Effect of Magnetic Fields on Martensitic Transformations in Alloys with a Paramagnetic to Antiferromagnetic Transition in the Austenitic State*

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The effect of magnetic fields on martensitic transformations in Fe-8.0Mn-4.5~5.3C(at%) alloys, which exhibit a paramagnetic to antiferromagnetic transition in the austenitic state, has been examined by means of differential scanning calorimetry, magnetic field susceptibility and magnetization measurements and optical microscopy, applying a pulsed ultra high magnetic field. As a result, it was found that the martensitic transformation was not thermally induced in all the alloys even at liquid helium temperature, but it occurred under magnetic fields higher than a critical one only in the alloy with 4.5 at%C. The critical magnetic field vs temperature relation in the 4.5 at%C alloy showed a C-curve, being largely different from that for all the ferrous alloys previously examined. Irrespective of the formation temperature, the amount of magnetic field-induced martensites was dependent on the strength of magnetic field near the critical one, but was independent on a little higher magnetic fields. Morphology of the magnetic field-induced martensites was the same irrespective of the formation temperature. Thermodynamic analysis suggested that an antiferromagnetic short range order which exists in the paramagnetic austenite suppressed the martensitic transformation.

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I. Introduction

Many studies have been carried out on magnetic field-induced martensitic transforma-
martensitic transformation, although the paramagnetic austenite has already been verified to exhibit the transformation to ferromagnetic martensite\(^{(11)}\). In the present study, therefore, the occurrence of martensitic transformations in the alloys has first been confirmed, and relation between \(M_s\) temperature and Néel temperature \(T_N\) has been examined by measuring those temperatures. Then, magnetic field-induced martensitic transformations have been examined, aiming at the critical magnetic field vs temperature relation, and the amount and morphology of the magnetic field-induced martensites have also been done by means of magnetization measurement and optical microscopy, respectively, applying an ultra high magnetic field. Finally, the results obtained have been compared with those in other ferrous alloys so far examined, and discussed thermodynamically about the effect of antiferromagnetism in the austenitic state on the martensitic transformation.

\section*{II. Experimental Procedure}

The alloys examined were Fe-8.0Mn-\(x\)C (\(x=3.1, 4.0, 4.5, 4.9\) and 5.3) (at%). They were produced by melting the component elements in a high frequency induction furnace under argon atmosphere and by casting into a water cooled iron mold. Details of the alloy production and specimen preparation of the five alloys were the same as those in the previous study\(^{(11)}\). From austenitized 0.3 mm thick sheets of those alloys, specimens were made by spark cutting into the size of 3 mm \(\times\) 3 mm \(\times\) 0.3 mm, 3.5 mm \(\times\) 3.5 mm \(\times\) 0.3 mm, and 3 mm \(\times\) 10 mm \(\times\) 0.3 mm, for differential scanning calorimetry (DSC) measurement (Rigaku Denki DSC 8131) to determine \(M_s\) temperature, magnetic field susceptibility measurement by a Faraday type magnetic balance (CAHN 2000) to determine \(T_N\) temperature, and magnetization measurement under high magnetic fields, respectively. Pulsed ultra high magnetic fields whose maximum strength was about 31 MA/m were applied to the austenitic alloy specimens at the Research Center for the Extreme Materials of Osaka University. Details of the ultra high magnetic field instru-

\section*{III. Results}

\subsection*{1. Transformation temperature and magnetic property of the austenitic state}

DSC measurements have been done in the temperature range from 293 to 77 K in order to determine \(M_s\) of the alloys. The determined \(M_s\) for two alloys (3.1 and 4.0 at% C) are shown in Fig. 1, as a function of carbon content. It is noted in the figure that the \(M_s\) lie on a dotted straight line which was obtained by calculating from an equation derived by Chang and Hsu\(^{(14)}\) to estimate the composition dependence of \(M_s\), that is, \(M_s\) linearly decreases with increasing carbon content. On the other hand, other three

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1}
\caption{Relation between \(M_s\) and \(T_N\) temperatures and carbon content. Symbols \(\bullet\) and \(\circ\) represent \(M_s\) and \(T_N\), respectively, and dotted line does calculated \(M_s\) by using an equation derived by Chang and Hsu\(^{(14)}\).}
\end{figure}
allies exhibited no martensitic transformation in the temperature range and even at liquid helium temperature of 4.2 K. This was also confirmed by observing the lack of the surface relief effect due to martensitic transformation by optical microscopy after the specimens were immersed into liquid helium and drawn up in the air, and also measuring no change in magnetic field susceptibility due to martensitic transformation in the temperature range from 300 to 4.2 K, as will be described later. Among these observations, the non-occurrence of martensitic transformation in the 4.5 at% C alloy seems to be a little strange, because the calculated $M_s$ was 32 K and a martensitic transformation would be induced below that temperature. This strange observation will be discussed later.

