Article ID: 1003 - 6326(1999)04 - 0723 - 05

Coherent strengthening of aging precipitation in rapidly solidified Cu-Cr alloy①

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Abstract: A single-roller melt spinning method was used to produce Cu-Cr microcrystalline alloy ribbons. Through 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 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.

Key words: rapid solidification; Cu-Cr alloys; aging precipitation; coherent strengthening

Document code: A

1 INTRODUCTION

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

Currently, the methods producing Cu-Cr alloy by rapid solidification (RS) are mainly single roller melt spinning[2,3] and atomization[4], which 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 reaches 3.3%Cr[3]. 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[5,6]. As far as the precipitation strengthening is concerned, different view points have been presented. Batawi *et al*[7] believed that the strengthening mechanism of RS Cu-Cr alloys conformed to Orowan strengthening mechanism. However, Correia *et al*[8] proposed that before the peak hardness in atomized Cu-Cr alloy

① Project 59671043 supported by the National Natural Science Foundation of China
Received Sep. 17, 1998; accepted Dec. 7, 1998

was reached the strengthening was caused by coherent strengthening mechanism upon aging and the growth of the precipitates upon over-aging might be explained by Orowan strengthening mechanism. In the present work, the properties and microstructures of a Cu-Cr alloy produced by single roller melt spinning method were studied and the specific strengthening mechanism and its effects were analysed.

2 EXPERIMENTAL

The Cu-0.66Cr alloy ingot, with the mass of 20 g, was induction melted in a quartz tube and then ejected under the pressure of pure Ar to a copper roller rotating at a velocity about 3 000 r/min. The resulting microcrystalline ribbons were 2 mm in width and 30 ~ 60 μm in thickness. The aging treatments were carried out in an electrical resistance furnace with a temperature accuracy of ± 5 ℃.

The electrical resistance was measured with a QJ42 type two probe electric bridge. The mean value of five measurements had an estimated accuracy within ± 0.000 2 Ω. The microhardness was determined with a 71-type microhardness tester under a load of 0.25 N and a holding time of 15 s. At least five samples were tested with an accuracy within ± 5%.

The ribbon samples for scanning electron microscopy (SEM) were mechanically and chemically polished before etched by the etch reagent of $\varphi(HNO_3) : \varphi(HCl) : \varphi(H_3PO_4) : \varphi(CH_3(COOH)) = 3 : 1 : 1 : 5$. The foil specimens used for the transmission electron microscopy (TEM) were obtained by double-jet electrolytic polishing at − 30 ℃ with the electric parameters of 2 V and 40 mA. The etching reagent was $\varphi(H_3PO_4) : \varphi(H_2O) = 7 : 3$. The resulting thin foil specimens were examined in a H-800 TEM operating at 200 kV.

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 spinned Cu-0.66Cr alloy ribbons after aging for 30 min. It is noted that both curves reach their maximum at 500 ℃ with tensile strength 478 MPa and microhardness HV185. Compared with the CSHT Cu-0.66Cr alloy, the tensile strength and microhardness were both considerably improved. The specific data are given in Table 1. It is found that in the as-cast state, the microhardness of the RS alloy is increased by 40%, and the electrical conductivity is lower (about 22% (IACS)) as compared with the alloy after conventional solution heat treatment (CSHT). However, upon aging at 500 ℃ 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 illustrates the SEM image of the microstructure corresponding to the peak value

