Journal of Alloys and Compounds 563 (2013) 85–90

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Pseudobinary eutectics in Cu–Ag–Ge alloy droplets under containerless condition

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ARTICLE INFO

Article history:
Received 13 November 2012
Received in revised form 4 February 2013
Accepted 9 February 2013
Available online 20 February 2013

Keywords:
Rapid solidification
Metals and alloys
Microstructure
Phase transitions

ABSTRACT

Pseudobinary eutectic generated by pseudobinary eutectic transition or peri-eutectic transition is a crucial structure in ternary alloy systems. Its formation mechanism strongly influences mechanical properties of these metallic materials. However, it was customarily neglected. In this paper, two pseudobinary eutectics, i.e. (Ag + ζ) and (Ag + ε_2), were investigated during the rapid solidification of Cu–Ag–Ge ternary alloy in a 3 m-drop tube. The sharp temperature variations and dramatic kinetic activities of the falling alloy droplets before solidification cause special microstructural characteristics. (Ag) dendrite is the heterogeneous nucleus for anomalous (Ag + ζ) pseudobinary eutectic in large droplets. Lamellar (Ag + ζ) pseudobinary eutectic grain forms independently on condition that primary (Ag) dendrite cannot form and its eutectic morphology becomes anomalous with the decrease of droplet size. Nanoscaled (Ag + ε_2) pseudobinary eutectic generating at the last stage of solidification is the product of both peri-eutectic and pseudobinary eutectic transitions. It distributes in the gaps of (Ag + ζ) pseudobinary eutectic grains and its morphology remains lamellar regardless of droplet size.

1. Introduction

Rapid solidification is a liquid to solid transformation process deviating far from the equilibrium situation. Compared with traditional solidification, rapid solidification provides a feasible way to prepare advanced metallic material with satisfactory mechanical properties by bringing new characteristics for microstructures, nanoscale for phases and special mechanisms for phase transitions. Many attempts have been made to study rapid solidification of pure metal and binary alloys for a long time [1–7]. The corresponding research on ternary alloys requires necessary information on related pure metals and binary alloys. It has burst in the last decade [8–14] for the reason that more and more ternary alloys are widely applied. In the case of a ternary alloy, the final microstructure composed of multiphase is determined by a series of participated phase transition events. The phase transitions involving three solid phases in the ternary alloy systems are summarized into three types, i.e. eutectic transition (E-type: $L \rightarrow \alpha + \beta + \gamma$), peritectic transition (P-type: $L + \alpha + \beta \rightarrow \gamma$) and peri-eutectic transition (U-type: $L + \alpha \rightarrow \beta + \gamma$, so-called quasi-peritectic transition). Consequently, the rapid solidification process of ternary alloy is more complicated.

Pseudobinary eutectic is a crucial structure existing in ternary alloy systems. It is generally formed by either pseudobinary eutectic transition or peri-eutectic transition. Unfortunately, pseudobinary eutectic has not been paid enough attention although ternary eutectic growth has been studied in the literatures [15–18]. When the composition of alloy melt varies along pseudobinary eutectic line with the decrease of temperature, pseudobinary eutectic is generated by pseudobinary eutectic transition. On condition that the composition of alloy melt reaches peri-eutectic transition point during solidification, it is formed by peri-eutectic transition. Drop tube, a kind of containerless technique, provides an approach to realize rapid solidification of metallic droplets with various micron sizes by solidifying them rapidly during a free fall [19,20]. The objective of this paper is to reveal the formation mechanism of two pseudobinary eutectics by performing rapid solidification of the alloy in the drop tube. The thermodynamic and kinetic features of the alloy droplets, which are the influencing factors of rapid solidification process, are also investigated.

