Martensitic Transformation of Antiferro-magnetic Fe Particles Embedded in a Cu Matrix in a Magnetic Field

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Abstract

Martensitic transformation of antiferro-magnetic Fe particles embedded in a Cu matrix has been studied in the presence of a magnetic field at low temperatures. The saturation magnetization increased when a magnetic field of 4.44MA/m was applied during deformation at 4.2K. Electron microscopic observation indicated that the increment of the transformed fraction by the magnetic field was greater for larger particles, in which transformation by plastic deformation is easier. Cooling down to 4.2K after deformation at room temperature induced additional transformation by a few percent. On the other hand, the application of a magnetic field during simple cooling did not cause any effect on the additional transformation. Since the chemical free energy difference between the γ and α phases has a maximum around the Neel temperature, the transformation of Fe particles below this temperature may be promoted by a magnetic field only when it is superimposed with a mechanical driving force.

1. Introduction

It is well recognized that the application of an external stress, particularly a shear stress, promotes the $\gamma \rightarrow \alpha$ martensitic transformation in steels and in Fe particles embedded in a Cu matrix [1-6]. In the case of the Fe particles, regions where the transformation takes place are pre-determined. Once the transformation starts in a particle it completes within the particle and, therefore, complicated interactions between transformed and untransformed regions, such as the one known as the autocatalytic effect [7,8], are not involved. Therefore, a Cu-Fe alloy is well suited for studying basic aspects of martensitic transformation.

Another interesting feature of the Cu-Fe alloy is that γ-Fe particles formed by aging undergo a magnetic transition, from para- to antiferro- magnetic state at about 70K on cooling [9,10]. Effects of a magnetic field on martensitic transformations in various ferrous alloys and steels have been extensively studied [11-17]. According to these studies, the magnetic field raises the starting temperature of the martensitic transformation (Ms) upon cooling and increases the amount of martensite. This effect is enhanced by the simultaneous

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application of an external stress [18]. However, most previous studies have been concerned with martensitic transformation from para- or ferro-magnetic austenite and very little studies have been performed to investigate the effect of a magnetic field on martensitic transformation from antiferro-magnetic austenite.

Simple application of a magnetic field below the Neel temperature is not, however, suitable, because the chemical free energy change accompanying the martensitic transformation decreases with decrease in temperature below the transition temperature [19,20]. In fact, Kakeshita et al. [17] did not detect the magnetic effect on the martensitc transformation in antiferro-magnetic Fe-Mn-C alloys even when a strong magnetic field was applied. In order to detect the magnetic effect, it is necessary that antiferro-magnetic austenite is in a transformable state. The antiferro-magnetic γ-Fe particles transform into α-Fe by application of external stress [19,20]. Therefore, in this study, tensile tests under a magnetic field are carried out below the Neel temperature and the effect of an external magnetic field on the martensitic transformation of Fe particles is examined in a Cu-Fe alloy. As will be shown later, a notable effect of a magnetic field on the martensitic transformation is found.

2. Experimental Procedure

Tensile specimens with 20 mm gage length and 2.5×2.0 mm^2 cross section were cut from single crystals of a Cu-1.50mass%Fe (1.70vol%Fe) alloy grown with a seed by the Bridgman method. All the specimens had approximately the same tensile axis, $[829]_f$, as shown in Fig. 1. (Hereafter, the subscript indices f and b denote fcc and bcc, respectively.) The $[829]_f$

Fig. 1 Stereographic presentation showing the orientation relationship between the Cu matrix (solid lines) and a Kurdjumov-Sachs variant (dotted lines). The tensile direction $[829]_f$ coincides with the easy magnetization direction, $[100]_b$, of the K-S variant.

