CRYSTALLOGRAPHY OF MARTENSITE IN A Cu-10Al-5Ni-5Fe ALLOY

F. Hasan, G. Lorimer, N. Ridley

JOURNAL DE PHYSIQUE

Colloque C4, supplément au n° 12, Tome 43, décembre 1982 *page* C4-653

CRYSTALLOGRAPHY OF MARTENSITE IN A Cu-10Al-5Ni-5Fe ALLOY

F. Hasan, G. W. Lorimer and N. Ridley

Department of Metallurgy, University of Manchester/UMIST, Grosvenor Street, Manchester M1 7HS, England

(Revised text accepted 1 October 1982)

Abstract. - The morphology and crystallography of quench-induced martensite in a Cu-10Al-5Ni-5Fe alloy has been studied using transmission electron microscopy. On quenching from 1000°C, the high temperature β-phase transformed to martensite based on the 3R-type structure. Numerous small iron-rich particles ∿0.1μm diameter, were observed within martensite plates. The parallel-sided martensite plates were twin-related. When the alloy was quenched from the α+β phase field, the β-phase, which now had a higher aluminium content, transformed to martensite based on either the ordered 3R or 2H type structure. On tempering, the martensite phase rejected Ni, Al and Fe as precipitates based on NiAl and the matrix transformed to a f.c.c. copper-rich solid solution.

Introduction. - Martensitic transformations in binary Cu-Al alloys and some multicomponent alloys based on the Cu-Al system essentially involve either bcc → 9R or bcc → cph transitions. However, some alloying elements can influence the crystallography and the microstructure of the product phases (1). Martensitic transformations in Cu-Al-Ni alloys have been studied by several workers (2,3), but little information has been published concerning Cu-Al-Fe alloys.

The object of the present work was to investigate the morphology and the crystal structure of quench-induced martensite, as well as the microstructural changes associated with the tempering of martensite, in a commercially based Cu-10%Al-5%Ni-5%Fe alloy.

Experimental. - The analysed chemical composition of the alloy examined was Cu-9.4 wt%Al-4.9wt%-Ni-4.4wt%Fe-1.2wt%Mn. For optical microscopy, specimens were polished using conventional procedures and etched in a 10% aqueous solution of ferric-nitrate. Thin foil specimens were prepared either by electropolishing with 7 vol% perchloric acid in acetic acid at room temperature using a potential of 30 volts, or by ion-beam thinning with 5.5 kV argon ions in an Ion-Tech Super Microlap apparatus. Some carbon extraction replicas of polished and etched specimens were prepared using standard techniques. Electron microscpy was carried out with either Philips EM301 or EM400T transmission electron microscopes. Chemical analyses of quenched, and quenched and tempered, thin specimens were made on EM400T fitted with an EDAX energy dispersive X-ray detector.

Results. - A light micrograph of a sample quenched from 1020°C, where the alloy consisted of bcc β phase, is shown in Figure 1a. The prior β grain-boundaries and groups of martensite plates can be seen.

Transmission electron microscopy of thin foils, Figure 1b, and extraction replicas, Figure 2a, revealed the presence of small, ∿0.1μm diameter, cuboidal precipitates uniformly distributed throughout the structure. The thin foil X-ray microprobe analysis of the precipitates extracted on carbon replicas indicated that they were rich in iron. On the basis of their chemistry, the precipitates were expected to have a bcc structure. However, the electron diffraction pattern, Figure 2b, showed weak superlattice reflections which indicated that the precipitates were

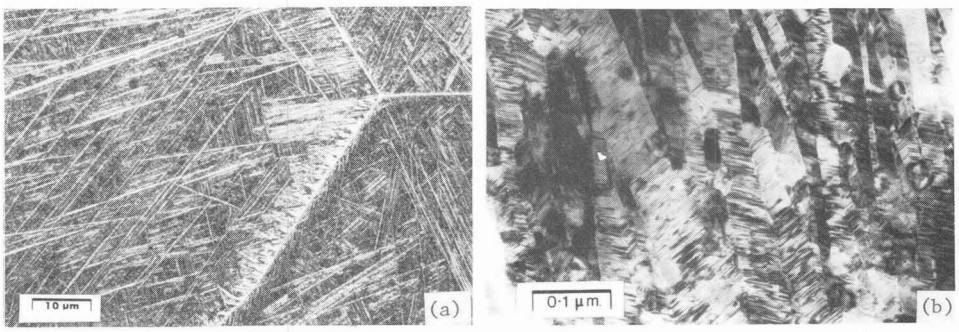

Figure 1. (a) Light micrograph of the sample quenched from 1020°C. (b) Transmission electron micrograph of the same sample as Figure 1a.

partially ordered. Attempts were made to suppress the formation of these iron-rich precipitates by employing fast cooling rates during quenching. These were not successful and the precipitates were formed even in splat-cooled samples*. The size of the precipitates decreased as the quenching rate was increased, while the shape and the distribution remained generally unaffected.

