Martensitic transformation of γ-Fe precipitates in a Cu 1.5 at % Fe Alloy

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In the present work, the mechanism of martensitic transformation, the influence of γ-Fe particle size on the martensitic transformation induced by cold working, and the transformation of γ-Fe into α-Fe by thermal treatment alone in a Cu–1.5 at% Fe alloy, was studied using field ion microscopy (FIM) and transmission electron microscopy (TEM). It has been found that γ-Fe precipitates smaller than about 10 nm did not transform martensitically to α-Fe by cold working. Precipitates larger than 10 nm adopted a Kurdjumov–Sachs orientation relationship with the copper matrix; and the martensitically transformed α-Fe precipitates were ellipsoidal in shape, with their major axes being oriented parallel to the ⟨1 1 0⟩ direction in the matrix. Dislocations were found in the matrix near the vicinity of transformed α-Fe precipitates, giving support to the dislocation cutting mechanism proposed by other workers for the transformation. In thermally aged alloys, no transformation of γ-Fe to α-Fe was observed during the coarsening of γ-Fe precipitates up to sizes as large as about 50 nm. These precipitates still remained coherent or semi-coherent with the copper matrix.

1. Introduction

Precipitation of almost pure b. c. c. α-Fe is expected to occur from supersaturated solid solution of the ε-phase in the Cu-rich side of the Cu–Fe alloy phase diagram [1]. However, owing to excellent coherency between f. c. c γ-Fe precipitates with the f. c. c ε-matrix, the precipitation of α-Fe is preceded by that of γ-Fe in Cu–Fe alloys [2]. In turn, transformation of the γ-Fe phase into an α-Fe phase is expected to occur during the coarsening stage in aged Cu–Fe alloys. Denney [1], however, using measurements of saturation magnetization never observed the transformation of coherent γ-Fe precipitates into ferromagnetic α-Fe, brought about by thermal treatment alone in the range 4–1073 K. On the other hand, Easterling and Miekk-Oja [2] found that loss of coherency in γ-Fe precipitates occurred by applying long ageing treatments, thereby causing their transformation to α-Fe. No experimental evidence, however, was given to support this contention.

The γ-Fe precipitates in aged Cu–Fe alloys have been observed to transform martensitically to α-Fe by the action of any of the following processes [3–8]:

1. cold working;
2. extraction of the precipitate; and
3. ion bombardment.

This transformation has been classified as martensitic because of its diffusionless nature [2].

The martensitic transformation of γ-Fe particles in Cu–Fe alloys has been extensively studied by TEM [3–8]. In early works, Easterling and Miekk-Oja [2] studied the martensitic transformation of γ-Fe precipitates by cold rolling of an aged Cu–1.95 at % Fe alloy, and found that the martensitic transformation did not occur by athermal treatment (continuous cooling), and cold working was necessary for it to occur. These authors also observed the existence of alternating dark and light bands in martensitically transformed α-Fe precipitates. These bands were perpendicular to the ⟨1 1 0⟩ direction of the copper matrix. They concluded that the dark bands were discs of martensite separated by retained austenite; in other words, the γ-Fe precipitates transformed only partially to α-Fe. This transformation was assisted by dislocations which transversed the precipitate during cold working [2]. Later studies by Easterling and Weatherly [3], and Easterling and Swann [4], showed that the transformation occurred by the formation of martensite laths with a Kurdjumov–Sachs orientation relationship to the matrix, $(1\,1\,1)_{matrix} \parallel (1\,0\,1)\ \alpha'$; $[0\,1\,1]_{matrix} \parallel [1\,1\,1]\ \alpha'$ (α′ = martensite), and that there existed a lower size limit of γ-Fe precipitates (about 20 nm), above which the martensitic transformation could be produced by cold mechanical working. It was also reported that the martensitic transformation took place when γ-Fe precipitates were extracted from the ε-matrix because of the removal of coherency strains [3]. Kubo *et al.* [5] and Kinsman *et al.* [6] showed that γ-Fe precipitates transformed fully to the α-Fe phase, and not partially

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as reported in reference [2]. These authors also observed that the alternating black and white bands corresponded to twins in the martensitically transformed precipitates, and the following mechanism was proposed to explain the martensitic transformation: the coherency strain between the γ-Fe precipitates and the ε-matrix was removed either during extraction of the precipitates or by dislocation cutting, inducing the martensitic transformation, and the lattice invariant shear was accommodated by twinning at low temperatures or by slip at high temperatures.

