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Determination of the enthalpy of fusion and thermal diffusivity for ternary $Cu_{60-x}Sn_xSb_{40}$ alloys

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ABSTRACT

The liquidus and solidus temperatures, enthalpy of fusion, and the temperature dependence of thermal diffusivity for ternary $Cu_{60-x}Sn_xSb_{40}$ alloys were systematically measured by DSC and laser flash methods. It is found that both the liquidus temperature and the enthalpy of fusion decrease with the rise of Sn content, and their relationships with alloy composition were established by polynomial functions. The thermal diffusivity usually drops from the solid toward the semi-solid state. The undercoolability of those liquid $Cu_{60-x}Sn_xSb_{40}$ alloys with primary Cu_2Sb solid phase is stronger than the others with primary β (SnSb) intermetallic compound, and the increase of cooling rate facilitates further undercooling. Microstructural observation indicates that both of the primary Cu_2Sb and β(SnSb) intermetallic compounds in ternary $Cu_{60-x}Sn_xSb_{40}$ alloys grow in faceted mode, and develop into coarse flakes and polygonal blocks.

1. Introduction

Ternary Cu-Sn-Sb alloys are applied extensively in mechanical and electronic industries because of their outstanding properties, such as high strength and thermal conductivity, excellent wear resistances and good weldability with high melting temperature. The investigations on thermodynamic properties and microstructures of Cu-Sn-Sb alloys are of significance for understanding the physical properties. Up to now, there are some literatures on Cu-Sn-Sb systems. For example, the phase transformation temperatures and the equilibrium phases at 423 K are experimentally measured [1]. By using the CALPHAD approach, the thermodynamic modeling of Cu-Sn-Sb ternary system is also carried out to calculate the liquidus projection and the isothermal sections [2,3]. Moreover, the activity of Sb element in liquid Cu-Sn-Sb alloys is determined by equilibrium saturation and Knudsen effusion mass spectrometric methods [4]. However, the research work on following aspects is still expected. Firstly, the enthalpy of fusion, which is one of the fundamental thermodynamic parameters determining the energy needed in melting the alloy, has not yet been available in the published literature. Although the enthalpy of fusion could be roughly estimated by Neumann–Kopp's rule from the values of the three pure components, this method usually brings in large discrepancy [5].Secondly, the thermal diffusivity $\alpha = \lambda/\rho C_P$ (λ is thermal conductivity, C_P is heat capacity and ρ is density), which indicates the rate of temperature changes [6] and reflects the correlation between thermal conductivity and heat capacity [7–9], is one of the crucial parameter to investigate thermal transportation process.

The differential scanning calorimetry (DSC) [10–14] and laser flash method are efficient techniques for quantitative thermal analysis [15,16]. The objective of this work is to determine the liquidus temperature, solid temperature and enthalpy of fusion for ternary $Cu_{60-x}Sn_xSb_{40}$ alloys by DSC method, and to measure the thermal diffusivity in a wide temperature range by laser flash method. Special attention is paid to the growth morphologies of primary intermetallic compounds in ternary $Cu_{60-x}Sn_xSb_{40}$ alloys.

2. Material and methods

Ternary $Cu_{60-x}Sn_xSb_{40}$ alloys with different compositions shown in the phase diagram [1] of figure 1(a) were investigated. The source and purity of the metal elements are presented in table 1, and they were used directly as received. Each DSC sample had a mass of about 150 mg and was melted by laser melting under the protection of argon gas. The uncertainty of the alloy composition $u_r(x) = 0.003$ is determined by comparing the mass weight of the sample before and after laser melting process. The DSC experiments were carried out with a Netzsch DSC 404C differential scanning calorimeter. The calorimeter was calibrated with the melting point and the enthalpy of fusion for high purity In, Sn, Zn, Al, Ag, Au

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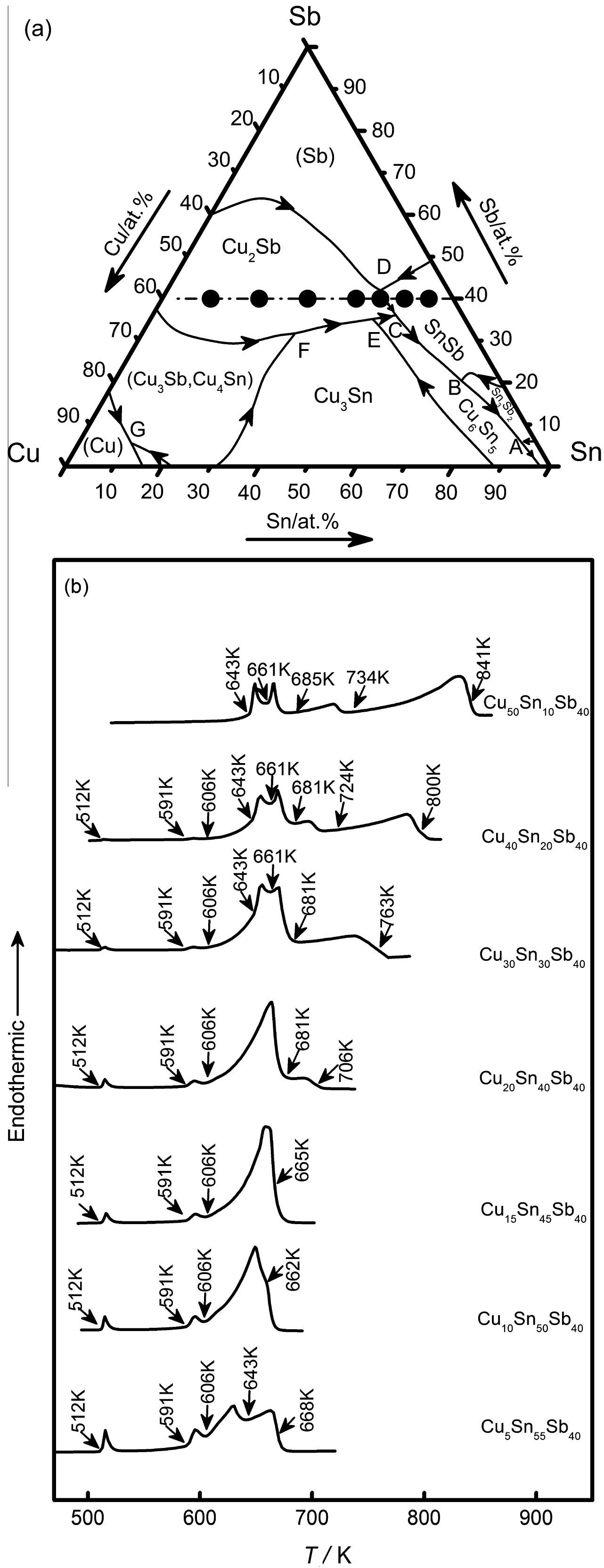