direction was chosen because it is close to the easy magnetization axis, $[100]_b$, of a specific
Kurdjumov-Sachs variant of α-Fe particles formed preferentially by the tensile deformation
[5] as shown in Fig. 1. They were solution treated at 1273K for 4 h in evacuated quartz
capsules, water quenched and subsequently aged at 973K for 3 days in vacuum. The heat
treatment produced coherent γ-Fe particles with the average diameter of 90 nm. The $\gamma \rightarrow$
α martensitic transformation in these particles did not occur by simple cooling down to 4.2K
[21]. Tensile tests were conducted at 4.2K at a strain rate of 1.7×10^{-4} s^{-1} by an Instron-
type testing machine. Tensile tests under a magnetic field of 4.44MA/m were carried out at
4.2K by using a super-conducting magnet. Figure 2 shows the cross sectional view of a
liquid He cryostat with a super-conducting magnet (max. 4.44MA/m) used in the tensile test.
Determination of the amount of liquid He in a cryostat was accomplished by measuring the
temperature of the cryostat with Matsushita carbon resistors (ERC-18SGJ). Resistance of
these carbon resistors in a magnetic field as high as $4 \sim 4.5$MA/m is known to be the same
as that without a magnetic field at 4.2K [22]. The magnetic field was applied along the
tensile axis shown in Fig. 2.
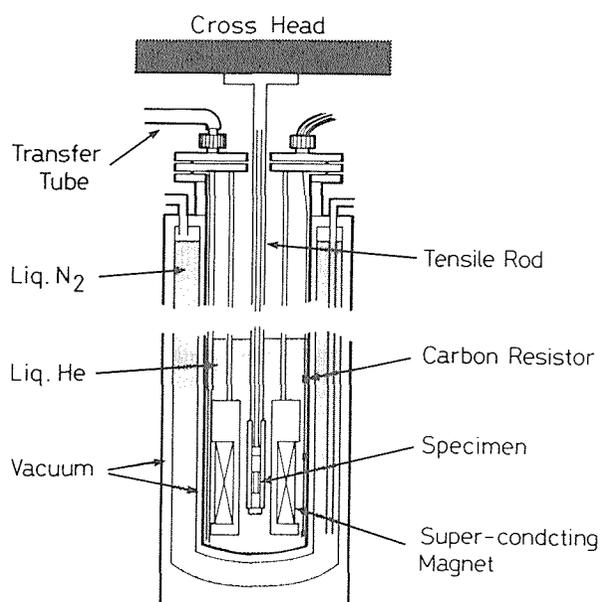
Fig. 2 The cross sectional view of a liquid He cryostat with a super-conduction magnet (max.
4.44 MA/m) used in the tensile test.

The effect of a magnetic field on the martensitic transformation by cooling was also
studied for pre-strained specimens. The dimensions of the pre-strained specimens were
$20 \times 6 \times 2$ mm^3. After straining by 5%, the center portion of the specimen was cut into two
pieces of $10 \times 3 \times 2$ mm^3 each. One was cooled to 4.2K in a magnetic field of 4.44MA/m and
the other was cooled without a magnetic field.

After the tensile deformation and cooling, the magnetization of the specimens was

measured by a Faraday-type magnetic balance at room temperature. The specimens were further sliced along the $(1\bar{1}1)_f$ primary slip plane for electron microscopic observation. Thin foils were prepared from the sliced pieces by electrolytic jet polishing and were examined by a 200kV transmission electron microscope (Hitachi H-700). Some of the specimens were annealed at 973K for 2 h prior to the microscopic observation in order to eliminate dislocations introduced around Fe particles during deformation and to make the identification of the particle phase easier.

