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High-temperature tensile properties of Cu–Ag composites prepared by solution–precipitation of electroformed multilayered alloys

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Appropriate heat treatments have been shown to convert Cu–Ag multilayered structures, obtained by a new electrochemical periodic displacement process, into homogeneous alloys or dispersed particle composites. The high-temperature tensile properties of the latter are comparable to those obtained for similar materials prepared by conventional metallurgical techniques. Preliminary data also indicate that the as-deposited material may exhibit superplastic behaviour under stress applied immediately at high temperature.

1. Introduction

Copper composites containing dispersed nanoscale particles of an immiscible metal that stabilizes the high-temperature mechanical properties, are currently of great interest for high-heat-flux applications in advanced aerospace engines and actively cooled leading-edge structures. One promising approach to the fabrication of the odd shapes often required is electrodeposition, which also has the potential of providing high-quality materials with particles of uniform size and distribution. However, co-deposition of metals having significantly different deposition potentials is usually plagued by nodule formation and variable composition associated with extremely fast deposition of the more noble metal at the relatively negative potentials required for deposition of the less noble component.

Recently, a new periodic displacement electroforming process has been described [1, 2] which permits deposition of high-quality Cu–Ag multilayered alloys of controlled composition. Essentially, a copper plating bath containing a small concentration of silver ions is employed and copper deposition is interrupted periodically to permit some of the deposited copper to be electrolessly displaced by silver from the electrolyte. In this case, appreciable amounts of silver can be included as multilayers in the copper matrix using a silver ion concentration sufficiently small to avoid nodule formation. Good control over the deposit composition is ensured by the relatively slow rate of the displacement process.

In the present paper, the microstructure and tensile properties of dispersion-strengthened Cu–Ag materials obtained by solution–precipitation heat treatments of electroformed Cu–Ag multilayers are presented.

2. Experimental procedure

The specimen preparation conditions used are described in detail elsewhere [2]. Deposition was performed at 60 °C from a standard copper cyanide bath containing 0.25 m*M* AgCN. The cathode was a rotating (750 r.p.m.) 304 stainless steel cylindrical mandrel (2.5 cm diameter, 7.6 cm long) protected from the cyanide electrolyte by a 2 μm thick pyrophosphate copper basal layer. Copper electrodeposition was performed at constant current ($-30\ \mathrm{mA\,cm^{-2}}$) and the "off time" for the displacement reaction was always 18 s. The deposited silver content was varied by adjusting the number of silver layers, which were calculated to be 2.5 nm thick (neglecting the porosity of the silver deposit).

Two silver contents, 3.8% and 6.5%, corresponding to 500 and 1000 silver layers, respectively, were investigated. Note that 1.0% Ag is co-deposited during copper deposition so that doubling the number of silver layers does not double the silver content. The amount of silver contained in the displacement layers (after subtraction of the 1.0% co-deposited silver is 2.8% for 500 layers and 5.5% for 1000 layers, as expected (within 0.1%).

Deposits were nominally 50 μm thick and yielded six test specimens, cut parallel to the axis of the cylindrical cathode. Specimen strips were clamped between dog-bone shaped case-hardened steel plates and ground to a dog-bone configuration having a reduced section width of 6.3 mm and a gauge length of 2.8 cm. Tensile testing was performed at a constant crosshead speed of $0.1\ \mathrm{mm\,min^{-1}}$ and inert gas purging was employed to prevent oxidation of the specimen at elevated temperatures.

The two solution-precipitation age-hardening treatments used in the present work are designated A and Z. They are typical of those used for dissolution and controlled precipitation of silver in the Naroly A and Naroly Z (zirconium added) Cu–Ag alloys often employed for high-heat-flux aerospace applications. The A-treatment involves solution at 900 °C for 20 min,

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relatively slow cooling (56 °C min^{-1}) to 538 °C, followed by holding the specimen at 482 °C for 8 h. In this case, much of the dissolved silver is precipitated during the slow cooldown. The Z-treatment involves solution at 927 °C for 2.0 h, a water quench to room temperature within 5 s, and holding at 482 °C for 4 h. Most of the silver presumably precipitates during the latter precipitation phase of the Z-treatment.

