JOURNAL OF MATERIALS SCIENCE LETTERS 11 (1992) 1104–1106

Development of high-strength, high-conductivity copper alloys by rapid solidification

J. A. JUAREZ-ISLAS, R. PEREZ, L. A. ALBARRAN, V. RIVERA*, L. MARTINEZ
*Lab. De Cuernavaca, Instituto de Fisica-unam, CP 62191, Apdo. Postal 139-B, Cuernavaca, Morelos, Mexico and *Instituto de Investigacion de Materials, Circuito Ext. Ciudad Universitaria, Del. Coyoacan, CP 04510, AP 70-360, Mexico*

Rapid solidification and mechanical alloying are being employed to develop high-strength, high-conductivity Cu alloys because they offer advantages not achievable by conventional ingot metallurgy practice. Most attention has been focused on rapid-solidification processing due to the beneficial effects of this technique on the structure and properties of such materials and as an alternative route to the production of engineering components. The effects of rapid solidification on structure include (among others) solid-solubility extension of alloying additions that are relatively insoluble at equilibrium and size refinement.

Cu alloys developed (with the aim of achieving high strength and high conductivity) via rapid solidification [1–9] include binary Cu–Cr [1, 5, 7], Cu–Zr [1, 3, 9], Cu–B [7] and ternary Cu–Cu–X (X = Zr, Ti or Mg) [5, 7], and Cu–Nb and Cu–Cr [8] via mechanical alloying.

This letter reports the mechanical and electrical properties of rapidly solidified Cu–Cr, Cu–Cr–Zr and Cu–Cr–Be alloys via microhardness and conductivity measurements before and after heat treatment. Lattice parameter determination and X-ray diffraction give details of the solid-solubility extention achievable in those alloys.

Cu alloys were prepared from oxygen-free high-conductivity Cu (99.99% purity), electrolytic Cr (99.8%), sponge Zr (99.99%) and ribbon of Be (99.99%) by induction vacuum melting. The chemical compositions were confirmed by wet analysis to an accuracy of ± 0.02% solute, as shown in Table I. Samples were melt-spun on to a Cu wheel at 3000 r.p.m. under an Ar atmosphere. The resultant ribbons were 3 mm wide and about 50 μm thick. Chemical analysis presented no significant losses of solute on remelting and spinning. Isochronal heat treatments were carried out on rapidly solidified ribbons 10 cm long, these ribbons being wrapped in Cu foil and sealed under Ar in silica capsules 15 mm in diameter. The specimens were then heat-treated in Ar in their capsules for 60 min at 100, 200, 300, 400, 500 and 600 °C in a resistance furnace. The capsules were then broken and the specimens directly water-quenched. X-ray diffraction was used with the purpose of determining the lattice parameter of the alloys and to identify any second phases in both the as-rapidly solidified and heat-treated conditions. A Siemens D500 X-ray diffractometer was used with Cu radiation. Vickers' microhardness measurements were made on transverse sections of the splats to evaluate their microhardness. Microhardness testing was performed using a Matzusawa MHT2 miniload Vickers' microhardness tester with a 10 g load. Microhardness values were the average of at least 20 measurements positioned so as to avoid occasional second-phase inclusions. The electrical resistivity was determined by measuring the resistance of the ribbon samples with a Hewlett-Packard 419 2A impedance analyser.

Table II shows the lattice parameter data for Cu–Cr, Cu–Cr–Zr and Cu–Cr–Be (data for as-rapidly-solidified pure Cu are also included) alloys with and without heat treatment. The lattice parameter, a_0, for the three alloys in their as-rapidly-solidified condition showed an increase compared with data for as-rapidly-solidified pure Cu. When the alloys are heat-treated up to 400 °C for 1 h, the values of a_0 for the three alloys were almost the same. At 500 °C the alloys showed a decrease in a_0 similar to the value of the as-rapidly-solidified pure Cu. Second phases identified by X-ray diffractometry in the three alloys at 500 °C were as follows: in the Cu–Cr and Cu–Cr–Be alloys only a Cr-rich phase was detected and for the Cu–Cr–Zr alloy the Cr-rich phase plus Cu_5Zr were detected. These values of lattice parameter, a_0, together with second-phases identification at 500 °C showed that extension of the solid-solubility of solute elements (Be, Cr or Zr) in the f c c α-Cu has already been