3. Experimental Results and Discussion

3. 1 The effect of a magnetic field on martensitic transformation

Figure 3 shows a pair of true stress-true strain curves obtained at 4.2K in the magnetic field and in the absence of a magnetic field. There is no observable difference in either yield stress or work hardening rate between these two conditions. Effect of a magnetic field on the mechanical properties is thus negligible. After the deformation, the specimens were annealed at 973K for 2 h prior to the electron microscopic observation described below.
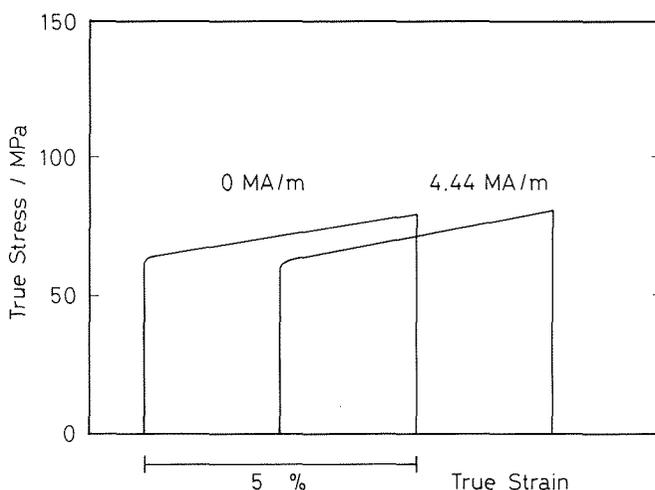

Fig. 3 True stress-true strain curves at 4.2K, without a magnetic field (left) and with a magnetic field of 4.44MA/m (right).

Despite the fact that no effect was found in the mechanical behavior, there was a notable difference in the amount of the $\gamma \rightarrow \alpha$ martensitic transformation between the above two conditions. The electron micrographs of α-Fe and γ-Fe particles taken with an incident beam perpendicular to the $(1\bar{1}1)_f$ primary slip plane are shown in Fig. 4.   The specimen in Fig. 4 (a) was deformed at 4.2K by 5% in a magnetic field and the specimen in Fig. 4 (b) was deformed by the same amount without a magnetic field.   In these figures, untransformed γ-Fe particles accompany a lobe contrast of coherent strain, while α-Fe particles are dark and elongated by the further annealing.   It is apparent that a larger fraction of Fe particles have transformed into α-Fe in (a) than in (b).

Figure 5 shows the fraction of martensitically transformed particles as a function of
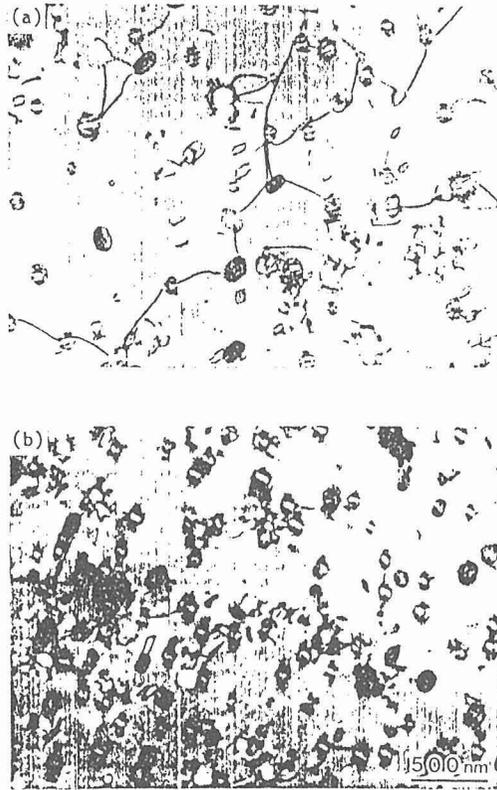
Fig. 4 Electron micrographs of α- and γ-Fe particles. Observation was made after annealing at 973K for 2 h. Transformed α-Fe particles are dark and elongated, while untransformed γ-Fe particles accompany a lobe contrast of coherent strain.
(a) Deformed in a magnetic field of 4.44MA/m.
(b) Deformed without a magnetic field.
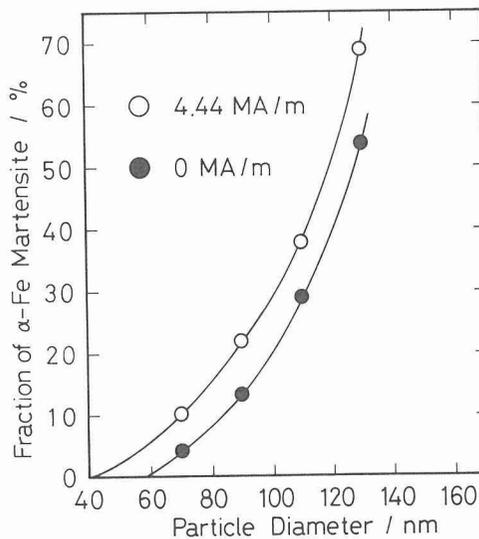
Fig. 5 Fraction of transformed particles plotted against the particle size.