All the above studies were carried out with precipitate sizes larger than 20 nm. In order to study the martensitic transformation of fine Fe precipitates, Ishida and Kiritani [9, 10] employed Cu–Fe alloys with additions of about 6 at % Al with the purpose of reducing the chance of cross-slip; thus giving more opportunity for a moving dislocation to cut through the γ-Fe precipitates and thereby causing the martensitic transformation. The lower limit in size of γ-Fe precipitates which could transform into α-Fe by dislocation cutting was not observed by direct TEM examination nor by means of magnetic measurement. They also reported that the majority of the martensitically transformed α-Fe particles had a pitch orientation relationship with the copper matrix, $(1\,0\,1)_{\text{matrix}} \parallel (1\,1\,1)\,\alpha$; $[0\,1\,0]_{\text{matrix}} \parallel [0\,1\,1]\,\alpha$, and that the shape of α-Fe particles was ellipsoidal with their longer axes along the matrix $\langle 0\,1\,1 \rangle$ direction.

Recently, Watanabe and Sato [11] found that the transformation of γ-Fe into α-Fe could be enhanced by the application of a magnetic field during cold working. This was attributed to an increase in the martensitic start-up temperature, M_s, which has been reported as about 773 K in Cu–Fe alloys [8].

It is well known that field ion microscopy (FIM) has high resolution, which can be used to analyse the martensitic transformation of γ-Fe particles in Cu–Fe alloys. Wendt and Wagner [12] carried out FIM observations of coherent γ-Fe particles, but their martensitic transformation was not studied. Yuchi *et al.* [13] and Wada *et al.* [14] studied by means of FIM the martensitic transformation of fine γ-Fe particles induced by thermal treatment alone, and found no transformation in fine γ-Fe particles. They also studied the martensitic transformation of large γ-Fe particles induced by cold rolling, and found that the transformation occurred following the Kurdjumov–Sachs orientation relationship with the copper matrix.

TEM studies of the mechanically induced martensitic transformation of γ-Fe precipitates in Cu–Fe alloys have been limited to sizes larger than about 10 nm [3–8]. The small volume fraction of Fe precipitates has made difficult the study of the martensitic transformation by TEM. Furthermore, the existence of a critical size for the martensitic transformation of γ-Fe precipitates, as reported through TEM observation, has not been confirmed by recent studies based on magnetic measurements [15]. It was thought, therefore, that the high resolution attainable by FIM could be used to advantage in the study of the martensitic transformation of γ-Fe precipitates smaller than 5 nm. In addition, the transformation of γ-Fe precipitates into an α-Fe phase by the effect of thermal treatment could be verified by FIM study.

2. Experimental procedure

A Cu–1.5 at % Fe alloy was prepared by vacuum melting pure Cu (99.99 %) and pure Fe (99.96 %) in an alumina crucible. A cylindrical ingot, 14 mm in diameter and 160 mm in height, was encapsulated in a quartz tube filled with argon gas, homogenized at 1273 K for 6.05×10^5 s, hot forged and then drawn into wires of 0.3–0.8 mm diameter. The wire specimens and thin disc specimens, of about 2 mm thickness and 12 mm diameter, were encapsulated in quartz tubes filled with argon gas, solution treated at 1323 K for 3600 s, and were then quenched in water. The quenched specimens were given ageing treatments at temperatures between 723 and 973 K for various periods of time. Aged wires of 0.8, 0.6 and 0.4 mm diameter were drawn down to 0.3 mm, in order to obtain cold worked specimens with different percentages of reduction in area. The aged discs were heavily cold rolled (95% reduction in thickness) at room temperature to produce foils of about 0.15 mm in thickness; some of these foils were again thermal treated to obtain TEM specimens in the aged condition alone.

