**Solidification microstructure of Cu–Cr and Cu–Cr-In alloys**

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**Abstract**

Solidification microstructure of Cu–Cr and Cu–Cr-In alloys has been characterized using scanning electron microscopy in the present work. Thermodynamic database has been established for the Cu–Cr binary system and Cu–Cr-In ternary system. Solidification behaviors of the two alloys have been simulated using the thermodynamic parameters based on Scheil model. The results show that the primary Cr phases with long and thin dendrites can be observed between Cu matrix grains for the Cu–Cr alloy, and the ‘flower-like’ coarsen dendrites primary Cr phases of the Cu–Cr-In alloy exist in the triangular grain boundary areas. The weight percent of indium element in the liquid phase of the Cu–Cr-In alloy during solidification continuously increases up. This will enlarge the solidification temperature range from 6 °C to 214 °C resulting in longer time for the dendrite growth and the alloying element indium with low melting point tends to segregate to the grain boundary region.

**1. Introduction**

As a typical type of aging hardening alloys, Cu–Cr based alloys have high strength and moderate electrical conductivity, thus they are being applied to contact wires for high speed trains [1–4], lead frames [5–7], heat transfer [1, 8], and so on. There are normally two ways to improve the alloy performance—optimization of heat treatment and addition of alloying elements [9–12]. For the Cu–Cr based alloys, common alloying elements include Zr [1, 13, 14], Ag [14–16], Mg [6, 7, 13], and Ti [17–19].

Alloying elements can have strong effect on the morphology of the primary phase—Cr phase in the Cu–Cr based alloys. For example, the equilibrium amount of solid phase decreases when adding Zr into Cu–Cr alloys, and the primary Cr phase reduces [20]. Element Zr is found to retard liquid phase separation in Cu–Cr alloys and refine the primary Cr phase at the same time [21]. Element Ag also has the effect of refining the primary Cr phase and leading to better processing flexibility [22, 23].

When investigating the solidification behaviors of the Cu–Cr based alloys containing micro-alloying elements, thermodynamics strengthens rationales for the analysis [24, 25], CALPHAD (Calculations of PHAse Diagram) approach definitely helps explain phase evolution and so on so forth [26]. In our previous work, a type of Cu–Cr-In alloy has been designed, which has good hot working formability and excellent comprehensive performance with high strength and high conductivity [27, 28], but little research has been carried out for its solidification behavior. Therefore, in the present work, the influence of element In on the solidification behavior of Cu–Cr alloys are investigated using experimental and thermodynamic methods.

**2. Experimental and thermodynamic calculations**

Pure copper (99.99 wt%), Cu–10wt%Cr alloy, and pure In (99.9 wt%) were used as raw materials. Two sets of alloys were melted and cast with measured compositions listed in table 1. Melting was carried out using a medium frequency induction furnace (KGPS 80/2500, Ningbo Shenguang). Molten was cast at 1150 °C into an
iron mold preheated to 50 °C followed by cooling in air. Ingots were in 40 mm × 80 mm size. The actual composition of the as-cast were determined via inductively coupled plasma emission spectroscopy (ICP, IRIS Intrepid II, Thermo Fisher Scientific).

Disk samples were cut from the as-cast ingots with diameter of 3 mm. Samples were then ground to 200 μm in thickness followed by thinning using 8 vol% HClO₃ + 92 vol% C₂H₅OH solution. Microstructure was observed using scanning electron microscopy (SEM, Mira 3 LMH, TESCAN) with energy dispersive spectrometer (EDS, 9806A-1UPS-SN, Thermo Fisher Scientific). Differential scanning calorimetry (DSC) was also used to study the phase transformation with 20 K min⁻¹ of heating and cooling rates.

Thermodynamic database for the Cu–Cr-In ternary system was established using CALPHAD method. The parameters of the Cu–Cr [29] and Cu–In [30] binary systems were adopted. For the Cr–In binary system, since there has been no phase equilibria information available, only solution phases were taken into account according to Dinsdale’s data [31]. Solidification curves for the Cu–Cr and Cu–Cr-In alloys were calculated using the above thermodynamic parameters in Pandat software [32] based on Scheil model [33].

3. Results and discussion

Figure 1 shows secondary electron (SE) images of microstructure of the as-cast Cu–Cr and Cu–Cr-In alloys. Large amount of primary Cr phases can be observed between Cu matrix grains for the Cu–Cr alloy as shown in figure 1(a). A magnified image for the red square in figure 1(a) is given in figure 1(b). Abundant of long and thin dendrites (<1 μm thick) exist along the primary dendrites which is somehow ‘leaf-like’. Figure 1(c) shows the morphology of the Cu–Cr-In alloy. Similar amount of primary Cr phases can also be clearly seen. In the
triangular grain boundary areas, dendrite arms are still fine (~1 μm thick), but those dendrites along the grain boundaries between two grains are obviously coarse. An enlarged area of the red square in figure 1(c) is shown in figure 1(d) where two ‘flower-like’ coarsen dendrites are present with ~3 μm in thickness.

