Effect of Magnetic Field on γ - α Transformation in Fe-Rh Alloys

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Effect of magnetic field on γ (austenite) $\leftrightarrow\alpha$ (ferrite) transformation has been studied by using Fe- x Rh alloys with $x = 2, 5, 10$ at%. In this system, the Curie temperature T_c of the α -phase is either above the $\gamma \leftrightarrow \alpha$ transformation temperature or below it depending on the Rh content. In the former case, the transformation temperature increases linearly with increasing magnetic field, while in the latter case, it increases almost proportional to square of magnetic field. Such difference has been discussed quantitatively on the basis of a Clausius-Clapeyron-like equation by using the magnetization and latent heat measured in the study. [doi:10.2320/matertrans.MI200713]

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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.

γ (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 α -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- x Rh alloys with $x = 2, 5, 10$ at% under various magnetic field by electrical resistivity measurement. We have also measured magnetizations of the α - and γ -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.

2. Experimental Procedure

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.

Electrical resistivity was measured under a magnetic field of up to 10 T applied parallel to the longest edge of the specimen by a direct current four probe method. In the measurements, platinum lead wires with a diameter of 0.1 mm were attached by spot welding at both ends of each specimen, and a direct current of 100 mA was passed through the specimen in the same direction. Temperature of the specimen was monitored by an R-type thermocouple welded at the center of each sample. The heating and cooling rates for the resistivity measurements were 1 K/min.

Magnetization of the above alloys was measured by using a vibrating sample magnetometer (VSM) and/or a superconducting quantum interference device (SQUID) magnetometer. Magnetization curve was corrected by considering the demagnetization coefficient of 0.1, which is evaluated by the magnetization curve of annealed pure iron with the same shape as the present specimens. DSC measurement was made in argon gas flow of 50 ml/min with a cooling and heating rate of 10 K/min by using a NETZSCH-STA449C/3/G Jupiter.

3. Results

Figures 1(a), 2(a), and 2(b) show temperature dependence of electrical resistivity of the Fe-2Rh, Fe-5Rh and Fe-10Rh

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Fig. 1 (a) 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.

Fig. 2 Temperature dependence of electrical resistivity of (a) Fe-5Rh alloy, and (b) Fe-10Rh alloy under magnetic field of 10 T and without magnetic field.

Table 1 The $\alpha \rightarrow \gamma$ and $\gamma \rightarrow \alpha$ transformation start temperatures of the present alloys under the magnetic fields H .

	Fe-2Rh		Fe-5Rh		Fe-10Rh	
$\mu_0 H$ / T	$T_s^{\alpha \rightarrow \gamma}$ / K	$T_s^{\gamma \rightarrow \alpha}$ / K	$T_s^{\alpha \rightarrow \gamma}$ / K	$T_s^{\gamma \rightarrow \alpha}$ / K	$T_s^{\alpha \rightarrow \gamma}$ / K	$T_s^{\gamma \rightarrow \alpha}$ / K
0	1115.7	1075.1	1046.6	990.6	963.2	905.1
1	1116.2	1076.2	1047.1	992.5	965.3	906.3
2	1117.0	1077.1	1048.1	994.9	966.9	909.1
3	1117.8	1077.9	1048.4	996.4	969.0	911.6
5	1120.0	1080.3	1051.2	1000.4	973.8	915.6
7	1122.1	1084.8	1052.9	1005.0	978.5	919.1
10	1126.5	1091.4	1058.4	1011.1	984.0	926.4

alloys, respectively, measured under magnetic field of 10 T and without applying magnetic field. 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 derive the Curie temperature T_C of the α -phase from the resistivity curves. The heating and cooling curves of the Fe-2Rh alloy measured under the field strength of $\mu_0 H = 0$ 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 Fig. 1(a). Considering the fact that the Curie temperature disappears under the magnetic field, the bend point corresponds to T_C of the α -phase. The heating curve of the Fe-5Rh alloy (Fig. 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 α -phase is not detected by resistivity measurement because the α -phase transforms to the γ -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 later in discussion. Concerning the γ -phase of the present alloys, the Curie temperature is expected to be far below the $\gamma \rightarrow \alpha$ trans-

formation temperature. Thus γ -phase is paramagnetic in the examined temperature range.

