Ordering in Copper-Titanium Alloys

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Copper base titanium alloys have recently received much attention. They are age hardening alloys, which decompose by the spinodal mechanism[1,2] into a periodic and aligned two phase mixture. The yield strength of the alloys can exceed 100,000 psi solely by the age hardening process.[1]

Buckle and Manenc[3] attempted to find evidence of ordering in the alloy because of its similarity to the nickel base titanium alloys they previously had studied. They found no evidence of ordering. However, they only looked for super-lattice reflections at positions in reciprocal space that corresponded to super-lattice reflections from the Ll_2 structure.

Saito, Iida and Watanabe[4] found some "unknown reflection at the lower angle side of the Debye Scherrer pattern," and suggested that the metastable phase was ordered, but no crystal structure was given.

Recent investigations[2,5] have shown that the metastable titanium rich phase is ordered with crystal structure of the type Dla. This communication will summarize our results in the study of the ordering reaction. The details of the spinodal decomposition reaction will be submitted elsewhere.

The copper-titanium alloys (1.55, 3.08 and 5.17 wt pct Ti) were solution treated at 900°C and rapidly quenched to room temperature. In the as-quenched condition, the 1.55 and 3.08 wt pct alloys showed evidence of phase separation (satellites), but no evidence of ordering (superlattice reflections). However the electron diffraction patterns of the 5.17 wt pct Ti alloy showed satellites around the fundamental reflections and faint superlattice reflections at the 1/5 {420} and 1/2 {210} positions (Fig. 1(*a*), (*b*)). The superlattice reflections were not visible on the screen of the microscope; they were only observed when the diffraction patterns were overexposed with respect to the fundamental reflections (see Fig. 1(*b*)). Fig. 1(*c*) is a schematic of the observed [002] diffraction pattern for the as quenched 5.17 wt pct Ti alloy.

After aging the 5.17 wt pct alloy at 400°C for 10 min, or at 450°C for 15 s, the 1/2 {210} superlattice reflections disappeared, leaving the 1/5 {420} reflections. These became more intense with aging, until they were readily observable on the screen of the microscope. Fig. 2 shows the Dla superlattice reflections for a 5.17 wt pct Ti alloy aged 15 s at 450°C.

Three extra types of reflections are present in Figs. 1(*b*) and 2, along the ⟨110⟩'s. Two of these are present near the {110}'s of the matrix, and the third type is present near the {220}'s of the matrix. These indicate the presence of an epitaxial film of Cu_2O on the surfaces of the specimen.[2,6] Two of the reflections can be indexed as {110} and {220} of the Cu_2O film,

