Martensitic Transformation in Shape Memory Alloys under Magnetic Field and Hydrostatic Pressure

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Effects of magnetic field and hydrostatic pressure on martensitic transformation have been examined by using Fe–Pt, Cu–Al–Ni, Ni2MnGa and Fe–Pd shape memory alloys and Fe–Ni alloys. Following results are obtained; (i) in Fe–Pt, Cu–Al–Ni and Fe–Ni alloys, the experimental magnetic field and/or hydrostatic pressure dependence of martensitic transformation start temperature, \( M_s \), is in good agreement with the dependence calculated by the equation previously proposed by our group to evaluate the relation between \( M_s \), and magnetic field and hydrostatic pressure. (ii) Giant magnetostriction has been observed in the martensite state of Ni2MnGa and Fe–31.2 at%Pd ferromagnetic shape memory alloy single crystals. The values (contraction of 3.8% for Ni2MnGa and expansion of about 3% for Fe–31.2 at%Pd) are nearly the same values as can be expected from the perfect conversion of variants, i.e., variants are converted to preferable variants whose magnetocrystalline anisotropy energy is minimum among them under the magnetic field.

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1. Introduction

Martensitic transformations are extensively influenced by external fields, such as temperature and uniaxial stress, modifying transformation temperatures, crystallography and amount and morphology of the product martensites.1,2) Therefore, to clarify the effect of external fields on martensitic transformations is very important to understand the essential problems of the transformation, such as thermodynamics, kinetics and the origin of the transformation, whose information is naturally useful to technological application field in using the transformation. Magnetic field and hydrostatic pressure are important in such external fields because there exist some significant differences in magnetic moment and atomic volume between the parent and martensitic states.3,4) In fact, many researchers3,3–9) have examined the effects of magnetic field and hydrostatic pressure on martensitic transformations. We also examined them systematically4–8) and found many interesting phenomena on them.

In the present paper, therefore, we show our following studies on the effects of magnetic field and hydrostatic pressure on martensitic transformations in some shape memory alloys; (i) effects of magnetic field and hydrostatic pressure on the martensitic transformation start temperature, \( M_s \), in Fe–Pt and Cu–Al–Ni shape memory alloys and Fe–Ni alloys and the validity of a new proposed relation by our group to evaluate the relation between \( M_s \), and magnetic field and hydrostatic pressure; (ii) giant magnetostriction caused by conversion of variants in the martensite state of Ni2MnGa and Fe–Pd ferromagnetic shape memory alloys exhibiting a thermoelastic martensitic transformation.

Incidentally, the study concerned with conversion of martensite variants under magnetic field has been recently attracted great interest and many studies have been made in Ni2MnGa,10–13) Fe–Pd14) and Fe3Pt15) ferromagnetic shape memory alloys. However, the magnetostriction of Ni2MnGa with stoichiometric composition is not reported, and perfect conversion of variants is not reported in Fe–Pd alloy until now. In the study of (ii) mentioned above, we show that nearly perfect conversion of variants is realized in stoichiometric Ni2MnGa and Fe–Pd alloys.

2. Experimental

Specimens used were Fe–24 at%Pt, Cu–28.6Al–3.2Ni (at%), Fe–31.2 at%Pd, Ni3MnGa and Fe–29.9 at%Ni. The Fe–24 at%Pt and Fe–29.9 at%Ni alloys were produced by melting the component metals in a high frequency induction furnace under argon atmosphere and casting into a water cooled iron mold. An ordering heat treatment was made in the Fe–24 at%Pt and its degree of order was 0.8 (the ordered Fe–24 at%Pt alloy thus obtained exhibits a thermoelastic martensitic transformation at \( M_s = 173 \text{ K} \)). Single crystals of Cu–28.6Al–3.2Ni (at%), Fe–31.2 at%Pd and Ni2MnGa were grown by a floating zone method. The Fe–31.2 at%Pd was solution treated at 1373 K followed by quenching into iced water, and Ni2MnGa was solution treated at 1073 K followed by ordering treatment at 873 K.

High field magnetization measurements were performed at Research Center for Materials Science at Extreme Conditions, Osaka University, the magnetic field being a pulsed one with its maximum strength of about 31 MA/m. Magnetic susceptibility measurements were made by a superconducting quantum interference device magnetometer. Magnetostriiction measurements were made by a sensitive three terminal capacitance method, where specimens were mounted in a parallel-
plate capacitance cell. Electrical resistivity measurements under a hydrostatic pressure were taken to obtain the hydrostatic pressure dependences of martensitic transformation temperatures in the above alloys. The hydrostatic pressures used in the measurements were generated by a piston cylinder type instrument, in which kerosine and transformer oil in a teflon capsule were used as liquid pressure medium and the applicable maximum pressure was 2.3 GPa.

