MELTING AND FREEZING BEHAVIORS OF Pb NANOPARTICLES EMBEDDED IN AN Al MATRIX

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Abstract—Dispersions of nanometer-sized Pb particles embedded in an Al matrix (10wt%Pb) have been synthesized by ball milling. It was found that the microstructure of Pb/Al mixture was refined with increasing milling time, resulting in nanometer-sized Pb particles homogeneously embedded in the Al matrix. The melting and freezing behaviors of the Pb particles were investigated by means of DSC. Calorimetry measurements indicated that both melting and freezing points of the Pb nanoparticles were depressed in comparison to the bulk Pb, and the melting and freezing point depressions were approximately proportional to the inverse particle size of Pb. The melting and freezing behaviors of Pb particles were analyzed in terms of thermodynamics. It was suggested that the melting and freezing point depression of the Pb nanoparticles results from their small size effects. © 1997 Acta Metallurgica Inc.

INTRODUCTION

Melting and freezing of materials have been under extensive considerations for a long time. Since experimental studies of the melting and freezing behavior of small particles began to appear in 1950, many pieces of evidence have shown that the melting temperatures of small particles can be well depressed in comparison to the bulk as the particle size is reduced (1). Although great efforts have been made, however, a complete understanding of the melting and freezing has yet to be achieved.

The embedded particles can offer a unique system in which the melting transformation can be studied, for the insulating matrix provides a degree of environmental protection. Approaches utilized to prepare the embedded particles are widely attempted, such as sputtering, rapid solidification, ion implantation or using porous glass etc. Recently, it has been reported that the ball milling technique (2) can also be used to synthesize two phase mixtures in immiscible binary systems. In particular, mean particle sizes in the regime of nanometers are easily obtained, which favors the study of the melting-freezing transition. The melting behavior of Sn in Ge/Sn (2) and In in In/Al (3) by ball milling has been reported. In this work, we synthesize dispersions of Pb/Al by ball milling. The melting and freezing behaviors of the embedded Pb particles were investigated by means of calorimetric measurements.

EXPERIMENTAL

Commercial elemental powders of Al and Pb with a composition of Al-10wt%Pb were used as starting materials for ball milling, which was performed in a vibratory ball mill. The
milling process was interrupted at various time intervals, and powder samples were removed for analysis.

The X-ray diffraction (XRD) was carried out on a Rigaku X-ray diffractometer (D/max-ra, 12 kW) with Cu Kα radiation. The microstructures of the Pb/Fe dispersions were examined by electron microscopy. Scanning electron microscopy (SEM) was performed on a Cambridge stereoscan-360 with a back-scattering mode. The transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HREM) were conducted on a Philips EM 420 microscope operated at 100 kV and a JEOL 2000 microscope with an accelerating voltage of 200 kV, respectively. Thermal analysis was performed in a Perkin-Elmer Differential Scanning Calorimeter (DSC-7) at a constant heating rate of 10 °C/min.

RESULTS AND DISCUSSION

Figure 1 displays the XRD spectra of Pb/Al samples milled for different times. Several features are noted from Fig. 1. Firstly, only diffraction peaks from Pb and Al are detected, showing that the ultimate milled products (10 h) are two phase mixtures of Pb and Al. Lattice parameters of Pb and Al in the as-milled products coincides well with the tabulated values, indicating that no solid solutions between Al and Pb are formed after ball milling. Secondly, the diffraction line profiles of both Pb and Al broaden with increasing milling time. The average grain sizes are calculated by using the Scherrer formula, as shown in Fig. 2. One can see that the grain sizes of both Al and Pb are continuously refined with prolonged milling time, and decreased into the nanometer regime. According to SEM observations, the Pb particles are gradually dispersed into the Al matrix. The microstructures of the as-milled sample of Pb/Al were revealed by TEM and HREM observations, which give evidence that the irregular Pb nanoparticles are mostly located at the grain boundaries of Al, and randomly oriented with the Al matrix (4).

Figure 1. X-ray diffraction patterns of Pb/Al samples with different milling times.  
Figure 2. Variation of the grain size of Pb as a function of milling time.

