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Influence of Grain Refinement on Oxidation Behavior of Two-Phase Cu–Cr Alloys at 973–1,073 K in Air

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Abstract: The oxidation behavior of grain-refined Cu–7.0 Cr alloy (GR Cu–7.0 Cr) in air at 973–1,073 K was investigated in comparison with normal casting Cu–7.0 Cr alloy (CA Cu–7.0 Cr). The oxidation of CA Cu–7.0 Cr alloy nearly followed parabolic law, while the oxidation kinetics of GR Cu–7.0 Cr slightly deviated from parabolic law. Both alloys almost produced multi-layered scales consisting of the outer layer of CuO and the inner layer of mixed Cr₂O₃ and Cu₂O oxides plus internal oxidation zones of chromium. The grain-refined Cu–7.0 Cr alloy produced a more amount of Cr₂O₃ in the inner layer of the scale, and thus was oxidized at much lower oxidation rate than that of CA Cu–7.0 Cr with normal grain size. The experimental results indicated that the differences in oxidation behavior between two alloys may be ascribed to the different size and spatial distribution of the second-phase particles and the reactive component contents in localized zone.

Keywords: Cu–Cr alloy, two-phase, oxidation, grain refinement, reactive elements

Introduction

Cu–Cr alloys are regarded as good materials for conducting and wear components, especially the promising vacuum contact materials with wide application perspective. However, the mutual solubility of chromium and copper is very low; for example, the solubility of chromium in copper was only 1.9×10^{-3} mol fraction at 1,173 K, high-temperature corrosion behavior of two-phase Cu–Cr alloy is quite different from that of single-phase copper

alloy, which is especially related to the microstructure, phase distribution, the size of crystalline grain and so on. Therefore, the corrosion behavior of Cu–Cr alloys at elevated operating temperature has been paid more attention from many material scientists in the past decade [1–6]. In particular, the high-temperature oxidation performance of Cu–Cr alloys with grain refining has been investigated by many researchers in recent years [7–9]. In case of Cu–Cr alloy, a technique by means of decreasing the grain size of the Cu–Cr alloy or increasing oxygen partial pressure at the oxide/metal interface is beneficial to enhance the outward diffusion of chromium and to produce a single protective Cr₂O₃ film on the Cu–Cr alloys. Equal channel angular pressing (ECAP) is a material processing method that can provide significant inner deformation and produce very fine grains without changing the material shape [10–13]. Therefore, ECAP was used to produce fine grains for Cu–Cr alloy in this study in order to investigate the influence of grain refinement on oxidation behavior of reactive component in Cu–Cr alloys. The oxidation of these Cu–Cr alloys in this study including normal casting Cu–7.0 Cr alloy and the grain-refined Cu–7.0 Cr alloy from four-pass ECAP was carried out in air at 973–1,073 K to elucidate the effect of grain refinement and distribution of second phase on the oxidation mechanism of the Cu–Cr alloy.

Experimental

The nominal composition and the actual average composition of the two-phase Cu–Cr alloys (at. %) selected in this present study were listed in Table 1.

The alloy ingots were prepared by arc-melting under a Ti-gettered Ar atmosphere from pure metals (99.99 % for chromium and copper) using non-consumable tungsten electrodes. The casting Cu–Cr alloys were then annealed in Ar at 873 K for 24 h to eliminate the residual mechanical stress and to achieve a better alloy equilibration. Here the cast Cu–Cr alloy was referred to as CA Cu–7.0 Cr in this study hereafter. The grain refinement of previous CA Cu–7.0 Cr alloy was achieved in the following step through four-pass

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Table 1: Actual composition (at. %) of CA Cu–7.0Cr and GR Cu–7.0Cr alloy.

