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Effect of Magnetic Fields on Martensitic Transformations in Ferrous Alloys and Steels

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The recent works carried out by the authors' research group on magnetic field-induced martensitic transformations are reviewed, which are concerned with various kinds of ferrous alloys, such as Fe–Ni poly- and mono-crystals, invar and non-invar Fe–Ni–C polycrystals, disordered and ordered Fe–Pt polycrystals, ausaged Fe–Ni–Co–Ti polycrystals and paramagnetic Fe–Mn–C polycrystals. The works clarified influences of composition, the existence of grain boundaries, crystal orientation, invar characteristic, thermoelastic nature and austenitic magnetism on the magnetic field-induced martensitic transformations. In the work on the ausaged Fe–Ni–Co–Ti alloy, the appearance of "magnetoelastic marten-sitic transformation" was newly found. By taking into account the influences of composition, grain boundaries, crystal orientation, invar characteristic, thermoelastic nature and austenite magnetism, a new and exact equation was proposed to generally explain the shift of M_s temperature as a function of critical magnetic field to induce martensitic transformations in those alloys, which consisted of three terms of the Zeeman energy, high field susceptibility energy and forced volume magnetostriction energy. The new and exact equation was experimentally verified to hold in all the alloys studied.

KEY WORDS: martensitic transformation; magnetic field inducement; ferrous alloy; invar alloy; steel.

1. Introduction

The martensitic transformation has been generally understood as a phenomenon which starts at the M_s temperature when a specimen is quenched or cooled from the austenitic temperature region, as is well known in ferrous alloys and steels. However, since it is a structural phase change involving a cooperative movement of atoms,[1] the martensitic transformation may be markedly affected by external forces such as uniaxial stress, hydrostatic pressure and magnetic field. In fact, M_s of ferrous alloys and steels has been reported to be decreased by hydrostatic pressure, and to be increased by uniaxial stress and magnetic field.[1] The decrease of M_s by hydrostatic pressure is because the volume change associated with martensitic transformation is inverse to the hydrostatic pressure in sense.[2] Therefore, if the sense of volume change is the same as that of hydrostatic pressure, M_s may be increased as actually reported on a Au–Cd alloy.[3] On the other hand, a uniaxial stress or magnetic field always results in an increase of M_s without regard to the sense of uniaxial stress or magnetic field or the type of specimen.

Very recently, uniaxial stress-, hydrostatic pressure- and magnetic field-induced martensitic transformations have been more actively studied, because they are expected to give much important information in developing functional and extreme materials. As a result, it has been clarified that a uniaxial stress brings in not only an increase of M_s but also the formation of various martensites with different crystal structures and morphologies depending on the deformation temperature. Moreover, stress-induced martensites at temperatures above A_f reversibly transform back to the parent phase only upon unloading, and pseudoelasticity is associated with the stress-induced martensitic and its reversible reverse transformations.[4,5] A martensitic transformation has also been found[6] to occur between martensites with different crystal structures. These phenomena are now widely known as fundamentals in functional shape memory alloys.[7]

Patel and Cohen[2] have analyzed quantitatively the decrease of M_s in an Fe–Ni alloy under a hydrostatic pressure, and confirmed theoretically and experimentally that the decrease of M_s was linear with hydrostatic pressure up to 0.2 GPa. However, it has recently been revealed[8] in a similar Fe–Ni alloy that M_s decreases nonlinearly with hydrostatic pressure higher than 0.2 GPa and that theoretically estimated M_s following the analysis by Patel and Cohen is largely different from the experimentally measured one. This means that other effects should be taken into consideration in addition to the effect that the volume change associated with martensitic transformation is inverse to hydrostatic pressure in sense.

The effects of uniaxial stresses and hydrostatic pressures on martensitic transformations should be referred to available papers, for example, Refs. 2) to 8) and others. In this paper, effects of magnetic fields on martensitic transformations will be reviewed centering around the results obtained by the authors' research group.

2. Previous Studies on the Effect of Magnetic Fields and Their Problems

As mentioned in the preceding section, magnetic field is known to be one of external forces affecting martensitic transformations in ferrous alloys and steels, because a large difference in magnetization exists between the austenitic and martensitic states. The first study on the effect of magnetic fields on martensitic transformations may be traced back to 1929 when Herbert[9] found that a quenched steel was increased in hardness under a magnetic field more than under no magnetic field. However, the origin of the hardness increase had not been clarified until 1961. In that year, Sadovsky et al.[10] in the U.S.S.R. found that the martensitic transformation in an Fe–Ni–Cr–C alloy was accelerated by a pulsed high magnetic field at temperatures above M_s of the alloy. Since then, many studies have been carried out on the effect of magnetic fields on martensitic transformations by applying a pulsed high magnetic field to various ferrous alloys and steels, especially by Sadovsky's group.[11-13] As a result, magnetic field-induced martensitic transformations were observed in Fe–Ni–Cr–C,[11] Fe–Ni–C,[12] Fe–Mn–C,[13] and other alloys; their M_s temperatures were elevated by about 60 K under the pulsed magnetic field of 27.8 MA/m. The amount of the magnetic field-induced martensites was dependent on the strength of pulsed magnetic field.

Furthermore, Sadovsky's group examined the effect of a static magnetic field (1.2 MA/m) on martensitic transformations in Fe–Ni–C alloys,[14] and showed that the amount of the martensites induced by the static magnetic field was the same as that induced by a pulsed magnetic field. Then, they concluded that there was no difference between the effects of static and pulsed magnetic fields on martensitic transformations. A similar study by using an Fe–Ni alloy was done by Saito and Suzuki.[15] Sadovsky's group also examined the effect of a pulsed magnetic field on the isothermal martensitic transformation in an Fe–Ni–Mn alloy,[16] and showed a magnetic field dependence of the amount of martensites. Korenko and Cohen[17] has done a similar study in more detail, and reported that a magnetic field influenced on the nucleation rate of martensitic transformation.

Taking account of the above characteristics of magnetic field-induced martensitic transformations, Krivoglaz and Sadovsky[18] concluded that the effect of magnetic fields was due only to the Zeeman energy. They proposed the following formula to estimate the shift of M_s, $\Delta M_s = M_s' - M_s$, due to the Zeeman energy as a function of critical magnetic field, H_c, for inducing martensitic transformation;

$$\Delta M_s = -\Delta M(M_s') \cdot H_c \cdot T_0/Q, \quad \dots\dots\dots(1)$$

where, $\Delta M(M_s') = M^r(M_s') - M^{\alpha'}(M_s')$

$M^r, M^{\alpha'}$: being spontaneous magnetizations of the austenitic and martensitic states at the shifted M_s, M_s', respectively

T_0: the equilibrium temperature of the two phases

Q: the latent heat of transformation.

In the above formula, $\Delta M(M_s')$ is negative in many ferrous alloys undergoing a martensitic transformation, because the spontaneous magnetization in the austenitic state is generally lower than that in the martensitic state, and therefore ΔM_s in those alloys are positive, that is, M_s is always raised under magnetic fields. Sadovsky's group reported that the propriety of the formula was confirmed by examining an Fe–Ni alloy.[18] Satyanaryan et al.[19] also confirmed that the increase of M_s under a magnetic field followed the formula. However, those confirmations were not sufficient because a large discrepancy was observed between experimentally measured and calculated ΔM_s in our works as will be mentioned, and also because of the following reasons.

Relation between ΔM_s and H_c was not examined over so wide ranges of temperature and magnetic field. Moreover, magnetic field dependences of the amount and morphology of magnetic field-induced martensites have not been systematically examined. The materials so far examined were mainly commercial ones including many elements, and thus magnetic properties of both austenitic and martensitic states and also thermodynamics and crystallographies of thermally-induced martensitic transformations in those materials have not been well clarified. Therefore, previous thermodynamical analyses for the effect of magnetic fields on martensitic transformations were not possibly exact. In addition to the above problems, there remain many questionable problems on magnetic field-induced martensitic transformations as follows.

All of previous studies were concerned with polycrystalline specimens and therefore the obtained information so far might be affected by the existence of grain boundaries. Moreover, no information has been obtained about the influence of crystal orientations on magnetic field-induced martensitic transformations. Some of ferrous alloys and steels undergoing martensitic transformation have an invar characteristic, and there may be an influence of the invar characteristic on magnetic field-induced martensitic transformations. However, there has been no report on this problem. All of the previous studies were concerned with disordered alloys, and there has been no information about the effect of degree of order on magnetic field-induced martensitic transformations. Many ferrous alloys and steels undergoing martensitic transformation are ferromagnetic or paramagnetic in the austenitic state, but they are all ferromagnetic in the martensitic state. Therefore, there may be some influence of the difference in austenitic magnetism on martensitic transformation. All of the previous studies were also concerned with the materials undergoing non-thermoelastic martensitic transformation, and there is no information on the effect of magnetic fields on thermoelastic martensitic transformations. Incidentally, thermoelastic martensitic transformation with a small temperature hysteresis is known to be

accompanied by a pseudoelastic effect.[4,5,7] That is, even if strain is generated by stress-induced martensitic transformation on loading, it disappears by the reverse transformation on unloading. It can therefore be expected that the magnetic field-induced martensite in thermoelastic alloys is similarly reversible under a magnetic field. As mentioned before, Sadovsky's group proposed a formula to estimate ΔM_s as a function of H_c.[18] However, its propriety was shown only for one value of magnetic field and temperature for a few alloys. Moreover, the formula was derived by assuming that the Gibbs chemical free energy of austenitic and martensitic phases is simply in a linear relation with temperature. However, the situation is not so simple in real alloy systems, and therefore the formula should be taken to be an approximation. Thus, the formula itself should be re-examined in the propriety.

In order to clarify the above problems, not only systematic detailed measurements but also precise analyses are needed by using suitable materials for solving respective problem. Thus, the authors and their coworkers have examined magnetic field-induced martensitic transformations in Fe–Ni poly- and monocrystals, invar and non-invar Fe–Ni–C polycrystals, disordered and ordered Fe–Pt polycrystals, ausaged Fe–Ni–Co–Ti polycrystals and paramagnetic Fe–Mn–C polycrystals, by carrying out magnetization measurements and optical microscopy observations, a precisely regulated magnetic field being applied at The High Magnetic Field Laboratory, Osaka University.

3. Effect of Composition on Magnetic Field-induced Martensitic Transformations in Fe–Ni Alloys

The martensitic transformation from fcc to bcc in Fe–Ni alloys with Ni content of 0 to 33 at% have been extensively studied by many researchers, and their thermodynamics and crystallography have been well clarified so far.[1] The Fe–Ni alloys with Ni content of 30 to 50 at% are known to have an invar characteristic, and various physical quantities of the alloys have been examined as a function of composition, such as the spontaneous magnetization in austenitic state and other.[20-23] Thus, the Fe–Ni alloys seem to be most suitable for investigating the effect of magnetic fields on martensitic transformations and its composition dependence. However, such an investigation has not been systematically done, and moreover the amount and morphology of magnetic field-induced martensites have not been examined by varying the formation temperature. Therefore, the author's group has first studied to make the above problems clearer.

The Fe–Ni alloys used in the study were 29.9, 31.7 and 32.5 at% in Ni content. Specimens of 3 mm × 20 mm × 0.3 mm size were cut from a sheet hot-forged, homogenized and hot- and cold-rolled, and then austenitized at 1 473 K for 1.08×10^4 s, followed by furnace-cooling to avoid quenching strain. All the austenitized specimens were cut into the half length

(3 mm × 10 mm × 0.3 mm) by a spark-cutting machine, and one was used for electrical resistivity vs. temperature measurements and the other for magnetization measurements. Details of the magnetization measurements under an ultra high magnetic field were described in Ref. 24).

3.1. Transformation Temperatures and Spontaneous Magnetization of Austenite

Electrical resistivity vs. temperature measurements were made in the temperature range from 293 to 77 K to determine M_s of the Fe–Ni alloys; M_s of the Fe–29.9, –31.7 and –32.5 at%Ni alloys were 223, 164 and 113 K, respectively. Next, the spontaneous magnetization of austenite of the three alloys were measured as a function of temperature difference from respective M_s, $\Delta T = T - M_s$, as shown in Fig. 1.[25] The figure indicates that the spontaneous magnetization of austenite decreases with decreasing Ni content and with increasing ΔT. On the other hand, according to an earlier paper,[20] the spontaneous magnetization of martensite of Fe–Ni alloys changes hardly (or slightly) with Ni content, and its value at 0 K is known to be about 2 μ_B/atom. This value may be valid in the temperature range examined in this study, because the Curie Point of the martensitic state is so high. Accordingly, ΔM becomes smaller with decreasing Ni content and/or with increasing ΔT. Therefore, if the contribution of magnetic fields on ΔM_s were only the Zeeman energy, ΔM_s would become larger with decreasing Ni content and/or with increasing ΔT, if T_0/Q is the same value irrespective of Ni content. However, ΔM_s does not change in such a way, as described below.

