Cu-Zr and Cu-Zr-Cr Alloys Produced from Rapidly Quenched Powders

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The production of alloys by means of ingot technology leads to micro- and macrosegregation, separation of phases and impurities, often into large, brittle particles, and coarse grain size. Alloy development is frequently restricted because of the coarseness of the structure and the resultant imposed limitations on hot and cold plasticity. One ready means of avoiding these problems is to produce the alloy in powder or pellet form; this permits attainment of high cooling rates in the liquid and solid, minimizes segregation, alters phase separation and distribution advantageously, and results in significantly finer structures. The powders utilized to produce wrought shapes may be much coarser than press-and-sinter powders, leading to important processing economies without sacrifice of structure refinement. The alloy systems Cu-Zr and Cu-Zr-Cr were selected for the present study; these are high conductivity, high strength alloys of commercial interest. Cooling rates for these specific powders using nitrogen atomization varied from about 10^3 to 10^4°C/sec. Powders were cleaned, canned, and hot extruded to produce bar stock; mechanical testing was performed on both as-extruded and thermomechanically-worked samples, with highly beneficial improvements in strength, ductility, and high-temperature structural stability.

SPLAT cooling, or rapid quenching of fine liquid metal droplets, has demonstrated an ability to control structure, and therefore properties, in ways and to a degree not previously possible by alternate casting methods. Solidification processes are primarily responsible for segregation and phase separation. The slower the solidification process, the greater the degree of segregation and separation, the coarser the grain size, and the coarser the excess phases. This damage to structure manifests itself to a greater degree the larger the ingot or casting. Prevention or minimization of such casting faults would improve hot and cold workability, enhance mechanical properties, decrease directionality effects, permit utilization of higher alloy content, and perhaps increase the reproducibility of properties.

The work reported here is the result of an investigation presently being conducted for the powder metallurgy production of wrought Cu-Zr and Cu-Zr-Cr alloys of higher alloy content than is now possible in ingot casting. The aims of the program are to produce high strength, high electrical conductivity copper alloys which will have excellent hot and cold working capability, while exhibiting highly improved structural stability in the temperature range of 500° to 750°C compared to present commercial alloys.

EXPERIMENTAL PROCEDURE

The starting materials used for this investigation were minus 100 mesh (−149 μ) nitrogen-atomized Cu-Zr and Cu-Zr-Cr alloy powders. The powders were given a reduction treatment in dry hydrogen (containing less than 0.0015 vol pct water vapor) for 10 hr at 450°C, and were subsequently compacted in copper cans (in a dry box with 0.0003 vol pct water vapor). The cans were evacuated and hot extruded, see Table I. Metallographic inspection and specific gravity measurements indicated that all alloys were essentially fully dense after extrusion.

Various thermomechanical treatments were used in order to optimize properties. These are listed in Table II.

The following properties were then determined:

1) hardness as a function of annealing temperature;
2) tensile properties at room temperature, and as a function of annealing temperature;
3) stress-to-rupture strengths at 400°and 650°C;
4) electrical conductivity.

RESULTS AND DISCUSSION

Dendrite arm spacing is a function of the degree of supercooling[1] and since the extent of supercooling depends on the cooling rate, one can expect a relationship between dendrite arm spacing and cooling rate. Experimental evidence available indicates that dendrite arm spacing in cast aluminum alloys is influenced only by cooling rate (or "local solidification time"). Bower *et al.*[2] plotted data obtained from a number of investigations with aluminum alloys, showing the relationship between secondary arm spacing d and local solidification time θ_f. Of the wide range of solidification rates examined, the dendrite arm spacing measurements were found to correlate linearly with θ_f on log-log coordinates:

Table I. Alloy Compositions and Fabrication Variables

Alloy	Zr, Wt Pct	Cr, Wt Pct	O_2, Wt Pct	Cu(bal) Wt Pct	Extr. Ratio	Extr. Temp, °C
ZA-2	0.20	–	0.04	99.76	25 to 1	600
ZA-3	0.37	–	0.03	99.60	25 to 1	650
ZA-8	0.80	–	0.08	99.14	25 to 1	650
ZAC-1	0.10	0.32	0.04	99.54	25 to 1	650