Next, we determine the $\gamma \rightarrow \alpha$ transformation temperature $T_s^{\gamma \rightarrow \alpha}$. This transformation is detected as a sharp decrease in resistivity for all the alloys, and we show $T_s^{\gamma \rightarrow \alpha}$ with an arrow on each cooling curve. Obviously, $T_s^{\gamma \rightarrow \alpha}$ under magnetic field of 10 T is higher than that under no magnetic field.

Finally, we determine the $\alpha \rightarrow \gamma$ transformation temperature $T_s^{\alpha \rightarrow \gamma}$. The resistivity heating curves of the Fe-5Rh and Fe-10Rh alloys show a sharp increase in association with the $\alpha \rightarrow \gamma$ transformation. Thus, $T_s^{\alpha \rightarrow \gamma}$ is easily determined as indicated by arrows in Fig. 2(a) and (b). In case of the Fe-2Rh alloy, however, the $\alpha \rightarrow \gamma$ transformation does not appear as a sharp increase in resistivity. Thus we determined $T_s^{\alpha \rightarrow \gamma}$ as the temperature at which the heating curve starts to deviate from a linear relation (dotted line) which is shown in Fig. 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 ($T_s^{\alpha \rightarrow \gamma}$ and $T_s^{\gamma \rightarrow \alpha}$) are summarized in Table 1. Also, they are plotted by square marks as a function of magnetic field in Fig. 3. In this figure, ΔT is the difference between the transformation start temperature under various magnetic field strengths $T_s(H)$ and the one measured under zero magnetic

Fig. 3 Magnetic field-dependence of transformation temperatures in Fe-2Rh, Fe-5Rh and Fe-10Rh alloys. Marks are obtained from Figs. 1 and 2. Error bars indicate precision for determining the transformation temperatures from the resistivity curves. Lines are calculated value using equation (2).

field $T_s(H=0)$. As known from the figure, the increase in $\alpha \rightarrow \gamma$ transformation start temperature $T_s^{\alpha \rightarrow \gamma}$ by the application of 10 T field is about 11 K for the Fe-2Rh, 12 K for the Fe-5Rh, and 21 K for the Fe-10Rh alloy. In case of $\gamma \rightarrow \alpha$ transformation start temperature $T_s^{\gamma \rightarrow \alpha}$, the increase is about 16 K for the Fe-2Rh, 21 K for the Fe-5Rh, and 21 K for the Fe-10Rh alloy.

Among the six panels in Fig. 3, it should be noted that $T_s^{\alpha \rightarrow \gamma}$ (a) and $T_s^{\gamma \rightarrow \alpha}$ (b) of the Fe-2Rh alloy and $T_s^{\alpha \rightarrow \gamma}$ (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 $T_s^{\gamma \rightarrow \alpha}$ (d) of the Fe-5Rh alloy, $T_s^{\alpha \rightarrow \gamma}$ (e), and $T_s^{\gamma \rightarrow \alpha}$ (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⁾

Considering the results obtained in the present study and that of the pure iron reported before,^{9,10)} we have plotted the transformation temperatures with and without applying magnetic field of 10 T as a function of Rh content, which is shown in Fig. 4. We know from the figure that the α -phase region is significantly expanded by the application of magnetic field of 10 T.

In the following we will show the results of magnetization and latent heat in the present alloys, which will be used for

Fig. 4 The Rh concentration dependence of the $\gamma \rightarrow \alpha$ and $\alpha \rightarrow \gamma$ transformation start temperatures under magnetic field of 10 T and without magnetic field.

Fig. 5 Magnetization curves of (a) Fe-2Rh, (b) Fe-5Rh, (c) Fe-10Rh alloys at various temperatures.

understanding quantitatively the magnetic field-dependence of γ - α transformation temperature.

