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Structure transformations of the decagonal and icosahedral phases in quaternary alloys

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An investigation of the phase transformations experienced by the decagonal and icosahedral phases in two different quaternary alloys is carried out. The transformation in the decagonal phase of Al–Cu–Co–Si alloy is induced by the electron radiation in a transmission electron microscope. However, in the icosahedral phase of Al–Cu–Co–Fe alloy this transformation is induced by annealing. Electron diffraction patterns obtained from both phases suggest that the deformation mechanism involved in these kinds of transition is related to twinning.

1. Introduction

There have been in the past few investigations on the nature of the transformations from quasicrystalline phases to crystalline structures. Most of these reports were mainly concerned with the binary Al–Mn system [1, 2]. In order to study these kinds of transition two different techniques have been mainly used [1, 2]. In some cases, the specimens with quasicrystalline phases are encapsulated in a vacuum and subsequently annealed or they are just annealed in an inert atmosphere. However, other studies involved the observation *in situ* of the transformations in a high-voltage transmission electron microscope. In this particular case, the transition induced by the electron radiation can be followed by observation of the morphological changes experienced by the quasicrystalline electron diffraction patterns [2].

Quasicrystalline phases in ternary alloys have also been widely studied in the literature; however, very few investigations on the transformation of quasicrystalline to crystalline structures have been carried out in this kinds of system [3, 4]. Ternary alloys which have attracted large attention in the literature due to the presence of quasicrystalline phases are the compounds $Al_{65}Cu_{20}Co_{15}$ and $Al_{65}Cu_{20}Fe_{15}$. These alloys have the characteristic that the quasicrystalline phases are formed under normal casting methods [5, 6]. Therefore, they do not require rapidly solidifying techniques to be formed. In the Al–Cu–Co alloys decagonal phases have been found; however, in Al–Cu–Fe only icosahedral phases can be obtained [5, 6].

In this work we report some preliminary results on the transition from quasicrystalline to crystalline phases in different quaternary alloys. Transformations in the decagonal phases from the alloy $Al_{62}Cu_{20}Co_{15}Si_3$ [7] have been observed *in situ* in the transmission electron microscope (TEM). Also, transitions of the icosahedral phase in alloys of $Al_{65}Cu_{22}Co_{6.5}Fe_{6.5}$ [8] have been studied. In this case, the normal cast specimens have been vacuum-encapsulated and subsequently annealed before the observations in the TEM have been carried out.

2. Experimental procedure

The Al–Cu–Co–Si quaternary alloy was obtained in a high-vacuum spherical mirror furnace. During heating the alloy took the shape of a spherical drop with small quasicrystalline decaprisms arranged in a radial manner. The cooling time to room temperature was approximately 300 s [7]. However, the Al–Cu–Co–Fe alloy was obtained by melting the high-purity elements in an arc furnace under an argon atmosphere. The resulting ingot was slowly cooled to room temperature. The observations were carried out in a Jeol 4000EX microscope. Specimens of the Al–Cu–Co–Fe alloy were annealed and subsequently observed in the microscope. The final preparation of the specimens was carried out using an ion-beam machine. However, the transitions in the Al–Cu–Co–Si alloy were observed *in situ* in the TEM. In this case the preparation of the specimens for the TEM observations were carried out just by mechanically grounding the small decaprisms and subsequently supporting them on Cu grids.

3. Results and discussion

3.1. Structure transformations in the decagonal phase of the Al–Cu–Co–Si alloy

The decagonal phase in alloys of Al–Cu–Co–Si was first reported by He *et al.* [9]. Since this report, there have been a large number of works concerning this type of quasicrystalline phase. Thus, for example, Zhang and Urban [10, 11] have pointed out the presence of planar defects and also dislocations in this structure. They also suggested that the diffraction patterns from this phase can be interpreted as the superposition of a decagonal and a b.c.c. structure. Steure and Kuo [12] have proposed a structure for

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this phase made of a stacking of quasiperiodic layers rotated 36° one from another along the tenfold axis.

In this report we present the results obtained from 2 mm length quasicrystalline decaprisms which were obtained with a melting and growth process carried out in a double-spherical mirror furnace [7]. The observations were carried out in a Jeol 4000EX microscope operated at 400 kV. At this accelerating voltage, the electron beam energies are able to induce phase transitions in this kind of alloy in just a few minutes.