Alloy designation	Cr	Cu
CA Cu–7.0	7.1	92.9
GR Cu–7.0 Cr	6.9	93.1

ECAP. The Cu–Cr alloy samples got by ECAP were referred to as GR Cu–7.0 Cr alloy. The different microstructures of CA Cu–7.0 Cr and GA Cu–7.0 Cr alloys were shown in Figure 1. It is concluded that Cu–7.0 Cr alloy is hypereutectic alloy and both alloys were composed of Cu-rich α phase matrix (solid solution of chromium in copper) and the dispersive distributed Cr-rich β phase (solid solution of copper in chromium), almost in agreement with the binary Cu–Cr phase diagram shown in Figure 2. In case of CA Cu–7.0 Cr, the average particle size for β phase is in the range of 10–20 μm ; they are basically in the presence of equiaxed grains in α phase matrix with a small amount of localized segregation (Figure 2(a)), while for the case of GR Cu–7.0 Cr, the Cr-rich β phase was broken and stretched due to ECAP, the particle size of β phase is in the range of 1–5 μm (Figure 2(b)). The two kinds of different Cu–7 Cr alloys were cut to flat slice with 1 mm thick and then ground down to 1,500 emery paper, washed in acetone and dried before testing. The oxidation test was carried out in air for 9 h at 973–1,073 K in horizontal furnace, and the mass gains of the tested Cu–Cr samples were measured by using an electronic balance with accuracy of 0.01 mg. After oxidation, the typical specimens were embedded in epoxy resin and then polished; finally, the microstructures of the scales were characterized by means of X-ray diffraction (XRD), scanning electron microscopy equipped with an energy-dispersive X-ray microanalysis system (SEM/EDX).

Figure 2: Phase diagram of the binary Cu–Cr alloy.

Results

Oxidation kinetics

The kinetics for the oxidation of the two different Cu–7.0 Cr alloys at 973 and 1,073 K in air are shown in Figure 3(a) as normal plots and in Figure 3(b) as the parabolic plots. It is observed that the oxidation rates for both alloys obviously increased with increased temperature. The kinetic curves of CA Cu–7.0 Cr almost followed parabolic law with the average parabolic rate constant (k_p) approximately equal to $5.61 \times 10^{-1} \text{ g}^2 \text{ m}^{-4} \text{ s}^{-1}$ at 973 K (listed in Table 2). Unlike the kinetic behavior of 973 K, the oxidation kinetic curves presented two different stages of parabolic curves at 1,073 K, the corresponding parabolic rate constants (k_p) are listed in Table 2, respectively. Moreover, the k_p values of 973 K are slightly smaller than that of 1,073 K, which is mainly related to the temperature effect. During the whole oxidation, the oxidation rates of the GR Cu–7.0 Cr alloy

Figure 1: Microstructures of Cu–Cr alloys (bright particle: β phase): (a) CA Cu–7.0 Cr and (b) GR Cu–7.0 Cr.

Figure 3: Oxidation kinetic curves for CA Cu-7.0Cr and GR Cu-7.0Cr in air at 973 and 1,073 K: (a) normal plots and (b) parabolic plots.

Table 2: Parabolic rate constant ($\text{g}^2 \text{m}^{-4} \text{s}^{-1}$) for the binary Cu-Cr alloys at 973–1,073 K in air.

Alloy designation	Oxidized at 973 K		Oxidized at 1,073 K	
	Initial	Average	Initial	Average
CA Cu-7.0Cr	4.70×10^{-2}	5.61×10^{-1}	4.54×10^{-1}	3.48
GR Cu-7.0Cr	2.21×10^{-2}	3.45×10^{-1}	5.31×10^{-1}	1.64

are smaller than that of CA Cu-7.0 Cr at both temperatures. The kinetic curves of GR Cu-7.0 Cr alloy approximately followed the parabolic law at 973 K; however, the kinetics of 1,073 K for GR Cu-7.0 Cr alloy deviated from the single parabolic plots, which was divided into two-stage parabolic plots, the first slope of the parabolic plots slowly increased with time within the initial stage approximately lasting 4 h, then rapidly increased to almost the constant values at second stage, which was possibly related to breakaway of scales during oxidation. When compared with the oxidation of CA Cu-7.0 Cr and GA Cu-7.0 Cr, it was observed

that the average parabolic rate constant (k_p) of GR Cu-7.0 Cr was lower than that of CA Cu-7.0 Cr alloy, which were mainly ascribed to the grain refinement and the smaller distributed β phase in the Cu-Cr alloy.

