Effects of magnetic field on martensitic transformations

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Abstract. Magnetic field is one of the intensive variables which influence phase transformations in solids. In the present study we will show how the characteristics of martensitic transformations are influenced by magnetic field, such as transformation temperature, morphology and kinetics.

1. Introduction
Martensitic transformation is one of typical first-order structural phase transitions without atom diffusion and has been widely studied to determine its characteristics from physical, metallographic, and crystallographic viewpoints[1]. According to studies by Patel and Cohen[2] and Otsuka et al.[3], some aspects of martensitic transformation such as transformation temperatures, crystallography, and morphology of the product martensites are strongly influenced by external field, such as temperature, hydrostatic pressure, and uniaxial stress. Thus, studies on the effects of these external fields are important to understand the essential problems of the martensitic transformation such as thermodynamics, kinetics, and the origin of the transformation. Magnetic field is one of such external fields because some difference in magnetic moment between the parent and martensite states exists[4]. We have especially investigated the effect of magnetic field on martensitic transformation in many alloys. Typical results are presented in the paper.

2. Effect of magnetic field on martensitic transformation temperature
We schematically show how the transformation temperature is influenced by magnetic field in Figure 1. Gibbs chemical free energy of the parent phase $G^P$ is lower than that of the martensite phase $G^m$ above equilibrium temperature $T_0$. Martensitic transformation starts at $M_s$ which is below $T_0$ because the interfacial energy and strain energy are needed to initiate the transformation. Under a magnetic field, the $G^m$ decreases mainly due to the magnetostatic energy (change in $G^P$ is neglected here for simplicity), resulting in increase in $T_0$. Also, the $M_s$ under the magnetic field increases to $M_s'$ if we assume that the martensitic transformation under the magnetic field occurs at the temperature where $G^m - G^P$ under magnetic field is the same as that under no magnetic field at $M_s$.

In the following, we will show the results for Invar Fe-Ni alloys, disordered and ordered Fe-Pt Invar alloys and non-Invar Fe-Ni-C alloys[5-7]. Their structural changes are basically those from fcc to bcc. High-field magnetization measurements were performed at Research Center for Materials Science at Extreme Conditions, Osaka University [8]. The solid marks in figure 2 show the change in martensitic transformation temperature $\Delta M_s$ ($= M_s' - M_s$) for Fe-Ni, Fe-Pt and Fe-Ni-C alloys. It is
known form the figure that $\Delta M_s$ increases with increasing magnetic field for all the alloys examined, and the rate of the increase against the magnetic field depends on the alloy system.

We have proposed [9] the following equation to estimate the relation between the critical magnetic field and the transformation temperature:

$$\Delta G(M_s) - \Delta G(M_s') = -\Delta M(M_s') H_c - \frac{1}{2} \chi_h P H_c^2 + \varepsilon_0 \left( \frac{\partial \omega}{\partial H} \right) H_c B,$$  \hspace{1cm} (1)

where $\Delta G(M_s)$ and $\Delta G(M_s')$ is the difference in Gibbs chemical free energy between the parent and martensite phases at $M_s$ and $M_s'$ temperatures, respectively, $\Delta M(M_s')$ is $M^p(M_s') - M^m(M_s')$ (where $M^p$ and $M^m$ are the spontaneous magnetization of the martensite and parent phases, respectively), $\chi_h$ is the high magnetic field susceptibility in the parent phase, $\varepsilon_0$ is the volume change associated with martensitic transformation, $\omega$ is the forced volume magnetostriction and $B$ is the parent bulk modulus.

The first term on the right-hand side of Eq.(1) represents the energy due to the magnetostatic effect, which was already proposed by Krivoglaz and Sadovsky[4]. The second and the third terms are introduced by our group, which represent the energies due to the high-field susceptibility and forced volume magnetostriction effects, respectively. The second term in Eq.(1) is related to the induced magnetic moment in the parent phase by applying magnetic field and is originally the same as magnetostatic energy like the first term. The third term in Eq.(1) is quite effective for the Invar alloys because $\omega$ in Invar alloys are larger by one order than those of non-Invar alloys.

Figure 1. Schematic Gibbs chemical free energy as a function of temperature under a magnetic field.

Figure 2. $\Delta M_s$ vs $H_c$ relation for Invar Fe-Ni and Fe-Pt alloys (a), non-Invar Fe-Ni-C (b). Solid marks are measured values and dotted lines are calculated relations.

