

Oxidation of two-phase Cu-Cr alloys with different microstructures^①

FU Guang-yan(付广艳)^{1,2}, NIU Yan(牛焱)²,
WU Wei-tao(吴维叟)², GUAN Heng-rong(管恒荣)²

(1. Department of Mechanical Engineering, Shenyang Institute of Chemical Technology,
Shenyang 110021, P. R. China;

2. State Key Laboratory for Corrosion and Protection, Institute of Metal Research,
Chinese Academy of Sciences, Shenyang 110016, P. R. China)

[Abstract] The oxidation of PM Cu-50Cr, MA Cu-40Cr and MS Cu-40Cr alloys at 800 °C in 0.1 MPa O₂ was studied. The most important difference of their oxidation behaviors is the formation of an exclusive chromia scale on the surface of the MS Cu-40Cr alloy and a continuous chromia layer beneath an outer CuO layer corresponding MA Cu-40Cr alloy, while a complex scale composing of CuO, Cu₂O, Cu₂Cr₂O₄ and Cr₂O₃ formed on the PM Cu-50Cr alloy. This result implies that alloy microstructure affects their oxidation behaviors largely. Microcrystalline structure provides numerous diffusion paths for reactive component chromium, shorter diffusion distance and rapid dissolution of Cr-riched second phase. All these favor the exclusive formation of the most stable oxide.

[Key words] oxidation; Cu-Cr alloys; powder metallurgy; mechanical alloying; sputtering

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1 INTRODUCTION

The purpose of this study is to examine the oxidation behavior of Cu-Cr alloys with different microstructures. Not only because Cu-Cr alloys are known candidate as vacuum electricity switch materials, but also ideal binary two-phase materials for illustrating the oxidation behaviors of two-phase alloys because the two metal elements have very small mutual solubility and do not form intermediate phases. Moreover the thermodynamic stability and the growth rates of their oxides are largely different^[1]. In previous investigation, it has been reported that many materials containing two or more different metal phases have different oxidation behaviors with respect to the common single-phase alloys^[2~4]. Especially the microstructure of an alloy has significant effects on its oxidation behavior^[5]. So that this paper examines the scaling behaviors of Cu-Cr alloys prepared by powder metallurgy (PM), mechanical alloying (MA) and magnetron sputtering technique (MS).

2 EXPERIMENTAL

Three Cu-Cr alloys with nominal chromium contents of 50%, 40% and 40% (mass fraction) have been prepared respectively by powder metallurgy (PM), mechanical alloying (MA) and magnetron sputtering technique (MS), and denoted as PM Cu-50Cr, MA Cu-40Cr and MS Cu-40Cr. The alloy microstructures are shown in Fig. 1. They all contain a

mixture of the solid solutions of chromium in copper (α phase, light) and of copper in chromium (β phase, dark), which are practically identical to the two pure metals as a result of the very low solubility of Cr and Cu.

For all alloys the α phase forms the matrix which contains a dispersion of the particles of the β phase. The main difference in the three alloys concerns the particle size of the β phase. PM Cu-50Cr alloy has phase particle size about 100 μm (Fig. 1(a)) and below 1 μm in MA Cu-40Cr alloy (Fig. 1(b)). But MS Cu-40Cr alloy is a coating that has a thickness of around 25 μm and has the same component with the substrate to eliminate the interdiffusion between the coating and the substrate. X-ray analysis (Fig. 2) shows that it contains α and β phases and they are too small to be observed by SEM. So only a bright layer can be seen for MS Cu-40Cr alloy.

Samples of about 2.5 cm² surface area were oxidized for 24 h in 0.1 MPa pure oxygen at 800 °C by means of a Cahn microbalance mod. 2000. Corroded samples were examined by means of X-ray diffraction (XRD), optical microscopy (OM) and scanning electron microscopy (SEM) for phase identification and structural analysis.

