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Thermodynamics and kinetics in liquid immiscible Cu–Cr–Si ternary system

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ABSTRACT

This work firstly focuses on the thermodynamic and kinetic studies of the liquid phase separation in the Cu–Cr–Si ternary system. On the thermodynamic aspect, four isothermal sections of the Cu–Cr–Si system at 900 °C, 1000 °C, 1100 °C and 1200 °C have been experimentally determined by X-ray diffraction (XRD) and electron probe microanalyzer (EPMA) on the equilibrated alloys, and the phase equilibria in the Cu–Cr–Si ternary system has been thermodynamically assessed by using the CALPHAD (*Cal*culation of *Pha*se *D*iagrams) technique on the basis of the presently obtained experimental results. The addition of Si can stabilize the metastable liquid phase separation in the Cu–Cr binary system, and increase its critical temperature. On the kinetic aspect, the formation of top–bottom and core–shell separated morphologies of the as-cast liquid immiscible Cu–Cr–Si alloys under various cooling rates have been detailedly analyzed.

1. Introduction

The Cu–Cr alloys with high Cr contents are predominant electrical contact materials and have been widely used for high voltage applications due to their considerably high interrupting ability, superior voltage withstanding stress, and excellent electric and thermal conductivities [1–3]. The Cu–Cr system displays a metastable liquid phase separation in the undercooled melt below the liquidus temperature and its binary phase diagram is characterized by a metastable liquid miscibility gap [4]. Early investigations have been performed on this alloy system in order to study the compositional ranges of the metastable liquid miscibility gap and solidified microstructures [5–10]. In addition, a third element was usually added to Cu–Cr alloy samples to enhance or reduce the extent of liquid phase separation [11–16]. In rapidly solidified Cu–Fe alloy samples, the addition of Si was found to stabilize the liquid miscibility gap [17–19]. Thus, the Cu–Cr–Si alloys may also display metastable liquid miscibility gap, which will extremely restrict the development of new high-temperature precipitation-aged Cu–Cr–Si alloys [20]. Therefore, it is important and necessary to investigate the effect of Si addition on the liquid phase separation in the Cu–Cr binary system.

Until now, no information about the liquid phase separation in the Cu–Cr–Si ternary system is available in the literature. Although the phase equilibria in the Cu–Cr–Si system were partially known [21–23], some uncertainties still remain and are summarized as follows: (i) the partial isothermal section at 800 °C in the composition range Cu–Cr–Cr_5Si_3 presented by Savitskii et al. [21] obviously differs from that compiled by Villars et al. [22]; (ii) the phase equilibria in the Cu-rich corner at 700 °C and 1000 °C determined by Roi et al. [23] show poor agreement with the solubility data of the (Cu) solid solution in the accepted Cu–Cr and Cu–Si binary systems; and (iii) both calculated isothermal sections of the Cu–Cr–Si system at 700 °C [24] and 1160 °C [25] are only predicted as tentative because they do not consider the solubility of third element in the binary phases. Thus, it is needful to experimentally determine the phase equilibria in the Cu–Cr–Si ternary system. Obtaining such information on the phase equilibria and phase transformations only from experiments is burdensome and expensive. The CALPHAD (Calculation of Phase Diagrams) technique, which is a powerful tool to reduce time and cost during the development of materials [26–28], and to predict metastable liquid miscibility gap at extremely high temperatures in the present work. Therefore, the thermodynamic description for the Cu–Cr–Si ternary system supported by key experiments is of great essence.

Research on Cu-based liquid immiscible alloys has focused mainly on the thermodynamic aspects, and great attention has recently been paid to investigate the kinetics of the liquid phase separation under rapid solidification conditions. Electromagnetic levitation, drop tube, gas atomization, and rapid quenching techniques have been used to experimentally explore the solidification behaviors of Cu-based liquid immiscible alloys [17–19,29,30], showing that the complex microstructure evolution during a cooling of an liquid immiscible alloy is the result of the concurrent action of the nucleation and diffusional growth of droplets, the

