

Precipitation hardening in Cu 1.81 wt % Be 0.28 wt % Co

Part 2 *Discontinuous precipitation*

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The discontinuous or cellular precipitation reaction in Cu 1.81 wt % Be 0.28 wt % Co has been investigated with transmission electron microscopy. The discontinuous precipitate, designated as γI , is nucleated at grain boundaries and grows into adjoining grains, in contrast to the continuously formed γ' intermediate precipitate, which has a similar structure, lattice parameter and orientation. After extensive ageing treatments at 425°C, a transformation to the equilibrium precipitate γ occurs. The extent of discontinuous precipitation depends upon temperature, as below 380°C continuous precipitation is the major mechanism, whereas above 380°C discontinuous precipitation predominates.

1. Introduction

Discontinuous (or cellular) precipitation [1] is a process requiring the nucleation and growth of duplex cells of the discontinuous precipitate and reorientated matrix, which in general are nucleated at grain boundaries and grow into the adjoining grains. The structural and compositional changes occur in regions immediately adjacent to the advancing interface. The parent phase remains unchanged until swept over by the interface and the reaction is complete in regions over which the interface has passed. The kinetics of the reaction depend on the growth of the cell as a whole, whereas in contrast the kinetics of continuous precipitation depend on the growth rate of individual precipitates.

In most treatments of discontinuous precipitation it has been assumed that the equilibrium phases are produced. Cahn [2], however, has shown that this is not the case for any non-zero growth rate, for which the discontinuous precipitate formed by the cellular reaction can only transform to the equilibrium precipitate by a slow lattice diffusion process.

Precipitation hardening copper-beryllium alloys (Be 0.5 to 2.0 wt %, Co 0 to 0.30 wt %) provide a system in which continuous and discontinuous precipitation may occur simultaneously. Support for this concept is provided

by the results of Entwisle and Wynn [3], on Cu 1.77 to 1.99 wt % Be 0.09 to 0.24 wt % Co, who noted, with optical microscopy, that a lamellar structure nucleated at ageing temperatures $\geq 380^\circ\text{C}$. In contrast, Wilkes and Jackson [4] reported a G.P. zone solvus for a binary Cu-Be alloy at 320°C, above which temperature the continuous precipitate γ' nucleated heterogeneously.

In this paper an electron microscopy study of discontinuous precipitation in a Cu 1.81 wt % Be 0.28 wt % Co alloy, as a function of ageing time, is reported. The effect of direct quenching to the ageing temperature was also evaluated, as a test for the presence of a G.P. zone solvus. The relative contributions of continuous precipitation, which was described previously [5], and discontinuous precipitation are discussed.

2. Experimental method

The alloy investigated was a commercial copper-beryllium alloy (Telcon 250) supplied by Telcon Metals Ltd, which had a composition of 1.81 wt % Be, 0.28 wt % Co.

Sheet material, 1.5 mm thick, was solution treated for 1 h at 800°C under an inert argon atmosphere. A supersaturated solid solution was obtained by quenching the homogenized solid solution into water at room temperature



Figure 1 The discontinuous precipitation reaction observed for the solution-treated condition aged for 20 h at 200°C.

or into a salt bath at the required temperature of ageing (175 to 425°C). The water-quenched material was subsequently aged at higher temperatures (175 to 425°C) in a horizontal tube furnace.

Thin foils were prepared for examination in the electron microscope by electropolishing by the method described previously [5].

3. Results

3.1. The discontinuous precipitate, γI

A prominent feature of the ageing process, for all the ageing temperatures studied, was a discontinuous precipitation reaction at the grain boundaries. Fig. 1 shows the discontinuous precipitation after ageing for 20 h at 200°C. The discontinuous precipitate, which was designated as γI to distinguish it from the continuous intermediate precipitate γ' , was present in the form of nodules ~ 150 nm in length. The nodules did not increase significantly in size for ageing times up to 125 h at 200°C. An important feature of the grain-boundary reaction in all the conditions investigated, was the absence of a precipitate free zone adjacent to the grain boundary.