Prior to heat treatment, specimens were usually sealed under argon in glass tubes. For rapid quenching, specimens were individually heat treated in a flowing argon atmosphere and then dropped into water at room temperature.

Specimens for scanning electron microscopy (SEM) examination were potted in acrylic resin and polished first on silicon carbide paper and then on successively finer aqueous alumina slurries (to 0.05 μm particle size). The polished cross-sections were etched in ammonium peroxide solution (40 ml concentrated NH_4OH and 2 ml 30% H_2O_2 in 40 ml water) to reveal the microstructure, silver segregations being particularly accented, because silver is not attacked by this solution.

3. Results and discussion

3.1. Deposit microstructure

As seen in Fig. 1, the as-deposited multilayered Cu–Ag material is extremely fine grained (average grain size less than 0.1 μm), as is generally the case for cyanide copper deposits. The individual 2.5 nm silver layers cannot be resolved via SEM, but distinct striations indicative of a layered structure can be developed by strong etching.

Fig. 2 shows that simple heat treatment at 528 °C for 5 h produces, in addition to copper grain growth, silver agglomeration into roughly spherical particles somewhat less than 1 μm diameter; white areas in the micrographs were shown by energy dispersive X-ray analysis (EDAX) to correspond to silver segregations. The latter are more obvious for the higher contrast micrograph shown as an insert in Fig. 2b. Note that the silver particles are more numerous (per unit area) in the specimen with the higher silver content, as expected. It is also apparent that the silver inhibits copper grain growth because the average grain size for the 6.5% Ag content (Fig. 2b) is obviously smaller than that for 3.8% Ag (Fig. 2a). This effect is probably attributable to the presence of a submicrometre grain-boundary layer of silver (evident as white lines along the grain boundaries), rather than to the larger silver particles which do not seem to form preferentially at grain boundaries.

Fig. 3 shows scanning electron micrographs for mildly etched Cu–Ag specimens after the solution phase of the age-hardening A-treatment (900 °C for 20 min; cool down at 56 °C min^{-1}), during which some silver precipitates. There is a relatively even distribution of silver particles but those at grain boundaries are larger (about 0.5 μm diameter), which is most evident for the higher silver concentration in Fig. 3b (note higher magnification). It is also clear that considerable grain growth has occurred during this solution treatment. Fig. 4 shows micrographs for the same specimens as in Fig. 3 after strong copper etching, which exposes more of the underlying silver (white areas). The silver precipitated within grains is seen to form thin filaments that are aligned for a given grain and seem to be longer and thicker for the higher silver content (Fig. 4b).

During the precipitation phase of the age-hardening A-treatment (482 °C, 8 h), the amount of silver precipitated at grain boundaries apparently increases, as is evident in Fig. 5a. At the higher silver content, such grain-boundary precipitation growth is obscured, even for lightly etched specimens (Fig. 5b), by the large density of silver present within grains. Comparison of the micrographs in Fig. 5 (note scale difference) reveals that the grain size after the age-hardening treatment is appreciably smaller for the higher silver content, 10–30 μm compared to 30–60 μm. This implies that the precipitated silver limits copper grain growth at