3. Results and Discussion

3.1 Effect of magnetic field on martensitic transformation temperature

Figure 1 shows a typical magnetization curve \((M(t) - H(t))\) for the Invar Fe–31.7 at%Ni alloy,\(^4\) where \(\Delta T\) represents the temperature difference between set temperature, \(T\), and \(M_s (\Delta T = T - M_s)\). In the figure, an abrupt increase in magnetization is recognized at a certain strength of magnetic field (indicating with an arrow). The strength of magnetic field at the abrupt increase in magnetization corresponds to \(M_s\) for inducing the martensitic transformation at \(T\), in other words the set temperature, \(T\), corresponds to the martensitic transformation start temperature under the strength of magnetic field of \(H_c\). The relation thus obtained between the critical magnetic field and the shift of \(M_c\), \(\Delta M_c (\Delta M_c = M_c' - M_c)\), is shown in Fig. 2(a) with solid circles for the Fe–31.7 at%Ni alloy, and is shown in Fig. 2(b) for the Fe–24.0 at%Pt shape memory alloy with \(S \sim 0.8\) (\(S\) is degree of order) with solid circles.\(^5\) It is known from the figures that the shift of \(M_c\) increases with increasing magnetic field for both the alloys irrespective of non-thermoelastic and thermoelastic martensitic transformation.

One of the authors proposed the following equation\(^4\) to estimate the relation between the critical magnetic field and the transformation start temperature:

\[
\Delta G(M_c) - \Delta G(M'_c) = -\Delta M(M'_c) \cdot H_c - \frac{1}{2} \cdot \chi_{hf}^p \cdot H_c^2 + \epsilon_0 \cdot \left( \frac{\partial \alpha}{\partial H} \right) \cdot H_c \cdot B, \quad \cdots \quad (1)
\]

where \(\Delta G(M_c)\) and \(\Delta G(M'_c)\) represent the difference in Gibbs chemical free energy between the parent and martensite phases at \(M_c\) and \(M'_c\) temperatures, respectively, \(\Delta M(M'_c)\) the difference in spontaneous magnetization between the parent and martensite states at \(M'_c\), \(\chi_{hf}^p\) the high magnetic field susceptibility in the parent phase, \(\epsilon_0\) the volume change associated with martensitic transformation, \(\alpha\) the forced volume magnetostriction and \(B\) the parent bulk modulus. The first, second and third terms on the right-hand side of eq. (1) represent the energies due to the magnetostatic, high field susceptibility and forced volume magnetostriction, respectively. Based on the equation, \(H_c\) vs. \(M'_c\) relations have been thermodynamically calculated for the present alloys by using the physical quantities involved in the equation; which were obtained by referring to the previous studies\(^2\) and by measuring in the present study.\(^4,5\) The calculated results are shown in Fig. 2, where the dotted lines indicated with M.S.E., H.F.E., F.M.E. and (M.S.E. + H.F.E. + F.M.E.) mean the \(H_c\) vs. \(M'_c\) relations calculated for the magnetostatic, high field susceptibility, forced volume magnetostriction and their total effects, respectively. As known from the figure, the calculated relations (M.S.E. + H.F.E. + F.M.E.) are in good agreement with the experimental ones for both the alloys. It should be noted that the shift of \(M'_c\) temperature due to the forced magnetostriction effect is nearly the same order as that due to the magnetostatic effect and the shift of \(M'_c\) due to this effect is a decrease in the ordered Fe–24 at%Pt alloy, although it is an increase in the Fe–Ni alloy.\(^5\) This difference is due to the fact that the volume change associated with martensitic transformation in the ordered Fe–Pt shape memory alloys is negative value, but positive in the Fe–Ni alloy.

It can thus be concluded from good agreement between calculated and measured relations that the propriety of the newly derived equation is quantitatively verified. We also applied pulsed high magnetic fields to the Ti–Ni and Cu–Al–Ni shape

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**Fig. 1** Magnetization curve of an Invar Fe–31.7 at%Ni.

**Fig. 2** Calculated and measured shifts of \(M'_c\) as a function of magnetic field for Invar Fe–31.7 at%Ni, (a), and Invar ordered Fe–24.0 at%Pt, (b), where M.S.E., H.F.E. and F.M.E. mean the effects of magnetostatic energy, high field susceptibility and forced volume magnetostriction, respectively.
memory alloys. However, magnetic field-induced martensitic transformations were not recognized in those alloys. The reason for this phenomenon can be explained by eq. (1), that is, the difference in magnetic moment between parent and martensite phases in Ti–Ni and Cu–Al–Ni alloys is so small for inducing martensitic transformation by applying magnetic field (31 MA/m) used in the experiment.