FIGURE 1. Selected alloys in the ternary Cu-Sn-Sb phase diagram and DSC heating curves: (a) the locations of selected alloys: (●), selected alloy compositions. (b) Heating curves of $Cu_{60-x}Sn_xSb_{40}$ alloys at a scan rate of 5 K/min. [a]Standard uncertainties are $u(p)$ = 1 kPa, $u_r(x)$ = 0.003 and $u(T)$ = 1 K.

TABLE 1
Metal elements used in experiments.

Chemical name	Source	Shape	Mass purity (%)
Copper (Cu)	Alfa-Aesar	Slug	99.999
Antimony (Sb)	Alfa-Aesar	Piece	99.999
Tin (Sn)	Alfa-Aesar	Shot	99.999

and Fe elements. As verified by the measurements with pure Cu, Sn and Sb elements, the standard uncertainty for temperature T measurement is $u(T)$ = 1 K, and the expanded uncertainty for enthalpy of fusion ΔH_m is $U_r(\Delta H_m)$ = 0.03 (level of confidence = 0.95). Before each DSC experiment, the alloy specimen was placed in an Al_2O_3 crucible. The chamber was evacuated and then backfilled with pure argon gas (99.999 vol.%, purification from oxygen, approx. 60 ml/min. The DSC thermal analyses were performed at 5 and 40 K/min scan rates, and the maximum heating temperatures were about 100 K higher than the liquidus temperatures. Each specimen was heated, isothermally held at predetermined temperature, and then cooled at given scan rate for 2 to 3 cycles while kept in the DSC calorimeter, and the DSC profiles obtained in the last cycle was applied for further analyses. After the DSC experiments, the alloy specimens were analyzed with a Vega 3 Tescan scanning electron microscope (SEM) and an INCA Energy 300 energy dispersive spectrometer energy dispersive spectrometer (EDS).

The thermal diffusivity α of ternary $Cu_{60-x}Sn_xSb_{40}$ alloys was measured between T = (300 and 900) K with a Linseis LFA 1000 standard laser flash thermal constants analyzer. The alloy samples were cut into Φ 12.7 × 4.0 mm in size, and clamped on a graphite sample holder. To stabilize the absorption of the incident energy, graphite is sprayed on the surface of the sample. The whole assembly was enclosed in a chamber evacuated to below 10^{-2} Pa and backfilled with the pure helium (99.99%) flow. The temperature was increased from 300 K to each test temperature with a heating rate of 5 K/min and the thermal diffusivity measurement was carried out and obtained from the average of three measurements. The expanded uncertainty in the measurements of thermal diffusivity is estimated to be $U_r(\alpha)$ = 0.05 (level of confidence = 0.95).

3. Results and discussion

Figure 1(b) shows the DSC heating curves of ternary $Cu_{60-x}Sn_xSb_{40}$ alloys at a slow scan rate of 5 K/min. From figure 1(a) and (b), it can be deduced that if the Sn content is lower than 45 at%, $Cu_{60-x}Sn_xSb_{40}$ alloys in whole or in part experience the following invariant transitions during heating, such as $Sn + Cu_6Sn_5 \rightarrow L + Sn_3Sb_2$ at T = 512 K, as marked point A in the phase diagram shown in figure 1 (a), $Sn_3Sb_2 + Cu_6Sn_5 \rightarrow L + \beta(SnSb)$ at T = 591 K (point B), $\beta(SnSb) + Cu_6Sn_5 \rightarrow L + Cu_2Sb$ at T = 643 K (point C), and $\beta(SnSb) + Cu_2Sb \rightarrow L + (Sb)$ at T = 661 K (point D), and the finally melted phase is the solid Cu_2Sb intermetallic compound. By contrast, if the Sn content is higher than 50 at%, the solid $Cu_{60-x}Sn_xSb_{40}$ alloys totally or partially undergo the two invariant transitions of $Sn + Cu_6Sn_5 \rightarrow L + Sn_3Sb_2$ at T = 512 K (point A) and $Sn_3Sb_2 + Cu_6Sn_5 \rightarrow L + \beta(SnSb)$ at T = 591 K (point B) on heating, and the solid to liquid transformation ends by the melting of solid β(SnSb) intermetallic compound. These invariant phase transitions are summarized in table 2.

The liquidus temperature T_L and solidus temperature T_S for ternary $Cu_{60-x}Sn_xSb_{40}$ alloys measured by DSC method are presented in figure 2(a). It should be mentioned that the liquidus temperature is determined by the inflection point of the last endothermic peak during melting process. The liquidus temperature shows a decreasing tendency with the increase of