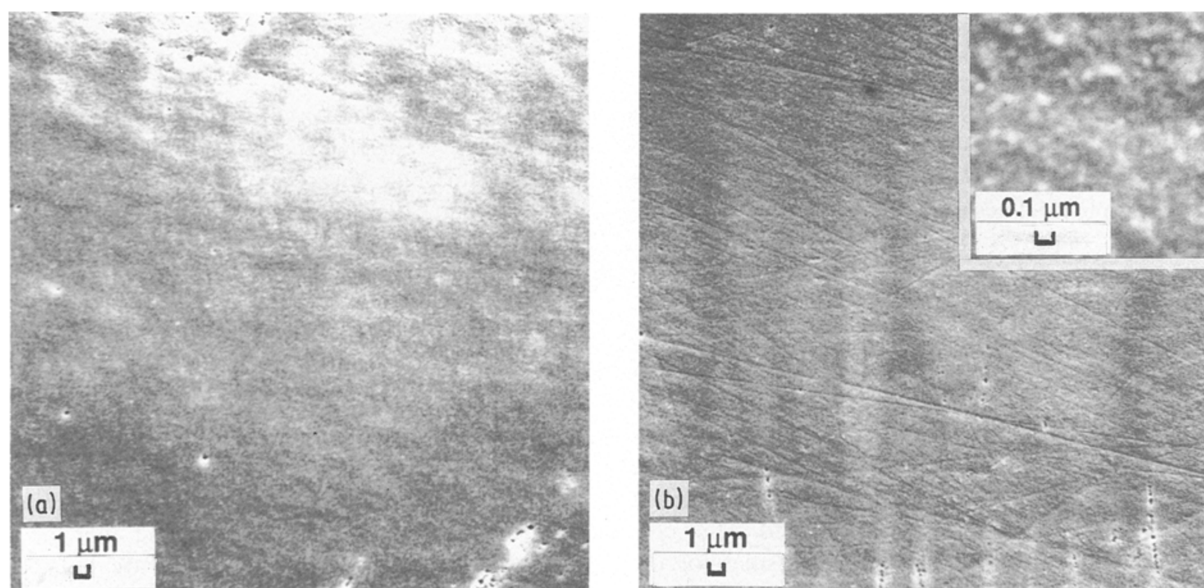


Figure 1 Scanning electron micrographs of as-deposited Cu–Ag multilayered materials. (a) 3.8% Ag, (b) 6.5% Ag.

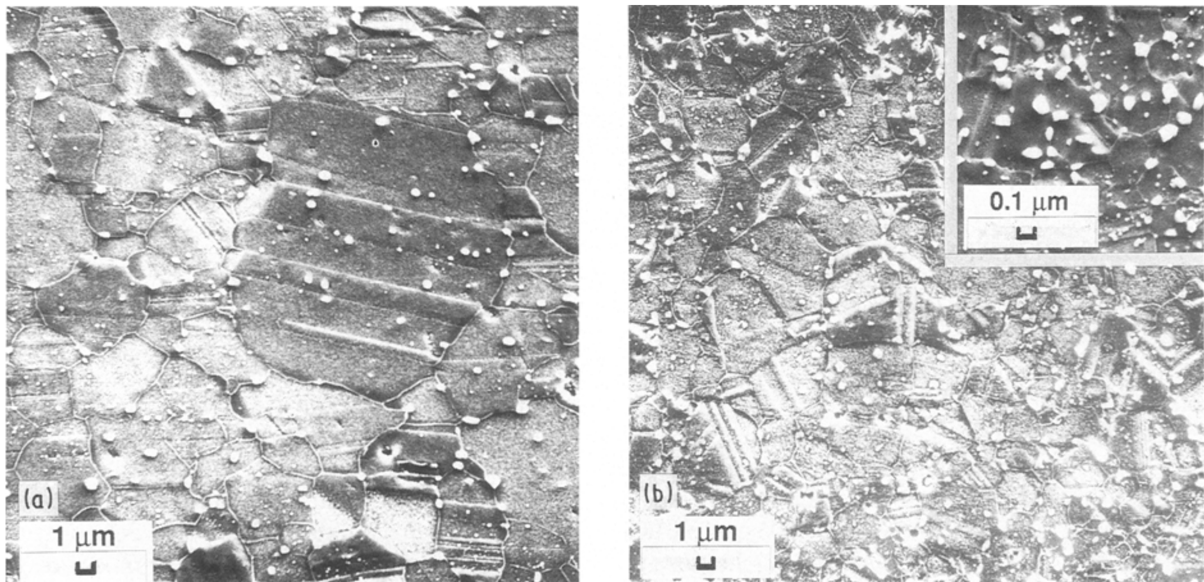


Figure 2 Scanning electron micrographs of electroformed Cu–Ag materials after 5 h at 538 °C. (a) 3.8% Ag, (b) 6.5% Ag.

