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Growth kinetics and martensitic transformation of large Fe particles in a Cu–1.5 mass % Fe alloy

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The growth kinetics and martensitic transformation induced by simple cooling of large Fe particles in Cu–1.5 mass % Fe single crystals aged at 973 K for up to 60 days are examined by transmission electron microscopy and magnetic measurement. The growth kinetics of large Fe particles can be described by the Lifshitz–Slyozov–Wagner theory and the interfacial energy between the Fe particles and the Cu matrix is estimated as 0.24 to 0.40 $\mathrm{J\,m^{-2}}$. The volume fraction of α-Fe particles increases with the mean particle size and with lowering of the cooling temperature. The critical sizes below which the transformation by simple cooling does not occur, are found to be 290 and 350 nm for specimens cooled to 77 K and room temperature, respectively. The saturation magnetization of the Cu–Fe alloy containing large α-Fe particles increases by further annealing of the cooled specimens. These facts imply that α-Fe particles are not produced during the prolonged ageing but are formed martensitically during the cooling process.

1. Introduction

In a Cu–Fe alloy with a few weight per cent of Fe, small metastable γ-Fe precipitate particles in the Cu matrix are known to martensitically transform into α-Fe either by plastic deformation or by extraction from the matrix [1–8]. In other words, these small γ-Fe particles in the Cu matrix do not transform into α-Fe by simple cooling even down to 4.2 K. Newkirk [9] found, by means of X-ray diffraction, that prolonged ageing (for about 34 days at 973 K) caused the existence of α-Fe particles in the Cu–Fe alloy at room temperature. Although he considered that the α-Fe particles grew during the ageing, it is not clear as to whether the α-Fe particles were actually formed during the prolonged ageing or during the cooling process to room temperature.

One of the purposes of the present research is to clarify how the α-Fe particles are formed in a long aged Cu–Fe alloy. For this purpose, however, transmission electron microscopy (TEM) observation is not necessarily very suitable. This is because when the particle size becomes comparable to the thickness of TEM specimens by the prolonged ageing, partial removal of the matrix constraint may cause the spontaneous $\gamma \rightarrow \alpha$ transformation.

The $\gamma \rightarrow \alpha$ structural transformation accompanies a para- or antiferro- to ferro-magnetic transition [1, 2, 6, 7, 10–12]. Therefore, taking advantage of such a magnetic change in the Fe particles, one can investigate the amount of transformed α-Fe particles in a bulk Cu–Fe alloy without removing the matrix constraint.

It is known that small and nearly spherical transformed α-Fe particles grow into elongated ellipsoids by annealing [5]. Moreover, it is found that the saturation magnetization of deformed Cu–Fe alloy specimens containing small α-Fe particles increases by annealing at 973 K for 2 h [7]. These morphological and magnetic changes in Fe particles have been investigated only for small Fe particles of less than about 150 nm. Therefore, in the present study, we have extended our investigation to larger Fe particles and their transformation behaviour by simple cooling and the effects of annealing have been studied.

It has been found [13, 14] that the growth kinetics of small γ-Fe particles obey the law of Ostwald ripening as described by Lifshitz and Slyozov [15] and Wagner [16]. The interfacial energy between small γ-Fe particles and the Cu matrix has been evaluated from the growth rate of the particles based on the Lifshitz–Slyozov–Wagner (LSW) theory [14]. In the present study, the applicability of the LSW theory for larger Fe particles will also be examined.

2. Experimental procedure

It is known that ageing at 973 K for 2 h produces α-Fe precipitates on the grain boundaries [17]. To eliminate the possible influence of grain boundaries on the precipitation of Fe particles, single crystals are used in the present study. Specimens (≃ 100 mm × 20 mm × 2 mm) of a Cu–1.5 mass % Fe alloy were cut from single crystals grown with a seed by the Bridgman

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method. They were solution treated at 1273 K for 4 h in evacuated quartz capsules and then water quenched. After the solution treatment, the specimens were aged at 973 K in vacuum for 1–60 days followed by air cooling to room temperature in order to obtain Fe precipitate particles of various sizes.

Smaller specimens for further cooling tests, 2.5 mm × 2.0 mm × 2–5 mm in size, were spark-cut from the aged specimens and immersed into liquid nitrogen (77 K) for 1 h.

