



Microstructure and melting behavior of tin nanoparticles embedded in alumina matrix processed by ball milling



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ABSTRACT

Tin dioxide and aluminum powders were ball milled for different time periods. Sn particles embedded in Al_2O_3 matrix formed through a displacement reaction after ball milling. However, SnO_2 cores remain within some larger particles, while in smaller particles pure Sn cores exist. The embedded Sn particle size was found to increase with the milling time, which is attributed to the thermal effect provided by the exothermic displacement reaction during prolonged milling. Melting point depressions were observed. The melting temperatures of the Sn particles scale linearly with the inverse particle sizes. The extent of melting point depressions is observed to be slightly larger than those in the literature. This is ascribed to the simultaneous presence of Sn– Al_2O_3 and Sn– SnO_2 interfaces.

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1. Introduction

In recent decades, nano-sized materials have become one of the major research topics. The physical and chemical properties of the nano-sized materials greatly influence their practical uses. Not surprisingly, much effort has been put on nanomaterials to unveil their unique properties, including melting. Melting is one of the important phase transformations in materials. It was found that melting preferentially nucleates at the surface of the solids due to reduced bonds of the surface atoms compared to the solid interior. Additionally, the summation of solid–liquid interfacial energy (γ_{sl}) and gas–liquid interfacial energy (γ_{gl}) are usually lower than the gas–solid interfacial energy (γ_{gs}). This facilitates the occurrence of surface melting [1]. Nanomaterials are known to have higher ratio of surface-to-volume compared to their bulk counterparts. It is expected that the abundant surface atoms having higher energy than those of interior atoms will depress melting point [2–6]. Lereah et al. [3] used dark field transmission electron microscopy (TEM) to observe the melting behavior of Sn nanoparticles embedded in SiO_2 . It was found that as the temperature approached bulk melting point, Sn particles with a bright ring around a dark core developed, which revealed that there was a liquid layer on the surface. The thickness of the liquid layer was observed to increase with increasing temperature. A similar

observation of surface melting of Sn particles embedded in Al matrix was reported by Chen et al. [6] in a high-temperature in situ X-ray diffraction (XRD) experiment. It was noted that there was a progressive decrease in the diffraction intensity at temperatures closer to the bulk melting point of Sn. This was attributed to the gradually decreased core volume fraction of the remaining solid Sn core as the fraction of surface liquid layer increased with increasing temperature. Eventually, the diffraction intensity vanished indicating complete melting of Sn nanoparticles [6]. Both of the aforementioned surface melting results show melting point depression, which denotes that melting starts at a temperature below the bulk equilibrium melting temperature (T_0).

In addition to melting point depression, some other interesting phenomena were observed in nano-sized materials. For example, the latent heat of melting of Sn particles was determined to be lower than its bulk value and scaled linearly with the inverse of particle size for particle sizes down to 20 nm [2,4–5,7]. The decrease of latent heat was attributed to the increase of the surface atom fraction and the increasing contribution of small size particles ($d < 5$ nm) with reducing particle size. It was reported that surface melting does not occur when the particle sizes are smaller than 5 nm. Instead, other mechanisms take place. For instance, Sn nanoparticles with sizes smaller than 5 nm were observed to exhibit an exothermic peak at a temperature around its bulk melting point during initial heating in a differential scanning calorimetry (DSC) test [4]. This phenomenon was attributed to partial coalescence of the small particles to reduce surface energy. For the same particle size of Sn ($d < 5$ nm), Oshima and Takayanagi [8] noticed the presence of a pseudo-crystalline

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structure in an in-situ heating experiment using high resolution (HR) TEM. This pseudo-crystalline structure solely exists in a certain temperature range and consists of crystalline embryos which change their configurations. These particles are practically in a liquid state at temperatures below the bulk melting temperature. Similarly, Lereah et al. [3] observed structural instability instead of surface melting in Pb particles with a radius smaller than 3 nm. It was suggested that the melting point of such fine particles became lower than the temperature for surface melting. Consequently, a sharp melting transition happened in place of surface melting.

Depressions of melting point of ball milled Sn particles were studied by several groups. Koch et al. [9] conducted ball milling experiments on the mixture of Sn and Ge powders. Finely dispersed Ge particles were found to be surrounded by Sn matrix after ball milling. Ge particle size decreased with increasing milling time and melting point depression was recorded. They concluded that most of the observed melting point depression was due to the increase of Ge/Sn interfacial area as Ge particle size decreased by mechanical milling. The vibrational instability induced at the Ge/Sn interfaces resulted in the melting of Sn. Sheng et al. [7], Liu et al. [10] and Chen et al. [6] conducted ball milling experiments on Al and Sn powder mixtures with different compositions. Nano-sized Sn particles embedded in Al matrix resulted after ball milling. These embedded Sn particles exhibit melting point well below the bulk equilibrium melting temperature (T_0). Both Liu et al. [10] and Chen et al. [6] suggested that the embedded Sn nanoparticles have larger interface-to-volume ratio and surface melting can occur on the surface atoms during heating processes. Sheng et al. [7] explained melting point depression based on a thermodynamic model. They found that the depression depends not only on particle dimension but also on particle/matrix interface structure and excess enthalpy of the interface.

