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# Magnetic Field-Induced Martensitic Transformations In Some Ferrous Alloys

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Effect of magnetic field on martensitic transformation has been examined in various kinds of ferrous alloys, such as Fe-Ni, Fe-Pt, Fe-Ni-C and Fe-Ni-Co-Ti alloys and non-ferrous alloys, such as Ti-Ni and Cu-Al-Ni shape memory alloys. Following results are obtained; (i) Transformation start temperatures in ferrous alloys examined increase with increasing magnetic field and their relations between transformation start temperature and critical magnetic field for inducing martensitic transformation are in good agreement with the relations calculated by the equation proposed by our group. On the other hand, the transformation temperatures in Cu-Al-Ni and Ti-Ni alloys are not influenced by magnetic field. (ii) The appearance of magnetoelastic martensitic transformation is newly found in the ausaged Fe-Ni-Co-Ti alloy. (iii) Isothermal martensitic transformation in an Fe-Ni-Mn alloy changes to the athermal one under magnetic fields.

Key words: martensitic transformation, magnetic field, transformation temperature, morphology, transformation process

## 1. INTRODUCTION

It is well known that martensitic transformation, which occurs in many Fe-, Cu- and Ti-based alloys and ceramics, is one of the most typical examples of the first order structural phase transformations without atom diffusion, and has been widely studied in order to know its characteristics from physical, metallographical and crystallographical points of view. In addition, martensitic transformation has also been studied from technological point of view, partly because fine martensites formed in quenched ferrous alloys and steels result in increase in hardness of the alloys and steels used as structural materials and partly because the shape memory effect and the pseudoelastisity effect have been found to appear in relation to the thermoelastic martensitic transformation and the shape memory alloys with these effects are now supplied to practical uses as functional materials. Thus, the martensitic transformation has recently been more actively studied. According to the studies[1,2], martensitic transformations are extensively influenced by external fields, such as temperature and uniaxial stress, in transformation temperatures, crystallography and amount and morphology of the product martensites. 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 and is also important to obtain technical information in developing structural and smart materials. Magnetic field is one of such external fields because there exists some difference in magnetic moment between the parent and martensitic states. Actually, the effect of magnetic field on martesitic transformations has been studied by many workers, especially in Sadovsky's group in Russia[3] and recently in our group[4-7]. As a result, we have found many interesting phenomena on them.

In the present paper, we will show some new findings on the effects of magnetic field on martensitic transformation temperature, morphology and distribution of the martensites, magnetoelastic martensitic transformation which occurs only while a magnetic field is applied and disappears when the magnetic field is removed, by using Fe-Ni, Fe-Pt, Fe-Ni-C, Fe-Co-Ni-Ti, Ti-Ni and Cu-Al-Ni alloys.

And the results will be discussed based on the equation previously derived by our group[4], to evaluate the relation between $M_s$ and critical magnetic field, $H_c$, for inducing martensitic transformation.

We have also investigated the effect of magnetic field on the martensitic transformation process in Fe-Ni-Mn alloys and discussed based on the phenomenological theory previously derived by our group[8], which may give a unified explanation for the two transformation processes, *i.e.*, isothermal and athermal ones.

## 2. EXPERIMENTAL

The specimens used were Fe-Ni, Fe-Pt, Fe-Ni-C, Ti-Ni, Cu-Al-Ni, Fe-Ni-Co-Ti and Fe-Ni-Mn alloys. The 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. 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 31MA/m. Details of the ultra high magnetic field instrument have been reported elsewhere[9]. The morphology of magnetic field-induced martensites has been observed by optical microscopy.

## 3. RESULTS AND DISCUSSION

3.1 Effect of magnetic field on martensitic transformation temperature

Figure 1 shows typical magnetization curve ( $M(t)$-$H(t)$ ) for the invar Fe-31.7at%Ni alloy, where $\Delta T$ represents the temperature difference between set temperature, $T$, and $M_s$ ( $\Delta T = T\text{-}M_s$ ). 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 the critical one, $H_c$, for inducing the martensitic transformation at $T$, inversely meaning that the set temperature, $T$, corresponds to the martensitic transformation start temperature under the strength of magnetic field of $H_c$, $M_s'$. The relation thus obtained between the critical magnetic field and the shift of $M_s$, $\Delta M_s$, ( $=M_s'\text{-}M_s$ ) is shown in Figs. 2 (a) with solid squares for the Fe-31.7at%Ni alloy, and is shown in Figs. 2(b) for the Fe-24.0at%Pt alloy with $S\sim 0.8$ ( $S$ is degree of order) with solid squares. It is known from the figures that the shift of $M_s$ increases with increasing magnetic field for both the alloys irrespective of non-thermoelastic and thermoelastic martensitic transformation.