After the cooling, some of the specimens were annealed at 973 K for 2 h and their saturation magnetization was measured with a Faraday-type magnetic balance at room temperature. Thin foils were prepared from the sliced pieces by electrolytic jet polishing and they were examined by a 200 kV TEM (Hitachi H-700). Since the particle size is comparable to the order of the transparency thickness of specimens at 200 kV, some of the specimens were examined using a high-voltage electron microscope operating at 1000 kV (H-1250S) with a double-tilt specimen holder.

3. Results

3.1. The relationship between Fe particle size and ageing time

Electron micrographs of aged specimens are shown in Fig. 1. The specimens in Fig. 1 were aged at 973 K for (a) 7 days, (b) 30 days, (c) 45 days and (d) 60 days. As can been seen, Fe particles become larger as ageing time increases. All Fe particles are spherical after ageing for 7 days as in Fig. 1a. However, ellipsoidal particles are also observed in (c) and (d). The number fractions of the ellipsoidal particles are about 8% (11 vol %) and 13% (20 vol %) in the specimens aged for 45 and 60 days, respectively. These shape changes of the Fe particles during ageing will be discussed later.

Fig. 2 shows the electron micrographs of the specimens aged at 973 K for 60 days, subsequently cooled to 77 K, kept at 77 K for 1 h and further annealed at 973 K for 2 h. A larger number of ellipsoidal particles are observed after the annealing in comparison with those before the annealing. The number fraction of the ellipsoidal particles after the annealing became about 27%. Therefore, this shape change of Fe particles partly occurred during annealing.

Mean particle radii were measured from these electron micrographs. Fig. 3 shows the growth curve of Fe particles in a Cu–1.5 mass % Fe alloy aged at 973 K. It is found that the mean particle radius, $\bar{r}$, is nearly proportional to $t^{1/3}$, where t is the ageing time. This indicates that the LSW theory for the coarsening of precipitates can be applied even for large Fe particles.