particle size. The fraction was obtained by dividing the number of the transformed α-Fe particles by the total number of Fe particles in a given particle size range. It can been seen that as the particle size becomes larger, the deformation-induced martensitic transformation becomes easier, in agreement with previous studies [6,23]. Figure 5 also shows that the Fe particles transform more easily in the applied magnetic field for all the particle sizes examined. The overall volume fractions of transformed particles were found to be 52vol% for a specimen strained in the magnetic field of 4.44MA/m and 30vol% for a specimen strained in the absence of a magnetic field.

When a magnetized specimen is placed in an inhomogeneous magnetic field, the specimen feels a force, F, given by,

$$F/v = I \times \frac{\delta H}{\delta x},$$ (1)

where v is the volume of the specimen, I the magnetization and $\delta H/\delta x$ the gradient of the magnetic field. Figure 6 shows the results of the magnetic measurement of the deformed specimens. Since the gradient of the magnetic field is in proportion to the strength of the magnetic field, the slope of these curves is proportional to the magnetization of the specimens. It can be seen that the magnetization of the specimen deformed with a magnetic field is greater than that without a magnetic field.
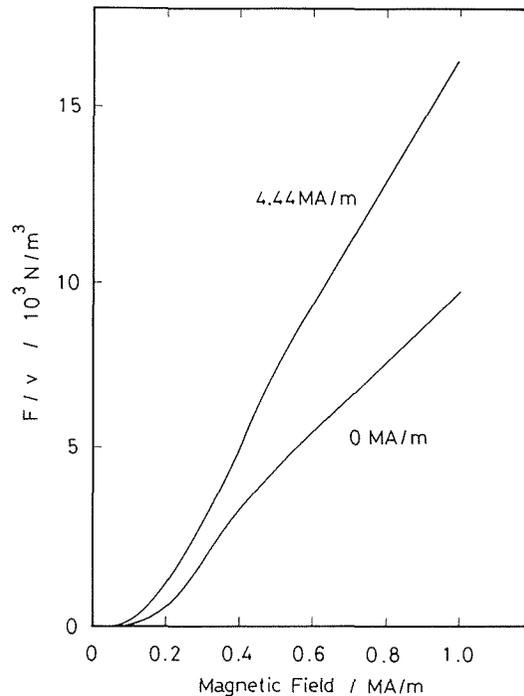

Fig. 6 The results of the magnetic measurement of the specimens deformed in tension with or without a magnetic field.

Moreover, as can be seen in Fig. 6, the magnetizations of the two specimens saturated at the magnetic field of 6.6×10^5A/m. This value is well correlated with the demagnetization as follows. The martensitically transformed α-Fe particles in a Cu-Fe alloy are nearly spherical in shape. Therefore, the demagnetizing factor, N, does not depend on the magnetization direction and its value is 1/3. Since I_s, the saturation magnetization of pure Fe at 293K is 2.16 tesla [24], the demagnetizing field, H_d, is,

$$H_d = -\frac{N}{\mu_0} \times I_s = -\frac{1}{3} \times \frac{1}{4\pi \times 10^{-7}} \times 2.16 = -5.8 \times 10^5 \,(\text{A/m}) \tag{2}$$