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$d = 7.5\theta_f^{0.39}$

This relationship was confirmed for a number of aluminum alloys over a wide range of cooling rates by Matyja *et al.*[3] They plotted dendrite arm spacing as a function of cooling rate, and obtained a similar linear corelation with a slope of 0.32. Such a relationship has been obtained in this work for Cu-Zr alloys, Fig. 1. The slope of this curve was found to be greater (approximately 0.48) than that observed for aluminum alloys (0.32).

It was found that the metastable extension of the solid solubility limit of zirconium in copper can be increased extensively by utilizing cooling rates of approximately 10^7 to 10^9°C/sec. Subsequent studies by Ray[4] showed that the solubility of zirconium in copper could be increased from a maximum equilibrium value of 0.2 to around 30 wt pct. From a practical point of view, fine splat foils formed through such rapid solidification rates are of limited commercial interest. On the other hand, intermediate cooling rates (10^2 to 10^5°C/sec) achieved by means of selected atomization techniques can result in powders suitable for consolidation and conversion to yield improved structures and properties.

To delineate the structure-property interplay, several quenching and atomization techniques are being examined. The results obtained from fine (−149 μ) nitrogen atomized powders are being reported here.

A typical microstructure of one of these powders is shown in Fig. 2; the average measured dendrite arm spacing of about 6 μ of these powders corresponds to cooling rates in the range 10^3 to 10^4°C/sec, Fig. 1. Table I summarizes the alloy compositions and fabrication variables.

The oxygen content of the alloys varied from 0.03 to 0.08 wt pct. This high oxygen content is due to the atomization process. If it is assumed (as is probable) that all the oxygen is tied up with zirconium to form ZrO_2, then the alloys contain 0.11 to 0.54 wt pct ZrO_2 (0.03 to 0.08 wt pct O_2). The presence of ZrO_2 has been confirmed by X-ray and chemical analysis.

In a preliminary evaluation of the stability of the extruded alloys, the effect of annealing (1 hr at temperature) on the room temperature hardness was examined. The results obtained are presented in Fig. 3, and it is clear that all the alloys are more stable above 600°C than the commercial ingot cast alloy.

All the as-extruded alloys were found to have a very fine grain size (5 to 10 μ) in the transverse direction Fig. 4 shows typical microstructures in the longitudinal and transverse direction of one of these alloys in the as-extruded condition. Table III lists the astruded properties of these alloys. As a result of the fine grain size, the increased alloy content, and the finely dispersed Cu_3Zr (or Cr + Cu_3Zr in ZAC-1) the as-extruded tension properties are slightly better than

Table II. Combinations of Processing Treatments

Designation	Treatment
A	As-extruded, 300°C anneal for 1 hr after each 10 pct strain increment at R T., continued to the desired degree of reduction.
B	As-extruded, solution treated at 980°C for 30 min, water quenched, followed by 50 pct R.A. at 20°C, then aged at 500°C for 3 hr, air cooled, and further reduced to 75 pct R.A. (from initial diameter).
C	As-extruded, solution treated at 980°C for 30 min, water quenched, followed by 50 pct R.A. at 20°C, then aged at 450°C for 1 hr, water quenched and further reduced to desired thickness.