3.2. Critical Magnetic Field to Induce Martensite

Magnetization vs. magnetic field relation ($M(t)$–$H(t)$) was measured by applying comparatively high magnetic fields to the three Fe–Ni alloys. The $M(t)$–$H(t)$ relations obtained at temperatures of $\Delta T = 50$, 50, and 40 K for the Fe–29.9, –31.7 and –32.5 at%Ni
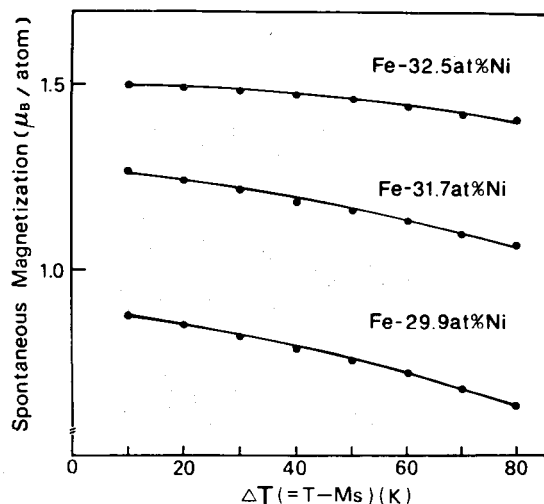
Fig. 1. Spontaneous magnetization of austenite as a function of temperature difference from M_s, $\Delta T = T - M_s$, for Fe–29.9, –31.7 and –32.5 at%Ni alloys.[25]

alloys, respectivity, are shown in Fig. 2.[25] In these curves, an increase of magnetization is recognized at a certain value of magnetic field for respective alloys. Such an increase was not observed when applied magnetic fields were lower than the certain field, H_c, which is probably critical to induce the martensitic transformation in each alloy at the above respective temperatures. Fig. 3[25] shows ΔM_s measured as a function of H_c for the three alloys. This figure shows that ΔM_s increases with H_c for all the alloys, forming a curve with a slightly downward convexity. Another characteristic feature noted in Fig. 3 is that
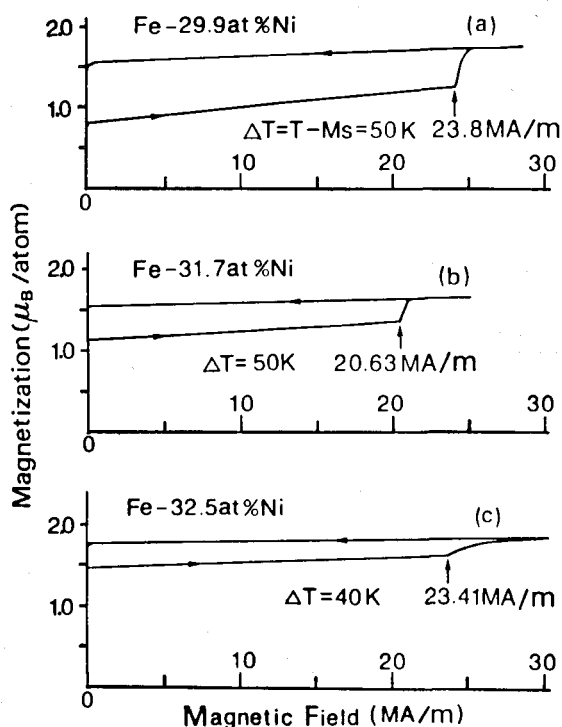
Fig. 2. Magnetization vs. magnetic field ($M(t)$–$H(t)$) relations of (a) Fe–29.9, (b) Fe–31.7, and (c) Fe–32.5 at%Ni alloys.[25]
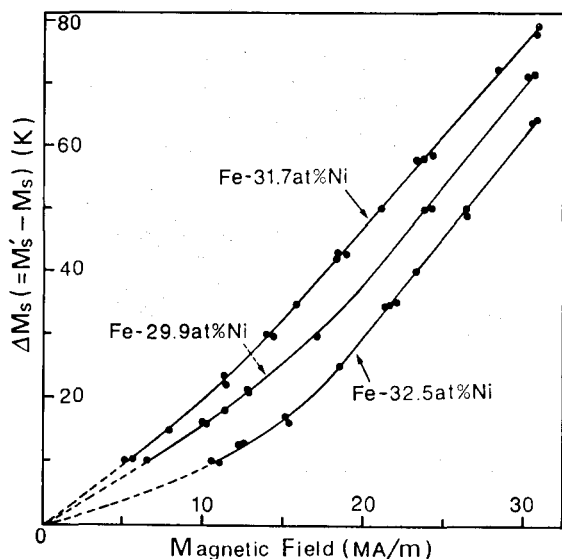

Fig. 3. Relation between the shift of M_s and the critical magnetic field (ΔM_s vs. H_c relation) for Fe–29.9, –31.7 and –32.5at%Ni alloys[25].

ΔM_s for the Fe–31.7at%Ni alloy are the largest among the three alloys all over H_c. This means that the influence of magnetic fields on ΔM_s is mostly effective in the Fe–31.7at%Ni alloy. This result is inconsistent with the formula proposed by Krivoglaz and Sadovsky,[18] which states that ΔM_s would become larger with decreasing ΔM or decreasing Ni content, if T_0/Q is the same value, as known from Fig. 1. Therefore, ΔM_s would become larger in the order of ΔM, namely, in the order of Fe–29.9, –31.7, and –32.5 at%Ni alloys.

However, the experimentally obtained ΔM_s as a function of H_c is not in that order (Fig. 3). This means that Krivoglaz and Sadovsky's formula does not hold in the Fe–Ni alloys. Moreover, ΔM_s calculated from the formula does not agree with the experimentally measured one, especially for high magnetic fields. For example, the calculated ΔM_s of the Fe–31.7at%Ni alloy under the magnetic field of about 30 MA/m was about 24 K, but it largely differs from the experimentally measured one, about 80 K. These results indicate that the effect of magnetic fields on martensitic transformations is not limited to the Zeeman energy.

3.3. Amount of Magnetic Field-induced Martensite

The amount of martensites induced by a magnetic field can be estimated by calculating from the result of magnetization measurements, because it is related to the magnetization. The amount of martensites thus obtained for the three Fe–Ni alloys are shown in Fig. 4,[25] as a function of the maximum strength of applied pulsed magnetic field at temperatures of given ΔT. In Fig. 4, when a magnetic field higher than H_c was applied to Fe–29.9 and –31.7at%Ni alloys at a given ΔT, the amount of martensites induced was constant without regard to the strength of applied magnetic field. This means that the martensitic transformation of an amount proper to a given ΔT is completed as soon as the magnetic field has reached H_c. That is, the amount of martensites does not depend on the maximum strength of magnetic field provided that the magnetic field is higher than H_c, because of a burst phenomenon as in the case of thermally-induced martensitic transformations of those alloys. On the other hand, the amount of magnetic field-induced martensites in the Fe–32.5at%Ni alloy gradually increases with increasing magnetic field beyond H_c, although it is saturated. This may be so, because the martensite in the alloy is partly thermoelastic. This thermoelastic nature was actually confirmed by an optical microscopy observation, as shown in Fig. 5.[25] Fig. 5(a) shows a martensite structure after the magnetic field of H_c has been applied at temperature of $\Delta T=25$ K, which was taken at room temperature after polishing and etching with 5 % nital, and Fig. 5(b) shows an unetched martensite structure after a magnetic field higher than H_c has been successively applied to the same alloy at the same temperature, which was taken from an identical place with Fig. 5(a). In Fig. 5(b), surface relief is observed at interfaces of the martensite indicated with
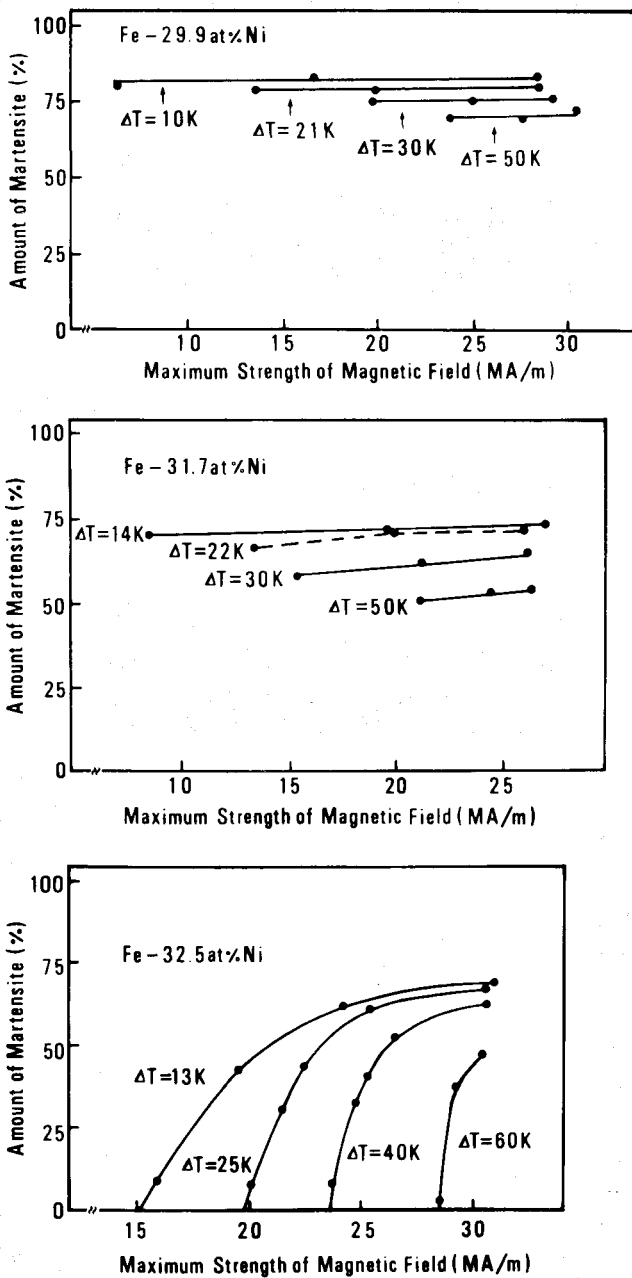
Fig. 4. Amounts of magnetic field-induced martensites, plotted as a function of maximum strength of pulsed magnetic field, in (a) Fe–29.9, (b) Fe–31.7, and (c) Fe–32.5at%Ni alloys.[25]
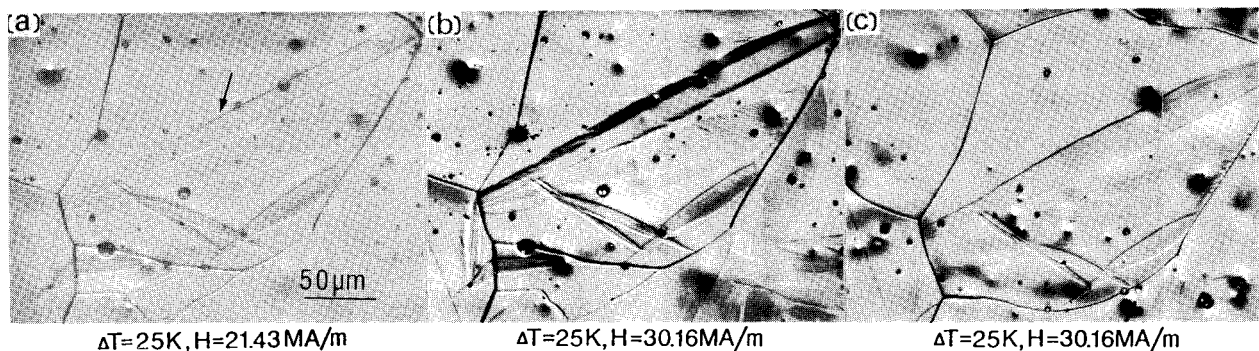
an arrow in Fig. 5(a). This suggests that the existed martensite plates can grow by applying a higher magnetic field. In order to make it clear, the specimen was etched, as shown in Fig. 5(c). Comparison between Figs. 5(b) and 5(c) clearly shows that the surface relief in Fig. 5(b) arises as a result of the growth of arrowed martensite in Fig. 5(a), that is, the martensite is partly thermoelastic. On the other hand, martensite plates in the Fe–29.9 and –31.7at%Ni alloys did not exhibit such a successive growth, that is, they were non-thermoelastic. However, all the alloys showed a similar tendency that the amount of magnetic field-induced martensites increases with decreasing ΔT.

3.4. Morphology of Magnetic Field-induced Martensite

Fig. 6[25] shows optical micrographs of thermally-induced lenticular martensites formed by cooling slightly below respective M_s of the three Fe–Ni alloys, (a), (d), and (g), and those of magnetic field-induced ones in those alloys, (b), (c), (e), (f), (h), and (i). The data of ΔT, formation temperature and H for the magnetic field-induced martensites are inscribed in each photograph. It is noted in the figure that the morphology (including internal structures) of the thermally-induced martensites is the same as that of the magnetic field-induced ones without regard to ΔT and H, provided that Ni content is the same. That is, the martensites are lenticular, and interfaces between the austenite and martensite crystals become more smooth and internally twinned regions corresponding to the mid-rib become wider with increasing Ni content, as previously observed by Patterson and Wayman.[26] Electron microscopic observations[25] also showed no difference between the magnetic field- and thermally-induced martensites even in finer scale.