where μ_0 is the parmeability in vacuum. The effective field inside the particle is always less than the external field by the amount of the demagnetic field. It is known that the minimum magnetic field necessary to induce the saturation magnetization of bulk α-Fe is about 0.5×10^5 A/m for the most difficult magnetization direction of $\langle 110 \rangle_b$. Therefore, the minimum magnetic field necessary to induce the saturation magnetization of spherical α-Fe particles is estimated to be,

$$5.8 \times 10^5 + 0.5 \times 10^5 = 6.3 \times 10^5 \,(\text{A/m}).$$

This value is in good agreement with the measured one.

The absolute values of the saturation magnetization were determined with reference to the F/v value of a standard specimen of pure Ni. The experimentally observed values of the saturation magnetization, I_s^{ex}, are shown in Table 1. Neither the as-solution treated specimens nor those aged at 973K for 3 days without tensile tests have shown detectable magnetization. In contrast, the specimens strained in the magnetic field of 4.44MA/m and in the absence of a magnetic field have shown the magnetization of 1.7×10^{-2} tesla and 1.0×10^{-2} tesla, respectively.

Table 1 Saturation magnetization and volume fraction of transformed particles. The volume fraction was estimated from the magnetization measurement and from the electron microscopic observation. The latter results are indicated with the * marks in the parentheses.

	No Magnetic Field		Magnetic Field of 4.44MA/m	
	I_s^{ex} (tesla)	Volume Fraction of α-Fe (%)	I_s^{ex} (tesla)	Volume Fraction of α-Fe (%)
Solution Treated	0	0	——	---
Aged at 973K for 3 days	0	0	——	---
Tensile Tested at 4.2K (5%)	1.0×10^{-2}	34	1.7×10^{-2}	58
Annealed at 973K for 2h after 4.2K Tensile Tests	1.3×10^{-2}	40(30*)	1.9×10^{-2}	59(52*)
Tensile Tested at R.T. (5%)	2.7×10^{-3}	9	——	---
Cooled to 4.2K after R.T. Tensile Tests	3.7×10^{-3}	13	3.6×10^{-3}	12

When the above experimental values of the magnetization is compared with the theoretical values, volume fraction of the transformed Fe particles must be estimated as follows. As in the previous studies [19,20,23,25], the solubility of Fe in Cu at 973K is taken as 0.34vol%.

Therefore, aging at 973K should produce the γ-Fe particles of 1.70−0.34=1.36 (vol%) in equilibrium. Since the saturation magnetization of Fe at 293K is 2.16 tesla [24], the saturation value of the magnetization of the present Cu-Fe alloy should be

$$I_s=2.16\times1.36\times10^{-2}=2.94\times10^{-2}\ \text{(tesla)} \tag{3}$$

when all the γ-Fe particles transform into the α-phase. Table 1 also shows the volume fraction (I_s^{ex}/I_s) of the α-Fe particles estimated from the magnetization measurement and the electron microscopic observation. The volume fractions of the transformed Fe particles are calculated to be 58vol% and 34vol% in the specimens deformed in the magnetic field and in its absence, respectively. These values agree well with those found from the direct TEM observation.

The effects of pre-deformation given at room temperature on the martensitic transformation by the further cooling are examined and the results are also shown in Table 1. The fraction of transformed particles in the 5% strained specimen was about 9%. Cooling down to 4.2K induced additional transformation by a few percent. However, the application of a magnetic field during cooling did not cause any additional transformation. This is in contrast to the notable magnetic effects found when a magnetic field was applied during deformation at 4.2K. During the cooling down to 4.2K, the specimen was exposed to Neel temperature without a magnetic field. As already mentioned the above, the chemical free energy difference between the γ and α phases shows a maximum around the Neel temperature. Therefore, most of the additional transformation may not be occurred at 4.2K (with a magnetic field) but around the Neel temperature (without a magnetic field). These facts also imply that the effect of a magnetic field on the transformation is smaller than that of a mechanical origin. Transformation of Fe particles is, thus, basically induced by deformation, during which glide dislocations cut or touch the particles to trigger the transformation [6]. Although the transformation is not promoted by a magnetic field alone, it is assisted by the magnetic field when major part of the driving force is provided mechanically.