On ageing for ~ 3 h at 315°C, lamellar

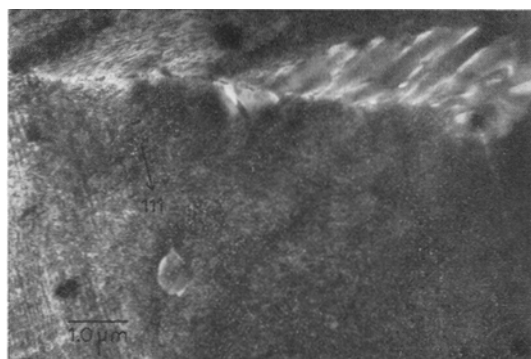


Figure 2 The discontinuous precipitation observed after ageing for 100 h at 315°C, with the continuously precipitated γ' present in the grain interior.

shaped precipitates were formed at the grain boundaries. After longer ageing times, up to 100 h at 315°C, the grain-boundary reaction advanced into the adjoining grains, with the lamellar precipitate increasing in size to ~ 1.0 μm , as shown in Fig. 2 (in which the structure associated with the continuous precipitation [5] within the grain can also be seen). The maximum thickness of a discontinuous cell was ~ 1.5 μm and the reaction was most advanced at the junction of several grains.

Similar observations to those for ageing at 315°C were made for ageing at 360°C, but at ageing temperatures $> 380^\circ\text{C}$ the discontinuous cells were not confined to relatively narrow regions about the grain boundary, and spread rapidly into the grains. For example, after 24 h at 425°C, the discontinuous reaction had completely engulfed the grains, and there was no



Figure 3 γI precipitates observed for the solution-treated condition aged for 24 h at 425°C. The selected-area diffraction pattern shows γI to have a similar orientation to the continuously precipitated γ' .

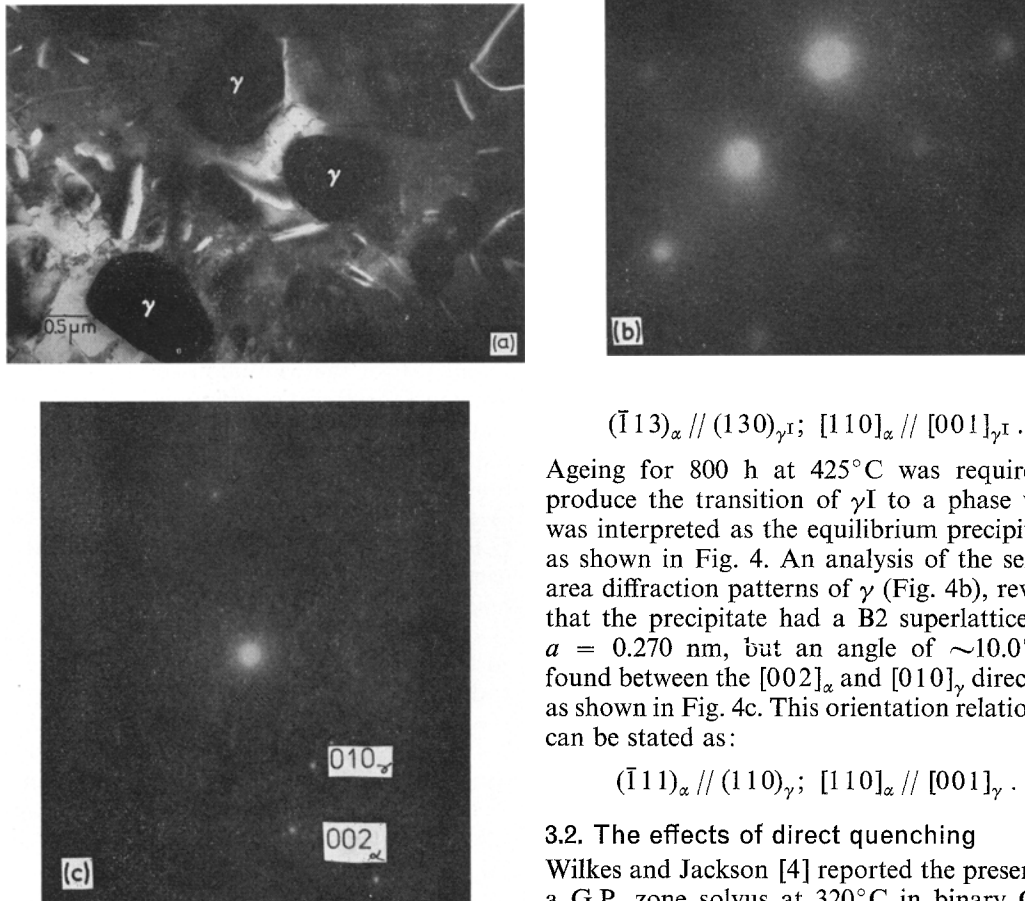


Figure 4 (a) The equilibrium precipitate γ observed for the solution-treated condition aged for 800 h at 425°C. (b) The selected-area diffraction pattern of a γ precipitate, $[100]_{\gamma}$ zone. (c) Selected-area diffraction pattern showing the orientation relationship of γ and the α matrix.