Figure 3. Shift of $M_s$ as a function of magnetic field for Invar Fe-31.7Ni (a), and Invar ordered Fe-24Pt alloys (b).
The calculated relation between $\Delta M_s$ and magnetic field based on Eq.(1) are shown in figure 2 with dotted lines, which are in good agreement with the experimental ones for all the alloys. We also show the calculated magnetic field dependence of transformation temperature for each term in Eq.(1) in order to know which term is effective in changing the transformation temperature by magnetic field. Typical calculated results for the Invar Fe-31.7at.%Ni alloy and the Fe-24.0at.%Pt alloy with $S = 0.8$ are shown in figure 3, where the dotted lines denoted by M.S.E., H.F.E., F.M.E. and (M.S.E.+H.F.E.+F.M.E.) are the $H_c$ vs $M_s$ relations calculated for the magnetostatic, high field susceptibility, forced volume magnetostriction and their total effects, respectively. As known form the figure, the calculated relations (M.S.E.+H.F.E.+F.M.E.) are in good agreement with the experimental ones for both alloys. It should be noted that the shift of $M_s$ due to the forced magnetostriction effect is nearly of the same order as that due to the magnetostatic effect for both alloys, and the shift of $M_s$ due to this effect is a decrease in the ordered Fe-Pt alloy, but an increase in the Fe-Ni alloy. This difference is due to the fact that the volume change associated with the martensitic transformation in the ordered Fe-Pt alloy is negative, but positive in the Fe-Ni alloy. Incidentally, in Eq.(1) we neglect the energies due to the magnetic anisotropy because these effects are small in many iron-based alloys. Recently, however, the magnetocrystalline anisotropy was found to play an important role in magnetic field-induced martensitic transformation in Co-Fe alloy[10] and in Ni-Mn-Ga alloy[11].

3. MagnetoeLASTIC MARTENSITIC TRANSFORMATION

In alloys exhibiting a thermoelastic martensitic transformation, each martensite crystal elastically responds to temperature to maintain the balance between thermal and elastic energies. If a uniaxial stress is applied to such an alloy at a temperature above $A_f$ and released, the forward and reverse transformation occur by a loading cycle. That is, the martensite is induced only while the stress is loaded. In analogy to this behavior, it is expected that if a magnetic field is applied to an alloy above $A_f$ and removed, martensite can be induced only while the magnetic field is applied. We found this type of martensitic transformation in an ausaged Fe-31.9Ni-9.8Co-4.1Ti (at.%) shape memory alloy and termed it as a magnetoelastic martensitic transformation[12] in analogy to the thermoelastic transformation.

![Figure 4. Spontaneous magnetization as a function of temperature in an ausaged Fe-Ni-Co-Ti alloy.](image)

![Figure 5. $M(t)$-$H(t)$ curves for an ausaged Fe-Ni-Co-Ti alloy at 163K above $A_f$.](image)

Figure 4 shows the spontaneous magnetization of the parent and the martensite phases as a function of temperature, which was obtained by magnetization measurements under low magnetic field. The difference in spontaneous magnetization between the two phases is about 0.3$\mu_B$/atom at $M_s$, which is of the same order as that in a previous Fe-32.5at.%Ni alloy. $M_s$ and $A_f$ shown with arrows are determined to be about 127 and 159K, respectively and $A_s$ is 60K. A pulsed high magnetic field was applied to a sample at a temperature above $A_s$, 163K ($\Delta T=(T-M_s)=36K$) and typical $M(t)$-$H(t)$ curves obtained are shown in figure 5(a) and (b). It is noted in figure 5(a) that there is no hysteresis in
magnetization when a pulsed magnetic field of 22.22MA/m is applied and removed. This means that
22.22MA/m is lower than the critical field, \( H_c \), for inducing the martensitic transformation, and
therefore no martensitic transformation occurs under the magnetic field of 22.22MA/m. Then, a higher
magnetic field was applied, and the obtained \( M(t) - H(t) \) curve is shown in (b), which reveals a
hysteresis of magnetization. That is, when a magnetic field is applied, the rate of increase of
magnetization against magnetic field changes at \( H_c = 23.08 \text{MA/m} \), as indicated with an arrow, and
when the magnetic field is removed, the increased magnetization returns to the initial value at about
\( H_f = 5 \text{MA/m} \) indicated with another arrow. This means that martensitic transformation is induced at
\( H_c \) and its reverse transformation is completed at \( H_f \). These observations show that the magnetoelastic
martensitic transformation is realized in the ausaged Fe-Ni-Co-Ti alloy.

4. Effect of Magnetic Field on Morphology of Martensites

Figure 6 shows optical micrographs of thermally-induced martensites formed by cooling a little below
the \( M_s \) temperature in Fe-Ni-C alloys ((a), (d) and (g)) and those of magnetic field-induced ones ((b),
(c), (e), (f), (h) and (i)). The formation temperature \( T, \Delta T (= T - M_s) \) and \( H \) are shown below each
photograph. Despite the different formation temperatures, the Fe-28.7Ni-1.8C mass% alloy exhibits
thin plate morphology and other two alloys do lenticular one. It is noted that the martensite
morphology is different even if the martensites are formed nearly the same temperature, as seen from
the comparison of (c) and (d). This result is contradictory to the proposition that the martensite
morphology in Fe-Ni-C alloys is decided only by the formation temperature[13]. The reason for this
difference is not known yet.

