Magnetic Field-induced Martensitic Transformations in Disordered and Ordered Fe-Pt Alloys*

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Magnetic field-induced martensitic transformations in disordered and ordered Fe-24 at%Pt alloys were studied to examine the effect of degree of order (S) on the transformations by measuring the magnetization and electrical resistivity, applying a pulsed ultra-high magnetic field. As a result, it is found that a magnetic field higher than a critical strength is needed to induce the martensitic transformations at temperatures above M_s without regard to the degree of order. The critical strength increases with increasing temperature difference from M_s , ΔT , and those plotted as a function of ΔT are found to lie on a straight line for the non-thermoelastic alloys with $S < 0.5$, but on a curved line for the thermoelastic ordered alloys with $S = 0.7-0.8$, as if the curve diverges near the respective T_0 temperature. The divergence phenomenon seems to suggest that the T_0 temperature is a maximum one above which martensites can not be induced even though any high magnetic field is applied. The amount of magnetic field-induced martensites increases linearly with increasing strength of the magnetic field for any ΔT and any degree of order, and the smaller the ΔT for a given degree of order and the lower the degree of order, the larger the amount of martensites becomes. A thermodynamic calculation for the increase of M_s temperature suggests that the effect of a magnetic field on martensitic transformations may result in not only the Zeeman effect but also another unknown effect.

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I. Introduction

In order to know the effects of magnetic field on martensitic transformations in ferrous alloys and steels, the present authors have recently studied on the increase of M_s temperature, amount of magnetic field-induced martensites, and martensite morphology by using an Fe-31.7 at%Ni alloy, applying a pulsed ultra-high magnetic field⁽¹⁾⁽²⁾. As a result, it was found that the martensitic transformation was able to be induced even at temperatures above M_s by applying a magnetic field higher than a

critical strength, and that the critical strength strongly depended on the temperature at which the magnetic field was applied. Similar results had already been obtained by Krivoglaz and Sadovsky⁽³⁾, who attributed the increase of M_s temperature to the Zeeman effect alone, and proposed that the increase of M_s temperature was expressed by the following formula;

$$\Delta T = \Delta M \cdot H \cdot T_0 / q,$$

where ΔM represents a difference in magnetic moment between the austenitic and martensitic states, H the strength of applied magnetic field, T_0 of temperature equilibrium between the austenite and martensite phases, and q the heat of transformation. However, the experimentally measured increase in M_s temperature of the Fe-Ni alloy was not in agreement with the calculated using the above formula, the former being about twice as large as the latter. This means that the effect of a magnetic field on martensitic transformations may result in not only the Zeeman effect but also another unknown effect.

In order to determine the unknown effect,

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further basic experiments are needed on magnetic field-induced martensitic transformations. One of such experiments is to clarify whether or not the M_s temperature can increase unlimitedly beyond the T_0 temperature, and whether or not there exists a maximum temperature above which martensites can not be induced even though a magnetic field of any strength is applied. In order to carry out such an experiment, disordered and ordered Fe–Pt alloys with a composition near Fe₃Pt are convenient, because the temperature difference between T_0 and M_s can be reduced arbitrarily by changing the degree of order, although it was unchangeable and as much as 200 K in the case of an Fe–Ni alloy. It is now well known that in the Fe–Pt alloy the temperature difference between T_0 and M_s decreases with increasing degree of order, and that the type of martensitic transformation changes from a non-thermoelastic one in the disordered state to a thermoelastic one in the ordered state. T_0 in such a thermoelastic martensitic transformation can be expressed as $(M_s + M_f)/2$ ⁽⁴⁾, being different from $(M_s + A_s)/2$ in the non-thermoelastic type case, and the difference between T_0 and M_s can be reduced to the order of a few degrees.

On the other hand, the difference in magnetic moment between the austenitic and martensitic states of an ordered Fe–Pt alloy is almost the same as that in the previous Fe–Ni alloy. Therefore, if such an ordered Fe–Pt alloy is used, magnetic field-induced martensitic transformations at temperatures near T_0 can be examined by applying the same order of strength of magnetic field as in the case of the Fe–Ni alloy. In this sense, the ordered Fe–Pt alloy is the only one on which magnetic field-induced martensitic transformations at temperatures near T_0 can be examined. However, there has been no report on the magnetic field-induced martensitic transformation in the Fe–Pt alloy. The present study is, therefore, conducted to make it clear by examining the increase of M_s temperature, critical strength of magnetic field to induce martensites, their degree of order dependence, and amount of martensites formed in Fe–24 at%Pt alloys with different degrees of order. The results are compared with those in the

previously studied Fe–Ni alloy.