Recently we have proposed the following equation[4] to estimate the relation between the critical magnetic field and the transformation start temperature:

$$\Delta G(M_s) - \Delta G(M_s') = - \Delta M(M_s')\cdot H_c - (1/2)\cdot\chi_{hf}\cdot H_c^2 + \varepsilon_0\cdot(\partial\omega/\partial H)\cdot H_c\cdot B \quad (1)$$

where $\Delta G(Ms)$ and $\Delta G(M_s')$ represent the difference in Gibbs chemical free energy between the parent and martensite phases at $M_s$ and $M_s'$ temperatures, respectively, $\Delta M(M_s')$ the difference in spontaneous magnetization between the parent and martensitic states at $M_s'$, $\chi_{hf}$ the high magnetic field susceptibility in the parent phase, $\varepsilon_0$ the volume change associated with martensitic transformation, $\omega$ 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 effects, respectively. Based on the equation, $H_c$ vs. $M_s'$ relations have been thermodynamically calculated for the present alloys. In the calculation, the Gibbs chemical free energies for Fe-Ni and Fe-Pt alloys have been obtained by following the equations de-

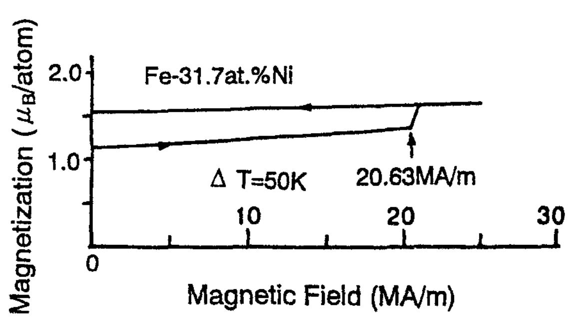


Fig. 1 Magnetization curve of an Invar Fe-31.7at.%Ni.

rived by Kaufman[10] and Tong and Wayman[11], respectively, and spontaneous magnetization in the martensitic states and $B$ for the alloys have been obtained by referring to the previous studies[12,13]. Other unknown physical quantities involved in the equation were set to be the ones measured in our studies[4-7]. 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. $M_s'$ 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 $M_s$ temperature due to the forced magnetostriction effect is nearly the same order as that due

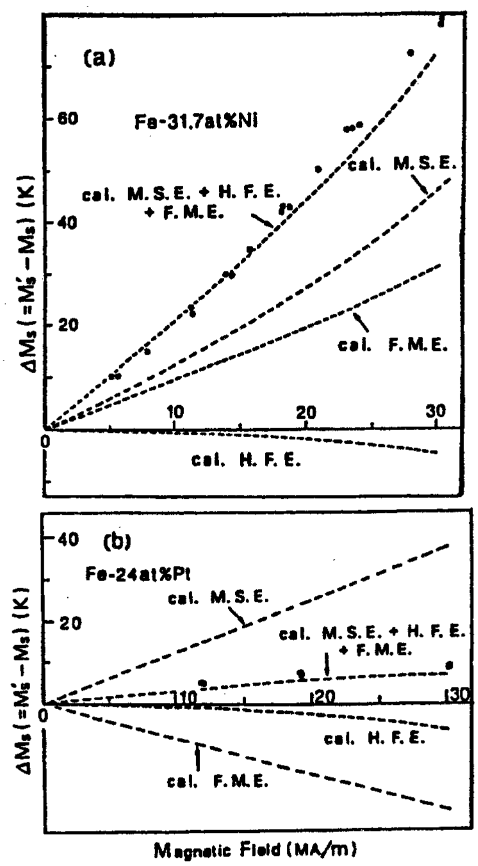


Fig. 2 Calculated and measured shifts of $M_s$ as a function of magnetic field for Invar Fe-31.7at.%Ni, (a), and Invar ordered Fe-24.0at.%Pt alloys, (b), where M.S.E., H.F.E. and F.M.E. mean the effects of magnetostatic energy, high field susceptibility and forced volume magnetostriction, respectively.

to the magnetostatic effect for both the invar 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 martensitic transformation in the ordered Fe-Pt alloy 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 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 ( 31MA/m ) used in the experiment.

