

Strengthening mechanisms in a rapidly solidified and aged Cu-Cr alloy

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A single-roller melt spinning method was used to produce Cu-Cr microcrystal alloy ribbons. Upon proper aging treatment, the strength and hardness of the alloy were remarkably enhanced while the conductivity only had a minimal decrease. Grain refinement and coherent dispersion strengthening were proved to be the major factors contributing to the improvement of strength and hardness of the alloy after aging. The degree of coherent strengthening was almost identical with that calculated by the Gerold equation. Compared with the solid solution quenched Cu-Cr alloy, the peak hardness was increased 2.6 times, in which about 27% was attributed to the grain refinement and 73%, in turn, provided by coherent strengthening due to aging precipitation. Neither the solid solution strengthening nor vacancy strengthening had detectable effect on the strength and hardness of the rapidly solidified Cu-Cr alloy. © 2000 Kluwer Academic Publishers

1. Introduction

Having high strength and good electrical and thermal conductivities, Cu-Cr alloys are used in a number of engineering applications, such as in electric resistance welding electrodes, the liner tube of continuous casting crystallizer, integrated circuit lead frame, aerial conductor of electric locomotive and so on. However, higher strength is more and more required for copper alloys with the rapid development of the electronic industry. For example, a tensile strength $\sigma_b > 600$ MPa, hardness $H_v > 180$ and conductivity $> 80\%$ IACS are demanded for lead frame materials on a very large scale integrated circuit [1] (VLSI). It is obvious that these property indices can not be reached by copper alloys produced by conventional solution heat-treatment (CSHT).

Rapid solidification (RS) can lead to a remarkable refinement of grain size and an obvious extension of the solid solubility of chromium in copper matrix, the maximum of which even reaching to 3.3% Cr [2]. Thus a great amount of dispersed precipitates is brought out upon aging with the simultaneous recovery of electrical conductivity. RS now has become one of the effective processes in obtaining high strength and high conductivity copper alloys. Many studies in this field

have been successively reported [3, 4]. As far as the precipitation strengthening is concerned, different view points have been presented. Batawi *et al.* [5] believed that the strengthening mechanism of RS Cu-Cr alloys conformed to the Orowan strengthening mechanism. However, Correia *et al.* [6] proposed that before the peak hardness in atomized Cu-Cr alloy was reached the strengthening was caused by a coherent strengthening mechanism upon aging and the growth of the precipitates upon over-aging might be explained by the Orowan strengthening mechanism. In the present work, the properties and microstructures of a Cu-Cr alloy produced by the single roller melt spinning method were extensively studied and the specific strengthening mechanism and its effects were analysed.

2. Experimental

The Cu-0.66Cr alloy ingots, weight of 20 g, were induction melted in a quartz tube and then jetted under the pressure of pure Ar on to a copper roller rotating at a velocity of about 3000 r/min. The resulting microcrystal ribbons were 2 mm wide and 30–60 μm thick. No oxidation was found on either side of the ribbons. The aging treatment were carried out in an electrical

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resistance furnace (with temperature accuracy $\pm 5^\circ\text{C}$) under a dynamic atmosphere of argon.

The electrical resistance was measured by the four probe test method using a Wayne Kerr bridge. The mean value of five measurements had an estimated accuracy of better than $0.0002\ \Omega$. The microhardness was carried out using a Vickers microhardness tester with a load of 25 g. At least five samples were tested with an accuracy about $\pm 5\%$.

The ribbon samples for scanning electron microscope (SEM) observation were mechanically and chemically polished before being etched in $\text{HNO}_3 : \text{HCl} : \text{H}_3\text{PO}_4 : \text{CH}_3(\text{COOH}) = 3 : 1 : 1 : 5$. The foil specimens used for transmission electron microscopy (TEM) were obtained by double-jet electrolytic polishing at -30°C and the electric parameters of 2 V and 40 mA. The etching reagent was $\text{H}_3\text{PO}_4 : \text{H}_2\text{O} = 7 : 3$. The resulting thin foil specimens were examined by transmission electron microscopy (TEM).