II. Experimental Procedures

An ingot of the Fe–Pt alloy with a nominal composition of 24 at%Pt was supplied by Prof. T. Tadaki at Osaka University, which was melted in a vacuum induction furnace by using 99.99% iron and 99.99% platinum. The ingot was hot-forged at 1273 K, homogenized at 1473 K for 6.0×10^5 s (168 h) in an evacuated silica capsule, and then hot- and cold-rolled into 0.3 mm thick sheet. Specimens $3 \times 20 \times 0.3$ mm³ in size were cut from the sheet and were austenitized at 1273 K for 1.08×10^4 s (3 h) in evacuated silica capsules, followed by quenching into iced water. Three kinds of specimens with different degrees of order were prepared by annealing at 923 K for 1.8×10^3 s (0.5 h), 2.9×10^4 s (8 h) and 3.8×10^5 s (108 h). In the present paper the three kinds of specimens will be labeled A, B and C in order of increasing annealing period. All specimens were cut into a half length ($3 \times 10 \times 0.3$ mm³) by a spark-cutting machine; one half was used for electrical resistivity measurements to determine transformation temperatures, and the other half for magnetic measurements. The size of the specimens was optimized to avoid Joule heating and a skin effect. High field magnetization measurements were performed at the Ultra-high Magnetic Field Laboratory, Osaka University, the magnetic field being a pulsed one with a maximum strength of 31.75 MA/m (400 kOe). Details of the pulsed magnetic field instrument have been described elsewhere⁽⁵⁾.

III. Results

1. Transformation temperatures and degrees of order

Prior to magnetic measurements, transformation temperatures (M_s , M_f , A_s and A_f), the equilibrium temperature (T_0), Curie point in the austenitic state (T_c), and the degree of order (S) were determined by measuring electrical resistivity-temperature relations and by referring to other data published so far, as described below.

The electrical resistivity of specimens A, B and C was measured as a function of temperature to determine respectively M_s , M_f , A_s and A_f temperatures. The electrical resistivity-temperature curves are shown in Fig. 1, (a), (b) and (c) being plotted for the specimens A, B and C, respectively, immediately after their annealing treatments for ordering. Transformation temperatures are indicated with arrows on each of the curves, and their values are listed with parentheses in Table 1. It is noted in Fig. 1 that the M_s temperature decreases and the type of transformation changes from a non-thermoelastic one in (a) to a thermoelastic one in (b) and (c) with increasing degree of order. However, the M_s temperatures of specimens B and C exhibiting thermoelastic type transformations increase by thermal cycling in the temperature range from 293 to 77 K. Such a thermal cycling effect on the M_s temperature can be clearly seen from the electrical resistivity-

temperature curves of Fig. 1(b') and (c') which were plotted after 15 thermal cycles for specimens B and C, respectively. The increased M_s temperatures are indicated with arrows on the curves, and their values are listed without parentheses in Table 1. The increase of M_s temperature is apparently saturated with these values, since it was not recognized even though the thermal cycling was repeated more than 15 times. It is thus noted from Table 1 that the M_s temperatures of thermoelastic specimens subjected to thermal cycling are higher than those not subjected to thermal cycling by 19 and 10 K for specimens B and C, respectively. Other transformation temperatures, M_f , A_s and A_f , however, are not much changed by thermal cycling in either specimen, as is seen in Table 1. Thus, specimens B and C used for magnetic measurements have beforehand been subjected to 15 times of thermal cycling to make their M_s temperatures remain constant.

The equilibrium temperature (T_0) was estimated from the formula $T_0 = (M_s + A_f)/2$ which was defined by Tong and Wayman⁽⁴⁾, by using the above transformation temperatures. The T_0 values for specimens B and C are shown in Table 1. The T_0 temperature thus obtained for those specimens subjected to 15 thermal cycles are higher than the M_s temperatures by about 20 and 12 K, respectively. The Curie temperature, T_c , was obtained by measuring the temperature dependence of magnetization in the austenitic state, (Table 1). It is noted that the Curie temperature are increased with increasing degree of order. The value of degree of order in each specimen was estimated from the data given in a previous paper by Tadaki *et al.*⁽⁶⁾ for an Fe-24 at%Pt alloy. Accordingly, the three kinds of annealing treatments at 923

Fig. 1 Electrical resistivity-temperature curves. (a), (b) and (c) are for specimens A, B and C, respectively, immediately after annealing treatments for ordering, and (b') and (c') are for specimens B and C, respectively, after 15 thermal cycles.

