Effect of TiC particles on the liquid–liquid decomposition of Al–Pb alloys

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ABSTRACT

The microstructure formation during a liquid–liquid phase transformation of immiscible alloys remains an unsolved scientific problem. In this work, casting experiments were carried out to investigate the effect of TiC particles on the liquid–liquid phase transformation of Al–Pb alloys. SEM and EDS investigations reveal that TiC particles can be used as inoculants for the nucleation of the Pb-rich droplets during the liquid–liquid decomposition of Al–Pb alloys and promote the formation of Al–Pb alloy with a dispersed microstructure. A model was developed to describe the kinetic behavior of TiC particles and the precipitation of the Pb rich droplets in the melt. The dissolution, coarsening and precipitation of TiC particles during the whole process from the very beginning of the addition of TiC into the melt till the liquid–liquid phase transformation of the Al–Pb alloy were calculated. It is demonstrated that if the number density of the TiC particles in the melt cooled to the binodal line temperature of Al–Pb alloys is high enough, the addition of TiC causes a refinement of the Pb-rich droplets/particles.

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1. Introduction

Immiscible alloys are characterized with a miscibility gap in the liquid state (as shown in Fig. 1 for Al–Pb alloy). Many of them have great potentials to be used in industry. For example, alloys based on Al–Pb and Al–Bi are candidates to be used as advanced bearing materials in automotive applications if the soft Pb or Bi phase is dispersed in the Al matrix [1–3]. Cu–Fe and Cu–Cr alloys are high-strength, high-conductivity materials [4–5], and Cu–Co alloy is excellent magneto-resistive material [6]. Unfortunately, these alloys have an essential drawback that just the miscibility gap in the liquid state poses problems. When a single-phase melt of these alloys are cooled into the miscibility gap, they transform into two liquids. The liquid–liquid phase decomposition generally causes the formation of a phase segregated microstructure [7–9]. In the last decades, the liquid–liquid phase transformation and separation of immiscible alloys have been a focus for material science [10–18]. It is demonstrated that the microstructure evolution during the liquid–liquid transformation is a result of the concurrent actions of the nucleation, growth, Ostwald ripening, motions and collision coagulations of the minority phase droplets [19–21]. The nucleation of the minority phase droplets has a dominant effect on the formation of the solidification microstructure of immiscible alloys [19]. Some techniques such as rapid solidification [21], inoculation [22] as well as solidification under effect of electric current pulses [23] may enhance the nucleation of the minority phase droplets and, thus, promote the formation of a well dispersed

microstructure. In the present work we investigate the effect of TiC particles on the microstructure formation of Al–Pb alloys.

2. Experimental procedure

Solidification experiments were carried out for Al–Pb alloys with different additive amounts of TiC particles. The experimental procedures are as follows. The pure Al (99.99%, mass percent, the same as below) and Pb (99.99%) were first melted and heated up to 1323 K in a graphite crucible. Proper amount of TiC particles was added into the melt. After that, the melt was held temperature and mixed for 30 min. Finally, the melt was poured into a graphite mold to form a cylindrical sample of 12 mm in diameter and 90 mm in length. The temperature at the center of the sample was measured using tungsten–rhenium thermocouple. The radius of the thermocouple is 0.2 mm. It is demonstrated that the cooling rate of the melt in the temperature range of 1023–1323 K, which corresponds to the miscibility gap in the liquid state for Al–Pb alloy, is about 90 K/s.

The TiC particles were added to the alloy by using the Al–1.35%Ti–0.33%C master alloy, which was manufactured in our laboratory. The microstructure of the master alloy consists of nano-sized TiC particles and α-Al matrix, as shown in Fig. 2. The molar fractions of Ti and C for the master alloy are approximately the same and, thus, there exists hardly TiAl$_3$ phase in the master alloy.

The Al–Pb alloy samples were sectioned longitudinally and metallographic specimens were prepared. Microstructure analyses were carried out by scanning electron microscope (HITACHI S-2400N SEM). The phase identifications were done by energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (Moldel D/Max 2500PC Rigaku
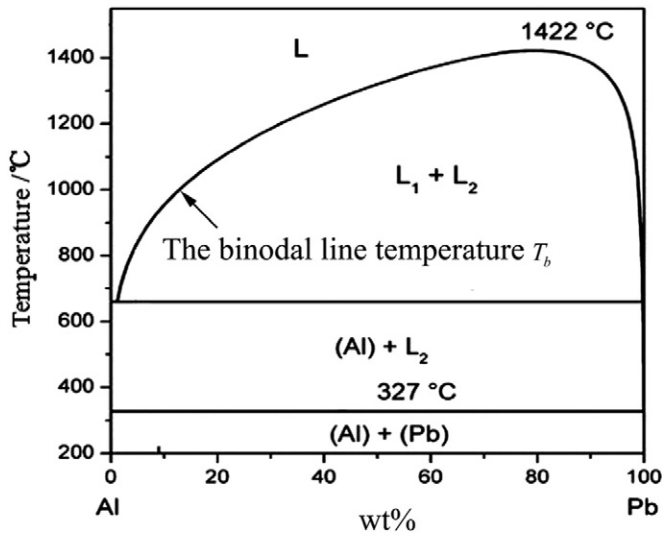
Fig. 1. Phase diagram for Al–Pb alloy [22]. T_b is the binodal line temperature of the alloy.

