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# Phase stability behavior of nanoscaled lead-bismuth peritectic alloys embedded in zinc matrix

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ABSTRACT

Pb-Bi alloy inclusions of nanometric size with peritectic composition embedded in zinc matrix are prepared by rapid solidification processing to study their phase stability and solid-state transformation behavior within the Zn matrix. The experimental results indicate the inclusions to be single phase having hcp crystal structure with a mode of size distribution of 25 nm. In-situ transmission electron microscopy using heating stage and high temperature X-ray diffraction results suggest that at small length scales of the confined inclusions, the coexistence of a liquid with two solid phases does not take place at the peritectic temperature.

When the geometric dimensions of a material decreases from the macroscopic scale to the nanoscale, its phase stability and phase transformation behavior can significantly get altered due to the additional effects from surfaces and interfaces. When the size of an alloy nanoparticle is reduced, the contribution to the interfacial energy from the interface between the two solid phases leads to an increase in the Gibbs free energy of the system and can result in a large variation in the properties such as melting point [1–4], crystal structure [5], crystal order parameter [6] as well as a significant change in the nature of the equilibrium phase diagrams at the nanoscale regime.

The use of monotectic alloy system containing a large miscibility gap can ensure that embedded particles are insoluble in the matrix at low temperature and consequently they provide an opportunity to study solid-solid and solid-liquid phase transformation behavior of nanoparticles. The bismuth–lead system is a part of low melting point metallic systems that are attractive for developing alloys for molten metal heat transfer system. It was also an important system for solder applications before the emergence of environmental concerns. The phases that appear in this system include liquid, rhombohedral Bi, fcc Pb and hcp $Pb_7Bi_3$ intermetallic compound. The intermediate hcp phase forms peritectically at about 30 at% Bi. This phase has an appreciable homogeneity range and is stable at lower temperatures. The maximum solubility of Bi in the fcc solid solution of Pb is about 24 at% Bi, whereas very little solubility exists for Pb in solid Bi. The eutectic temperature and compositions are 125 °C and Bi-44.5 at% Pb respectively [7]. Zn is immiscible with Bi and Pb both in liquid and solid states.

Significant amount of work is available on the superheating and suppression of the melting point of pure metal particles, eutectic phase transformation as well as phase stability studies in alloy nanoparticles [8,9]. The superheating phenomenon has been observed in metals such as In, Pb embedded in Al, Pb in Zn, Cu and Ag in Ni matrix [10–18]. Significant depression of melting point was observed in the case of Bi embedded in Al and Zn matrices and Pb in Ni matrix [16,19,20]. Two-phase inclusions of Pb–Cd, Pb-Sn and Bi-Sn and In-Sn in Al matrix have been synthesized by non-equilibrium processing techniques and their eutectic phase transformation behavior has been well studied [21–25]. Single phase inclusions of Pb–In in Al synthesized by rapid solidification have also been studied [26]. Jesser et al. [27] studied the melting behavior of isolated nanoparticles of Pb-Bi alloys using heating stage transmission electron microscopy and consequently arrived at the phase diagrams from the experimental data on individual, isolated nanoparticles as a function of the size of the nanoparticle. Several deviations from the melting behavior of bulk materials were observed. Lee et al. [28] reported the formation of an amorphous phase in nanoscaled bismuth-tin alloys (<8 nm) produced by in-situ vapor deposition of bismuth on tin and tin on bismuth. Srivastava et al. studied the evolution of microstructure in Ag–Ni nanoparticles as a function of size [29].

In the present work we report the experiments designed to probe and understand the phase stability and transformation behavior of the alloy phases at the peritectic composition as a function of temperature using both in-situ and ex-situ studies. To the best of authors' knowledge,

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the detailed study of peritectic transformation behavior of embedded particles is not available.