Table 1 Data on transformation temperatures, T_0 temperature, Curie temperature of austenite (T_c), and degree of order (S) for specimens used in the present study.

Sample	M_s (K)	M_f (K)	A_s (K)	A_f (K)	T_0 (K)	T_c (K) (austenite)	S
A	(255)	(198)				288	<0.5
B	203 (184)	160 (158)	183 (181)	243 (245)	223 (214.5)	321	~0.7
C	153 (143)	123 (120)	139 (138)	177 (183)	165 (163)	333	~0.8

K, which were adopted in the present experiment, will bring the degrees of order, less than 0.5, nearly equal to 0.7 and 0.8 for specimens A, B and C, respectively, as shown in Table 1.

2. Critical strength of magnetic field to induce martensitic transformation.

A pulsed magnetic field $H(t)$ whose maximum strength is higher than the critical one to induce the martensitic transformation was applied for the specimens, and the magnetization $M(t)$ was recorded as a function of strength in one pulse. Typical examples of the M - H curves obtained for the specimens A and B are shown as (a) and (b), respectively, in Fig. 2, in which there are inscribed experimental conditions such as degree of order, maximum strength of pulsed magnetic field, and temperature difference between M_s and a temperature at which the magnetic field is applied. The curve (c) in Fig. 2 is shown as reference, which is a similar M - H curve for a previously examined Fe-31.7 at%Ni alloy. It is noted in (c) that the magnetization abruptly changes at $H=20.63$ MA/m (260 kOe) due to the occurrence of martensitic transformation, as indicated by an arrow. The strength of the magnetic field exhibiting such an abrupt change in magnetization was previously described to correspond to the critical one to induce the martensitic transformation at $\Delta T=50$ K.

However, such an abrupt change in magnetization is not recognized in (a) and (b) for the present specimens A and B, respectively, and therefore, no information exists on the occurrence of martensitic transformation. Nevertheless, some hysteresis of magnetization curves can be observed, being representative of the occurrence of martensitic transformation. These results suggest that critical strengths of the magnetic field can not be determined from magnetization measurements alone even if martensitic transformation occurs, and this result is greatly different from that obtained in the previous Fe-Ni alloy. Thereupon, in order to determine critical strengths of the magnetic field to induce martensitic transformations, electrical resistivity measurements have been carried out in combination with magnetization measurements, because the electrical resistivity

Fig. 2 Magnetization curves as a function of strength of magnetic field in one pulse. (a) and (b) are for specimens A ($S < 0.5$) and B ($S \approx 0.7$), respectively, and (c) is for a previously examined Fe-31.7 at%Ni alloy.

change is very sensitive to the occurrence of martensitic transformations. The electrical resistivity ratio was measured for every rise of 0.8 MA/m (10 kOe) in maximum strength of the pulsed magnetic field, and plotted as a function of the maximum strength of pulsed magnetic field. Figure 3 shows such a plot for the specimen B ($S=0.7$) at $\Delta T=15$ K, where $R(H)$ means the electrical resistivity when the maximum strength of the magnetic field is H . This figure indicates that the ratio $R(H)/R(0)$ begins to decrease at a certain maximum strength of magnetic field, corresponding to the occurrence of martensitic transformation. Such a maximum strength in magnetic field is defined as a critical field to induce the marten-

Fig. 3 Electrical resistivity ratio as a function of maximum strength of pulsed magnetic field at $\Delta T = 15$ K for specimen B ($S \approx 0.7$), from which the critical strength of the specimen B was determined.

sitic transformation at a given ΔT . In this way, the critical maximum strength of pulsed magnetic field was determined as a function of ΔT for each of the specimens A, B and C, as shown in Fig. 4. In the figure, those for the previous Fe-Ni alloy are also shown for comparison. Figure 4 clearly indicates that the critical strengths of magnetic field to induce martensitic transformations increase with increasing ΔT for all specimens. Comparing the increases of M_s temperatures of the specimens with one another as to the same strength of magnetic field, they decrease with increasing degree of order, as easily seen from Fig. 4. For example, when 20 MA/m (252 kOe) of strength of magnetic field is applied, the M_s temperatures of specimen A ($S < 0.5$) and C ($S \sim 0.8$) are 28 and 7 K, respectively, which decrease as much as 21 K with increasing degree of order.