3. Results

Curves showing the variations in tensile strength and microhardness with the aging temperature are given in Figs 1 and 2, respectively, for the melt spun Cu-0.66Cr alloy ribbons after aging for 30 min. It is noted that both curves reach their maximum at 500°C , with a tensile strength of 478 MPa and microhardness Hv185. Compared with the CSHT Cu-0.66Cr alloy, the tensile

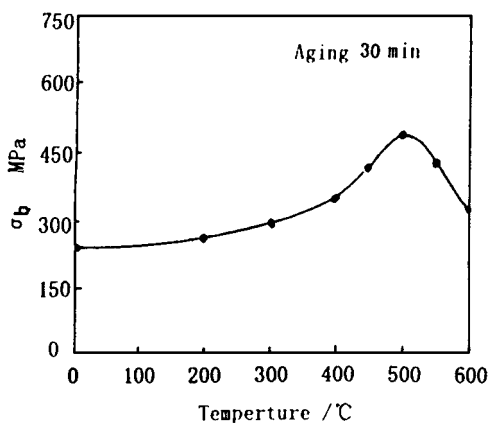


Figure 1 Tensile strength vs. aging temperature.

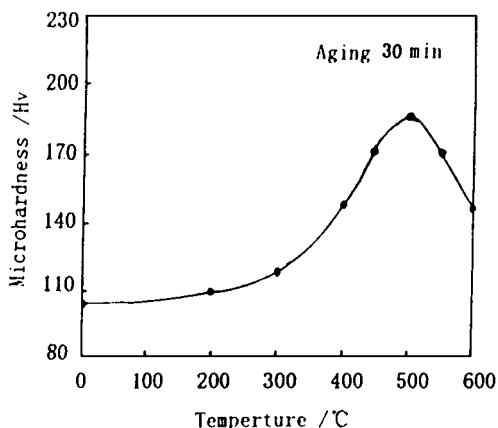


Figure 2 Microhardness vs. aging temperature.

TABLE I Properties of CSHT and RS Cu-0.66Cr in the as-cast and aging conditions

	CSHT 1000°C quenched in water	Aging 500°C, 30 min	RS 10 ⁶ °C/s	Aging 500°C, 30 min
Tensile strength (MPa)	235	350	236	478
Microhardness (Hv)	75	126	105	185
Conductivity (%IACS)	40%	80%	22%	76%

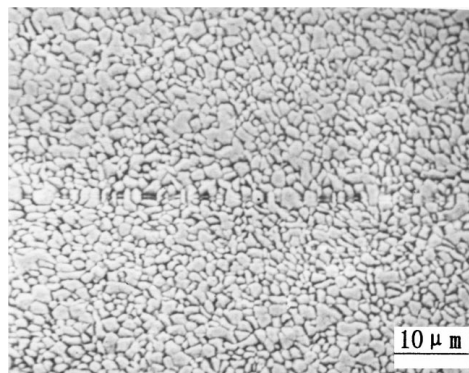


Figure 3 SEM image showing the grains for RS Cu-0.66Cr alloy upon aging 500°C for 30 min.

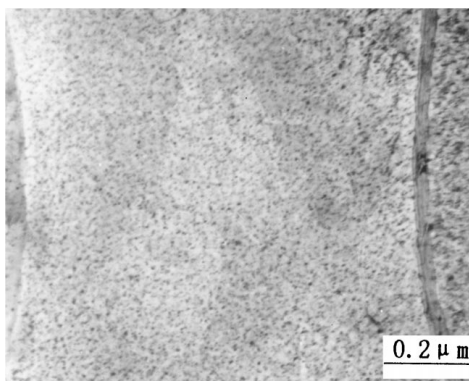


Figure 4 The precipitates in RS Cu-0.66Cr alloy upon aging 500°C for 30 min.

strength and microhardness were both considerably improved. The specific data are given in Table I. It is found that in as-cast state, the microhardness of the RS alloy is increased by 40%, but only possess lower electrical conductivity of about 22% IACS as compared with the alloy after conventional solution heat treatment (CSHT). However, upon aging at 500°C for 30 min, the tensile strength and microhardness are increased by 47% and 37%, respectively. Meanwhile, an obvious recovery to 76% IACS in electrical conductivity is obtained.

Fig. 3 shows the SEM image of the microstructure corresponding to the peak value upon aging at 500°C for the RS Cu-0.66Cr alloy. It can be seen that even after aging the fine grain size has no visible growth with respect to the as-cast state. The homogeneously distributed globular precipitates of size about 6 nm are observed by TEM as illustrated in Fig. 4. No two-lobe contrast caused by coherent distortion was observed in the microstructure. Many investigators believed that for RS Cu-Cr alloys the precipitates, corresponding to