Fig. 1 shows a sequence of diffraction patterns of the decagonal phase along the twofold axis. In Fig. 1a, the decagonal diffraction spots and also those corresponding to the (1 1 1) zone axis in the b.c.c. superimposed structure can clearly be seen. Fig. 1b and c show the diffraction patterns after different electron radiation times *in situ* in the microscope. These figures clearly show the systematic disappearance of the diffraction spots which correspond to the decagonal phase. In Fig. 1d practically all the phases are

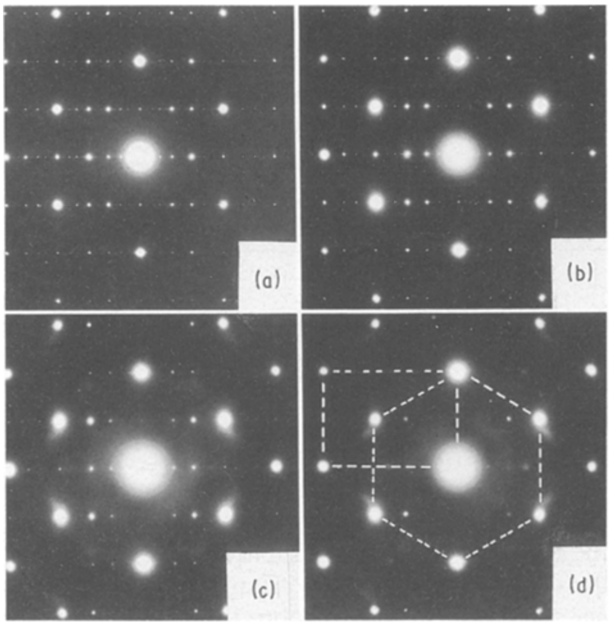

Figure 1 Diffraction patterns from the decagonal phase of Al–Cu–Co–Si along a twofold axis. (a) Diffraction pattern at the beginning of the experiment; (b, c, d) diffraction patterns which correspond to different electron radiation times. The exposure time is increased from (b) to (d).

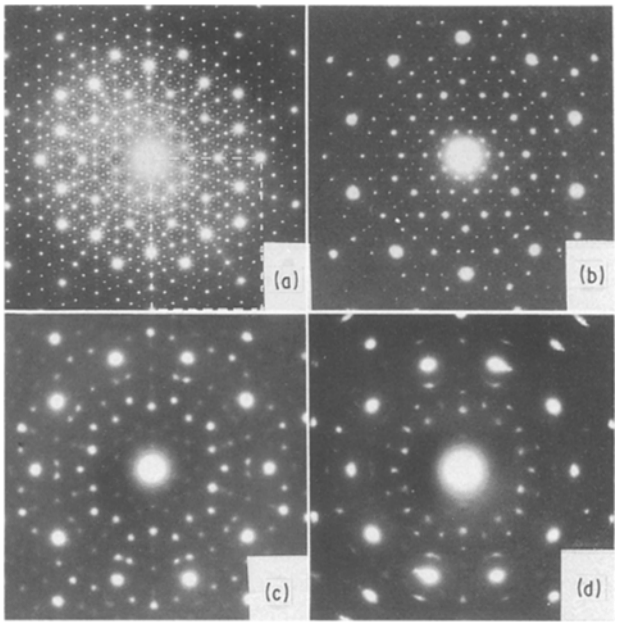

Figure 3 Diffraction patterns from the decagonal phase of Al–Cu–Co–Si along a tenfold axis. (a) Diffraction pattern at the beginning of the experiment; (b, c, d) same diffraction patterns at different electron radiation times. The exposure time is increased from (b) to (d).