Foil and wire specimens in the aged condition, and in the aged plus cold worked condition, were prepared for FIM observation by electropolishing in a solution of 20 vol % HNO_3 at 10 V d.c. FIM observation of both types of specimens was carried out using a mixture of Ne and H_2 as the imaging gas. The tip temperature and vacuum level during FIM observation were 20 K and 4×10^{-6} Pa, respectively.

TEM specimens were prepared using the twin jet electropolishing technique, in a solution of 33 vol % HNO_3 in methanol at 233 K at a voltage of 12 V d.c. TEM observation was performed in a Jeol JEM-200B electron microscope, operated at 200 kV.

3. Results

3.1. FIM and TEM observations of aged specimens

A FIM micrograph of the Cu–1.5 at % Fe alloy aged at 773 K for 46.7×10^5 s (54 days) is shown in Fig. 1. Since no dislocations are observable in the interface between the brightly imaged spherical Fe precipitates and the ε-matrix (copper matrix), and the concentric rings of the Fe precipitates show continuity with the concentric rings of the ε-matrix, it is deduced that the Fe precipitates are coherent with the matrix and, hence, they must be γ-Fe precipitates. The mean size, *d*, of these γ-Fe precipitates is 27 nm. The size of these precipitates was measured by the persistence size technique [16] using video-recorded FIM, by calibration with a lattice parameter of 0.361 nm for the ε-matrix, as measured by TEM electron diffraction. It is interesting to note that no martensitic transformation took place to reach the equilibrium α-Fe phase, though the aged specimens were cooled down to 20 K during

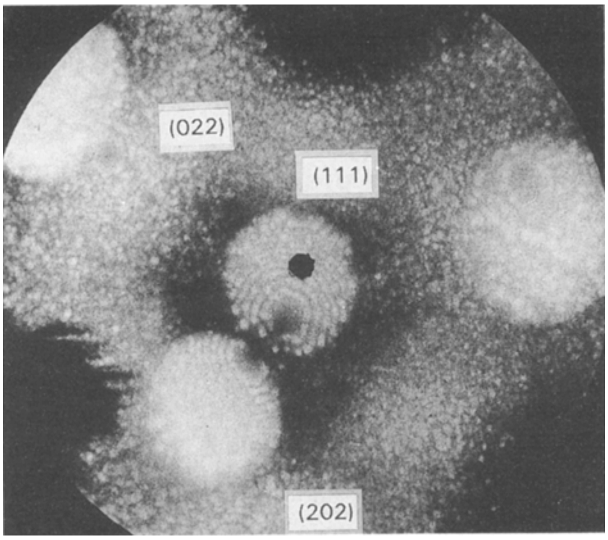

Figure 1 FIM micrographs of Cu–1.5 at % Fe alloy aged at 773 K for 46.7×10^5 s ($d = 27$ nm).

FIM observation. Furthermore, not even field evaporation of the specimens during FIM observation, or the mechanical stresses generated by the high electric field, induced the transformation of γ-Fe precipitates into α-Fe. These facts agree with FIM observations of the γ-Fe precipitates, of sizes between 2 and 12 nm, by Wada *et al.* [14].

Fig. 2 shows an FIM micrograph of γ-Fe precipitates larger than those observed in Fig. 1, found in a specimen aged at 823 K for 70×10^5 s (81 days). The average size of the precipitates in this specimen was about 45 nm. It can be observed that the shape of the precipitates is now ellipsoidal; such a shape change has been observed by TEM in martensitically transformed α-Fe precipitates by Ishida and Kiritani [10]. However, examination of Fig. 2 shows no dislocations in the precipitate–matrix interface, and the concentric rings of the Fe precipitates coincide with the position of the concentric rings of the f.c.c. structure of the ε-matrix. This means that the γ-Fe precipitates are still coherent with the matrix after prolonged ageing and even after maintenance at a temperature of 20 K.