The transmission electron micrograph shown in Figure 1b, provides a link with the light micrograph (Figure 1a) revealing the groups of martensite plates. The internal striations within individual plates arise from faulting (4).

The results of the electron diffraction investigation were interpreted, by following the analysis of Sato et al (5,6). Electron diffraction patterns taken from the individual martensite plates were indexed as disordered 3R (or 9R) structure; the diffraction pattern along the [010] zone axis is shown in Figure 3a. The diffraction patterns obtained along [210] or [$\bar{2}$10] zone axes were similar to that of Figure 3a. In the literature, this type of martensite is usually referred to as β'-martensite (1,4). Electron diffraction, Figure 3b, revealed that the parallel-sided martensite plates were twin-related.

---

* This experiment was carried out in co-operation with Dr. H.A. Davies in the Department of Metallurgy at the University of Sheffield.

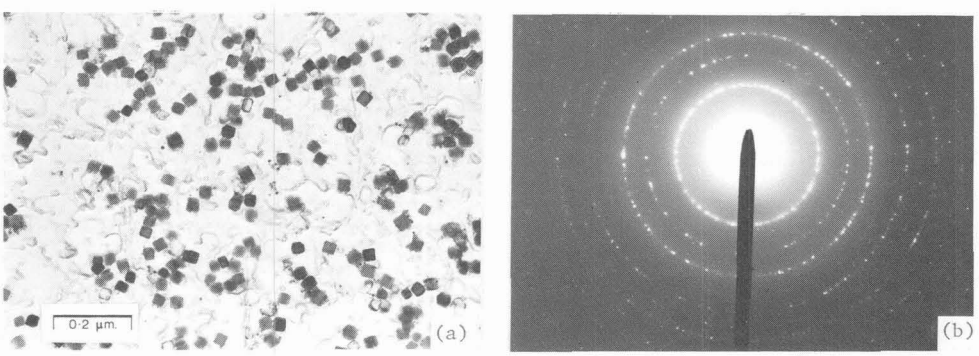

Figure 2. (a) Carbon extraction replica of the specimen quenched from 1020°C, showing the cuboidal precipitates. (b) Electron diffraction ring pattern, taken from a large number of precipitates shown in Figure 2a, which can be indexed as a B2 structure.

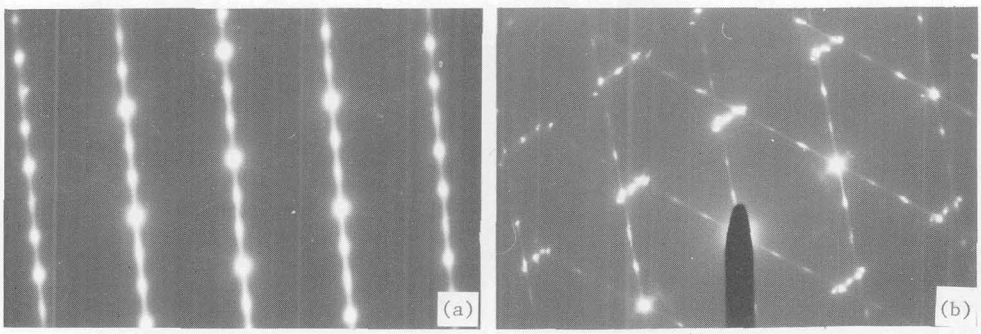

Figure 3. (a) Electron diffraction pattern taken along $[010]_o$ zone-axis, from one of the martensite plates of Figure 1b; 9R structure. (b) Electron diffraction pattern *along* $[210]_o$ zone-axis, obtained from a group of parallel-sided martensite plates.

Some of the specimens were quenched from $\alpha+\beta$ phase-field and in this case the martensite derived from β exhibited two distinct morphologies, as shown in Figure 4a. One type, which showed internal striations, was similar in appearance to that of Figure 1b, and the electron diffraction patterns taken from this type of martensite, β_1', (Figure 4b) were indexed as ordered3R (or 18R) structure. The superlattice reflections in the diffraction patterns obtained from β_1' martensite were very weak, and it was difficult to establish whether the crystal structure of the parent phase was B2 or DO_3. However, considering the aluminium content of the parent β, it is reasonable to assume that it had the DO_3 crystal structure. In the second type, γ', the individual plates were internally twinned but showed no internal striations; the corresponding electron diffraction patterns, Figure 4c, were indexed as 2H structure. The two types of martensite, i.e. 18R and 2H, are commonly referred to as β_1' and γ', respectively.