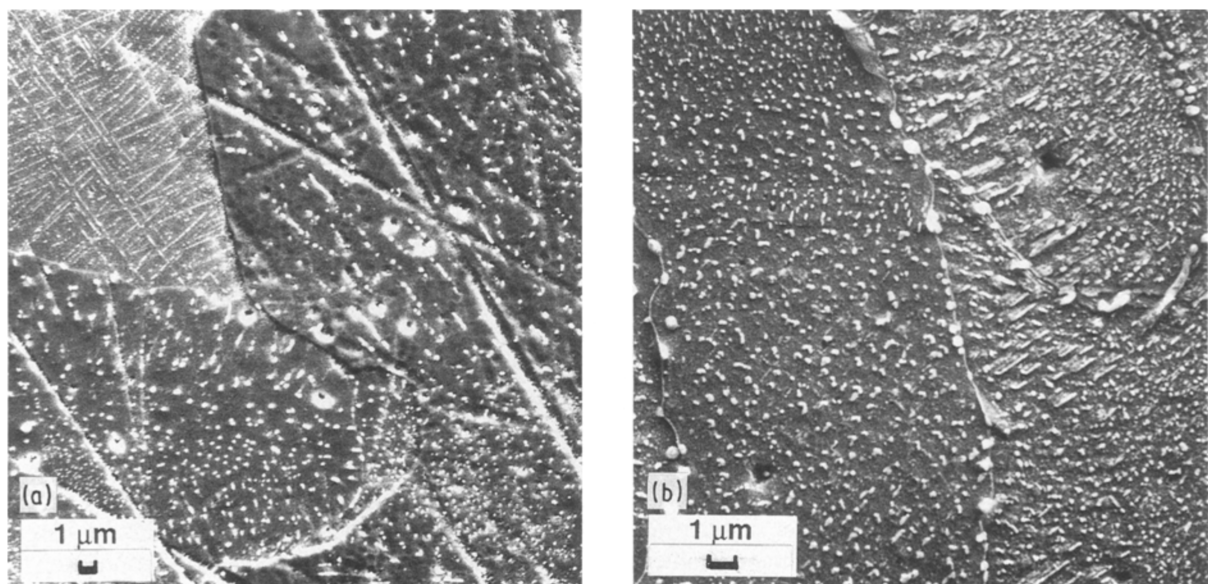


Figure 3 Scanning electron micrographs of electroformed Cu–Ag materials after the solution phase of the age-hardening A-treatment (specimen lightly etched). (a) 3.8% Ag, (b) 6.5% Ag.

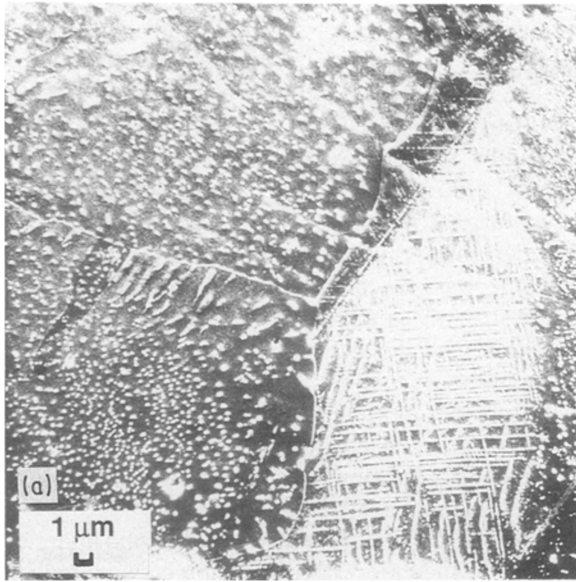
high temperatures and that the optimum silver level is certainly more than 4% for the A-treatment. Note that some grain boundaries in the 3.8% material span the 50 μm sample thickness, as shown in Fig. 5a.

3.2. Deposit texture

The X-ray diffraction data in Table I show that as-deposited Cu–Ag material exhibits the preferred orientation typical of cyanide copper deposits, i.e. (1 1 1) planes aligned parallel with the Cu–Ag layers (perpendicular to the deposition direction). Note that the relative intensity value corresponding to the dominant crystallographic orientation is underlined. After correction for the differences in atom densities for the various planes, the Cu(1 1 1) diffraction intensity is an order of magnitude greater than those for the other two principal copper orientations. It is also evident that the silver displacement layers grow epitaxially and exclusively on the Cu(1 1 1) planes; the Ag(1 1 1)/Cu(1 1 1) intensity ratio of 6.6% agrees well with the percentage of silver present as multilayers (5.5%). The age-hardening A-treatment practically eliminates this (1 1 1) texture for both copper and silver (Table I).