A TEM micrograph, with its corresponding diffraction pattern, of the specimen aged at 823 K for 14.7×10^5 s (17 days) is shown in Fig. 3. The diffraction pattern indicates that the foil surface is parallel to a {100} plane and that the Fe precipitate structure is f.c.c. The dark field showed a reversed contrast effect in the precipitates. The observed image contrasts are the same as those reported for Cu–Co alloys by Ashby and Brown [16]. According to these authors, the contrast effects are due to the coherency strains around a spherical particle coherent with the matrix. The diffraction patterns of the γ-Fe precipitates and the ε-matrix are superimposed in Fig. 3 because of the similar lattice parameter of the γ-Fe phase, 0.365 nm [17], and the ε-matrix, 0.361 nm.

3.2. FIM and TEM observation of cold worked specimens

A FIM micrograph of the Cu–1.5 at % Fe alloy aged at 723 K for 1.7×10^5 s (2 days) and then wire drawn (75% reduction in area) is shown in Fig. 4. The average diameter of the γ-Fe precipitates in this specimen is 4 nm, and it can be observed that they are still coherent with the ε-matrix. Hence, the martensitic transformation has not been induced by plastic deformation in aged specimens containing γ-Fe precipitates of 4 nm. Similar results were obtained in a specimen aged at 823 K for 5.2×10^5 s (6 days) and then cold rolled (95% reduction in thickness) as shown in Fig. 5. In this case, the average diameter of the γ-Fe precipitates is about 7 nm; the Fe precipitates are again still coherent with the ε-matrix, in spite of heavy plastic deformation, and have not transformed martensitically to the α-Fe phase. This is verified by the (1 1 0) electron diffraction pattern for this specimen shown in Fig. 6, where no extra spots from the b.c.c. α-

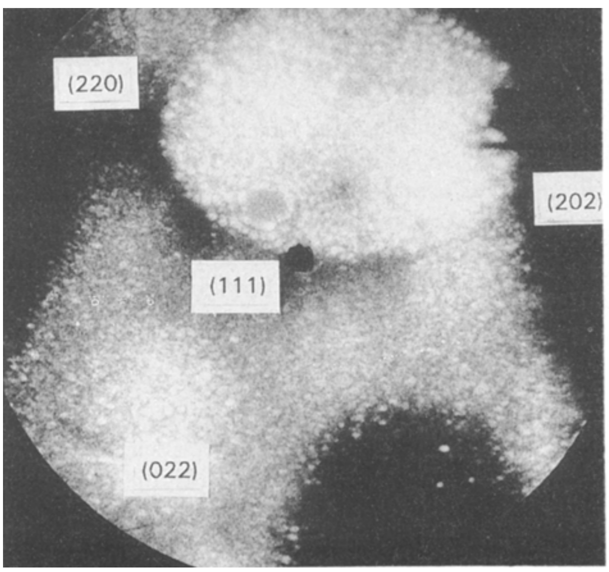

Figure 2 FIM micrograph of Cu–1.5 at % Fe alloy aged at 823 K for 70×10^5 s ($d = 45$ nm).