In order to analyze element segregation during solidification, EDS mapping for the Cu–Cr and Cu–Cr–In alloys are compared. A SE image for ‘leaf-like’ dendrite of the Cu–Cr alloy with corresponding EDS mapping of elements Cu and Cr are shown in figure 2. Cu atoms are locating in the matrix and Cr atoms are mainly in the primary phase. For the Cu–Cr-In alloy case, a SE image for ‘flower-like’ dendrite is shown in figure 3 with corresponding EDS mapping of elements Cu, Cr, and In. The distribution of Cu and Cr atoms are the same as that in the Cu–Cr alloy. No segregation has been found for the In atoms.

Since the content of In is low (no greater than 0.18 wt%), noise can cover the signals of In atoms for the EDS mapping. Another EDS point analysis has been carried out for a dendrite in figure 4(a) of the Cu–Cr–In alloy. No In has been detected on the dendrite (figure 4(b) referring to Point 1 in figure 4(a)), while 0.76 wt% In has been found in the area in the matrix near the dendrite as illustrated in figure 4(c) referring to Point 2 in figure 4(a). This indicates possible segregation of In atoms which needs further investigation.

Solidification behaviors of the Cu–Cr and Cu–Cr–In alloys are analyzed using Scheilmodel [33]. Volume fraction of solid phase of the Cu–Cr and Cu–Cr–In alloys are plotted against temperature during solidification in figure 5. The temperature range for solidification of the Cu–Cr alloy is between 1083 °C and 1077 °C. The onset temperature of solidification of the Cu–Cr–In alloy is still 1083 °C, however, the offset temperature drops to 869 °C. This means that the solidification window has been enlarged from 6 °C to 214 °C, which provides sufficient time for dendrite growth. This is consistent with the experimental observation in figure 1 showing much coarser dendrites in the Cu–Cr–In alloy than those in the Cu–Cr alloy. Figure 6 shows the DSC curves of the Cu–Cr and Cu–Cr–In alloys. It is clear that for the Cu–Cr alloy in figure 6(a), the onset point for melting is 1079 °C. However for the case of the Cu–Cr–In alloy in figure 6(b), the onset point for melting is 1054 °C, consistent with the value of ~1050 °C (99% solid phase) as shown in figure 5(b).

The calculated phase diagram of the Cu–Cr and Cu–Cr–In are shown in figure 7. The DSC data of Cu0.34Cr is closer to the liquidus temperature. Moreover, it can be seen that the as-cast microstructure of Cu-0.34Cr as show in figure 1(a) is consistent with calculated Cu–Cr–Phase diagram. However, due to non-equilibrium solidification and composition segregation of the Cu0.34Cr0.18In, the DSC data is lower than the liquidus temperature. And the as-cast microstructure of Cu-0.34Cr-0.18In as shown in figure 1(b) is fcc-Cu and bcc-Cr rather than fcc-Cu, bcc-Cr and CuIn binary compound. This is mainly because the segregation temperature of CuIn phase is too lower to occur phase transition and the high temperature structure has been contained in the room temperature.

Weight percent of different elements in the liquid phase of the Cu–Cr–In alloy during solidification have also been calculated and plotted in figure 8. With temperature decreasing, weight percentage of Cr atoms increases first and then decreases from 1070 °C at which bcc-Cr phase starts to form. It is interesting to see that element In continuously increases up to 22.8 wt% during solidification. Although no such high content of element In has been detected using EDS, the Cu matrix near grain boundary regions has higher In content ~0.76 wt% as illustrated in figure 4. This is because element with lower melting point is prone to be expelled into the liquid phase and get solidified at grain boundary regions. Element In has a melting point of 157 °C, much lower than Cu and Cr, which results in segregation of In atoms in liquid phase and thus larger solidification temperature range. Similarly, the concentration of element Cu in the liquid phase during solidification also decreases gradually with the concentration change of element Cr and element In.
4. Summary

In the present work, experimental observation and thermodynamic calculations have been conducted for investigation of solidification behaviors of Cu–Cr and Cu–Cr–In alloys. Different morphologies of dendrites have been observed for the two alloys. The role of element In has been analyzed using simulation of solidification process based on Scheil model with the thermodynamic database of the Cu–Cr–In ternary system. This work can be helpful for the further processing steps during manufacturing high strength high conductivity Cu–Cr–In alloys. The following conclusions can be obtained:
The primary Cr phases with long and thin dendrites exist between Cu matrix grains for the Cu-0.43Cr alloy. However, with adding In element, the elongated primary Cr phases are replaced by 'flower-like' coarsen dendrites in the triangular grain boundary areas of the Cu-0.43Cr-0.18In alloy.

(1) The solidification window of Cu–Cr alloy has been enlarged by adding In element. As the solidification interval of Cu0.34Cr0.18In alloy reach 214 °C, Cr atoms and In atoms are enriched at the front edge of solid-liquid interface during solidification, which provides sufficient time for Cr dendrite growth and results in segregation of In atoms nears the dendrite of the Cu-0.43Cr-0.18In alloy.

(2) The calculated phase diagram shows that the Cu–Cr and Cu–Cr-In alloys have different phase compositions. The Cu–Cr-In alloy has a wider solidification interval compared to the Cu–Cr alloy.
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Figure 8. Weight percentage of different elements in the liquid phase during solidification. (a) All elements; (b) Cu; (c) Cr; (d) In.
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