Magnetic field-control of microstructure and function of materials exhibiting solid–solid phase transformation

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Abstract

We have investigated effects of magnetic field on transformation temperatures of a pure iron specimen and selection of variants formed by martensitic transformation in a Fe–31.2Pd (at.%) alloy single crystal and disorder–order transition in a CoPt single crystal. Following results are obtained: (i) the equilibrium temperature of austenite to ferrite transformation in the pure iron specimen increases by about 7 K when a magnetic field of 10 T is applied, and the result is discussed on the basis of the Clausius–Clapeyron equation; (ii) the rearrangement of martensite variants driven by magnetic field is confirmed to occur in the Fe–31.2Pd (at.%) ferromagnetic shape memory alloy, and the behavior is discussed quantitatively by introducing magnetic shear stress acting across the twinning plane; (iii) single variant of L10-type ordered phase in a CoPt is obtained by ordering heat-treatment under a magnetic field.

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1. Introduction

Solid–solid phase transformations are usually classified into two groups from a view point of atom diffusion: diffusionless (martensitic) transformation and diffusion transformation. For both transformations, their characteristics are well known to be influenced by external fields such as temperature and pressure. Magnetic field is one of such fields and expected to be effective especially, when there exists a large difference in magnetization between the high temperature and low temperature phases.

In fact, concerning the martensitic transformation, effects of magnetic field have been intensively studied by Sadovsky’s group in Russia [1] and by our group [2,3] using iron based alloys and steels whose transformations are associated with a large difference in magnetic moment between the high temperature and low temperature phases. As a result, magnetic field is found to promote extremely the martensitic transformation in many iron-based alloys and steels. For example, the transformation temperature increases by about 80 K, when a magnetic field of 38 T is applied in Fe–Ni and Fe–Mn–C alloys. In addition, the magnetic field influences kinetics of martensitic transformation. That is, an isothermal transformation in an Fe–Ni–Mn alloy change to an athermal one under a magnetic field. These characteristics under a magnetic field have been well explained by thermodynamical and statistical method by our group [2,3].

On the other hand, concerning the diffusion transformation, there have been not so much investigations although an extreme magnetic effect can be also expected using iron-based alloys [4,5], as in the martensitic transformation mentioned above. In this paper, therefore, we will examine the effect of magnetic field on equilibrium temperature of diffusion transformation. Among many diffusion transformations, we selected austenite (γ) to ferrite (α) transformation in a pure iron, because we can expect a significant change in transformation temperature by the application of magnetic field in this system as previously estimated by Enemoto et al. [4] and Choi et al. [5]. Moreover, the increase of γ→α transformation temperature in a pure iron specimen was experimentally confirmed by Hao and Ohtsuka [6]. However, to evaluate the equilibrium temperature under a magnetic field, there needs both the γ→α and α→γ transformation temperatures. In the present study, therefore, we will determine both the γ→α and α→γ transformation temperatures in a pure iron specimen by applying various magnetic fields and analyze the field dependence of equilibrium temperature based on the Clausius–Clapeyron equation.
In addition to the change in transformation temperature, magnetic field is also expected to be effective for controlling the microstructure of transformation products with a large magnetoocrystalline anisotropy. The reason is as follows: an alloy exhibiting a solid-solid transformation usually forms a crystallographic domain structure in its low temperature phase. Such crystallographic domain has a common crystal structure but has different orientation, and is frequently referred to as a variant. For example, when an alloy transforms from a cubic structure to a tetragonal one, three variants are formed in the tetragonal phase irrespective of whether the transformation is associated with diffusion of atoms or not. Every variant has a common free energy unless external field is applied. However, under a magnetic field, there arises a significant difference in magnetic energy among them, especially when the low temperature phase is ferromagnetic with a large magnetoocrystalline anisotropy. Then, a specific variant with lowest magnetic anisotropy energy will be selected to grow under a magnetic field [7,8].

In the present study, we will show that such selection of variant is actually realized for two cases. One is the rearrangement of martensite variants driven by magnetic field in an Fe–31.2Pd (at.%) ferromagnetic shape memory alloy. The process of this rearrangement is diffusionless one. Another is the selected growth of a specific variant during ordering heat-treatment in a CoPt single crystal under a magnetic field. This selection process is diffusion one.

2. Experimental procedure

The transformation temperatures of pure iron under a magnetic field were detected by electrical resistivity measurement. A rectangular high purity (99.99%) iron specimen of 20 mm in length, 2 mm in width and 0.5 mm in thickness was inserted at the center of both the hot-zone of a furnace and a superconducting magnet. Magnetic field was applied along the longest direction of the specimen and the resistivity was measured along the same direction using a direct current four probe method. The heating and cooling rates were 1 K/min.