TABLE I Chemical analysis of the Cu alloys

Alloy	Cr (wt %)	Zr (wt 5)	Be (wt %)
Cu–Cr	1.02		
Cr–Cr–Zr	2.72	0.25	
Cu–Cr–Be	0.975		0.215

TABLE II Variation in lattice parameter, a_0 (nm) for the f c c α-Cu alloys as a function of temperature of heat treatment (1 h)

Alloy (wt %)	As-rapidly-solidified	200 °C	400 °C	500 °C
Cu	3.6148			
Cu-1.02Cr	3.61484	3.6188	3.6187	3.6147
Cu-2.72Cr-0.25Zr	3.6205	3.6210	3.6205	3.6150
Cu-0.98Cr-0.2Be	3.6175	3.6175	3.6172	3.6147

achieved by rapid solidification and retained in solid solution up to 400 °C.

Table III shows the microhardness Vickers response of the three melt-spun Cu alloys in their as-rapidly-solidified condition and after heat treatment at 100, 200, 300, 400, 500 and 600 °C for 1 h. These data are plotted in Fig. 1, which shows that the Cu–Cr–Zr alloy was the alloy which showed the best response to the ageing treatment, with a peak hardness of 261 $kg\,mm^2$ at 400 °C. The same figure includes microhardness data for an argon-atomized Cu–10Ni–8Fe alloy [10] in which the microhardness value is at its maximum in the as-rapidly-solidified condition (about 159 $kg\,mm^{-2}$) and then decreases progressively as the temperature of heat-treatment increases, being its value of microhardness at 400 °C (1 h) 56% lower than that obtained for the Cu–Cr–Zr alloy under the same conditions of heat-treatment.

Fig. 2 shows data for electrical conductivity (International Annealed Copper Standard; % IACS) of melt-spun Cu alloys as a function of temperature up to 600 °C (1 h) of heat-treatment. The Cu–Cr and Cu–Cr–Zr alloy showed similar behaviour of electrical conductivity (and superior to that of Cu–Cr–Be alloy) up to 600 °C. It was in all cases the Cu–Cr alloy that showed better values of electrical conductivity than the other two alloys and its value was superior (by 15%) to that reported in [1] for Cu–Cr alloy.

The lattice parameter and microhardness data shown in Tables II and III indicate that a metastable extension of the maximum solubility up to 2.7 wt % Cr and 0.25 wt % Zr can be achieved in melt-spun Cu-alloy ribbons. As mentioned above, the microhardness values for the Cu–Cr–Zr alloy increase as the heat-treatment temperature increases up to 400 °C, and alloys of the Cu–Ni–Fe type under similar conditions of rapid solidification show the opposite behaviour, which gives the advantage to Cu–Cr–Zr alloys in order to be consolidated in its softest condition and its full strength to be developed by a subsequent age-hardening treatment. As shown in Fig. 2, the values of electrical conductivity increase as the heat-treatment temperature increases, but the resultant electrical conductivities are lower than that desired for industrial applications, such as resistance-welding electrodes in which an electrical conductivity of approximately 90% IACS is desired, but this set of alloys have shown better values of electrical conductivity (76% IACS for the Cu–Cr–Zr alloy at 600 °C) than those reported in [1] for Cu–Cr and in [9] for Cu–Zr alloys.

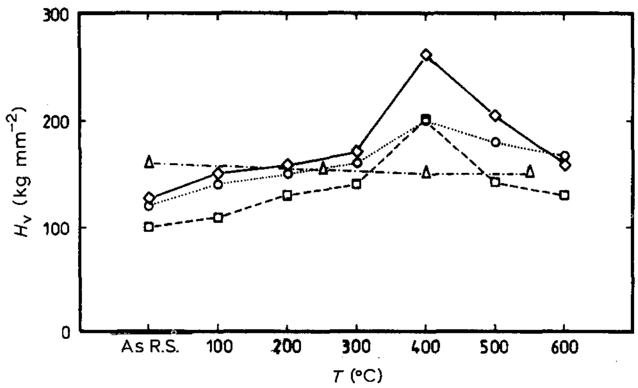

Figure 1 Microhardness Vickers' response of melt-spun Cu alloys in their as-rapidly-solidified condition and after heat treatment at 100, 200, 300, 400, 500 and 600 °C (1 h heat treatment). (○) Cu–Cr, (◇) Cu–Cr–Zr, (□) Cu–Cr–Be and (△) [10].