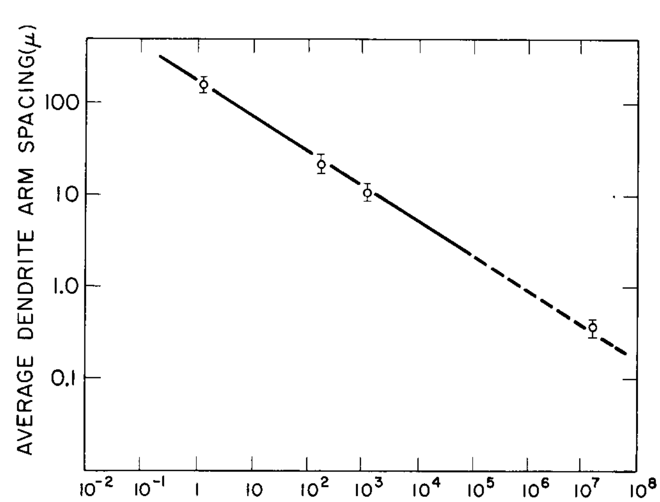

Fig. 1—Variation of dendrite arm spacing as a function of cooling rate for Cu-Zr alloys.

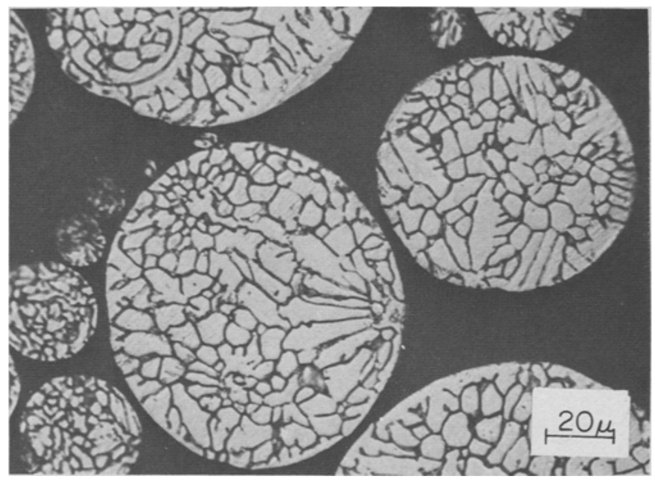

Fig. 2—Microstructure of nitrogen-atomized Cu-0.2 pct Zr powder(Etch $FeCl_3$).

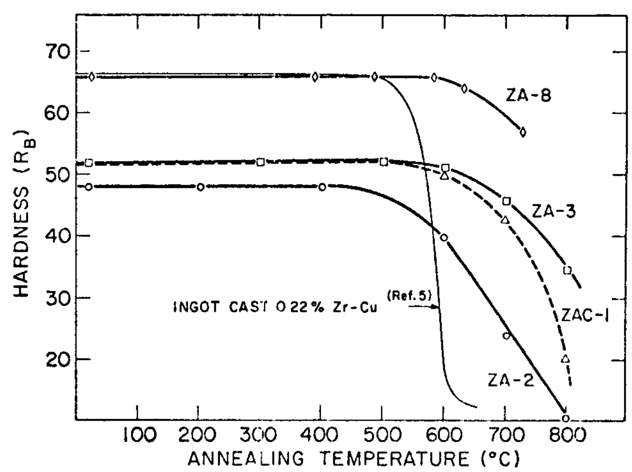

Fig. 3—Hardness at 20°C as a function of annealing temperature (1 hr at temperature) of as-extruded alloys.