Rearrangement of martensite variants in an Fe–31.2Pd (at.%) alloy single crystal was examined, which was grown by floating zone method. Two parallelepiped specimens were cut out of the crystal: one is 3.7 mm × 3.7 mm × 3.7 mm in dimension and each edge being parallel to one of (100) of the parent phase were cut out from the single crystal. After homogenization at 1373 K for 24 h, they were quenched into iced water. Ordering heat-treatment was made with and without applying a magnetic field.

3. Results and discussion

3.1. Effect of magnetic field on austenite–ferrite equilibrium temperature of pure iron

Fig. 1 shows electrical resistivity curve of a pure iron measured in the heating (a) and cooling (b) processes under various magnetic fields. The $\alpha \rightarrow \gamma$ transformation is detected as a decrease in resistivity heating curve, and the transformation start temperature $T_{s}^{\alpha \rightarrow \gamma}$ is indicated by an arrow on each curve in Fig. 1(a). The $\gamma \rightarrow \alpha$ transformation is also detected as an increase in resistivity cooling curve, and the transformation start temperature $T_{s}^{\gamma \rightarrow \alpha}$ is indicated by an arrow on each curve in Fig. 1(b). The values of $T_{s}^{\alpha \rightarrow \gamma}$ and $T_{s}^{\gamma \rightarrow \alpha}$ obtained from Fig. 1(a) and (b) are plotted as a function of magnetic field in Fig. 2. It should be noted in the figure that both $T_{s}^{\alpha \rightarrow \gamma}$ and $T_{s}^{\gamma \rightarrow \alpha}$ increase monotonically with increasing magnetic field. Concerning $T_{s}^{\gamma \rightarrow \alpha}$, it increases nearly linearly with increasing magnetic field, and the value increases by 8.2 K when the magnetic field of 10 T is applied. This result is in good agreement with that reported by Hao and Ohtsuka [6]. On the other hand, the $\alpha \rightarrow \gamma$ transformation temperature $T_{s}^{\alpha \rightarrow \gamma}$ shows a different field dependence. That is, the increasing rate in low field range ($H < 5 \ T$) is smaller than that in the high field range ($H > 5 \ T$). In addition, the increase of $T_{s}^{\alpha \rightarrow \gamma}$ is about 6.4 K, when the magnetic field of 10 T is applied, being smaller than the increase of $T_{s}^{\gamma \rightarrow \alpha}$. The reason of different field dependencies between the $\gamma \rightarrow \alpha$ and $\alpha \rightarrow \gamma$ transformations is possibly related to the temperature dependence of magnetization of the $\alpha$-phase. At the present stage, however, we assume that the degree of superheating needed to initiate the $\alpha \rightarrow \gamma$ transformation is equal to that of supercooling needed to initiate $\gamma \rightarrow \alpha$ one. Under this assumption, the equilibrium temperature $T_{0}$ is approximated as $(T_{s}^{\alpha \rightarrow \gamma} + T_{s}^{\gamma \rightarrow \alpha})/2$. The field dependence of $T_{0}$ thus obtained from Fig. 2 is shown by solid circles in Fig. 3. In the figure, the results obtained by repeating the same experiment are also shown with solid triangles and solid

![Fig. 1. Temperature dependence of electrical resistivity near the $\alpha \rightarrow \gamma$ (a) and $\gamma \rightarrow \alpha$ (b) transformation temperatures under various magnetic fields (0, 3, 5, 7, 10 T).](image-url)
squares. Obviously, $T_0$ increases parabolically with increasing magnetic field.

Generally, the equilibrium temperature $T_0$ of the first order transformation is known to satisfy the Clausius–Clapeyron equation, which is expressed as

$$\frac{dT_0}{dH} = -\frac{\Delta M}{\Delta S},$$

where $\Delta M$ and $\Delta S$ are the difference in magnetization and entropy between the two phases considered, respectively. In the following, we will show that the field dependence of $T_0$ shown in Fig. 3 is in good agreement with that calculated by the equation. The value of $\Delta S$ under a magnetic field is approximated to the value under zero field, which is evaluated using a reported latent heat of $-0.92$ kJ/mol [9]. In evaluating $\Delta M$, we neglected the magnetization of the $\gamma$-phase, because the magnetization of the $\gamma$-phase is very small compared with that of the $\alpha$-phase. The magnetization of the $\alpha$-phase is calculated by using the Weiss mean-field theory, where we used the spontaneous magnetization of the $\alpha$-phase at 0 K to be $2.219$ $\mu_B/\text{atom}$ by referring to a data book [10] and assumed the total angular momentum number to be $1/2$, although it is a rough approximation. The calculated equilibrium temperatures under magnetic fields are shown by a solid line in Fig. 3. As known from the figure, the calculated result is in good agreement with experimental results. In this way, the magnetic field dependence of equilibrium temperature is well explained by thermodynamic analysis.