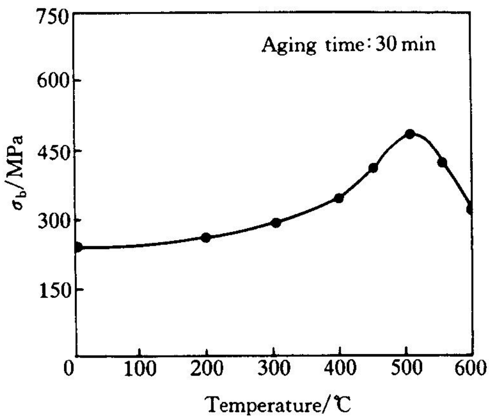

Fig. 1 Tensile strength vs aging temperature

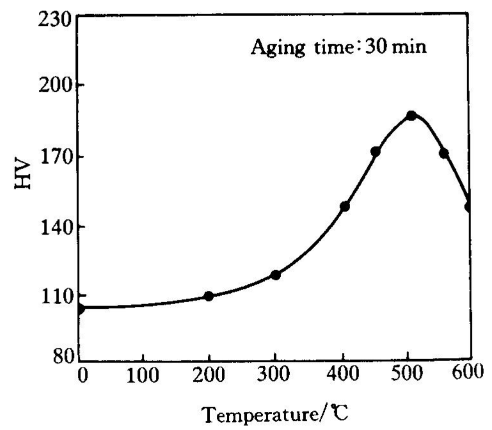

Fig. 2 Microhardness vs aging temperature

Table 1 Properties of CSHT and RS Cu-0.66Cr in as-cast and aging conditions

Property	CSHT at 1 000 ℃ and quenched in water	Aging (500 ℃, 30 min)	RS (10^6 ℃/s)	Aging (500 ℃, 30 min)
Tensile strength/MPa	235	350	236	478
Microhardness HV	75	126	105	185
Conductivity(IACS)/%	40	80	22	76

upon aging at 500 ℃ 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 with the size of ~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 the peak strength or hardness upon aging, are probably coherent ones[9], 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 for the sample which was over-aged at 600 ℃ for 1 h, although 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 the precipitates in the present work. Usually, the two-lobe type contrast can only be observed when the size of precipitates is larger 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[10] believed that the two-lobe type strain field and its shape mainly depended on r^3.

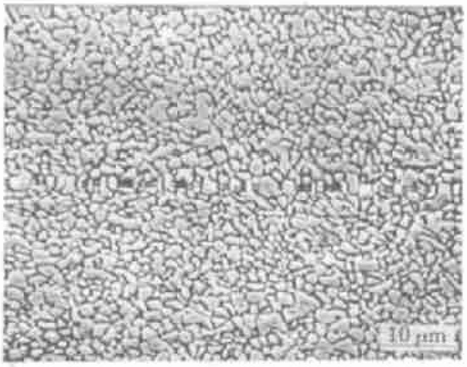

Fig.3 SEM image showing grains for RS Cu-0.66Cr alloy after aging at 500 ℃ for 30 min

