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Liquid phase separation of ternary Al–In–Sn/Ge monotectic type alloys investigated with calorimetric method

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ABSTRACT

The phase equilibrium, thermodynamic properties and liquid demixing patterns for binary $Al_{100-x}In_x$, ternary $(Al_{100-x}In_x)_{90}Sn_{10}$ and $(Al_{100-x}In_x)_{90}Ge_{10}$ (x = wt.%) alloys are investigated by differential scanning calorimetry (DSC) method. The corresponding phase diagrams are experimentally established, and it is found that both monotectic temperature and critical temperature for immiscibility gap decrease when either Sn or Ge is added to binary $Al_{100-x}In_x$ alloys. The enthalpy of fusion for binary Al–In alloys, ternary Al–In–Sn and Al–In–Ge alloys shows linear functions with In content, and the introduction of Sn and Ge elements decreases the enthalpy of fusion. The liquid phase separation mechanism is discussed in relation to the DSC curves and solidified microstructures. It is demonstrated that the core and shell phases can be altered by the addition of Ge element in $(Al_{100-x}In_x)_{90}Ge_{10}$ alloys as compared with those in binary $Al_{100-x}In_x$ and ternary $(Al_{100-x}In_x)_{90}Sn_{10}$ alloys. This provides an effective way to switch the inner and outer phases for core–shell structure.

1. Introduction

Monotectic alloys arouse great scientific interest because of the existence of two immiscible liquid phases prior to monotectic solidification, which usually cause various liquid phase separation patterns in the solidified structures [1–5]. Up to now, dispersive and core–shell structures are two kinds of favorable demixing patterns with great application potentials. The former one is characterized by the minor liquid phase finely dispersed as small particles within the matrix of the major liquid phase [6], whereas in the latter case the core and the shell are composed of the two immiscible liquid phases respectively and have distinctive boundaries [7]. Numerous experimental [8–17] and calculated work [18–22] indicates that both the thermodynamic properties and kinetic factors, such as enthalpy, diffusion coefficient, viscosity, density, interfacial tension, cooling rate, undercooling level and velocities of Marangoni and Stokes motions greatly affect the liquid phase separation process. Therefore, to study the thermodynamic property and liquid phase separation pattern of immiscible alloys under different dynamic conditions are essential for a comprehensive understanding of liquid phase separation mechanism.

Binary Al–In immiscible alloys are promising in many fields extending from the advanced self-lubricating bearings up to superconductors [7,8]. Though the Al–In phase diagram is well established in the solid state, there are some discrepancies on the location of the liquid–liquid miscibility gap, particularly close to the critical point [8,23–25]. For thermodynamic properties, the surface tension, interfacial tension between two liquids, and the density of liquid Al–In alloys have been experimentally measured [8]. However, the enthalpy of fusion and the enthalpy of liquid demixing for Al–In monotectic alloys, which are indispensable for determining the nucleation rate of second liquid phase are still unknown and needs to be measured experimentally. Furthermore, if a small amount of a third element is introduced to binary Al–In alloys, it may change the phase equilibria, the location of liquid immiscibility gap, as well as the related thermodynamic properties. On the other hand, the liquid phase separation pattern may differ from the binary monotectic alloy due to the addition of a third element. It has been proved that it is a promising way to tune the liquid phase separation pattern and optimize their performance by adding a suitable third element to other binary monotectic alloys [26,27]. Nevertheless, there are few reports on the Al–In–X ternary monotectic system till now. Therefore, it is of great importance to experimentally investigate both thermodynamics and liquid phase separation mechanism for ternary Al–In-X systems.

