Effect of magnetic field on solid-solid phase transformations in iron-based ferromagnetic alloys

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Abstract. We have investigated the effect of magnetic field on phase transformation of iron-based ferromagnetic alloys. Two systems are selected. One is Fe-Rh alloys exhibiting a diffusional transformation from an austenite phase to a ferrite phase on cooling. The field dependence of the transformation temperature is well explained thermodynamically. The other is an Fe-31.2Pd alloy exhibiting a martensitic transformation. In this system, rearrangement of martensite variants occurs by the application of the magnetic field, and this behaviour is quantitatively explained by considering magnetic shear stress, which is expressed by the magnetic energy difference between variants divided by twinning shear.

1. Introduction
Solid-solid phase transformations are usually classified into two groups from a viewpoint of atom diffusion: diffusionless (martensitic) transformation and diffusional transformation. For both transformations, their characteristics are known to be influenced by external fields such as temperature, hydrostatic pressure and uniaxial stress. Magnetic field is one of such fields, and especially effective for changing the transformation temperature when there is a large difference in magnetization between the high- and low-temperature phases. In fact, concerning diffusionless (martensitic) transformations, the effects of magnetic field have been intensively studied in some iron based alloys[1-3]. Through the studies, the field-dependence of transformation temperature and also transformation kinetics have been quantitatively clarified until now. On the other hand, concerning diffusional transformations, the effect of magnetic field has not been so clarified yet.

$\gamma$(austenite)$\leftrightarrow\alpha$(ferrite) transformation in Fe-based alloys is one of representative diffusional transformations, in which the transformation temperature is considerably influenced by magnetic field[4-6], because there exists a large difference in magnetization between the two phases. Among various Fe-based alloys, Fe-Rh system is especially of interest because the Curie temperature $T_c$ of the $\alpha$-phase becomes higher than the $\gamma\leftrightarrow\alpha$ transformation temperatures when Rh content exceeds a certain value while the relation reverses when the content is below it. Then we can expect that the field-dependence of $\gamma\leftrightarrow\alpha$ transformation temperatures in the former case differs from that in the latter case.

In the present study, therefore, we have examined the $\gamma\rightarrow\alpha$ and $\alpha\rightarrow\gamma$ transformation temperatures in Fe-xRh alloys with x = 2, 5, 10 at.% under various magnetic field by electrical resistivity measurement. We have also measured magnetizations of the $\alpha$- and $\gamma$-phases near the transformation...
temperature as well as the latent heats of the transformations. Then the field-dependence of the \( \gamma \rightarrow \alpha \) and \( \alpha \rightarrow \gamma \) transformation temperatures is discussed on the basis of a Clausius-Clapeyron-like equation.

In addition, we will show rearrangement of variants by magnetic field observed in Fe-31.2Pd alloy, and make a quantitative analysis on this behavior by introducing a magnetic shear stress.

2. Effect of magnetic field on \( \gamma - \alpha \) transformation of Fe-Rh alloys

2.1. Sample preparation

Ingots of Fe-Rh alloys with Rh content of 2, 5, 10 at.% were prepared by arc melting. They were homogenized in vacuum for 72 h at 1273 K followed by quenching into iced-water. From each ingot, specimens for electrical resistivity measurement, magnetization measurement and differential scanning calorimetry (DSC) were cut out. The size of the specimen is 20 mm \( \times \) 2 mm \( \times \) 1 mm for electrical resistivity measurement, 5 mm \( \times \) 3 mm \( \times \) 1 mm for magnetization measurement, and 3 mm \( \times \) 3 mm \( \times \) 1 mm for DSC measurement. After cutting out these specimens, they were subjected to a heat-treatment for 1 h at 1273 K.

2.2. Transformation temperatures under magnetic field

Figure 1(a) shows temperature dependence of electrical resistivity of the Fe-2Rh alloy, and figure 2 shows that of the Fe-5Rh and Fe-10Rh alloys. Measurements have been made under magnetic field of 10 T and without applying magnetic field. The heating and cooling rate is 1 K/min, and the resistivity curve under magnetic field of 10 T is shifted upward by a constant value of \( \beta = 0.3 \mu \Omega \text{m} \) to separate the curves.