Zn-2 at% ($Pb_{70}Bi_{30}$) alloy was chosen for the present experiment and rapid solidification from the alloy melt using melt-spinning technique was carried out to synthesize nanometer sized alloy dispersions in an aluminum matrix. The alloy melt was ejected through a 0.5 mm diameter orifice quartz nozzle using Ar gas over a pressure of 15–20 kPa onto the surface of the polished copper wheel rotating at a speed of 18 m/s. The samples thus obtained were in the form of ribbons of thickness 60–80 μm and width of 2.5–3.0 mm. The samples for transmission electron microscopy (TEM) investigations were prepared using a Gatan Duo ion mill operated at a voltage of 5 kV and a current of 0.25 mA in each gun. The morphological studies including high-resolution lattice imaging and elemental mapping were performed in a field-emission TEM operated at 300 kV (FEI Tecnai F30). In-situ electron microscopy studies were carried out using a double tilt heating holder (GATAN model 628-0500). In situ X-ray studies were carried out using X'pert PRO instrument with Cu Ka radiation (40 kV, 30 mA) and a high temperature X-ray diffractometer attachment SHT-1500.

Microstructural analysis from the melt-spun sample Zn-2 at% ($Pb_{70}Bi_{30}$) shows the presence of single-phase particles embedded in zinc matrix. A typical bright-field image (Fig. 1a) taken along [0001] axis of the matrix zinc, shows a distribution of $Pb_7Bi_3$ single phase particles embedded in the matrix. The corresponding selected area diffraction pattern is presented in Fig. 1c. Fig. 1b shows dark field image captured using $(01\overline{1}0)$Pb7Bi3 reflection. From the analysis of these electron diffraction patterns obtained along major zone axes, we conclude that $Pb_7Bi_3$ possesses an orientation relation with zinc matrix given by

$$[0001]\mathrm{Zn}//[0001]\mathrm{Pb_7Bi_3}$$

$$\sim 19^{\circ} \text{ between } \left(01\overline{1}0\right)\mathrm{Zn}, \left(01\overline{1}0\right)\mathrm{Pb_7Bi_3}$$

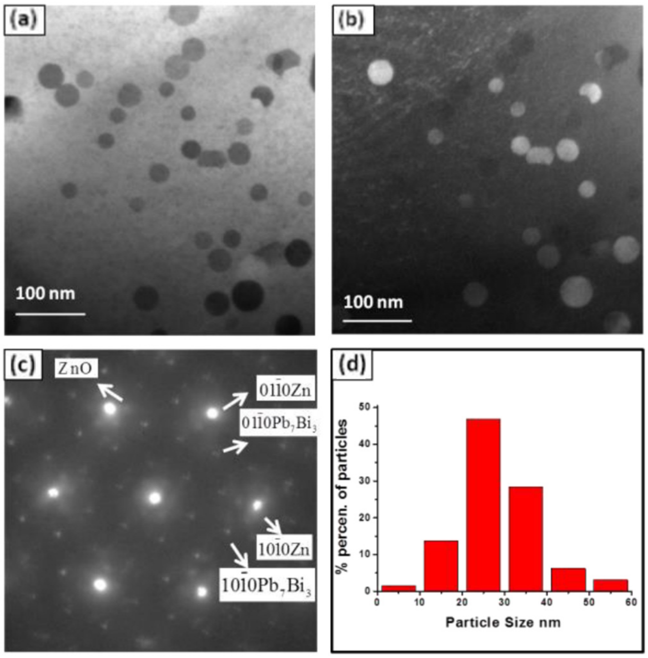

**Fig. 1.** (a) Bright field image of single phase $Pb_7Bi_3$ particles in Zn-2 at% ($Pb_{70}$-$Bi_{30}$) sample. (b) Dark field image using $(01\overline{1}0)$-$Pb_7Bi_3$ reflection from the secondary spot shown in SADP. (c) Selected area diffraction pattern taken from the bi-phase particle along [0001] Zn. (d) Typical size distribution histogram shows that the mode is 25 nm. Size distribution measurements were carried out by imaging the particles along the [0001] zone axis of Zinc and determining the maximum diagonal of each particle.

