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Liquid phase separation of Cu-Cr alloys during rapid cooling

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Abstract: The ribbons of Cu-Cr alloys with high Cr content (15%−35%, mass fraction) were prepared by rapid solidification. The microstructures of solidified samples were analyzed by scanning electron microscopy and transmission electron microscopy. The results reveal that a representative liquid phase separation microstructures are observed in Cu75Cr25 ribbons solidified at a cooling rate of about 10^4 K/s. The liquid phase separation is not restrained when the cooling rate is enhanced to about 10^7 K/s. However, the size of Cr particles solidified from Cr-rich liquid or Cr-rich regions in alloy melts could be refined by increasing the cooling rates. The size of Cr particles increases with increasing Cr contents when the ribbons contain 15% to 35%Cr.

Key words: Cu-Cr alloy; liquid phase separation; melt spinning; rapid cooling

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1 Introduction

Cu-Cr alloys containing 20%−50%Cr have been widely investigated because they are the most important contact materials used in high voltage vacuum switches. It has been well known that the smaller the Cr particles in Cu-Cr alloys are, the better the contact electric properties of contact materials can be exhibited[1−3]. Because the ordinary microstructures of the as-cast Cu-Cr alloys consist of bcc Cr dendrites distributed in fcc Cu matrix and heat treatments can not be used to change the as-cast microstructures, many special preparation processes, such as powder sintering[2,4], molten metal infiltrating [5, 6], self-consuming electrode [7], arc-melting[8] and low-segregation molten-casting[9] have been used to improve the microstructures of Cu-Cr contact alloys. However, the size of Cr particles in these products is still in micron-scale. While by mechanical alloying[1], some nano-scale Cr particles were obtained after the Cu-Cr powders were pressed and sintered. The samples exhibited some excellent electric properties, but the lower productivity and higher residual gas made this process not widely used.

In order to obtain refined microstructures, in our prior work[10] we prepared Cu-Cr ribbons containing 3%−25%Cr by melt spinning. It was found that a lot of larger Cr particles were observed in melt-spun Cu-Cr ribbons besides some Cr precipitations in nano-scale. The diameters of these large Cr particles could be refined to 200 nm when Cr content was 25%. However, the formatting mechanism of these large Cr particles in melt-spun Cu-Cr ribbons has not been understood clearly. In this paper, the formatting mechanism of Cr particles is investigated by the use of rapid solidification at different cooling rates. The results indicate that the larger Cr particles solidify from liquid phase separated Cr-rich melt.

2 Experimental

Purity copper (99.95%, mass fraction) and purity chromium (99.98%) were used to prepare Cu-Cr alloys. The starting materials were arc melted employing a non-consumable tungsten electrode. In order to obtain homogeneous samples, several remelting cycles were performed with the ingots turned upside down before each remelting. Subsequently, the ingots with a mass of 20 g were inserted into a quartz tube. After the ingots had melted they were heated by high frequency induction to the required temperature, the alloy ribbons were then prepared by single roller melt spinning under a pressure of 5.05×10^4Pa Ar gas. Three velocities of cooling roller, 0.8、8 and 33 m/s, were chosen. The thickness of obtained ribbons is 1 mm, 200 μm and 40 μm, respectively. The microstructures of the rapid solidification

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samples were analyzed by JSM 6460 scanning electron microscope(SEM) equipped with an energy dispersive spectrometer (EDS) and a Hitachi H-800 transmission electron microscope(TEM). The foil specimens used for transmission electron microscopy(TEM) were obtained by ion polishing.

3 Results

The microstructure of a Cu75Cr25 (mass fraction, %) ribbon is shown in Fig.1. The cooling roller velocity of 0.8 m/s was used to prepare this sample. The cooling rate calculated is about 1.2×10^4 K/s according to Ref.[11]. Fig.1 shows that a lot of particles distribute in the matrix. The diameter of the largest particle is about 10 μm and the smallest one is about 0.5 μm. It is obvious that the largest particles are surrounded by a lot of smaller spheres. Some of the smaller particles joined together with the larger particles. EDS analysis indicates that the composition of these spheres or particles was about 13 % Cu and 87%Cr, the matrix was 97%Cu-3%Cr (mass fraction). These results mean that these particles are Cr-rich, then named as Cr particles. Fig.1 also indicates that another phase, noted by an arrow, distributes in the large Cr particles. They can be determined to be Cu-rich phase by EDS.

