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THE CRYSTAL STRUCTURE OF THE METASTABLE PRECIPITATE IN COPPER-BASED COPPER-TITANIUM ALLOYS

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In a recent paper, Knights and Wilkes (1) (KW) have reported that the metastable ordered phase which forms by precipitation from copper-rich copper-titanium binary alloys is of the type $L1_2$ (Cu_3 Au; Pm3m) with lattice parameter a = 4.1 A (0.41 nm). They based this on the indexing of a $[020]_m$ (matrix) electron diffraction pattern shown schematically in Figure 1.

Hakkarainen and ourselves have investigated this same system (2, 3, 4) and have reported that the precipitate is the body centered tetragonal D1a structure (Ni_4 Mo; I4/m). Comparison of our $[020]_m$ electron diffraction patterns with that of KW reveal no differences with respect to the position of the precipitate reflections. However, the two proposed precipitate crystal structures are so different from one another that quite different diffraction patterns should be observed. It is the purpose of this note to demonstrate that certain reflections expected for the $L1_2$ structure are missing from the observed $[020]_m$ electron diffraction patterns, thus ruling out the assignment of the $L1_2$ structure to the ordered phase. Furthermore, it will be shown that the D1a structure is fully consistent with all the experimental findings.

KW claim that the $[020]_m$ diffraction pattern arises from $L1_2$ precipitates with two equivalent orientations with respect to the matrix:

$$\text{(i)}\quad [100]_{ppt} \;//\; [201]_{matrix}$$

$$[010]_{ppt} \;//\; [\bar{1}02]_{matrix}$$

$$\text{(ii)}\quad [100]_{ppt} \;//\; [102]_{matrix}$$

$$[010]_{ppt} \;//\; [\bar{2}01]_{matrix}$$

Both of these have $[001]_{ppt}$ // $[010]_{matrix}$.

However, there are four other equivalent orientations of the $L1_2$ precipitate with the matrix, one pair with $[001]_{ppt}$ // $[100]_{matrix}$:

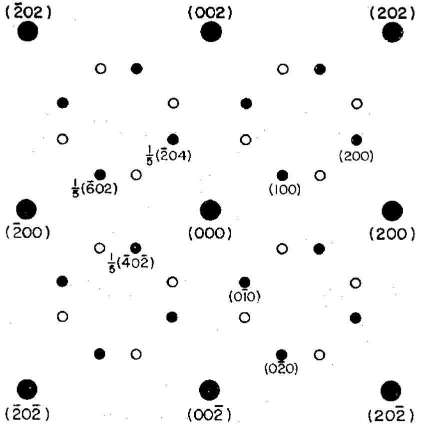

FIG. 1

Schematic of observed $[020]_m$ diffraction pattern. Right hand side shows $L1_2$ indexing of both fundamental and superlattice precipitate reflections based on a = 4.1A (0.41 nm). Left hand side shows Dla indexing of superlattice reflections based on the f.c.c. lattice. Open circles are from a second variant.

(iii) $[100]_{ppt}$ // $[0\bar{2}1]_{matrix}$

$[010]_{ppt}$ // $[012]_{matrix}$

(iv) $[100]_{ppt}$ // $[0\bar{1}2]_{matrix}$

$[010]_{ppt}$ // $[021]_{matrix}$

and the other pair with $[001]_{ppt}$ // $[001]_{matrix}$:

(v) $[100]_{ppt}$ // $[2\bar{1}0]_{matrix}$

$[010]_{ppt}$ // $[\bar{1}\bar{2}0]_{matrix}$

(vi) $[100]_{ppt}$ // $[1\bar{2}0]_{matrix}$

$[010]_{ppt}$ // $[\bar{2}\bar{1}0]_{matrix}$

Because of the symmetry of the matrix, all six orientations are equally likely. Only $(hk0)_{ppt}$ reflections for orientations (i) and (ii) are seen in the $[020]_m$ reciprocal lattice. With the other equivalent orientations, "extra" reflections should appear in the $[020]_m$ reciprocal lattice, as shown in Figure 2. In this figure, the +'s represent $(h\ 2h\ \ell)_{ppt}$ reflections ($h=0,\pm1,\pm2,\ \ldots;\ \ell\neq0$) from orientations (iii) and (iv) while the x's represent the $(h\ 2h\ \ell)_{ppt}$ reflections ($h=0,\pm1,\pm2,\ \ldots;\ \ell\neq0$) from the orientations (v) and (vi).