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\begin{align*}
\text{Fe-28.7Ni-1.8C, (A) Fe-29.0Ni-1.4C, (B) Fe-24.7Ni-1.8C, (C)} \\
\Delta T = 30 \text{K}, H = 11.11 \text{MA/m} \\
\Delta T = 30 \text{K}, H = 17.46 \text{MA/m} \\
\Delta T = 50 \text{K}, H = 15.87 \text{MA/m} \\
\Delta T = 88 \text{K}, H = 30.16 \text{MA/m} \\
\Delta T = 65 \text{K}, H = 28.97 \text{MA/m} \\
\Delta T = 94 \text{K}, H = 30.16 \text{MA/m} \\
\end{align*}
\]

Figure 6. Optical micrographs of thermally-induced martensites ((a), (d), (g)) and magnetic field induced-ones ((b), (c), (e), (f), (h), (i)) in Fe-Ni-C alloys.

Figure 7 is an optical micrograph showing the morphology of magnetic field-induced martensites in Fe-31.6Ni (at.%) alloy single crystal. It is known from the figure that several martensite plates grow
nearly parallel to the direction of magnetic field. Such a directional growth of martensite plates does not appear in thermally-induced martensite. Therefore, the directional growth appears to be
characteristic of magnetic field-induced martensites. We also notice that other plates terminate at the
directionally grown plates. This means that the directionally grown plates were first formed and the
other plates followed. The reason for such lengthwise growth of martensite plates under magnetic field
is not clear, but shape magnetic anisotropy effect plays an important role.
5. Kinetics of Martensitic Transformation
Martensitic transformations are frequently classified into two groups with respect to kinetics: athermal and isothermal transformations. The former type has a well defined transformation temperature $M_s$ and occurs spontaneously at $M_s$, while the latter does not have $M_s$ but occurs after some finite incubation time during isothermal holding.

Fe-Ni-Mn is an alloy system in which both the athermal and isothermal transformations occurs depending on composition. For example, Fe-31.4Ni-0.5Mn alloy has a clear $M_s$ temperature at 195 K, while Fe-29.4Ni-3.9Mn (mass%) alloy does not. The latter alloy exhibits a C-curve in the TTT diagram as shown in figure 8. We applied a pulsed magnetic field on these alloys. Figure 9 (a) is a $M$-$H$ curve of the former alloy obtained 23 K above its $M_s$, and (b) is a $M$-$H$ curve of the latter alloy at 4.2 K. Note that the same increase in magnetization is observed in both alloys. The increase in magnetization is due to martensitic transformation. The time required for the formation of all the martensite is about 20 $\mu$s. This result means that isothermal transformation in the Fe-29.4Ni-3.9Mn alloy changes to athermal one. On the basis of this finding, we have constructed a phenomenological theory which gives a unified explanation for the two transformations[14]. The dotted curve in figure 8 is calculated C-curve by using this model, which agree well with experimental result.

![Figure 8. TTT diagram of the isothermal martensitic transformation in Fe-29.4Ni-3.9Mn (mass%) alloy.](image)

![Figure 9. Magnetization vs magnetic field curves showing field-induced transformation.](image)

6. Giant Magnetic Field-Induced Strain in Ferromagnetic Shape Memory Alloys
Shape memory alloys exhibit a large recoverable strain of several percent in association with rearrangement of martensite variants. Recently, it was found by Ullakko et al. that the large strain can be induced by applying a magnetic field in ferromagnetic shape memory alloy of Ni$_2$MnGa. After that, similar results were found in other shape memory alloys, such as Fe-Pd alloys[16, 17] and in Fe$_3$Pt[18]. In this section, we will show our results of magnetic field-induced strain (MFIS) in these alloys, and explain the condition for realizing the large magnetic field-induced strain.

Figure 10 shows the MFIS obtained in single crystals of Fe-31.2Pd, Fe$_3$Pt and Ni$_2$MnGa. In all the measurements, the specimen was cooled down to 4.2 K or 77 K without applying magnetic field. Then the magnetic field was applied in the [001]$_P$ direction. This direction corresponds to easy axis or hard axis depending on variants. The strain starts to appear at a field of about 0.25MA/m and then saturates. The strain is due to rearrangement of martensite variants, which has been confirmed by optical microscopy or by x-ray diffraction.

The reason for the rearrangement of martensite variants by magnetic field is essentially explained by magnetocrystalline anisotropy constant $K_u$ and the twinning stress. The magnetic field will exert a
magnetic shear stress across the twinning plane, and the maximum of it should be $|K_u|/s$, where $s$ is twinning shear. In order to realize the rearrangement of martensite variants, $|K_u|/s$ should be larger than the stress required for twinning plane movement. We have confirmed that this condition is actually realized when the MFIS occurs in the three alloys shown in figure 10 regardless of temperature.

![Figure 10. The longitudinal magnetic field-induced strain along the [001]p direction of Fe-31.2Pd at 77 K(a), Fe3Pt at 4.2 K (b), and Ni2MnGa at 77 K(c).](image)

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