Effects of Cr content and electromagnetic stirring on the phase separation of Cu-Cr alloy

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Abstract

The Cu-Cr immiscible alloys were prepared by arc melting. The effects of Cr addition and electromagnetic stirring on the phase separation, microstructure were examined. The results show that serious phase segregation occurs at the center of the sample with increasing Cr contents, forming a sandwich like structure. The shape of the primary Cr transforms from fine dendrite to more developed dendrite. Thermodynamic analysis indicates that Cr addition increases the driving force for the liquid phase separation. The electromagnetic stirring can facilitate relative motion between the Cr droplets and the melts, and thus intensify the segregation phenomenon. With Cr additions, the hardness in non-segregated area shows only slight increase, and in Cr segregated area shows a significant increase. While the electrical conductivity shows only slight decrease with increasing Cr content.

1. Introduction

High-performance Cu-Cr alloys are widely used as electrical contact materials due to their combined properties of high mechanical strength and high electrical conductivity [1–3]. However, due to the poor solubility of Cr in Cu and the density difference between Cu and Cr, it is difficult to prepare this alloy under conventional smelting and casting conditions [4, 5].

The binary Cu-Cr alloy system has a large positive mixing heat in the supercooled melt [6], and this results in a metastable miscibility zone below its liquidus [7–9]. As shown in figure 1, when the alloy is cooled to miscibility zone, the alloy will undergo liquid phase separation, resulting in two immiscible liquid phases: Cr-rich droplets in copper melt. During the subsequent cooling process, the Cr-rich droplets undergo migration motion and collision in the Cu melt [10]. As the maximum solubility of Cr in Cu is only 0.7% [11], and the density of Cu is greater than that of Cr, the Cu-Cr alloy ingots produced by conventional casting are prone to serious segregation and even two-phase stratified solidification structure [12, 13]. For this reason, Cu-25Cr and Cu-50Cr alloy, which are commonly used as contact material, are mainly produced by powder sintering and infiltration method [14].

The size and distribution of the primary Cr phase in Cu-Cr alloy have significant impacts on the performance of the contact material. Therefore, it is of great significance to further understand the microstructure evolution and the segregation behavior of alloying elements during the solidification of immiscible Cu-Cr alloys. In this paper, the Cu-Cr alloys were prepared by arc melting method, and the effects of Cr content and magnetic stirring current on the microstructure evolution of Cu-Cr alloys were investigated.

2. Experimental materials and methods

Using electrolytic copper with purity of 99.99%, and chromium particles with purity of 99.99% as raw materials, the experimental alloys were prepared by vacuum arc melting in argon atmosphere, under the conditions of melting current of 250A and magnetic stirring current of 0–10A. prepared four Cu-Cr alloy samples with
chromium contents range from 5 wt% to 20 wt%. The sample mass was 45g, and the diameter was about 30mm. The samples were cut along the longitudinal sections and after grinding and polishing, etched with a corrosive solution composed of 5 g FeCl$_3$ + 10 ml HCl + 100 ml C$_2$H$_5$OH. The microstructure and element distribution of the samples were analyzed by an optical microscope (Nikon MA-200) and a scanning electron microscope (Zeiss EVO-18) equipped energy dispersive analyzer. The orientation relationship of the grains was characterized by scanning electron microscope (Hitachi S3400N) equipped with EDAX-TSL EBSD system. The hardness of the sample was measured using Vickers hardness tester (HMV-G-FA) with a 0.5-Kg load, and holding time of 15 s. All the reported hardness values are the mean value from at least 7 places. The electrical conductivity of the sample was determined using a digital eddy current metal conductivity tester (Sigma-2008).

Figure 1. Phase diagram of Cu-Cr binary alloy with metastable immiscible gaps.

Figure 2. Effect of Cr content on microstructure and morphology of Cu-Cr alloy. (a) 5 wt%, (b) 10 wt%, (c) 15 wt%, (d) 20 wt%.

Figure 3. Inverse pole figure of Cu-20Cr alloy, at the position of the red rectangular in figure 2 d.
3. Experimental results and discussion

3.1. Effect of Cr content on the solidification structure

Figure 2 shows the macroscopic morphology of the Cu-Cr alloy. It can be seen that when the Cr content reaches 10 wt%, there occurs serious phase segregation at the center of the sample forming a sandwich-like structure. Depending on the degree of segregation, the color of the segregation area changes from white gray to dark gray. From the inverse pole figure of Cu-20Cr alloy shown in figure 3, it can be seen that the segregation area is mainly composed of Cr dendrites with different orientations.

