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Temperature dependence of the amount of transformed Fe particles in a Cu–1.5–mass% Fe Alloy

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The temperature dependence of the amount of martensitic transformation in Cu–1.5–mass% Fe has been examined by transmission electron microscopy (TEM) and magnetic measurements. It was found that the temperature dependence of the amount of deformation-induced martensite for smaller (< 160 nm) Fe particles exhibits a maximum at a transition temperature. The transition temperature increases as the mean transformable-particle size increases. The evolution of the transition has been explained by incorporating the effect of paramagnetic to anti-ferromagnetic transitions in the γ-phase into thermodynamic considerations.

1. Introduction

Without plastic deformation, small γ-Fe particles in a Cu–Fe alloy do not transform into α-Fe when simply cooled to 4.2 K [1]. In contrast, large γ-Fe particles produced by high-temperature and long-time ageing transform into α-Fe by simple cooling alone [2].

It is known [3–5] that γ-Fe particles in Cu–Fe alloys undergo a magnetic transition, from the disordered paramagnetic to the ordered anti-ferromagnetic state, below 100 K on cooling. For example, Gonser *et al.* [4] found by means of Mössbauer spectroscopy that the Néel temperatures of γ-Fe particles in a Cu–Fe alloy aged at 920 K for 4 h and at 950 K for 50 h are 55 K and 67 K, respectively.

Since the configurational entropy of paramagnetic γ-Fe particles is larger than that of anti-ferromagnetic γ-Fe particles, the temperature dependence of the chemical free energy of the γ-phase should become weaker below the Néel temperature, T_N. The general appearance of the chemical-free-energy difference between the γ- and α-phases is anticipated to have the form shown in Fig. 1. Therefore, the temperature dependence of the amount of martensites is expected to show a transition in the vicinity of this temperature. Kakeshita *et al.* [61] have found that the $\gamma \rightarrow \alpha$ martensitic transformation of an Fe–8.0–mass % Mn–1–mass % C alloy, which exhibits a paramagnetic to anti-ferromagnetic transition at 30 K in the parent austenitic state, is suppressed below 100 K. They attributed this suppression to the occurrence of short-range spin order even above the Néel temperature.

The purpose of the present study is to find whether the martensitic transformation of Fe particles in a Cu matrix is affected by the magnetic transition. On the basis of quantitative analysis of the variation in the saturation magnetization caused by the $\gamma \rightarrow \alpha$ transformation, the origin of the free-energy change due to the $\gamma \rightarrow \alpha$ transformation is discussed by taking account of the magnetic-energy contribution.

2. Experimental procedure

Single crystal sheets of $100 \times 20 \times 2\ mm^3$ were grown from a Cu–1.50–mass % Fe (1.70 vol % Fe) alloy with a seed by the Bridgman method. The specimens were oriented to have approximately the same tensile axis, $[829]_f$, as shown in Fig. 2a and they were solution treated at 1273 K for 4 h in evacuated quartz capsules and subsequently quenched in water at room temperature.

Some of the specimens used for the tensile tests were aged at 973 K for 3 days in vacuum, resulting in the introduction of γ-Fe particles with an average diameter of 90 nm. The γ-Fe particles of this size are known to be untransformable by simple cooling down to 4.2 K [1]. The $\gamma \rightarrow \alpha$ martensitic transformation was introduced to these small Fe particles by plastic deformation at various temperatures. Since the amount of martensite depends on the amount of

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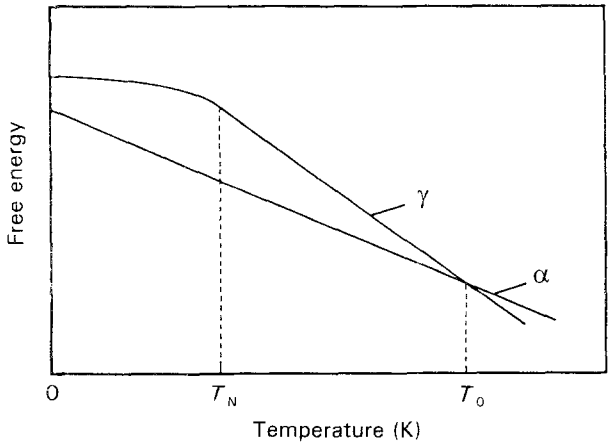
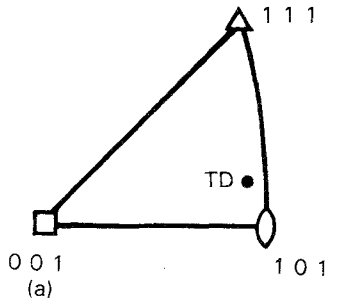


Figure 1 The general appearance of the free-energy difference between the γ- and α-phases. See Section 4.