3.2 Giant magnetostriction in ferromagnetic shape memory alloys

In this section, we describe giant magnetostriction caused by conversion of martensite variants in Ni$_2$MnGa and Fe–Pd ferromagnetic shape memory alloys. According to previous studies, these alloys transform from cubic structures to tetragonal structures, and their tetragonality ($c/a$) are slightly smaller than a unity (precisely speaking, the martensite of Ni$_2$MnGa is reported to has a monoclinic structure, but we treat it as a quasi-tetragonal structure here.). Thus, there are three lattice correspondence variants for the Ni$_2$MnGa and Fe–Pd alloys. The easy axis of martensite state is the $c$-axis for Ni$_2$MnGa, and is the $a$-axis for Fe–Pd. However, the magnetostriction of Ni$_2$MnGa with stoichiometric composition is not reported, and perfect conversion of variants is not reported in Fe–Pd alloy until now. Whereupon, we will show their results as below.

3.2.1 Magnetostriction of Ni$_2$MnGa

Figure 3 shows temperature dependence of magnetic susceptibility of the Ni$_2$MnGa measured by applying a magnetic field of 80 kA/m. In the cooling process, a sharp decrease of susceptibility appears at 202 K. This decrease is due to the martensitic transformation. The temperature hysteresis of martensitic transformation is about 6 K, being a characteristic value of thermoelastic martensitic transformation. It is also noted in the figure that a small dip corresponding to an intermediate transformation is observed at 250 K. These transformation behavior is in good agreement with that reported previously.

We measured magnetostriction of Ni$_2$MnGa along [001]$_P$ direction by applying a magnetic field along [001]$_P$ direction at 286 K (parent phase), 240 K (intermediate phase) and 77 K (martensite phase) after cooling down to these temperatures without magnetic field (the subscript "P" means the symbol of abbreviation of the parent phase.). As a result, magnetostrictions at 286 and 240 K are of about $7 \times 10^{-5}$ (contraction) and about $3 \times 10^{-5}$ (contraction), respectively, being larger than that of conventional ferromagnetic materials, but nearly the same order of that of Invar alloys. A characteristic feature is that a large magnetostriction appeared at 77 K, as shown in Fig. 4. In the field applying process, the specimen starts to contract at about 0.3 MA/m, and saturated to the value of about 3.7% at 0.7 MA/m. This contraction is nearly the same value as can be expected from the perfect conversion of variants, i.e., variants are converted to a preferable variant whose magnetoelastic anisotropy energy is the smallest among them under the magnetic field. In this case, the easy axis of the preferred variant is almost parallel to the direction of the magnetic field. In the field removing process, the specimen does not change its shape. These results are in good agreement with those reported in non-stoichiometric Ni$_2$MnGa alloys examined at room temperature. In this way, we certainly confirm a perfect conversion of martensite variants under a relatively low magnetic field. It should be noted in Fig. 4 that the conversion of variants proceeds in multi steps (probably in three steps). Such behavior may relate to accumulation of the elastic energy introduced in the specimen through the conversion of variants.

3.2.2 Magnetostriction of Fe–31.2 at%Pd

Figure 5 shows temperature dependence of magnetic susceptibility of the Fe–31.2 at%Pd alloy measured by applying a magnetic field of 40 kA/m. In the cooling process a sharp decrease of susceptibility appears at 225 K. This decrease is due to the martensitic transformation. The temperature hysteresis of martensitic transformation is very small, meaning that the transformation is close to the second order.

We measured magnetostriction of the Fe–31.2 at%Pd alloy along [001]$_P$ direction by applying the magnetic field along the [001]$_P$ direction at 77 K.
1.5 \times 10^{-4} \text{ appeared. Such a large magnetostriction is due to}
the Invar effect of this alloy. At 77 K, a large magnetostriction
appeared as shown in Fig. 6. In the field applying process, the
specimen starts to expand at about 0.3 MA/m, and saturated
to the value of about 3% at about 1 MA/m. This expansion
is nearly the same value as can be expected from the perfect
conversion of variants, i.e., variants are converted to prefer-
able variants whose magnetocrystalline anisotropy energy is
the smallest among them under the magnetic field. In this
case, the easy axis of the preferred variant is almost parallel
to the direction of the magnetic field. In the field removing
process, the specimen contracted about 0.1%. This contrac-
tion will also be caused by the conversion of variants.

