

THE EFFECT OF RARE EARTH ELEMENTS ON Cr PRECIPITATIONS IN A Cu-0.8WT%Cr ALLOY

GEWANG SHUAI¹, MENG ZHANG¹ AND YONGLI YAN²

¹School of Materials Science and Engineering, Nanchang University, 330047 Nanchang, China, ²Department of Basic Courses, Northeastern University at Qinhuangdao, 066000 Qinhuangdao, China
e-mails: shuaigw@126.com, zhhmeng@ncu.edu.cn, qhdyyl@126.com
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ABSTRACT

The microstructural evolution of Cu-based alloys during aging was studied using a quantitative metallographic method. Samples were cut from ingots of Cu-0.8wt%Cr and Cu-0.8wt%Cr-RE alloys. These were solution treated at 1000 °C for 1.5h and subsequently quenched in water, then separately aged at 480 °C for different durations. The microstructures were observed by optical microscope, and the characteristic geometric parameters of precipitated Cr phase, including volume fraction V_V , face density N_A , mean diameter and roundness, were measured. These data provided more details about the process of aging. The results showed that precipitation of Cr phase occurred in the form of particles during aging. Rare earth elements promoted the precipitation of Cr phase and dispersed Cr particles. The phenomenon of overaging came earlier in Cu-Cr-RE than in Cu-Cr. In the present work, the optimal aging time at 480 °C was 2 hrs for the Cu-0.8wt%Cr-RE alloy and 3 hours for the Cu-0.8wt%Cr alloy.

Keywords: CuCrRE alloy, precipitation, quantitative metallographic analysis.

INTRODUCTION

Cu-based alloys have many important applications because of their high strength and excellent conductivity. Many methods of alloy preparation have been developed to improve strength, such as aging-hardening, rapid solidification, solid solution hardening and mechanical alloying (Morris and Morris, 1989; Batawi *et al.*, 1990; Szablewski and Kuznicka, 1991; Lopez *et al.*, 1997; Jin and Adachi, 1998; Liu *et al.*, 2000). Cu-Cr alloy, as a typical age-hardened alloy, can be strengthened by precipitation of Cr phase in a copper matrix without impairing its good electrical and thermal conductivities. The morphology, size and distribution of the precipitated Cr phase have a significant influence on the ultimate properties of the Cu-Cr alloy. It has been a topic of great interest of how to control the process of precipitation of Cr phase (Tang *et al.*, 1985). Previous research showed that the Cu-Cr alloy is very sensitive to aging temperature and aging time and easily inclined to overaging under an unsuitable heat treatment program. It also has been discussed that a small addition of other elements to a Cu-Cr alloy can improve its properties (Ferneer *et al.*, 2001). We have

focused on the addition of rare earth elements to the Cu-Cr alloy. RE additives have been applied in many alloys and showed good effects of cleaning the matrix and microalloying (Du, 1996; Tan *et al.*, 1999), but little applied research of RE elements in Cu-Cr alloys has been carried out.

It is well known that the distribution of the secondary phase in the matrix has a very important influence upon the properties of materials. Some previous research has described methods for the spatial distribution of the secondary phase and the effects on properties of materials including ferrous metals and composites (Horalek *et al.*, 1988; 1989a,b; Liu and Yu, 1996; Wang *et al.*, 2000; Popa and Chaix, 2002). There were few reports dealing with the distribution of secondary precipitation in Cu-Cr-RE alloys after being aged by using quantitative metallographic analysis. In this paper, characteristic geometric parameters of precipitated Cr particles in Cu-Cr and Cu-Cr-RE alloys have been measured using quantitative metallographic method. The results provide valuable information for choosing the optimal procedure for aging treatment and to obtain a suitable Cu-Cr alloy with better properties.

MATERIAL AND METHODS

SAMPLE PREPARATION

Cu-0.8wt%Cr-RE alloy was prepared by vacuum induction melting from electrolytic copper, Cu-4wt%Cr and Cu-10wt%RE alloys. A Cu-0.8wt%Cr alloy was also prepared for comparison. Samples cut from the cross section of ingots were solution treated at 1000 °C for 1.5 h followed by water quenching. The solution-treated samples were separately aged at 480 °C for 1h, 2h, 3h and 4h. The specimens for observation by optical microscope were polished and etched in a solution of FeCl₃, HCl and absolute alcohol. In order to examine the crystal structures of phases in the samples, X-Ray diffraction was carried out by D/max-3B diffractometer.