evidence for the presence of the continuously precipitated γ' , as shown in Fig. 3. An analysis of the diffraction patterns revealed that the discontinuous precipitate γ I, had a B2 superlattice structure with $a = 0.270$ nm. A determination of the habit plane of γ I revealed it to be close to $\{113\}_{\alpha}$. This result was supported by the orientation relationship found from the diffraction patterns, Fig. 3, in which the $[002]_{\alpha}$ direction was found as $\sim 7.0^{\circ}$ from $[010]_{\gamma}$. An approximate orientation relationship can be stated as:

$$(\bar{1}13)_{\alpha} // (130)_{\gamma I}; [110]_{\alpha} // [001]_{\gamma I}.$$

Ageing for 800 h at 425°C was required to produce the transition of γ I to a phase which was interpreted as the equilibrium precipitate γ as shown in Fig. 4. An analysis of the selected area diffraction patterns of γ (Fig. 4b), revealed that the precipitate had a B2 superlattice with $a = 0.270$ nm, but an angle of $\sim 10.0^{\circ}$ was found between the $[002]_{\alpha}$ and $[010]_{\gamma}$ directions, as shown in Fig. 4c. This orientation relationship can be stated as:

$$(\bar{1}11)_{\alpha} // (110)_{\gamma}; [110]_{\alpha} // [001]_{\gamma}.$$

3.2. The effects of direct quenching

Wilkes and Jackson [4] reported the presence of a G.P. zone solvus at 320°C in binary Cu-Be alloys. However, in the present investigation it was found that G.P. zones were present, as revealed by striations and diffuse diffraction effects, on ageing the solution-treated and water-quenched material for short ageing times in the temperature range 315 to 425°C. This observation was not conclusive by itself as the possibility existed that the zones were formed on heating from room temperature, with only zones below a critical size being dissolved on heating above the "solvus". To resolve this problem a series of direct quench experiments were performed, which involved quenching the solution-treated material into a salt bath at the required ageing temperature.

Ageing at 425°C for 5 min revealed the presence of G.P. zones, as shown in Fig. 5 with $[001]$ reldods and the related striations. In addi-

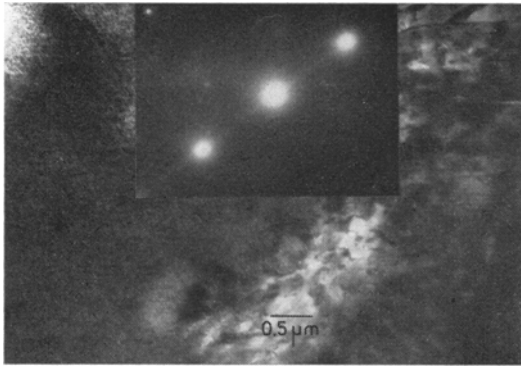


Figure 5 The solution-treated material directly quenched to 425°C and aged for 5 min.

tion to the striations, the discontinuous precipitate rapidly formed at the grain boundary.

In general, it was found that the modes of precipitation, both continuous and discontinuous, were similar to those noted for the water-quenched material [5] and thus a detailed discussion of the directly quenched material is not given.

4. Discussion

Discontinuous precipitation was found to commence by the initial nucleation of the γI precipitate at the grain boundary. The mechanism of the growth is in agreement with the model first proposed by Smith [6], namely that the orientation of the precipitate was not related in any way to the grain into which it was growing, but was found to have an orientation relationship with the supersaturated solid solu-

tion on the other side of the boundary, an example of which is shown in Fig. 2. This observation indicates that the reaction is controlled by diffusion along the cell boundary and that the role of lattice diffusion is not significant.

Cahn's [2] theory of the cellular reaction predicts many of the observed features of the present investigation. First, the equilibrium phase was not formed for a non-zero growth rate, second, the discontinuous precipitate γI was formed in a reorientated α matrix and third, platelets of γI were nucleated in order to maintain a constant inter-precipitate spacing at a given ageing temperature.

From an analysis of the selected-area diffraction patterns and habit plane, a similar structure and orientation relationship to that found [5] for the continuous precipitate γ' was obtained for the discontinuous precipitate γI . Hence, the distinction in terminology is only required to distinguish between the different modes of formation of the two precipitates. The essential difference is that γ' was nucleated by G.P. zones, whereas γI was nucleated heterogeneously from the solid solution at the grain boundary.