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 Fig. 5(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 α -phase. On the other hand, in the case of the Fe-10Rh alloy the magnetization curve at 983 K is of the γ -phase while others are of the α -phase. Obviously, the magnetization of the γ -phase is negligibly small compared to that of the α -phase regardless of whether the α -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 $2.25 \mu_B/\text{atom}$ for Fe-2Rh, $2.27 \mu_B/\text{atom}$ for Fe-5Rh, and $2.33 \mu_B/\text{atom}$ for Fe-10Rh alloy. These values lie on the Slater-Pauling curve.¹¹⁾ The spontaneous magnetization of the α -phase near Curie temperatures have been evaluated by Arrott plot. In this plot the square of magnetization M^2 is plotted as a function of magnetic field over magnetization

Fig. 6 Temperature dependence of spontaneous magnetization (0 T, shown with solid marks) and magnetization at $\mu_0 H = 1$ T (shown with open marks) for the Fe-2Rh, Fe-5Rh and Fe-10Rh alloys. The value is normalized by spontaneous magnetization at 4.2 K, M_0 , and the temperature is normalized by the Curie temperature T_c .

Fig. 7 DSC curves of Fe-2Rh, Fe-5Rh and Fe-10Rh alloys.

H/M . The spontaneous magnetization (indicated with 0 T) thus obtained is shown in Fig. 6 together with the magnetization at 1 T. In this figure the temperature is normalized by T_c and magnetization by M_0 of each alloy. We know from the figure that the M/M_0 (normalized magnetization) of the three alloys shows the same T/T_c (normalized temperature) dependence.

Differential scanning calorimetry (DSC) has been made with a heating and cooling rate of 10 K/min to obtain the latent heat of the transformation, which is shown in Fig. 7(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. The latent heat evaluated by the DSC curve is summarized in Table 2. We notice in Table 2 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 α -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 $T_s^{\alpha \rightarrow \gamma}$. Incidentally, the $\alpha \rightarrow \gamma$ and $\gamma \rightarrow \alpha$ transformation start temperatures and the Curie temperature evaluated from

Table 2 Latent heat L (kJ/mol) for $\alpha \rightarrow \gamma$ and $\gamma \rightarrow \alpha$ transformations, spontaneous magnetization M_0 (μ_B /atom) at 4.2 K, Curie temperature T_c (K) of the present alloys.

Alloy	L ($\alpha \rightarrow \gamma$)	L ($\gamma \rightarrow \alpha$)	M_0	T_c
Fe-2Rh	1.13	-1.69	2.25	1036
Fe-5Rh	1.63	-3.36	2.27	1029
Fe-10Rh	2.93	-4.43	2.33	1015*

*estimated value.

Fig. 8 Magnetoresistance of the α -phase in (a) Fe-2Rh, (b) Fe-5Rh, (c) Fe-10Rh alloys.

the DSC curves are in good agreement with those obtained from the electrical resistivity measurement.

By the way, we notice in Figs. 1 and 2 that the resistivity of the α -phase decreases with increasing magnetic field while that of the γ -phase is almost independent of magnetic field. To see the behavior more clearly, we have plotted the normalized magnetoresistance of present alloys in Fig. 8. We notice a monotonic decrease in magnetoresistance with increasing magnetic field strength for all the alloys. Such a negative magnetoresistance of the α -phase will be due to the increase in magnetic order with increasing magnetic field. The evaluated value of magnetoresistance at the Curie temperature under magnetic field of 10 T is about 0.955 for the Fe-2Rh and 0.954 for the Fe-5Rh. In case of Fe-10Rh the magnetoresistance is evaluated to be about 0.968 at 960 K under 10 T field.

4. Discussion

In this section we will discuss the effect of magnetic field on the γ - α transformation temperature of Fe- x Rh alloys ($x = 2, 5, 10$) based on magnetostatic energy. As known from Figs. 1 and 2, all the alloys examined here exhibit a large temperature hysteresis. Thus we discuss magnetic field-dependence of $T_s^{\alpha \rightarrow \gamma}$ and $T_s^{\gamma \rightarrow \alpha}$ instead of equilibrium temperature, as in martensitic transformations of 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.³⁾ Under the assumption, we can derive the following equation to estimate the field-dependence of transformation temperature, as in martensitic transformations.

$$\Delta G(T_s) - \Delta G(T_s') = - \int_0^H \Delta M dH, \quad (1)$$

where ΔM is the difference in magnetization between γ - and α -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 ΔS and ΔM .