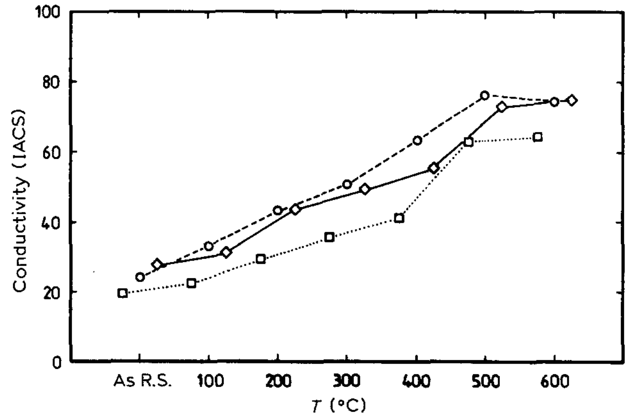

Figure 2 Electrical conductivity of melt-spun Cu alloys as a function of temperature up to 600 °C (1 h) heat treatment. (○) Cu–Cr, (◇) Cu–Cr–Zr and (□) Cu–Cr–Be.

In conclusion, an extended solid solution of Cr, Cr–Zr and Cr–Be in Cu has been achieved by rapid solidification. A peak age-hardening temperature of 400 °C was found for the rapidly solidified Cu–Cr–Zr alloy, being at its peak hardness 56% higher than alloys of the Cu–Ni–Fe type under similar conditions. Finally, the electrical conductivity values of alloys of the Cu–Cr and Cu–Cr–Zr types were superior to those reported for Cu–Cr [1] and Cu–Zr [9], but still need to be improved for industrial applications.

Acknowledgement
We thank the participation of Mr Anselmo Gonzalez Trujillo during the melt-spinning and heat-treatment experiments.

TABLE III Microhardness Vickers (10 g load) response of melt-spun copper alloys in their as-rapidly solidified condition and after heat treatment at 100, 200, 300, 400, 500 and 600 °C (1 h).

Microhardness ($kg\,mm^{-2}$)							
Alloy (wt %)	As-rapidly solidified	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C
Cu-1.02Cr	127.6 ± 9	104.4 ± 8	157.4 ± 9	168.6 ± 11	261.3 ± 13	205.2 ± 13	162.2 ± 7
Cu-2.72Cr-0.25Zr	120.4 ± 4	141.3 ± 4	149.1 ± 6	159.1 ± 6	199.4 ± 13	243.4 ± 12	166.7 ± 8
Cu-0.98Cr-0.2Bc	100.6 ± 9	109.5 ± 7	130.3 ± 7	138.8 ± 8	200.5 ± 14	143.8 ± 14	129.4 ± 9

References

1. M. J. TENWICK and H. DAVIES, *Mater. Sci. Eng.* **98** (1988) 543.
2. M. A. MORRIS and D. G. MORRIS, *Acta Metall.* **35** (1987) 2511.
3. M. BLANK, C. CAESER and U. KOSTER, in "Rapidly quenched metals", (edited by S. Steeb and H. Warlimont North-Holland, Amsterdam, 1985) p. 883.
4. L. ARNBERG, U. BACKMAN, N. BACKSTROM and J. LANGE, *Mater. Sci. Eng.* **83** (1986) 115.
5. E. BATAWI, D. G. MORRIS and M. A. MORRIS, *Mater. Sci. Technol.* **6** (1990) 892.
6. J. V. WOOD and C. Y. ELVIDGE, *MRS Symp. Proc.* **58** (1986) 451.
7. E. BATAWI, M. A. MORRIS and D. G. MORRIS, *Mater. Sci. Eng.* **98** (1988) 161.
8. M. A. MORRIS and D. G. MORRIS, *ibid.* **A111** (1989) 115.
9. R. N. WRIGHT and L. E. ANDERSON, *ibid.* **A111** (1989) 167.
10. S. H. LO, W. M. GIBBON and R. S. HOLLINGSHEAD, *ibid.* **98** (1988) 441.

Received 16 July
and accepted 12 September 1991