

Rapid Solidification of Copper Alloys with High Strength and High Conductivity

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Rapid solidification has been employed to develop high-strength/high-conductivity copper alloys, because it offers advantages not achievable by conventional ingot metallurgy practice. The effect of rapid solidification on mechanical properties and electrical conductivity on copper alloys (with and without heat treatment) has been studied. Results indicated that alloys of the Cu-Cr-Zr type, rapidly solidified and aged, show a good combination of electrical conductivity [45.82×10^6 (1/Ω · m)] and microhardness Vickers (24.46×10^6 Pa) values. These values are superior to those of optimally aged conventional copper alloys for resistance welding electrode applications.

Keywords electrical conductivity, high conductivity, high strength, International Annealed Copper Standard (IACS), microhardness

1. Introduction

One of the effects of rapid solidification on structure is solid solubility extension of alloying additions that are relatively insoluble at equilibrium and size refinement. Rapid solidification processing of copper alloys (Ref 1-12) has included binary Cu-Cr (Ref 1, 2, 4, 5, 7), Cu-Zr (Ref 2-3, 7), Cu-B (Ref 5), Cu-Ni (Ref 5, 8, 10), and Cu-Fe (Ref 5) and ternary Cu-Cr-X (X = Zr, Ti, or Mg) (Ref 1, 4-5, 8), Cu-Ni-Sn (Ref 9), Cu-Nb (Ref 6), and Cu-Cr (Ref 6) processed via mechanical alloying. In addition, it has been reported (Ref 1) that a thermomechanical process for spray-forming ternary Cu-Cr-Zr alloys was applied to reach interesting combinations of strength and conductivity, giving values of strength in excess of 800 MPa with conductivities in excess of 43.5×10^6 (1/Ω · m).

Research has also continued on thermomechanically processed powders of Cu-Nb (Ref 11), Cu-Ta (Ref 11), Cu-Cr (Ref 11), and Cu-Fe binary alloys (Ref 12), reporting strength values in the range of ~750 to 900 MPa and conductivities in the range of $\sim 42.34 \times 10^6$ to 46.98×10^6 (1/Ω · m) for the Cu-Fe alloys. This study reports data on the mechanical and electrical properties obtained in: (a) Cu-Cr, Cu-Cr-Zr, and Cu-Cr-Be alloys (with and without heat treatment) processed by using the melt spinning technique; and in (b) commercial Cu-Cr-Be electrodes commonly used in a Japanese assembly car industry in Mexico. It also compares the values of strength and conductivity obtained in those copper alloys with those reported in the literature.

2. Experimental Procedure

Cu-1.0wt%Cr, Cu-2.7wt%Cr-0.25wt%Zr, and Cu-1.0wt%Cr-0.2wt%Be alloys were prepared by vacuum induction melting in alumina crucibles. The chemical composition of the resulted ingots were confirmed by wet analysis to an accu-

racy of $\pm 0.02\%$ solute. Samples were melt spun onto a copper wheel under an argon atmosphere to ribbons $\sim 3 \times 10^{-5}$ m thick and 3×10^{-3} m wide. Isochronal heat treatments were carried out on rapidly solidified ribbons 0.10 m long under an argon atmosphere for 1 h, at 373, 473, 573, 673, 773, and 873 K in a resistance furnace and the ribbons were water quenched. X-ray diffraction (Siemens D-5000) and scanning electron microscopy (SEM) (Stereoscan 440) were employed with the aim of determining solid solubility extension, identifying second-phase particles in the as-rapidly solidified and heat-treated ribbons, and identifying second-phase particles in commercial electrodes, whose analyzed composition was Cu-0.3wt%Cr-0.3wt%Be. Microhardness (Matzusawa MHT-2872, 147 N load) Vickers measurements were carried out on transverse sections of ribbons and of commercial electrodes. The electrical resistivity of ribbons and of commercial electrodes of 5×10^{-5} by 3×10^{-3} by 0.10 m and 1×10^{-3} by 3×10^{-3} by 0.10 m, respectively, was determined by measuring the resistance of the samples in a Hewlett Packard 4192 A impedance analyzer.