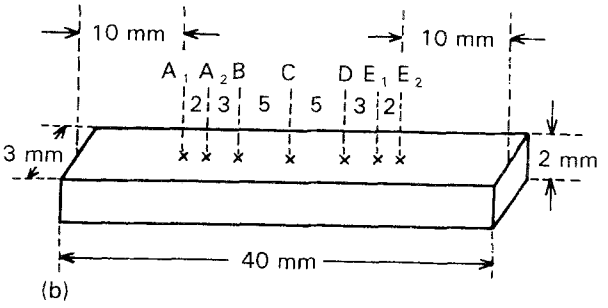


Figure 2 Orientation and dimension of a specimen used for tensile tests. (a) The tensile direction (TD) is shown in a standard triangle of a stereographic projection. (b) Point markings were introduced by a micro-Vickers hardness tester for the precise determination of the plastic strain.

plastic deformation [7], precise determination of the plastic strain was necessary to compare the amounts of martensite formed at different temperatures. Therefore, point marks were made by a micro-Vickers hardness tester before each tensile test as shown in Fig. 2b. Tensile tests were conducted at various temperatures between 4.2 K and 273 K at a strain rate of $1.7 \times 10^{-4}\ s^{-1}$ with an Instron-type testing machine. Test temperatures were controlled by using a liquid-helium cryostat and open dewar as listed in Table I. Specimens with 20 mm gauge length and $2.5 \times 2.0\ mm^2$ cross-section were deformed by 5% in nominal tensile strain. Although the exact strain varied from specimen to specimen and also from place to place within the gauge length, the error due to this deviation was corrected by taking account of the overall strain dependence of the transformation.

In order to study the temperature dependence of the martensitic transformation by simple cooling, one specimen ($2.5 \times 2 \times 7\ nm^3$) aged at 973 K for 30 days was repeatedly cooled to various temperatures between 293 K and 4.2 K. This ageing produced γ-Fe particles with an average diameter of about 200 nm. It is known [8] that γ-Fe particles larger than 290 nm transform into α-Fe by simple cooling to 77 K without deformation. Since some Fe particles in the above specimen aged for 30 days were larger than 290 nm, they were susceptible to spontaneous transformation into α-Fe by simple cooling.

After the tensile deformation or cooling, magnetization of these specimens was measured at room temperature with a Faraday-type magnetic balance. The amount of α-Fe particles was estimated from the value of the saturation magnetization as described previously [8]. Thin foils were prepared from the sliced pieces by electrolytic jet polishing and they were examined by a 200 kV transmission electron microscope (Hitachi H-700).

TABLE I Temperature control for tensile tests

Temperature (K)	Bath
4.2	Liquid He
4.2 ~ 77	He gas
77	Liquid N_2
77 ~ 173	N_2 gas
173 ~ 293	Alcohol

3. Experimental results

Fig. 3a and b shows the electron micrographs of the specimens aged at 973 K for 3 days and for 30 days, respectively. Fe particles are nearly spherical and become larger as the ageing time increases. Untransformed small γ-Fe particles aged for 3 days accompany a lobe contrast of coherent strain, while α-Fe particles exhibit dark contrast with many dislocations.

Fig. 4 shows growth of Fe particles with ageing. The mean particle sizes are also shown. The γ-Fe particles in the specimens aged for 3 days should not transform into α-Fe by simple cooling to 77 K, since all the particles are smaller than the critical size, 290 nm, for spontaneous transformation by simple cooling to 77 K. In fact, spontaneously transformed particles were not found in the specimen aged at 973 K for 3 days. The specimen aged at 973 K for 30 days, however, contained transformed particles as large as 340 nm.

Fig. 5 shows the volume fraction of transformed particles in aged (973 K, 3 days) and deformed (5% plastic strain) specimens as a function of transformation (deformation) temperature. It is seen that the fraction increases with decreases in the transformation temperature above 90 K, while it decreases below the transition temperature at 90 K.