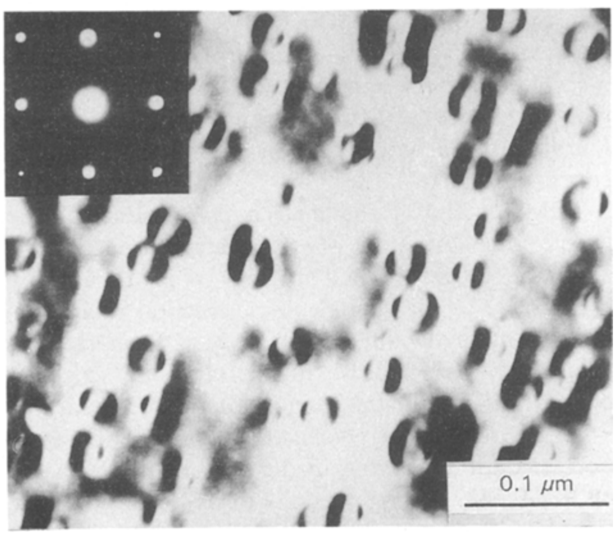

Figure 3 Bright field TEM micrograph and diffraction pattern of Cu–1.5 at % Fe alloy at 823 K for 14.7×10^5 s.

Fe phase are found. The bright field image of this specimen shows a high density of dislocations, which tends to mask the contrast from the γ-Fe precipitates in this micrograph.

The FIM image of the specimen aged at 723 K for 24.2×10^5 s (28 days) and then wire drawn (50% reduction in area) is shown in Fig. 7. The γ-Fe precipitates of about 10 nm are now observed to be incoherent with the ε-matrix. Therefore, the precipitates in this specimen have transformed martensitically into the α-Fe phase, due to plastic deformation applied to the aged specimen.

The FIM image of precipitates about 19 nm in diameter in a specimen aged at 723 K for 95.8×10^5 s (138 days) and then wire drawn (75% reduction in area) is shown in Fig. 8. It is evident that the Fe

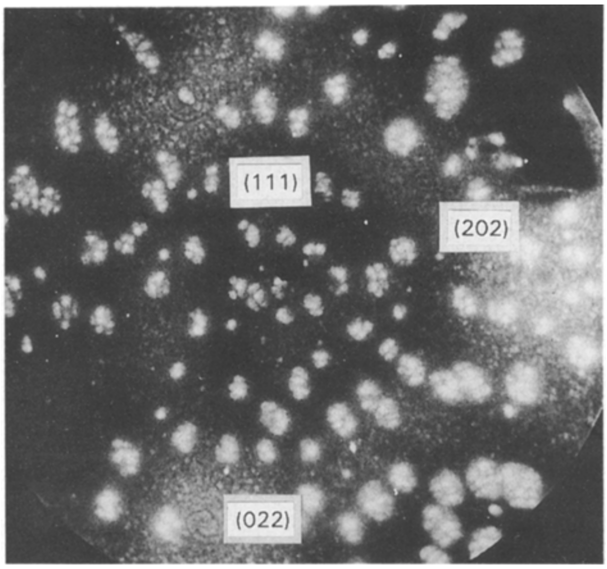

Figure 4 FIM micrograph of Cu–1.5 at % Fe alloy aged at 723 K for 1.7×10^5 s ($d = 4$ nm) and then wire drawn (75% reduction in area).

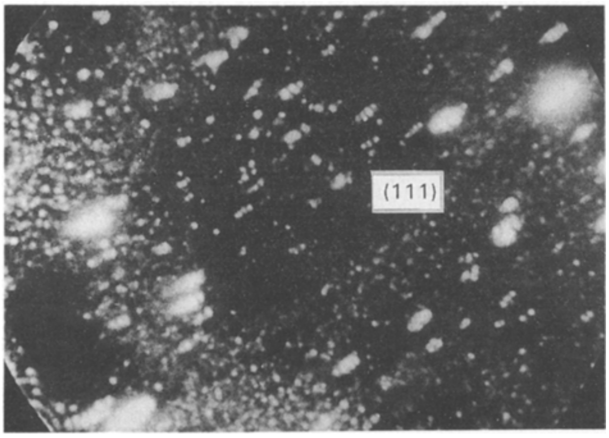

Figure 5 FIM micrograph of Cu–1.5 at % Fe alloy aged at 823 K for 5.2×10^5 s ($d = 7$ nm) and then cold rolled (95% reduction in thickness).