First, we determine the Curie temperature \( T_c \) of the \( \alpha \)-phase from the resistivity curves. The heating and cooling curves of the Fe-2Rh alloy measured under the field strength of \( \mu_0H = 0 \text{T} \) (without magnetic field) exhibits a bend at about 1036 K, which is indicated by a double arrow. The bend point disappears when magnetic field of 10 T is applied as seen in figure 1(a). Considering the fact that the Curie temperature disappears under the magnetic field, the bend point corresponds to \( T_c \) of the \( \alpha \)-phase. The heating curve of the Fe-5Rh alloy (figure 2(a)) also exhibits a bend point at 1029 K as indicated by a double arrow, and the bend point disappears when the magnetic field is applied. From the result, \( T_c \) of the Fe-5Rh alloy is determined to be 1029 K. In case of the Fe-10Rh alloy, \( T_c \) of the \( \alpha \)-phase is not detected by resistivity measurement because the \( \alpha \)-phase transforms to the \( \gamma \)-phase on heating before \( T_c \) is reached. Thus, we have roughly estimated \( T_c \) of the Fe-10Rh alloy by extrapolating \( T_c \)'s of pure Fe (1044 K)[7], Fe-2Rh and Fe-5Rh alloys. The estimated value is about 1015 K, which will be used for a thermodynamic analysis later. Concerning the \( \gamma \)-phase of the present alloys, the Curie temperature is expected to be far below the \( \gamma \rightarrow \alpha \) transformation temperature. Thus \( \gamma \)-phase of the present alloys is paramagnetic in the examined temperature range.

![Figure 1](attachment:image.png)

**Figure 1.** Temperature dependence of electrical resistivity of a Fe-2Rh alloy measured under magnetic field of 10 T and without magnetic field. (b), and (c) show the \( \alpha \rightarrow \gamma \) transformation start temperature clearly as a deviation from linear relation (dotted lines) under magnetic field of 10 T and without magnetic field.
Next, we determine the γ→α transformation temperature $T_s^{γ→α}$. This transformation is detected as a sharp decrease in resistivity for all the alloys, and we show $T_s^{γ→α}$ with an arrow on each cooling curve. Obviously, $T_s^{γ→α}$ under magnetic field of 10 T is higher than that under no magnetic field for each alloy.

Finally, we determine the α→γ transformation temperature $T_s^{α→γ}$. The resistivity heating curves of the Fe-5Rh and Fe-10Rh alloys show a sharp increase in association with the α→γ transformation. Thus, $T_s^{α→γ}$ is easily determined as indicated by arrows in figure 2 (a) and (b). In case of the Fe-2Rh alloy, however, the α→γ transformation does not appear as a sharp increase in resistivity. Thus we determined $T_s^{α→γ}$ as the temperature at which the heating curve starts to deviate from a linear relation (dotted line) which is shown in figure 1(b) and (c) under magnetic field of 10 T and without magnetic field, respectively.

Similar measurements have been made by varying the magnetic field, and the transformation start temperatures ($T_s^{α→γ}$ and $T_s^{γ→α}$) are plotted by square marks as a function of magnetic field in figure 3. In the figure, Δ$T$ is the difference between the transformation start temperature under various magnetic field strengths $T_s(H)$ and the one measured under zero magnetic field $T_s(H = 0)$. As seen in the figure, Δ$T$ increases with increasing magnetic field as reported previously in some iron based alloys. [4-6]

Among the six panels in figure 3, it should be noted that $T_s^{α→γ}$ (a) and $T_s^{γ→α}$ (b) of the Fe-2Rh alloy and $T_s^{α→γ}$ (c) of the Fe-5Rh alloy are above $T_c$ of each alloy. Thus the α-phase is paramagnetic at these transformation temperatures. In this condition, the transformation temperatures increase parabolically with increasing magnetic field. On the other hand, it should be noted that $T_s^{γ→α}$ (d) of the Fe-5Rh alloy, $T_s^{α→γ}$ (e), and $T_s^{γ→α}$ (f) of the Fe-10Rh alloy are below $T_c$ of each alloy. Thus the α-phase is ferromagnetic at these transformation temperatures. In this case, the transformation temperatures increase linearly with increasing magnetic field. In this way, the field-dependence of transformation temperature for the former case (α-phase is paramagnetic) is obviously different from the latter case (α-phase is ferromagnetic), as in the Fe-Co alloys reported previously [8].
2.3. Magnetization and latent heat

Magnetization measurement of the Fe-2Rh, Fe-5Rh, and Fe-10Rh alloys has been made in the heating process near the transformation temperature and at 4.2 K. Typical results of magnetization curves are shown in figure 4(a), (b), and (c) for the Fe-2Rh, Fe-5Rh, and Fe-10Rh, respectively. In the figure, the Curie temperature $T_c$ is also shown. In the case of the Fe-2Rh and Fe-5Rh alloys, all the curves are of the $\alpha$-phase. On the other hand, in the case of the Fe-10Rh alloy the magnetization curve at 983 K is of the $\gamma$-phase while others are of the $\alpha$-phase. Obviously, the magnetization of the $\gamma$-phase is negligibly small compared to that of the $\alpha$-phase regardless of whether the $\alpha$-phase is ferromagnetic or paramagnetic. The spontaneous magnetization at 4.2 K, $M_0$, for each alloy is obtained from the magnetization curve to be 2.25 $\mu_B$/atom for Fe-2Rh, 2.27 $\mu_B$/atom for Fe-5Rh, and 2.33 $\mu_B$/atom for Fe-10Rh alloy. These values lie on the Slater-Pauling curve.[9]