### 3.2. Selection of crystallographic domain by magnetic field in an Fe–31.2Pd (at.%) ferromagnetic shape memory alloy

Fig. 4 shows the temperature dependence of lattice parameter of the Fe–31.2Pd (at.%) alloy [11], which exhibits a thermoelastic martensitic transformation from a ferromagnetic parent phase to a ferromagnetic martensite phase. As known from the figure, the transformation temperature $T_M$ is about 230 K, and the lattice parameters change gradually below $T_M$. Since, the parent phase is cubic and the martensite phase is tetragonal whose $c$-axis (hard axis) corresponds to one of the three equivalent $a$-axes of the parent phase, there are three corresponding variants as mentioned before.

Then, we measured a magnetic field-induced strain (MFIS) of the Fe–31.2Pd (at.%) alloy associated with the rearrangement of martensite variants (RMV). In the measurement, the strain was detected along $[001]$P direction (P stands for the parent phase) by a capacitance method after cooling down to 77 K without applying magnetic field. So, the starting point of the specimen is multi-variant state (three variants exist). Then, we applied a magnetic field along the $[001]$P direction and measured the strain along the field direction. The result is shown in Fig. 5, where we notice that the specimen expands...
The value of $\tau_{\text{mag}}$ will be evaluated by $\Delta U_{\text{mag}}/s$, where $\Delta U_{\text{mag}}$ is the magnetic energy difference per unit volume between the two variants separated by the twinning plane considered, and $s$ is the corresponding twinning shear. Assuming that the magnetic energy is mainly composed of magnetocrystalline anisotropy energy and Zeeman energy, the maximum of $\Delta U_{\text{mag}}$ is equal to the uniaxial magnetocrystalline anisotropy constant $|K_u|$ under the [001]$_p$ field. Then, the maximum value of magnetic shear stress, $\tau_{\text{mag}}^m$, will be $|K_u|/s$ under the [001]$_p$ field.

The value of $|K_u|$ is obtained from the area enclosed by the two magnetization curves: along hard magnetization axis and along easy magnetization axis. In order to obtain these curves, we must make magnetization experiments of a single variant state in martensite phase, which is realized by applying a compressive stress along one of (001)$_p$ directions. An example of the magnetization curves along the $a$ and $c$-axes is shown in Fig. 6. By making the same experiment at various temperatures below $T_M$, we obtained temperature dependence of $|K_u|$ as shown in Fig. 7. The amount of twinning shear for the present alloys is express as $s = (1 - (c/a)^2)/(c/a)$, because the twinning plane is {101}$_M$. Then, we can easily calculate $s$ from the lattice parameters shown in Fig. 4. Using the value of $|K_u|$ and $s$ thus obtained, we calculated the maximum of magnetic shear stress $\tau_{\text{mag}}^m$, which is shown as a function of temperature in Fig. 8. As known form the figure, the value of $\tau_{\text{mag}}^m$ increases monotonically with decreasing temperature.

In evaluating $\tau_{\text{req}}$, we made tensile tests along the [001]$_p$ direction. At any temperature examined, a stage corresponding to the RMV by the external stress appears. From the stress of the stage, we obtained temperature dependence of $\tau_{\text{req}}$, which is also shown as a function of temperature in Fig. 8. Comparing $\tau_{\text{mag}}^m$ and $\tau_{\text{req}}$ shown in Fig. 8, it is obvious that the value of $\tau_{\text{mag}}^m$ is larger than $\tau_{\text{req}}$ at any temperature below $T_M$. In this way, we have confirmed that the condition for the RMV by magnetic field mentioned before is quantitatively satisfied below $T_M$ in the Fe–31.2Pd (at.% alloy). The same condition was confirmed.