It has been demonstrated that the $\gamma \rightarrow \alpha$ transformation in an Fe particle is triggered when a glide

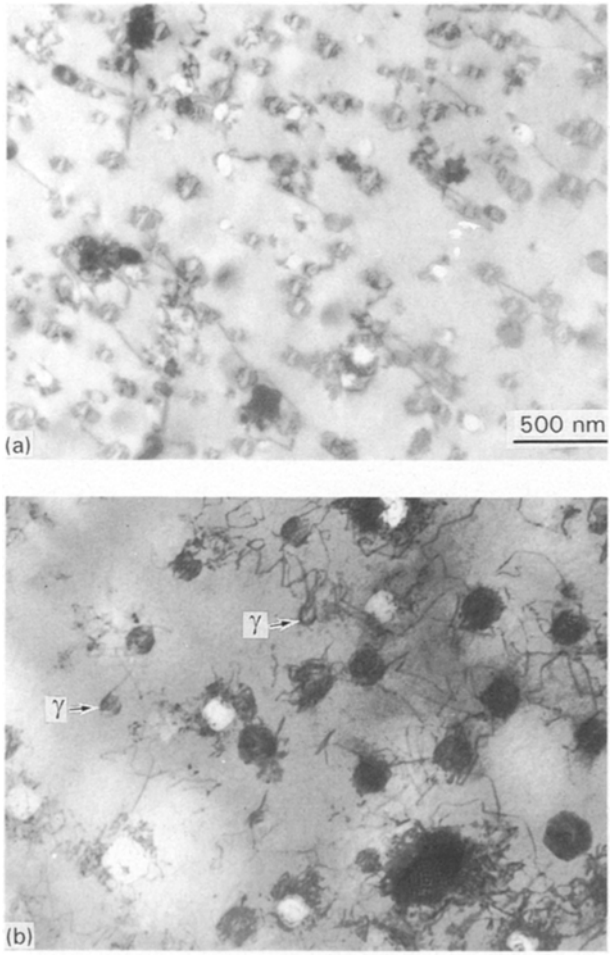


Figure 3 Electron micrographs of the specimens aged at 973 K for: (a) 3 days and (b) for 30 days. Particles in (a) are identified as mostly γ-Fe and only small particles, denoted by γ, are the γ-Fe in (b).

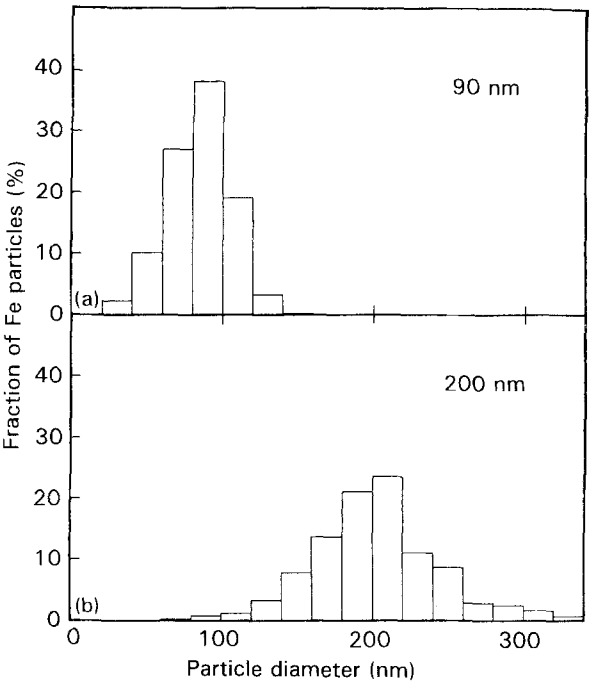


Figure 4 Growth of Fe particles by ageing. Aged at 973 K for: (a) 3 days, and (b) 30 days. The mean particle sizes are shown on the figure.

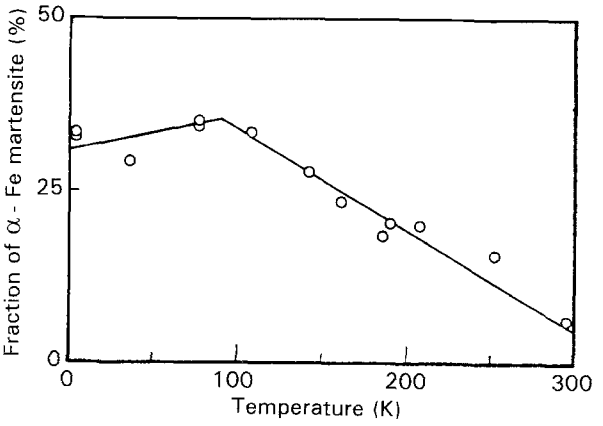


Figure 5 Volume fraction of transformed particles in aged (973 K, 3 days) and deformed specimens plotted against the transformation (deformation) temperature.

dislocation or a set of glide dislocations meets the particle [7–9]. Since the same amount of plastic strain, 5 %, was applied to all the specimens tested, the probability of the collision of glide dislocations with γ-Fe particles should be the same regardless of the test temperature in Fig. 5. Moreover, the particle size distribution should not vary from specimen to specimen. Under these circumstances, it is conceivable that the amount of martensite reflects the relative magnitude of the chemical-free-energy change associated with the $\gamma \rightarrow \alpha$ transformation. Therefore, this rather unusual transformation behaviour below 90 K is considered to be closely related to the paramagnetic to anti-ferromagnetic transition of γ-Fe particles, provided that the Néel temperature of this specimen lies around 90 K. It is imagined that the chemical-free-energy difference between γ- and α-phases becomes smaller at a lower temperature below 90 K. This point will be further discussed in a later section.