Scale morphology and composition

Micrographs of the scales produced on the two binary Cu-7.0 Cr alloys with different grain sizes after oxidation at 973–1,073 K are shown in Figures 4 and 5, respectively. As shown in Figure 4, oxidation of CA Cu-7.0 Cr at 973 K formed scales composed of a thin outermost layer of CuO (gray) plus the thick inner layer of Cu₂O with an irregular dispersive distribution of unoxidized β phase particles, particularly, a very thin layer of Cr₂O₃ formed on the surface of β phase particles was also found, and some cracks and gaps were observed from the cross-sectional morphology. Unlike the oxidation at 973 K, the considerable thin outmost layer of CuO was observed in scales at 1,073 K; the inner layer of the scales was mostly composed of Cu₂O plus internal oxidation zone; a non-continuous Cr₂O₃ layer was partly detected in the scale/alloy interface; at the same time, an obvious Cr-depleted zone was observed in front of internal oxidation zone.

Differing from the scale structures of CA Cu-7.0 Cr at 973 K, the scales formed on GR Cu-7.0 Cr alloy was composed of a very thick outermost layer of CuO, then followed by a relative thin inner layer of mixed Cu₂O and Cr₂O₃ zones, a clear Cr-depleted zone was partly observed in the alloy matrix; meanwhile, the internal oxidation zone was detected beneath the scales, and the obvious cracks were present at the alloy/scale interface (Figure 5). For oxidation of GR Cu-7.0 Cr alloy at 1,073 K, the outer layer of mainly CuO (gray color) was considerably thin, almost absence of the outmost layer of the scale (Figure 5 (b)), the scales were mostly composed of the thick Cu₂O layer mixed with some small and dispersive particles of Cr₂O₃. In particular, locally continuous Cr-rich oxides were detected in the scale/alloy interface; at the same time, a continuous Cr-depleted zone was observed in matrix. When compared with the oxidation of the two different Cu-Cr alloys at both temperatures, oxidation of GR Cu-7.0 Cr alloy produced the relative thinner scales and more volume fraction of chromium oxides in the inner layer of scale than CA Cu-7.0 Cr alloy, which effectively hinder inward penetration of oxygen and the outward diffusion of metal ion through the scales; these are related to the differences of grain size and the distribution of β phase

Figure 4: Cross-sectional micrograph (SEM/BEI) of CA Cu-7.0 Cr alloys oxidized in air at 973 and 1,073 K for 9 h: (a) at 973 K; (b) enlarged view of region A in (a); and (c) at 1,073 K.

Figure 5: Cross-sectional micrograph (SEM/BEI) of GR Cu-7.0 Cr alloys oxidized in air at 973 and 1,073 K for 9 h: (a) at 973 K; (b) at 1,073 K; and (c) enlarged view of region A in (b).

between two alloys. However, the cracking and scaling-off of GR Cu–7.0 Cr was more serious than that of CA Cu–7.0 Cr, which was possibly related to the internal residual stress resulting from the ECAP process.

