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Complex phase separation of ternary Co–Cu–Pb alloy under containerless processing condition

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ABSTRACT

The macrosegregation and solidification processes of ternary $Co_{43}Cu_{40}Pb_{17}$ alloy have been investigated under the containerless processing condition in drop tube. The addition of Pb element is found to be quite effective to promote the phase separation of Co–Cu alloy, resulting in a macroscopic segregation pattern in ternary $Co_{43}Cu_{40}Pb_{17}$ alloy. The rapidly solidified alloy droplets are characterized by core–shell structures due to the combined effects of reduced gravity and containerless state during free fall. When the droplet diameter is smaller than 450 μm, a kind of three-layer core/shell structure is formed, which consists of a Co-rich core, a Cu-rich intermediate layer and a Pb-rich surface shell. EDS analyses show that the Pb solute has a stronger affinity with Cu-rich liquid and a repulsive interaction with Co-rich liquid. The solidification process of $Co_{43}Cu_{40}Pb_{17}$ ternary alloy involves two successive phase separation events, a subsequent peritectic transformation and a final monotectic transformation.

1. Introduction

Liquid phase separation is a commonly observed phenomenon in various condensed matter systems such as polymers, oxides, metallic glasses and alloys [1–5]. Within metallic systems, this kind of liquid–liquid phase transformation is not only characteristic of stable immiscibility gap in monotectic alloys but also typical of metastable immiscibility gap in peritectic alloys with large positive mixing enthalpy, such as Co–Cu and Fe–Cu alloy systems which have been investigated intensively [6–8]. It has aroused great research interest in the field of material science and technology [9–13]. Due to the giant magnetoresistance (GMR) property of nanostructured Co–Cu alloy with a significant volume of Co-rich particles, the decomposition of liquid Co–Cu based alloys has been widely investigated experimentally in recent years [5,14]. In order to control the liquid phase separation, different kinds of third element, like Ni and B [14,15], have been introduced to the binary Co–Cu system. It has been reported that liquid phase separation can be restrained and GMR property can be improved by addition of Ni. In contrast, the addition of B, which can reduce the liquidus temperature and enhance the metastable phase separation temperature, is quite effective for the promotion of liquid phase separation of Co–Cu-based system. The addition of third element has shown great influence on the phase separation and solidification process as well as the final microstructure and related properties.

Containerless processing is an important technique to obtain large undercooling of alloy melts due to the avoidance of heterogeneous nucleation caused by the crucible walls. Among those methods of containerless processing, the drop tube is a very promising way [8]. It has a major characteristic of subdividing metallic alloy melt into fine droplets. Under this condition, two distinct advantages are produced: one is high cooling rate, the other is less catalysis in the small droplets. The two effects will enhance the undercooling level obtained in the small droplets. Only the high undercooling can induce the possible metastable phase separation in Co–Cu based peritectic alloys. In this paper, we introduce the Pb element to binary Co–Cu alloy and the drop tube technique is used to investigate the phase separation and microstructure evolution of rapidly solidified ternary $Co_{43}Cu_{40}Pb_{17}$ alloy in undercooled state during free fall. The chemical composition of ternary $Co_{43}Cu_{40}Pb_{17}$ alloy locates near the middle line between Co and Cu vertexes in the composition triangle of ternary Co–Cu–Pb alloy system, as shown in Fig. 1 [6,16–18].

2. Experimental procedure

The bulk samples were prepared from pure Co (99.95%), Cu (99.999%) and Pb (99.999%). Co and Cu were primarily melted in an arc-melting furnace, and then were melted together with Pb by induction heating under the protection of B_2O_3 fluxing and argon atmosphere. As the ternary Co–Cu–Pb phase diagram has not been available, the solidification event of ternary $Co_{43}Cu_{40}Pb_{17}$ alloy was measured by a kind of thermal analysis. A large sample with the mass of 10 g was contained in a 13 mm ID × 15 mm OD × 120 mm quartz tube. It was melted by radio frequency induction heating and protected from oxidation by flowing argon gas. A Pt Rh_{30}–Pt

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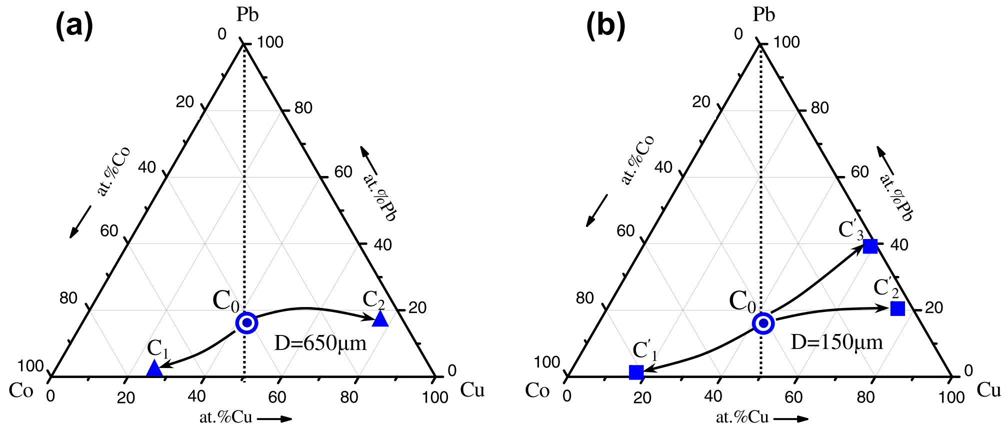

Fig. 1. Schematic of alloy composition selection and phase separation process of ternary $Co_{43}Cu_{40}Pb_{17}$ alloy droplets: (a) two separated phases in a large alloy droplet with D = 650 μm, and (b) three separated phases in s small alloy droplet with D = 150 μm.

