

## A study of the nucleation characteristics of discontinuous precipitation in a pro-eutectic Cu-Ag alloy

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The formation of a solute-depleted matrix and a precipitate phase as a duplex product behind a boundary advancing into a supersaturated matrix is termed as discontinuous precipitation (DP) [1]. The initiation of DP naturally involves the nucleation of heterogeneous grain boundary precipitates and the motion of these grain boundaries which act as the sweeping short-circuit paths for solute transport [1, 2]. These processes, in turn, depend on the structure of individual boundaries [1, 3-5]. Studies on grain boundary and interphase interface structures have indicated that the two may not be identical in nature [6-10]. Information on the relative effectiveness of different types of interfaces in initiating DP is, however, not well documented, and this has provoked the present investigation on a Cu-7.7 at % Ag alloy. The pro-eutectic alloy [11] can provide a sample surface with or without strain, grain boundaries, eutectic boundaries with various curvature and discontinuous reaction fronts as the available sites for the onset of DP. Moreover, it is possible to generate artificial interfaces in this alloy quite easily, as follows. At the precipitation temperature (say, 400°C) the terminal solid solutions in the Cu-Ag system are almost pure copper or silver [11]. Thus, a coating of copper on a very large-grained polycrystalline specimen of copper-rich supersaturated solid solution may provide numerous grain boundaries at the precipitation temperature, whereas a similar coating with silver may generate incoherent precipitate-matrix type interfaces. It was also proposed to study the initiation of DP at these "synthetic interfaces" to obtain a better insight of the nucleation process.

About 300 g Cu-7.7 at % Ag alloy was prepared from 99.99% pure copper and 99.99% pure silver by induction melting. A large-grained ingot of diameter 10 mm was grown from this alloy under argon atmosphere by the vertical Bridgeman technique. Semicircular discs of thickness 5 mm were cut from the ingot by a low-speed diamond saw, and these specimens were homogenized at  $775 \pm 10^\circ\text{C}$  for 5 h under protective cover before quenching in water at room temperature. The flat faces of these specimens were polished to 0.5  $\mu\text{m}$  diamond followed by electropolishing in concentrated (about 85%)  $\text{H}_3\text{PO}_4$  for 20 min, using a stainless steel cathode with a d.c. potential of 2 V, which eventually removed all traces of surface strain on the specimens.

One of the two semicircular faces of a selected set of samples was cleaned with acetone and coated with pure copper (1.2  $\mu\text{m}$  thick) or pure silver (0.3  $\mu\text{m}$  thick) by a vapour deposition technique. The strain-free

surface of another uncoated specimen was scratch-strained by means of a Vickers pyramid indenter subjected to 5 kg load. All of the samples were encapsulated in evacuated Pyrex tubes, precipitated at 400°C for different lengths of time and finally quenched in water to room temperature. For metallographic studies, the specimens were polished with 0.5  $\mu\text{m}$  diamond and etched with a solution containing 200 g  $\text{CrO}_3$ , 20 g  $\text{Na}_2\text{SO}_4$ , 17 ml HCl (35%) and 1000 ml distilled water. All metallographic observations were made on the rectangular face of semicircular discs. A few elemental analyses were carried out with a Camscan-2DV scanning electron microscope fitted with a Link AN 10/25 energy-dispersive X-ray analysis system using the software package ZAF-4/FLS.

The microstructure of the specimens solution treated at  $775 \pm 10^\circ\text{C}$  for 5 h has the typical appearance of a "burnt structure", where the "nodules" of dark-coloured eutectic are distributed uniformly in the matrix (seen also in Fig. 1a), and most parts of the grain boundaries are covered with a layer of eutectic. The X-ray microanalyses reveal that the intergranular nodules and the eutectic at the grain boundaries are free from the "halo effect" often observed in the Cu-Ag alloys [12], where a broad region between the primary copper crystals and eutectic tends to be very low in copper content.