To obtain the size distribution, measurements were carried out by imaging the particles along the [0001] zone axis of zinc and determining the maximum diagonal of each particle. From the size distribution, the mode of the size distribution is found to be 25 nm as shown in Fig. 1d.

In order to understand the phase stability and peritectic phase transformation behavior of these embedded alloy nanoparticles, in-situ hot-stage TEM experiments are carried out. Fig. 2 shows sequence of micrographs showing melting behavior of a single-phase hcp $Pb_7Bi_3$ phase particle of size around 23 nm during in situ heating experiments. Fig. 2a shows a high-resolution transmission electron microscope (HRTEM) image of $Pb_7Bi_3$ single-phase particle obtained along [0001] zone of the Zn matrix. As the temperature is increased from room temperature to 165 °C, no major change in the morphology of the particle could be observed. However, at 168 °C which is 19 °C below the bulk peritectic temperature, melting is initiated at the particle-matrix interface. This is evident from Fig. 2c as the high-resolution fringes start vanishing at particle-matrix interface. While the absence of fringes is by no means a confirmation of melting, the observation of the microstructure on further heating substantiates this claim. On further increase in temperature from 168 °C to 192 °C, one can observe wetting of the particle by the melt and growth of melt into the interior of the particle leading to a core-shell structure. The entire melting event is completed at 208 °C, which is approximately 30 °C below the liquidus temperature of lead rich solid solution. The complete melting of the inclusion ensemble was found to be spread out over an interval of about 40 °C around the peritectic temperature. It should be noted here that the formation of second solid is not observed during melting between peritectic temperature and Pb liquidus temperature. This is expected according to equilibrium phase diagram.

High temperature X-ray diffraction experiments were carried out to know the phase evolution and the peritectic phase transformation of $Pb_7Bi_3$ inclusions (Fig. 3a) in large number of particles that can confirm whether the second phase suppression during peritectic reaction is occurring in a few particles or in all the particles. For clarity, we only present the reflections in the range 28°–34° in 2θ values. X-ray diffraction study revealed that the melt-spun samples Zn-2 at% ($Pb_{70}Bi_{30}$) contain peaks corresponding to the hcp $Pb_7Bi_3$ phase. During heating up to the temperature of 175 °C, a minor shift of peaks belonging to $Pb_7Bi_3$ phase towards lower 2θ side could be observed. However, the intensities of reflections of $Pb_7Bi_3$ phase remain unaltered. As the temperature increases from 175 °C to 220 °C, the intensities of $Pb_7Bi_3$ phase peaks start decreasing that suggest the initiation of melting of peritectic inclusions. The continuous decrease in peak intensities also indicate a size-dependent melting behavior that occurs over a temperature range. The XRD peaks from the inclusions disappeared completely at 234 °C which indicates a complete melting of all the $Pb_7Bi_3$ phase inclusions. It should be noted here that during heating, the peaks corresponding to lead-rich solid solution could not be observed indicating suppression of the formation of the pre-peritectic solid phase in the inclusions around peritectic temperature.

In situ XRD studies are further carried out to study the peritectic phase transformation of the alloy inclusions during cooling (Fig. 3b). During cooling the first $Pb_7Bi_3$ intermetallic peaks appear at 200 °C which is approximately 40 °C below the lead liquidus temperature but 13 °C above the peritectic temperature. This is a surprising result since the nucleation of peritectic phase above the peritectic temperature is generally not anticipated. The only way to rationalize this observation is to visualize the scenario where Pb FCC could not nucleate from PbBi melt. In that case it is possible for PbBi intermetallic phase to extend close towards temperature higher than peritectic temperature and can nucleate directly from the melt without any partitioning from the liquid. On further cooling to 150 °C, the intensities of $Pb_7Bi_3$ phase peaks increases (Fig. 3b) indicating occurrence of the solidification in different inclusions over a temperature range. Below 150 °C, the peak intensities did not change significantly as the temperature decreases to room temperature. It should be noted that during cooling the peaks