3.3 The effect of hydrostatic pressure on martensitic
transformation temperature

Figure 7 shows a typical electrical resistivity vs. temper-
ature curve under a pressure of 1.0 GPa for the Invar Fe–
29.9 at%Ni alloy.22) In the figure, a curve under no pressure
is also shown for comparison, and the $M_s$ temperature is
indicated with an arrow on each curve. As determined from
the figure, $M_s$ temperature under pressure shifts from that
under no pressure. The shift of the $M_s$ temperature, $\Delta M_s$
($= M_s - M_s'$), was plotted as a function of pressure, as shown
in Fig. 8. The same measurement has been made for non-
Invar Cu–Al–Ni shape memory alloys7) and the measured
shifts of equilibrium temperature of Cu–28.6Al–3.2Ni (at%)
single crystal, $\Delta T_0$ ($\Delta T_0 = T_0 - T'_0$, where $T_0$ is defined as
$(M_s + A_f)/2$), is shown in Fig. 9. It is found from Figs. 7
and 8 that the transformation temperature in the Fe–Ni al-
loy decreases parabolically with increasing pressure, while
transformation temperature in the Cu–Al–Ni alloy increases
linearly with increasing pressure. This difference is qualita-
tively explained by the difference in $\Delta V$, which is $V^{\text{m}} - V^{\text{p}}$,
where $V^{\text{m}}$ and $V^{\text{p}}$ are the volumes of martensite and parent
phases, respectively; $\Delta V$ is positive (2%) for the Fe–Ni al-
loys and negative ($-0.3\%$) for the Cu–Al–Ni alloy. A char-
acteristic feature is that the measured hydrostatic pressure de-
pendence of the martensitic transformation start temper-
ate Invar Fe–Ni alloys is not in good agreement with the one
calculated using Patel & Cohen’s equation,1) which is shown
in Fig. 8 with the dotted line. However, the measured hy-
drostatic pressure dependence of the equilibrium temperature
in the non-Invar Cu–Al–Ni alloy is in good agreement with
the one calculated using Patel & Cohen’s equation,\(^1\) which is shown in Fig. 9 with the dotted line. Such good agreement has been obtained for another non-Invar Ti–Ni alloys exhibiting B2 ↔ R and R ↔ B19′ transformations.\(^8,9\) The results described above clearly indicate that the Invar effect plays an important role in the martensitic transformation of Invar alloys under hydrostatic pressures. We speculated\(^23\) that the disagreement for Invar alloys was due to the existence of spontaneous volume magnetostriction, \(\omega_s\), which leads to the Invar effect and directly influences the volume change associated with the martensitic transformations.

Considering the Invar nature on martensitic transformation under hydrostatic pressure mentioned above, we derived the following equation\(^23\) including a term due to \(\omega_s\) to estimate the hydrostatic pressure dependence of transformation start temperatures, by referring to Patel & Cohen’s equation,\(^1\)

\[
\Delta G(M_s, 0) - \Delta G(M_s', 0) = \int_0^P \left\{ \frac{1 + \omega_s(M_s', P')}{1 + \omega_s(M_s', 0)} V_p(M_s', 0) \left( 1 - \frac{P'}{B^p} \right) \right. \\
- \left. V_m(M_s', 0) \left( 1 - \frac{P'}{B^m} \right) \right\} dP', \ldots \tag{2}
\]

where \(\Delta G(M_s, 0)\) and \(\Delta G(M_s', 0)\) represent the differences in Gibbs chemical free energy between austenite and martensite phases under no pressure at \(M_s\) (transformation start temperature under no pressure) and \(M_s'\) (transformation start temperature under a pressure, \(P\)), respectively, \(\omega_s(M_s', P')\) the spontaneous volume magnetostriction at \(M_s'\) under \(P'\), \(V_p(M_s', 0)\) and \(V_m(M_s', 0)\) the atomic volumes of austenite and martensite phases at \(M_s'\) under no pressure, respectively, and \(B^p\) and \(B^m\) the bulk moduli of the austenite and martensite phases, respectively. This equation tells us that the atomic volume of austenite phase decreases by the factor of \((1 + \omega_s(M_s', P'))/(1 + \omega_s(M_s', 0))\), due to a decrease in \(\omega_s\) caused by applied hydrostatic pressure.

In order to confirm the validity of the proposed equation, we calculated the hydrostatic pressure dependence of the transformation temperature based on the equation for the Invar Fe–Ni alloy\(^22\) and another Invar Fe–24.0 at%Pt shape memory alloy with \(S \sim 0.8\).\(^23\) In the calculation, temperature and hydrostatic pressures dependences of \(\omega_s\) and \(V\) are obtained in the present study\(^23\) and other physical quantities involved in the equation were set to be the measured in the previous studies.\(^21\) The calculated relations are shown in Fig. 9 with the dotted lines, which are in good agreement with the experimental ones for all the alloys. Thus, the newly derived equation is quantitatively verified.

As described above, magnetic field and hydrostatic pressure extremely influence martensitic transformations. So we can produce new structural materials with excellent mechanical properties and new smart materials by the combination of magnetic field and hydrostatic pressure as well as temperature and stress conventionally used.

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REFERENCES