3 RESULTS

The oxidation kinetics of the three Cu-Cr alloys is shown in Fig. 3. The oxidation kinetics of the PM Cu-50Cr alloy is approximately parabolic, for MA Cu-

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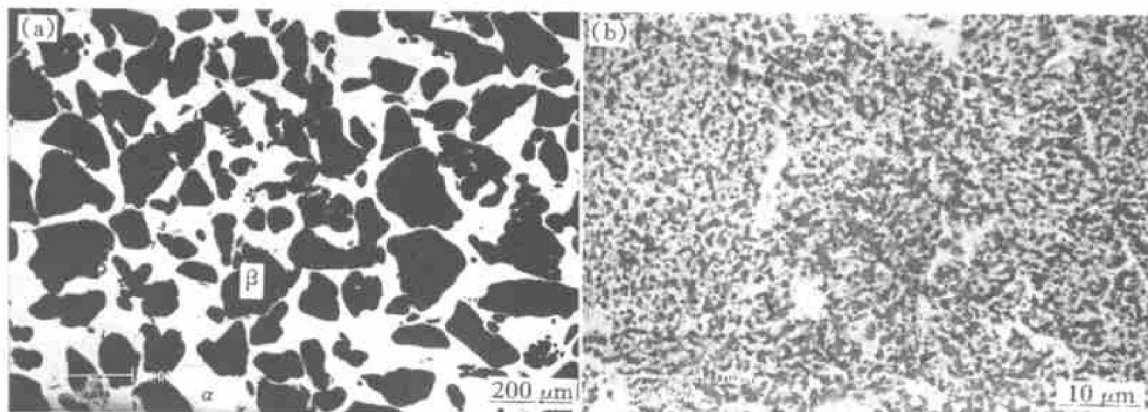


Fig. 1 Microstructures (SEM/BEI) of Cu-Cr alloys
(a) —PM Cu-50Cr; (b) —MA Cu-40Cr

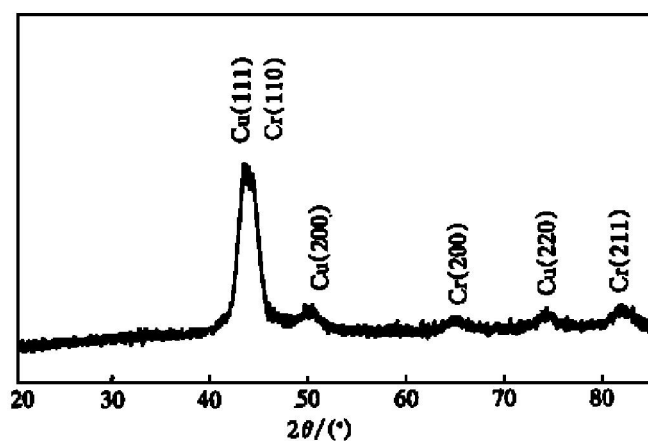


Fig. 2 X-ray diffraction pattern of MS Cu-40Cr alloy

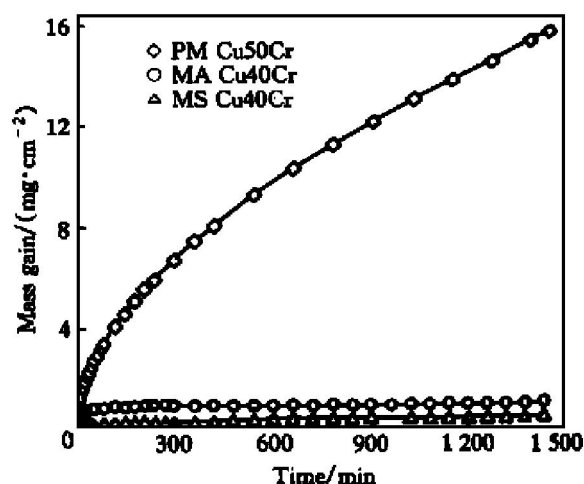


Fig. 3 Oxidation kinetics of three Cu-Cr alloys in 0.1 MPa pure oxygen at 800 °C

40Cr and MS Cu-40Cr alloys the oxidation rate decreases with time at the beginning, then tends to a constant. The mass gain of the MS Cu-40Cr alloy is less than the MA Cu-40Cr alloy and the mass gains of the MS Cu-40Cr and the MA Cu-40Cr alloy are much less than the PM Cu-50Cr alloy.

The scale structures grown on the three Cu-Cr alloys after 24 h oxidation are shown in Fig. 4.