QUANTITATIVE METALLOGRAPHIC ANALYSIS

The microstructures were observed with a MeF3 optical microscope and objective with 50× magnification equipped with a digital camera having a resolution of 800×1000 pixels. Quantitative metallographic analysis was carried out using Image-Pro Plus (IPP) software for image analysis. For our work, IPP was used for the preparation of task-oriented functions, based on the principle of stereology and quantitative metallography, used to perform the measurements of characteristic geometric parameters. In order to assure appropriate accuracy of the results, 30 fields randomly selected in each sample were analyzed. Due to the limit of resolution of the optical microscope, the parameter of area identifying S_{min} was set to 1 μm^2 , so that only particles with an area larger than 1 μm^2 were measured and noise was almost eliminated.

RESULTS

The scans of X-Ray diffraction showed both face-centered cubic (fcc) Cu and body-centered cubic (bcc) Cr in all of the samples. After aging treatment, the intensity of diffraction peaks of Cr became larger. The results suggested that precipitation of Cr phase occurred during aging. The microscopy observation showed that the precipitated Cr phase was in the form of particles distributed in the copper matrix. Scans carried out on the peaks of all samples did not show evidence of additional peaks for RE, because RE content was too low.

Optical microscopic examination showed that the microstructures of both alloys were dendritic, with some Cr particles homogeneously distributed in the material prior to solution treatments. We selected four figures (Figs. 1-4) to show the microstructures of Cu-0.8wt%Cr and Cu-0.8wt%Cr-RE alloys before and after aging. After solution treatment, the number of Cr particles was lower, as shown in Figs.1 and 3. There is no evident difference between the two alloys.

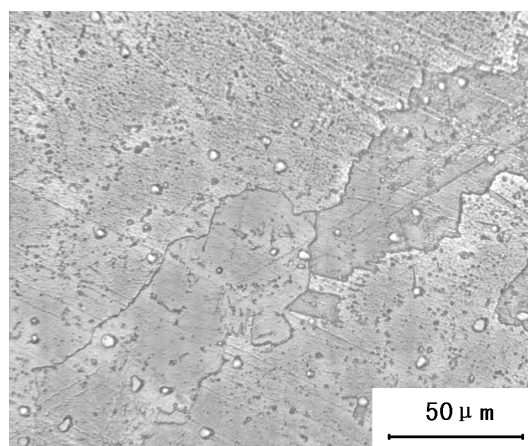


Fig. 1. Microstructure of Cu-0.8Cr after 1000 °C ×1.5h-solution heat treatment.

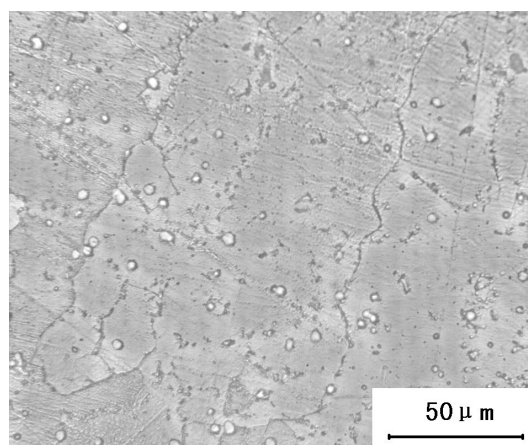


Fig. 2. Microstructure of Cu-0.8Cr after 480 °C ×2h-aging treatment.

After aging at 480 °C more and more particles appeared in the matrices and the number increased with increasing aging time in both Cu-Cr and Cu-Cr-RE alloys. Figs. 2 and 4 showed the typical microstructures of Cu-Cr and Cu-Cr-RE alloys after being aged at 480 °C for 2h. It indicated that Cr precipitation occurred. There are more particles in Fig. 4 than in Fig. 2, and the particles in Fig. 4 are much finer.

Curves in Figs. 5-8 show the variations in volume fraction V_V , face density N_A , mean diameter and roundness of Cr particles with aging time for the two alloys.

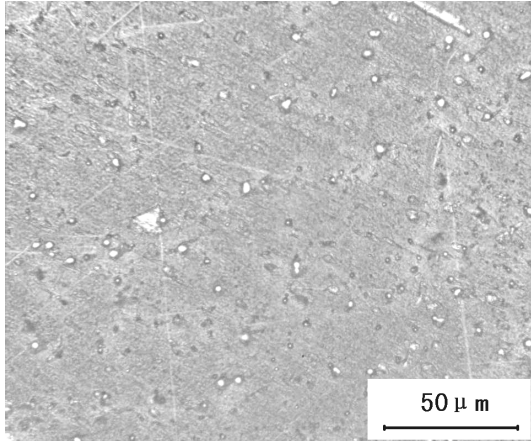


Fig. 3. Microstructure of Cu-0.8Cr-RE after 1000 °C × 1.5h-solution heat treatment.