Along the field direction and its value is about 3% at 1.0 T. Considering the value of 3%, we can say that the RMV driven by magnetic field is certainly realized in the Fe–31.2Pd (at.%) alloy. In this case, the fraction of the variant whose easy axis (a-axis) lies along the field direction (the variant whose magnetocrystalline anisotropy energy is lowest among the three variants) increases by the field application and it reaches 100%, which is calculated by the strain shown in Fig. 5 and the lattice parameters shown in Fig. 4. We also confirmed such a complete RMV by magnetic field in the Fe–31.2Pd (at.%) alloy by optical microscope observation.

In order to derive the condition for RMV by magnetic field, we introduce a magnetic shear stress $\tau_{\text{mag}}$ acting across the twinning plane. The reason for introducing $\tau_{\text{mag}}$ is that we usually evaluate a shear stress for analyzing a twinning plane. The reason for introducing $\tau_{\text{mag}}$ is that we usually evaluate a shear stress for analyzing a twinning plane movement, by which the RMV proceeds. Using the value of $\tau_{\text{mag}}$, the condition for RMV by magnetic field will be given as: the value of $\tau_{\text{mag}}$ is larger than the shear stress required for the RMV, $\tau_{\text{req}}$. In the following, we will show that this condition is certainly satisfied when RMV occurs by a magnetic field.

Fig. 5. Magnetic field-induced strain of an Fe–31.2Pd (at.%) alloy.

Fig. 6. Magnetization curve of an Fe–31.2Pd (at.%) alloy at 77 K measured along the $a$ and $c$-axes.

Fig. 7. Temperature dependence of uniaxial magnetocrystalline anisotropy $|K_u|$ for an Fe–31.2Pd (at.%) alloy.
3.3. Growth of a specific crystallographic domain in CoPt during the ordering heat-treatment under a magnetic field

A Co-50 at.\% Pt alloy transforms from a disordered A1-type (cubic) structure to an ordered L10-type (tetragonal) structure at 1100 K, and the tetragonal phase has three variants, as in the Fe-31.2Pd (at.\%) alloy mentioned before. The ordered phase has a Curie temperature of about 760 K, and has a high magnetocrystalline anisotropy of 4.1 MJ/m$^3$ [14] at room temperature, where the easy axis is the c-axis and the hard axis is the a-axis. Therefore, there arises a significant magnetocrystalline anisotropy energy difference between variants under a magnetic field below the Curie temperature, and the variant with the lowest magnetic energy is expected to grow preferentially compared with other variants.

In order to confirm the above expectation, we have made ordering heat-treatment of a CoPt with and without applying a magnetic field. The specimens used in the study are cube ones with each edge parallel to (100); the directions of the three edges are termed as $X$-, $Y$-, $Z$-directions. The specimens were first solution-treated at 1273 K followed by quenching into iced water to obtain the disordered state. The specimen was then subjected to the following ordering heat-treatment: heating up to 1023 K with a heating rate of about 150 K/min and keeping at 1023 K for 3 h. This heat-treatment was made under a magnetic field of 10 T applied along the Z-direction. The same heat treatment without applying magnetic field was also made for comparison.

After the ordering heat treatment, magnetization curves were measured along the X-, Y-, Z-directions, which are shown in Fig. 9. When the ordering heat-treatment were made without applying the magnetic field, the magnetization curves measured along the three directions are almost the same with one another as seen in Fig. 9(b). This means that the three variants are almost equivalently formed by this heat-treatment. On the other hand, when the ordering heat-treatment was made under the magnetic field of 10 T applied along the Z-direction, the magnetization measured along the Z-axis saturates easily compared with that measured along the $X$- and $Y$-directions as seen in Fig. 8(a). This means that almost single variant, whose easy axis (c-axis) lies along the Z-direction, is formed by the ordering under the magnetic field. The same selection of specific variant was reported in FePd by Tanaka et al. [15] At the present stage, the mechanism of the selected growth of the preferable variant under a magnetic field is not clear, and it is a subject in the future.

4. Summary

Effects of magnetic field on transformation temperature in iron and selection of variants in an Fe–31.2Pd (at.\%) ferromagnetic shape memory alloy and also in ordering process of a CoPt have been examined. As a result, following conclusions were obtained.

The austenite-ferrite equilibrium temperature of pure iron increases by about 7 K when a magnetic field of 10 T is applied. The change in equilibrium temperature is well explained by the Clausius–Clapeyron equation.

Rearrangement of martensite variants driven by magnetic field occurs in the Fe–31.2Pd (at.\%) ferromagnetic shape memory alloy. The condition is expressed as follows: the magnetic shear stress should be larger than the shear stress required for the twinning plane movement.

The selected growth of the variant with the lowest magnetic anisotropy energy is realized in the CoPt when the ordering heat-treatment is made under a magnetic field.

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