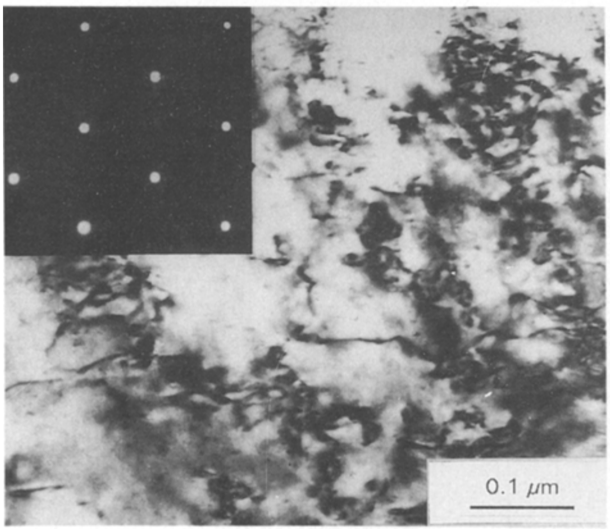

Figure 6 Bright field TEM micrograph and diffraction pattern of Cu–1.5 at % Fe alloy aged at 823 K for 5.2×10^5 s and then cold rolled (95% reduction in thickness).

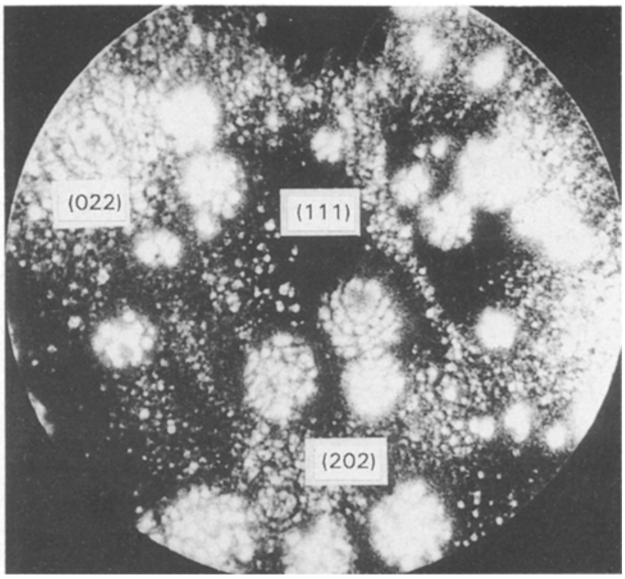

Figure 7 FIM micrograph of Cu–1.5 at % Fe alloy aged at 723 K for 24.2×10^5 s ($d = 10$ nm) and then wire drawn (50% reduction in area).

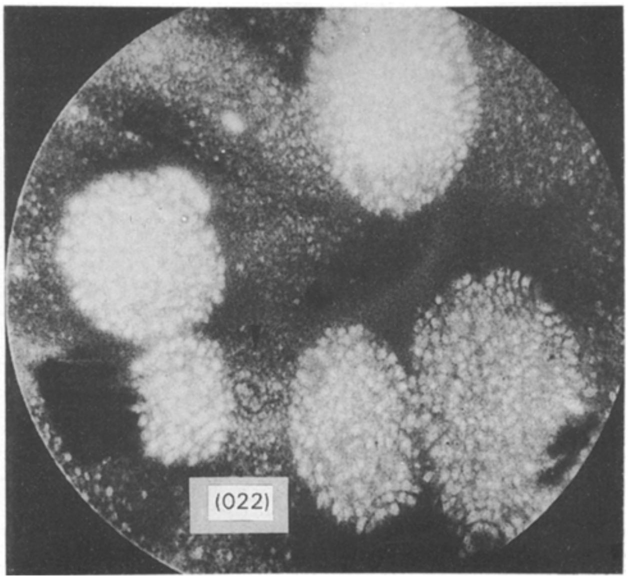

Figure 8 FIM micrograph of Cu–1.5 at % Fe alloy aged at 723 K for 95.8×10^5 s ($d = 19$ nm) and then wire drawn (75% reduction in area).

precipitates located near the (1 1 0) plane of the matrix are again incoherent in the specimen; thus, they must have transformed martensitically into the α-Fe phase.