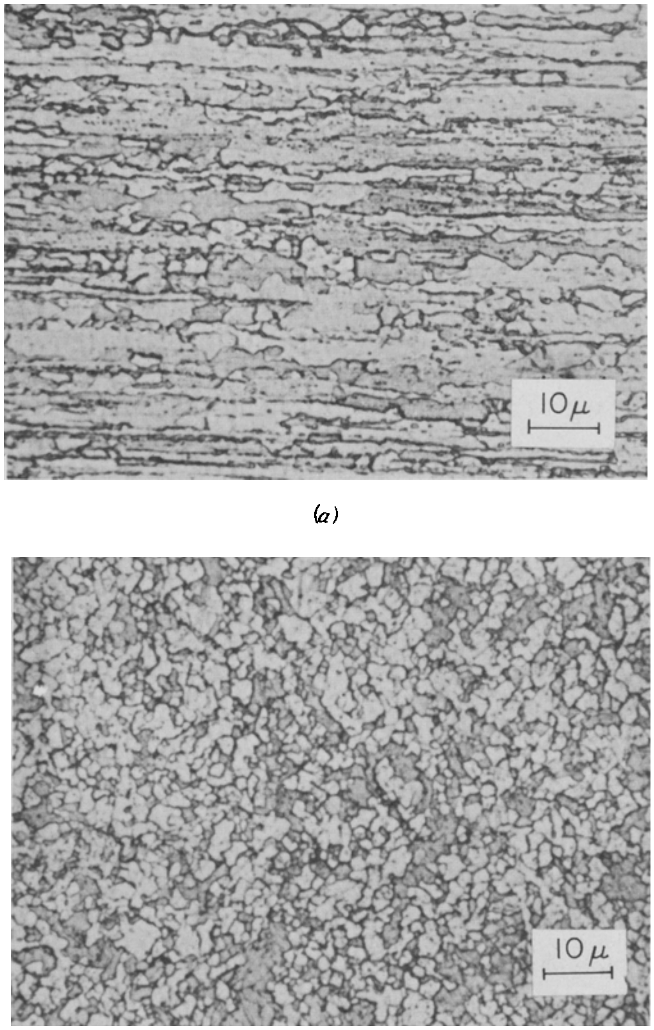

Fig. 4—Typical microstructures of ZA-2 alloy in the as-extruded condition. (*a*) Longitudinal, (*b*) transverse section. (Etch $FeCl_3$).

Table III. Properties of As-Extruded Cu-Zr and Cu-Cr-Zr Alloys

Alloy	Approx G.S., μ	Hardness, R_B	Y.S., psi	U.T.S., psi	Elong., Pct	Red. Area, Pct	Elec. Cond., Pct IACS
ZA-2	2 to 5	48	28,000	37,000	34.0‡	84 5	94.6
ZA-3	2 to 5	52	25,000	37,000	34.0‡	88.0	92.0
ZA-8	2 to 5	65	47,000	60,500	30.5‡	65.6	91.2
ZAC-1	5 to 10	52	35,000	37,000	22.6‡	86 5	82.6
AMZIRC*	–	42	19,000	37,000	19.0¶	–	90.0
0.19 pct Zr†	–	–	45,800	45,500	6.0¶	–	
0 40 pct Zr†	–	–	46,900	47,800	5.0¶	–	
0 74 pct Zr†	–	–	45,800	49,800	5.0¶	–	

*0 15 pct Zr, solution annealed at 980°C, aged 1 hr at 500°C.[6]

†Experimental ingot type alloys produced by M. J. Saarivirta.[7] Material solution annealed at 900°C and quenched, cold rolled 25 pct.

‡Gauge length 0.7 in; equals 4D.

¶Gauge length 2 0 in, equals 4D.

those of the commercial ingot alloys.

Except in the alloy ZA-2 (which was extruded at a temperature 50°C lower than the other alloys), Laue diffraction on all other extrusions showed the absence of cold work since the K_α doublets could be clearly

Table IV. Effect of Thermomechanical and Age-Hardening Treatments on Strength of ZA-2

Condition	Y.S., psi	U.T.S., psi	Elong, Pct	Reduction in Area, Pct	Elec. Cond., Pct IACS
As-extruded	28,000	37,000	34.0	84.5	93.6
Ext. + 50 pct R.A. (A)	47,000	47,500	23.0	82.5	93.0
Ext. + 80 pct R.A. (A)	49,000	52,500	21.4	88.0	92 5
Ext. + 90 pct R.A. (A)	47,500	53,000	17.6	90.5	91.6
Ext. + 75 pct R.A. (C)	56,000	58,000	16.4	90.5	–
Ext. + 90 pct R.A. (C)	57,000	58,000	16.6	90.5	88.1

Table V. Effect of Thermomechanical and Age-Hardening Treatments on Strength of ZAC-1