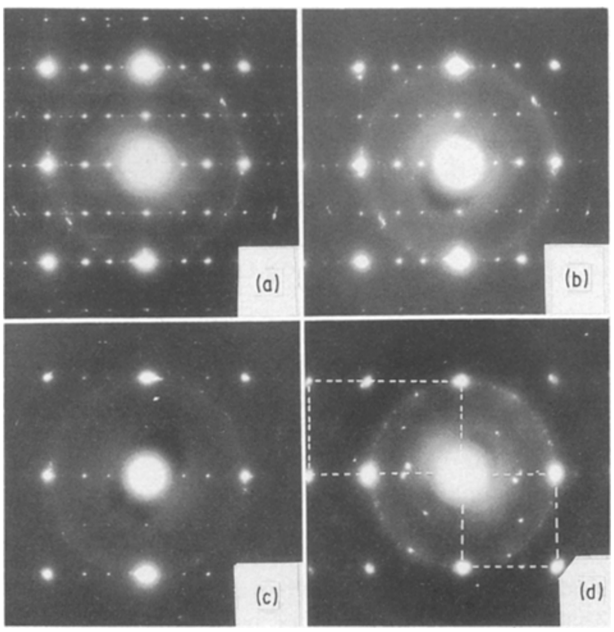

Figure 2 Diffraction patterns from the decagonal phase of Al–Cu–Co–Si along a twofold axis. (a) Diffraction pattern at the beginning of the experiment; (b, c, d) same diffraction patterns at different electron radiation times. The exposure time is increased from (b) to (d).

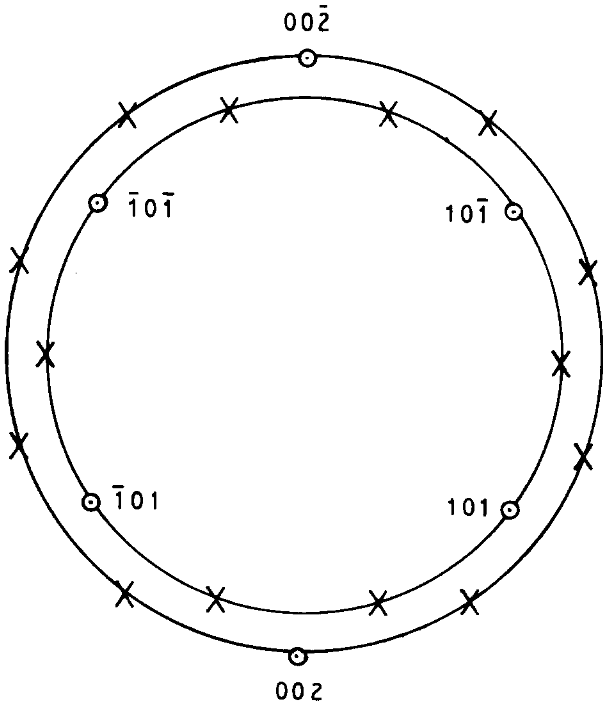

Figure 4 Kinematic electron diffraction pattern of a twinned arrangement of cubic crystals predicted by the twinned model [13].

crystalline in nature. In this figure, two crystalline phases can clearly be seen. The b.c.c. (1 1 1) zone axis diffraction pattern is superimposed on a rectangular pattern. The sequence in Fig. 1 also shows an increase in intensity and a large spread in reciprocal space of the crystalline reflections.

The same behaviour can be obtained in the decagonal diffraction pattern along the others twofold axis. After some time of electron radiation there are clear signs of disappearance of the decagonal spots; however, the spots in the (1 0 0) b.c.c. zone axis still remain. This is shown in Fig. 2. Although Fig. 2d shows few quasicrystalline spots, there is a clear tendency to crystallization. It is important to mention the final appearance of two different crystalline structures; the b.c.c. (1 0 0) zone axis diffraction pattern and a superimposed rectangular diffraction pattern. Similar intensity and spread behaviour of the crystalline reflections are also obtained along this quasicrystalline orientation. However, these two quasicrystalline orientations do not give clear information on the deformation mechanism involved for the quasicrystalline–crystalline transformation. Partial information on this mechanism can be obtained from diffraction patterns along the ten-fold axis.

Fig. 3a illustrates the tenfold pattern at the beginning of the experiment; however, Fig. 3d shows the same diffraction pattern after some electron radiation time. In this case there is also a clear disappearance of the tenfold diffraction spots, the only remaining spots strongly resembling the diffraction spots kinematically simulated for twinned crystalline specimens. A schematic diagram based on the results of Yang *et al.* [13] is illustrated in Fig. 4. This figure shows the diffraction pattern obtained from an arrangement of twinned f.c.c. cubic crystals.