By the way, it is well known in Fe–Ni alloys that lath and lenticular martensites are thermally-induced at temperatures above and below 273 K, respectively. However, the magnetic field-induced one in Fig. 6(c) exhibits a lenticular morphology even though they are formed at 293 K. This suggests that the formation temperature itself is not an essential factor to determine the morphology of martensites in Fe–Ni alloys, being different from an observation that the martensite morphology in Fe–Ni–C alloys is determined only by the formation temperature.[27] As will

Fig. 5. Optical micrographs showing the growth of existing martensite plates in an Fe–32.5at%Ni alloy, by successively applying a higher magnetic field. (c) is the etched structure of (b).[25]

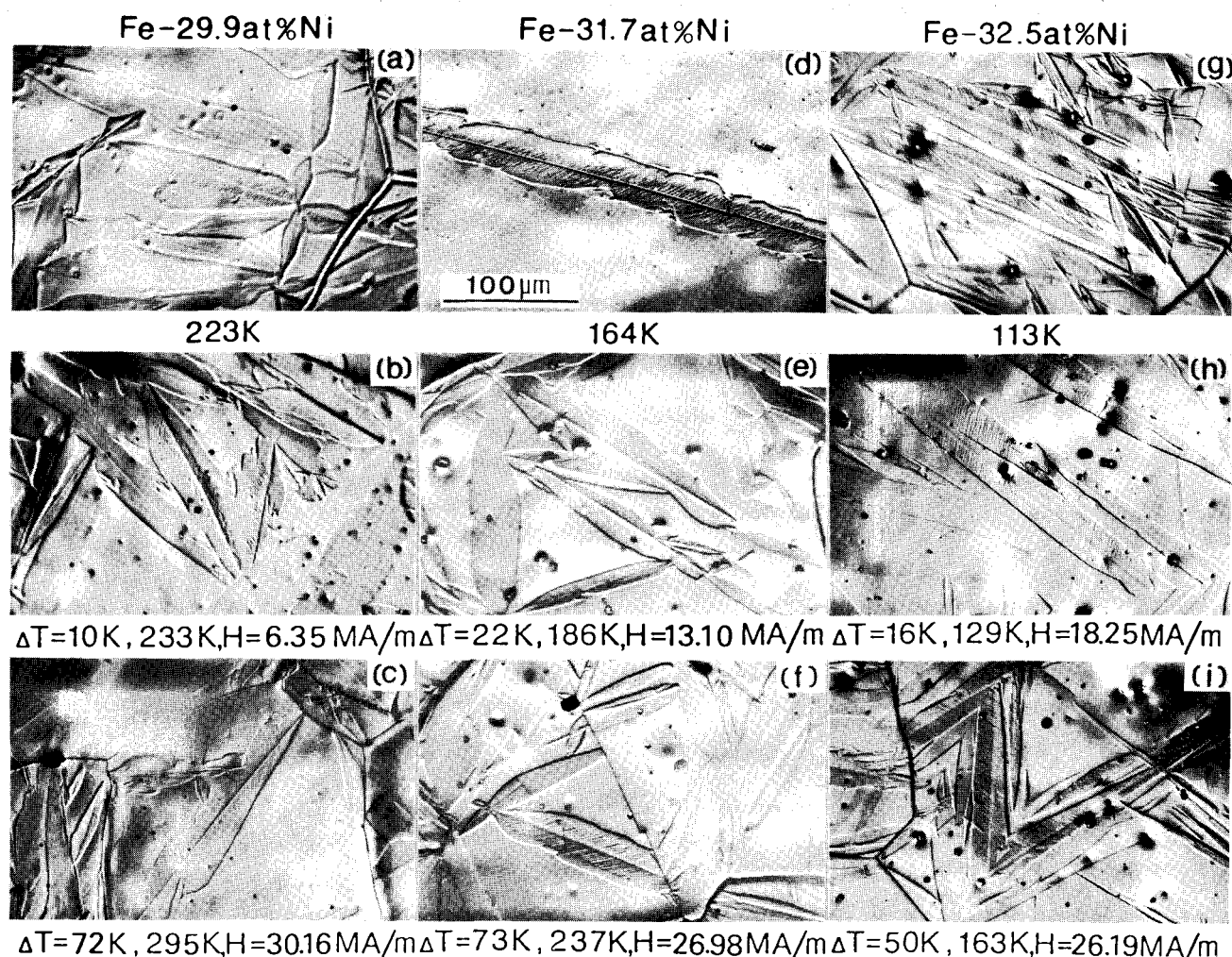Fe-29.9at%Ni   Fe-31.7at%Ni   Fe-32.5at%Ni

Fig. 6. Optical micrographs of thermally-induced martensites, (a), (d), and (g), formed by cooling a little below re-spective M_s of Fe-29.9, -31.7 and -32.5at%Ni alloys, respectively, and of magnetic field-induced ones, (b), (c), (e), (f), (h), and (i). $\varDelta T$ and H for the magnetic field-induced martensites are inscribed in each photograph.[25]

be mentioned later, uniaxially stress-induced marten-sites exhibit different morphologies depending on the deformation temperature. On the other hand, hy-drostatic pressure-induced martensites exhibit the identical morphology without regard to the formation temperature like the magnetic field-induced ones.[28] These facts seem to suggest that strain field accumu-lated in the austenite before martensitic transforma-tion controls the martensite morphology. That is, in the case of uniaxially stress-induced martensitic trans-formation, the austenite before martensitic transfor-mation may be subjected to some strain with a shear component, while hydrostatic pressure- and magnetic field-induced transformations may occur without any shear component. This will be discussed later again.

4. Influence of Grain Boundaries and Crystal Orientations on Magnetic Field-induced Martensitic Transformation

All of previous studies on magnetic field-induced martensitic transformations were concerned with poly-crystalline specimens, and therefore the information obtained so far might be influenced by the existence of grain boundaries. Moreover, no information has

been obtained about the effect of crystal orientations on magnetic field-induced martensitic transforma-tions. Thus, magnetic field-induced martensitic trans-formations in single crystals of an Fe–Ni alloy with different orientations were examined to make those problems clearer, and the results obtained were com-pared with previous ones for polycrystalline specimens with nearly the same composition.

From a large grain of Fe–31.6at%Ni alloy, ribbon-shaped specimens (2 mm × 7 mm × 0.3 mm) were cut so that their length-wise direction was parallel to the ⟨100⟩, ⟨110⟩ and ⟨111⟩ directions of austenite crys-tal. Pulsed high magnetic fields whose maximum strength was about 31.75 MA/m were applied along the length-wise direction of single crystals of three orientations.

First, electrical resistivity was measured as a func-tion of temperature in the range from 77 and 800 K, in order to determine transformation temperatures of each single crystal. The M_s temperature was nearly the same as M_f due to a burst phenomenon in single crystals, and those of three single crystals were con-sistent within 5 K, being nearly the same as M_s of polycrystalline alloys with nearly the same composi-tion.

Next, magnetization in the austenitic state was measured as a function of ΔT. It was found from the measurement that the spontaneous magnetization of austenite was in good agreement with that of the Fe–31.7at%Ni alloy polycrystal examined in the preceding section.

4.1. Critical Magnetic Field to Induce Martensites in Single Crystal

The $M(t)$–$H(t)$ relation was examined applying a magnetic field whose maximum strength was higher than H_c, as done for polycrystalline alloys. Typical $M(t)$–$H(t)$ curves are shown in Fig. 7,[29] (a), (b), and (c) being for single crystals with $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ orientations, respectively. An abrupt increase in magnetization is recognized at a certain strength of magnetic field, as indicated with an arrow on each curve. Such an abrupt increase in magnetization was not observed when the applied magnetic field was lower than a certain value which corresponds to H_c, as in the case of polycrystalline alloys. Fig. 8[29] shows
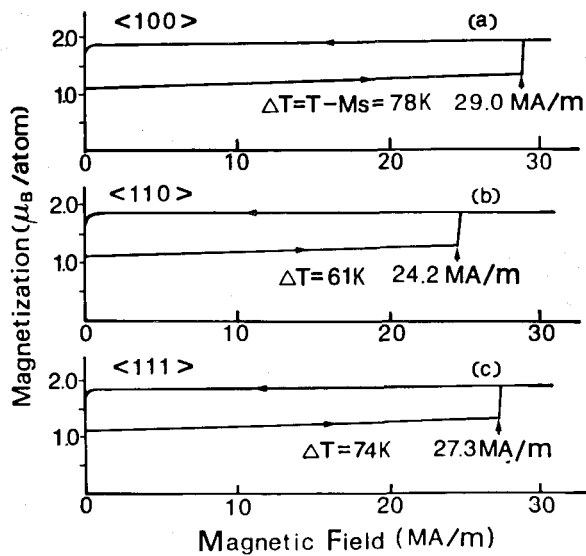

Fig. 7. $M(t)$–$H(t)$ curves for 3 single crystals of an Fe–31.6at%Ni alloy, (a), (b), and (c) being of $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ orientations, respectively.[29]
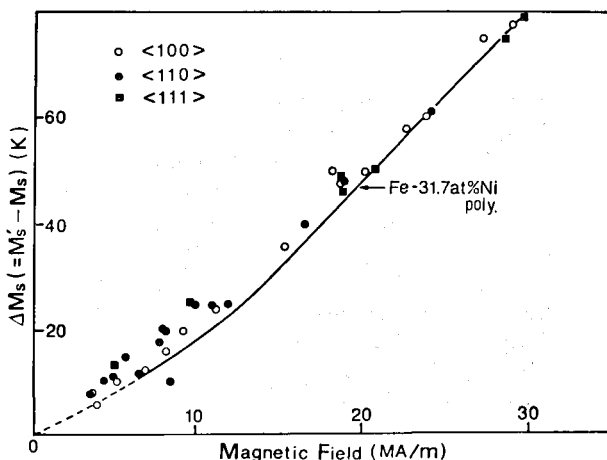

Fig. 8. ΔM_s vs. H_c relation for 3 single crystals of an Fe–31.6 at%Ni alloy.[29]

ΔM_s measured as a function of H_c. In the figure, symbols ○, ● and ■ represent the ΔM_s vs. H_c relation for the single crystals with $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ orientations, respectively, and the solid line represents the previous one for the Fe–31.7at%Ni alloy polycrystalline specimen. It is seen from the figure that ΔM_s increases with H_c for all the single crystals, and they lie nearly on a solid line irrespective of crystal orientations. That is, the ΔM_s vs. H_c relation is independent of the existence of grain boundaries and of the crystal orientations.

4.2. Amount of Magnetic Field-induced Martensites in Single Crystal

The amount of magnetic field-induced martensites was obtained in the same way as in the preceding section. The obtained amounts for the three single crystals under respective H_c are shown in Fig. 9,[29] as a function of ΔT. This figure indicates that the martensite amount is almost constant (about 80 %) without regard to ΔT and crystal orientation. Moreover, it does not increase even if any magnetic field higher than H_c is applied from the beginning. This can be seen from the magnetization curves in Fig. 7, that is, an abrupt increase of magnetization is observed at respective H_c. Such a burst phenomenon of magnetic field-induced martensitic transformation under H_c is very similar to that of thermally-induced one at normal M_s. Incidentally, the amount (80 %) of martensites in single crystal specimens is larger than that (75 %) in polycrystalline Fe–Ni alloys in the preceding section. This difference in martensite amount may be attributed to the existence of grain boundaries. Moreover, it is noted from Fig. 7 that the magnetic field-induced martensites are all formed within 10^{-6} s, because the magnetization increases in that period. This formation period is consistent with that previously reported for thermally-induced martensites.[30]

4.3. Morphology and Arrangement of Martensites in Single Crystal

The morphology of magnetic field-induced martensites was the same as that of thermally-induced one irrespective of crystal orientation, ΔT and H, as in polycrystalline Fe–Ni alloys. Fig. 10[29] shows ma-
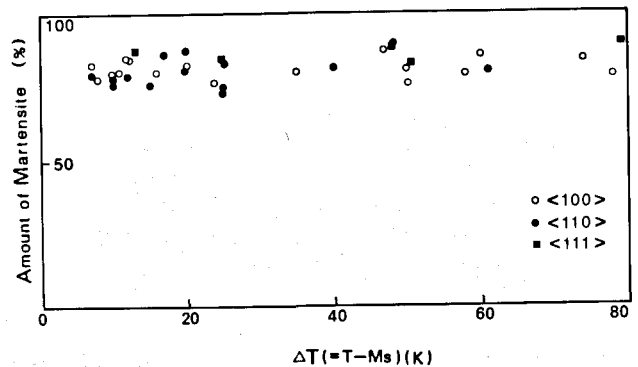

Fig. 9. Amount of magnetic field-induced martensites at the critical magnetic field, plotted as a function of ΔT, showing independence of crystal orientation.[29]
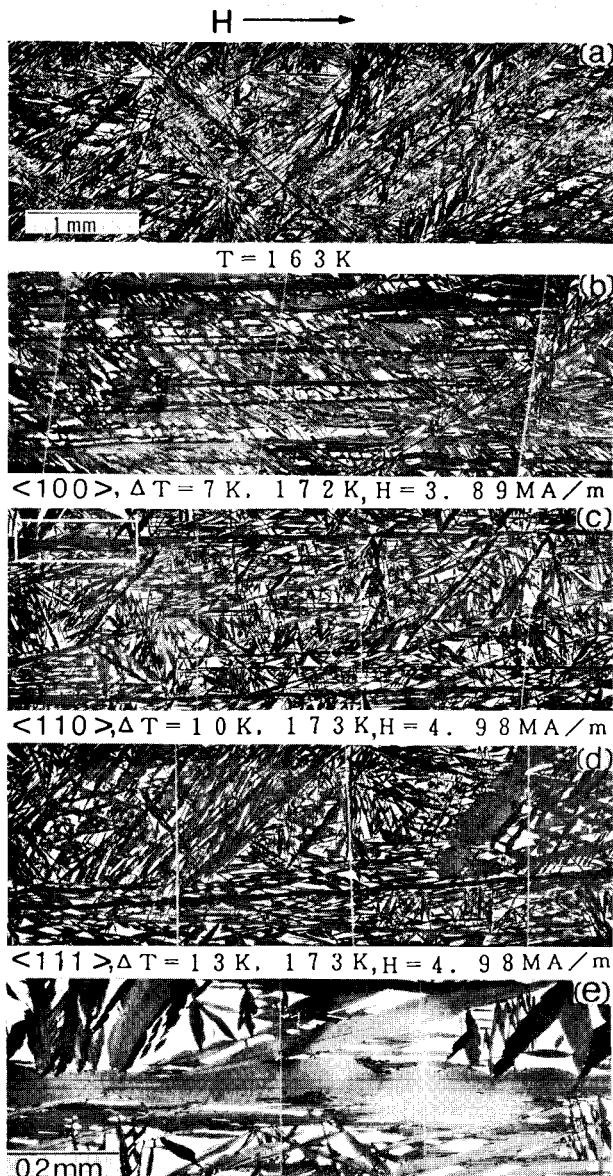
H ———→