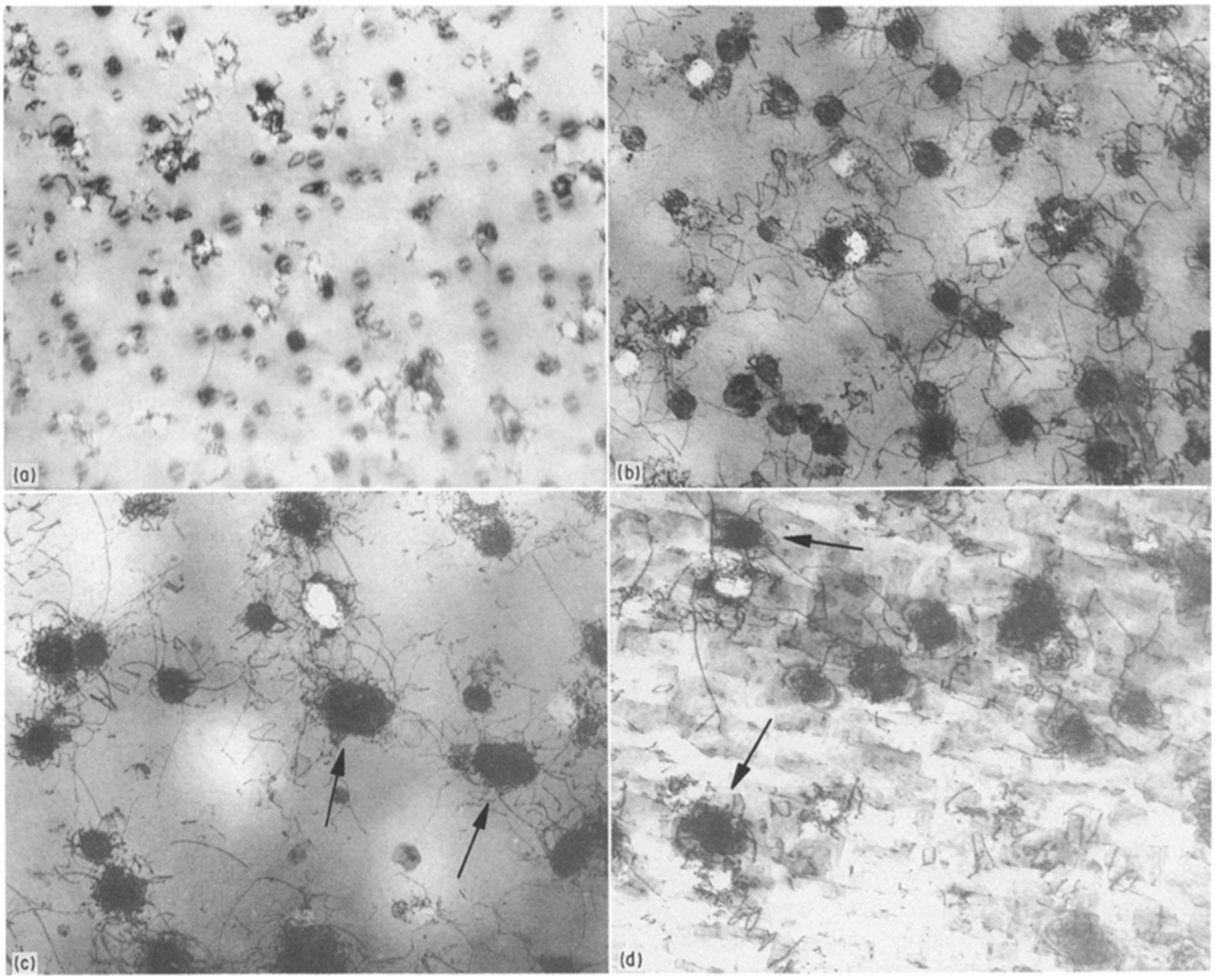

Figure 1 Transmission electron micrographs of Fe particles in a Cu–Fe alloy aged at 973 K and subsequently cooled to room temperature. Some particles (arrowed) in (c) and (d) have become ellipsoidal in shape.

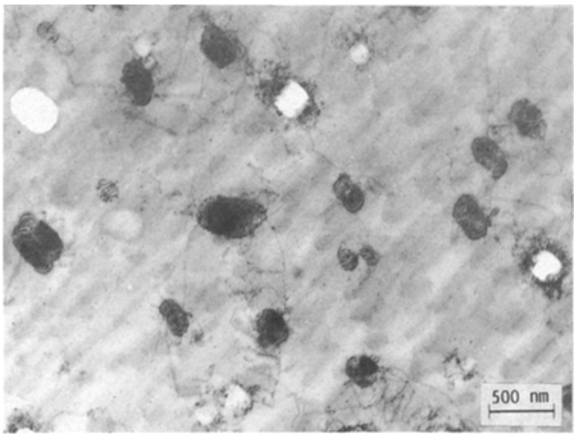

Figure 2 Transmission electron micrograph of a specimen aged at 973 K for 60 days, cooled to 77 K and further annealed at 973 K for 2 h.

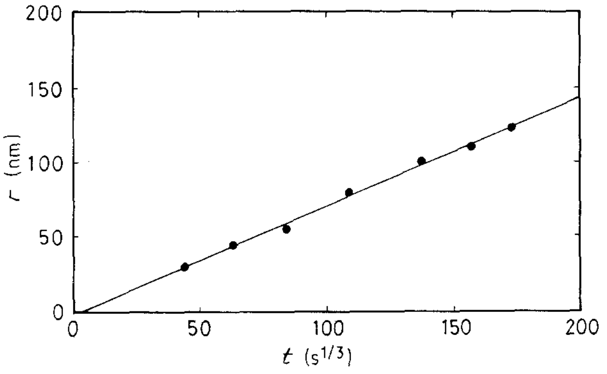

Figure 3 The growth curve of Fe particles in a specimen aged at 973 K. $\bar{r}$ = mean particle radius, t = ageing time.

According to the LSW theory, the relationship between $\bar{r}$ and t is expressed as

$$\bar{r}^3 = kt \tag{1}$$

where

$$k = \frac{8}{9}\frac{Dx^{\alpha}\Gamma^{\gamma/\mathrm{Cu}}V_m^2}{RT} \tag{2}$$

where D is the diffusion constant of a solute (Fe) in a solvent (Cu), x^{α} the solubility of Fe in Cu, $\Gamma^{\gamma/\mathrm{Cu}}$ the interfacial energy between γ-Fe and Cu, V_m the molar volume of the precipitate and RT has its usual meaning.