Magnetic field susceptibility of the austenite of the five alloys has been measured by a Faraday type magnetic balance method in order to determine $T_N$, a low steady magnetic field being applied to the alloys. A typical result of the measurements on the 4.5 at% C alloy is shown in Fig. 2, as a function of temperature. The figure indicates that the magnetic field susceptibility has a broad peak near 30 K, which was reversible in the temperature range from 300 to 4.2 K. This suggests that the 4.5 at% C alloy does not exhibit any martensitic transformation but shows a paramagnetic to antiferromagnetic transition in the austenitic state. The broad peak makes the determination of $T_N$ not so easy, but the $T_N$ may be defined to be about 30 K, which corresponds nearly to the peak temperature of the magnetic field susceptibility. A similar broad peak was observed for the 4.9 and 5.3 at% C alloys. On the other hand, the magnetic field susceptibility of other two alloys (3.1 and 4.0 at% C) was constant in the temperature range from 300 to respective $M_s$, this being the same as that for the paramagnetic austenitic alloys previously examined(11). Therefore, the other two alloys are surely paramagnetic in the austenitic state. $T_N$ thus determined for the former three alloy are plotted in Fig. 1, which are constant (about 30 K) irrespective of carbon content in the range from 4.5 to 5.3 at%. However, the 4.5 at% C alloy is of a delicate composition, because its $T_N$ (30 K) is a little lower than the calculated $M_s$ (32 K) or they are almost the same, as seen from Fig. 1. Therefore, the non-occurrence of martensitic transformation in the 4.5 at% C alloy may be attributed to the antiferromagnetism in the austenitic state.

Next, magnetic field-induced martensitic transformation has been examined in order to know the effect of antiferromagnetism of the austenitic state on martensitic transformation. It was observed in the 4.5 at% C whose $T_N$ was almost the same as calculated $M_s$, but not in other alloys (4.9 and 5.3 at%) whose $T_N$ were much different from their calculated $M_s$. Results of the examination on the 4.5 at% C alloy will be described below.

2. Critical magnetic field for inducing martensite

Magnetization $M(t)$ has been measured as a function of magnetic field $H(t)$ in one pulse. Typical $M(t)$-$H(t)$ curves at temperatures lower (4.2 K) and higher (50 K) than $T_N$ are shown in Fig. 3(a) and (b). The curve in (a) shows no hysteresis even when maximum strength of magnetic field of 31 MA/m has been applied, suggesting that no martensitic transformation occurs under the magnetic field. On the other hand, the curve in (b) shows an increase in magnetization at a certain magnetic field, as indicated by an arrow. This indicates that martensitic transformation is induced by a magnetic field and the product phase is ferromagnetic. Such an increase in magnetization due to martensitic transformation was not observed when the maximum
strength of applied pulsed magnetic field was lower than the certain one. Therefore, the certain magnetic field should correspond to the critical one for inducing the martensitic transformation. In this way, in the 4.5 at%C alloy, the martensitic transformation was induced by a magnetic field even though it was not thermally induced. Then, the critical magnetic field has been measured as a function of temperature, as shown in Fig. 4. The relation between the critical magnetic field and temperature forms a C-curve, being quite different from that in the ferrous alloys previously examined(1)-(11). That is, the critical magnetic field takes a minimum at about 100 K, and it again increases with decreasing temperature. This means that the martensitic transformation is suppressed as temperature decreases below 100 K. The suppression may be attributed to the antiferromagnetism, as mentioned before, because no other change in physical property is expected except the antiferromagnetism. However, the critical magnetic field starts to increase at about 100 K higher than $T_N$, not at $T_N$. This strange increase may be explained by an antiferromagnetic short range order in the paramagnetic austenite, as will be discussed later. The antiferromagnetic short range order is supposed to be a precursor of the observed paramagnetic to antiferromagnetic transition in the austenitic state, or to be a local one of the transition due to the compositional fluctuation.

3. Amount and morphology of magnetic field-induced martensite

The amount of magnetic field-induced martensites has been calculated in the same manner as in the previous study(5)(6), that is, by using the result of magnetization measurement. In the calculation, the spontaneous magnetization in martensitic state was assumed to be originated in magnetic atoms, that is, to depend only upon the compositions of Fe and Mn atoms. Then, referring to the Slater-Pauling curve(15), the value of about 2.0 $\mu_B$ was adopted for the present Fe-Mn-C alloys at 0 K, and considered to be valid in the temperature range where the magnetization measurements have been made, although this is very rough approximation. The calculated martensite amount is shown in Fig. 5, as a function of maximum strength of the applied pulsed magnetic field. It is seen in the figure that the amount slightly increases in the vicinity of the critical magnetic field and abruptly under a little higher magnetic fields, but it is saturated under much higher fields. Such a magnetic field...
dependence of the martensite amount is commonly observed for all the formation temperature, and it is also seen in the magnetization curve in Fig. 3(b). It is also noted in Fig. 5 that the saturated amount increases with decreasing temperature.