The FIM micrograph of the specimen aged at 823 K for 14.7×10^5 s (17 days) and then cold rolled (95% reduction in thickness) is shown in Fig. 9. The average size of Fe precipitates is about 32 nm. It can be observed that the major axes of the ellipsoidal α-Fe precipitates is parallel to the ⟨1 1 0⟩ direction of the matrix as shown in Fig. 9. The orientation of the ε-matrix in relation to the martensitically transformed α-Fe precipitates seems to agree with the Kurdjumov–Sachs orientation relationship, since the $(1\,1\,1)_{f.c.c}$ plane of the ε-matrix is parallel to the $(1\,1\,0)_{b.c.c.}$ plane of the α-Fe precipitate and the $[1\,1\,0]_{f.c.c.}$ direction in the matrix is parallel to the $[1\,1\,1]_{b.c.c.}$ direction of the α-Fe precipitate. The presence of a screw dislocation can be observed near the martensitically transformed α-Fe precipitate in Fig. 9.

4. Discussion

4.1. Transformation of α-Fe into γ-Fe in aged specimens

FIM and TEM observations of the Cu–1.5 at % Fe alloy aged for long periods of time showed that γ-Fe precipitates were fully coherent with the ε-matrix and did not transform into the α-Fe phase. This agrees with the results of the magnetic measurements by Denney [1], who observed no ageing transformation at temperatures between 4 and 1073 K. A more recent study by Watanabe and Sato [11] showed no transformation of γ-Fe precipitates even as large as 200 nm. However, they pointed out that about 4% fraction of the γ-Fe precipitates transformed martensitically to α-Fe by cooling down to 70 K after ageing. The present work has shown that in the specimen with γ-Fe precipitates as large as 45 nm, they do not transform martensitically to the α-Fe phase by cooling down to 20 K during FIM observation. This agrees with the results by Wada *et al.* [14] dealing with γ-Fe precipitate sizes between 2 and 12 nm. The TEM observations reported here also confirm the lack of transformation in long aged specimens. In all, transformation of γ-Fe precipitates into an α-Fe phase seems difficult to occur during reasonable periods of ageing because of the high stability of γ-Fe precipitates in the ε-matrix. Such a stability can be attributed to excellent coherency of the γ-Fe precipitates with the matrix, which should produce low values of interfacial and strain energies [18]. This, in turn, facilitates the formation of the γ-Fe precipitates instead of the equilibrium α-Fe precipitate.

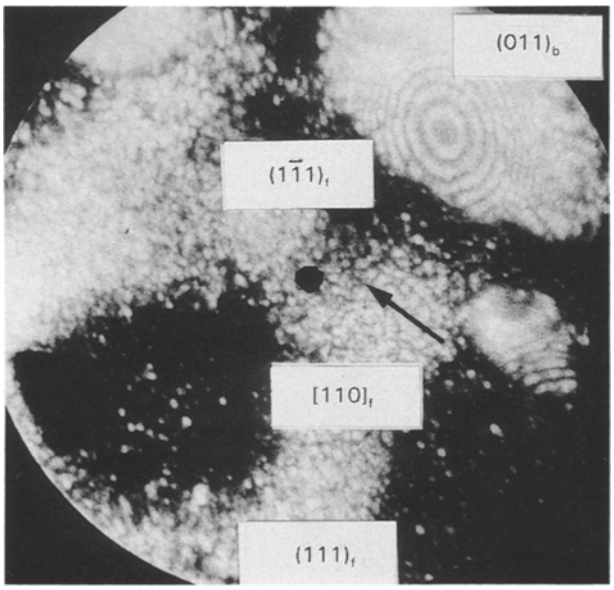

Figure 9 FIM micrographs of Cu–1.5 at % Fe alloy aged at 823 K for 14.7×10^5 s ($d = 32$ nm) and then cold rolled (95% reduction in thickness).