One of the characteristic features in Fig. 4 is

Fig. 4 Critical strengths of magnetic fields to induce martensitic transformations, plotted as a function of ΔT ($T - M_s$).

that the critical strengths of the magnetic field for specimens B and C lie on a curved line, and that the curves appear to diverge near their proper temperatures. This characteristic is greatly different from the fact that the critical strengths of the magnetic field for specimen A and the previously studied Fe-Ni alloy lie on a straight line and a bent straight line, respectively, and appears as if they increase unlimitedly. The temperature at which the curved lines diverge seems to correspond to the respective T_0 temperature of specimen B and C, as indicated in Fig. 4. This means that a maximum temperature may possibly exist, above which no martensitic transformation can be induced even if any high magnetic field is applied. This result seems to be very important in determining the effect of a magnetic field on thermodynamics or kinetics of martensitic transformations, and will be discussed later in detail.

3. Amount of magnetic field-induced martensites

The amount of magnetic field-induced martensites has been determined by calculation, using magnetic moments in the austenitic and martensitic states, in the same way as that described in a previous paper⁽²⁾. The calculated amounts for specimens A, B and C are shown as a function of the maximum strength of the pulsed magnetic field in Fig. 5. This figure shows that the amounts linearly increase with the maximum strength of magnetic field independent of the degree of order and ΔT . Such

Fig. 5 Amounts of magnetic field-induced martensites, plotted as a function of maximum strength of the pulsed magnetic field.

a magnetic field dependence of the amount of martensite can also be recognized from the magnetization curves in Fig. 2(a) and (b), which exhibit a gradual increase. This result is different from that for the previous Fe-Ni alloy in which the amount of martensite is nearly the same without regard to the strength of applied magnetic field, provided that ΔT is kept constant. According to the figure, the amounts of martensites also increase with decreasing ΔT when the degree of order is kept constant, as is easily seen if those of specimen A are compared at $\Delta T=15, 24$ and 32 K. Furthermore, they also increase with decreasing degree of order when ΔT is kept constant, as is seen from a comparison between the amounts of martensites of specimens A and B at $\Delta T=15$ K. In this way, the amounts of magnetic field-induced martensites are dependent on the strength of magnetic field, being greatly different from the case of previous Fe-Ni alloy. The reason for such a difference between the Fe-Pt and Fe-Ni alloys is not known yet, but may be attributed to the difference in mechanical strength of the matrix γ phases and/or in martensite growth mechanism in these different alloys.

IV. Discussion

It has been found above that the martensitic transformations in nearly disordered and ordered Fe-24 at%Pt alloys can be induced even at temperatures well above M_s by applying a magnetic field higher than a critical strength, and that the critical strengths of the magnetic field for the thermoelastic ordered alloys appear to diverge near the T_0 temperatures. This result suggests that the martensitic transformations can not be induced at temperatures above T_0 , even if any high magnetic field is applied.

Incidentally, there have been two viewpoints concerning an inducement of martensitic transformations at temperatures above M_s . Taking these two viewpoints, some discussion will be presented concerning the divergence phenomenon of the critical strengths of a magnetic field to induce martensitic transformations. The first viewpoint comes from an

analogy with that on deformation-induced martensitic transformations. It has been considered in the deformation-induced transformations that the stress or strain caused by deformation reduces the driving force necessary for martensite nucleation but does not effect the energy states of the matrix γ and martensite α' phases. As a result, the M_s temperature is raised by some degrees corresponding to a reduction in the driving force, and the T_0 temperature is not changed. However, the increase of M_s temperature is limited to T_0 at most, because the M_d temperature has been proposed to be close to $T_0^{(7)}$, which is defined as the maximum one above which no martensitic transformation can be induced by any amount of deformation. If this viewpoint is applied to magnetic field-induced martensitic transformations, a magnetic field may be considered to induce martensitic transformations only at temperatures below T_0 by reducing the driving force for martensite nucleation. This consideration is seemingly reasonable, since the martensitic state is thermodynamically more stable than the austenitic state only below the T_0 temperature. Thus, the divergence phenomenon of critical strengths of magnetic field near the T_0 temperature may be tentatively explained, as also actually observed in Fig. 3. However, this explanation seems not to be right, since the energy states of the matrix γ and martensite α' phases should be affected by a magnetic field and the driving force for martensite nucleation should be unchangeable, provided that a structural change is given, as discussed below.