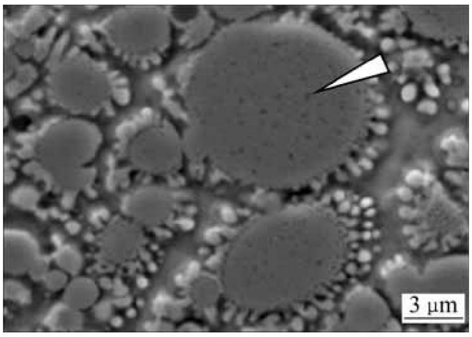

Fig.1 SEM image of melt-spun Cu75Cr25 ribbon (Velocity of cooling roller is 0.8 m/s)

For Cu75Cr25 alloy, when the velocity of cooling roller increases to 8 m/s (1.86×10^5 K/s), the size of these particles, as shown in Fig.2, is from 100 to 500 nm. The electronic diffraction indicates that these spheres are bcc Cr. When the velocity of cooling roller increases to 33 m/s (6.86×10^6 K/s), the Cr particles in Cu75Cu25 ribbons, as shown in Fig.3, were refined to 100−200 nm. Both the X-ray and electronic diffraction revealed that these particles were bcc Cr[10]. Figs.4 and 5 show the microstructures of the rapid solidification Cu85Cr15 and Cu65Cr35 ribbons. The velocity of cooling roller used to prepare these ribbons is also 33 m/s (6.86×10^6 K/s). It is obvious that decrease of Cr content has resulted in refining of Cr particles, while increase of which makes the Cr particles grow.

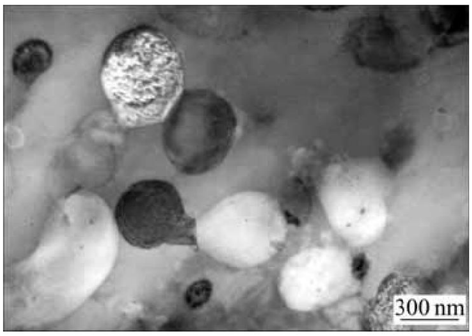

Fig.2 TEM image of melt-spun Cu75Cr25 ribbons (Velocity of cooling roller is 8 m/s)

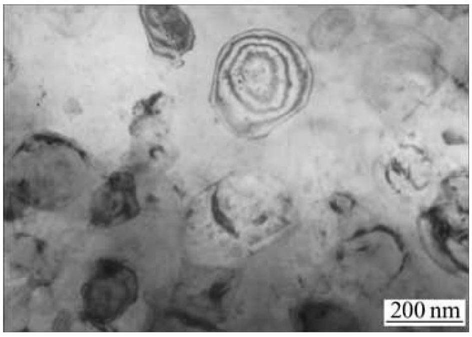

Fig.3 TEM image of melt-spun Cu75Cr25 ribbon (Velocity of cooling roller is 33 m/s)

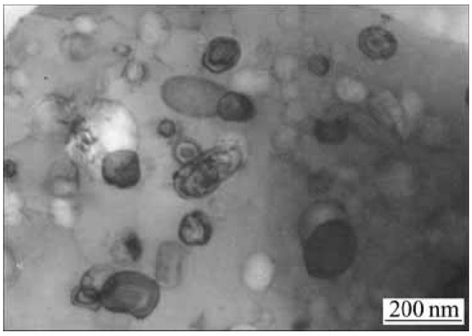

Fig.4 TEM image of melt-spun Cu85Cr15 ribbon (Velocity of cooling roller is 33 m/s)

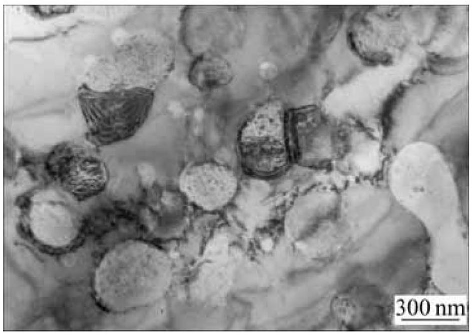

Fig.5 TEM image of melt-spun Cu65Cr35 ribbon (Velocity of cooling roller is 33 m/s)

The observations also indicate that an accumulation of Cr particles can always be present in the ribbons when the velocities of cooling roller are slower than 33 m/s, as shown in Figs.2−5. Further observations reveal that the crystallographic orientations of the accumulated Cr particles, as shown in Fig.6, are different. Fig.6 also shows that a lot of second phase particles distribute in the large Cr particles in nano-scale. The electronic diffraction testifies that these small particles are fcc Cu. Similar phenomenon can also be observed in Figs.3 and 5.