Cu–Ag–Ge alloy is selected to achieve it. First of all, the growth morphologies of the phases occurring in the Cu–Ag–Ge ternary alloy system can be distinguished by optical microscope or scanning electron microscope. It is possible for us to investigate its solidification process in detail. It had been confirmed that ternary eutectic in Cu–Ag–Ge alloy transforms from regular to anomalous under far from equilibrium condition, meanwhile the cooperative growth of two non-faceted eutectic phases is replaced by the independent nucleation and growth of three eutectic phases [19,21]. Furthermore, Cu–Ag–Ge alloy system has three peri-eutectic transitions and one ternary eutectic transition, as shown in Fig. 1 [22,23]. The solidification process of $Cu_{54}Ag_{33.5}Ge_{12.5}$ alloy may involve

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http://dx.doi.org/10.1016/j.jallcom.2013.02.021

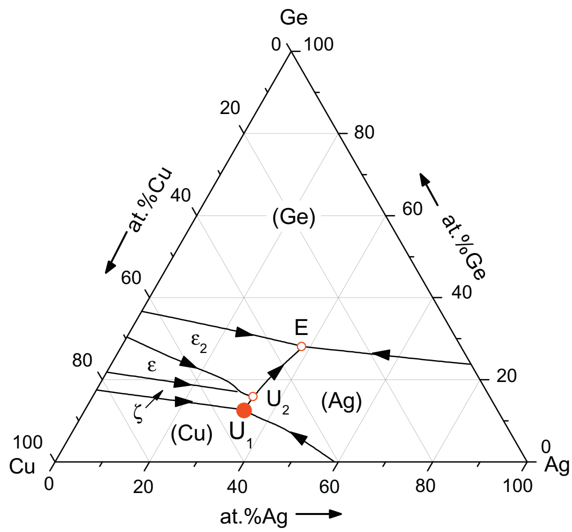

Fig. 1. Location of $Cu_{54}Ag_{33.5}Ge_{12.5}$ ternary alloy in the Cu–Ag–Ge phase diagram [22,23]. Point U_1 is $L + (Cu) \rightarrow (Ag) + \zeta$ peri-eutectic transition point, point U_2 is $L + \zeta \rightarrow (Ag) + \varepsilon_2$ peri-eutectic transition point and point E is $L \rightarrow (Ag) + (Ge) + \varepsilon_2$ ternary eutectic transition point.

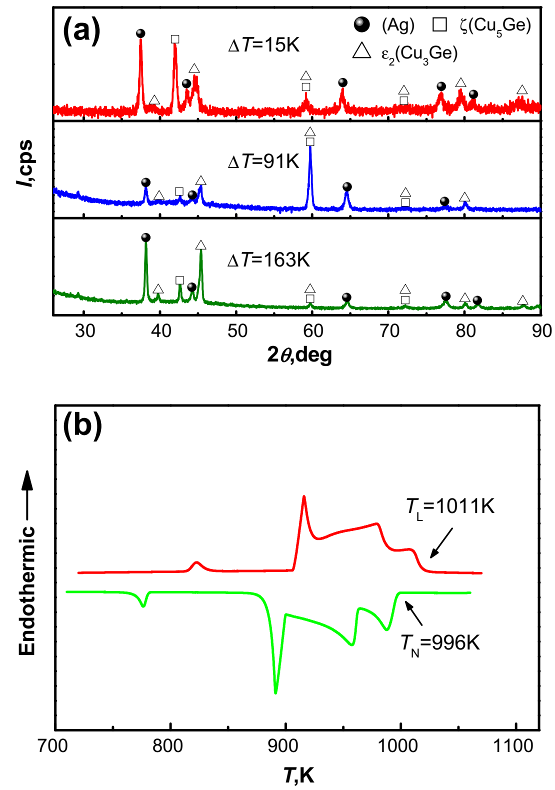

Fig. 2. XRD and DSC analyses of $Cu_{54}Ag_{33.5}Ge_{12.5}$ alloy [24]: (a) XRD patterns at different undercoolings; (b) DSC curve with the heating-cooling rate of 10 K min^{-1}.

two peri-eutectic transitions and two pseudobinary eutectic transitions. Therefore, the investigation on two kinds of pseudobinary eutectics formed by different phase transitions during different solidification stages was carried out comparatively.

2. Experimental procedure

$Cu_{54}Ag_{33.5}Ge_{12.5}$ ternary alloy sample prepared from pure Cu (99.999%), pure Ag (99.99%) and pure Ge (99.999%) has a mass of about 1 g. The rapid solidification of alloy droplets was accomplished in a 3 m-high drop tube. In an experiment, the sample was placed in a ϕ 16 × 150 mm quartz tube with a nozzle of ϕ 0.3 mm size at its bottom. The quartz tube was then installed in the induction coil on the top of the drop tube. The drop tube was evacuated to 2×10^{-4} Pa and backfilled with the mixture gas of highly purified Ar and He gases to about 1×10^5 Pa. The pressure ratio of Ar to He is 2:1. After that the sample was melted by induction heating and superheated by about 200 K above its liquidus temperature for several seconds. Finally, the melt was ejected through the nozzle and dispersed into fine liquid droplets. These liquid droplets solidified rapidly during free fall.