Apart from the aforementioned research using powder mixtures of Sn/Al and Ge/Sn, the present work aims at understanding the melting behavior of Sn nanoparticles embedded in a rigid ceramic matrix. It was demonstrated that less reactive oxides can react with aluminum through thermite reactions [11–13]. In the present study tin dioxide and aluminum powder mixtures were ball milled for different time periods and a displacement reaction took place, in which SnO₂ was reduced while Al was oxidized. These Sn nanoparticles are therefore embedded in an Al₂O₃ matrix. The microstructure evolution and melting behavior of the embedded Sn particle sizes will be delineated.

2. Experimental

Four grams of powder mixture containing 1 g of tin dioxide (SnO₂, purity 99.99%, 50–100 nm) and 3 g of aluminum (purity 99.9%, particle size smaller than 200 mesh) were used as the starting materials. The Al–Sn binary system was chosen because the metals are essentially immiscible. The powder mixtures were loaded and sealed within a tool steel vial along with 10 hardened steel balls in a glove box under pure argon atmosphere. Ball-to-powder weight ratio was measured to be 5:1. The powder mixtures were milled for 5–20 h using a Spex 8000-D milling machine with revolutions per minute (rpm) of 1725. The powder mixtures were milled for 30 min with an interruption of 15 min to avoid heat effect. The milling process was repeated until the desired milling time was achieved. According to Takacs's detailed review paper [11], ball milling induced self-sustaining reactions can occur in many exothermic powder mixtures. Therefore, tin dioxide and aluminum powders undergo the following displacement reaction:



The reaction heat ($-\Delta H$) was calculated to be 260.6 kJ/per oxygen atom. Consequently, Sn nanoparticles embedded in Al₂O₃ matrix can be achieved.

A Bruker D8 SSS X-ray diffractometer was employed to identify phases of the milled powder mixtures. The X-ray diffractometer was operated at an output voltage of 40 kV and current of 10 mA with Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$). The particle size of tin was calculated from the full-width at half-maximum (FWHM) of the diffraction planes using Scherrer's equation. The powder mixtures for TEM observations were cold compacted with a uniaxial stress of 100 MPa. Focused ion beam (FIB) was used to prepare TEM samples. A thin carbon film was deposited on the sample surface prior to FIB milling in order to minimize beam damage. A Ga⁺ ion source was used to mill the specimens. Different milling conditions were employed for rough and final milling. Rough milling was carried out with an operating voltage of 30 kV and a beam current of 6.8 nA. Final polishing on the sample surface was performed with an operating voltage of 5 kV and a rather low beam current of 40 pA. Microstructure characterizations of the Sn nanoparticles embedded in Al₂O₃ matrix were conducted using an FEI Tecnai F20 TEM at 200 kV.

The melting temperatures of the ball milled Sn nanoparticles were measured by a TA Instrument MDSC 2920 DSC. DSC heating scan was conducted from 0 °C to 400 °C and subsequently cooled to 0 °C with a heating or cooling rate of 10 °C/min. It may be suggested that the DSC scan includes the stored energy of ball milling, and therefore it cannot be used to solely present the melting behavior of the Sn nanoparticles. To eliminate this effect, two continuous DSC scans were carried out on each condition and the second scan data will be used in the following discussions. To ensure that all the stored energy of ball milling was released during the first DSC run and an equilibrium phase was obtained, five continuous DSC heating and cooling cycles were also carried out on some selected ball milled powder mixtures. The powder mixture for X-ray diffraction and TEM analysis of each ball milling condition was also heated and cooled in accordance with DSC heating and cooling rates. In the following, the powder mixtures subjected to zero and one DSC heating and cooling scan will be denoted as *as-milled* and *nanoconfined* samples, respectively. The present work emphasizes the nanoconfined samples and most of the results are related to these samples.

3. Results

The XRD diffraction patterns of the as-milled and nanoconfined Sn in Al₂O₃ matrix are given in Fig. 1a and b, respectively. It can be observed that SnO₂, Sn and Al diffraction peaks coexist in the as-milled (Fig. 1a) and nanoconfined (Fig. 1b) samples. Additionally, the diffraction intensities of SnO₂ decrease, while the intensities of Sn increase gradually with increasing milling time. These trends of reduced SnO₂ and raised Sn diffraction intensities indicate that the formation of Sn phase progresses with increasing milling time. However, a noticeable SnO₂ phase could still be found after the powder mixture was ball milled for 20 h. This implies that the SnO₂ phase was not fully consumed. According to formula (1), Al₂O₃ forms as a result of the displacement reaction. The absence of the Al₂O₃ phase on the XRD patterns is due to the formation of amorphous Al₂O₃ phase, which was also observed in the Al–CuO displacement reactions [14,15]. The existence of amorphous Al₂O₃ phase was also proved by HRTEM data and this will be provided in the following section.

It was determined that stored energy of ball milling could contribute up to 25% of the observed melting point depression before the Sn particle was melted [9]. Therefore, nanoconfined samples were used for the following analyses. The particle sizes of Sn and Al phases calculated from the FWHM of diffraction planes and substituted to Scherrer's equation are plotted as a function of milling time (Fig. 2). Sn particle size of the 5 h milled sample was

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