In the present work, 10%Sn and 10%Ge elements were added into binary $Al_{100-x}In_x$ monotectic alloys to study the phase

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equilibria, thermodynamics and liquid demixing characteristics of ternary $(Al_{100-x}In_x)_{90}Sn_{10}$ and $(Al_{100-x}In_x)_{90}Ge_{10}$ alloys. The selection of these two elements depends mainly on their different affinities with Al and In elements. The Sn element has a stronger affinity with In element than that of Al element. This is due to the fact that the binary In-Sn alloy is eutectic type which is homogeneous in liquid state whereas the Al–Sn system displays a metastable liquid miscibility gap. On the contrary, Ge element prefers to be trapped in Al-rich phase when phase separation occurs between Al-rich and In-rich liquid phases. The selected Al–In, Al–In–Sn and Al–In–Ge alloys have been investigated by differential scanning calorimetry (DSC) to measure phase transformation temperatures and to establish the vertical sections of ternary Al–In–Sn/Ge alloys. Meanwhile, thermodynamic properties such as enthalpy of fusion and enthalpy of liquid demixing are determined as functions of In content. The solidification morphology of alloy samples after DSC experiment is discussed in relation to the DSC curves. Special attention has been paid to the effect of Sn and Ge elements on demixing pattern and monotectic solidification structure. It also needs to be mentioned that all the alloy compositions in the present work are defined by weight percent.

2. Experimental

Binary $Al_{100-x}In_x$, ternary $(Al_{100-x}In_x)_{90}Sn_{10}$ and $(Al_{100-x}In_x)_{90}Ge_{10}$ (x = wt.%) alloys with different compositions were prepared from metal elements of Al, In, Sn and Ge by laser melting under the protection of argon gas. The Source and purity of the metal elements are presented in table 1.

The DSC experiments were carried out with a Netzsch DSC 404C differential scanning calorimeter made in Germany. The calorimeter was calibrated with the melting temperatures and the enthalpy of fusion of standard In, Sn, Zn, Al, Ag, Au and Fe samples provide by Netzsch Company. The measuring accuracies of temperature and enthalpy of fusion are determined to be ±1 K and ±3% respectively, as verified by the measurements with pure Al and In elements. Before each DSC experiment, the alloy specimen was placed in an Al_2O_3 crucible, and the chamber was evacuated to about 0.1 Pa. The DSC thermal analyses were performed at given scan rates under Ar flow (99.999 vol.%, purification from oxygen, approx.60 ml/min), and the maximum heating temperatures were about 150 K higher than the liquidus temperatures. Each specimen was heated, isothermally held at predetermined temperature, and then cooled at given scan rate for 2∼3 cycles, and the DSC profiles obtained in the last cycle was applied for further analysis. After the DSC experiments, the alloy specimens were cut by transverse section and polished. The solidification microstructures were analyzed with an optical microscope and a scanning electron microscope. The solute distribution profile was investigated with an INCA Energy 300 energy dispersive spectrometer.