With the separation of the liquid phase, the Cr-rich droplets migrate to the core of the sample under the action of Marangoni and Stokes motions\cite{15} as shown in figure 2. Since the melting point of Cr is higher than that of Cu, the liquid Cr will solidify before liquid Cu. During the subsequent solidification process, Cr-rich droplets will attach to the previously solidified Cr phase. Such solidification behavior eventually results in a randomly distributed grain orientations, as shown in figure 3.

According to the regular solution model in thermodynamics, the mixing free energy of a binary system is\cite{16}:

$$
\Delta G_m = RT \left( X_{Cu} \ln X_{Cu} + X_{Cr} \ln X_{Cr} \right) + \Omega_{CuCr} X_{Cu} X_{Cr}
$$

where $R$ is the gas constant, $T$ is the absolute temperature, $X_{Cu}$ and $X_{Cr}$ are the mole fractions of Cu and Cr components respectively, and $\Omega_{CuCr}$ is the interaction coefficient between the components Cu and Cr. The weight percentage and mole percentage conversion of Cu-Cr alloy is shown in table 1. According to the reference\cite{7}, the interaction coefficient between Cr-Cr can be expressed as:

$$
\Omega_{Cu-Cr} = (60880 - 18750X_{Cr}) - T \left( 16.25 - 7.55X_{Cr} \right) (J/mol)
$$

Table 1. Comparison table of weight percentage and mole percentage of Cu-Cr alloy.

| wt % | 5  | 10 | 15 | 20 |
|------|----|----|----|----|
| at.% | 0.0604 | 0.1196 | 0.1774 | 0.2340 |

Figure 4. Relationship between free energy of mixing and composition of Cu-Cr alloy.

Figure 5. Effect of Cr content on microstructure of non-segregated areas of Cu-Cr Alloys. (a) (e) 5 wt%, (b) (f) 10 wt%, (c) (g) 15 wt%, (d) (h) 20 wt%.

(a) (b) (c) (d) (e) (f) (g) (h)
Combining formula (2) and (1), the relationship between the mixed free energy and the composition can be obtained, as shown in figure 4, where $\Delta g$ is the difference of mixed free energy before and after liquid phase separation. According to the principle of minimum energy, the alloy components located in the range A to B will undergo liquid phase separation to reduce the free energy of the system. It can be seen from figure 4, the driving force for the liquid phase separation $\Delta g$ increases with the Cr addition within the composition range of the alloys in this paper (5wt%-20wt%).

Figure 5 shows the microstructure of the non-segregated area of the Cu-Cr alloy. It can be seen that with the increase of Cr content, the primary phase (blue color) is gradually transformed from fine dendrites to more developed dendrites, and the grains of the matrix are also gradually refined with the increase of Cr content. According to the element distribution of the Cu-Cr alloy shown in figure 6, it can be determined that the primary phase is Cr dendrite and the matrix is Cu. As indicated in the phase diagram of Cu-Cr alloy (figure 1), it can be seen that the liquidus temperature increases with the Cr addition, and therefore the primary Cr dendrites will start nucleating at a higher temperature. This means the primary Cr dendrites will have more time to grow and to be more developed.
3.2. Effect of electromagnetic stirring current on the microstructure

Figure 7 a, b, and c shows the effect of electromagnetic stirring on the macro-structure of Cu-20Cr alloy. It can be observed that with increasing electromagnetic stirring current, the phase separation is more pronounced. Under the electromagnetic stirring, the alloy melt usually performs centrifugal motion [17], which makes the two phases with different densities move relative to each other: The Cu melt with higher density move toward the edge of the sample, while the Cr-rich droplets with lower density moves toward the center of the sample, resulting in segregation of Cr phase in the center of the sample. As the electromagnetic stirring current increases, the refinement of Cr dendrites in non-segregated areas can be observed, as shown in figures 7(e)–(g). The refinement of the Cr dendrites microstructure is considered to be the combining effect of mechanical fracture and fusion [18–20].

3.3. Effect of Cr content on electrical conductivity and hardness of Cu-Cr alloy

Figure 8 compares the electrical conductivity of the Cu-Cr alloy with pure copper. It can be seen that the Cr addition significantly reduces the conductivity of pure copper from 97.5%IACS to 53.3%IACS of Cu-5Cr alloy. And further increasing Cr content to 20 wt%, the electrical conductivities show only slight decrease from 53.3%IACS to 47.6%IACS. This is considered to be associated with solubility limit of Cr in copper. As the maximum solubility of Cr in copper is 0.7 wt%, the increasing of Cr content has no effect on the solubility of Cr in copper matrix, and thus the conductivity of Cu-Cr alloy.