It is important to point out the qualitative agreement between the diffraction pattern from the twinned

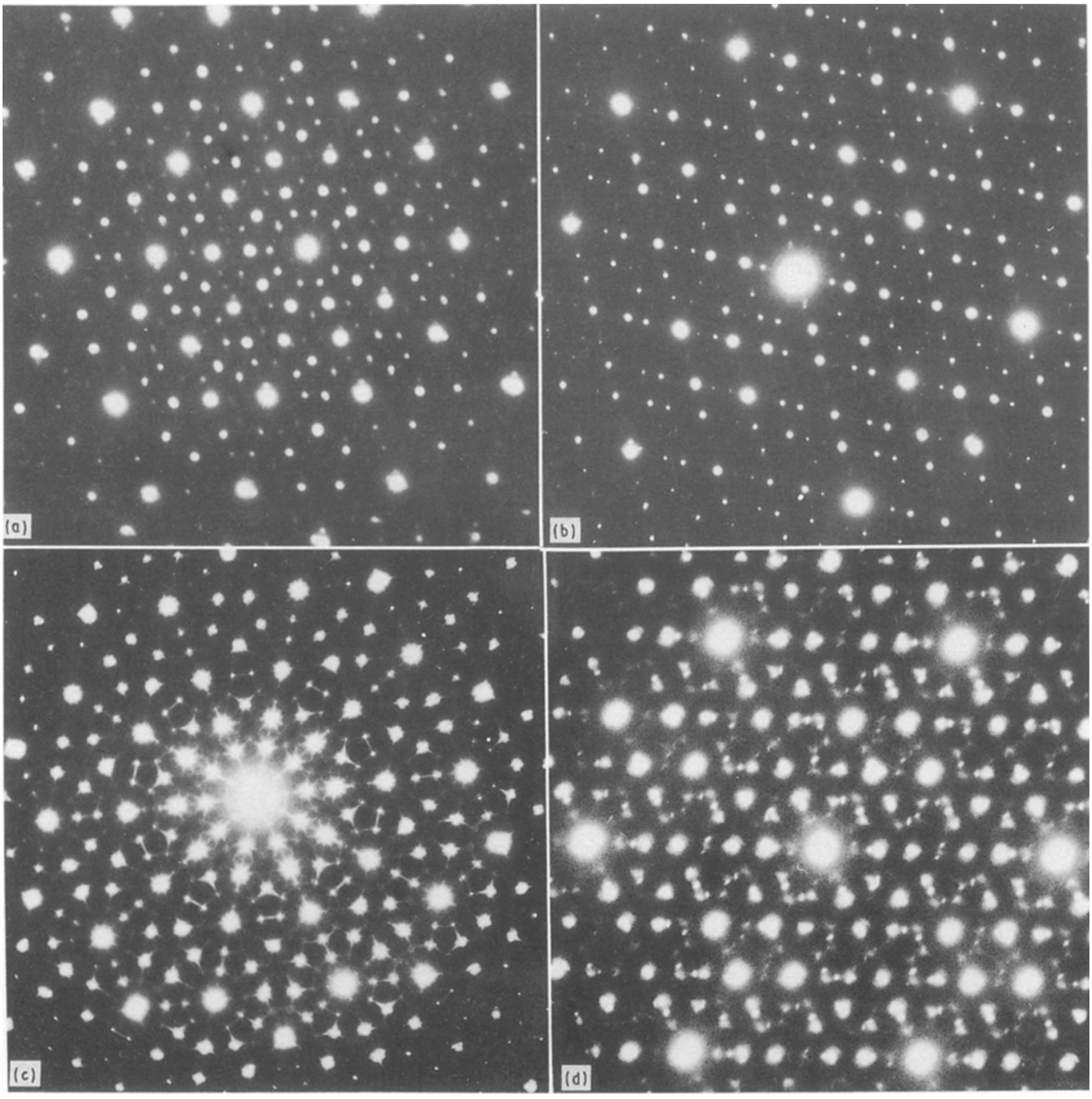

Figure 5 Diffraction patterns from the icosahedral phase of Al–Cu–Co–Fe alloy (a) along the fivefold axis, (b) along the twofold axis, (c) along the fivefold axis after annealing at 800 °C for 24 h, (d) along the twofold axis after annealing.

model and the first two inner rings of spots shown in Fig. 3d. It is also important to mention that Field and Fraser [14] and Idziak and Heiney [15] have simulated diffraction patterns from twinned cubic crystals and there is also qualitative agreement between their predictions and the experimental results given in Fig. 3d. It therefore seems to be possible that the deformation mechanism which is involved in this kind of phase transition could be related to twinning. It is finally important to realize that the crystalline rectangular pattern shown in Fig. 3a is able to generate the two external circular array of spots; however, the inner circles can be obtained by double diffraction mechanisms.