Discussion

The scale structures of CA Cu–7.0 Cr and GR Cu–7.0 Cr oxidized in air at 973–1,073 K could be nearly described by the schematic diagram shown in Figure 6. The oxide scales from the outer layer to the inner layer in the scales are generally following the sequence of $\text{CuO} \rightarrow \text{Cu}_2\text{O} \rightarrow \text{Cu}_2\text{O} + \text{Cr}_2\text{O}_3 \rightarrow$ internal oxidation zone. However, the scale structure can be changed with the elevated temperature, grain size and the distribution of second phase in alloy. For example, the outer CuO layer of GR Cu–7.0 Cr became considerably thin and almost tended to disappear from the scale at 1,073 K (shown in Figure 5(b)); meanwhile, more volume fraction of Cr_2O_3 was formed in the inner layer close to the scale/alloy interface, which was clearly different from the scale structure for CA Cu–7.0 Cr alloy. Although GR Cu–7.0 Cr and CA Cu–7.0 Cr contained the same chromium content, the big differences in scale structure and kinetics between them still lie at both temperatures, which are mainly ascribed to the change of grain size and the different distribution of β phase and so on.

Figure 6: Schematic diagram of scale structure in cross section for CA Cu–7.0 Cr and GR Cu–7.0 Cr oxidized in air at 973–1,073 K.

For GR Cu–7.0 Cr and CA Cu–7.0 Cr, the presence of 7 at. % chromium in Cu–Cr alloy is insufficient to hinder the growth of the external scales mostly composed of copper oxides, mainly as a result of the limited solubility of chromium in copper, judged from phase diagram shown in Figure 2. Therefore, in the present alloys the chromium element is mostly present in form of particles of a second Cr-rich β phase dispersed in the copper matrix, which is clearly observed from Figure 1.

As predicated on a classical theoretical basis of the binary Cu–Cr alloy [14–16], the critical content of the reactive component B of binary A–B alloys required for forming the exclusive external scale of BO oxides is much higher for the two-phase alloy than for the corresponding single-phase alloy, where A is regarded as the more noble and B the more reactive component in the alloys. Here, the treatments for the previous oxidation theory of binary solid solution alloys cannot directly be applied for predicting oxidation of Cu–Cr alloy in the present study as a result of the very small mutual solubility of chromium and copper. Thus, the oxidation behavior of Cu–Cr alloys is considerably more complex than that of the Fe–Cr and Cu–Al alloys. The literature [17] reported that the binary Cu–Cr alloy with a normal grain size still produced the incomplete external chromia scales under chromium contents as high as 75 at. %; conversely, the alloys tended to undergo the internal oxidation of chromium of the in situ type, which is in good agreement with the predications of a theoretical treatment of the oxidation of binary two-phase alloys reported in these literatures [14, 15].

In general, the critical B concentration N_B^0 required for the transition from mixed scales (AO + BO) to a single external oxide BO in binary A–B solid solution can be calculated according to the Wagner formula as follows [18]:

$$N_B^0 = \frac{V}{M_O Z_B} \left(\frac{\pi k_p}{D_B} \right)^{\frac{1}{2}} \quad (1)$$

where k_p is the parabolic rate constant of BO film growth calculated according to the weight gain on unit surface area, V the molar volume of alloy, Z_B the valence of B in the scale, M_O oxidation of atomic mass, D_B the diffusion coefficient of B in the alloy. Some specific measures for transformation to the external oxidation at low concentration are suggested as follows: (1) reduce the factors of oxygen inward flux, such as reducing P_{O_2} (partial pressure of oxygen); (2) improve the factors of B outward flux, such as grain refining of alloy substrate or surface modification which can contribute to short circuit diffusion, etc., so as to raise D_B . Therefore, the formation of the

external chromia scale or increasing oxidation resistance of Cu–Cr alloy may depend on either by decreasing the oxygen pressure or by preparing alloy with very small grain size.

In the present study, the ECAP method was used to obtain the small grain size for Cu–Cr alloy. The boundaries between two phases increased after the phase particles were refined by ECAP. Then, a great deal of grain boundaries may act as preferential diffusion channels, which further reinforced the short-circuit diffusion of Cr. The grain boundaries took larger proportion in the bulk alloy, and grain boundary diffusion made bigger contribution, i. e. D_B increased, therefore, outward transportation rate of selective component increased accordingly, which was desirable for the formation of external Cr_2O_3 . However, for the present Cu–Cr system, the increase of the effective diffusion coefficient of chromium has not resulted in the transformation from internal oxidation to external oxidation, which is mainly due to the lack of chromium in the alloy or the grains were not refined to sufficient degree [18].