Fig. 10. Macroscopic optical micrographs of thermally-induced, (a), and magnetic field-induced martensites in 3 single crystal specimens with ⟨100⟩, ⟨110⟩, and ⟨111⟩ orientations, (b), (c), and (d), respectively. (e) is an enlargement of the framed area of (c). The direction of magnetic fields, crystal orientations, transformation temperatures, ΔT, and H are inscribed on each photograph.[29]

from which it is clearly known that one plate grows lengthwise along the direction of magnetic field, and that other plates terminate at the directionally grown plates. This means that the directionally grown plates were first formed and then the other plates followed. The reason for such a formation of lengthwise grown plates under a magnetic field is not clear now, but a shape magnetic anisotropy effect seems to play an important role.[29]

In the above examination, no difference was found between poly- and mono-crystalline Fe–Ni alloys in the ΔM_s vs. H_c relation. That is, the effect of magnetic fields on ΔM_s is not influenced by the existence of grain boundaries, and the magnetic contribution to ΔM_s must be isotropic because it is independent of crystal orientations. It was already mentioned that the magnetic contribution to ΔM_s was due to not only the Zeeman energy but also other energies. The Zeeman energy is isotropic under magnetic fields higher than about 1 MA/m, and therefore the magnetic contribution due to the other energies must be also isotropic under that region of magnetic fields.

5. Effect of Invar Characteristic on Magnetic Field-induced Martensitic Transformation in Fe–Ni–C Alloy

In the above, magnetic field-induced martensitic transformations in Fe–Ni alloys have been clarified not to be influenced by the existence of grain boundaries and by the crystal orientations. By the way, the Fe–Ni alloys so far examined have an invar characteristic, and therefore the other energies besides the Zeeman energy affecting ΔM_s might be related to the invar characteristic. In order to evaluate directly such an effect of invar, Fe–Ni and Fe–Pt alloys appears to be suitable, because they become invar or non-invar depending on their composition. However, M_s of the non-invar alloys is higher than room temperature, and they are not suitable because our instrument can not apply magnetic fields at temperatures above room temperature. In this sense, Fe–Ni–C alloys are most suitable for our instrument, because those invar or non-invar alloys can easily be prepared by varying the compositions of Ni and C, and their M_s can be lowered below room temperature. However, the preceding studies on magnetic field-induced martensitic transformations in the Fe–Ni–C alloys were not performed from such a point of view, and the amount and morphology of the magnetic field-induced martensites were not examined systematically by varying temperature.

Three Fe–Ni–C alloys, Fe–28.7Ni–1.8C, Fe–29.0 Ni–1.4C, and Fe–24.7Ni–1.8C (at%), were prepared. According to a previous study,[31] the former two alloys are invar and the last one is non-invar (the three alloys will be labeled A to C, respectively, for simplicity in this section).

5.1. Transformation Temperature and Spontaneous Magnetization of Austenite

After M_s and M_f of the three alloys were deter-

croscopic morphologies, exhibiting the whole view of thermally-induced martensites, (a), and magnetic field-induced ones, (b) to (d). Crystal orientation, formation temperature, H and its direction for the magnetic field-induced martensites are inscribed in each photograph. Figs. 10(b) to 10(d) reveal that several martensite plates grow nearly parallel to the direction of applied magnetic field, and some of them run through from one end to the other of the single crystals. However, such a directional growth of martensite plates is not observed in Fig. 10(a). Therefore, the directional growth seems to be characteristic of magnetic field-induced martensites. Fig. 10(e)[29] is an enlargement of the framed area of Fig. 10(c),

mined by electrical resistivity *vs.* temperature measurements, the spontaneous magnetization of austenite was measured as a function of ΔT, as shown in Fig. 11.[32] The figure reveals that it decreases with increasing ΔT and in the order of A to C alloys. On the other hand, the spontaneous magnetization of martensite was assumed to originate in magnetic atoms and so depend only upon the composition of Fe and Ni atoms. The assumption was almost valid for the Fe–Ni–C alloys[33] whose C content was within 2 at%, as in the present case of the Fe–Ni–C alloys. Thus, the spontaneous magnetization of martensite was estimated to be about 2.0 μ_B/atom for the invar alloys and about 2.2 μ_B/atom for the non-invar alloy, in the same way as before. Accordingly, ΔM increases in the order of A to C alloys in the temperature range examined.

5.2. Critical Magnetic Field to Induce Martensite

As in the previous Fe–Ni alloys, $M(t)$–$H(t)$ relation in one pulse was measured in magnetic fields higher than H_c. Typical $M(t)$–$H(t)$ curves at $\Delta T = 50$ K are shown in Fig. 12,[32] (a) to (c) being for alloys A to C, respectively. An increase in magnetization is similarly recognized at a certain strength of magnetic field, as indicated with an arrow on each curve. Such an increase was not observed below the certain magnetic fields for each alloy at the same temperature. Therefore, the certain magnetic field corresponds to H_c at $\Delta T = 50$ K, and the ΔM_s *vs.* H_c relation is shown for the three alloys in Fig. 13.[32] In the figure ΔM_s increases with H_c for all the alloys, and lies on a curve with a slightly downward convexity (similarly to the case of Fe–Ni alloys) for the two invar alloys (A, B), while those for the non-invar alloy (C) lie on a single straight line. This suggests that the effect of magnetic fields on ΔM_s differs significantly between invar and non-invar alloys.

Another characteristic noted in Fig. 13 is that ΔM_s for alloy A is larger than that for alloy B over the whole range of applied magnetic field. Since ΔM for alloy A was larger than that for alloy B, ΔM_s for alloy A would be smaller than that for alloy B under a given H, as mentioned before. Such an incom-
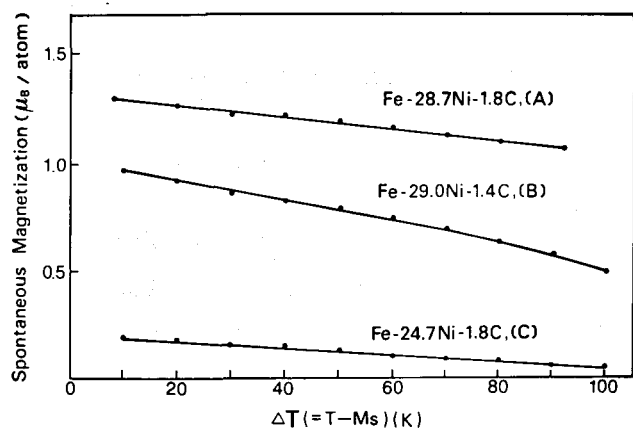
patibility means that martensitic transformations under a magnetic field are influenced not only by the Zeeman energy but also by the other energies, as in the case of Fe–Ni alloys, which may be related to the invar characteristic, because a large difference in the magnetic field dependence of ΔM_s was observed between invar and non-invar alloys.

5.3. Amount of Magnetic Field-induced Martensite

The amount of magnetic field-induced martensites estimated in the same way as before was found to in-
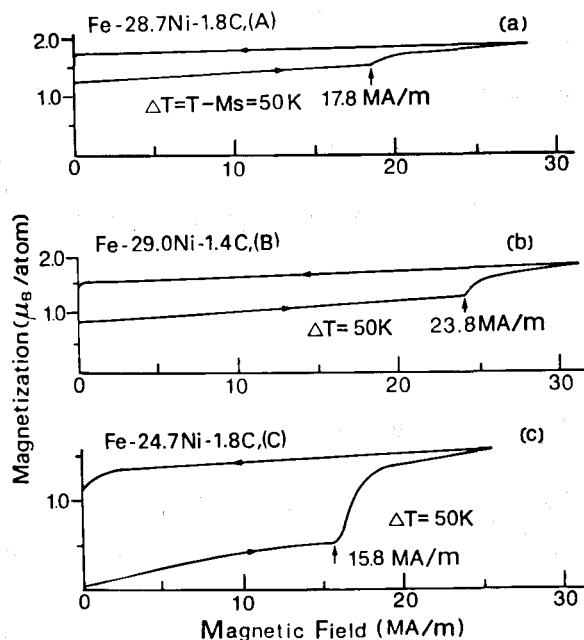
Fig. 12. $M(t)$–$H(t)$ curves for three Fe–Ni–C alloys, the composition being inscribed.[32]

Fig. 11. Spontaneous magnetization of austenite as a function of ΔT for three Fe–Ni–C alloys.[32]
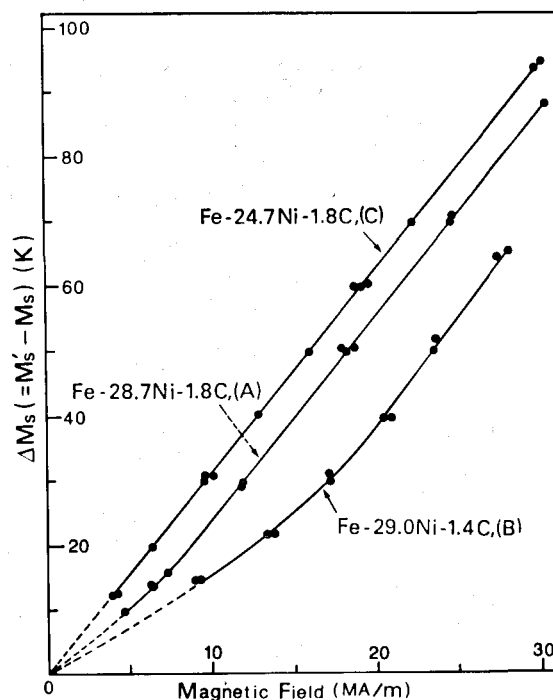
Fig. 13. ΔM_s *vs.* H_c relation for three Fe–Ni–C alloys.[32]

crease with the maximum strength of pulsed magnetic fields for all the alloys. Such a field dependence of the martensite amount is also seen in the magnetization curves in Fig. 12, since all the alloys exhibit a gradual increase of magnetization after the magnetic field has reached respective H_c. However, some difference is observed between alloy A and the other two alloys; the martensite amount in alloy A increases gradually on reaching H_c, but in the other two alloys it increases abruptly to a certain amount at respective H_c and continuous gradual increase. This difference seems to be due to a difference in morphology of the martensites.

5.4. Morphology of Magnetic Field-induced Martensite

The morphology of magnetic field-induced martensites was compared with that of thermally-induced ones formed by cooling slightly below respective M_s, as before. Both the martensites were the same in morphology despite the different formation temperature, alloy A being of thin plate and the other two alloys of lenticular. As mentioned before, this difference in martensite morphology between alloy A and the other two alloys is considered to be the origin of the difference in increasing manner of martensite amount at H_c. Because, thin plate martensites in alloy A may grow thermoelastically, whereas lenticular martensites in the other alloys may grow instantaneously to some amount at respective M_s due to the burst nature.

The comparison also revealed that the martensite morphology is different even if the formation temperature is nearly the same. This result is contradictory to a previous proposition[27] that the martensite morphology in Fe–Ni–C alloys is determined only by the formation temperature. In order to check further this point, the magnetic field-induced martensites were compared with deformation-induced ones at the same temperature. Figs. 14(a) and 14(c)[32] are optical micrographs of the magnetic field-induced martensites in alloys A and C at 181 and 273 K, respectively, and Figs. 14(b) and 14(d) are those of deformation-induced ones in alloys A and C at 181 and 273 K, respectively. The formation temperatures of those martensites are the same for respective alloys, but their morphologies are largely different, Figs. 14(a) and 14(b) showing plate and lenticular morphologies, respectively, and Figs. 14(c) and 14(d) lenticular and butterfly morphologies, respectively. This observation clearly indicates that the martensite morphology in Fe–Ni–C alloys is not determined only by the formation temperature.

