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Silver dissolution on copper-based alloys

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Electrical resistivity measurements and scanning electron microscopy was used to study the dissolution of silver on Cu–Ag and Cu–Al–Ag alloys. The results seem to indicate that the dissolution temperature is affected by the addition of aluminium.

1. Introduction

It is known that the bronzes show important characteristics, such as chemical stability (Cu–Al), good mechanical properties (Cu–Al, Cu–Si), and that small additions of silver to the aluminium bronzes improve some of their properties, e.g. hardness [1] and stress corrosion [2] without appreciable modification in their plasticity and workability. The Cu–Al–Ag alloy can also be used to study the influence of the electronic and size effects in the presence and ranges of stability of various typically metallic phases [3].

In this work, the distribution of silver precipitates and the influence of the composition in the electrical resistivity of some copper-based alloys were studied, using scanning electron microscopy (SEM), energy-dispersive X-ray microanalysis (EDX) and the measurement of electrical resistivity changes with the equilibrium temperature.

2. Experimental procedure

Cylindrical rods and wires of about 3.0 and 0.5 mm diameter, respectively, were prepared according to the procedure described elsewhere [4]. Table I shows the compositions of the alloys studied, determined by chemical analysis.

The samples were annealed at 750 °C for 240 h for homogenization, and water quenched from 420, 500, 530 and 750 °C, after 1 h annealing at each temperature. The identification of the phases was made by optical and electronic microscopy and microprobe analysis, using a Neophot 30 Carl Zeiss, a Jeol JSM-840 and a JSM-T30 SEM.

The electrical resistivity measurements were made at equilibrium temperatures using a Leeds-Northrup potentiometer with precision up to 10^{-7} V.

3. Results and discussion

Fig. 1 shows the electrical resistivity versus temperature curves for pure copper (Curve 1) and for the Alloys A (Curve 2), B (Curve 3), C (Curve 4) and

TABLE I Compositions of the alloys (wt %)

Alloy	Copper	Silver	Aluminium
A	95.1	–	5.2
B	95.0	5.0	–
C	91.3	4.7	4.3
D	86.6	5.3	8.4

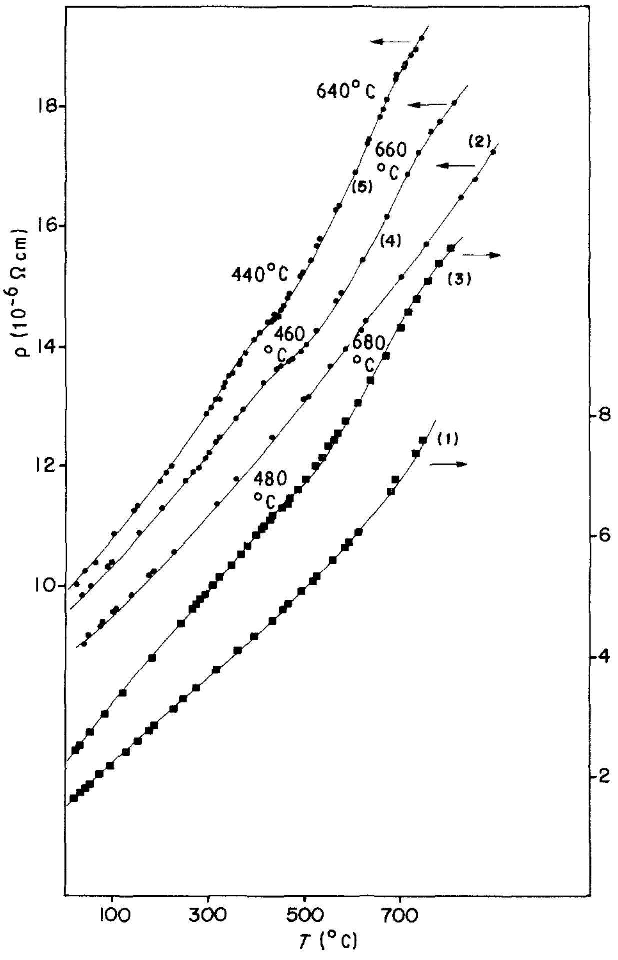


Figure 1 Electrical resistivity changes with the equilibrium temperature.