In Equation 1, k can be evaluated from Fig. 3 as $k = 3.91 \times 10^{-28}\ \mathrm{m^3\,s^{-1}}$ by the least square method. This value is in good agreement with the value obtained by Matsuura *et al.* [14]; $k = 3.89 \times 10^{-28}$ $\mathrm{m^3\,s^{-1}}$. Different from the present study, the largest mean particle radius observed by Matsuura *et al.* is about 50 nm and particles remained as γ-Fe after cooling to room temperature. This means that Matsuura *et al.* have examined the growth of γ-Fe particles. Therefore, the excellent agreement of the k values suggests that the growth curve in Fig. 3 is also that for γ-Fe particles. If α-Fe particles were formed during the prolonged ageing in the present study, the k value would have been significantly different from that obtained in [14]. This is because the interfacial energy between α-Fe and Cu, $\Gamma^{\alpha/\mathrm{Cu}}$, is significantly larger than $\Gamma^{\gamma/\mathrm{Cu}}$ [14]. Therefore, we conclude that the large Fe particles obtained in the present study are still γ-Fe at the ageing temperature.

Let us evaluate the magnitude of the interfacial energy $\Gamma^{\gamma/\mathrm{Cu}}$ using Equation 2. The diffusion constant of Fe in Cu at 973 K in [14] is evaluated as

$$\begin{aligned} D &= 1.01 \times 10^{-4}\exp\left(-\frac{213(\mathrm{kJ\,mol^{-1}})}{R\,973(\mathrm{K})}\right)^2 \\ &= 3.71 \times 10^{-16}\ \mathrm{m^2\,s^{-1}} \end{aligned} \tag{3}$$

The solubility of Fe in Cu at 973 K is reported to be between 480 and 800 $\mathrm{mol\,m^{-3}}$ [18, 19]. Using these values together with $V_m = 7.1 \times 10^{-6}\ \mathrm{m^3}$, the interfacial energy of large Fe particles is evaluated to be $\Gamma^{\gamma/\mathrm{Cu}} = 0.24\text{–}0.40\ \mathrm{J\,m^{-2}}$. This range of the value of $\Gamma^{\gamma/\mathrm{Cu}}$ is in good agreement with the previously reported value for small γ-Fe particles, $\Gamma^{\gamma/\mathrm{Cu}} \simeq 0.25$ $\mathrm{J\,m^{-2}}$ [14]. On the other hand, $\Gamma^{\alpha/\mathrm{Cu}}$ has been reported to be larger than 0.5 $\mathrm{J\,m^{-2}}$ [20]. Therefore, we can also conclude from the values of the Fe/Cu interfacial energy that large Fe precipitate particles formed during the prolonged ageing are γ-Fe.

3.2. Volume fraction of transformed α-Fe particles

Fig. 4 shows the values of the saturation magnetizations of specimens as a function of ageing time. Curves a and b were obtained from the specimens which were cooled to room temperature and to 77 K, respectively, and Curve c from the specimens which were cooled to 77 K and subsequently annealed at 973 K for 2 h. Since a saturation magnetization value is considered to be proportional to the volume fraction of transformed ferro-magnetic α-Fe particles, it can be seen