Condition	Y.S. psi	U.T.S., pis	Elong., Pct	Reduction in Area, Pct	Elec. Cond., Pct IACS
As-extruded	35,000	37,000	22.6	86.5	82.6
Ext. + 60 pct R.A. (A)	42,000	44,500	21 2	84.5	80.9
Ext. + 90 pct R.A. (A)	50,000	51,500	14.0	89.0	80.1
Ext. + 75 pct R.A. (B)	63,000	66,000	14.6	85.0	85.8
Ext. + 75 pct R.A. (C)	73,000	76,000	14.0	85.0	85.0

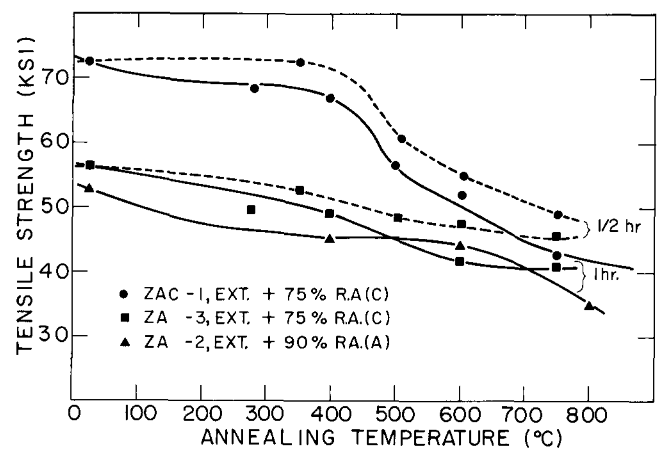

Fig. 5—Tensile strength at 20°C as a function of annealing temperature (for $\frac{1}{2}$ hr and 1 hr periods at temperature).

resolved. In the case of ZA-2 slight-line broadening was obtained. Therefore, it is felt that stored energy due to extrusion did not contribute to any great extent to the mechanical properties of the alloys. The ductility values of the powder-based alloys are relatively higher than those obtained from the ingot-cast alloys.

All alloys were subsequently thermomechanically worked and the effects on mechanical properties determined. The effects of combined solution treatment, thermomechanical work, and precipitation hardening were investigated. These treatments are defined in Table II.

Although zirconium additions to copper produce an age-hardening effect, response to precipitation hardening (unlike Cu-Cr alloys) is slight, and the mechanical properties are developed primarily by cold working. Alloy ZAC-1 utilizes a third element, chromium, which results in pronounced improvement in precipitation hardening. A comparison between the tensile data for ZA-2, Table IV, and ZAC-1, Table V, clearly

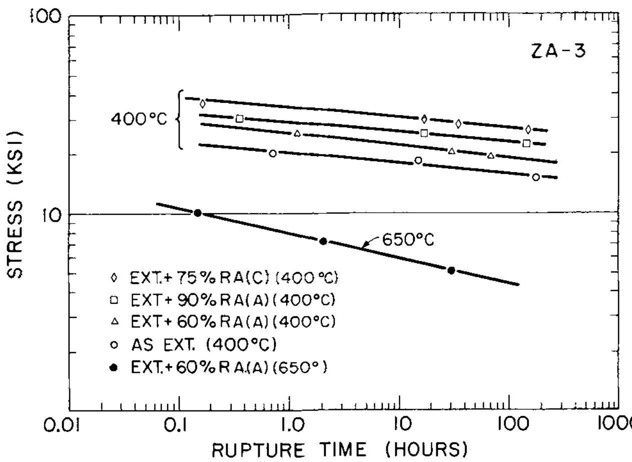

Fig. 6—Stress-rupture plot for alloy ZA-3 at 400° and 650°C.