4.2. Martensitic transformation induced by plastic deformation

In the present work it was confirmed by FIM observation that the martensitic transformation of γ-Fe precipitates induced by mechanical working of aged samples requires a minimum (critical) precipitate size of about 10 nm in order for the transformation to occur. Easterling and Weatherly [3] found a critical precipitate size of about 20 nm using TEM. However, their study was confined to precipitate sizes larger than 10 nm. Using magnetic measurements, Ishida and Kiritani [9] found no critical size for the γ-Fe precipitates in order to transform martensitically into the α-Fe phase in Cu–Fe alloys with small additions of aluminium. However, the addition of aluminium could have facilitated the martensitic transformation of γ-Fe precipitates because the atomic size of Al is larger than those of Cu and Fe atoms, thus promoting the loss of coherency. In this way, the critical size for the occurrence of the martensitic transformation could have been reduced below the usual resolution in TEM.

The morphology of the martensitically transformed α-Fe precipitates has been observed to be ellipsoidal by FIM observation in the present work. The major axes of the ellipsoids are parallel to the ⟨1 1 0⟩ direction of the ε-matrix. Similar results were found by Ishida and Kiritani [10] using TEM. The ellipsoidal shape has been associated [10] with the mechanism of transformation of the γ-Fe phase into the α-Fe phase, but not with plastic deformation applied during mechanical working. It can be explained by the transformation mechanism proposed by Kurdjumov and Sachs [19], in which the shape of the martensitically transformed α-Fe precipitates projected on the $(1\,1\,1)_{f.c.c.} \parallel (1\,0\,1)_{b.c.c.}$ interface is elliptical with an axial ratio value of 1.10. In the case of FIM, an accurate axial ratio cannot be measured because of the image distortion caused by the rounded shape of the FIM specimen.

A mechanism for the martensitic transformation of the γ-Fe precipitates into α-Fe precipitates, induced by plastic deformation in Cu–Fe alloys, has been proposed by Easterling and Swann [4]; the cutting of precipitates by glide dislocations causes the nucleation of lath-shaped martensite. However, Kato *et al.* [8] suggested that the martensitic transformation is induced by applied stresses during plastic deformation, without the need for cutting by dislocations. In the present work, several screw dislocations have been observed at the interface between the matrix and martensitically transformed α-Fe precipitates by FIM. Thus, the cutting action of dislocations on γ-Fe precipitates seems necessary in order to disrupt their coherency and to nucleate the martensite. The mechanism for the nucleation of martensite has not been well understood as yet, although several models have been proposed [19]. After nucleation of the martensite, the habit plane is accommodated by lattice invariant strains obtained by twinning at low temperatures or by slip at high temperatures. Twins have been observed in several TEM studies of the martensitic transformation in Cu–Fe alloys [5, 6]. However, no twins were detected in this study by FIM observation in specimens deformed plastically after ageing.

The Kurdjumov–Sachs orientation relationship between the α-Fe precipitate and the ε-matrix has been found in these specimens observed by FIM. This finding agrees with previous TEM work [3, 6, 7].

5. Conclusions

FIM was employed to study the transformation of γ-Fe precipitates into the α-Fe phase in a Cu–1.5 at % Fe alloy and conclusions are summarized as follows:

1. The martensitic transformation of γ-Fe precipitates into α-Fe precipitates did not occur during the ageing process in a Cu–1.5 at % Fe alloy. However, it took place during mechanical working of the aged alloy, containing γ-Fe precipitates larger than 10 nm.

2. The martensitically transformed α-Fe precipitates possess an ellipsoidal shape with their major axes along the ⟨1 1 0⟩ direction of the copper matrix. The orientation relationship of Kurdjumov–Sachs was verified in the martensitic transformation of γ-Fe precipitates into the α-Fe phase.

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