D (Curve 5). Curves 1 and 2 have no inflection points, indicating that Alloy A has no phase change over all the studied temperature range. As expected, this curve is a little higher than that for the pure copper, owing to the higher electrical resistivity of the copper–aluminium solid solution. Curve 3, which corresponds to Alloy B, shows two inflection points, which indicate the occurrence of some transformation in the copper–silver solid solution. Curves 4 and 5, corresponding, respectively, to Alloys C and D, also show two inflection points at temperatures a little lower than those for Curve 3.

Fig. 2 shows the scanning electron micrographs for Alloys A and C after annealing. Alloy A has only one phase and Alloy C has two phases, the dark one corresponding to a solid solution of silver and aluminium in copper and the light one corresponding to a silver-rich phase.

Fig. 3 shows the aluminium-mapping for Alloy A and the silver-mapping for Alloy C. It is possible to see that aluminium is homogeneously distributed on Alloy A and to see the formation of silver-precipitates on Alloy C.

Figs 4 and 5 show, respectively, the scanning electron micrographs obtained for Alloys A and C quenched from temperatures a little lower and higher than those at which the inflection points were verified (see Fig. 1). From these micrographs one can see that Alloy A stays monophasic at all temperatures studied and Alloy C shows an alteration in the silver-rich phase distribution: at 420 °C, it shows a linear silver distribution and at 500 °C it shows silver precipitates.

This redistribution probably occurs with a silver absorption by the matrix due to the increase in its solubility with temperature, and with the growth of some precipitates by silver diffusion. The silver solubility continues to increase with the temperature until its total dissolution, as shown by the micrograph for the alloy quenched from 750 °C.

The curves from Fig. 1 show that aluminium, in addition to increasing the electrical resistivity of the alloys, also affects the localization of the inflection points.

From Figs 4 and 5 the inflection points on Curve 3, which corresponds to the Cu–5.0 wt % Ag alloy, may be related to the dissolution of silver in the copper matrix.

According to Hansen and Anderko [5], at the composition studied here (5.0 wt % Ag), the silver dissolution in the Cu–Ag alloy starts at about 700 °C.

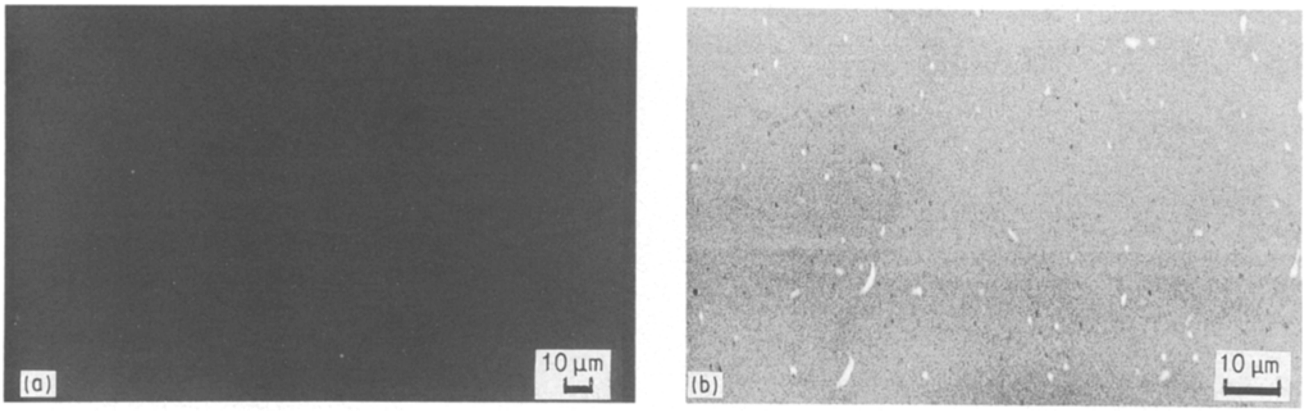


Figure 2 Scanning electron micrographs for (a) Alloy A and (b) Alloy C after annealing.