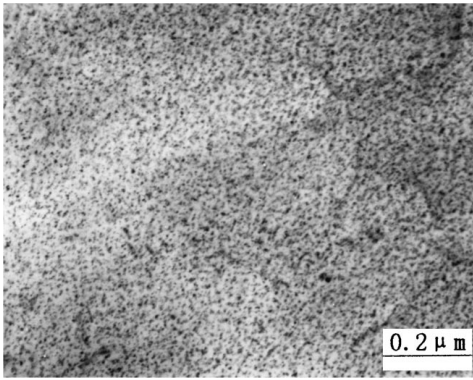


Figure 5 The precipitates in RS Cu-0.66Cr alloy upon aging 600°C for 1 h.

the peak strength or hardness upon aging, are probably coherent ones [7], which was proved by the fact that the two-lobe type contrast was clearly observed in the later stages of the aging process. However, in the present work, no obvious two-lobe type contrast was observed even the sample were over-aged at 600°C for 1 h besides the precipitates, with a small change in the shape, were slightly larger than those in peak hardness condition as illustrated in Fig. 5. This phenomenon is probably due to the smaller size of precipitates in the present work. Usually, the two-lobe type contrast can only be observed when the size of precipitates is more than 30 nm. For example, Correia *et al.* have reported that the appearance of the two-lobe type contrast corresponds to the precipitates with the size about 40–50 nm in an atomized Cu-Cr alloy. Furthermore, McIntyre [8] believed that the two-lobe type strain field and its shape mainly depended on the size of precipitates.

The selected area electron diffraction (SAED) analyses of the microstructures corresponding to the peak hardness did not show any sign of the bcc Cr phase. It is obvious that the coherent precipitates are not bcc Cr. It is probable that the crystal structure of the precipitates is identical with that of the matrix, that is, the coherent precipitates is the fcc Cr. This has been confirmed by Knight in his study on a Cu-Cr alloy [9]. Upon further aging, the fcc coherent precipitates lost the coherency with the matrix and transformed to a bcc structure.

4. Discussion

The above results have shown that the microhardness (Hv105) of RS Cu-Cr alloy was higher than that (Hv85) of CSHT Cu-Cr alloy. According to the microstructure analyses there were three possible strengthening mechanisms i.e. fine grain strengthening, solid solution strengthening and vacancy strengthening. To further determine the specific effects of the three strengthening mechanism, ribbons of pure copper were prepared by RS in the same manner as the RS Cu-Cr alloy. The properties of the RS pure copper ribbons are summarized in Table II. The microhardness and tensile strength of the RS pure copper only had a negligible decrease upon aging at 500°C for 1 h in spite of the complete decay of vacancies. Thus, it was proved that the large amount of vacancies do not give a strong vacancy strengthening.

TABLE II The experimental data for RS pure copper

State	Microhardness Hv	Tensile strength MPa	Resistivity Ω m
RS (10 ⁶ °C/sec)	103	208	1.85×10^{-8}
Aging (500 °C × 1 h)	101	203	1.81×10^{-8}

Furthermore, the slight difference of both microhardness and tensile strength between the RS Cu-Cr alloy and pure copper (comparing the property data in Table I and II) suggests that the effect of solid solution strengthening have been small, which can be interpreted by the minimal difference in the radius of Cu and Cr atoms. However, the great extension in the solubility of Cr in Cu resulted in a remarkably increase of electrical conductivity. Therefore, the enhancement of microhardness in RS Cu-0.66Cr alloy was mainly attributed to the fine grain strengthening mechanism. As far as the tensile strength (in Table I) was concerned, that of RS Cu-Cr alloy was not improved as expected with respect to that of CSHT Cu-Cr alloy, which was inconsistent with the changes in microhardness. This was caused by the experimental conditions. In the present work, the tensile samples were directly cut from the melt-spun ribbons. In this case, the structural defects, mainly on the free surface of the RS ribbons, should be taken into consideration. Although the surface of the ribbons were carefully mechanically polished, it is still difficult to completely remove the defects. Moreover, the tensile tests for such thinner ribbons were quite sensitive to small defects. Therefore, the real properties of thinner RS ribbons could only exactly reflected by microhardness measurement.

The strength and hardness of the RS alloy have been greatly enhanced with respect to CSHT alloy after aging treatment. In peak hardness or slight over-aging conditions, the precipitates remain coherent with the matrix. The increment of shear stress caused by the coherent dispersion strengthening can be expressed as [10]

$$\Delta\tau_{cs} = X(\varepsilon G)^{3/2} \left(\frac{r f b}{\Gamma} \right)^{1/2} \quad (1)$$

Where ε is the function of the degree of misfit δ , G and b are the shear modulus and Burgers Vector of the matrix, respectively, r and f are the mean radius and volume fraction of the precipitates, respectively, Γ is the line tension of the dislocations pinned by the precipitates, X is a coefficient varying between 2 and 3, usually, $X = 2.6$ is selected. $\Gamma = \alpha G b^2$, α variates between 0.089–0.5.