3. Results and Discussion

For ribbons of Cu-Cr, Cu-Cr-Zr, and Cu-Cr-Be alloys in the as-rapidly solidified condition, and after heat treatment at up to 673 K, the main phase detected was the face-centered cubic (fcc) α -Cu solid solution. SEM carried out in ribbons in the as-rapidly solidified and heat-treated conditions showed that extension of the solid solubility of solute elements (Be, Cr, or Zr) in the fcc α -Cu had already been achieved by rapid solidification and had been retained in solid solution at up to 673 K.

At temperatures above 673 K, for the Cu-Cr and Cu-Cr-Be alloys, a copper-rich phase (96.3 ± 0.4 at.%) was detected, and for the Cu-Cr-Zr alloy a copper-rich phase (96.5 ± 0.5 at.%) plus Cu_5Zr (83.7 ± 0.7 at.% Cu, 16.6 ± 0.4 at.% Zr) were detected.

In the resistance welding electrodes for industrial applications, a copper-rich precipitate in the matrix was detected, whose composition was close to the stoichiometric compound Cr_3Cu (73.2 ± 2.3 at.% Cr and 25.8 ± 0.7 at.% Cu).

Figure 1 shows a representative microstructure of ribbons in the as-heat-treated condition, which corresponds in this case to the Cu-Cr-Zr alloy. This figure includes the morphology of the main precipitates observed in ribbons. Figure 2 shows the

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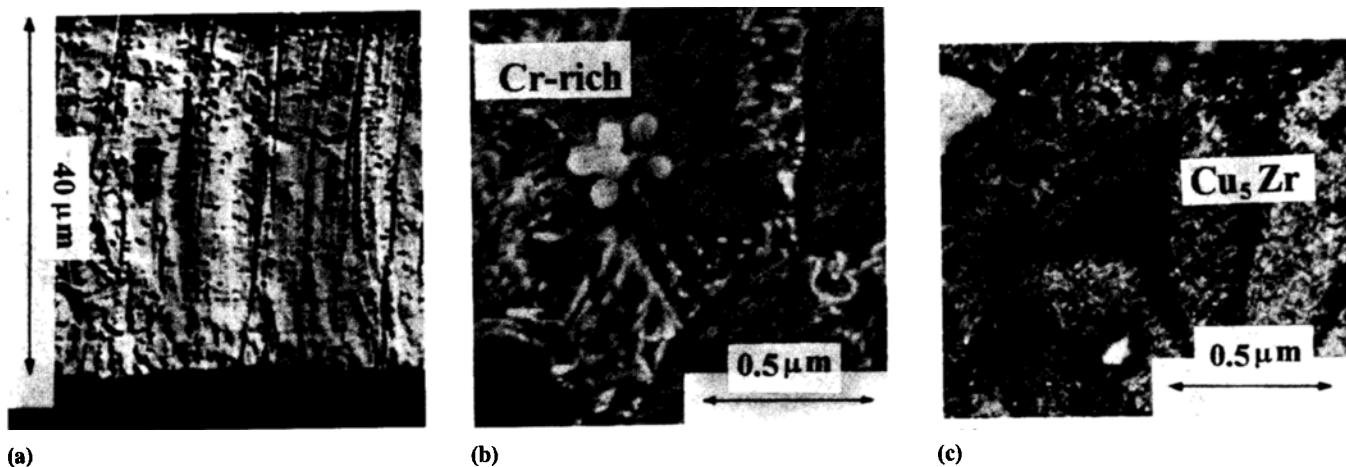


Fig. 1 (a) A representative microstructure of heat-treated ribbons in which second-phase particles were observed. This photomicrograph corresponds to a Cu-Cr-Zr ribbon heat treated at 773 K for 1 h. (b) Morphology of the copper-rich precipitate observed in alloys of Cu-Cr, Cu-Cr-Zr, and Cu-Cr-Be. (c) Morphology of the Cu₅Zr precipitate observed in the Cu-Cr-Zr alloy

Table 1 Microhardness Vickers (H_V), ultimate tensile strength (UTS), and electrical conductivity (σ for several copper alloys