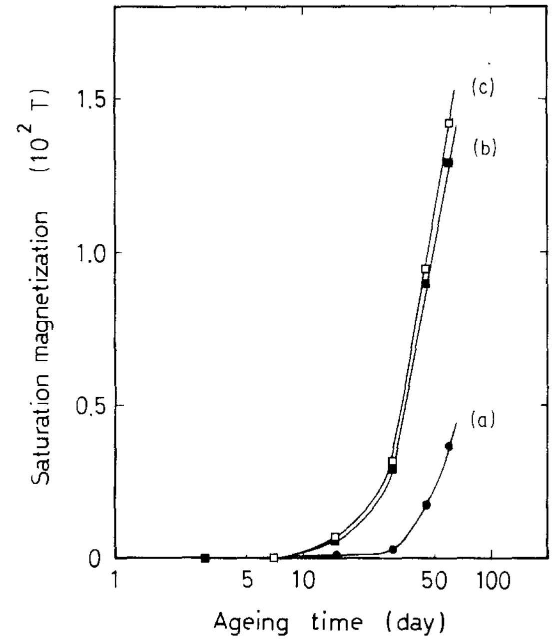

Figure 4 The values of saturation magnetization of a Cu–1.5 mass % Fe alloy as a function of ageing time. Specimens which were cooled to (a) (●) room temperature (b) (■) 77 K, and (c) (□) 77 K and subsequently annealed at 973 K for 2 h.

from Fig. 4 that larger particles obtained by prolonged ageing for more than 30 days have transformed into α-Fe by simple cooling to room temperature alone. Newkirk also found that the prolonged ageing caused the existence of α-Fe particles at room temperature. However, as mentioned in the previous section, we believe that the α-Fe particles were not formed during ageing but were formed martensitically during the cooling process.

The volume fraction of α-Fe martensite particles can be found from the saturation magnetization values. As in the previous studies [6, 7], the solubility of Fe in Cu at 973 K is taken as 0.34 vol %. Therefore, the ageing of the present Cu–1.5 mass % Fe alloy at 973 K should produce the γ-Fe particles of 1.36 vol % in equilibrium. Because the saturation magnetization of Fe at 293 K is 2.16 T [21], the saturation value of the magnetization of the present Cu–Fe alloy should be $I_s = 2.16 \times 1.36 \times 10^{-2} = 2.94 \times 10^{-2}$ T when all the γ-Fe particles transform into the α-phase. The volume fraction V_f was thus calculated as $V_f = I/I_s$, where I is the measured saturation magnetization of a specimen.

Fig. 5 shows the volume fraction of α-Fe particles as a function of the mean particle size. It is seen that the volume fraction increases with mean particle size in qualitative agreement with the work by Newkirk [9]. The volume fraction also increases as the cooling temperature becomes lower.

Fig. 6 shows the ratio of the saturation magnetization after annealing to that before the annealing. The ratio does not depend on the particle size and the average ratio of the magnetization is about 1.1. This result indicates that the total volume of the α-Fe particles is increased by the annealing. The implication of this will be discussed later.

Fig. 7 shows the size distributions of Fe particles in aged specimens. The volume fractions of transformed α-Fe particles estimated by the magnetic measurement are also indicated. From Fig. 7, only a very small fraction of transformed particles are found in specimens aged for 15 days (maximum particle size is 260 nm) and 30 days (maximum particle size is 340 nm) by simple cooling to 77 K and room temperature, respectively. Because the γ → α transformation occurs more easily in larger particles than in smaller ones, it is reasonable to assume the existence of a critical size below which transformation by simple

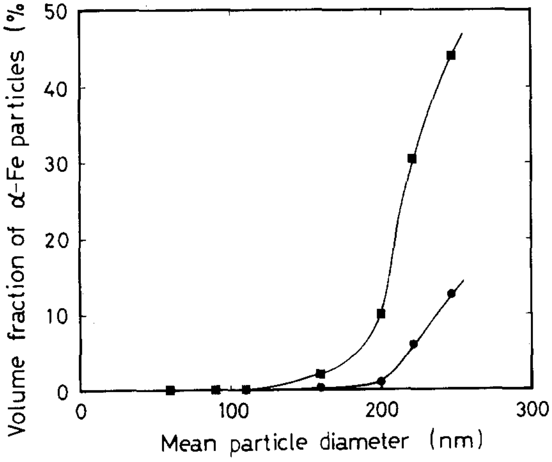

Figure 5 The volume fraction of α-Fe martensite particles as a function of mean particle size, at (●) room temperature, and (■) 77 K.