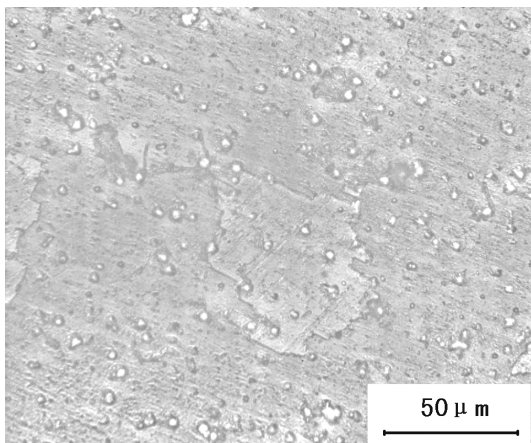


Fig. 4. Microstructure of Cu-0.8Cr-RE after 480 °C × 2h-aging treatment.

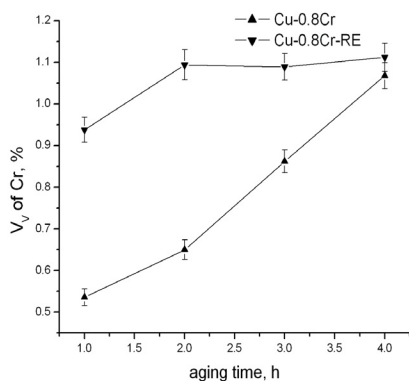


Fig. 5. Volume fraction V_V of Cr as a function of aging time.

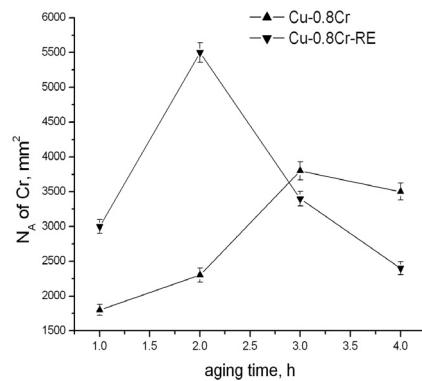


Fig. 6. Face density N_A of Cr as a function of aging time.

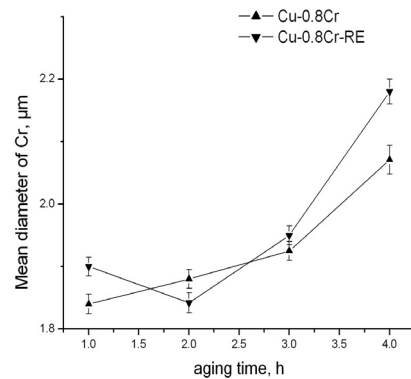


Fig. 7. Mean diameter of Cr as a function of aging time.

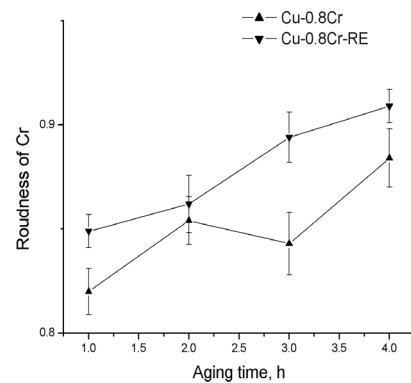


Fig. 8. Roundness of Cr as a function of aging time.

V_V of Cr particles in two sample alloys increased with increasing aging time (as shown in Fig. 5). In the Cu-Cr-RE alloy, it reached the maximum value after aging for 2 hrs, then tended to be stable. In the Cu-Cr alloy, it increased as a function of aging time and approached the value of Cu-Cr-RE after aging for 4 hrs.

N_A of Cr particles in these samples increased at the beginning and then decreased after reaching the maximum value, as shown in Fig. 6. The peak value of N_A in the Cu-Cr-RE alloy was higher and appeared earlier than in the Cu-Cr alloy. Table. 1 gives the rates of increase and decrease of N_A of Cr particles in these two alloys. It shows that the rates changed faster in Cu-Cr-RE than in Cu-Cr.