Tempering of the martensite was carried out at various temperatures. The resultant structures consisted of a matrix phase which was a fcc copper-rich solid solution (α), and precipitates based on NiAl with a B2 structure. Samples tempered at low temperatures ($\sim$500°C) for short times revealed that the precipitates of NiAl nucleated either on martensite plate boundaries or on the surface of pre-existing iron-rich particles, Figure 5.

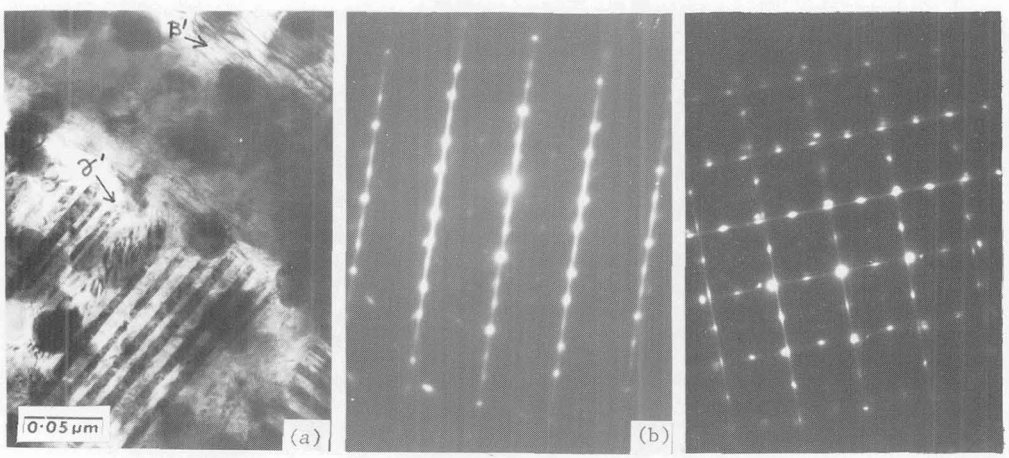

Figure 4. (a) Transmission electron micrograph of a sample quenched from 850°C, showing β_1' and γ' martensites. (b) Electron diffraction pattern along [010] zone axis, obtained from β_1'-martensite. (c) Electron diffraction pattern along [010] zone·axis, obtained from two γ'-martensite plates which were at an angle of $\sim$90° with respect to each other.

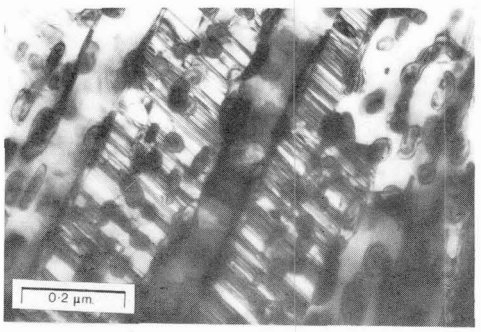

Figure 5. Transmission electron micrograph of a sample, quenched from 1020°C and tempered at 500°C for 1 hour, showing the precipitation on martensite plate-boundaries and on the surface of iron-rich particles within the martensite-plates.

Discussion

The formation of iron-rich precipitates in Cu-Al-Fe alloys prior to the martensitic transformation, has been repofted by Delaey and Olaerts (7). Indirect microscopic evidence has been obtained during the present work which supports the proposal that the iron-rich precipitates form prior to the martensitic transformation. The dark-field images, e.g. Figure 6, as obtained with any reflection from the iron-rich precipitates contained within the martensite matrix, show that all the particles have the same orientation relative to the electron-beam. These precipitates are cubic and if they form with a cube-cube orientation-relationship with the β-phase then all the variants will be parallel as illustrated by Figure 6. On the contrary, if the precipitates do not have a cube-cube relationships with β, or if they form in the martensite, then the multiplicity of the orientations would mean that only a fraction of the total number of precipitates will be visible in the dark-field, using single precipitate reflection. It should be noted that there is a slight shift in the orientation between the precipitates in adjacent martensite plates, but this can be explained in terms of the differences in lattice strain between adjacent plates.

Additional evidence that the iron-rich precipitates formed prior to the martensitic transformation is provided by the average size of individual martensite plates Figure 1b, which was considerably smaller than that reported for Cu-Al and Cu-Al-Ni alloys, and indicated that the presence of the precipitates affected the nucleation and/or growth of the martensite.

When the alloy was quenched from β phase-field, the β'-martensite with 9R structure was obtained, Figure 1b and 3a. This observation is consistent with most of the previous work (1,4), except that some workers have described the β'-martensite as consisting of 11H-type crystal structure (8) or a mixture of 9R and 11H structure (1). The parallel-sided martensite plates were found to be twin-related, Figure 3b. The details of the crystallography of twinning will be presented elsewhere.