Alloy, %	H _V , Pa × 10 ⁻⁶		UTS, MPa		σ, (1/Ω · m) × 10 ⁻⁶		Process	Ref
	Min	Max	Min	Max	Min σ (IACS)	Max σ (IACS)		
Cu-1.9Zr	...	34.6	23.2 (40.0)	MS + AH	2
Cu-4.6Zr	29.0 (50.0)	MS + AH	2
Cu-1.6Cr-0.4Zr	800	...	43.7 (75.5)	A + T	1
Cu-15Vol%Nb	700	1575	30.1 (52.0)	47.5 (82.0)	A + C + A	11
Cu-15Vol%Ta	750	1220	38.2 (66.0)	47.2 (81.5)	A + C + A	11
Cu-15Vol%Ni	775	1000	44.0 (76.0)	47.2 (81.5)	A + C + A	11
Cu-Be-Ni	...	40.7	800	1025	34.2 (59.0)	47.2 (81.5)	C(T)	14
Cu-15Vol%Fe	800	1450	29.0 (50.0)	47.2 (81.5)	A + C + A	12
Cu-0.5Zr	420	...	48.1 (83.0)	A + C + A	15
Cu-2.7Cr-0.25Zr	24.4	27.8	...	850	43.1 (75.0)	MS + A	PW	
					40.6 (70.0)	45.8 (79.0)	,	
Cu-0.5Cr-0.3Be	...	17.3	27.2 (47.0)	C(T)	PW
Cu-2.5Co-0.4Be	...	17.3	23.2 (40.0)	CA	2
Cu-2Be	...	34.6	29.0 (50.0)	C(T)	2

IACS, International Annealed Copper Standard; MS + AH, melt spinning + age hardening; CA, conventional aging; C(T), commercial electrode but toxic; A + T, atomization + thermomechanical treatment; A + C + A, atomization + consolidation + aging; MS + A, melt spinning + aging; PW, present work

shapes of the resistance welding electrodes (designated as 1, 2, and 3) and the morphology of their precipitates. Identification of the copper-rich and Cu₅Zr precipitates in the heat-treated ribbons are in agreement with those reported in the literature (Ref 13).

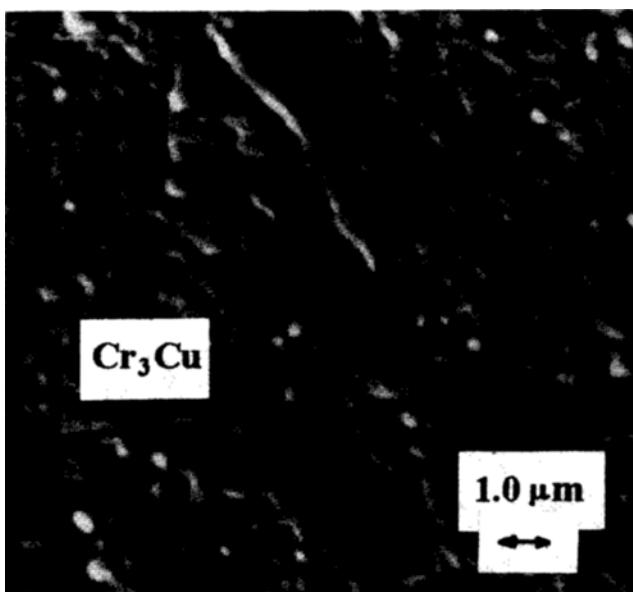
With regard to the aging response, Fig. 3 shows the microhardness Vickers values of the three melt-spun copper alloys in their as-rapidly solidified condition and after heat treatment from 373 to 873 K for 1 h, together with the microhardness values of three resistance welding electrodes in their as-received condition for industrial applications. According to Fig. 3, the ternary Cu-Cr-Zr and Cu-Cr-Be alloys showed a continuous increase in their microhardness values until they reached a peak hardness at 673 K. The Cu-Cr binary alloy showed the same behavior until it showed its best aging response at 773 K. The Cu-Cr-Zr alloy showed the highest microhardness value of the three alloys, $27.52 \times 10^4 \pm 10$ Pa at 673 K for 1 h. Microhardness values measurements of the three commercial electrodes

showed an average value of 17.73×10^6 Pa. This microhardness value is 35% lower than that obtained in the Cu-Cr-Zr alloy in its peak condition. Microhardness Vickers values obtained in the Cu-Cr-Zr alloy at its peak aging condition were superior to the reported values for the commercial Cu-Cr-Be and Cu-Co-Be alloys, as shown in Table 1.