After that, the solidified droplets were cross-sectioned, polished and etched with a mixture of 30 ml 30% H_2O_2 + 10 ml saturated NaOH solution for about 3 min and followed by 5 g $FeCl_3$ + 10 ml HCl + 50 ml H_2O. The thermodynamic properties, phase constitution and microstructures were analyzed by Netzsch DSC 404C apparatus, Rigaku D/max 2500 V X-ray diffractometer, Zeiss Axiovert 200 MAT optical microscope, FEI Sirion 200 scanning electron microscopy, and Oxford INCA 300 energy dispersive spectroscopy fitted in SEM, respectively.

3. Results and discussion

3.1. Near-equilibrium solidification of master alloy

In order to compare with the rapid solidification of alloy droplets in the drop tube, the solidification of master alloy was investigated at the first. The master alloy was prepared by arc melting with the protect of Ar gas. According to XRD and DSC analyses as shown in Fig. 2 [24], $Cu_{54}Ag_{33.5}Ge_{12.5}$ alloy consists of (Ag), ζ (Cu_5Ge) and ε_2 (Cu_3Ge) phases and its liquidus temperature is 1011 K. The detailed discussion is given in Ref. [24].

Fig. 3 is the optical micrographs for the solidified master alloy. The white phase is (Ag) phase, the grey one ζ phase and the dark one ε_2 phase, which were further distinguished by EDS analysis. Primary (Ag) dendrite, (Ag + ζ) and (Ag + ε_2) pseudobinary eutectics coexist in the microstructure. Due to the similarity of ζ and ε_2 phases, both (Ag + ζ) and (Ag + ε_2) pseudobinary eutectics grow with rod-shape. (Ag + ε_2) pseudobinary eutectics with relative small sizes distribute in the gaps between primary (Ag) dendrites and (Ag + ζ) pseudobinary eutectics. Based on the microstructure and Cu–Ag–Ge phase diagram (Fig. 1), it can be concluded that the solidification pathway of the master alloy is: primary (Ag) dendrite → (Ag + ζ) pseudobinary eutectic → (Ag + ε_2) pseudobinary eutectic, which has been explained in detail in Ref. [24]. Four phase transitions take place continuously during the solidification, i.e. $L \rightarrow (Ag)$, $L \rightarrow (Ag) + \zeta$, $L + \zeta \rightarrow (Ag) + \varepsilon_2$ and $L \rightarrow (Ag) + \varepsilon_2$. Among these, $L + \zeta \rightarrow (Ag) + \varepsilon_2$ is peri-eutectic transition.

Another peri-eutectic transition $L + (Cu) \rightarrow (Ag) + \zeta$ does not happen in the solidification process of the alloy, for the reason that (Cu) phase is not the constituent phase of the alloy according to XRD analysis [24]. Furthermore, no trace in the microstructure shows that (Cu) phase ever formed at the initial stage of solidification. Therefore, the composition of the alloy is more likely to be located in the (Ag) phase region where is near point U_1.

Two pseudobinary eutectics, (Ag + ζ) and (Ag + ε_2), exist in the microstructure of the alloy. (Ag + ζ) pseudobinary eutectic is the product of $L \rightarrow (Ag) + \zeta$, whereas (Ag + ε_2) pseudobinary eutectic is generated by both peri-eutectic transition $L + \zeta \rightarrow (Ag) + \varepsilon_2$ and subsequent pseudobinary eutectic transition $L \rightarrow (Ag) + \varepsilon_2$. The related discussion can be found in Section 3.4.

3.2. Thermodynamic and kinetic characteristic of droplets

$Cu_{54}Ag_{33.5}Ge_{12.5}$ alloy had been dispersed into the droplets with diameter sizes ranging from 100 to 1200 μm, then solidified rapidly during free fall in the drop tube. Dramatic temperature drop and rapid free fall during solidification, which are the key thermodynamic and kinetic factors for the alloy droplets, strongly influence their microstructural characteristics and solidification pathways.

The temperature variation of the droplets during free fall is difficult to be measured accurately. We turn to calculate the