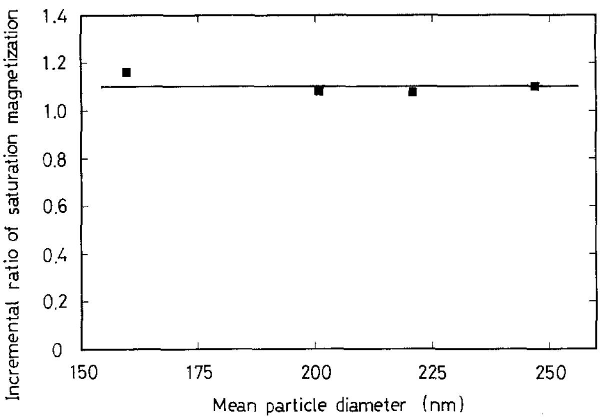

Figure 6 The ratio of the saturation magnetization after the annealing at 973 K for 2 h to that before the annealing.

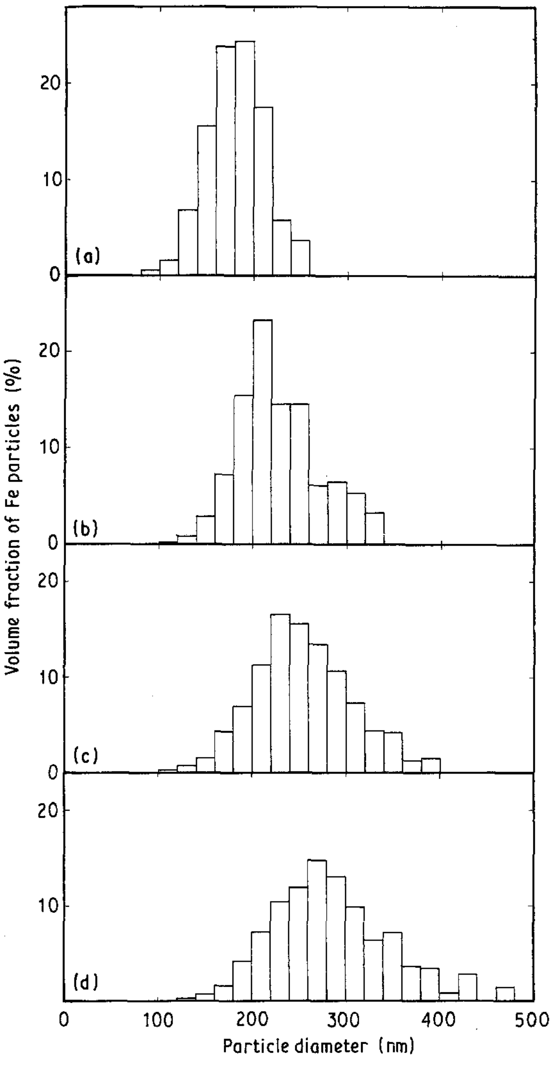

Figure 7 The size distributions of Fe particles in specimens aged for (a) 15, (b) 30, (c) 45 and (d) 60 days. The volume fractions of transformed α-Fe particles estimated by the magnetic measurement are: (a) room temperature 0.3%, 77 K 2.0%; (b) room temperature 1%, 77 K 10%; (c) room temperature 6%, 77 K 31%; (d) room temperature 13%, 77 K 44%.

cooling does not occur. The critical sizes thus estimated from Fig. 7 and from the measured volume fraction values are 290 nm for the specimens cooled to 77 K and 350 nm for the specimens cooled to room temperature.

4. Discussion

4.1. Size dependence of the $\gamma \rightarrow \alpha$ martensitic transformation in Fe particles

In the present study, we have found that the $\gamma \rightarrow \alpha$ martensitic transformation by simple cooling occurs more easily in larger Fe particles. Because the total Fe/Cu interfacial area decreases as Fe particles become larger, it can be imagined that the transformation barrier of the interfacial energy becomes less important and the transformation becomes easier when the particles are larger.