Figure 4 shows data for electrical conductivity [in $(1/\Omega \cdot m)$] of melt-spun copper alloy ribbons in their as-rapidly solidified condition and after heat treatment at up to 873 K for 1 h, together with electrical conductivity data for the resistance welding electrodes in the as-received condition for industrial applications. The Cu-Cr, Cu-Cr-Be, and Cu-Cr-Zr alloys showed similar electrical conductivity (the Cu-Cr and Cu-Cr-Zr alloys had slightly higher conductivity than the Cu-Cr-Be alloy) up to 873 K. Commercial resistance welding electrodes showed electrical conductivity values from 12.76×10^6 to 27.26×10^6 $(1/\Omega \cdot m)$, in comparison to the value of 45.82×10^6 $(1/\Omega \cdot m)$ obtained for the Cu-Cr-Zr alloy in its peak aged



(a)



(b)

Fig. 2 (a) Shapes of resistance welding electrodes for industrial applications. (b) Morphology of Cr_3Cu precipitates observed in resistance welding electrodes

condition (773 K, 1 h). If we compare the electrical conductivity value of this Cu-Cr-Zr alloy with those shown in Table 1, it can be observed that in terms of this property this alloy showed a good response to the rapid solidification and aging treatment.

The values of microhardness and electrical conductivity obtained for the Cu-Cr-Zr alloy were superior than those obtained for commercial resistance welding electrodes normally used in a Japanese assembly car industry based in Mexico, in which the highest value of microhardness was $18.04 \times 10^6 \text{ Pa}$ and the highest value of electrical conductivity was $27.26 (1/\Omega \cdot \text{m})$.

4. Conclusions

As can be observed from Table 1, the alloys (in particular, the Cu-Cr-Zr alloy) showed an outstanding response with re-

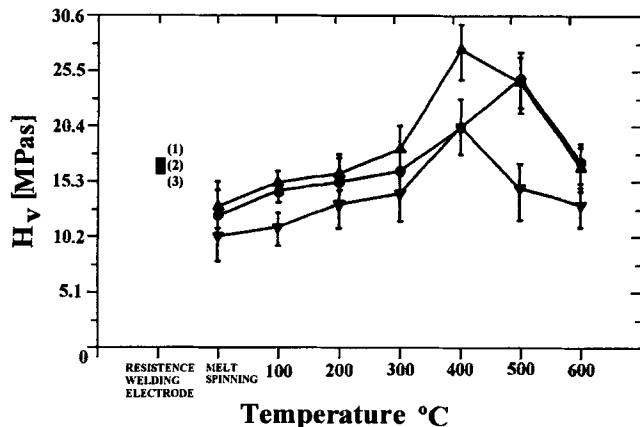


Fig. 3 Microhardness Vickers (147 N load) measurements as a function of heat treatment. Solid square, (1, 2, and 3) resistance welding electrode; solid triangle (base down), Cu-Cr-Zr; open circle, Cu-Cr; solid triangle (tip down), Cu-Cr-Be

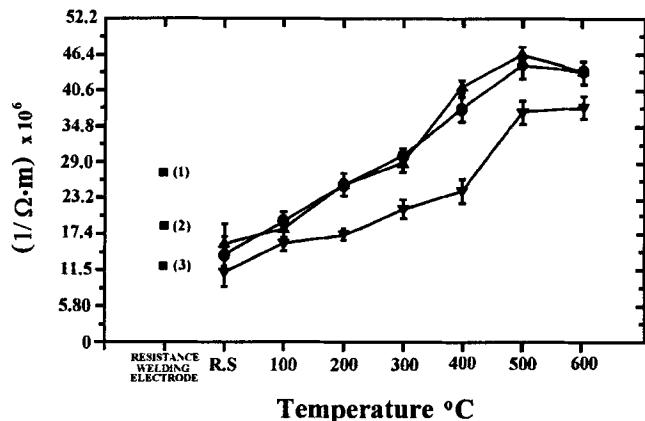


Fig. 4 Electrical conductivity measurements in $(1/\Omega \cdot \text{m})$ as a function of heat treatment. Solid square, (1, 2, and 3) resistance welding electrode; solid triangle (base down), Cu-Cr-Zr; open circle, Cu-Cr; solid triangle (tip down), Cu-Cr-Be

gard to electrical conductivity and microhardness Vickers values, being superior in both properties when compared with commercial resistance welding electrodes used for daily industrial applications.

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