Figure 6(a), (b) and (c) show optical micrographs of magnetic field-induced martensites. Formation temperature $T$ and strength of applied magnetic field $H$ are indicated on the micrographs. It is known from the figure that the morphology is the same irrespective of the wide range of formation temperatures. This result is the same as that for Fe-Ni and Fe-Ni-C alloys previously examined$^{6,9}$.

IV. Discussion

It has been shown in the above that martensitic transformation was not thermally induced in Fe-8.0Mn-4.5C(at%) alloys exhibiting a paramagnetic to antiferromagnetic transition in the austenitic state, but that it was induced by magnetic fields higher than a critical one only in the 4.5 at%C alloy whose $T_N$ was almost the same as calculated $M_s$. The critical magnetic field vs temperature relation in the 4.5 at%C alloy was quite different from that in all the ferrous alloys previously examined. That is, the critical magnetic field decreases and increases above and below 100 K, respectively, with decreasing temperature, showing a minimum value at about 100 K, whereas that for the previous alloys only decreases with decreasing temperature toward $M_s$. The in-
crease in the critical magnetic field between 100 K and $T_N$ was then attributed to the existence of an antiferromagnetic short range order in the paramagnetic austenite, as explained below.

The critical magnetic field vs temperature relation has first been calculated by using the equation previously derived by the present authors\(^{6(10)}\), assuming that the austenitic state of the present alloys is paramagnetic. In the calculation, therefore, the effect of an antiferromagnetic short range order in the austenitic state on the martensitic transformation is neglected. The neglected effect may then be revealed by subtracting the calculated critical magnetic field from the measured one. According to the previous study on magnetic field-induced transformation from paramagnetic austenite to ferromagnetic martensite, the critical magnetic field vs temperature relations was found to be reduced as follows\(^{6(10)}\):

$$\Delta G(M_s) - \Delta G(M'_s) = -\Delta M(M'_s) \cdot H_c,$$

where $M_s$ and $M'_s$ represent transformation temperatures without and with a magnetic field, respectively, $\Delta G(M_s)$ and $\Delta G(M'_s)$ the difference in Gibbs chemical free energy between the austenite and martensite phases at $M_s$ and $M'_s$, respectively, $\Delta M(M'_s)$ the difference in spontaneous magnetization between the austenitic and martensitic states at $M'_s$, and $H_c$ the critical magnetic field. $M_s$ and Gibbs chemical free energy have been obtained by following the equation derived by Chang and Hsu\(^{14}\), and spontaneous magnetization in the martensitic state was obtained to be 2.0 $\mu_B$ by referring to the Slater-Pauling curve\(^{15}\), as mentioned before. The relation thus calculated is shown with the dotted line in Fig. 4. It appears to coincide with the measured relation in the high temperature region, but becomes largely different from the measured one in the lower temperature region. The difference between the calculated and measured critical magnetic fields ($H_{\text{cal.}}$ and $H_{\text{meas.}}$, respectively) is shown in Fig. 7 as a function of temperature. The figure shows that $H_{\text{meas.}} - H_{\text{cal.}}$ curvilinearly increases with decreasing temperature, although the temperatures are much higher than $T_N$. This increase manner is very similar to that for an antiferromagnetic short range order in paramagnetic austenite, which is well known for ferrous alloys exhibiting a paramagnetic to antiferromagnetic transition in the austenitic state. So, the increase of $H_{\text{meas.}} - H_{\text{cal.}}$ may probably be attributed to a short range order of antiferromagnetism in the austenitic state, as mentioned before. Besides the increase in $H_{\text{meas.}} - H_{\text{cal.}}$, the broad peak of magnetic field susceptibility over the wide temperature range in Fig. 2 may possibly be another evidence for the existence of an antiferromagnetic short range order.