The morphology of magnetic field-induced martensites was the same as that of thermally-induced one irrespective of formation temperature and the strength of magnetic field for Fe-Ni and Fe-Ni-C alloys examined. However, we found that magnetic field influences the distribution of martensite plates in Fe-31.6at.%Ni single crystals[14]. That is, martensite plates grow nearly parallel to the direction of applied magnetic field irrespective of the difference in crystal orientation, although such amount of martensite plates is a few. This directional growth of martensite plates is not observed in thermally-induced martensites. Therefore, the directional growth seems to be characteristic of magnetic field-induced martensites. The reason for such a formation of lengthwise grown plates under magnetic field is not clear yet, but a shape magnetic anisotropy effect seems to play an important role.

## 3.2 Magnetoelastic martensitic transformation

In the alloy exhibiting a thermoelastic martensitic transformation, it is known that a martensite crystal grows or shrinks with temperature cycling, that is, it responds to temperature change in a balance between thermal and elastic energies. If a uniaxial stress is applied to such an alloy at temperature above $A_f$ and released, the alloy exhibits pseudoelastic behavior due to the stress-induced martensitic and its reverse transformation upon loading cycle. Considering this behavior, it can be expected that if a magnetic field is applied to the alloy exhibiting a thermoelastic martensitic transformation above $A_f$ and removed, martensites may be induced only while a magnetic field is applied and revert to the parent phase when the magnetic field is removed. We define this type of martensitic transformation as a magnetoelastic martensitic transformation, and actually have found it in an ausaged Fe-31.9Ni-9.8Co-4.1Ti(at.%) shape memory alloy, as will be described below.

A pulsed high magnetic field was applied to the specimen at a temperature above $A_f$, 163K ( $\Delta T$ ( $=T-M_s$ ) = 36K, $T > A_f$ ) and typical $M(t)$-$H(t)$ curves obtained are shown in Figs.3 (a) and (b). It is noted in (a) that there is no hysteresis of magnetization when a pulsed magnetic field whose maximum strength is 22.22MA/m has been applied and removed. This means that the maximum strength is lower than a critical magnetic field, $H_c$, to induce martensitic transformation, and therefore that 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

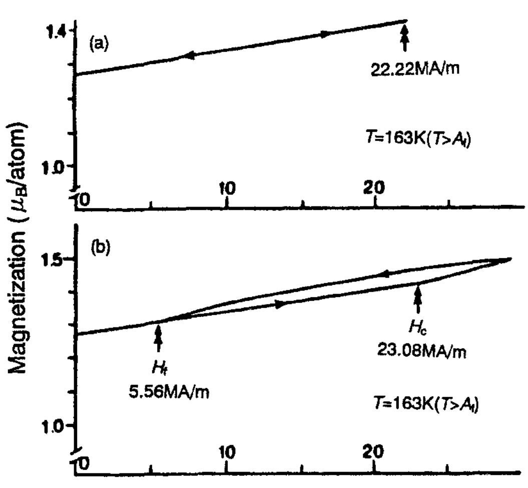


Fig. 3 $M$(t)-$H$(t) curves for an ausaged Fe-Ni-Co-Ti alloy at 163K ($T$>$A_f$), (a) and (b).

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 $H_c$=23.08MA/m, as indicated with an arrow, and when the magnetic field is removed, the increased magnetization returns to the initial value at about $H_f$ = 5.56MA/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 certainly realized in the ausaged Fe-Ni-Co-Ti alloy, and such behavior is always realized at temperatures above $A_f$.

3.3 Kinetics of martensitic transformation

Martensitic transformations are well known to be classified into two groups with respect to the kinetics, athermal and isothermal ones. The former transformation has a well defined transformation temperature, $M_s$, and occurs instantaneously at $M_s$, while the latter one does not have a definite $M_s$ temperature but occurs after some finite incubation time during isothermal holding[15]. Very few materials exhibit an isothermal transformation, and Fe-Ni-Mn and Fe-Ni-Cr alloys are considered to be typical such materials. Many studies on isothermal martensitic transformation in Fe-Ni-Mn and Fe-Ni-Cr alloys have been made so far[15-17]. According to the study by Kurdjumov and Maksimova[15], isothermal transformations are considered to be the general and athermal ones the special case, speculating that the incubation time necessary for an athermal transformation is undetectably short. However, this view has not been verified yet, and further investigation is needed. Thus, we investigated the influence of a magnetic field on the athermal and isothermal martensitic transformations in Fe-30.3Ni-0.5Mn(at.%) and Fe-24.0Ni-4.0Mn(at.%) alloys[8], respectively, which will be described below.