The simple cooling tests were carried out for a specimen aged at 973 K for 30 days. The aged specimen was cooled to a desired temperature, held for 20 min and the saturation magnetization was measured at room temperature. Subsequently the same specimen was cooled to a lower temperature and the magnetic measurement was made at room temperature. Such cooling and heating cycles were repeated down to 4.2 K. Fig. 6 shows the fraction of transformed particles as a function of the cooling temperature. In this specimen, the relationship between the amount of martensite and the transformation temperature again exhibited a transition but at a higher temperature around 100 K. The observed difference in the transition temperature possibly comes from the particle size dependence of the Néel temperature as reported by Gonser *et al.* [4].

Comparing the Figs 5 and 6, the temperature dependence of the amount of transformed particles behaves differently, since the amount of martensite continued to increase even below 100 K in Fig. 6. If the chemical-free-energy change associated with the $\gamma \rightarrow \alpha$ transformation decreases below the Néel temperature, as suggested in the previous paragraph, the amount of transformed particles should remain unchanged below 100 K in Fig. 6. Therefore, the observed slight increase in the amount of transformed particles below 100 K is

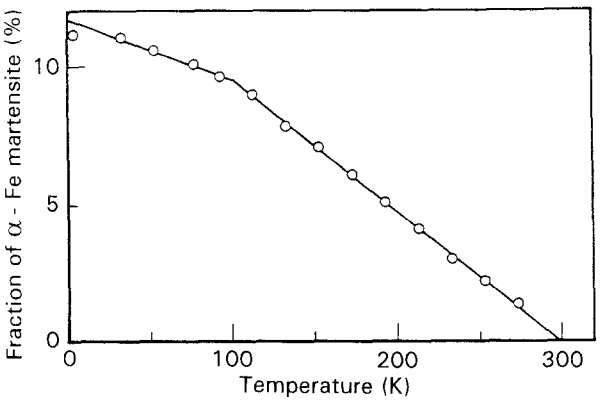


Figure 6 Fraction of transformed particles in aged (973 K, 30 days) and cooled specimens as a function of the cooling temperature.

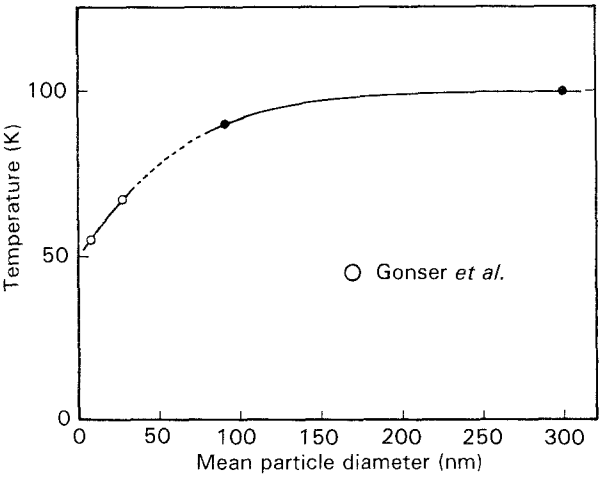


Figure 7 Particle size dependence of the transition temperature and the Néel temperature reported by Gonser *et al.* [4].

not consistent with the thermodynamic argument mentioned above. This increase may be attributed to the thermal cycles imposed on the specimen, since dislocation motion (possibly induced by a thermal stress) may trigger off the martensitic transformation. Glide dislocations should be generated at the particles upon martensitic transformation as, for example, observed in Fig. 3b.

As mentioned in the Introduction, the Néel temperature of γ-Fe particles in a Cu–Fe alloy depends on the ageing conditions. This may come from the particle size dependence of the Néel temperature. In order to examine this possibility, the transition temperature is plotted against the transformable particle size in Fig. 7 together with the Néel temperature reported by Gonser *et al.* [4]. The transition temperature increases with the particle size in qualitative agreement with the increase in the Néel temperature. This correspondence provides further confirmation of our understanding that the temperature dependence of the amount of transformed particles reflects the temperature dependence of the chemical-free-energy difference between γ- and α-Fe particles.