XRD). SISC IAS V8.0 software developed by the Chinese Academy of Sciences was used for the quantitative metallographic analysis to determine the size distribution and the average diameter of the Pb-rich particles in Al–Pb alloys and TiC particles in the Al–1.35%Ti–0.33%C master alloy.

3. Experimental results

Fig. 3 shows the solidification microstructures of the samples. The black phase and white phase are the Al-rich matrix and Pb-rich phase particles, respectively. Fig. 4 shows the quantitative metallographic result of the size distribution of the Pb-rich phase particles.

Both Figs. 3 and 4 demonstrate that the particles can be divided into two classes. The larger particles (the primary particles) are the product of the liquid–liquid decomposition. They have some time to grow before being engulfed by the solidification interface. The smaller particles (the secondary particles) are the product of the monotectic reaction. They are engulfed by the solidification interface almost immediately after their nucleation. Here we care mainly about the "primary particles". These particles will simply be called "Pb-rich particles" in the following. The average size of these particles ($<d_{Pb}>_{2D}$) in samples with different additive amounts of TiC (or C_{TiC}, wt.%) is given in Table 1. Fig. 3 and Table 1 demonstrate that the average size of the Pb-rich particles remains approximately unchanged when C_{TiC} is below 0.076. It then shows a tendency of increase with C_{TiC} when $0.076 < C_{TiC} < 0.093$ and a tendency of decrease with C_{TiC} when $0.093 < C_{TiC} < 0.125$. The average size of the Pb-rich particles keeps almost constant when C_{TiC} is beyond 0.125.

The FESEM line-scanning analyses were carried out to identify the locations of TiC particles in the Al–Pb alloy. One result is shown in Fig. 5. It demonstrates that the TiC particles are located inside the Pb-rich particles, indicating that the Pb-rich droplets are formed by the heterogeneous nucleation on TiC particles during the liquid–liquid phase decomposition.

Fig.6 shows the solidification microstructures of the Al–7%Pb alloys with different additive amounts of TiC particles. It shows a similar refining effect of TiC particles on the Pb-rich particles.

These experimental results demonstrate that TiC particles can work as the heterogeneous nucleation sites for the Pb-rich droplets and catalyze the nucleation of the Pb-rich droplets during cooling an Al–Pb alloy in the miscibility gap.

4. Discussions

In order to understand the detailed effect of TiC particles on the microstructure formation of Al–Pb alloys, a model is developed to calculate the kinetic behavior of TiC particles during the whole process from the very beginning of the addition of TiC into the melt till the liquid–liquid phase transformation as well as the precipitation of the Pb-rich droplets under the effect of TiC particles during the liquid–liquid phase transformation.

A function $f_i(R,t)$ is defined to describe the size distribution of the Pb-rich droplets (i = 1) or the TiC particles (i = 2). $f_i(R,t)dR$ gives the number of the precipitated droplets/particles of phase i per unit volume in a radius range between R and $R + dR$ at time t. According to this definition, the number density N_i, average radius $\langle R_i \rangle$ and volume fraction ϕ_i of the droplets/particles of the precipitated phase i are given by the following equations:

$$N_i = \int_0^\infty f_i(R,t)dR \tag{1}$$

$$\langle R_i \rangle = (1/N_i) \int_0^\infty R f_i(R,t)dR \tag{2}$$

$$\phi_i = (4\pi/3) \int_0^\infty R^3 f_i(R,t)dR. \tag{3}$$

The size distribution function $f_i(R,t)$ satisfies Eq. (4) during the whole process of heating and cooling of the melt [19]:

$$\frac{\partial f_i(R,t)}{\partial t} + \frac{\partial}{\partial R}(v_i f_i(R,t)) = \left.\frac{\partial I_i(R,t)}{\partial R}\right|_{R=R_i^*} \tag{4}$$

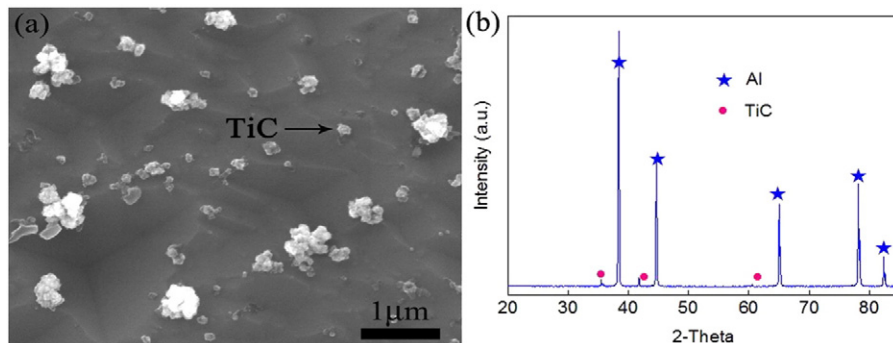**Fig. 2.** Microstructure (a) and XRD pattern (b) of the Al–1.35%Ti–0.33%C master alloy. The 2D average diameter of the TiC particles is about 100–200 nm.