As discussed before,[32] in the case of deformation-induced martensitic transformation, a considerable amount of plastic deformation may be introduced in the austenite before martensitic transformation. On the other hand, magnetic field-induced martensites may be produced without any plastic deformation. In the former case, it may be possible that a particular arrangement of dislocations has been formed in the austenite to influence the martensite morphology. It is well known that a large number of dislocations
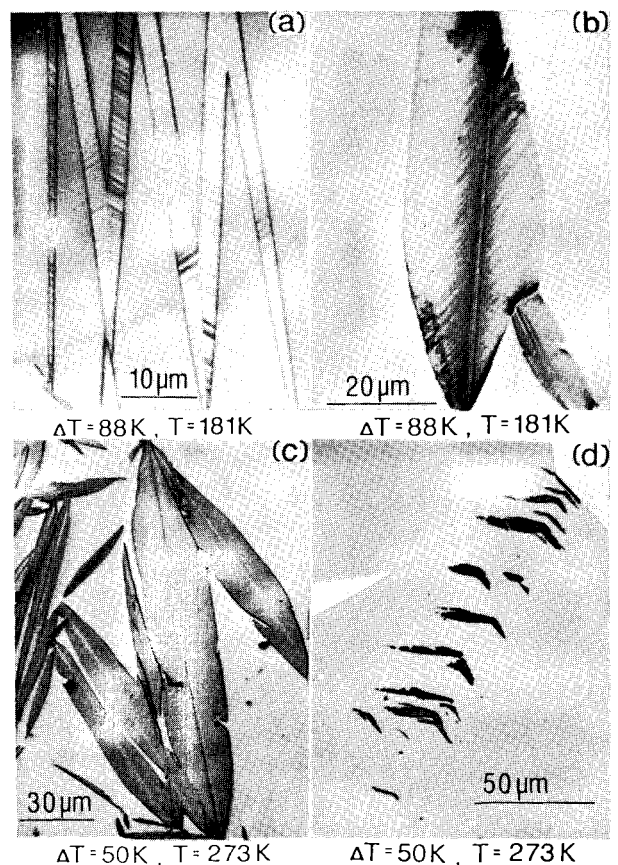

Fig. 14. Optical micrographs of magnetic field-induced martensites, (a), (c), and of deformation-induced ones, (b), (d), in Fe–28.7Ni–1.8C (at%) alloy, (a), (b), and Fe–24.7Ni–1.8C (at%) alloy, (c), (d), at 181 and 273 K, respectively.
Note the different morphologies in the alloys even though the formation temperatures are the same for each alloy.[32]

are observed in ferrous martensites as the formation temperature becomes higher and as the martensite morphology changes from thin plate to lenticular, butterfly and finally lath. Taking account of these facts, it may be assumed that the martensite morphology is related to the dislocation structure in the austenite before martensitic transformation, and therefore the morphology may be changed by varying the austenite dislocation structure even in an alloy with the same composition and even at the same temperature. However, detailed relation between the martensite morphology and dislocation structure in austenite is not yet clear.

6. Effect of Degree of Order or Volume Change during Martensitic Transformation in Fe–Pt Alloy

It has been revealed in the above that invar characteristic seems to play an important role on ΔM_s under a magnetic field. Fe–Pt alloys are also invar, but their martensitic transformations are different from those in the previous Fe–Ni and Fe–Ni–C alloys. The Fe–Pt alloys with compositions near Fe_3Pt are ordered into the $L1_2$ type, and the degree of order can

easily be changed by varying the annealing period for ordering. It is now known in the Fe–Pt alloys that the temperature hysteresis between M_s and A_f can be controlled by increasing the degree of order, although in Fe–Ni and Fe–Ni–C alloys it is unchangeable amounting to 400 K. The type of martensitic transformation in the Fe–Pt alloys can be changed from non-thermoelastic in the disordered state to thermoelastic in the ordered state. Moreover, in the Fe–Pt alloys the volume change associated with martensitic transformation becomes negative by increasing the degree of order. On the other hand, difference in spontaneous magnetization between the austenitic and martensitic states of Fe–Pt alloys is almost the same as that in Fe–Ni and Fe–Ni–C alloys. Therefore, magnetic field-induced martensitic transformations in ordered and disordered Fe–Pt alloys, whose volume changes are negative and positive, respectively, can be examined by applying the same order of magnetic field as in Fe–Ni and Fe–Ni–C alloys. An Fe–Pt alloy is, thus, the only one for which the difference in magnetic field effect between non-thermoelastic and thermoelastic martensitic transformations can be investigated. However, there has been no report on the magnetic field-induced martensitic transformations in Fe–Pt alloys.

The Fe–Pt alloy used was an Fe–24.0at%Pt, and three levels of ordered state were prepared by annealing at 923 K for 1.8×10^3 s, 2.9×10^4 s and 3.8×10^5 s; they are labeled A, B, and C, respectively, for simplicity in this section.

6.1. Various Characteristic Values and Spontaneous Magnetization of Austenite and Martensite

Prior to magnetization measurements, characteristic values such as transformation temperatures (M_s, M_f, A_s, and A_f), equilibrium temperature (T_0), Curie temperature of austenitic state (T_c), and degree of order (S) were measured or determined by referring to available data. The value of S was obtained from the data by Tadaki and Shimizu.[34] The transformation temperatures were determined by electrical resistivity vs. temperature measurements, and T_0 was estimated from the formula, $T_0 = (M_s + A_f)/2$, which was defined by Tong and Wayman.[35] A specimen with a degree of order less than 0.5 has a large temperature hysteresis, and so its A_s and A_f could not be measured. On the other hand, highly ordered specimens B and C become thermoelastic, exhibiting small temperature hysteresis as shown in Table 1, where other data are also inscribed. In the ordered specimens, M_s increases with thermal cycling in the tem-

perature range from 293 to 77 K, but the increase is apparently saturated after 15 cycles, although other transformation temperatures, M_f, A_s, and A_f, were not changed so much as M_s by thermal cycling. Thus, in Table 1, the values of the temperatures in parentheses are for specimens immediately after the annealing treatments for ordering, and those without parentheses are for specimens after 15 thermal cycles. Magnetization measurements were carried out for the specimens B and C after 15 thermal cycles. The Curie temperature T_c was measured by magnetization measurements under low magnetic fields which was listed in Table 1.

Spontaneous magnetization of austenite was measured as a function of ΔT as before, and its values are shown in Fig. 15.[36] Spontaneous magnetization of martensite measured at temperatures below M_f was 2.22 and 2.44 μ_B/atom for thermoelastic specimens B and C, respectively, although it was not measured for non-thermoelastic specimen A, because two phases coexist in the specimen. Then, the spontaneous magnetization of martensite of specimen A was about 2.0 μ_B/atom on the assumption as before.

6.2. Critical Magnetic Field to Induce Martensite

A pulsed magnetic field $H(t)$ whose maximum strength was higher than H_c was applied to each of the three specimens, and magnetization $M(t)$ was measured as a function of $H(t)$. Typical $M(t)$–$H(t)$ curves for specimens A to C are shown in Fig. 16,[36] respectively, along with inscribed experimental con-
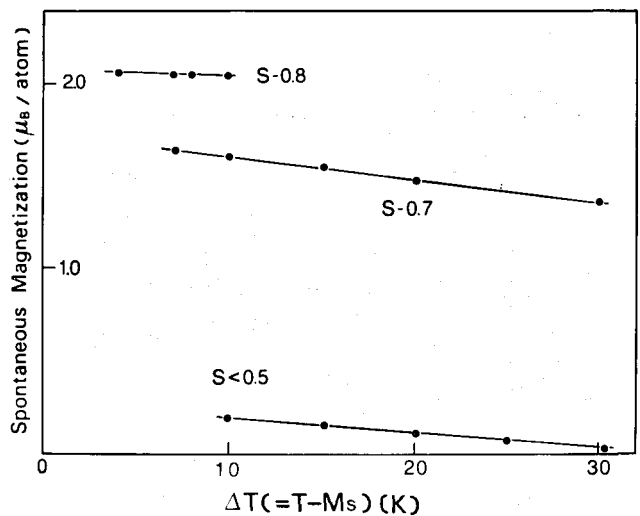
Fig. 15. Spontaneous magnetization of austenite as a function of ΔT for three Fe–Pt alloy specimens whose degrees of order are 0.8, 0.7, and <0.5.[36]

Table 1. Data on transformation temperatures, T_0 temperature, Curie temperature (T_c), and degree of order (S) for three kinds of specimens of an Fe–24.0at%Pt alloy.[36]

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

ditions such as *S*, ΔT and maximum strength of applied pulsed magnetic field. It is noted in the figure that the increase in magnetization as in the previous Fe–Ni and Fe–Ni–C alloys is not recognized. Therefore, no information is derived from the figure as to the occurrence of martensitic transformation. Nevertheless, some hysteresis can be found on the magnetization curves as a representative of the occurrence of martensitic transformation. These results suggest that H_c can not be determined only from magnetization measurement even if martensitic transformation occurs. Therefore, in order to determine H_c, electrical resistivity *vs.* temperature measurements were carried out in combination with magnetization measurements, because electrical resistivity change was more sensitive for the occurrence of martensitic transformations.[36]

The critical field H_c thus defined was measured as a function of temperature, and ΔM_s was plotted as a function of H_c, as shown in Fig. 17.[36] This figure clearly indicates that ΔM_s increases with H_c in all the specimens. Comparisons of ΔM_s among the three specimens at a given H_c indicates the decrease of ΔM_s with increasing order. One characteristic in Fig. 17 is that ΔM_s *vs.* H_c relation for specimens B and C is of a curve with an upward convexity, and it appears to saturate near their proper temperature (about T_0). This nonlinearity is largely different from the linearity for specimen A.
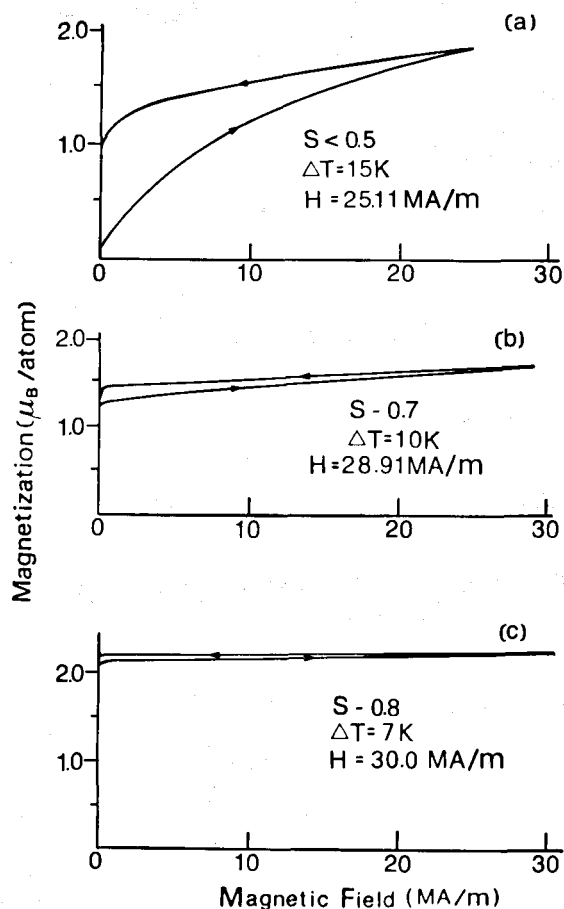
The nonlinear relations between ΔM_s and H_c have also been observed for Fe–Ni and Fe–Ni–C alloys, but the convexity of curves for those alloys was inverse to that for the Fe–Pt alloys. The downward convexity of curves of the previous Fe–Ni and Fe–Ni–C alloys seems to correspond to the non-thermoelastic nature or a positive volume change associated with martensitic transformations, and the upward one of the Fe–Pt alloys represents the thermoelastic nature or a negative volume change, even though all of those alloys are similarly invar.

6.3. Amount of Magnetic Field-induced Martensite

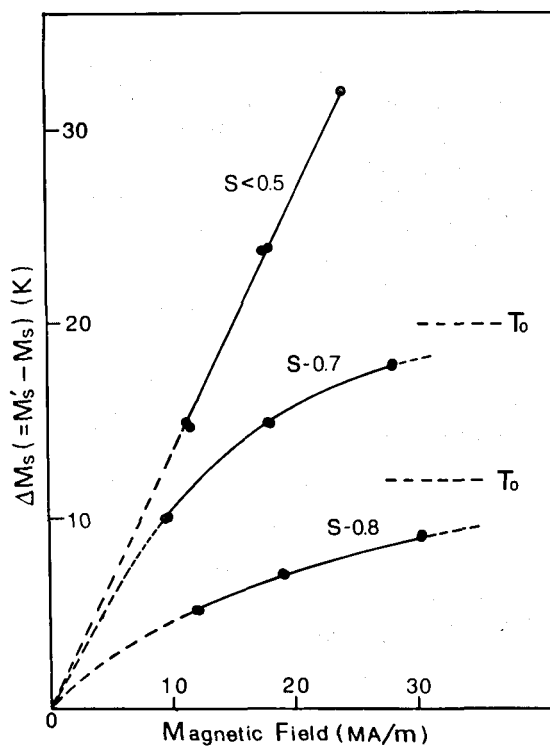The amounts of magnetic field-induced martensites were estimated in the same way as before, and those

Fig. 16. $M(t)$–$H(t)$ curves of Fe–24.0 at%Pt alloy specimens whose degrees of order are (a) <0.5, (b) 0.7, and (c) 0.8.[36]

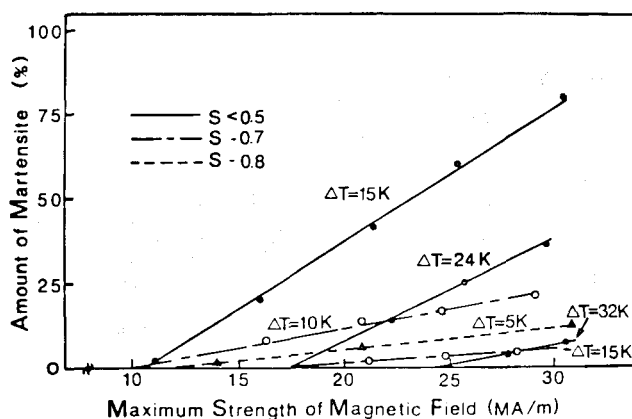Fig. 17. ΔM_s *vs.* H_c relation for Fe–24.0at%Pt alloys with three kinds of degrees of order.[36]

Fig. 18. Amount of magnetic field-induced martensites in Fe–Pt alloys with three kinds of degrees of order, plotted as a function of maximum strength of pulsed magnetic field.[36]

for specimens A to C are shown in Fig. 18,[36] as a function of the maximum strength of pulsed magnetic field. This figure shows that the martensite amount linearly increases with magnetic field irrespective of the degree of order and ΔT. This increasing tendency is different from that for the previous Fe–Ni alloys whose martensite amount was nearly the same irrespective of the applied magnetic field at a constant ΔT. In the figure, the martensite amount also increases with decreasing ΔT at a given degree of order, as easily seen by comparing the amount of specimen A at temperatures of ΔT=15, 24, and 32 K. Furthermore, it also increases with decreasing degree of order at a constant ΔT of 15 K, as seen from comparison between the martensite amounts of specimens A and B. In this way, the martensite amount is dependent on the magnetic field, being greatly different from the previous Fe–Ni alloys. The reason for such a difference between the Fe–Pt and Fe–Ni alloys is not yet clear, but may be attributed to a difference in mechanical strength of austenite matrix and/or in the growth mechanism of martensite.