3.3. High-temperature tensile properties

Table II gives the tensile test data for electroformed Cu–Ag specimens pull tested at 538 °C in argon after a simple heat treatment (538 °C, 5 h), and after the two solution–precipitation age-hardening treatments (A and Z). If the thinness of the specimens (50 μm) and unoptimized heat treatments are taken into account,



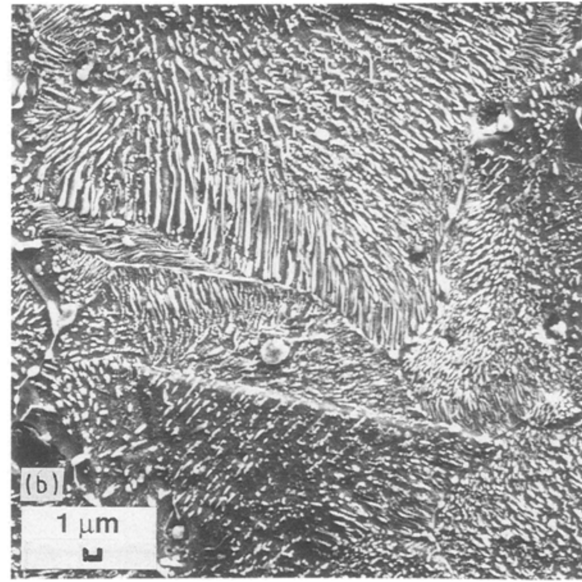
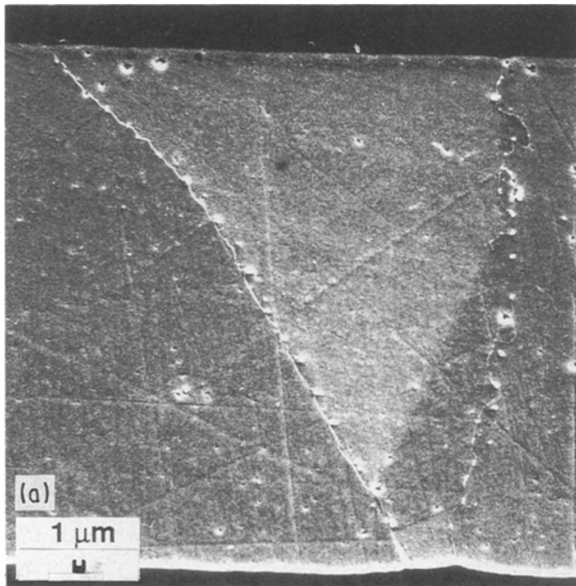


Figure 4 Same as Fig. 3, but specimens strongly etched.



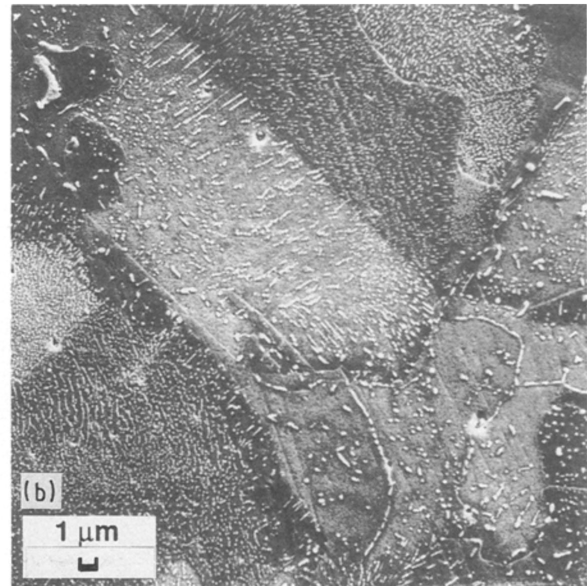


Figure 5 Scanning electron micrographs of electroformed Cu–Ag materials after the complete age-hardening A-treatment. (a) 3.8% Ag, (b) 6.5% Ag.

these results are very encouraging. In all but one case, the yield strength (YS) exceeds the minimum acceptable value for Naroly A, i.e. 60 MPa, and some of the Z-treated specimens would also qualify in terms of the ultimate tensile strength (UTS) requirement for Naroly A (90 MPa).