The discontinuous precipitate γI approached equilibrium by a slow lattice diffusion process and the transformation to the equilibrium phase γ was observed only after ageing for 800 h at 425°C. The unit cells of the γI and γ precipitates with their relative orientations are shown in Fig. 6. The structure and orientation of γ is in good agreement with that proposed by Geisler *et al* [7].

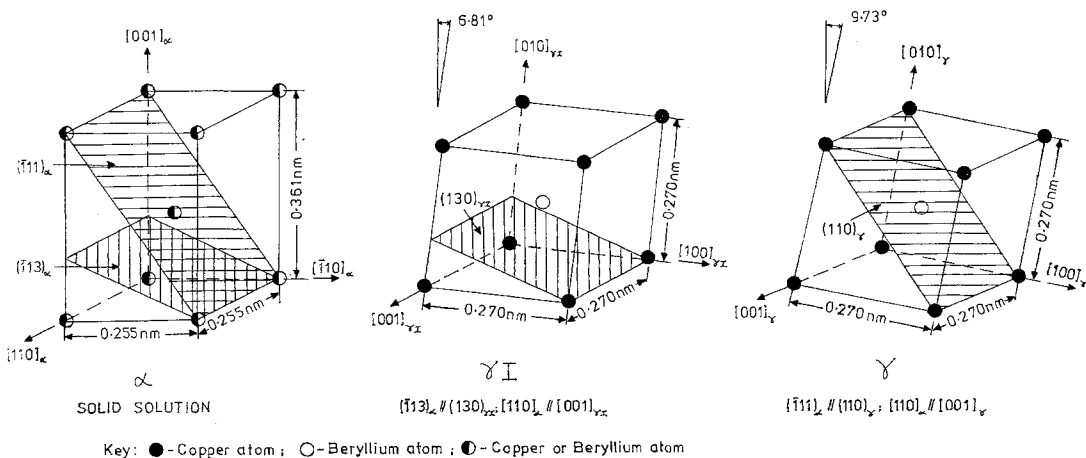


Figure 6 The unit cells and relative orientations of the γI and γ precipitates.

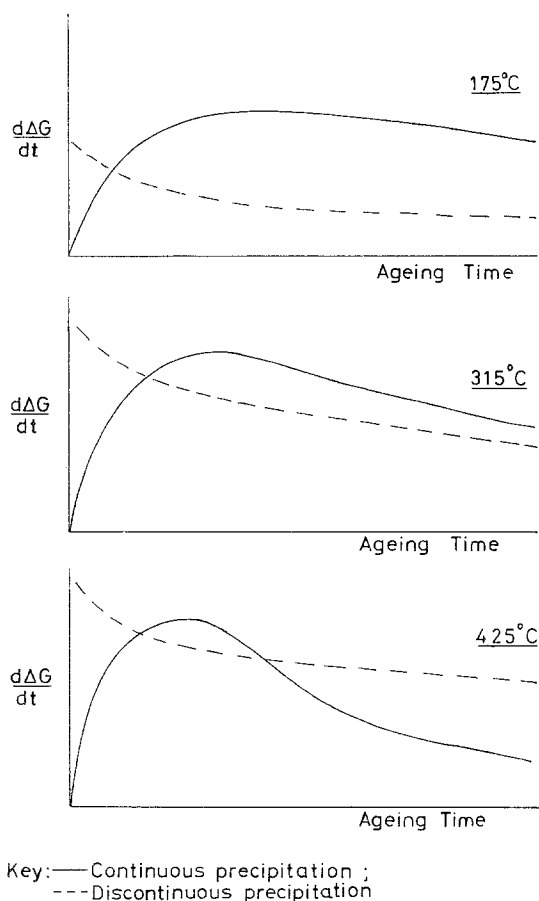


Figure 7 Schematic representation of the rate of change of free energy as a function of ageing time and temperature.

These results, together with the results on continuous precipitation [5] indicate that two distinct modes of precipitation are present in the ageing of copper-beryllium-cobalt alloys. The predominant mode depends on the ageing temperature and the relationship may be considered schematically in terms of the rate of change of free energy [8], as shown in Fig. 7. For ageing below 380°C the cellular reaction was confined to relatively small areas around the grain boundary and continuous precipitation was the major mode. Ageing above 380°C initially produced both continuous and discontinuous precipitation, but for longer ageing times the discontinuous mechanism was predominant and completely transformed the grain to γ I precipitates in a reorientated α matrix. At a later stage γ I transformed to the equilibrium γ precipitate.