3. Results and discussion

3.1. Phase transition and immiscibility gap

In order to precisely determine the phase transition characteristics, the DSC experiments at a scan rate of 5 K/min were performed on all the selected alloys presented in tables 2–4. The obtained DSC curves show that for the three alloy systems, when In content x is lower than 17.3%, no liquid phase separation can be detected. Figure 1 shows the DSC curves of binary $Al_{90}In_{10}$, ternary $(Al_{90}In_{10})_{90}Sn_{10}$ and $(Al_{90}In_{10})_{90}Ge_{10}$ alloys as examples. As seen in figure 1(a), there are three endothermic events in the melting process of binary $Al_{90}In_{10}$ alloy. According to binary Al–In phase diagram [23], the first endothermic peak at T = 429 K corresponds to the eutectic melting of (Al) + (In) → L_2(In-rich). When temperature rises to 910 K, reverse monotectic reaction L_2 + (Al) → L_1(Al-rich) occurs, which is followed by the melting of (Al) solid solution phase at T = 926 K. It needs to be mentioned that the second and third endothermic peaks overlap due to their very narrow temperature gap. For ternary $(Al_{90}In_{10})_{90}Sn_{10}$ alloy, the first endothermic peak at 393 K indicates the eutectic transformation (Al) + (In) → L_2. The next endothermic event at T = 888 K demotes the reverse monotectic reaction L_2 + (Al) → L_1. Then, the remaining (Al) solid solution phase transfers into liquid phase at T = 920 K. Therefore, it can be summarized that all the three phase transitions for $(Al_{90}In_{10})_{90}Sn_{10}$ alloy during melting are similar to those of binary $Al_{90}In_{10}$ alloy except for a slight decrease in each transformation temperature. This is probably due to the dissolution of Sn element in (In) phase. As mentioned above, binary Al–Sn alloy is a monotectic system whereas binary In–Sn system is a eutectic one, in which In and Sn elements can be soluble with each other at any proportion in liquid state. For ternary $(Al_{90}In_{10})_{90}Ge_{10}$ alloy, the first endothermic peak for this alloy at 429 K is evidently due to the eutectic melting of (Al) + (In) → L_2. Upon heating, there appears a rather large peak at T = 685 K. According to the invariant reactions in the binary phase diagrams of Al–In, Al–Ge and In–Ge systems, this reaction is predicted to be eutectic transformation (Al) + (Ge) → L_1, which is confirmed by the solidified structure observation in Section 3.3. If temperature continuously rises, the DSC base line is deviated and monotectic melting (Al) + (In) → L_2 takes place at T = 858 K. After this, residual (Al) solid phase melts, and the liquid temperature of this alloy is determined to be T = 902 K. Figure 1(b) plots the DSC cooling curves of these alloys. During cooling process of binary $Al_{90}In_{10}$ alloy, primary (Al) phase precipitates form the liquid alloy at T = 910 K. When temperature drops to T = 896 K, monotectic reaction L_1 → L_2 + (Al) takes place. Finally, the eutectic solidification L_2 → (In) + (Al) occurs at T = 428 K. The solidification route for $(Al_{90}In_{10})_{90}Sn_{10}$ alloy is the same as that of binary $Al_{90}In_{10}$ alloy. For ternary $(Al_{90}In_{10})_{90}Ge_{10}$ alloy, the solidification path differs. When temperature decreases to 895 K, primary (Al) solid phase nucleates initially from the liquid alloy, and then monotectic reaction takes place L_1 → L_2 + (Al) at T = 854 K. Once temperature drops down to 672 K, eutectic reaction L_1 → (Al) + (Ge) occurs in the residual L_1 phase, and finally (Al + In) eutectic structure forms from L_2 phase at T = 426 K.

When In content is larger than 20%, all the three alloy systems exhibit liquid homogenization upon heating. Figure 2 presents the DSC traces of $Al_{50}In_{50}$ based alloys as examples to show their phase transition characteristics. For $Al_{50}In_{50}$ alloy, as shown in figure 2(a), the first endothermic peak at T = 429 K is still due to the eutectic meting (Al) + (In) → L_2. The second signal with a peak at T = 910 K corresponds to the monotectic reaction L_2 + (Al) → L_1. After this, the alloy consists of two immiscible liquids L_1(Al-rich) and L_2(In-rich), which mix upon heating and homogenize at T = 1075 K. Similar to binary $Al_{50}In_{50}$ alloy, ternary $(Al_{50}In_{50})_{90}Sn_{10}$ alloy also experiences the same phase transitions in melting process except for a slight decrease in each transition temperature owing to the dissolution of Sn element in (In) phase. For $(Al_{50}In_{50})_{90}Ge_{10}$ alloy, the (Al) + (In) → L_2 eutectic melting occurs at T = 429 K with a small endothermic peak, and then the followed eutectic melting of (Al) + (Ge) → L_1 at T = 685 K yields a sharp peak. On continuously heating, the monotectic melting (Al) + L_2 → L_1 produces a relatively

TABLE 1
Meatal elements used in experiments.

Chemical Name	Source	Shape	Mass purity
Alumina (Al)	Alfa-Aesar	Slug	99.9999%
Indium (In)	Alfa-Aesar	Shot	99.9999%
Tin (Sn)	Alfa-Aesar	Shot	99.9999%
Germanium (Ge)	Alfa-Aesar	Piece	99.9999+%