4. Discussion

The temperature dependence of the free energy of the γ-phase should be smaller in the anti-ferromagnetic state than in the paramagnetic state, because the entropy of the anti-ferromagnetic γ-phase is smaller than that of the paramagnetic γ-phase. The magnitude of the free-energy decrease, arising from the magnetic transition, may be most easily evaluated at absolute zero temperature (0 K). As is well known [10], the magnetic contribution to the free-energy decrease at 0 K is of the order of RT_N per mole of a substance, where R is the gas constant and T_N is the Néel temperature. An assignment of $T_N = 70$ K leads to $RT_N = 580$ J mol^{-1}.

Johansson [11] and Zener [12] have calculated the chemical-free-energy change accompanying the $\gamma \rightarrow \alpha$ transformation in pure Fe, $\Delta F_{Fe}^{\gamma \rightarrow \alpha}$, from specific-heat measurements. Using their results, Fisher [13, 14] derived the following expression which is applicable below 500 K,

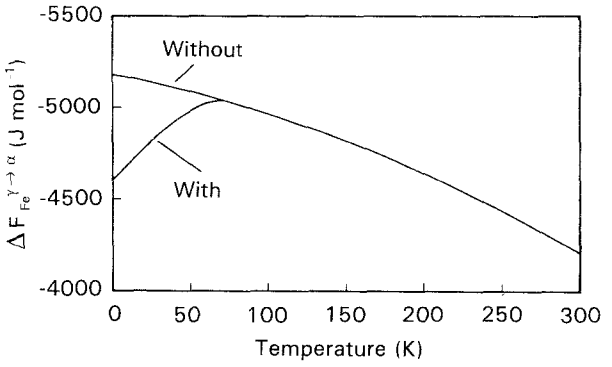


Figure 8 Schematic representation of $\Delta F_{Fe}^{\gamma \rightarrow \alpha}$ as a function of temperature with and without magnetic transition in the γ-phase.

$$\Delta F_{Fe}^{\gamma \rightarrow \alpha} = -5180 + 1.653T + 52.3 \times 10^{-4} T^2 \quad (\text{J mol}^{-1}) \qquad (1)$$

The anti-ferromagnetism of γ-Fe, however, is not taken into account in this equation. If the magnetic transition were absent, the $\gamma \rightarrow \alpha$ chemical-free-energy difference would be -5180 J mol^{-1} at 0 K and -5039 J mol^{-1} at 70 K from Equation 1. Since the magnetic transition stabilizes the γ-phase by 580 J mol^{-1} at 0 K, the chemical-free-energy difference for the transformation from anti-ferromagnetic γ to α becomes -4600 J mol^{-1} at 0 K. This energy gain is smaller than that for the transformation from paramagnetic γ to α at 70 K (-5039 J mol^{-1}). Therefore, it is likely that the $\Delta F_{Fe}^{\gamma \rightarrow \alpha}$ versus T curve should be similar to that depicted schematically in Fig. 8. In fact, the data calculated by Johansson [11] indicates that the $\Delta F_{Fe}^{\gamma \rightarrow \alpha}$ at 0 K is smaller than that at 100 K. It follows that the chemical driving force, $|\Delta F_{Fe}^{\gamma \rightarrow \alpha}|$, should exhibit a maximum around T_N. Thus, the present experimental result that the fraction of martensite decreases with a decrease in the transformation temperature below the Néel temperature is rationalized. A similar effect of suppression of the martensite transformation by anti-ferromagnetism has also been found in Fe–Mn–Si alloys [15] and in a Fe–Mn–C alloy [6].

5. Conclusions

The temperature dependence of the amount of martensitic transformation in Cu–1.5–mass % Fe was examined by TEM and magnetic measurement. The results are summarized as follows.

1. Smaller γ-Fe particles (< 160 nm) transform martensitically into α-Fe only when plastic deformation is applied. Larger particles (> 290 nm), however, transform by simple cooling. The amount of transformed Fe particles is found to depend on the deformation temperature, cooling temperature and particle size.

2. The amount of transformed particles showed a transition on the temperature dependence curve at 90 $\sim$ 100 K. The temperature dependence for the smaller Fe particles showed a maximum at the transition temperature.

3. The transition temperature increased with increasing mean transformable-particle size.

4. All the characteristic features relating to the transition are well explained by taking account of paramagnetic to anti-ferromagnetic transition in γ-Fe particles.

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