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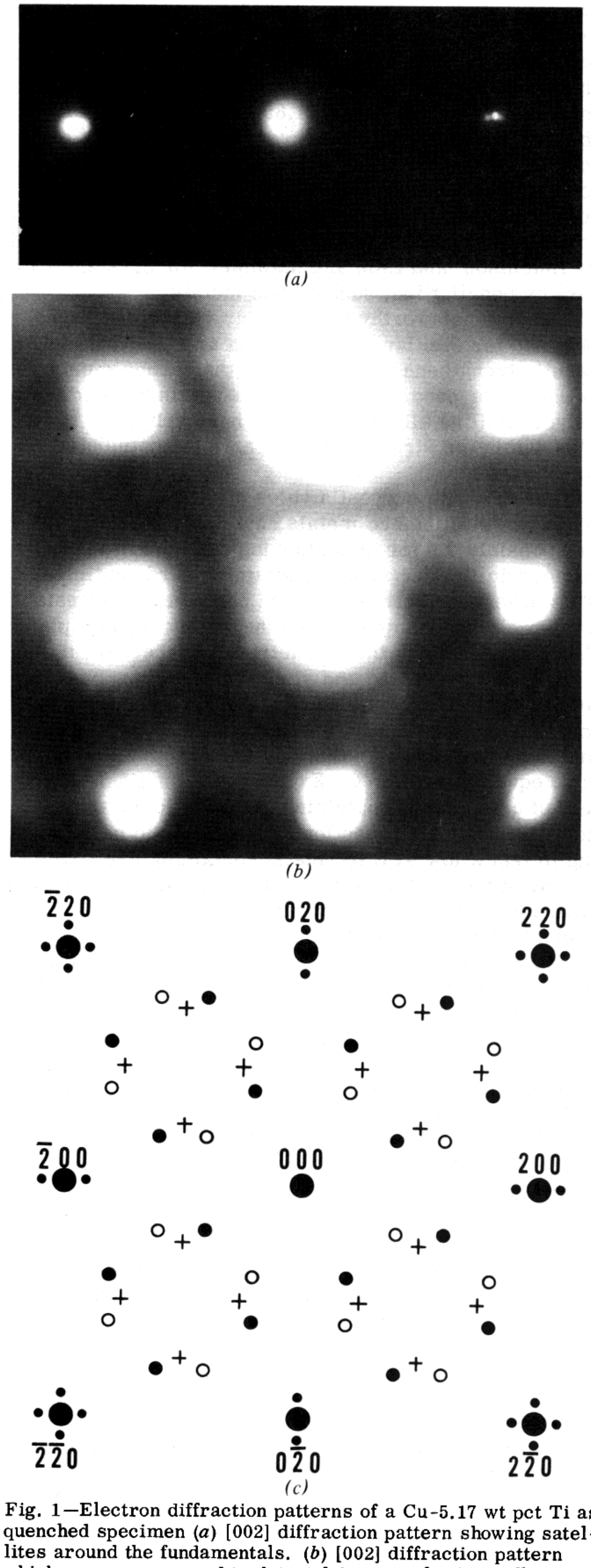

Fig. 1—Electron diffraction patterns of a Cu-5.17 wt pct Ti as quenched specimen (*a*) [002] diffraction pattern showing satellites around the fundamentals. (*b*) [002] diffraction pattern which was overexposed to detect faint superlattice reflections. (*c*) Schematic of the observed [002] diffraction pattern of the as quenched Cu-5.17 wt pct Ti alloy. The positions of the satellites spots are not to scale. The open and filled circles are super-lattice positions for two variants of the Dla structure.

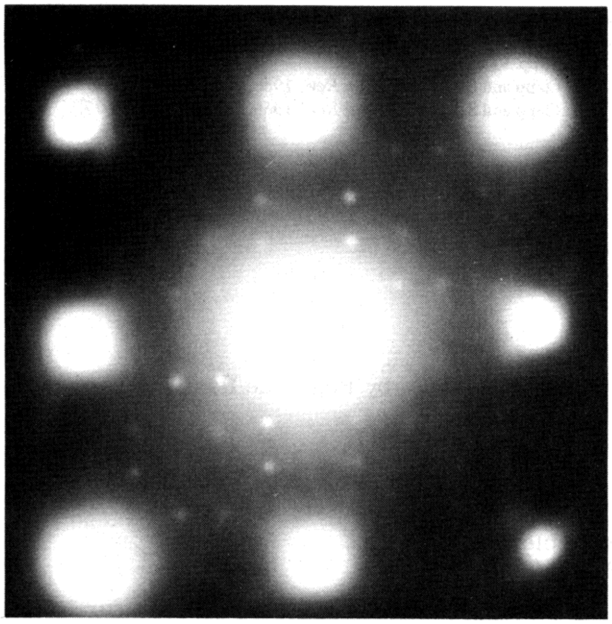

Fig. 2—Cu-5.17 wt pct Ti specimen aged 15 s at 450°C. [002] diffraction pattern, showing the Dla superlattice reflections. Also visible are faint reflections from Cu_2O epitaxial film. See text.