Table 1. Rates of increase and decrease of N_A of chromium particles for two alloys.

	Cu-0.8wt%Cr	Cu-0.8wt%Cr-RE
rate of increase, /mm ² ·h	1000	2500
rate of decrease, /mm ² ·h	500	1550

From Fig. 7 it can be seen that the mean diameter of chromium particles increased with increasing aging time and the size of particles in Cu-Cr-RE was larger than in the Cu-Cr alloy except at 2h. The rate of coarsening of precipitated Cr particles in Cu-Cr-RE (0.093 $\mu\text{m}/\text{h}$) was higher than that in Cu-Cr (0.077 $\mu\text{m}/\text{h}$).

The roundness we measured is defined by the following formula:

$$\text{Roundness} = \frac{4 \cdot \text{Pi} \cdot \text{area}}{\text{Perimeter}^2}$$

where perimeter is the length of the object's outline, and area is the surface of each object. Circular objects will have a roundness = 1; other shapes will have a roundness < 1.

The variations of roundness of chromium particles are presented in Fig. 8. Roundness increased with increasing aging time in both alloys in a general way, except that it decreased abnormally at 3h in the Cu-Cr alloy. The value of roundness in the Cu-Cr alloy was smaller than that in Cu-Cr-RE.

DISCUSSION

From Figs. 1 and 3 it is obvious that solution treatment did not dissolve all of the Cr particles in the copper matrices. The maximum equilibrium solubility of chromium in copper is only about 0.8 wt% even at 1070 °C (Tenwick and Davies, 1988), which is higher than the temperature of solution treated in this paper. Cr particles existed in all samples. They could be divided into two groups: finer ones and coarser ones. The finer ones were the result of solid-state precipitation

during aging, while the coarser ones were created directly from melting during casting. After solution treatment, these unresolved Cr particles did not affect the subsequent quantitative analysis because they kept almost stable during the aging processes.

Figs. 2 and 4 show that the two alloys behaved differently during aging. Comparing the micrographic image of the Cu-Cr-RE and Cu-Cr alloys, we could find no evident difference of precipitated Cr particles in these two alloys. However, the results of quantitative analysis showed more details.

Fig. 5 shows that V_V of Cr phase was about 1.094% in Cu-Cr-RE after being aged for 2h and about 1.068% in Cu-Cr after aging for 4h. It is obvious that rare earth elements promoted the process of precipitation. Also, these results suggest that the Cr phase had precipitated completely after aging.

According to the theory of precipitation hardening (Porter, 1981), a large number of nuclei appeared in the matrices due to the severe driving force at the early aging stage and the size of precipitated particles was small. Then they grew with time and the spacing between the precipitates became large. The processes of precipitating and coarsening of the secondary phase were accompanied by the process of long-distance diffusing of secondary phase atoms. These evolutions of microstructures during the aging process would lead to the conclusion that the hardness of material increased at first and then decreased. Specimens aged beyond peak hardness were referred to as overaged. Comparing these curves in Figs. 5-7, RE elements speeded the processes of aging including nuclei and growth of precipitated particles.

It should be further noted that the phenomenon of overaging came earlier in Cu-Cr-RE than in Cu-Cr. It suggests that although we can get a finer precipitate distribution in the Cu-Cr-RE alloy, we should perform aging operations on this kind of alloy much more carefully.

As we know, in the early stage of aging, the morphology of the second phase is usually plates and pillars with bad roundness because of the influence of strain energy. With the coarsening of the second phase, the morphology of the precipitated phase becomes spheres with good roundness in order to decrease the total interface energy. Therefore, the two factors of precipitating and coarsening have opposite influences on roundness. Roundness as a statistical parameter is determined by the dominant factor.

CONCLUSION

A systematic study of microstructure evolution by using a quantitative metallographic method has enabled the determination of the characteristics of precipitated Cr phase in Cu-Cr and Cu-Cr-RE alloys. The data of volume fraction V_V , face density N_A , mean diameter and roundness of Cr particles measured from microscopy morphologies can provide more details about the processes of aging. The main effect of rare earth additives is that REs promote the processes of aging including nuclei and the growth of precipitate particles. The phenomenon of overaging comes earlier in Cu-Cr-RE than in Cu-CR. Consideration must be given to the effects of rare earth elements when deciding on the best aging operation in practice. In the present work, the optimal aging time at 480 °C is 2 hours for Cu-0.8wt%Cr-RE alloy and 3 hrs for Cu-0.8wt%Cr alloy.

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