3. 2 The effects of annealing on saturation magnetization

It is known that the saturation magnetization of simply cooled specimens with transformed α-Fe particles increases by the further annealing at 973K for 2 h [25]. The saturation magnetization of the deformed and annealed specimens is shown in Table 1. The saturation magnetization also increases by the further annealing of a deformed specimen containing small Fe particles. According to the microscopic observations, the α-Fe particles in the deformed specimen, which had been nearly spherical after the $\gamma\rightarrow\alpha$ transformation, grew into elongated ellipsoids by the annealing. This shape change by the annealing would occur by the diffusional relaxation of the elastic energy stored upon the $\gamma\rightarrow\alpha$ transformation [26] and by the anisotropy of the interfacial energy between the α-Fe particles and the Cu matrix [27]. However, a dominant cause in a very early stage of the annealing may be that the α-Fe particles absorb dissolved Fe atoms in the matrix during the annealing because of the change in the solubility limit due to the presence of the α-Fe particles of a

lower energy state than the γ-Fe particles. The solubility of Fe in Cu at 973K in the presence of α-Fe particles was estimated to be 0.18mass% (0.20vol%) [25]. This means that volume fraction of the α-Fe particles is $1.70-0.20=1.50$ (vol%) in equilibrium at 973K. Therefore, the saturation value of the magnetization of the annealed Cu-Fe alloy should be

$$I_s = 2.16 \times 1.50 \times 10^{-2} = 3.24 \times 10^{-2} \text{ (tesla)} \tag{4}$$

when all the γ-Fe particles transform into the α-phase. This value gives the volume fractions of 59vol% and 40vol% for the specimens strained in the magnetic field and in its absence, respectively, as shown in Table 1. The agreement between the magnetic measurements and the microscopic observations is, thus, excellent.

Some words should be added for the structure of as-transformed α-Fe particles. It is known that the transformed particles have a band structure. These bands were initially thought as alternating layers of transformed α-Fe and untransformed γ-Fe by Easterling and Miekk-Oja [28]. Later, it was shown by Kinsman et al. [29] that, these bands were made of micro-twinned α-Fe martensite variants. The agreement between the magnetic measurements and the microscopic observations supports the conclusion by Kinsman et al. [29]. This is because if the bands were made of the alternating layers of α-Fe and γ-Fe of approximately equal volume, the volume fraction of martensite estimated by the magnetic measurement cannot be larger than half of that estimated by microscopic observation. The above conclusion is also supported by the previously mentioned fact that the experimentally observed minimum magnetic field necessary for the saturation magnetization of the α-Fe particles is in agreement with the theoretically estimated ones. Here, the spherically-shaped (not the layered discs) fully-transformed α-Fe particle was assumed in the theoretical estimation.

4. Conclusions

Martensitic transformation of Fe particles embedded in a Cu matrix has been studied in the presence of a magnetic field at low temperatures. The experimental results are summarized as follows.
(1) The saturation magnetization, indicating the amount of transformed α-Fe particles, increased when a magnetic field of 4.44MA/m was applied during deformation at 4.2K.
(2) Electron microscopic observation indicated that the increment of the transformed fraction by the magnetic field was greater for larger particles, in which transformation by plastic deformation is easier.
(3) Cooling down to 4.2K after deformation at room temperature induced additional transformation by a few percent. However, the application of a magnetic field during cooling did not cause any effect on the additional transformation.
(4) Since the effect of a magnetic field on the martensitic transformation is much smaller than that of a mechanical origin, the transformation of Fe particles is promoted by a magnetic field only when it is superimposed with a mechanical driving force.

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