Differential scanning calorimetry (DSC) has been made with a heating and cooling rate of 10 K/min by using a NETZSCH-STA449C/3/G Jupiter to obtain the latent heat of the transformation, which is shown in figure 5 (a), (b), and (c) for the Fe-2Rh, Fe-5Rh, and Fe-10Rh alloy, respectively. A clear peak due to the $\gamma\rightarrow\alpha$ transformation is seen in the cooling curves and that due to the $\alpha\rightarrow\gamma$ one is seen in the heating curves. We notice that the absolute value of latent heat $|L|$ in the cooling process is larger than that in the heating process for all the alloys. The difference is especially large for the Fe-5Rh alloy in which the $\alpha$-phase is ferromagnetic at $T_s^{\gamma\rightarrow\alpha}$ although it is paramagnetic at $T_s^{\alpha\rightarrow\gamma}$. The large difference in $|L|$ means that the change in magnetic entropy at $T_s^{\gamma\rightarrow\alpha}$ is larger than that at $T_s^{\alpha\rightarrow\gamma}$ probably due to magnetic entropy change. Incidentally, the $\alpha\rightarrow\gamma$ and $\gamma\rightarrow\alpha$ transformation start temperatures and the Curie temperature evaluated from the DSC curves are in good agreement with those obtained from the electrical resistivity measurement.
2.4. Thermodynamic analysis

In this section we will discuss the effect of magnetic field on the $\gamma$-$\alpha$ transformation temperature of Fe-xRh alloys ($x = 2, 5, 10$) considering magnetostatic energy. As known from figures 1 and 2, all the alloys examined here exhibit a large temperature hysteresis. Thus we discuss magnetic field-dependence of $T_s^{\gamma\rightarrow\alpha}$ and $T_s^{\alpha\rightarrow\gamma}$ instead of equilibrium temperature, as in martensitic transformations in ferrous alloys.

The existence of temperature hysteresis means that a driving force is required for the transformation. The driving force is given by the difference in chemical free energy between the two phases $\Delta G(T_s)$ at the transformation start temperature $T_s$. Let the transformation start temperature under a magnetic field of $H$ be $T_s'$ and we assume that the driving force at $T_s'$ under the magnetic field is equal to $\Delta G(T_s)$. That is, we assume that the driving force does not change by the application of magnetic field. This assumption has been confirmed to be appropriate for martensitic transformation in some iron based alloys. Under the assumption, we can derive the following equation to estimate the field-dependence of transformation temperature, as in martensitic transformations.

$$\Delta G(T_s) - \Delta G(T_s') = \int_0^{T_s'} \Delta M dH \quad (1),$$
where $\Delta M$ is the difference in magnetization between $\gamma$-and $\alpha$-phases. The left hand side of the equation can be approximated as $\Delta S (T_s' - T_s)$ if the change in transformation temperature is small. Then the field-dependence of transformation temperature is given by

$$\Delta T = T_s' - T_s = -\frac{1}{\Delta S} \int_0^H \Delta M dH \quad (2).$$

We can calculate field-dependence of transformation temperatures if we know $\Delta S$ and $\Delta M$. The change in entropy $\Delta S$ has been evaluated as $\Delta S = L/T_s$, where $L$ is the latent heat of $\gamma \rightarrow \alpha$ ($\alpha \rightarrow \gamma$) transformation in case we are considering $T_s^\alpha \rightarrow \gamma$ ($T_s^\gamma \rightarrow \alpha$).

In obtaining the change in magnetization $\Delta M$, we neglect the magnetization of the $\gamma$-phase because it is small compared with the magnetization of the $\alpha$-phase. The magnetization of the $\alpha$-phase for $H < 1.2$ T is obtained by the magnetization curves shown in figure 4. However, that for $H > 1.2$ T has not been obtained in the present study. To evaluate the value in the high field region, we assumed that the linear relation of $M^2$ vs $H/M$ (Arrott plot) obtained for $H < 1.2$ is also satisfied for $H > 1.2$ T. In this approximation, we can calculate the field-dependence of $\Delta M$ at the transformation start temperatures of the present alloys, which is shown in figure 6.

Putting the values of $\Delta S$ and $\Delta M$ thus obtained into equation (2), the field-dependence of the shift in transformation temperature ($\Delta T$) has been calculated for the present alloys, and the results are shown by solid curves in figure 3. The calculated value is in good agreement with experimental result for all the alloys.