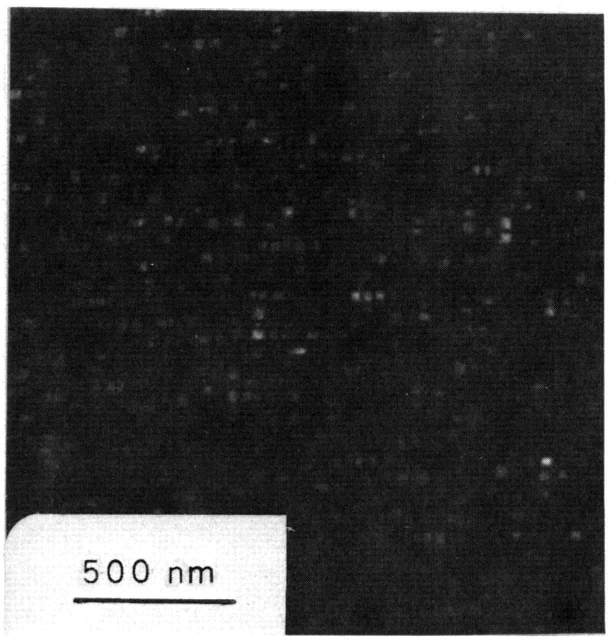

Fig. 3—A dark field electron micrograph of a Cu-5.17 wt pct alloy aged at 450°C for 1000 min. The image was formed from one of the superlattice reflections. The foil normal is [002], and the particles lie along the [020] and [200] directions. (1000 nm = 1 μm).

and the third type occurs from the diffraction of the {220} matrix reflections, by {110} oxide planes.

After further aging, the ordered Cu_4Ti particles could be imaged by using a superlattice reflection. Fig. 3 shows the ordered particles that exist after aging a 5.17 wt pct Ti alloy 1000 min at 450°C.

The 1.55 and 3.08 wt pct alloys both have been observed[2] to order after aging at temperatures above 375°C. Comparison of satellite and superlattice intensities implies that the spinodal reaction occurs

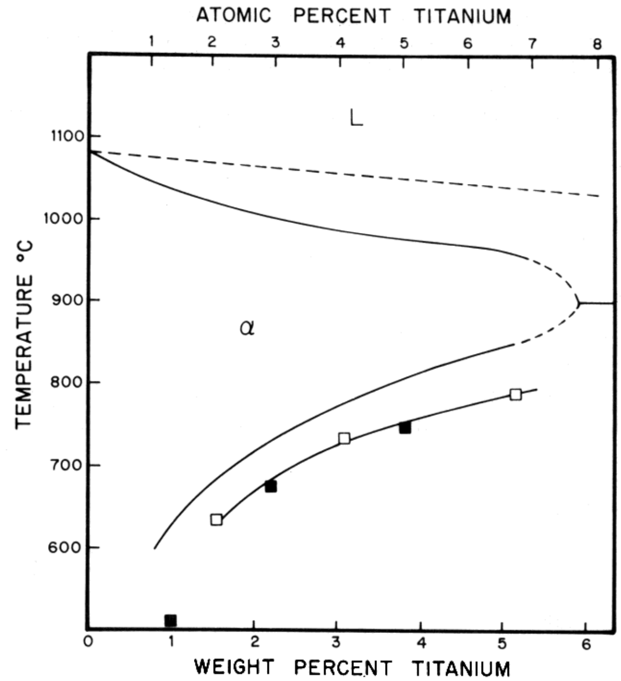

Fig. 4—The copper rich side of the copper-titanium phase diagram. The equilibrium solvus was determined by Saarivirta and Cannon.[9] The line through the squares is the coherent solvus for the metastable Dla phase. Temperatures marked by filled squares were determined by Hakkarainen[5] Those marked by open squares were determined in this investigation.

first. The ordering reaction begins in the titanium enriched regions probably after a certain critical titanium composition is reached in them. The two reactions then occur together. The Cu-Ti binary is therefore an example of an alloy in which both phase separation and ordering occur simultaneously, consistent with recent theoretical predictions.[7]

The Cu_4Ti phase is metastable. Upon prolonged aging it is replaced by a more stable incoherent phase.[2,3,8] The solvus of the metastable Dla phase was determined by reversion treatments and found to lie within the stable two phase region of the phase diagram.[2,5] (See Fig. 4.)