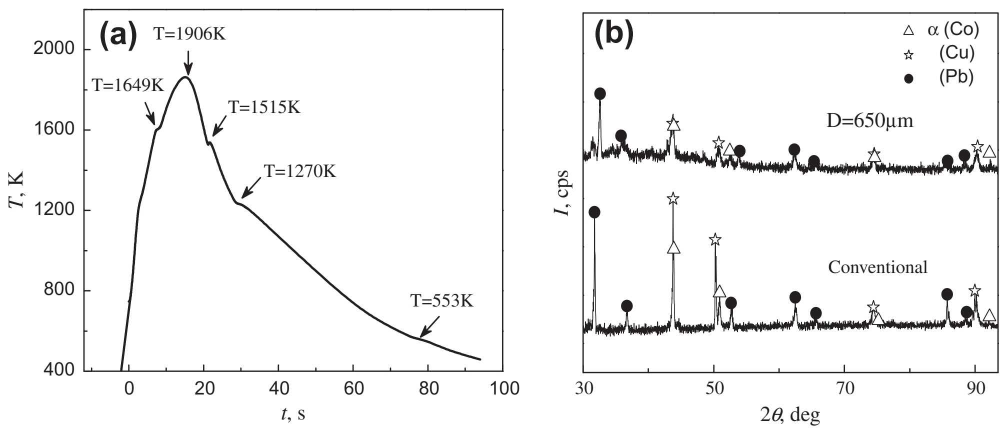

Fig. 2. Thermal analysis and XRD patterns of ternary $Co_{43}Cu_{40}Pb_{17}$ immiscible alloy. (a) Thermal analysis and (b) XRD patterns.

Rh_6 thermal couple was inserted into this alloy to measure its heating and cooling curves. The measured liquidus temperature of this alloy is 1649 K, as presented in Fig. 2a.

Each sample for drop tube experiments had a total mass of about 1 g. The sample was contained in a 13 mm ID × 15 mm OD × 160 mm quartz tube with a small orifice about 0.4 mm in diameter at its bottom. The quartz tube was placed at the top of drop tube and the drop tube was evacuated to 2.0×10^{-4} Pa before being backfilled with He (99.995%) and Ar (99.999%) gases to about 0.1 MPa. The alloy sample melted by induction heating was superheated to 150–300 K above the liquidus temperature. It was then ejected from the nozzle and dispersed into many fine droplets after being blown by a gas flow of highly purified Ar gas into the quartz tube. After the experiments, the microstructures of the solidified alloy were analyzed by a Zeiss Axiovert 200 MAT optical microscope (OM) and an FEI Sirion 200 scanning electron microscope (SEM). The phase constitutions and composition profiles were analyzed by Rigaku D/max 2500 V X-ray diffractometer (XRD) and Oxford INCA Energy300 energy dispersive spectrometry (EDS).

3. Results and discussion

3.1. Phase constitution and cooling rate

X-ray diffraction analyses were performed to determine the phase constitution of $Co_{43}Cu_{40}Pb_{17}$ alloy droplets formed in drop tube. The XRD patterns are illustrated in Fig. 2b, which indicate that the solidification microstructure of $Co_{43}Cu_{40}Pb_{17}$ alloy is composed of α(Co), (Cu) and (Pb) solid solution phases under both reduced gravity and conventional gravity conditions.

During the experiments, a bulk sample of alloy melt is firstly dispersed into a great number of small droplets. It is very difficult to measure the actual thermal process of tiny droplets during free fall inside a drop tube. Because the thermal radiation and convection are the dominant approaches for the heat transfer process from alloy droplet to its environment, theoretical estimations are performed based on Newtonian heat transfer model [19,20]. The cooling rate R_c of alloy droplet during free fall is described as

$$R_c = \frac{6}{\rho_d C_{PL} D}[\varepsilon\sigma_{SB}(T^4 - T_g^4) + h(T - T_g)] \tag{1}$$

where ρ_d is the droplet density, C_{pL} is the specific heat, D is the droplet diameter, ε is the emissivity of melts, σ_{SB} is the Stefan–Boltzmann constant, T is the droplet temperature during free fall, h is the heat transfer coefficient of droplet, T_g is the gas temperature. In calculation, the physical parameters listed in Table 1 are derived from Ref. [21].

Fig. 3 shows the calculated cooling rate during free fall of $Co_{43}Cu_{40}Pb_{17}$ alloy droplets. Evidently, the initial cooling rate

Table 1
Physical parameters of ternary $Co_{43}Cu_{40}Pb_{17}$ alloy.

Physical parameter	Value
Heat conductivity, λ (W m^{-1} K^{-1})	93.88
Surface emissivity, ε_h	0.176
Specific heat, C_{PL} (J kg^{-1} K^{-1})	456.6
Density, ρ_d (kg m^{-3})	8.39×10^3
Heat transfer coefficient, h (W m^{-2} K^{-1})	206.9
Stefan–Boltzmann constant, σ_{SB} (W m^{-2} K^{-4})	5.67×10^{-8}
Initial temperature, T_0 (K)	1800