The electrical resistivity measurements showed that the Fe-30.3Ni-0.5Mn(at.%) alloy has a clear transformation start temperature at 195 K, but the Fe-24.0Ni-4.0Mn(at.%) alloy does not. Then, the Fe-24.0Ni-4.0Mn(at.%) alloy was isothermally held at several tempera-

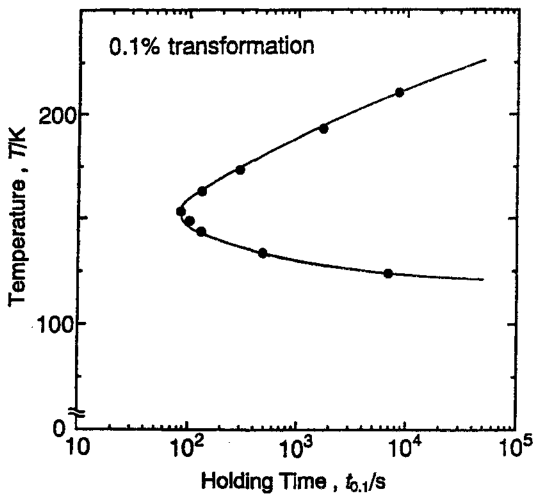


Fig. 4 *T T T* diagram of the isothermal martensitic transformation in an Fe-24.0Ni-4.0Mn(at.%) alloy.

tures between 4.2 and 293K. A typical *T T T* ( Time, Temperature, Transformation ) diagram obtained is shown by the closed circles in Fig. 4. As seen in the figure, one should note that martensitic transformation occurs after some incubation time and the *T T T* diagram clearly forms a C-type of curve whose nose temperature, at which the incubation time is shortest, is about 153K. Then, we applied a pulsed magnetic field to these alloys. Figs. 5(a) is a typical *M*(*t*)-*H*(*t*) curve for the Fe-30.3Ni-0.5Mn(at.%) alloy at 218K, which is 23K higher than the $M_s$ temperature and Figs. 5(b) is that for the Fe-24.0Ni-4.0Mn(at.%) alloy at 4.2K. In (a), an instantaneous increase in the magnetization due to a martensitic transformation is recognized at a critical magnetic field (indicated by an arrow), like in the alloys previously investigated, which exhibit an athermal martensitic transformation[5]. Note that the same increase in magnetization as seen in (a) ( the time required for the formation of all the martensites is about 20 $\mu$ s ) is observed in the Fe-24.0Ni-4.0Mn (at.%) alloy, as seen in (b), although no martensitic transformation was observed in the Fe-24.0Ni-4.0Mn(at.%) alloy down to 4.2K in zero magnetic field, despite an isothermal holding longer than 8.64 x $10^4$ s. These results are the same as in the athermal and isothermal martensitic transformations in Fe-Ni-Mn alloys previously studied[18] and suggest that the isothermal martensitic transformation changes to an athermal one under a high magnetic field. This means that the two transformation processes are closely related to each other and that their differences are not intrinsic but the two transformation processes may be explained by one basic rule. On the basis of this finding, we constructed a phenomenological theory[18], which gives a unified explanation for the two transformation processes. More details of the theory has been reported elsewhere[18]. Based on the theory, we could prove that in the materials which exhibits an isothermal martensitic transformation, a static magnetic field lowers the nose temperature and reduces the incubation time and a hydrostatic pressure raises the nose temperature and increases the incubation time. In fact, we found the prediction certainly realized in the Fe-Ni-Mn alloy, which will be described below.