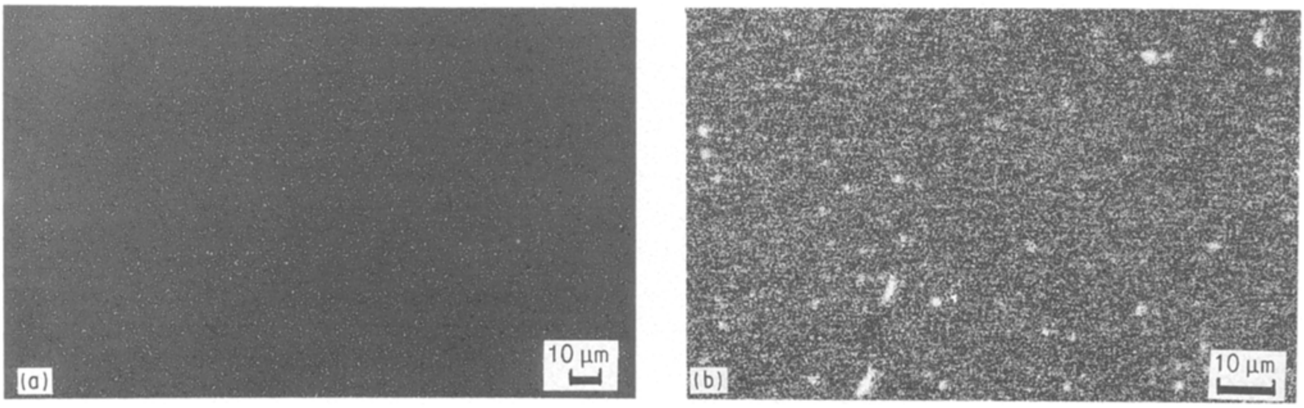
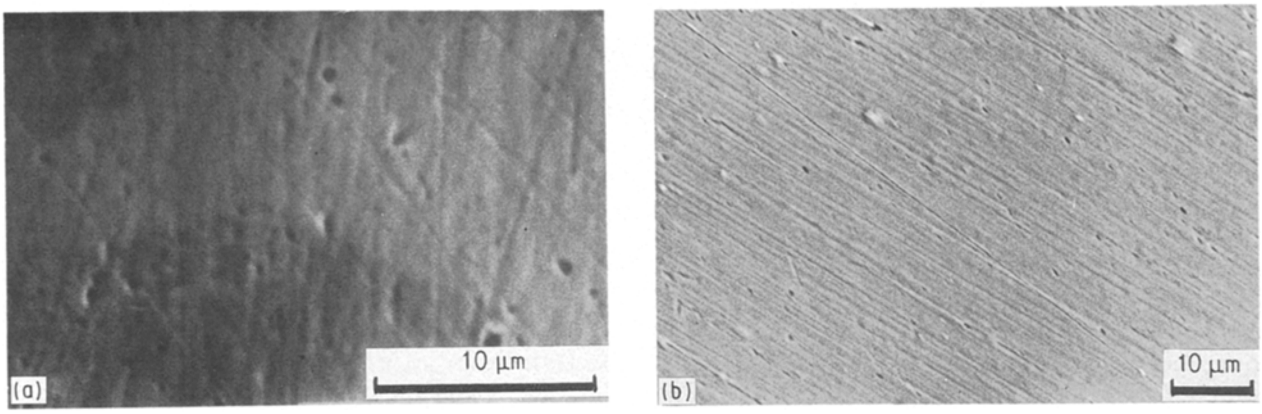


Figure 3 (a) Aluminium-mapping for Alloy A and (b) silver-mapping for Alloy C.



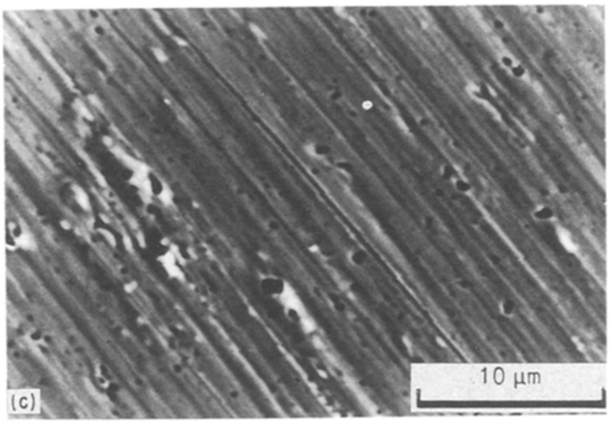


Figure 4 Scanning electron micrographs for Alloy A quenched from (a) 420 °C, (b) 500 °C and (c) 750 °C.

This seems to indicate that the first inflection point on Curve 3, at about 480 °C, is produced by a rearrangement of the silver atoms at the beginning of the dissolution process, which lowers the electrical resistivity of the alloy. The second inflection point, at about 680 °C, may indicate the passage from the solid solution to the copper-dissolved silver phase and then the electrical resistivity of the alloy takes a slightly higher value.