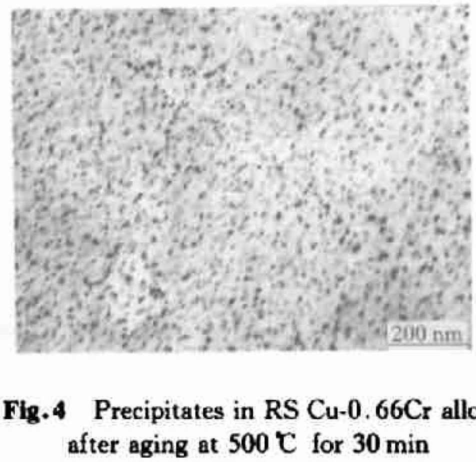

Fig.4 Precipitates in RS Cu-0.66Cr alloy after aging at 500 ℃ for 30 min

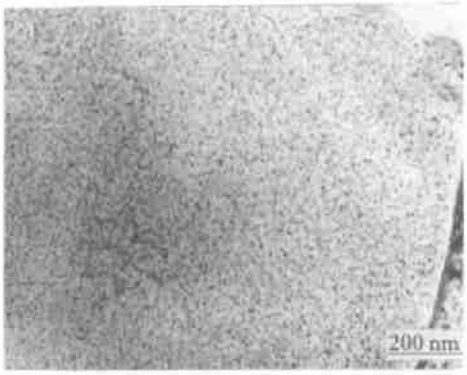

Fig.5 Precipitates in RS Cu-0.66Cr alloy after aging at 600 ℃ for 1 h

The selected area electron diffraction (SAED) analyses on 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 seems that the crystal structure of the precipitates is identical with that of the matrix, that is, the coherent precipitates are fcc Cr. This has been confirmed by Knights in his study on a Cu-Cr alloy[11~14]. 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, the 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 2. The microhardness and tensile strength of the RS pure copper only had negligible decrease after aging at 500℃ 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. Furthermore, the slight difference of both microhardness and tensile strength between the RS Cu-Cr alloy and pure copper (comparing the property data in Tables 1 and 2) 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 remarkable increase of electrical conductivity. Therefore, the enhancement of mircrohardness in RS Cu-0.66Cr alloy was mainly attributed to the fine grain strengthening mechanism. As far

Table 2 Experimental data for RS pure copper

State	Microhardness HV	Tensile strength/MPa	Resistivity /(Ω·m)
RS (10^6℃/s)	103	208	1.85×10^{-8}
Aging (500℃, 1 h)	101	203	1.81×10^{-8}

as the tensile strength (see Table 1) 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-spinned 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 mechanically polished carefully, 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 be exactly reflected only by microhardness measurement.

The strength and hardness of RS alloy have been greatly enhanced with respect to CSHT alloy after aging treatment. In peak hardness or slight over-aging conditions, the precipitates kept coherent with the matrix. The increment of shear stress caused by the coherent dispersion strengthening can be expressed as[15]

$$\Delta\tau_{cs} = X(\varepsilon G)^{3/2}(r\varphi b/\Gamma)^{1/2} \qquad (1)$$

where ε is the function of the degree of misarrangement δ; G and b are the shear modulus and Burgers vector of the matrix, respectively; r and φ are the mean radius and volume fraction of the precipitates, respectively; Γ is the line tension of the dislocations pinned by the precipitates, $\Gamma=\alpha Gb^2$, and α varies between 0.089~0.5; X is a coefficient varying between 2 and 3, usually, $X=2.6$ is selected.

The maximum mutual action force F_m between the coherent precipitates and a straight edge dislocation has been calculated by Gerold and Haberkovn[16], using the isotropical elastic theory:

$$F_m = 4G\varepsilon br \qquad (2)$$

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

$$r_{max} = \Gamma/2Gb\varepsilon \qquad (3)$$

By inserting Eq. (3) into Eq. (1), one gets the estimated maximum increment of the shear stress resulted from the coherent dispersion strengthening, which is written as

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

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 approximation, the lattice constant α = 0.368 nm[17] of the rich fcc Cr phase in Cr-Ni alloy is inserted into Eq.(5):

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

The value $\delta = 0.018$ is obtained. By inserting it into Eq.(6):

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

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

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

If inserting the volume fraction $\varphi = 67\%$ of the precipitates in RS Cu-Cr alloy after aging at 500 ℃ for 30 min (in peak hardness state) into Eq.(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 peak hardness condition. It is very close to the tensile strength 478 MPa obtained in this work.

Through regressing large amount of experimental data, Correia *et al*[8] have given an empirical relation between the increment of microhardness and the volume fraction of the precipitates for Cu-Cr alloy upon aging:

$$\Delta HV = 94\varphi^{1/2} \quad (8)$$

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

It is noted from the variation of microhardness that compared with CSHT, the fine grain strengthening brought by RS may increase the microhardness by ΔHV = 30, which contributes about 27% to the increment of the microhardness. In the later aging at 550 ℃ for 30 min, no obvious grain growth was found. The fine grain strengthening machanism still worked. Therefore, the coherent dispersion strengthening leads to an increment of microhardness about ΔHV = 80, which contributes about 73% to the increment of the microhardness. Both the solid solution and vacancy strengthening have little effects on the microhardness.

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(Edited by Peng Chaoqun)