We have made isothermal holding measurements of the Fe-24.0Ni-4.0Mn (at.%) alloy exhibiting an isothermal martensitic transformation have been made in order to produce *T T T* diagrams under static magnetic fields and hydrostatic pressures. The *T T T* diagrams ob-

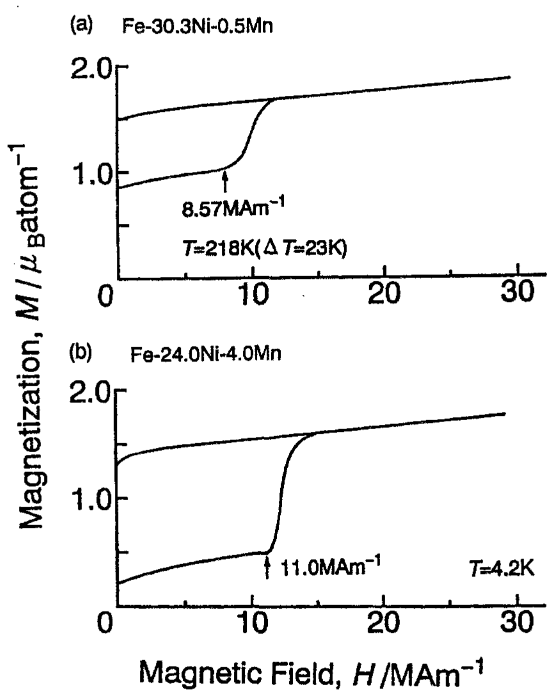


Fig. 5 Magnetization vs magnetic field curves of an Fe-30.3Ni-0.5Mn(at.%) alloy at 218K, (a), and Fe-24.0Ni-4.0Mn(at.%) alloy at 4.2K, (b), the magnetization increases instantaneously at a critical magnetic field induced by arrows.

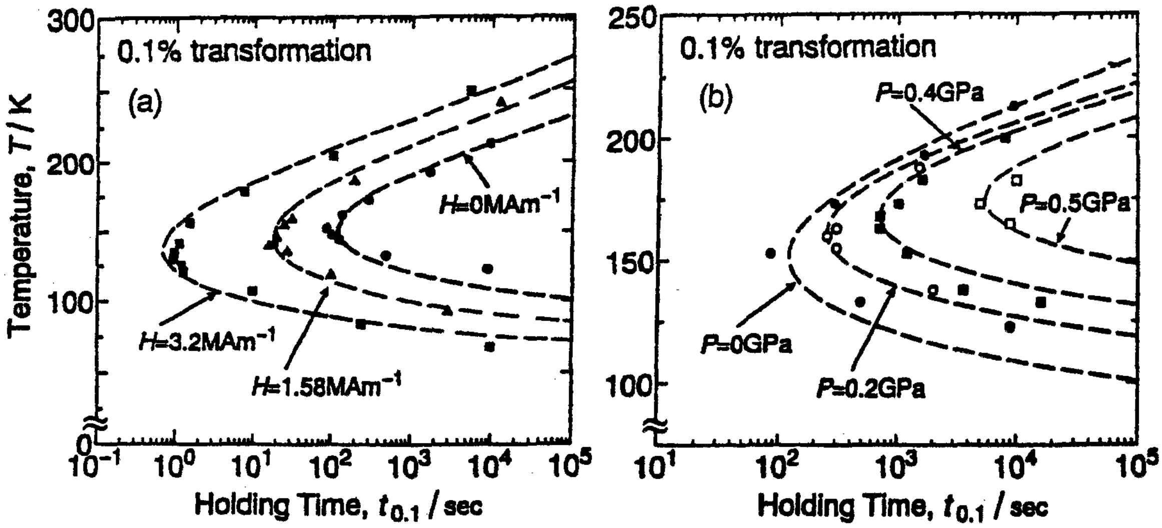


Fig. 6 *T T T* diagrams of the martensitic transformation in an Fe-24.0Ni-4.0Mn(at.%) alloy under static magnetic fields, (a), and that under hydrostatic pressures, (b), and the dotted lines represent the calculated *T T T* diagrams with the theory previously proposed.

tained are shown in Figs. 6(a) and (b) for the case of magnetic field and that of hydrostatic pressure, respectively, where the dotted lines represent the calculated *T T T* diagrams based on the equation previously derived by our group[18]. As known from the figures, the behavior of isothermal martensitic transformation under those external fields is similar to that predicted by the theory previously derived[18], suggesting that the theory is confirmed to be appropriated.

In this way, by using magnetic field, we can control not only the martensitic transformation temperatures but also the distribution of martensites and transformation process.

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