Precipitation in uncoated strain-free specimens shows that the free surface (marked by the arrow in Fig. 1a) does not initiate the DP, except where a grain boundary meets the surface, whereas extensive precipitation takes place at the grain boundaries (e.g. Fig. 1b). Similar observations have also been reported for Ni-In and Ni-Sn alloys [13]. When the surface of the solution-treated strain-free specimen is mechanically polished before precipitation at 400°C, the DP starts at the surface (cf. Fig. 2a), possibly due to the strain induced by the mechanical polishing. This postulate is supported by the result of precipitation in the scratch-strained sample (cf. Fig. 2b), where well-developed precipitate colony forms around the scratch marking.

Two possible ways the strain can promote nucleation are: (1) by introducing grain boundaries as a result of recrystallization at the precipitation temperature which, in turn, provide the nucleation sites for DP, and (2) by enhancement of the driving force for nucleation of the precipitates caused by the stored energy of cold work. The extensive precipitation at the copper-coated strain-free specimen surface shown in Fig. 3a evidences the dominant role of the former factor, because copper-coating can generate large

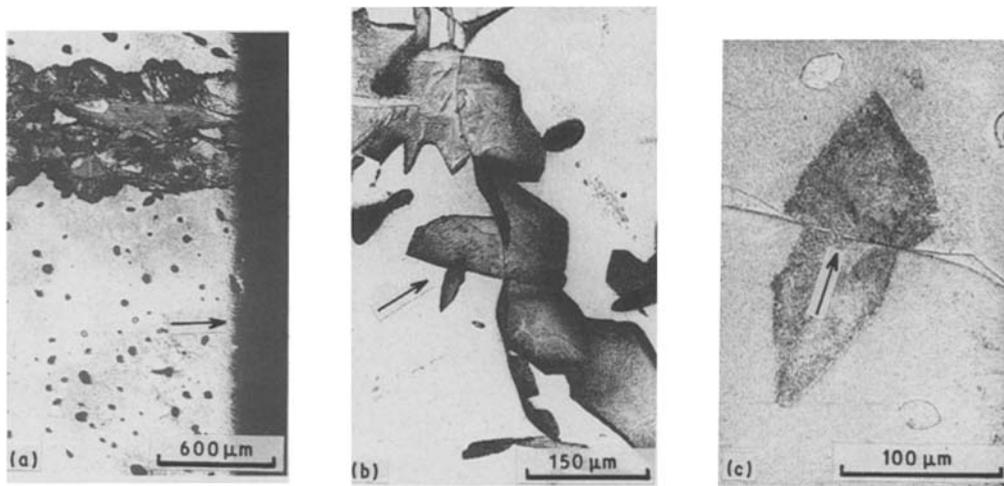


Figure 1 Microstructures of strain-free specimens precipitated at 400°C for 6 h (see text). The mottled appearance of the micrographs is due to the colour-tinting effect of chromic acid.

numbers of grain boundaries at the bulk-coating interface without straining the sample. In fact, any diffusion of copper from the coating into the supersaturated matrix (at the precipitation temperature) would reduce the driving force for precipitation by diminishing the local solute supersaturation. It may be mentioned that in the Cu-Ag system the diffusion of silver (i.e. the faster-diffusing species) does not cause diffusion-induced grain boundary migration (DIGM) in copper [14] and hence, DIGM cannot account for the present observations.

The microstructure of the silver-coated strain-free specimen precipitated at 400°C shows precipitate colonies at some isolated patches of the coated surface (cf. Fig. 3b). The silver coating on the supersaturated solid solution can readily provide incoherent precipitate-matrix type interfaces for the deposition of silver-rich phase (about 98.2 at% silver [11]) at 400°C. Any such precipitation should move the bulk-

coating interface into the bulk material. In contrast to grain boundaries, however, such moving interphase interfaces cannot move without long-range mass transport. Since the silver coating is not as effective as copper coating in triggering the DP (cf. Fig. 3), it appears that the nucleation of the second phase may not be the rate-limiting step for the onset of DP in the Cu-Ag alloy.