Figure 9 shows the Vickers hardness with Cr content. As seen, the hardness in non-segregated area shows only slight increase. This is consistent with the increasing of Cr content (in the composition range of this study) has no effect on the solubility of Cr in copper matrix. The hardness in segregated areas, however increase significantly from 88.09 HV to 180.47 HV. It is considered that the degree of segregation, and thus the compactness of the separated Cr phase improved significantly, as shown in figure 2. This results in increased hardness in Cu-Cr alloys with higher Cr content.

4. Conclusion

(1) The addition of Cr results in serious phase separation in the Cu-Cr alloys prepared by arc melting. This is consistent with the thermodynamic analysis that the Cr addition increases the driving force of the phase separation in Cu-Cr alloy.

(2) The increase of the electromagnetic stirring current promotes the relative motion between the Cr droplets and the copper melt. This results in a more serious Cr segregation at the core of the sample. The electromagnetic stirring refines the Cr dendrites in the non-segregated areas.

(3) With Cr additions, the hardness in non-segregated area shows only slight increase, and in Cr segregated area shows a significant increase. While the electrical conductivity shows only slight decrease with increasing Cr content.
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

[1] Cao W et al 2011 Effect of Mo addition on microstructure and vacuum arc characteristics of CuCr50 alloy Vacuum 85 943–8
[2] Zhao Z et al 2015 Micro-structure and liquid phase separation of Cu–Cr alloys treated high current pulsed electron beam Materials research 18 34–9
[3] Xiu S X et al 2011 Microstructure and properties of CuCr contact materials with different Cr content Trans Nonferrous Met. Soc. 21 (China: Engl. Ed.) 389–93
[4] Shi R P et al 2013 Formation mechanisms of self-organized core/shell and core/shell/corona microstructures in liquid droplets of immiscible alloys Acta Mater. 61 1229–43
[5] Lu W Q, Zhang S G and Zhang W 2015 Direct observation of the segregation driven by bubble evolution and liquid phase separation in Al–10 wt% Bi immiscible alloy Scr. Mater. 102 19–22
[6] Liu S C et al 2018 Novel insight into evolution mechanism of second liquid-liquid phase separation in metastable immiscible Cu-Fe alloy Mater. Des. 156 71–81
[7] Jacob K T, Priya S and Waseda Y 2000 A thermodynamic study of liquid Cu-Cr alloys and metastable liquid immiscibility Z. Metallk. 91 594–600
[8] Wei C, Wang J and He Y 2020 Liquid-liquid phase separation in immiscible Cu-Co alloy Mater. Lett. 268 127585
[9] Liu S C et al 2018 A surface energy driven dissolution model for immiscible Cu-Fe alloy J. Mol. Liq. 261 232–8
[10] Zhang L T et al 2019 Phase separated characteristics affected by cooling rate of immiscible Cu-Cr alloy by laser surface melting J. Alloys Compd. 772 209–17
[11] Pang Y et al 2014 Effects of Zr and (Ni, Si) additions on properties and microstructure of Cu–Cr alloy J. Alloys Compd. 582 786–92
[12] Wu Y and Li C 2012 Investigation of the phase separation of Al-Bi immiscible alloy melts by viscosity measurements J. Appl. Phys. 111 073521
[13] Zhao Z, Ratke L and Feuerbacher, B 1998 Microstructure evolution of immiscible alloys during cooling through the miscibility gap Modelling & Simulation in Materials Science & Engineering 6 123–39
[14] Zhang C Y et al 2006 Preparation of CuCr25 contact materials by vacuum induction melting Journal of Materials Processing Technology 178 283–8
[15] Wei C, Wang J and He Y 2020 Influence of high magnetic field on the liquid-liquid phase separation behavior of an undercooled Cu–Co immiscible alloy J. Alloys Compd. 842 155902
[16] Sun Z et al 2008 Effects of Zr addition on the liquid phase separation and the microstructures of Cu–Cr ribbons with 18–22 at.% Cr J. Alloys Compd. 455 243–8
[17] Zhao I Z et al 2010 Microstructure formation in centrifugally cast Al-Bi alloys Comput. Mater. Sci. 49 121–5
[18] Xu Y et al 2016 Analysis of cracking phenomena in continuous casting of 1Cr13 stainless steel billets with final electromagnetic stirring International Journal of Minerals, Metallurgy and Materials 23 334–41
[19] Xu Y et al 2017 Effects of vertical electromagnetic stirring on grain refinement and macrosegregation control of bearing steel billet in continuous casting Iron and Steel Research, International 24 463–9
[20] Kobayashi S et al 1988 Factors affecting equiaxed zone generation in electromagnetic stirring Transactions of the Iron and Steel Institute of Japan 28 939–44