The change in the interfacial energy per unit area of the Fe/Cu interface, $\Delta\Gamma$, associated with the $\gamma \rightarrow \alpha$ transformation in [14] is estimated as

$$\Delta\Gamma = \Gamma^{\alpha/\mathrm{Cu}} - \Gamma^{\gamma/\mathrm{Cu}} = 0.2\ \mathrm{J\,m^{-2}} \qquad (4)$$

For the average particle radius of $\bar{r}$, the total interfacial area per unit volume of Fe, A, becomes $A = 4\pi\bar{r}^2/(4\pi\bar{r}^3/3) = 3/\bar{r}$. Therefore, the total changes in the interfacial energy when all the γ-Fe particles transform into α-Fe become $A\Delta\Gamma = 4.1 \times 10^6\ \mathrm{J\,m^{-3}}$ for $\bar{r} = 145$ nm (the critical radius at 77 K) and $A\Delta\Gamma = 3.4 \times 10^6\ \mathrm{J\,m^{-3}}$ for $\bar{r} = 175$ nm (the critical radius at 293 K). On the other hand, the chemical driving forces of the transformation estimated from the temperature dependence of the $\gamma \rightarrow \alpha$ chemical free energy difference [22, 23] are $-7.1 \times 10^8\ \mathrm{J\,m^{-3}}$ at 77 K and $-6.0 \times 10^8\ \mathrm{J\,m^{-3}}$ at 293 K. Because the interfacial energy is negligibly small compared with the magnitude of the chemical driving force, we conclude that the easier transformability in larger particles is not caused by the thermodynamic effect of the decreasing interfacial energy. Moreover, no size effect can be expected for the thermodynamic role of the misfit elastic strain energy on the transformation. This is because both the elastic strain energy and the driving force have the same dependence on the volume of Fe particles.

It is true that the interfacial energy could play an important role on the nucleation process of the α-Fe martensite. For example, when $\bar{r} = 1$ nm, $A\Delta\Gamma = 6.0 \times 10^8\ \mathrm{J\,m^{-3}}$ and this value is comparable to the magnitude of the chemical driving force. As the particle size becomes larger, the number of "nucleation sites" in one particle should increase. This may explain the size effect of the transformability of the Fe particles like the well-known grain size effect. However, because the "nucleus" or "embryo" of a martensite is still not well understood, we will not discuss the possible nucleation stage any further.

Rather, we would like to point out that the martensitic transformation in small particles (in which the transformation occurs only by plastic deformation) depends on the probability of the collision of glide dislocations in the Cu matrix with Fe particles [5]. Although plastic deformation was not introduced in the present study, some dislocations are generated during the cooling process owing to the difference in the thermal expansion coefficients of Cu and γ-Fe. Fig. 8a demonstrates an example of the formation of arrays of dislocation loops punched out around Fe particles by thermal stress. In the thicker region of the foil specimen (1–2 μm), a large number of dislocations are observed throughout the entire region of the matrix as shown in Fig. 8b. These micrographs substantiate the importance of the glide dislocations in triggering off the martensitic transformation [5] even in a simply cooled specimen. The larger the particles, the wider the ranges of internal stresses to generate dislocations. Therefore, the origin of the size effect of the transformability may lie in the increasing degree of the dislocation generation in larger Fe particles during the cooling process.

4.2. The effects of annealing on saturation magnetization

It is known that small α-Fe particles induced by deformation, which were nearly spherical after the $\gamma \rightarrow \alpha$ transformation, grow into elongated ellipsoids by the annealing [5]. This shape change by annealing may partly occur by the diffusional relaxation of elastic strain energy created upon the transformation. However, it may also occur if α-Fe particles absorb