Comparing the oxidation of CA Cu–7.0 Cr and GR Cu–7.0 Cr at the two temperatures, it is observed that oxidation rate of GR Cu–7.0 Cr was lower than that of CA Cu–7.0 Cr, which was mainly associated with the more amount of Cr_2O_3 formed in the inner layer of scale for GR Cu–7.0 Cr than for CA Cu–7.0 Cr, effectively hindering the outward diffusion of copper from substrate. Here the effect of grain refinements on the oxidation behavior of binary Cu–Cr alloys may be discussed from two aspects [4]. On the one hand, the positive effect of grain refinement is to accelerate transportation of the reactive component (Cr) in the alloys, contributing to fast formation of Cr_2O_3 oxides in the scales and even connected to a continuous Cr_2O_3 film (Figure 5(c)), which can then act as a barrier preventing further oxidation. On the other hand, the negative effect of grain refinement was to increase the diffusion coefficient of all the elements (including oxygen from environment), resulting in faster oxidation of all the components of the alloys, and then weight gains of alloy became much larger than before. Key point in evaluating the oxidation resistance of the grain-refined Cu–Cr alloy is to know whether positive or negative effect prevails [19]. From the oxidation curves of GR Cu–Cr alloy shown in Figure 3, it was observed that the total mass gains of GR Cu–7.0 Cr were lower than that of CA Cu–Cr alloy with normal grain size after 10 h; therefore, it can be concluded that grain refinement was helpful to improve oxidation resistance of Cu–Cr alloys.

Furthermore, the main difference between these two alloys lies in the amount and existing form of Cr_2O_3 , it

can be observed from the micrographs that volume fraction of Cr_2O_3 formed in grain-refined Cu–7.0 Cr is obviously more than that of CA Cu–7.0 Cr, and more continuous Cr_2O_3 in the form of thin lines was detected close to the scale/alloy interface. Although CA Cu–7.0 Cr contained almost the same amount of Cr as grain-refined Cu–7.0 Cr alloy, the in situ oxidation of β (Cr) phase in CA Cu–7.0 Cr was wrapped in CuO or Cu_2O in the form of metal after oxidation at 973 K, when the temperature elevated to 1,073 K, the alloy mostly formed dispersive distribution of Cr_2O_3 -rich particles in the scales instead of continuous Cr_2O_3 lines. Conversely, grain-refined Cu–7.0 Cr produced thick mixed oxidation zone of Cu_2O plus Cr_2O_3 after oxidation at both 973 and 1,073 K; in particular, there were locally continuous Cr_2O_3 in the form of thin lines in the scales. When compared with the microstructures of CA Cu–7.0 Cr, the grains in GR Cu–7.0Cr were much finer than CA Cu–7.0 Cr, and the average size of Cr-rich second phase was below 2 μm . These big differences in the microstructure of two alloys caused different structures of oxidation scale formed on Cu–Cr alloy. The main reason is that, in the binary Cu–Cr alloys with the same content of chromium, if the Cr-rich β particles distributed in α matrix are bigger, the constant dissolving and transportation speed of chromium particles to alloy surface is lower; on the contrary, if the Cr-rich β particles are smaller and well distributed, the distance of adjacent two Cr particles becomes shorter; meanwhile, smaller Cr particles cause bigger surface area and dissolve faster to supply sufficient chromium to alloy surface, then contributes to the formation of Cr_2O_3 film. The presence of Cr-depleted zone in the Cu–Cr alloy substrate was attributed to insufficient Cr amount needed to form continuous protective Cr_2O_3 film on two-phase binary Cu–Cr alloys in this study, when chromium was supplied to the alloy surface for growth of Cr_2O_3 , the concentration of Cr in the front of base material decreased considerably and no sufficient Cr in the alloy to complement, as a result, the Cr-depleted zone appeared with extended oxidation time.