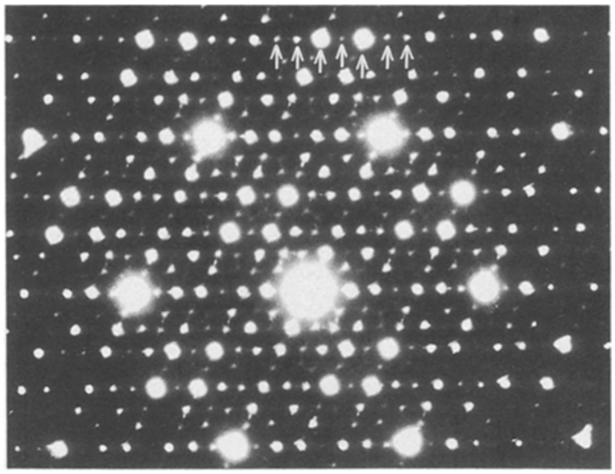

Figure 6 Diffraction pattern from the icosahedral phase along the twofold axis. Periodicity is indicated by the arrows.

3.2. Structure transformations in the icosahedral phase of the Al–Cu–Co–Fe alloy

The icosahedral phase in ternary alloys of Al–Cu–Fe has been widely studied in the literature [5, 6]. This phase is also found in alloys of Al–Cu–Co–Fe [8]. The results presented in this section relate to icosahedral phases found in this kind of quaternary alloy. The alloy was obtained by melting the high-purity elements in an arc furnace with an argon atmosphere. For annealing the specimens were encapsulated in a vacuum and subsequently annealed at 800 °C for 24 h. The observations were carried out in a Jeol 4000EX microscope operated at 200 kV. For electron microscope observations the specimens were thinned using an Ar ion-beam milling machine.

Fig. 5 shows the fivefold and twofold diffraction patterns before and after being annealed at 800 °C for 24 h. The first interesting feature of the patterns obtained after annealing the specimens is related to the pronounced spread of the diffraction spots in reciprocal space. This effect can qualitatively be understood as being produced by the deformation of the icosahedral phase giving rise to larger values of the "interplanar" spacings and therefore increasing the orientations over which the electron intensity around the diffraction spots can be appreciable [16]. There are, on the other hand, a large number of new diffraction spots which appear in the diffraction patterns. In some cases a continuous spread of electrons is found between some reflections (Fig. 1c).

Extra reflections are sometimes arranged periodically in reciprocal space. This is clearly illustrated in Fig. 6, where a twofold icosahedral diffraction pattern shows clear signs of crystallization along one of the fivefold axes. Another interesting feature of the electron diffraction patterns from the icosahedral annealed specimens is illustrated in Fig. 7. This figure shows three different twofold diffraction patterns. Fig. 7a was obtained from an icosahedral specimen before annealing. However, Fig. 7b and c were obtained from different icosahedral grains in the same specimen after annealing. Fig. 7b and c show different degrees of crystallization. Fig. 6, on the other hand, has already shown clear indications of periodicity along the fivefold axis for this kind of quasicrystalline zone axis.