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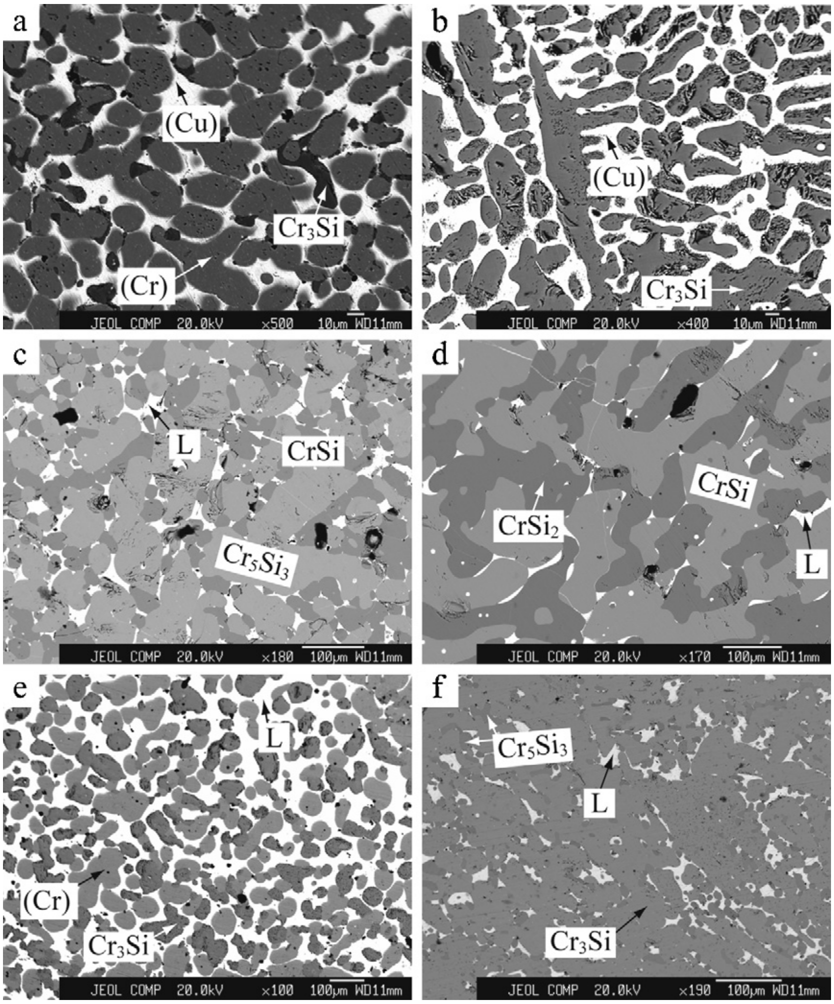

Fig. 1. BSE images of the typical ternary Cu–Cr–Si alloys: (a) the $Cu_{47}Cr_{47}Si_6$ (wt.%) alloy annealed at 1000 °C for 60 days, (b) the $Cu_{46}Cr_{46}Si_8$ (wt.%) alloy annealed at 1000 °C for 60 days, (c) the $Cu_8Cr_{65}Si_{27}$ (wt.%) alloy annealed at 1100 °C for 30 days, (d) the $Cu_7Cr_{54}Si_{39}$ (wt.%) alloy annealed at 1100 °C for 30 days, (e) the $Cu_{48}Cr_{48}Si_4$ (wt.%) alloy annealed at 1200 °C for 4 days, and (f) the $Cu_{11}Cr_{72}Si_{17}$ (wt.%) alloy annealed at 1200 °C for 15 days.

collisions and coagulation and the spatial phase separation due to the Stokes and Marangoni motions of droplets. Studying the solidification mechanism of the liquid immiscible alloy only by experiments is an extremely tough work, thus kinetic simulation of the microstructural evolution of the liquid immiscible alloy during cooling is of increasing interest. Zhao et al. made great efforts to study the kinetic models of the microstructure evolution in several liquid immiscible alloys by numerical simulation [31–37], and Wang and Shi et al. firstly developed a model to describe the formation mechanism of core–shell and core–shell–corona structures in liquid immiscible Cu–Fe base alloys by phase field simulation [38,39]. All of the above-mentioned kinetic studies by both experiments and simulations have indicated that, gravity and cooling rate are two of the most important affecting factors during the solidification process of the liquid immiscible alloys under Earth's gravity condition. However, for the liquid immiscible Cu–Cr–Si alloys, no information about the co-effect of gravity and cooling rate during the solidification process was available, which will obviously restrict the development of the high-performance Cu–Cr–Si alloys. Thus, comparative experimental studies of the solidification behaviors of the liquid immiscible Cu–Cr–Si alloys supported by kinetic calculation are necessary.

The purpose of the present work is to deal with the thermodynamic and kinetic studies of the liquid phase separation in the Cu–Cr–Si ternary alloys by both experiments and calculation. The paper is organized as the following. The experimental details and results are described in Section 2. The thermodynamic model and calculated results using the CALPHAD method are presented in Section 3. The fluid kinetic equations and major calculation results are provided and analyzed in Section 4. Major findings are finally summarized in Section 5.

2. Experimental details and results

2.1. Experimental procedure

Electrolytic copper (99.99 wt.%), chromium (99.99 wt.%) and silicon (99.99 wt.%) were used as starting materials. Bulk buttons were prepared from pure elements by arc melting under high purity argon atmosphere using a non-consumable tungsten electrode, and some liquid immiscible alloy buttons were expected to appear top–bottom separated macroscopic morphologies after cooling in the arc-melting furnace. The ingots were melted at least six times in order to achieve their homogeneity. The sample weight was around 20 g and the weight loss during melting was generally <0.20% of the sample weight. Afterwards, the ingots were cut into small pieces for heat treatments and further observations. Plate-shaped specimens were wrapped in W foil in order to prevent direct contact with the quartz ampoule, and put into quartz ampoule evacuated and backfilled with argon gas. The specimens were annealed at 1200 °C, 1100 °C, 1000 °C and 900 °C, respectively. The time of the heat treatment varying from several days to several months depends on the annealing temperature and the composition of the specimen. After the heat treatment, the specimens were quenched into ice water.

For the purpose of comparing solidified microstructures between cooling in the arc-melting furnace and cooling in the high frequency induction furnace, Cu–Cr–Si alloys of about 350 g/ingot were prepared in alumina crucibles by melting pure elements in a high frequency induction furnace under an argon atmosphere by the following process. The molten alloys were heated to about 1800 ± 50 °C in the