The presence of the 1/2 {210} superlattice reflections is of interest. They are present in other alloys which order to the Dla structure[10,11] both above and below the critical ordering temperatures. Their origin is presently under debate: It has been suggested that they arise either from local statistical order[12,13] or from "microdomains" with non-conservative antiphase boundary faults.[10,11]

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1. J. A. Cornie, A. Datta, and W. A. Soffa: *Met. Trans.*, 1973, vol. 4, pp. 727-33.
2. D. E. Laughlin: Ph.D. Thesis, Massachusetts Institute of Technology, 1973.
3. C. Buckle and J. Manenc: *Mem. Sci. Rev. Met.*, 1960, vol. 57, pp. 435-49.
4. K. Saito, K. Iida, and R. Watanabe: *Trans. Nat. Res. Instit. Metals*, 1967, vol. 9, pp. 21-27.
5. T. Hakkarainen: Doctor of Technology Thesis, Helsinki University of Technology, 1971.

6. H. Sato, S. A. Werner, and M. Yessik: *Z. Metallkde.*, 1973, vol. 64, pp. 427-29.
7. M. J. Richards: Sc.D. Thesis, Massachusetts Institute of Technology, 1971.
8. H. T. Michels, I. B. Cadoff, and E. Levine: *Met. Trans.*, 1972, vol. 3, pp. 667-74.
9. M. J. Saarivirta and H. S. Cannon: *Metal Progr.*, 1959, vol. 76, no. 2, pp. 81-84.
10. P. R. Okamoto and G. Thomas: *Acta Met.*, 1971, vol. 19, pp. 825-41.
11. S. D. Das, P. R. Okamoto, P. M. J. Fisher, and G. Thomas: *Acta Met.*, 1973, vol. 21, pp. 913-28.
12. P. C. Clapp and S. C. Moss: *Phys. Rev.*, 1966, vol. 142, pp. 418-27.
13. P. C. Clapp and S. C. Moss: *Phys. Rev.*, 1968, vol. 171, pp. 754-77.

Corrections to *Met. Trans.*, 1973, vol. 4

Diffusion Creep by Dislocation Climb in Beryllium and Be-Cu Single Crystals, by Roger Le Hazif, Gerard Edelin, and Jean Michel Dupouy, pp. 1275-1281.

Page 1280
Should read

$$D_{\perp} = 45 \pm 3 \text{ kcal/mole}$$
$$D_{\parallel} = 48.1 \pm 0.8 \text{ kcal/mole}$$

Page 1281

Should read

$$D_{\perp} = 2.75 \pm 0.5 \exp\left(-\frac{45 \pm 3 \text{ kcal/mole}}{RT}\right)\text{cm}^2 \cdot \text{s}^{-1}$$

$$D_{\parallel} = 7.4 \pm 3.5 \exp\left(-\frac{48.1 \pm 0.8 \text{ kcal/mole}}{RT}\right)\text{cm}^2 \cdot \text{s}^{-1}$$

Nucleation Limitation and Hardenability, by R. C. Sharma and G. R. Purdy, pp. 2303-2311.

This entire paper is published correctly in this issue (April, pp. 799-807) since many paragraphs were out of sequence in the original publication.

Deformation Mechanisms in Commercial Ti-50A (0.5 at. pct O_{eq}) at Intermediate and High Temperatures (0.3 – 0.6 T_m), by M. Doner and H. Conrad, pp. 2809-2817.

Page 2815, Table IV

The expression for "Subgrain Creep for Pile-up" should be:

$$\frac{\dot{\epsilon}_s kT}{D\mu b} \simeq 2.1 \times 10^2 \, (\sigma/\mu)^3$$