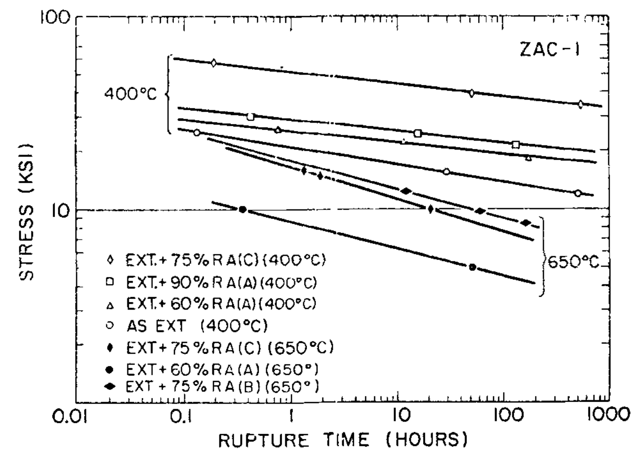

Fig. 7—Stress-rupture plot for alloy ZAC-1 at 400° and 650°C.

shows this effect. ZAC-1 was also found to be stronger in stress-rupture than any of the other alloys.

As a further measure of stability, the alloys were annealed at various temperatures for $\frac{1}{2}$ hr and 1 hr periods, and then their tensile strength values were measured at room temperature, Fig. 5. Again, as is the case with all the other mechanical properties, the alloys were found to be very stable above 400°C. This may be due in part to the presence of ZrO_2.

Stress-rupture tests were performed on all the alloys, in air, between 400° and 650°C. It was found that a considerable increase in stress-rupture life was obtained through thermomechanical and precipitation-hardening treatments. Plots of initial stress vs time-to-rupture are presented for alloys ZA-3 and ZAC-1 in Figs. 6 and 7. All the alloys were found to be significantly stronger in stress-rupture above 400°C than any ingot-cast Cu-Zr alloys so far reported. Fig. 8 makes such a comparison. Elongation and reduction of area measurements from stress-rupture tests showed considerable scatter, but on the whole the ductility was found to be excellent. The range in which most values fell was 4 to 10 pct elongation and 30 to 85 pct reduction of area.

The effect of thermomechanical treatments on electrical conductivity of the alloys was found to be small. For example, values fell from 94 pct IACS for the as-

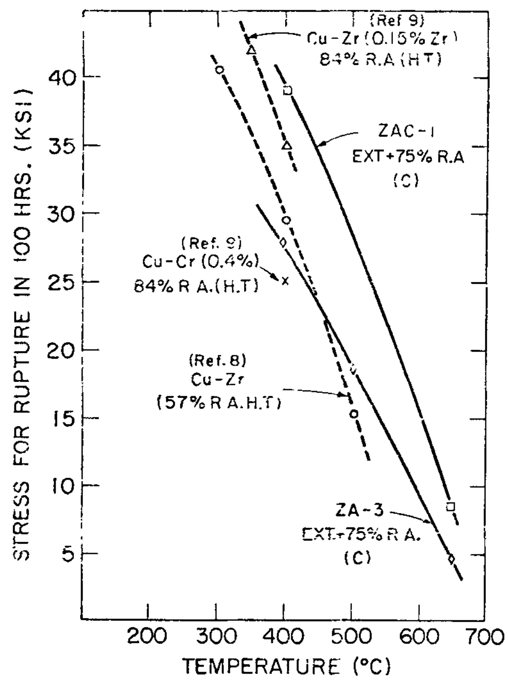

Fig. 8—Plot showing stress for 100 hr rupture life at several temperatures.

extruded condition to 92 pct IACS after 90 pct reduction of area in ZA-2; see Tables IV and V.

SUMMARY

Powder production by means of nitrogen atomization of Cu-Zr and Cu-Zr-Cr alloys, followed by thermomechanical working and heat treatment, results in fine wrought structures with excellent mechanical properties. The resultant ductility values obtained are superior to those of conventional ingot-type material; hot and cold plasticity are excellent. The addition of chromium to Cu-Zr, combined with solution treatment, thermomechanical work, and precipitation hardening, yields the best overall properties. The high-temperature stability of the alloys, as measured by the extreme flatness of the stress-rupture data plots at 400° and 650°C, and by the retention of room temperature properties after exposure at 400° to 800°C, is excellent.

ACKNOWLEDGMENTS

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