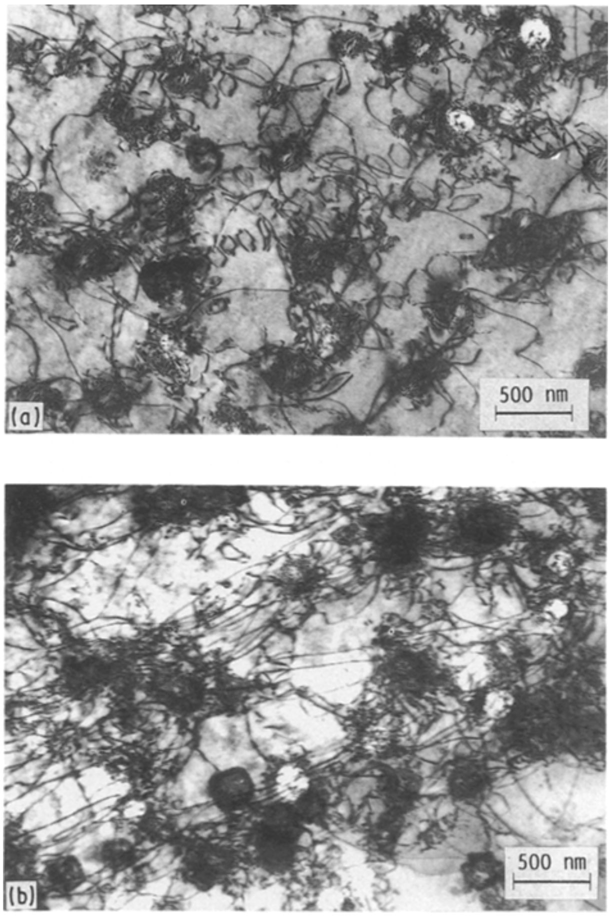

Figure 8 Transmission electron micrographs of specimen aged at 973 K for 30 days and subsequently cooled to room temperature. (a) Arrays of dislocation loops punched out by thermal stress. (b) A larger number of dislocations observed at a thicker region.

dissolved Fe atoms in the matrix during the annealing. In a previous study [7], it was found that the saturation magnetization of deformed specimens with small transformed α-Fe particles increased by further annealing at 973 K for 2 h. As has been found in Fig. 4, the saturation magnetization after the annealing is also larger than that before annealing in the Cu–Fe alloy containing large Fe particles. Because the annealing was performed at the same temperature as that of the ageing, new precipitation of α-Fe particles is very unlikely to occur during the annealing. Therefore, the increase in the saturation magnetization should be caused by the difference in the solubility of Fe atoms between the α and γ phases in Cu. In fact, Matsuura *et al.* also suggested that the solubility of Fe in the γ phase is smaller than that in the α phase [14]. This fact also supports our previous conclusion that even prolonged ageing does not produce equilibrium α-Fe particles: the saturation magnetization is always increased regardless of the particle size. Because the ratio of the saturation magnetization after the annealing to that before the annealing is 1.1 as noted in Fig. 6, the solubility of Fe in Cu at 973 K in the presence of α-Fe particles is estimated as

$$1.5\text{ mass \%} - (1.5\text{ mass \%} - 0.3\text{ mass \%}) \times 1.1 = 0.18\text{ mass \%} \qquad (5)$$

It should be noted, however, that this solubility value is considered to be meaningful only if both the solubility value of γ-Fe in Cu, 0.3 mass % (0.34 vol %), and the composition of the present alloy, Cu–1.5 mass % Fe, are accurate.

4.3. Shape changes of the Fe particles

As shown in Fig. 1, ellipsoidal Fe particles were observed in the specimens aged for more than 45 days. So far, it has been tacitly believed that the spherical to ellipsoidal shape change occurs either in the transformed α-Fe particles during annealing [5] or by shear deformation. An alternative possibility is that the spherical to ellipsoidal shape change takes place in the γ-Fe particles during the prolonged ageing. In fact, a previous calculation based on anisotropic elasticity revealed that the elastic strain energy of a coherent γ-Fe particle embedded in a Cu matrix becomes smaller if it takes a needle shape rather than a spherical shape [24]. When γ-Fe particles are small, however, the stronger effect of the interfacial energy stabilizes the spherical shape of the γ-Fe particles.

5. Conclusions

The growth kinetics and the martensitic transformation by simple cooling of large Fe particles in Cu–1.5 mass % Fe single crystals aged at 973 K up to 60 days were examined by transmission electron microscopy and magnetic measurement. The results and conclusions are summarized as follows.

1. The growth kinetics of large Fe particles obeyed the law of Ostwald ripening described by the Lifshitz–Slyozov–Wagner theory. The interfacial energy between the Fe particles and the Cu matrix was estimated to be 0.24 to 0.4 $\mathrm{J/m^{-2}}$.
2. The volume fractions of α-Fe particles in aged and cooled specimens increased with increasing particle size and with lowering of the cooling temperature. The critical sizes below which the transformation by simple cooling does not occur, were found to be 290 and 350 nm for the specimens cooled to 77 K and room temperature, respectively.
3. The saturation magnetization of aged and cooled specimens increased by further annealing at 973 K for 2 h.
4. These facts imply that α-Fe particles are not produced during prolonged ageing but are formed martensitically during the cooling process.

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