The above results indicate that magnetic effect due to the invar characteristic must be different between Fe–Pt and Fe–Ni alloys, even though they are all invar. That is, the invar characteristic in thermoelastic ordered Fe–Pt alloys may decrease ΔM_s due to the Zeeman energy, as seen from the saturation phenomenon of ΔM_s, whereas that in non-thermoelastic disordered Fe–Pt and Fe–Ni(–C) alloys may increase ΔM_s due to the Zeeman energy. Such decrease and increase in M_s may be related to the negative and positive volume changes associated with the martensitic transformations, respectively, as will be shown later.

7. Appearance of Magnetoelastic Martensitic Transformation in Ausaged Fe–Ni–Co–Ti Alloy

Magnetic field-induced martensitic transformations in thermoelastic alloys have been described in the preceding section. In the thermoelastic alloys, it is known that a single martensite crystal grows or shrinks gradually with temperature cycling, that is, it elastically responds to temperature in a balance between thermal and elastic energies.[37] If a uniaxial stress is applied to such a thermoelastic alloy at a temperature above A_f and then released, the alloy exhibits pseudoelastic behavior due to the stress-induced martensitic and reverse transformations upon load cycling.[4,5,7] The stress-induced martensite above A_f may thus be called "mechanoelastic", because it elastically responds to an applied mechanical stress.

If a magnetic field is applied to thermoelastic ferrous alloy above A_f, martensites which elastically respond to the magnetic field may be induced similarly to the mechanoelastic martensite. In such a "magnetoelastic martensitic transformation", martensites may be induced only while a magnetic field is applied, and they may revert to the austenite when the magnetic field is removed. In order to clarify the

appearance of such a magnetoelastic martensitic transformation, the ordered Fe–Pt alloys seem to be suitable because of the thermoelastic nature. However, the magnetoelastic transformation may not be realized in the alloy, because the martensitic transformation was not induced at temperatures nearly above T_0 ($<A_f$) because of a saturation in ΔM_s, as seen in Fig. 17. Fortunately, however, an ausaged Fe–Ni–Co–Ti alloy was recently found to exhibit a thermoelastic martensitic transformation.[38] Moreover, a difference in magnetization exists between the austenitic and martensitic states. In this section, therefore, the appearance of magnetoelastic martensitic transformation will be examined by using an Fe–Ni–Co–Ti alloy, as well as transformation characteristics such as ΔM_s vs. H_c relation, the amount of magnetic field-induced martensites and so on.

The alloy used is an Fe–31.9Ni–9.8Co–4.1Ti (at%), and it was shaped into 3 mm × 10 mm × 0.28 mm size plates from its ingot by hot- and cold-rolling after homogenization. The plate specimens were aged at 973 K for 10.8 ks after the austenitization for partial ordering by precipitation of the γ' phase (Ni$_3$Ti).

7.1. Transformation Temperatures and Magnetic Properties of Austenitic and Martensitic Phases

Fig. 19[39] shows an electrical resistivity vs. temperature curve, from which M_s and A_f were determined to be about 127 and 159 K, respectively, although M_f and A_s were not determined because they were lower than 77 K. The curve is very similar to that for the ordered thermoelastic Fe–Pt alloys in the preceding section, the temperature difference between M_s and A_f being only 32 K. Thus, the martensitic transformation in the ausaged Fe–Ni–Co–Ti alloy is certainly thermoelastic, as also previously verified by an optical microscopy observation.[38] The spontaneous magnetization of austenitic and martensitic states was measured as a function of temperature, as shown in Fig. 20. According to the figure, M_s and A_f shown with arrows are consistent with those determined by the electrical resistivity vs. temperature measurement, and A_s is known to be 60 K. It is also noted in this figure that the difference in spontaneous magnetization between
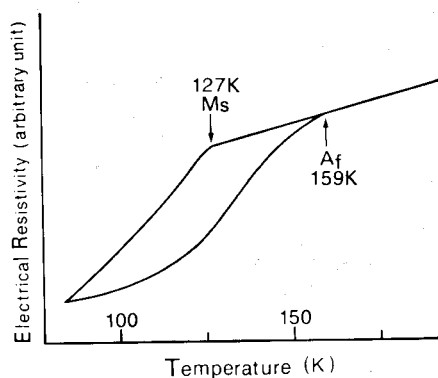

Fig. 19. Electrical resistivity vs. temperature curve of an Fe–31.9Ni–9.8Co–4.1Ti (at%) alloy ausaged at 973 K for 10.8 ks, showing a small temperature hysteresis.[39]

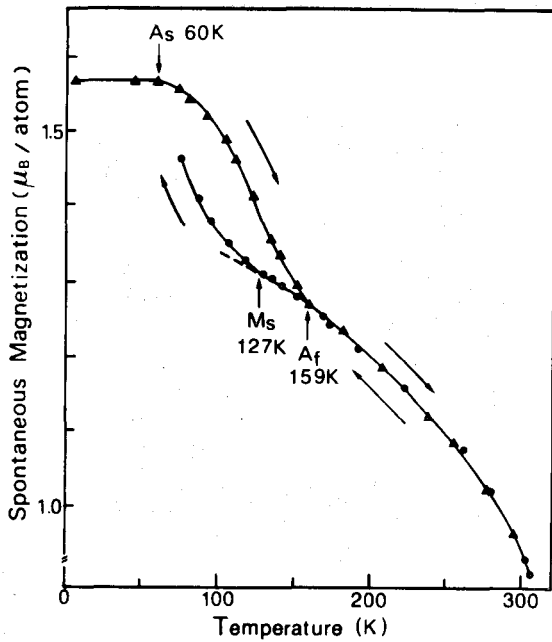Fig. 20. Spontaneous magnetization as a function of temperature in an ausaged Fe–Ni–Co–Ti alloy.[39]

the two phases is about 0.3 μ_B/atom at M_s which is the same order as that in the previous Fe–32.5at%Ni alloy. Therefore, the magnetoelastic martensitic transformation may occur by applying the same order of magnetic field as before.

7.2. Critical Magnetic Field to Induce Magnetoelastic Martensite

Typical $M(t)$–$H(t)$ curves obtained at 163 K ($\Delta T = 36$ K, $T > A_f$) are shown in Figs. 21(a) and 21(b)[39]; (a) shows no hysteresis when a pulsed magnetic field whose maximum strength is 22.22 MA/m has been applied and then removed. This means that the maximum strength is lower than H_c and no martensitic transformation occurs. Then, higher magnetic field was applied, and the obtained $M(t)$–$H(t)$ curve is shown in (b), which reveals a hysteresis with a discontinuity of magnetization at $H_c = 23.08$ MA/m, as indicated by an arrow. When the magnetic field was removed, the increased magnetization restores to the initial value at about $H_f = 5$ MA/m indicated by 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 expected magnetoelastic martensitic transformation is certainly realized in the ausaged Fe–Ni–Co–Ti alloy, and that it is always realized at temperatures above A_f. On the other hand, when magnetic fields were applied at temperatures between M_s and A_f, the reverse transformation was not completed, as follows; Typical $M(t)$–$H(t)$ curves obtained at $T = 138$ K ($\Delta T = 11$ K, $M_s < T < A_f$) are shown in Figs. 21(c) and 21(d). Fig. 21(c) shows no hysteresis when the pulsed magnetic field of 9.52 MA/m was applied, suggesting no martensitic transformation, as in Fig. 21(a). However, when applied magnetic field was increased above H_c, a hysteresis was observed on the $M(t)$–$H(t)$ curve, as shown in Fig. 21(d), but the
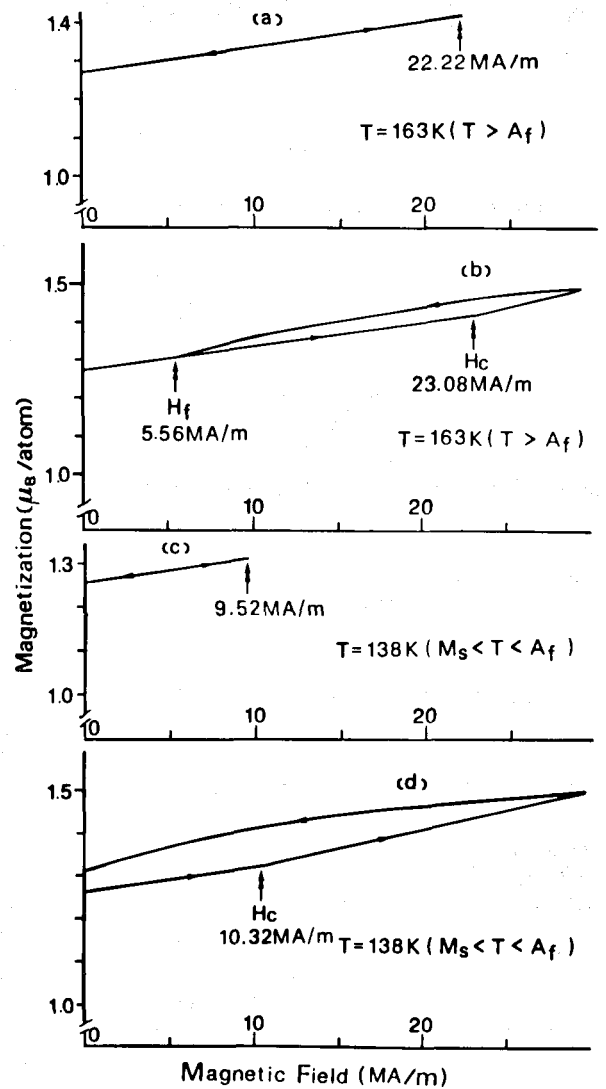

Fig. 21. $M(t)$–$H(t)$ curves for an ausaged Fe–Ni–Co–Ti alloy at temperatures of (a) and (b) 163 K ($T > A_f$), and (c) and (d) 138 K, ($M_s < T < A_f$).[39]

curve is somewhat different from Fig. 21(b). That is, the magnetization after removing the magnetic field was larger than that in the initial state. However, this increased magnetization disappears if the specimen is heated up beyond A_f. These results mean that a part of magnetic field-induced martensites remains after removing the magnetic field, that is, the reverse transformation is not completed. This is reasonable because the martensite is still thermodynamically stable in this temperature range. Fig. 22[39] shows the relation between ΔT vs. H, which is similar to that in Fe–Ni and Fe–Ni–C alloys previously examined, probably because the positive volume change associated with transformation inverse to the ordered thermoelastic Fe–Pt alloy. In Fig. 22, critical magnetic field for the reverse transformation, H_f, is also plotted. The hysteresis between H_c and H_f is nearly the same when the magnetic field was applied at temperatures above A_f, but not so at temperatures between M_s and A_f.