Comparing scale structures of CA Cu–7.0 Cr and grain-refined Cu–7.0Cr, it can be easily observed that the thickness of their scales was significantly different, mainly due to the formation of mixed oxide of $\text{Cu}_2\text{O} + \text{Cr}_2\text{O}_3$ in inner layer of scales, which may effectively prevent flux rate of reactants to some extent. However, in most cases, Cr_2O_3 mostly present in the form of single particles in inner oxidation zone of CA Cu–7.0 Cr, even occasionally Cr_2O_3 connected together to form continuous lines. Whereas much longer and thin lines of Cr_2O_3 appeared apparently on the bottom of

scale in GR Cu–7.0 Cr alloy. This is the contribution of grain refinement in the above-mentioned analysis. Grains in GR Cu–7.0 Cr are thinner and smaller, with bigger surface area; the dissolving speed is higher than the bigger ones in CA Cu–7.0 Cr alloy, and transporting of Cr particles to alloy surface is faster as well, correspondingly, the Cr_2O_3 particles formed are smaller and surface areas become bigger, contributing to the formation of uniform and continuous line-form Cr_2O_3 film; on the other hand, the Cr particles are bigger in CA Cu–7.0 Cr alloy than GR Cu–7.0 Cr alloy, and the Cr_2O_3 particles produced are bigger as well, which laid a relatively longer distance between the two adjacent Cr_2O_3 particles, causing it more difficult for them to be connected to a continuous line of Cr_2O_3 .

Observed from micrographs of oxidized Cu–Cr alloys, the previous stretched Cr particles became oval shape, indicating that recrystallization of chromium occurred during oxidation test. As the grain size of the second phase was getting bigger and bigger, the advantage of grain refinement was getting less and less, and even disappeared. In addition, the easily cracking and scaling-off of the oxide scales formed GR Cu–7.0 Cr alloy that could be explained from the following factors: (1) the grains of GR Cu–7.0 Cr alloy partly slid, and stretched, broken and fiberized because of the ECAP processing, the lattice distortion and dislocation tangles caused the presence of certain amount of residual stress in the metal; thus, the scale became easily spalling off during oxidation. (2) Although grain-refined Cu–Cr alloys obtained better strength but at the cost of causing residual stress, meantime, the growth of oxides of copper and chromium also produced great stress because Pilling Bedworth Ratio (PBR) of copper and chromium oxides is far more than 1.0, which is not beneficial for the oxidation resistance of Cu–Cr alloy, easily inducing cracking and peeling off from base material. In a word, the grain-refined Cu–Cr alloy is more conducive to the promotion of selective oxidation of reactive Cr component and enhances the oxidation resistance.

Conclusions

In the present study, the microstructures of binary two-phase Cu–Cr alloys significantly affected their oxidation performance. The oxidation behavior and scale structures formed on Cu–Cr alloy closely depended on the size of Cr-rich second phase and the distribution of α and β phases in matrix. Both CA Cu–7.0 Cr and GR Cu–7.0 Cr alloys produced multi-layered scales, but the volume fraction of Cr_2O_3 formed on GR Cu–7.0 Cr is

apparently more than that of CA Cu–7.0 Cr, and the Cr_2O_3 particles in GR Cu–7.0 Cr are finer and better distributed. In particular, many continuous Cr_2O_3 zones were locally obtained on GR Cu–7.0 Cr alloy, reducing the oxidation rates, but cracking and scaling-off of the oxide scales was very serious, which was owing to the residual stress in grain-refined Cu–7.0 Cr alloys. Regarding grain refinement induced by ECAP technology, it would be preferable to adjust the passes of pressing and relieve the residual stress by proper technique with goal to get the desirable microstructures and good oxidation resistance for Cu–Cr alloy.

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