3. Rearrangement of martensite variants in Fe-Pd under a magnetic field

A ferromagnetic shape memory alloy of Fe-31.2(at.%)Pd exhibits a thermoelastic martensitic transformation [10] from a cubic phase (Fm$\overline{3}$m) to a tetragonal phase (I$4/mmm$) at 230 K ($T_M$) as shown in the figure 7. The tetragonal phase is ferromagnetic with a large uniaxial magnetocrystalline anisotropy, and its $a$-axis is the magnetization easy axis.
The thermally-induced martensite phase usually composed of several orientation variants, which are connected one another by a twinning plane. Figure 8(b) shows such a multi-variant state of the martensite phase of Fe-31.2Pd formed from a plane matrix of the parent phase (figure 8(a)) by cooling. The specimen used was a single crystal, which was grown by a floating zone method from an ingot prepared by arc melting. We applied a magnetic field in the [001] direction of the parent phase and observed the change in microstructure. This direction corresponds to the magnetization easy axis for one variant and hard axis for another variant. When the magnetic field exceeded about 0.28 MA/m, rearrangement of variants initiates by the movement of twinning planes as reported previously in Ni-Mn-Ga alloys [11-14] and a Fe-30Pd alloy[11]. When the field exceeds about 0.4 MA/m, the whole area comprises the dark region as shown in figure 8(d), meaning that the rearrangement of variants is realized. In association with the rearrangement, the specimen elongated by about 3% in the field direction, the strain of which was measured by a capacitance method.

**Figure 9.** Magnetization curves of Fe-31.2Pd alloy measured in the $a$-axis and $c$-axis at 77 K and 200 K.
In order to understand the rearrangement of variants 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 movement, by which the rearrangement of variants proceeds. Using the value of $\tau_{\text{mag}}$, the condition for rearrangement of variants by magnetic field will be given as: the value of $\tau_{\text{mag}}$ is larger than the shear stress required for the twinning plane movement, $\tau_{\text{req}}$ ($\tau_{\text{mag}} > \tau_{\text{req}}$). In the following we will show that this condition is certainly satisfied in the present Fe-31.2Pd alloy.

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 $|K_u|$ in the case that a magnetic field is applied to $[001]_p$. The value of $s$ is given by the lattice parameters shown in figure 7 as $s = \{1-(c/a)^2\}/(c/a)$. 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 $|K_u|$ was 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 was realized by applying a compressive stress along one of $<001>_p$ directions. Examples of the magnetization curves along the $a$ and $c$ axes are shown in figure 9. By making the same experiment at various temperatures below $T_M$, we obtained temperature dependence of $|K_u|$ as shown in figure 10. Then, using the value of $|K_u|$ and $s$, $\tau_{\text{mag}}^m$ is calculated and the result is shown in figure 11.

The other important quantity is the shear stress required for the twinning plane movement. In evaluating this $\tau_{\text{req}}$, we have made tensile tests along the $[001]_p$ direction. At any temperature

![Figure 10. Temperature dependence of uniaxial magnetocrystalline anisotropy constant $K_u$.](image)

![Figure 11. Relation between the maximum of magnetic shear stress $\tau_{\text{mag}}^m$ and the stress required for twinning plane movement $\tau_{\text{req}}$ in Fe-31.2Pd alloy.](image)
examined, a stage corresponding to the rearrangement of variants appears. From the stress of the stage, we have obtained the stress of $\tau_{req}$, and its temperature dependence is shown in figure 11. Comparing $\tau_{mag}$ and $\tau_{req}$ shown in figure 11, it is obvious that the value of $\tau_{mag}$ is larger than $\tau_{req}$ at any temperature below $T_M$. In this way, we have confirmed the propriety of the condition for the occurrence of rearrangement of variants by magnetic field mentioned before regardless of temperature and orientation of magnetic field.

4. Conclusions

We have investigated effects of magnetic field on the $\gamma \rightarrow \alpha$ and $\alpha \rightarrow \gamma$ transformation temperatures in Fe-2Rh, Fe-5Rh and Fe-10Rh alloys by electrical resistivity measurements under magnetic field. As a result, we found that the change in transformation temperature $\Delta T$ is almost proportional to magnetic field when the $\alpha$-phase is ferromagnetic at the transformation temperature. On the other hand, $\Delta T$ is proportional to square of magnetic field when the $\alpha$-phase is paramagnetic. These field-dependencies of transformation temperature are well explained by Clausius-Clapeyron-like equation. We also examined the rearrangement of martensite variants by magnetic field in Fe-31.2Pd alloy and found that magnetic shear stress is larger than the shear stress required for the twinning plane movement in this alloy.

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