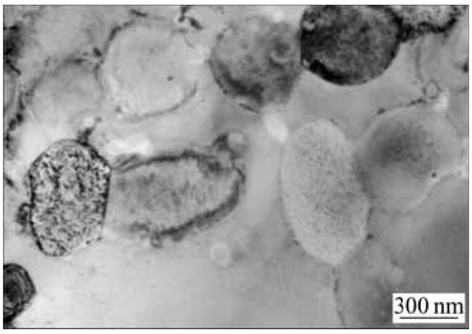

Fig.6 TEM iamge of melt-spun Cu65Cr35 ribbon (Velocity of cooling roller is 33 m/s)

4 Discussion

It is well known that the Cu-Cr, similar to Cu-Co and Cu-Fe, is a liquid metastable binary system with large positive mixing heat. By thermodynamic calculation, ZENG et al[12] obtained a liquid metastable miscibility gap in 1997. Lately, JACOB et al[13] measured the thermodynamic activity of Cr in Cu-Cr liquid alloys and revised the liquid metastable miscibility gap. Fig.7 shows the Cu-Cr binary phase diagram[13]. In the diagram, the dash lines are the liquid metastable miscibility gap (MG, bimodal line) and liquid spinodal line. The Cr content of the MG peak is 43.6%Cr. According to thermodynamics theories and the work in Cu-Co and Cu-Fe systems[14−20], when the alloy melts with positive mixing heat are undercooled to below a fixed temperature, depending on their compositions, the liquid phase will enter into the MG zone and separate into two liquids (L1+L2), one is Co-rich or Fe-rich and the other is Cu-rich. There is an interface between the two liquids. Liquid phase separation will occur. The liquid phase separation dealt with here is different from the monotectic systems. The melt of a monotectic system will separate into two liquids in equilibrium state depending on the composition and temperature. The liquid separation of Cu-Co or Cu-Fe system occurs at a temperature that is lower than that of liquidus or occurs in supercooled melts. The liquid phase separation of Cu-Co, Cu-Fe and Cu-Co-Fe systems have been studied in detail by CAO et al[14,15], ROBINSON et al[19], ELDER et al[20] and SUN et al[16−18] by using deep supercooling technologies. SONG et al[21] studied the liquid phase separation of melt-spun Cu-Co alloys in detail. Based on these studies, it is known that the process of the liquid phase separation in alloys under deep supercoolings can be divided into several steps: the formatting of Co-rich or Fe-rich liquid droplets, the growth of the droplets, the accumulation of smaller droplets, the second liquid phase separation and solidification of two liquids. Another character of liquid phase separation is that the compositions of the two liquids will be on the MG at different temperatures under slow cooling. This effect will result in that the solute contents in solids from liquid phase separation are higher than those from ordinary solidification (Fig.7). Moreover, Co-rich and Fe-rich liquids will solidify firstly because they have larger supercoolings. In this way, the solids in liquid phase separation alloys will solidify from liquid phase separated liquids. The different phase separation steps can be observed in solidified samples prepared at different cooling rates. By comparing Cu-Cr with Cu-Co and Cu-Fe systems, it can be known that the temperature difference between liquidus and MG is much less, so the liquid phase separation should take place more easily.

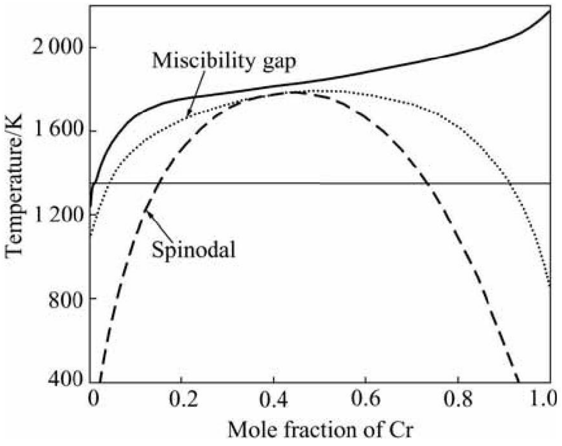

Fig.7 Cu-Cr binary phase diagram with metastable miscibility gap[13]

The image shown in Fig.1 is typical liquid separation microstructure consulting the results of liquid phase separated Cu-Co[16,19,20] alloys. The Cr-rich droplets had formed and the smaller Cr-rich droplets were accumulating into larger ones when the Cr-rich liquid started to solidify. The second phase separation occurred too. The EDS results can also prove that the Cr particles shown in Fig.1 are from liquid phase separation, because the Cu content in Cr particles is about 13%, which is much higher than the solubility of Cu in Cr in equilibrium phase diagram (Fig.7) and accords with the character of liquid phase separation. It is obvious that the Cu75Cr25 melt enters into the MG zone during the rapid solidification and liquid phase separation has occurred.