The maximum mutual action force F_m between the coherent precipitates and a straight edge dislocation has been calculated by Gerd and Haberkora [11], using isotropic elastic theory giving

$$F_m = 4G\varepsilon b r \quad (2)$$

If $\beta c = \sin(\theta/2) = Fm/2\Gamma = 1$, the radius r_{\max} of the maximum coherent precipitates that can be cut by dislocations is given as

$$r_{\max} = \frac{\Gamma}{2Gb\varepsilon} \quad (3)$$

By inserting Equation 3 into Equation 1, one gets the estimated maximum increment of the shear stress resulting from coherent dispersion strengthening, which is written as

$$\Delta\tau_{\text{csmax}} = 1.84G\varepsilon f^{1/2} \quad (4)$$

As far as the Cu-Cr alloy system is concerned, the lattice constant of fcc Cr is required in calculating the value of ε . However, the lattice constant of fcc Cr in Cu-Cr alloy has not been reported. As an approximation, the lattice constant $\alpha = 0.368$ nm [12] of the rich fcc Cr phase in Cu-Ni alloy is inserted into the following equation:

$$\delta = \frac{|a_p - a_m|}{a_m} \quad (5)$$

The value $\delta = 0.018$ is obtained. By inserting this into Equation 6

$$\varepsilon = |\delta|[1 + 2G(1 - 2\nu_p)/Gp(1 + \nu_p)] \quad (6)$$

One gets $\varepsilon = 0.015$ for fcc Cr phase. By inserting the related parameters ($M = 3.06$, $G = 42.1$, $\varepsilon = 0.015$) into Equation 1, the increment of maximum strength contributed by coherent precipitates is obtained as

$$\Delta\sigma_{\text{csmax}} = 356f^{1/2} \quad (7)$$

By inserting the volume fraction $f = 67\%$ of the precipitates in RS Cu-Cr alloy after aging at 500°C for 30 min (in peak hardness state) into Equation 7, the increment of the maximum tensile strength is obtained to be about 291 MPa. The sum of this value and the strength of pure copper under the same aging condition becomes 496 MPa, which gives the tensile strength of the alloy in the peak hardness condition. It is very close to the tensile strength 478 MPa obtained in this work.

By regression analysis of a large amount of experimental data J. B. Correia *et al.* [5], have given an empirical relation between the increment of microhardness and the volume fraction of the precipitates for Cu-Cr alloy upon aging

$$\Delta H_v = 94f^{1/2} \quad (8)$$

From Equation 8 the maximum increment of the peak hardness in this work is obtained to be $\Delta H_{v\text{max}} = 77$. The sum of this value and microhardness of the RS pure copper is $H_v = 180$, which is the microhardness in the peak condition. It is quite consistent with the measured microhardness $H_v = 185$.

It is noted from the variation of microhardness that compared with CSHT, the fine grain strengthening brought out by RS may increase the microhardness

by $\Delta H_v = 30$, which contributed about 27% to the increment of the microhardness. In the later aging at 550°C for 30 min, no obvious grain growth was found. The fine grain strengthening mechanism still worked. Therefore, the coherent dispersion strengthening leads to an increment of microhardness about $H_v = 80$, which contributes about 73% to the increment of the microhardness. Both the solid solution and vacancy strengthening have little effects on the microhardness.

5. Conclusions

1. The microhardness of RS Cu-0.66Cr alloy can be increased by 40% as compared with that of the CSHT Cu-Cr alloy.

2. Upon aging at 500°C for 30 min, the tensile strength of RS Cu-0.66Cr alloy is increased by 46% with respect to the CSHT Cu-Cr alloy. Meanwhile, a recovery of electrical conductivity reaching about 76% IACS obtained.

3. Two-lobe type contrast is not found in the peak hardness condition and even in the later stages of the ageing process for the RS Cu-0.66Cr alloy due to the very fine precipitates.

4. The estimated maximum strength by using coherent precipitation theory is quite consistent with the experimental results.

5. The variations of microhardness indicate that upon aging the fine grain strengthening contributes to about 27% enhancement of microhardness. While the coherent dispersion strengthening contributes to about 73%. Both the solid solution and vacancy strengthening only have a minimal effect on the microhardness.

Acknowledgement

This work was supported by the National Natural Science Foundations of China under Contract No. 59671043.

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Received 29 September 1998

and accepted 23 June 1999