The oxidation of the PM Cu-50Cr alloy produces complex scales (Fig. 4(a)). The outer region is composed of a thin continuous CuO (gray) and a uniform Cu₂O layer (light) beneath it. The inner region corresponding to the alloy-consumption zone contains a Cu₂O matrix, inside which there are bigger particles of chromium metals still unoxidized surrounded by a thin layer of chromia and then by an outer thick layer of the double oxide Cu₂Cr₂O₄. The oxidation of the MA Cu-40Cr alloy forms simple scales, the outer layer is a continuous CuO and the inner layer is a continuous Cr₂O₃, a Cr-depleted region forms beneath it (Fig. 4(b)). But the oxidation of the MS Cu-40Cr alloy only forms an external chromia layer and a Cr-depleted region beneath it (Fig. 4(c)).

4 DISCUSSION

The scaling behaviors of the three Cu-Cr alloys with different microstructures after 24 h oxidation are obviously different. The PM Cu-50Cr alloy produces a complex scale containing the pure oxides of both copper and chromium (Cu₂O, CuO and Cr₂O₃) as well as the double oxide Cu₂Cr₂O₄. The CuO is only present in the outmost layer of the scales, where the oxygen activity is sufficient for its stability. The outer region of the scales contains only copper, while chromium is confined in the inner-scale region in the form of its oxide or of the double Cu-Cr oxide. It is result of the fact that diffusion through the scale is faster for copper than for chromium and the two pure metal oxides have the larger difference between their growth rates. Except at places where the chromium concentration is sufficient to prevent the oxidation of copper completely or when the amount of copper and chromium in the scale is sufficient to produce a single layer of double oxide surmounting a continuous chromia layer. Finally, particles of chromium still partly in the metallic state are observed inside the

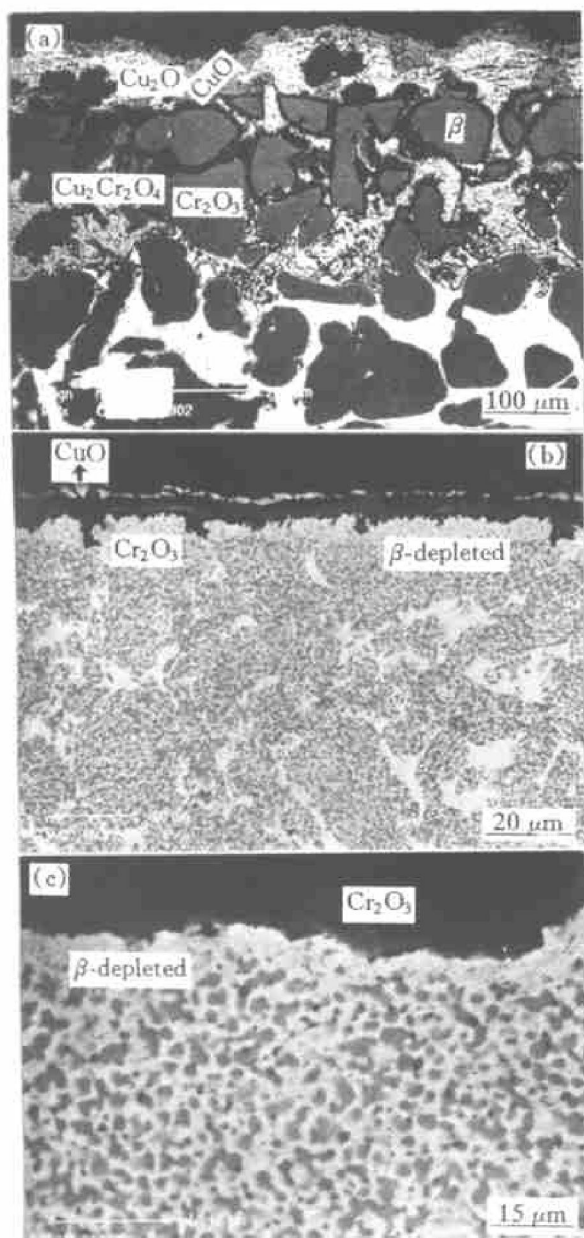


Fig. 4 Micrograph of cross section of Cu-Cr alloys oxidized in 0.1 MPa O₂ at 800 °C for 24 h (SEM/BEI)

(a) —PM Cu-50Cr; (b) —MA Cu-40Cr; (c) —MS Cu-40Cr

scale. Generally, the chromium-metal particles are surrounded by a layer of chromia and then by a double oxide and often by a matrix of copper oxide. This depends on the large difference between the rates of oxidation of copper and chromium. The matrix of the alloy nearly always made of the alpha phase is oxidizing more rapidly than the chromium particles, the chromium particles are then incorporated still not completely corroded into the scale, where they may be preserved for some time due to kinetics reasons. The corrosion behavior of these chromium particles will then depend also on their size, because large particles will take a longer time than smaller particles to be converted into the oxide.