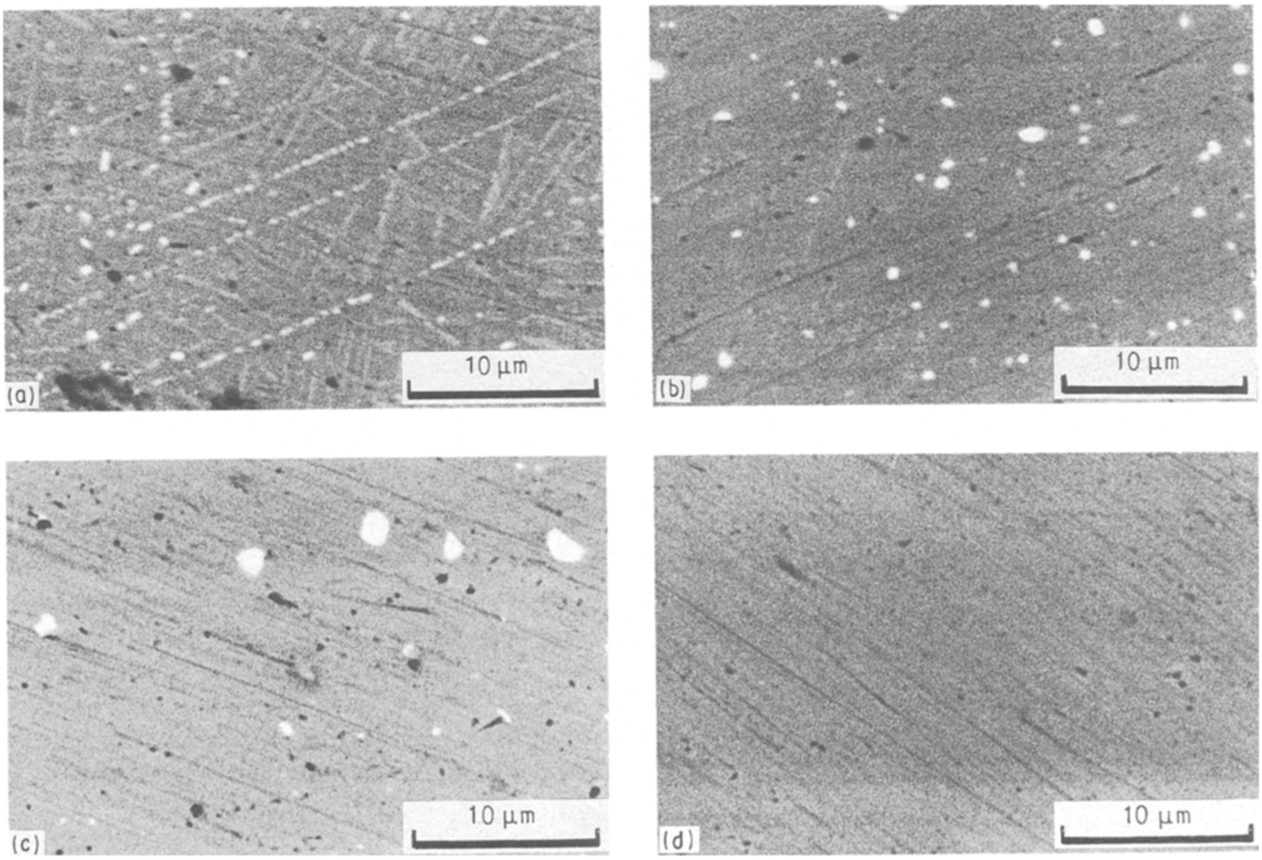


Figure 5 Scanning electron micrographs for Alloy C quenched from (a) 420 °C, (b) 500 °C and (c) 530 °C and (d) 750 °C.

The presence of inflection points on Curves 4 and 5 seems to be related to the same mechanism described for Curve 3 and their occurrence at lower temperatures may be due to differences in the composition.

The effect of aluminium addition to the Cu–Ag alloy seems to be to produce an enlargement of the copper-dissolved silver region and this would explain the lowering of the inflection temperatures with increasing aluminium contents, because with this the passage from the solid solution of silver in copper to the copper-dissolved silver phase must occur at a lower temperature.

Acknowledgements

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