The second viewpoint is that an external force such as magnetic field and stress may change the energy states of the matrix γ and martensite α' phases and accordingly may raise the T_0 temperature. In such a case, the M_s temperature is increased in response to the increase in T_0 temperature, because the driving force for martensite nucleation is unchanged. The M_s temperature may rise unlimitedly, if the external force is increased. This may correspond to the case reported by Krivoglaз and Sadovsky⁽³⁾, who considered the effect of a magnetic field on martensitic transformations to be due only to the Zeeman effect, and hence

proposed the formula $\Delta T = \Delta M \cdot H \cdot T_0 / q$ for the increase in M_s temperature. According to their formula, ΔT increases unlimitedly with H , as long as ΔM has a finite value, as described above. However, the critical strengths of the magnetic field actually diverge near the T_0 temperature, and this can not be explained by the formula. Moreover, ΔT calculated from the formula is not consistent with that experimentally obtained. Taking specimen C as an example, its T_0 is obtained to be 165 K, and the heat of transformation, q , is estimated to be about 330 J/mol, according to Tong and Wayman⁽⁸⁾. When 23.81 MA/m (300 kOe) of magnetic field is applied for specimen C, ΔT can be calculated by putting the values, $0.4 \mu_B$, 23.81 MA/m, 165 K and 330 J/mol, for ΔM , H , T_0 and q , respectively, and turns out to be about 33 K. But, this value is greatly different from that (less than 10 K) experimentally obtained. This means that the effect of a magnetic field on martensitic transformations may not result in the Zeeman effect alone, and that there may be another unknown effect. However, this does not mean that the second viewpoint above can not explain the divergence phenomenon of critical strengths of the magnetic field.

If the unknown effect is assumed to be such that the M_s temperature is decreased by a magnetic field for the present ordered Fe-Pt alloys, the divergence phenomenon of critical strengths of the magnetic field near the T_0 temperature may be explained, as schematically shown in Fig. 6. That is, a linear increase of M_s temperature due to the Zeeman effect (Z.E. line in Fig. 6) may be reduced by a parabolic decrease of M_s temperature due to the unknown effect (U.E. line in Fig. 6), and consequently the resultant increase of M_s temperature or critical strengths of magnetic field may diverge near the T_0 temperature (the dotted line in Fig. 6), as actually observed in Fig. 3. If a parabolic increase of M_s temperature is inversely assumed for the previous Fe-Ni alloy, such may explain the bent phenomenon in the linear relation between the critical strength and ΔT in the alloy (Fig. 4). However, the nature of the unknown effect and why the effect decreases the M_s

Fig. 6 Schematic explanation of the divergence phenomenon for critical strengths of magnetic field near the T_0 temperature. Z.E. and U.E. correspond to an increase due to the Zeeman effect and a decrease due to an unknown effect, respectively.

temperature are not yet clear at present. To clarify these are very important in knowing the basic effect of a magnetic field on martensitic transformations.

V. Conclusion

The results obtained in the present experiment are summarized as follows;

(1) A magnetic field higher than a critical strength is needed to induce martensitic transformations in disordered and ordered Fe-24 at%Pt alloys without regard to the degree of order. The critical strengths for the thermoelastic ordered alloys with $S=0.7$ and 0.8 lie on a curve when they are plotted as a function of ΔT , and the curves appear to diverge near the respective T_0 temperature of the alloys. On the other hand, those for the non-thermoelastic (nearly) disordered alloys with S less than 0.5 lie on a straight line.

(2) The amount of magnetic field-induced martensites linearly increases with increasing strength of the magnetic field for any ΔT and any degree of order, being greatly different from the behavior found in a previously examined Fe-Ni alloy. The smaller the ΔT for a given degree of order and the lower the degree of order, the larger the amount of martensites becomes.

(3) The formula $\Delta T = \Delta M \cdot H \cdot T_0 / q$ given

by Krivoglaz and Sadovsky can not account for the increase of M_s temperature determined in the present experiments, as well as in the previous experiment for an Fe-Ni alloy. This suggests that the effect of a magnetic field on martensitic transformations may result in not only the Zeeman effect but also another unknown effect which may bring about an increase or decrease of M_s temperature, depending on the alloy system.

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