The oxidation of the MA Cu-Cr alloy with similar chromium contents in the same experiment condi-

tions formed the external scales containing outer layer CuO and inner layer Cr₂O₃ and produces a depletion of chromium in the alloy. The formation of a continuous external layer of chromia on this alloy is rather surprising in view of the low solubility of chromium in copper and of the consequent two-phase nature of these materials. In fact the exclusive growth of an external scale composed of the most stable oxide is much more difficult for two-phase than for solid-solution binary alloy, as already predicted and observed in various cases^[6–8]. For many two-phase alloys, such as Cu-Ag, Fe-Cu and Fe-Ce, this type of scale structure was not achieved even under quite high concentrations of the most reactive component. This difference between the scaling behavior of the two kinds of Cu-Cr alloys is attributed to the small particles of the β phase in the alloy. The scaling behavior of alloys with small grains and phase particles can differ from that of corresponding alloys with large grain and phase particles, as already observed in a number of studies concerning alloys presenting very small or even extremely small grain sizes^[9]. In fact, for MA Cu-Cr alloy mechanical alloying process introduces large amount of grain and particle boundaries that act as preferential diffusion paths and increase the rate of transport of chromium to the interface alloy/scale. Another possible effect is related to the fact that the solubility of Cr in the grain and particle boundaries is certain larger than in the bulk. An increase of the solubility favors again the transition from the internal to the external oxidation of the reactive element. Finally, the rate of dissolution of the β phase particles should increase as a consequence of their much larger surface area as compared to samples with the same composition but containing coarse particles. At the same time the distance between two β phase particles is shorter. All these are effective in increasing the flux of Cr to the surface to produce a protective Cr₂O₃ scale. For MS Cu-40Cr alloy the particles of β phase are small to nanometer to more quicken the diffusion of Cr and the dissolution of β phase and provide the more short distance between the two β phases. The flux of Cr to the surface is sufficient to produce a protective Cr₂O₃ scale that cuts off the growth of transient Cu-oxides. This implies that microcrystalline reduces the critical concentration of the most-reactive component needed for the transition from the internal to the external oxidation, as proposed by WANG et al^[9, 10].

The scaling rates of the present MA Cu-40Cr alloy and MS Cu-40Cr alloy are lower than those measured for PM Cu-50Cr alloy of similar compositions, as shown in Fig. 3. The difference is small for MA Cu-40Cr and MS Cu-40Cr, which is in agreement with the scale morphologies. A complex scale containing amount of CuO and Cu₂O occurs on the PM Cu-50Cr alloy, while a simple scales forms on MA Cu-40Cr and MS Cu-40Cr alloys, especially a contin-

uous external layer of chromia which protect the alloy substrate from being corroded further formed on MS Cu-40Cr alloy. So the scaling rate of the latter is lower.

5 CONCLUSIONS

1) The oxidation behaviors of the three Cu-Cr alloys are quite different. The oxidation of PM Cu-50Cr alloy forms a complex scale containing CuO, Cu₂O, Cu₂Cr₂O₄ and Cr₂O₃, while MA Cu-40Cr and MS Cu-40Cr alloys form simple scales containing a continuous Cr₂O₃ layer and a Cr-depleted layer beneath it. Especially an exclusive scale of chromia is produced on the MS Cu-40Cr alloy.

2) The mass gains of MA Cu-40Cr and MS Cu-40Cr alloys are much less than that of PM Cu-50Cr alloy. The mass gains of MS Cu-40Cr alloy are even less than that of MA Cu-40Cr alloy. The difference is mainly attributed to different microstructures.

3) The MA Cu-40Cr and MS Cu-40Cr alloys have more grain and phase particle boundaries than PM Cu-50Cr alloy, which can act as preferential diffusion path for chromium. At the same time the small particles of chromium can dissolve into copper phase rapidly and provide shorter diffusion distance. So the supply of chromium to the external scale becomes much more effective.

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