Figure 3 shows the DSC curves upon heating Pb/Al samples with different milling times. For the sample at the early stage of ball milling (0.5 h), there is one sharp endothermal peak in the heating DSC curve with an onset temperature of 327.0°C, which is virtually the melting temperature of bulk Pb. With an increasing milling time, or the refinement of Pb particles, the melting peak shifts to lower temperatures and asymmetrically broadens. For instances, the
melting peak of Pb/Al sample milled for 10 h spans over a temperature range of 305.5-322.0°C. Evidently, the melting temperatures of the Pb nanoparticles are significantly depressed as the particle size is reduced. Several heating/cooling cycles have been performed for each sample, and subsequent melting sequences hardly change the shape of the melting curve in DSC.

Classical thermodynamic treatment which predicts the size dependence of the melting point of fine particles can be described by Couchman-Jesser equation (5):

\[ \frac{T_m}{T_0} = 1 - 3(\sigma_{sm} - \sigma_{lm}) / \rho Lr \]

where, \( \rho = (\rho_s + \rho_l)/2 \), \( T_m \) is the melting point of the Pb particles, \( T_0 \) is the equilibrium melting temperature of the bulk Pb. \( \sigma_{sm} \) and \( \sigma_{lm} \) are the interface energies of solid-Pb/solid-Al and Liquid-Pb/solid-Al. \( L \) is fusion enthalpy of the bulk Pb at the equilibrium state, and \( r \) is the mean particle size of Pb.

The predicted \( r^{-1} \) size dependence of the melting temperature can be experimentally verified by plotting the measured melting temperature as a function of the inverse particle size, as shown in Fig. 4. The best fit to the data is a straight line, indicating the data is clearly consistent with a dependence of the melting temperatures. According to the slope of the best fit straight line and above equation, with available data of \( L, \rho \) of Pb, one may calculate the value for \( \sigma_{sm} - \sigma_{lm} \) to be 13.3 kJ/m². This result indicates that the solid Pb particle/Al matrix interface energy is larger than the liquid Pb particle/matrix energy, which might be the origin of the melting point depression of Pb particles.

Previously, it has been reported that the faceted Pb nanoparticles, epitaxially oriented with the Al matrix by rapid solidification, are much superheated (4). The different melting behaviors of Pb particles might be attributed to the unlike interfacial structures. In the case of rapid solidification, the ordered Pb/Al interfaces always have lower interfacial energy in comparison to the disordered Pb/Al interfaces in the as-milled Pb/Al samples, which consequently leads to different values for \( \sigma_{sm} - \sigma_{lm} \) and thus different melting behaviors for Pb particles according to the above equation.

Figure 5 displays the DSC curves showing the freezing behavior of Pb particles in the as-milled Pb/Al samples as a function of milling times. For Pb/Al sample milled 2 h, the Pb particles solidify with an undercooling of about 30°C, which is nearly similar to the
undercooling of micrometer sized Pb droplets in cast Al-Pb samples reported previously (6). This undercooling results from the heterogeneous nucleation by the surrounding Al matrix. As the particle size of Pb is decreased with increasing milling time, the freezing peak of Pb broadens and shifts to lower temperatures, suggesting the size dependence of the undercoolings of the nanoparticles, and that finer particles will have larger undercoolings.

Since the solidification of liquids undergoes a process of nucleation and growth, if the nucleation of the liquids is prohibited, then the solidification may take place at lower temperatures. With regard to the nanoparticles, such as Pb embedded in the Al matrix, the fine particles will be affected by an additional pressure due to the large surface tension, which makes nucleation of Pb droplets difficult and thus leads to the solidification at lower temperatures. In other words, the freezing of nanoparticles will have larger undercoolings than of microparticles, as is actually observed in Fig. 5 that the undercooling of Pb particles increases with decreasing particle size.

CONCLUSIONS

1. Nanometer sized Pb particles are homogeneously embedded in an Al matrix by means of ball milling, and the irregular Pb particles are found to be randomly oriented with the Al matrix.

2. The melting point of Pb particles is significantly depressed as the particle size is reduced, which fundamentally agrees with the thermodynamic prediction that the melting temperature is inversely proportional to the particle size.

3. The freezing temperature of Pb nanoparticles is also found to be decreased with the refinement of the particles, which might be attributed to the size effects. It was suggested that the nanoparticles will have larger undercoolings.

References

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5. P.R. Chouchman and W.A. Jesseer, Phil. Mag., 35, 787 (1977)