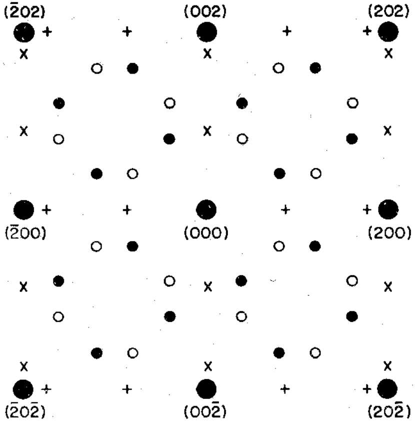

FIG. 2

With all six variants of the proposed $L1_2$ phase, additional reflections are expected in a $[020]_m$ diffraction pattern. (+ from variants iii and iv; x from variants v and vi.)

The missing reflections should have had comparable intensities. For instance {ℓoo} occurs both among the reflections indexed by KW and among the missing ones. Actually, because two variants would contribute to each of the missing reflections these should have higher intensities than the observed reflections. Their absence in KW's own $[020]_m$ pattern thus rules out the assignment of the $L1_2$ structure.

If for some reason, KW's specimens formed only two out of the six equivalent variants, they would have observed not only the reported $[020]_m$ diffraction pattern, but also $\langle 200 \rangle_m$ diffraction patterns in which only the + or x precipitate reflections appear. We have never observed such a pattern, and neither was one reported by KW. Also, as discussed below, dark field microscopy indicates that other variants are present.

Furthermore, the proposed $L1_2$ $\{200\}_{ppt}$ reflections should be more intense than the $L1_2$ $\{100\}_{ppt}$ reflections, since the former are fundamental reflections while the latter are superlattice reflections. No such differences in intensities have been observed by us, or were reported by KW.

The claim (2, 3, 4) that the ordered phase is of the type D1a with lattice parameter a = 5.84A (0.584 nm) and c = 3.62A (0.362 nm) is based on electron diffraction and coherency evidence. It is consistent with all known data, but careful x-ray diffraction experiments may eventually be required to remove all possible doubt. The symmetry of our diffraction patterns is such that the structure is known to belong to the tetragonal Laue class that includes 4/m.

The $[020]_m$ reciprocal lattice section of the D1a structure is exactly that shown in Figure 1 (5, 6). Furthermore, the tetragonality is consistent with the early x-ray work on CuTi (7) and previous electron microscopy results (2, 8). It should be noted that our work (3, 4) showed that the ordered tetragonal phase was present from the very early stages of the transformation.

There are six variants for the D1a as well, but only two contribute to a $[020]_m$ diffraction pattern. Dark field analysis shows that the superlattice reflections present in such a pattern account for approximately one-third of the precipitate particles (3).

Quite apart from the diffraction evidence, both KW and ourselves found that this precipitate is initially fully coherent. For the D1a structure, full coherency is easy to understand, since it is a derivative of f.c.c. with the same interatomic spacing as the matrix and oriented in such a way that the matrix and precipitate would be part of the same single crystal if one ignores the difference between the copper and titanium atoms. For the $L1_2$ structure, oriented in the way suggested by KW, coherence is not possible. The lattice parameter of their proposed precipitate structure was chosen to be $\sqrt{5}/2$ times the lattice parameter of the matrix so that two of the cube axes of the precipitate correspond in direction and length to two perpendicular <1 1/2 0> lattice vectors of the matrix. The third cube axis is parallel to but incommensurate with the [010] of the matrix. Because of the incommensurability, there exist no planes of true coherence, except possibly the $(020)_m$. Even for the $(020)_m$, only one atom in five of the matrix coincides with an $L1_2$ precipitate position. It would be very unlikely that such a precipitate is coherent.

We conclude that the data contradict the assignment of an $L1_2$ structure and that they are fully consistent with the D1a structure.

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