The results of the direct quenching experi-

ments showed that for the ternary alloy studied, no G.P. zone solvus existed up to temperatures of 425°C, in contrast to the results of Wilkes and Jackson [4] and Gruhl and Wassermann [9] on the binary Cu-Be alloy. An alternative explanation of their results may be that the "transition" temperature of 320°C observed was not a G.P. zone solvus, but the temperature at which the discontinuous precipitation mode became preferred. However, the interesting difference from the present results is the suggestion, that the presence of 0.28 wt% Co suppresses the discontinuous mode until an ageing temperature of 380°C is reached. The optical observations of Entwisle and Wynn [3], on the ternary alloy, may also be interpreted as due to a "transition" temperature at \sim 380°C.

Resistivity measurements [10-12] have also shown that the presence of cobalt in copper-beryllium alloys retards continuous precipitation at ageing temperatures \leq 350°C but has no effect on the ageing process at higher temperatures [11].

It is suggested that the presence of cobalt modifies the grain-boundary structure and vacancy concentration obtained during solution treatment, and ageing influences the grain size. The presence of cobalt at the grain boundary may also effect the step density and, hence, the boundary mobility, in a manner analogous to the effect of third elements on recrystallization [13]. For ageing temperatures below 380°C it is then suggested that cobalt diffuses with the boundary, whereas at higher temperatures the boundary moves at a faster rate than the diffusing cobalt atoms and the cobalt segregation effectively "evaporates", with the result that the boundary mobility is similar to that of the binary alloy. This effect will be further investigated.

5. Conclusions

1. The ageing of Cu 1.81 wt% Be 0.28 wt% produces, in addition to continuous precipitation, a discontinuous precipitation reaction which is nucleated at grain boundaries and grows into the adjoining grains.

2. The lamellar discontinuous precipitate designated for convenience as γ I, has the same structure, lattice parameter and orientation to the continuously precipitated γ' intermediate precipitate. γ I has a B2 superlattice structure with $a = 0.270$ nm and an orientation $(\bar{1}13)_\alpha // (130)_{\gamma I}$; $[110]_\alpha // [001]_{\gamma I}$.

3. The extent of the discontinuous precipita-

tion is strongly dependent upon temperature. Below 380°C the major mode is continuous precipitation, whereas above 380°C discontinuous precipitation predominates.

4. The equilibrium phase γ is formed only after extensive ageing treatments, e.g. 800 h at 425°C. γ has a B2 superlattice with $a = 0.270$ nm and with an orientation $(\bar{1}11)_\alpha // (\bar{1}10)_\gamma$; $[110]_\alpha // [001]_\gamma$.

5. A series of direct quench experiments showed that no G.P. zone solvus existed in the alloy at ageing temperatures up to 425°C.

6. In comparison with earlier work on the binary alloy the presence of cobalt was found to suppress the discontinuous precipitation mode for ageing temperatures $\leq 380^\circ\text{C}$.

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References

1. E. HORNBOGEN, *Met. Trans.* **3** (1972) 2717.
2. J. W. CAHN, *Acta Metallurgica* **7** (1959) 18.
3. A. R. ENTWISLE and J. K. WYNN, *J. Inst. Metals* **89** (1960) 24.
4. P. WILKES and M. M. JACKSON, *Met. Sci. J.* **3** (1969) 130.
5. W. BONFIELD and B. C. EDWARDS, *J. Mater. Sci.* **9** (1974) 398.
6. C. S. SMITH, *Trans. ASM* **45** (1953) 533.
7. A. H. GEISLER, J. H. MALLERY and F. E. STEIGERT, *Trans. Met. Soc. AIME* **194** (1952) 307.
8. A. KELLY and R. B. NICHOLSON, *Prog. Mat. Sci.* **10** (1963) 151.
9. W. GRUHL and G. WASSERMAN, *Metall.* **5** (1949) 141.
10. P. A. BECK, *J. Appl. Phys.* **20** (1949) 666.
11. H. THOMAS and U. WILKE-DORFURT, *Metal* **50** (1959) 466.
12. Y. MURAKAMI, H. YOSHIDA and S. YAMAMOTO, *Trans. Jap. Inst. Met.* **9** (1968) 11.
13. K. LUCKE and K. DETERT, *Acta Metallurgica* **5** (1957) 628.

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