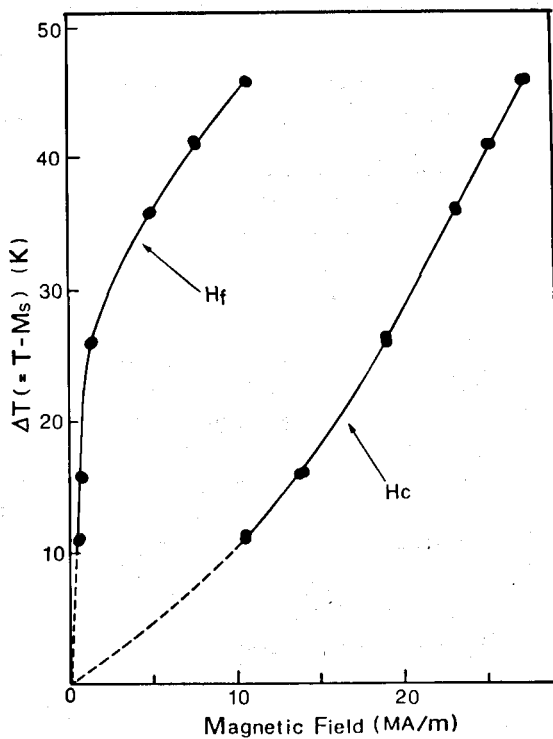Recently, some structural steels used as a supporter for super-conducting magnets have come into ques-

Fig. 22. ΔT vs. H relation of an ausaged Fe–Ni–Co–Ti alloy.[39]

tion in research field on fusion reactors. They exhibit an irreversible magnetic field-induced martensitic transformation, which causes cracking along the interfaces of martensite and austenite. Such a question may be solved if the cracking is prevented or a stabler austenitic steel is adopted. Then, if an Fe–Ni–Co–Ti alloy strengthened by ausaging is used as such a supporter, no crack may be caused because a reversible magnetoelastic martensitic transformation is realized in the alloy, as mentioned above. The ausaged Fe–Ni–Co–Ti alloy is thus now known to exhibit a magnetoelastic martensitic transformation as well as shape memory effect, and therefore, the alloy may be utilized as a magnetically sensitive device in addition to a thermally sensitive one.

8. Effect of Paramagnetic Nature of Austenite on Martensitic Transformation

All of the above studies on magnetic field-induced martensitic transformations were concerned with ferrous materials undergoing a transformation from ferromagnetic austenite to ferromagnetic martensite. Therefore, the obtained information may be different from that for materials undergoing another type of transformation from paramagnetic austenite to ferromagnetic martensite. An experiment is, therefore, needed to examine the magnetic field-induced martensitic transformation in such materials. An Fe–Mn–C alloy is suitable for such an experiment, because the alloy exhibiting a transformation from paramagnetic austenite to ferromagnetic martensite can easily be prepared by varying the composition of Mn and C atoms, and also because its thermody-

namics and crystallography of thermally-induced martensitic transformation have already been well examined.[40,41] However, the previous studies on magnetic field-induced martensitic transformations in Fe–Mn–C alloys were not done from such a point of view.

The alloy used was an Fe–3.9Mn–5.0C (at%), and $3 \, \text{mm} \times 10 \, \text{mm} \times 0.5 \, \text{mm}$ size specimens were prepared for magnetization measurement. First, differential scanning calorimetry measurements were made in the temperature range from 293 to 77 K in order to determine transformation temperatures and the latent heat of transformation, by using the specimens cut into 3 mm square. The measurements shows M_s as 223 K and the latent heat of transformation as 2 518 J/mol.[42] Next, the susceptibility in austenitic state obtained by magnetization measurement at a low magnetic field was 3.2×10^{-13} H·m²/kg, independent of temperature in the range from 253 to 293 K. This temperature independency of susceptibility means that the Fe–Mn–C alloy is surely paramagnetic in the austenite state. The spontaneous magnetization of martensite was obtained on the assumption that it originates in magnetic atoms and therefore it depends only on the composition of Fe and Mn atoms. Thus, by referring to the Slater–Pauling curve, the spontaneous magnetization of martensite was obtained to be about 2.0 μ_B/atom.

8.1. Critical Magnetic Field to Induce Martensite

Typical $M(t)$–$H(t)$ curves obtained at temperatures of $\Delta T = 60$ and 80 K are shown in Fig. 23.[42] In this figure, an increase in magnetization is recognized at a certain magnetic field, as indicated by an arrow on each curve. In this way, the martensitic transformation is surely induced even in the paramagnetic austenite, in the same manner as in the ferromagnetic austenite previously examined. The certain magnetic field corresponds to H_c of this alloy at the above two temperatures, and the ΔM_s vs. H_c relation is shown in Fig. 24.[42] It is seen from the figure that ΔM_s increases linearly with H_c. This linearity is different from the nonlinearity in non-thermoelastic invar Fe–Ni and Fe–Ni–C and thermoelastic invar Fe–Pt alloys, and rather similar to that in non-thermoelastic non-invar Fe–Ni–C alloys.

8.2. Amount and Morphology of Magnetic Field-induced Martensite

The martensite amount estimated in the same way as before is shown in Fig. 25[42] as a function of the maximum strength of pulsed magnetic field. The amount increases with the maximum strength of magnetic field for all ΔT; that is, it increases slightly near H_c, abruptly under a slightly higher field than H_c and linearly under higher fields. This increasing tendency of the martensite amount was examined by optical microscopy observation, as shown in Fig. 26.[42] Fig. 26(a) shows a martensite structure observed at room temperature after polishing and etching after applying a magnetic field near H_c at a temperature of $\Delta T = 35$ K, and Fig. 26(b) shows an unetched structure

after successive application of a magnetic field higher than H_c to the same alloy at the same temperature as in Fig. 26(a) (which was taken from the identical
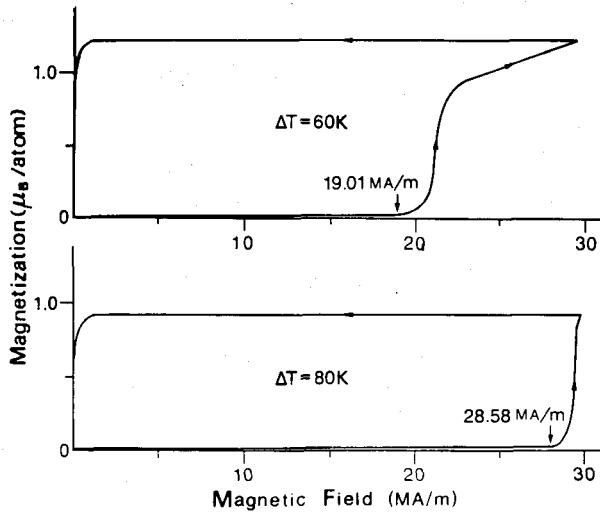

Fig. 23. $M(t)$–$H(t)$ curves for a paramagnetic Fe–3.9Mn–5.0C (at%) alloy at temperatures of $\Delta T=60$ and 80 K.[42]
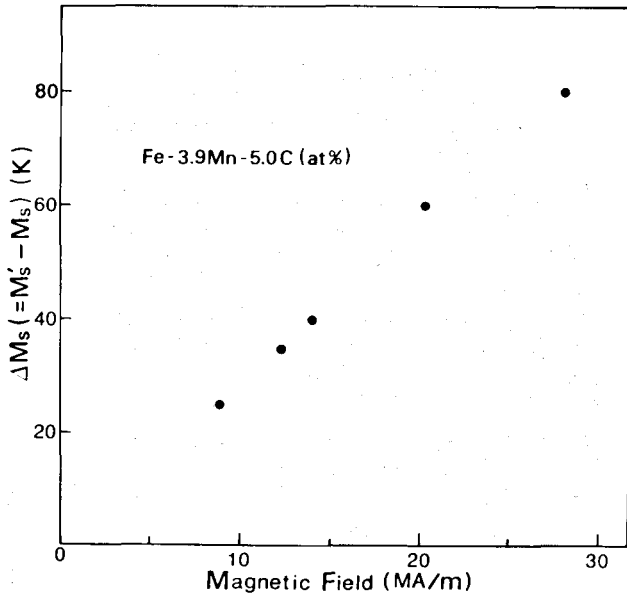
place as in Fig. 26(a) at room temperature). Surface relief newly arises at interfaces of martensites as indicated with an arrow in Fig. 26(a). This may be due to the growth of existing plates and/or the formation of new martensite plates. In order to make it clear, the specimen was observed after polishing and etching, as shown in Fig. 26(c). Comparison of Fig. 26(b) with Fig. 26(c) indicates that the surface relief in Fig. 26(b) is caused not only by a slight growth of existing plates but also by the formation of many small plates.

The morphology of the magnetic field-induced martensites was the same as that of thermally-induced ones irrespective of temperature, as in the previous Fe–Ni and Fe–Ni–C alloy polycrystals. Several martensite plates were observed growing nearly parallel to the direction of applied magnetic field, as in the previous Fe–Ni alloy single crystals.

9. Exact Formulation of Magnetic Effects on Martensitic Transformation

In the above, effects of magnetic fields on martensitic transformations in various ferrous alloys have
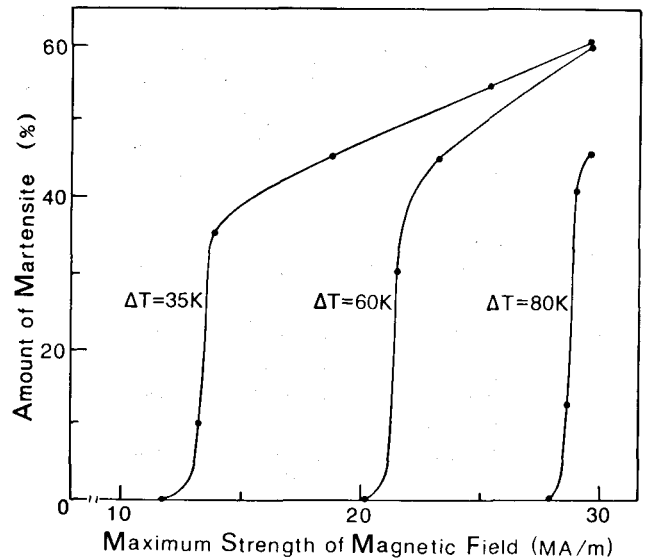

Fig. 24. ΔM_s vs. H_c relation of a paramagnetic Fe–Mn–C alloy.[42]

Fig. 25. Amount of magnetic field-induced martensites in a paramagnetic Fe–Mn–C alloy at three temperatures, plotted as a function of maximum strength of pulsed magnetic field.[42]

T=258K, ΔT=35K
H=14.29MA/m

T=258K, ΔT=35K
H=23.81MA/m
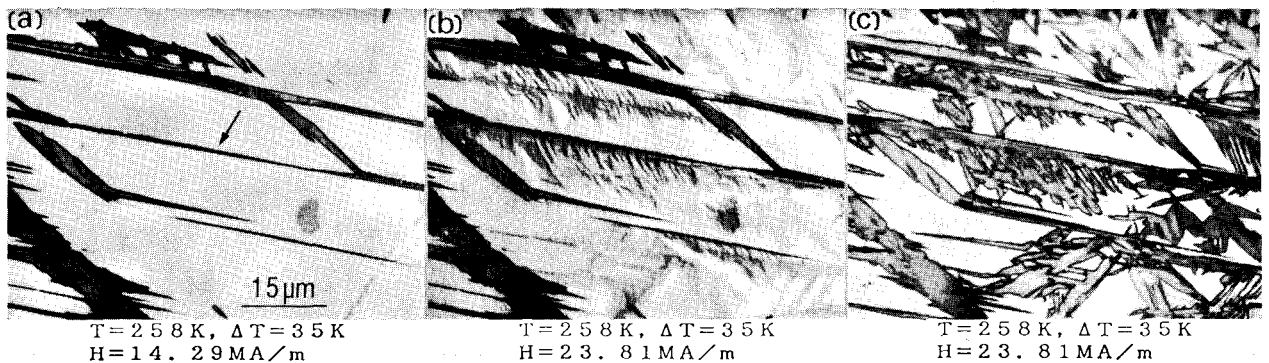
T=258K, ΔT=35K
H=23.81MA/m

Fig. 26. Optical micrographs showing the growth of existing martensite plates in a paramagnetic Fe–Mn–C alloy by successively applying a magnetic field higher than H_c. (c) is the etched structure of (b).[42]

been described, and much important information has been obtained on the ΔM_s vs. H_c relation and the amount and morphology of magnetic field-induced martensites. Of these, the ΔM_s vs. H_c relations have typically been revealed to differ among non-thermoelastic invar (Fe–Ni, Fe–Ni–C, disordered Fe–Pt), thermoelastic invar (ordered Fe–Pt), non-thermoelastic non-invar (Fe–Ni–C) and non-thermoelastic paramagnetic (Fe–Mn–C) alloys. In this section, the difference will be discussed, and a new and more exact formula will be developed for unified explanation of all of the ΔM_s vs. H_c relations of those alloys.

To begin with, it should be pointed out that two important things were not taken into consideration in the formula first proposed by Krivoglaz and Sadovsky.[18] One is that the Gibbs chemical free energies of austenitic and martensitic phases are simply assumed to be a linear relation with temperature. However, the situation is not so simple in real alloy systems, and a more exact expression must be used for the Gibbs chemical free energy, as derived by Kaufman and Cohen,[43] and other researchers. The other thing is that magnetic energy due to the high field susceptibility of austenite was neglected, even though it was fairly large. As typically seen in Figs. 2(a) and 12(c), the magnetization in austenitic state before martensitic transformation increases considerably with magnetic field, while that in martensitic state does not so much. This means that the high field susceptibility in austenitic state, $\chi_{hf}^{\gamma}(T)$, is substantially large and that in martensitic state is negligibly small, $\chi_{hf}^{\gamma}(T)$ being an increment of magnetization per unit strength of magnetic field at temperature T. However, the effect of the high field susceptibility on martensitic transformation was not taken into consideration in the previous formula. On the other hand, the high field susceptibility in Fig. 23 is very small compared with that in Figs. 2(a) and 12(c), and therefore it may be neglected for paramagnetic alloys.

