b). In a zero field, the schematic image of $G_\varepsilon$, $G_\beta$, $G_\beta$, and $G_\gamma$, which are the free energies of the quenched $\varepsilon$-phase, equilibrium $\gamma$- and $\beta$-phase, and the metastable $\tau$-phase, respectively, are shown in solid curves. At both temperatures, with an applied magnetic field, the gain in $E_M$ for the ferromagnetic $\tau$-phase is much larger than those for non-ferromagnetic $\beta$- and $\gamma$-phases, resulting in a large decrease in $G_\varepsilon$, shown by the broken curves. As a result, the dip in the $G_\varepsilon$ under magnetic fields brings it close to the common tangent for $G_\beta$ and $G_\gamma$. In other words, the $\tau$-phase becomes close to the equilibrium phase under magnetic fields. Therefore, the driving force of $\varepsilon$-$\tau$ and $\tau$-$\beta$ transformation is enhanced and decreased by IFHT, respectively, resulting in acceleration of the $\varepsilon$-$\tau$ phase transformation and suppression of the $\tau$-$\beta$ phase transformation. Furthermore, based on the magnetic contribution on $G$, magnetic field is ineffective for $\varepsilon$-$\beta$, $\gamma$ transformation because $\varepsilon$-, $\beta$- and $\gamma$-phase do not have large $M$. On the other hand, although $E_M$ for the $\tau$-phase at 573 K was larger than that at 623 K, $G_\beta$ and $G_\gamma$ become more stable than those at 623 K. Therefore, the gain in the Zeeman energy becomes ineffective for enhancement of the $\varepsilon$-$\tau$ transformation. In addition, thermal activation of the transformation decreased because of the low $T_C$ and the transformation becomes sluggish. For these reasons, in-field annealing-induced enhancement of the $\varepsilon$-$\tau$ phase transformation was smaller than that for $T_C = 623$ K. It is noted that the gain in the Zeeman energy is less than 0.1 kJ/mol. This value is quite small and may only have a small effect on the phase equilibrium. Thus, the $\tau$-phase is metastable but probably close to the equilibrium.

Compared Fig. 6 with Fig. 10, the behaviors of $M_t$ seems to be different each other. As seen in Fig. 6, decrease in $M_t$ appeared for IFHT sample, whereas monotonically increase in $M_t$ was observed for the sample annealed in 0 T. Meanwhile, IFHT sample showed the increase in $M_t$ for as-melt one. The annealing of as-melt sample in 0 T led the decrease in $M_t$ for $12 \leq t \leq 24$ h. These differences were explained by the residual fraction of $\varepsilon$-phase. Based on the above transformation model of Mn-Al alloys under magnetic fields, the kinetics of the in-field transformation for single $\varepsilon$-phase and as-melt sample at 623 K is discussed. In this model, magnetic-field-induced stabilization of $\tau$-phase led the acceleration of $\varepsilon$-$\tau$ transformation and suppression of $\tau$-$\beta$ transformation. As seen in Fig. 6, $M_t$ in 15 T increased for $t \leq 48$ h and decreased for $48 \leq t \leq 168$ h, whereas $M_t$ in 0 T increased for $t \leq 168$ h. Here, as seen in Fig. 2 (b), small fraction of $\varepsilon$-phase was remained at 48 h in 15 T. Residual $\varepsilon$-phase was almost vanished for $48 \leq t \leq 168$ h, and $\tau$-phase was no longer synthesized. Thus, the decrease of $M_t$ under 15 T was due to the disappearance of $\varepsilon$-phase and following $\tau$-$\beta$ transformation. Meanwhile, the $\varepsilon$-$\tau$ transformation in 0 T was slower than 15 T, $M_t$ increased for $48 \leq t \leq 168$ h, due to $\varepsilon$-$\tau$ transformation. According to the XRD pattern (see Fig. 7), although the fraction of $\beta$-phase seemed to be larger than that in 15 T, residual $\varepsilon$-phase was also larger than 15 T. As a result, increase of $M_t$ due to $\varepsilon$-$\tau$ transformation was more effective than decrease of $M_t$ due to $\beta$-$\gamma$ transformation during the initial condition. As seen in Fig. 9, the fraction of residual $\varepsilon$-phase was small, suggesting the slight occurrence of $\varepsilon$-$\tau$
transformation in following heat treatment. $M_t$ in 15 T did not decreased for $t \leq 24$ h, whereas $M_t$ in 0 T decreased for $12 \leq t \leq 24$ h. Monotonically increase of $M_t$ for IFHT sample was due to the $ε$–$τ$ transformation and the suppression of $τ$–$β$ transformation. Meanwhile in 0 T, decrease of $M_t$ was due to the decrease of $τ$-phase. As residual $ε$-phase was small and the $τ$-phase was enough large that $τ$–$β$ transformation became dominantly for $12 \leq t \leq 24$ h, leading the decrease of $M_t$ in 0 T.

In this study, no crystal orientation was induced by IFHT for Mn-Al alloys. This was a result of the $ε$–$τ$ solid-phase transformation. The $ε$–$τ$ transformation was reported to be a massive transformation\(^{33}\). During the massive transformation, $ε$-phase with disordered hcp structure became ordered hcp-L1\(_0\) transformation. The relationship of the axis between the $ε$- and $τ$-phase is shown in Fig. 13. When there is an $ε$–$τ$ transformation, the $ε$-plane of the $ε$-phase with hcp structure is compressed and a L1\(_0\) structure is formed. Therefore, the axis of the formed L1\(_0\) structure was determined by that of the $ε$-phase. Consequently the solid-state $ε$–$τ$ transformation caused the no IFHT-induced crystal orientation.

5. Conclusions

In-magnetic-field heat treatment (IFHT) effects for the phase formation of $τ$-phase Mn-Al were investigated. The drastic improvement of the ferromagnetic properties was observed by IFHT because of the acceleration and the suppression of the $ε$- and $τ$-phase transformation, respectively. These IFHT effects on the selected phase formation of $τ$-phase can be explained by the stabilization of the ferromagnetic $τ$-phase by contribution of $E_M$ for the free energy under magnetic fields.

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Fig. 12 Schematic diagrams of the energy states of the phases at $T_s = 623$ K (a) and 573 K (b). $G_ε$, $G_τ$, $G_β$, and $G_γ$ are the free energies of the $ε$-, $γ$-, $β$-, and $τ$-phases, respectively. The solid curve indicates the free energy of the phases at a zero field. The broken curve is the $G_τ$ in magnetic fields. The solid line indicates the common tangent of $G_β$ and $G_ε$.

Fig. 13 The relationship between the $ε$-phase with a hcp structure (broken lines) and the $τ$-phase with a L1\(_0\) structure (solid lines).

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