The change in entropy ΔS has been evaluated as $\Delta S = L/T_s$, where L is latent heat of transformation shown in Table 2.

In obtaining the change in magnetization ΔM , we neglected the magnetization of the γ -phase because it is small compared with the magnetization of the α -phase. The magnetization of the α -phase for $H < 1.2$ T is obtained by the magnetization curves shown in Fig. 5. 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 situation, we can calculate the field-dependence of ΔM at the transformation start temperatures of the present alloys, which is shown in Fig. 9.

Putting the values of ΔS and ΔM thus obtained into equation (2), the field-dependence of the shift in transformation temperature (ΔT) has been calculated for the present alloys, and the results are shown by solid curves in Fig. 3. The calculated value is in good agreement with experimental result for all the alloys. For further discussion, magnetization of the α -phase under high magnetic fields should be measured experimentally, which is a future subject.

5. Conclusions

We have investigated effects of magnetic field on the $\gamma \rightarrow \alpha$ and $\alpha \rightarrow \gamma$ transformation temperatures ($T_s^{\gamma \rightarrow \alpha}$ and $T_s^{\alpha \rightarrow \gamma}$) in Fe-2Rh, Fe-5Rh and Fe-10Rh alloys by electrical resistivity measurements under magnetic field up to 10 T. As a result, we have confirmed that both $T_s^{\gamma \rightarrow \alpha}$ and $T_s^{\alpha \rightarrow \gamma}$ increase by magnetic field for the three alloys. The change in transformation temperature ΔT is almost proportional to magnetic field when the α -phase is ferromagnetic at the transformation temperature. On the other hand, ΔT is proportional to square of magnetic field when the α -phase

Fig. 9 Magnetic field-dependence of the difference in magnetization ΔM between γ - and α -phases of the present alloys calculated from the Arrott plot. The left panels are ΔM 's at temperatures near $T_s^{\alpha \rightarrow \gamma}$ and the right panels are those at temperatures near $T_s^{\gamma \rightarrow \alpha}$.

is paramagnetic. These field-dependencies of transformation temperature are well explained by Clausius-Clapeyron-like equation.

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REFERENCES

- 1) V. D. Sadovsky, L. V. Smirov, Ye. A. Fokina, P. A. Malinen and I. P. Soroskin: *Fiz. Met. Metalloved* **27** (1967) 918.
- 2) T. Kakeshita, K. Kuroiwa, K. Shimizu, T. Ikeda, A. Yamagishi and M. Date: *Mater. Trans. JIM*, **34** (1993) 423–428.
- 3) T. Kakeshita, T. Saburi, K. Kindo and S. Endo: *Phase Transitions* **70** (1999) 65–113.
- 4) M. Enomoto, H. Guo, Y. Tazuke, Y. R. Abe and M. Shimotomai: *Metall. Mater. Trans.* **32A** (2001) 445.
- 5) J.-K. Choi, H. Ohtsuka, Y. Xu and W.-Y. Choo: *Scripta Mater.* **43** (2000) 221–226.
- 6) X. J. Hao and H. Ohtsuka: *Mater. Trans.* **45** (2004) 2622–2625.
- 7) H. P. J. Wijn (Ed.): *Magnetic Properties of Metals, d-Elements, Alloys and Compounds*, (Springer-Berlin 1991), p. 12.
- 8) T. Fukuda, M. Yuge, J.-H. Lee, T. Terai and T. Kakeshita: *ISIJ Int.* **46** (2006) 1267–1270.
- 9) T. Kakeshita and T. Fukuda: *Sci. Technol. Adv. Mater.* **7** (2006) 350–355.
- 10) H. Miyauchi, T. Fukuda and T. Kakeshita: *CAMP-ISIJ* **17** (2004) 1227.
- 11) C. Kittel: *Introduction to Solid State Physics*, 7th edition, (Wiley, New York, 1996), p. 627.