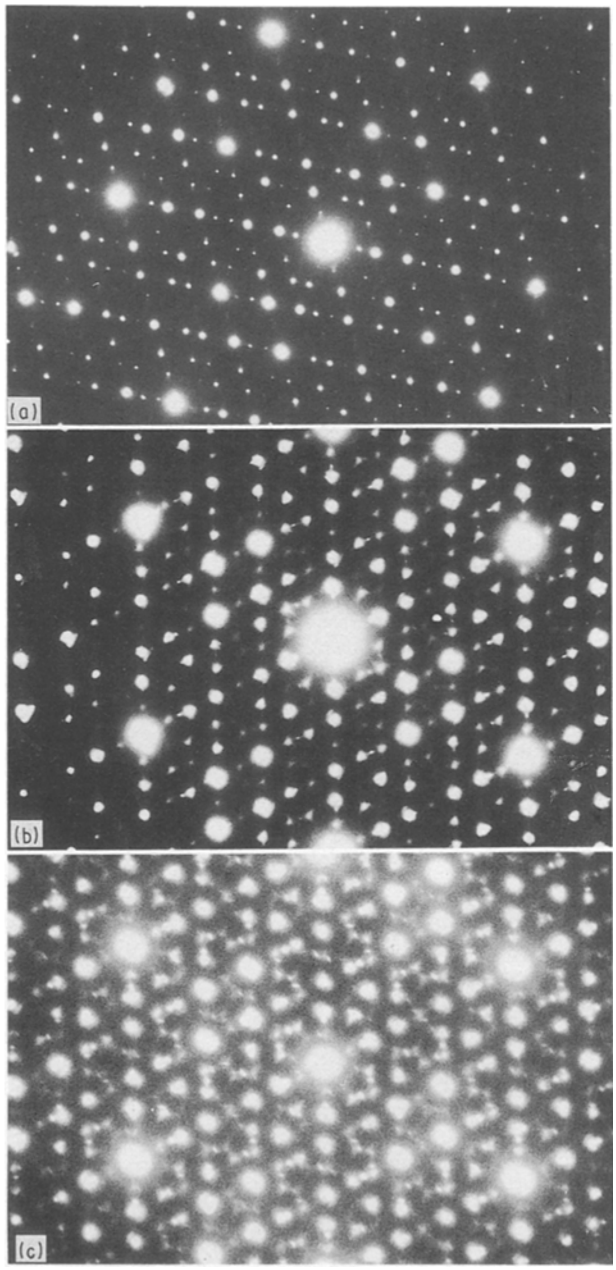

Figure 7 Diffraction patterns from the icosahedral phase along the twofold axis. (a) Before annealing; (b, c) after annealing at 800 °C for 24 h.

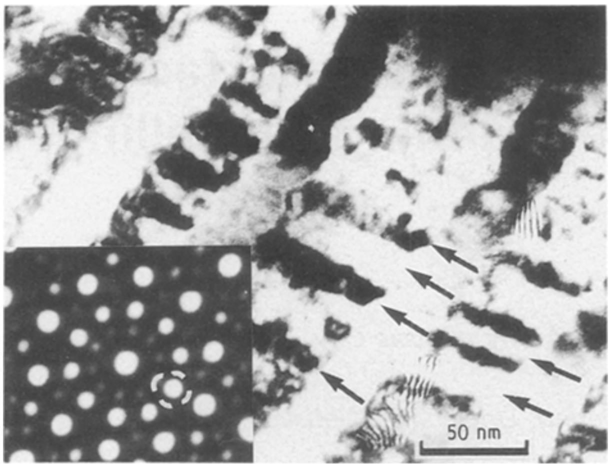

Figure 8 Dark-field image under fivefold diffraction conditions. The dark field is formed with a spot from the second ring of reflections. The contrast features are similar to twinned regions in crystalline specimens.

Although the twofold diffraction pattern illustrates clear indications of transitions from quasicrystalline to crystalline structures, the diffraction patterns alone are not able to provide information on the deformation mechanism which induces the transformation. However, dark-field images can give insights into this aspect. This is shown in Fig. 8, which corresponds to a low-magnification dark-field image from the annealed specimen. The image was obtained under fivefold diffraction conditions using one of the second-ring spots to generate the image. The contrast features displayed by this figure have strong similarities with those of twinned crystalline regions. Dark features in this image correspond to crystalline specimen areas unable to scatter electrons along the beam used for the dark-field imaging.

4. Conclusions

The electron radiation in the TEM induces transformations from the quasicrystalline decagonal phase to crystalline structures in alloys of Al–Cu–Co–Si. This kind of transformation seems to be induced by a deformation mechanism based on twinning. The twofold quasicrystalline zone axis show two different crystalline phases, the b.c.c. (1 1 1) and (1 0 0) diffraction patterns and also a rectangular pattern which in Fig. 1 has dimensions of $0.2\ \text{nm}^{-1} \times 0.12\ \text{nm}^{-1}$ and in Fig. 2 of $0.2\ \text{nm}^{-1} \times 0.14\ \text{nm}^{-1}$. On the other hand, diffraction patterns obtained from annealed icosahedral phases in alloys of Al–Cu–Co–Fe show diffraction spots which are considerably spread out in reciprocal space. This effect suggests deformations in the icosahedral phases due to changes in the "interplanar" spacings. The twofold diffraction pattern from the icosahedral phase after annealing shows clear indications of crystallization along the five-fold axis. Image-contrast features obtained under fivefold diffraction conditions suggest also that twinning could be the deformation mechanism involved in the phase transformation.

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