Then, the magnetic energy due to the high field susceptibility will be introduced besides that due to the Zeeman energy. It may be expressed approximately as $-1/2 \cdot \chi_{hf}^{\gamma}(T) \cdot H^2$, because the magnetization increases linearly with magnetic field, as seen in many $M(t)$–$H(t)$ curves. Incidentally, the Zeeman energy is a magnetostatic energy, and was defined as a bilinear product of the magnetization with the magnetic field. Therefore, $\Delta M(M_s') \cdot H_c$ in the Krivoglaz and Sadovsky formula corresponds to the Zeeman energy. In such sense, $1/2 \cdot \chi_{hf}^{\gamma}(T) \cdot H^2$ is also a kind of the Zeeman energy, because it is a bilinear product of the magnetization with the magnetic field, $1/2 \cdot \{M^{\gamma}(T, H) - M^{\gamma}(T, 0)\} \cdot H$, where $M^{\gamma}(T, H)$ means an austenite magnetization under a magnetic field H at a temperature T. However, in this paper, the two Zeeman energies of $\Delta M(T) \cdot H$ and $1/2 \cdot \chi_{hf}^{\gamma}(T) \cdot H^2$ will be distinguished as those due to the Zeeman effect and high field susceptibility effect, respectively.

Patel and Cohen[2] developed a theory to explain the shift of M_s when a uniaxial stress or hydrostatic pressure was applied to an alloy system. By analogy

with the theory, ΔM_s vs. H_c relation may be expressed as follows;

$$\Delta G(M_s) - \Delta G(M_s')$$
$$= -\Delta M(M_s') \cdot H_c - 1/2 \cdot \chi_{hf}^{\gamma}(M_s') \cdot H_c^2, \quad \ldots\ldots(2)$$

where, $\Delta G(M_s') = G^{\gamma}(M_s') - G^{\alpha'}(M_s')$, G^{γ} and $G^{\alpha'}$ being the Gibbs chemical free energies of austenite and martensite phases at temperature M_s', respectively, and the other notations are as defined already. This equation is a quadratic one of H_c, which can be obtained by solving it for a specific M_s', if ΔG, ΔM, and χ_{hf}^{γ} are known as a function of temperature. The Gibbs chemical free energies can be obtained by following the equations proposed by Kaufman and Cohen,[43] and other researchers. The value of $\Delta M(T)$ can be known from the measured spontaneous magnetization of austenite (such as Fig. 1) and estimated one of martensite, and $\chi_{hf}^{\gamma}(T)$ from $M(t)$–$H(t)$ curves (such as Figs. 2 and 12). By substituting these known values into Eq. (2), ΔM_s vs. H_c relations were calculated for Fe–Ni, Fe–Ni–C, Fe–Pt, and Fe–Mn–C alloys. The calculated relations were almost consistent with measured ones for non-thermoelastic non-invar Fe–Ni–C and paramagnetic Fe–Mn–C alloys, but not for other alloys which were all invar. Therefore, the inconsistency between the calculated and measured ΔM_s vs. H_c relations may be related to the invar nature of those alloys.

It is well known that invar alloys have a large forced volume magnetostriction, which is defined as field-induced volume change, $\partial \omega / \partial H$, where ω is a volume change per unit volume. The $\partial \omega / \partial H$ has been measured for invar and non-invar alloys such as Fe–Ni[21,22,44] and for metals such as Ni.[45] According to the measurements, it is isotropically positive, that is, the austenite is subjected to a volume expansion, and it is about 10^{-10} m/MA for invar alloys and about 10^{-11} m/MA for non-invar metals and alloys. In a microscopic point of view, the volume expansion comes from the Pauli repulsion in the induced magnetization. In a phenomenological point of view, it can be regarded as a negative hydrostatic pressure for the austenite. This means that $\partial \omega / \partial H$ corresponds to $-\partial \omega / \partial P$ under hydrostatic pressure. The only difference between the $\partial \omega / \partial H$ and $\partial \omega / \partial P$ is their sign; namely $\partial \omega / \partial H > 0$ while $\partial \omega / \partial P < 0$.

The effect of hydrostatic pressures on ΔM_s was quantitatively studied by Patel and Cohen,[2] as mentioned before. They proposed the following equation to estimate ΔM_s when a hydrostatic pressure P was applied to a ferrous alloy;

$$\Delta G(M_s) - \Delta G(M_s') = -\varepsilon_0 \cdot P, \quad \ldots\ldots\ldots(3)$$

where, ε_0: the volume change associated with martensitic transformation.

The negative sign on the right-hand side is due to the fact that ε_0 is inverse to P in sense. On the other hand, when a negative hydrostatic pressure (that is, isotropic expansion) is produced by the forced volume magnetostriction effect, the negative term $-\varepsilon_0 \cdot P$ must be replaced by the positive term $\varepsilon_0 \cdot (\partial \omega / \partial H) \cdot H \cdot B$,

since $(\partial\omega/\partial H)\cdot H\cdot B=(\varDelta V/V)\cdot B$ corresponds to the hydrostatic pressure, where B is the bulk modulus. Hence, taking account of the magnetic energies due to the forced volume magnetostriction effect as well as the Zeeman and high field susceptibility effects, the relation between $\varDelta M_s$ and H_c in invar alloys must be represented by the following equation;

$$\varDelta G(M_s)-\varDelta G(M_s')$$
$$=-\varDelta M(M_s')\cdot H_c-1/2\cdot\chi_{hf}^{\tau}(M_s')\cdot H_c^2$$
$$+\varepsilon_0\cdot(\partial\omega/\partial H)\cdot H_c\cdot B\ .\ \ ....(4)$$

In the case of the thermoelastic martensitic transformation in an invar Fe–Pt alloy, ε_0 becomes negative, as mentioned before, and so the positive sign of the last term must be replaced by a negative sign.

In order to prove quantitatively the propriety of the above new equation consisting three terms of magnetic energies, physical quantities involved in the equation must be known. Of those quantities, the Gibbs chemical free energies were obtained from the equation by Kaufman and Cohen[43] for Fe–Ni alloys, as mentioned already, and by Fisher *et al.*[46,47] for Fe–Ni–C alloys, Tong and Wayman[48] for Fe–Pt alloys, and Chang and Hsu[40] for Fe–Mn–C alloys. The values of $\varDelta M(T)$ and $\chi_{hf}^{\tau}(T)$ were obtained from the magnetization measurements and $M(t)$–$H(t)$ curves, as before, and B was obtained by referring to previous works by Oomi and Mōri.[49] The volume change ε_0 in non-thermoelastic invar Fe–Ni and non-invar Fe–Ni–C alloys were recently measured by X-ray diffraction,[50] and that in thermoelastic invar Fe–Pt alloys were referred to a work by Tadaki and Shimizu.[34] The final forced volume magnetostrictions were also recently measured by Fabry–Pérot interferometry for all of the above alloys.[50]

The $\varDelta M_s$ vs. H_c relations were thus calculated for the two non-thermoelastic invar Fe–Ni, one thermoelastic invar Fe–Pt, one non-invar Fe–Ni–C and one paramagnetic Fe–Mn–C alloys by substituting the above known and measured values of physical quantities of those alloys into Eq. (4). The calculated $\varDelta M_s$ vs. H_c relations are shown with dotted lines in Fig. 27,[50] together with the measured ones (small closed circles), Fig. 27(a) being for invar Fe–31.7 and –32.5at%Ni and Fe–24at%Pt alloys, Fig. 27(b) for a non-invar Fe–24.7Ni–1.8C (at%) alloy, and Fig. 27(c) for a paramagnetic Fe–3.9Mn–5.0C (at%) alloy. It is clearly seen from the figures that the calculated relations are essentially in good agreement with the measured ones over the wide ranges of $\varDelta M_s$ and H_c.

Numerical values of calculated $\varDelta M_s$ are shown in Table 2 together with measured ones when a pulsed magnetic field of the nearly maximum strength (about 30 MA/m) was applied to 5 kinds of alloys. It is known that $\varDelta M_s$ due to the forced volume magnetostriction effect for invar Fe–Ni and Fe–Pt alloys are larger than that for non-invar Fe–Ni–C alloys, and that they are nearly the same order in magnitude as those due to the Zeeman and high field susceptibility effects. This is due mainly to the fact that the forced volume magnetostriction in invar alloys is larger than
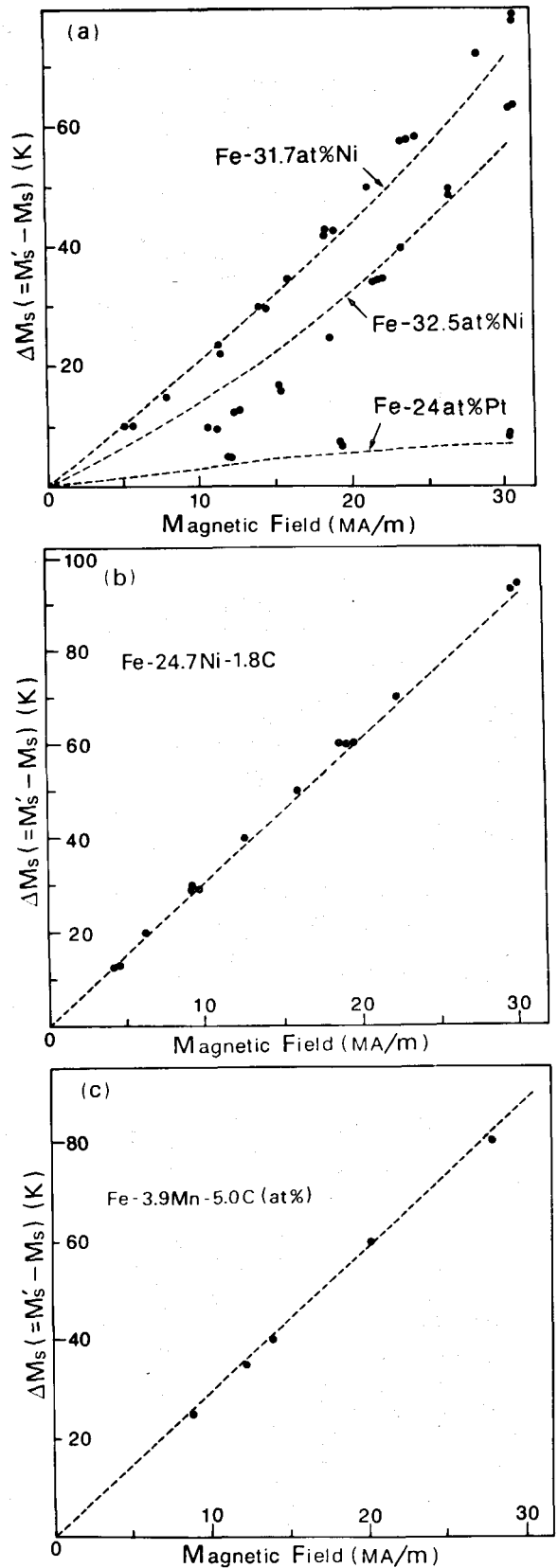

Fig. 27. Comparison between calculated (---) and measured (●) $\varDelta M_s$ vs. H_c relations for (a) invar Fe–Ni and Fe–Pt alloys, (b) one non-invar Fe–Ni–C alloy, and (c) one paramagnetic Fe–Mn–C alloy.[50]

that in non-invar alloys, although other quantities such as $(\varDelta G(M_s)-\varDelta G(M_s'))$ must be also taken into account. It is also noted in the table that $\varDelta M_s$ due

Table 2. Numerical values of calculated and measured ΔM_s, when about 30 MA/m of magnetic field was applied to three invar Fe–Ni alloys, one ordered invar Fe–Pt alloy and one non-invar Fe–Ni–C alloy.[50]

Composition	Fe–29.9at%Ni	Fe–31.7at%Ni	Fe–32.5at%Ni	Fe–24at%Pt	Fe–24.7Ni–1.8C
H (MA/m)	30.16	30.95	30.95	30.16	30.16
$-\Delta M \cdot H - \frac{1}{2}\chi_{hf}^r H^2$, $\Delta M_{s,1}$ (K)	43	41	30	31	83
$\varepsilon_0\left(\frac{\partial \omega}{\partial H}\right)\cdot H \cdot B$, $\Delta M_{s,2}$ (K)	28	31	28	-25	9
$\Delta M_{s,1}+\Delta M_{s,2}$ (K)	71	72	58	6	92
$\Delta M_{s \text{ obs.}}$ (K)	72	80	65	9	94

to the forced volume magnetostriction effect shows a decrease in thermoelastic invar Fe–Pt alloy. This is due to the fact that ε_0 in the Fe–Pt alloy has a negative value, as mentioned before. Therefore, it can be concluded that the propriety of the newly proposed equation (4) by the author's group for the ΔM_s vs. H_c relation is quantitatively verified. In other words, the effect of magnetic fields on ΔM_s for invar alloys consists of the Zeeman, high field susceptibility and forced volume magnetostriction effects, and that for non-invar ferromagnetic alloys of the first two effects, and also that for non-invar paramagnetic alloys of only the first one effect.

Readers who want to know more details of the above study should refer to Ref. 51) as well as the others.

Note

As known from the above description, the effect of magnetic fields on martensitic transformations shifts the equilibrium temperature between austenite and martensitic phases and consequently the M_s temperature. However, how the magnetic field affects the premartensitic phenomena such as lattice softening and the nucleation mechanism by a dissociation of dislocations has not yet been clarified. This clarification may be one of important future research subjects in the field of martensitic transformations.

Acknowledgements

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