When the alloy is heated to α+β phase-field, partitioning of alloying elements occurs and the β phase becomes richer in aluminium and nickel. In the temperature range of 840-870°C, the composition of β is approximately Cu-12.5wt%Al-6wt%Ni-2.5wt% Fe. On quenching from such temperatures, a mixture of β_1' and γ' was obtained. The co-existence of two different types of martensite has been reported for Cu-Al binary alloys (1,4) and for a Cu-12.8wt%Al-6.6wt%Ni alloy (2). Hull and Garwood (2) proposed that the two types of martensite were formed as a result of the partitioning of aluminium into aluminium-rich and aluminium-poor zones. It is difficult to correlate this interpretation with the scale of the microstructure in the present alloy since the regions containing β_1' and γ' were of the order of a few microns in dimension. The proposal of Delaey and Warlimont (1) that in the composition range, where β-type and γ-type martensites may be formed concurrently, small local changes in internal stresses are sufficient to transform the β-phase to either of the two structures, could explain the present observations.

Although the structure of β-type martensite was characterized as disordered,

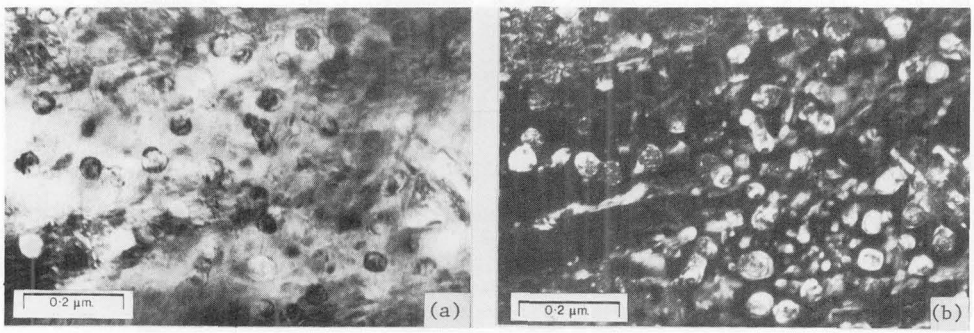

Figure 6. (a) Bright-field image of β'-martensite. (b) Dark-field image of the same area as Figure 6a, obtained with a reflection from the iron-rich precipitates.

by Hull and Garwood (2), they reported faint superlattice relfections in a sample which had been quenched from 950°C. During the present work the observation of the weak superlattice reflection in an electron diffraction pattern taken from β'-martensite, Figure 4b, supports the observation of Hull and Garwood. In binary alloys of similar aluminium-contents, distinct superlattice reflections were reported by Swann and Warlimont (4). However, it is possible that the presence of nickel (or nickel and iron) may effect the ordering reaction which takes place prior to the martensitic transformation.

On tempering, the martensite rejected nickel, aluminium and iron as precipitates based on NiAl and the matrix transformed to fcc copper-rich solid solution (α). Precipitation of the solute-rich phase on the martensite plate boundaries has been reported to occur in a number of alloy systems (1). In the present case, the pre-existing iron-rich precipitates also acted as favourable sites for the nucleation of NiAl because of the similarity between their crystal structures and lattice parameters (9).

Conclusions. - Upon quenching the alloy of composition Cu-10wt%Al-5wt%Ni-5wt%Fe, from the β phase-field, small iron-rich precipitates, ∿0.1μm diameter, formed prior to the martensitic transformation. The martensite had a 9R structure and the parallel-sided plates were twin-related.

When the alloy was quenched from α+β phase-field, the β-phase which had an enhanced aluminium concentration, transformed to either 18R or 2H martensite.

On tempering, the β'-martensite rejected aluminium, nickel and iron as precipitates based on NiAl and the matrix transformed to fcc copper-rich solid solution. The NiAl precipitates nucleated either on martensite plate-boundaries or on the pre-existing iron-rich particles.

Acknowledgements. - This investigation was supported by the Ministry of Defence,U.K. The EM400T was purchased with grants from SRC and NERC.

References

1. Delaey L. and Warlimont H.: Prog.in Mater.Sci., 18 (1974) 32.

2. Hull D. and Garwood R.D.: J.Inst.Met., 86 (1957/58) 485.

3. Duggin M.J.: Acta Met., 14 (1966) 123.

4. Swann R.P. and Warlimont H.: Acta Met., 11 (1963) 511.

5. Sato H., Toth R.S. and Honjo G.: J.Phys.Chem.Solids, 28 (1967) 137.

6. Sato H., Toth R.S. and Honjo G.: Acta Met., 15 (1967) 1381.

7. Delaey L. and Olaerts J.: Leuven Univ., Unpublished research, 1967/68.

8. Wilkens M. and Warlimont H.: Acta Met., 11 (1963) 1099.

9. Hasan F., Lorimer G.W. and Ridley N.: Manchester Univ., Unpublished research, 1982.