Investigations of DP in Al-Li [5], Al-Zn [15], Cu-In [16] and Fe-Mn-V-C [17] alloys have indicated that the type of boundary curvature may have some influence on the development of precipitate colonies. The eutectic nodules in the present alloy provide interfaces with convex forward curvature (e.g. Fig. 1a). Moreover, the constituent phases in the eutectic and in the discontinuous precipitate colonies are also identical [11]. Yet, in experiments performed here, none of the nodules are found to initiate DP (e.g. Fig. 1a).

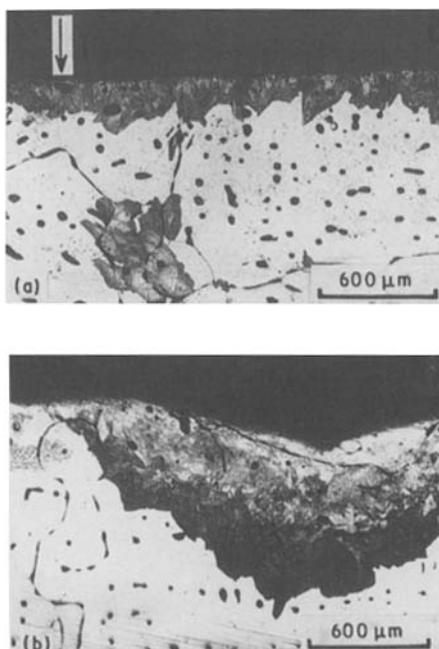


Figure 2 Microstructures of the Cu-Ag alloy precipitated for 4 h at 400°C, showing discontinuous precipitation triggering (a) at the surface (shown by arrow) as a consequence of prior mechanical polishing and (b) around the scratch marking.

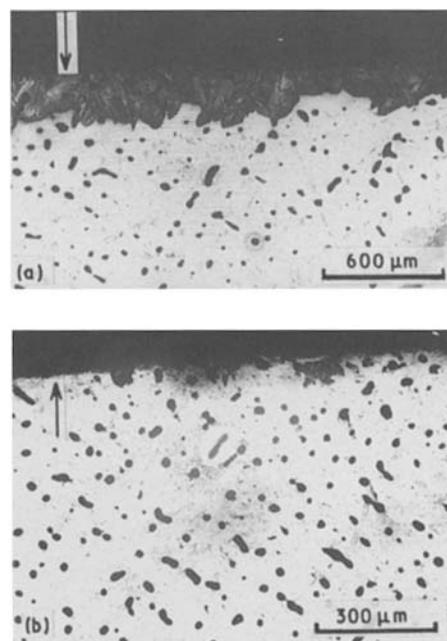


Figure 3 Microstructures displaying the nucleation characteristics in the (a) copper-coated and (b) silver-coated specimens, precipitated at 400°C for 4 h (see text). The arrows point to the coated surfaces.

In contrast to eutectic nodules, the grain boundary eutectic regions can have interfaces with convex forward, as well as concave forward, curvatures. The inability of these eutectic–matrix interfaces to initiate DP is borne out by the fact that the segment of the grain boundaries free from eutectic (e.g. the portion indicated by the arrow in Fig. 1c) appear to be the favoured site for the onset of DP.

Fig. 1b shows that the discontinuous reaction fronts in the present alloy are usually faceted, and here the arrow illustrates that they can act as the nucleation site for newer colonies. The analogous mode of nucleation, termed “budding” [1, 18], has been reported in a high-strain system like Ni–Au, where growth fronts are also distinctly non-planar. It may be pointed out that the discontinuous reaction fronts also contain interphase interfaces similar to the eutectic boundaries in the Cu–Ag systems. The theory of precipitation on migrating boundaries [16] emphasizes the ability of the reaction fronts to undergo small thermally activated movement and, perhaps, the mobility of the discontinuous reaction fronts is instrumental in initiating newer colonies by them. The inability of eutectic–matrix interfaces to nucleate precipitate colonies may indicate their lack of mobility compared with that of discontinuous reaction fronts.

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