Here, a thermodynamic explanation will be given for the effect of an antiferromagnetic short range order on martensitic transformation, as schematically shown in Fig. 8(a) and (b). $G_1$ and $G_2^+$ in (a) mean the Gibbs chemical free energies for the paramagnetic austenite and ferromagnetic martensite phases, respectively, $T_0$ the equilibrium temperature of these two phases, and $\Delta G_1(M_s) = G_1 - G_2^+$ the chemical driving force. Judging from the fact that the present Fe–Mn–C alloys exhibited a paramagnetic to antiferromagnetic transition in the austenitic state at $T_N$, the Gibbs chemical free energy for the austenite with an antiferromagnetic short range order, $G_2$, may be lower than $G_1$ below $T_N$ (where the antifer-
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romagnetic short range order starts to exist), and the energy due to the antiferromagnetic short range order may decrease with decreasing temperature toward $T_N$. The difference in Gibbs chemical free energy, $\Delta G_2 = G_2^\alpha - G_\alpha$, may thus form a parabolic curve with an upward convexity against temperature, as shown in Fig. 8(b). Then, $\Delta G_2$ is smaller than the chemical driving force $\Delta G_1(M_s)$ over the whole range of temperature, bringing in no thermal inducement of martensitic transformation, as actually confirmed in the present study. However, if the energy of $\Delta G_1(M_s) - \Delta G_2$ is supplied by a magnetic field, martensitic transformation may be induced, and the critical magnetic field vs temperature relation may form a similar curve to the $\Delta G_1(M_s) - \Delta G_2$ vs temperature relation, as observed as a C-curve in the present study as well. In this way, the effect of antiferromagnetic short range order on the martensitic transformation is qualitatively explained from a thermodynamic point of view.

The paramagnetic austenite with an antiferromagnetic short range order eventually transforms to antiferromagnetic one at $T_N$. This means that the degree of antiferromagnetic short range order increases with decreasing temperature toward $T_N$ and the antiferromagnetic austenite is stabilized over the long range at $T_N$. Thus, magnetic field inducement of martensitic transformation may become to be very difficult below $T_N$. Here, the magnitude of critical magnetic field for inducing martensitic transformation in the antiferromagnetic austenite will be estimated in terms of the magnetic structure, and then that in the austenite with an antiferromagnetic short range order will be evaluated. According to a molecular field approximation(16), antiferromagnetic austenite transforms to paramagnetic one if a magnetic field nearly two times higher than the exchange field, $2H_E$, is applied. This means that $G_2^\alpha$ below $T_N$ in Fig. 8(a) may be changed into $G_1^\alpha$ under the magnetic field of $2H_E$, and that a martensitic transformation may be induced by magnetic fields higher than $2H_E$, because $\Delta G_2$ becomes larger than the chemical driving force $\Delta G_1(M_s)$ at temperatures below $M_s$. Therefore, the magnetic field of $2H_E$ may roughly be regarded as a critical one for inducing martensitic transformation at those temperatures.

Thereupon, the exchange field $H_E$ at 0 K has been calculated for the Fe-Mn-C alloys whose magnetic structure has been studied by Endo and Ishikawa(12). According to them, number of the nearest neighbor for antiferromagnetic and ferromagnetic spins are eight and four, respectively. Putting these numbers into equations for $T_N$ and $H_E$ given by using a mean field approximation, the $T_N$ and $H_E$ are expressed as follows:

$$T_N = 2S(S+1)(-8J_0 + 4J_0)/3k_B, \quad (1)$$
$$H_E = 2S(-8J_0)/g\cdot\mu_B, \quad (2)$$

where $S$ represents the spin quantum number, $J_0$ the exchange energy, $g$ the Landé $g$-value, $\mu_B$ the Bohr magneton, and $k_B$ the Boltzmann's constant. From eqs. (1) and (2), $H_E$ is expressed as
\[ H_E = \frac{6k_B \cdot T_N}{g \cdot \mu_B (S + 1)}. \]  
(3)

The quantities of \( g \) and \( S \) may be assumed to be 2 and 1/2, respectively, for simplicity, and \( T_N \) has been measured to be 30 K in the present study. Putting these values into (3), one obtains that \( H_E \) is about 70 MA/m. Then, \( 2H_E \) is about 140 MA/m, being much higher than the maximum strength of applied magnetic field of 31 MA/m in the present study. Therefore, the present result that martensitic transformation has not been induced below \( T_N \) even under the maximum magnetic field is reasonable. However, strictly speaking, the value of 140 MA/m is not exactly the critical magnetic field for inducing martensitic transformation, because a decrease of \( G^\alpha \) under a magnetic field has been neglected. Taking into account the decrease, the critical magnetic field may be somewhat lower than 140 MA/m. Anyhow, the critical magnetic field becomes lower than 140 MA/m with increasing temperature, that is, with decreasing degree of antiferromagnetic long or short range order. If the critical magnetic field is thus lowered below the maximum strength of magnetic field of 31 MA/m, martensitic transformation may be induced by magnetic fields, as actually observed above \( T_N \).

As discussed above, the difference in Gibbs chemical free energy between austenites in the antiferromagnetic long or short range order state and the paramagnetic state should be quantitatively correlated with the magnitude of critical magnetic field. Therefore, a further quantitative evaluation for the Gibbs chemical free energy and critical magnetic field is now under way.

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