The liquid phase separation in Cu-Cr system is that the Cu-Cr melts are separate into two liquids, one is Cr-rich (L1) and the other is Cu-rich (L2). The Cr particles shown in Fig.1 are solidified from Cr-rich liquid and the Cu matrix from Cu-rich liquid. The second phase distributed in Cr particles, as shown in Fig.1 is Cu-rich from second liquid phase separation of Cr-rich liquid.

The liquid phase separation regions of the phase diagrams of Cu-Co, Cu-Fe and Cu-Cr are in liquid and solid two-phase regions. However, once the liquid phase separation takes place, the solidification of primary crystals would stop or not occur because the Gibbs free energy of the coexistence of two liquids is less than that of a liquid and a solid[17]. When the cooling rates are enhanced, 1.2×10^4 K/s for example, the Cr particles can be refined. However, the accumulations of Cr particles in Cu75Cr25 ribbons still exist. But the accumulations do not perform well due to the increase of cooling rates. So the larger Cr particles shown in Fig.3 are also solidified from the Cr-rich melt of liquid phase separation. The accumulation of Cr particles is the result of accumulations of Cr-rich droplets. The experiments reveal that the accumulated Cr particles, as shown in Fig.6, have different crystallographic orientations. The reason lies in that the Cr particles nucleate respectively and non-synchronously in several accumulating Cr-rich droplets during rapid cooling because the Cr-rich have different Cr contents or supercoolings. It have not been confirmed that the Cu particles distributed in Cr particles are from second phase separation of Cr-rich liquid or from precipitation in solid state, but at least, it can be known that much more Cu dissolved in Cr solution when Cr particles finished the solidification.

The liquid metastable miscibility gap(MG) has the character of spinodal separation. When Cr contents are less than 43.6% (mole fraction), Cr-rich liquid can be formed by two ways: liquid Spinodal separation and nucleation and growth, depending on alloy composition and supercooling. For Cu75Cr25 alloy, the liquid phase separation during rapid cooling would be Spinodal separation in the initial stage. When the cooling rates were very large, only the Cu-rich and Cr-rich regions might form, and the interfaces between Cr-rich and Cu-rich liquid might appear unnecessarily，unless the cooling rates were enhanced large enough to restrain the liquid phase separation completely. However, the supercoolings of the Cr-rich regions, the difference between the temperatures of alloy melts and that of liquidus will increase with the increase of Cr contents in Cr-rich regions. The Cr particles will also solidify from the Cr-rich liquid. Then the particles, as shown in Fig.3, are also from the liquid phase separation.

Fig.7 shows that, when Cr contents are less than 43.6% (mole fraction) the liquid phase separation starts at a higher temperature with the increase of Cr content. The Cr particles, as shown in Fig.5, will become larger for Cu65Cr35 ribbons because a higher temperature can accelerate the diffusions of atoms in liquids. However, when Cr contents are decreased, Cu85Cr15 ribbons for example, the liquid phase separation occurs at a lower temperature, and the formation of Cr-rich liquid may be nucleation and growth, the formation rates of Cr-rich liquid would slow down. Therefore, the liquid phase separation of Cu85Cr15 ribbons would not carry out fully in rapid cooling. The Cr particles, as shown in Fig.6, will be finer.

Due to the liquid phase separation, the supersaturation solid solution of Cr in Cu was obtained. The separation of this solution has been investigated[22]. Although the liquid phase separation occurred, for Cu75Cr25 ribbons, the Cr particles were refined to less than 200 nm by melt spinning. This will be beneficial to the improvement of electric contact properties.

5 Conclusions

The liquid phase separation can occur in Cu-Cr melts during rapid cooling. Several liquid phase separation steps can be observed in solid microstructures. Enhancement of cooling rate can refine the Cr particles from liquid phase separation, while increase of Cr content will result in growth of the Cr particles.

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