It is likely that thicker specimens would yield higher values for both strength and elongation, and more consistent results. As discussed above, the grain size for heat-treated material is comparable to the deposit thickness so that failure can occur via fracture or slippage at only one weak grain boundary. Fatal edge flaws are also more likely for thin specimens and probably account for the wide variation in measured elongation values. In addition, because even a small amount of necking represents an appreciable fraction of the deposit thickness, measured elongations probably approach true strain values and should be lower than those obtained when appreciable necking occurs.

3.4. Apparent superplastic behaviour

For two Cu–3.3%Ag specimens tensile tested under argon at 540 °C without prior heat treatment, extremely high elongation values were obtained. An elongation of 84% was observed for one specimen which was subsequently found to have failed at the sample gripping device rather than within the gauge length. In the second case, the tensile test was stopped at an elongation of 125% because the operator mistakenly thought that the specimen must have slipped from the grips. A more systematic study is required but such high values suggest superplastic behaviour.

TABLE I Relative intensities of diffracted X-rays for electroformed Cu–6.5% Ag materials

	Lattice spacing	As-deposited multilayer	After A-treatment
Cu(1 1 1)	2.09	13 290	3830
Cu(2 0 0)	1.81	1 610	4430
Cu(2 2 0)	1.28	950	1930
Ag(1 1 1)	2.36	880	530
Ag(2 0 0)	2.04	0	490
Ag(2 2 0)	1.45	0	490
Ag(3 1 1)	1.23	0	520

TABLE II Tensile test data for Cu–Ag alloys at 538 °C

Ag (%)	Heat treatment (°C/h)		YS (MPa)	UTS (MPa)	Elongation (%)
3.8	538/5		59	76	15
			50	64	2.4
		Average	55	70	8.7
6.5	538/5		43	62	3.6
			34	37	3.7
		Average	39	50	3.7
3.8	A		60	80	6.0
			72	74	1.6
		Average	66	77	3.8
3.8	Z		74	103	11
			55	61	0.8
		Average	65	82	5.9
6.5	Z		88	90	2.4
			72	77	3.7
		Average	80	84	3.1

A = 900 °C (20 min); cool 56 °C min^{-1} to 538 °C; 482 °C (8 h)
Z = 927 °C (2 h); water quench within 5 s; 482 °C (4 h)

4. Conclusions

Solution–precipitation heat treatments can be used to convert Cu–Ag multilayered alloys prepared by a new periodic displacement electroforming process into materials containing dispersed silver particles. Based on SEM analysis, 2.5 nm silver layers agglomerate to roughly spherical particles (about 1 μm diameter) over 5 h at 538 °C, and dissolve readily (within 20 min) in the copper matrix at 900 °C. The dissolved silver precipitates at grain boundaries as both continuous grain-boundary films and spherical particles, and as thin filaments within grains. For one solution–precipitation treatment of a 6.5% Ag specimen, silver precipitated at grain boundaries apparently limited the copper grain growth to the 10–30 μm range.

The mechanical properties measured at 538 °C for the silver-stabilized copper material, e.g. yield strengths of 70–90 MPa, are comparable to those obtained for similar alloys prepared by conventional metallurgical methods. This is especially remarkable because the specimens were only 50 μm thick so that necking was presumably negligible and the average grain size was comparable to the sample thickness. In addition, the deposition conditions and heat-treatment cycles were chosen somewhat arbitrarily and are certainly not optimum. Significant improvement in the deposit mechanical properties can be expected as the process conditions are optimized and thicker specimens become available.

Because the strength of Cu–Ag (Naroly) materials is known to increase with decreasing copper grain size, improved tensile properties could presumably be obtained for electroformed materials if the initial fine grain structure could be retained through the solution–precipitation process. This may be possible because the nanoscaled silver layers presumably would dissolve in the copper matrix at much shorter times (or lower temperatures) than those used in the present work. Because most of the grain coarsening occurred during the solution phase, limiting the time for the solution treatment would probably result in finer copper grains and better tensile properties.

Finally, the as-plated Cu–Ag layered material is apparently superplastic when deformed immediately at high temperatures. It may be possible to exploit this property to form odd-shaped Cu–Ag parts whose properties would then be improved and stabilized via appropriate solution–precipitation treatments.

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