Pressure-induced superheating of Al nanoparticles encapsulated in Al₂O₃ shells without epitaxial interface

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Abstract

Quantitative measurements were carried out on the pressure effect of superheating of Al nanoparticles encapsulated in Al₂O₃ shells without epitaxial interfaces. In situ XRD experiments revealed that encapsulated Al nanoparticles with different particle sizes can be superheated to 7–15 K beyond the bulk equilibrium melting point of Al, and that this is accompanied by a suppressed thermal expansion behavior. A value for the pressure build-up on the Al core due to the constraint of the rigid Al₂O₃ shell of up to 0.25 GPa was derived from the temperature dependence of the lattice spacing for the superheated samples. The correlation between the measured pressure and superheating verified that the observed superheating is a pressure-induced phenomenon which follows the Clausius-Clapeyron relation. It was demonstrated that substantial superheating can be achieved by a pressure build-up even without confinement of epitaxial interfaces for a metal/ceramic system.

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Keywords: Melting; Superheating; In situ X-ray diffraction; Nanoparticles; Pressure effect

1. Introduction

Melting of solids usually initiates at the surface where the barrier for melt nucleation vanishes [1,2]. One may not expect to be able to prevent solids from melting when temperature exceeds the equilibrium melting point \( T_0 \), i.e. superheating of solids is usually not feasible experimentally, in contrast to the supercooling of liquids. However, when a solid is coated with another material with a higher melting point, superheating is achievable when melting nucleation at the surface is effectively suppressed. This kind of superheating phenomenon was firstly reported by Daeges et al. [3], who observed superheating of Ag particles coated with Au. Since then, superheating in various systems with embedded (or encapsulated) metal particles in metal matrices has been investigated extensively [4–9]. Superheating in Pb thin films sandwiched by Al films with epitaxial interfaces was also observed [10]. In addition, a hierarchy of superheating limits for solids has been established in terms of thermodynamic consideration, analysis of kinetics, as well as via computer simulations [11–17].

Previous investigations revealed that one of the key factors dominating the superheating of encapsulated particles is the structure characteristics of the interface between the particle and the matrix (coating) [2]. When the interface is coherent or semi-coherent with a low interfacial energy, nucleation and/or growth of the liquid phase at the interface can be effectively suppressed; hence melting of the particles will be shifted to higher temperatures that may exceed the bulk equilibrium melting point \( T_0 \). Otherwise, incoherent interfaces with high interfacial energies will permit melting below \( T_0 \), i.e. a pre-melting of solid occurs. In this circumstance, the
melting temperature of small particles will be lower than $T_0$, and the smaller the particle size, the lower the melting point, analogous to the observations in free-standing small particles. This has been clearly demonstrated with experimental observations by Sheng et al. [9]. Therefore, formation of epitaxial interfaces is always considered to be necessary for achieving superheating in particle/matrix systems.

Indeed, due to the difference in thermal expansion coefficients (TECs) between the particles and the matrix, a compression pressure is generated on the embedded particles upon heating. The pressure build-up was considered to be effective in elevating the melting point of the encapsulated nanoparticles [5–8], following the classical thermodynamic consideration as in bulk solids. However, while the effect of epitaxial interfaces on superheating of encapsulated nanoparticles has been experimentally demonstrated in numerous systems [7–9], the pressure effect on superheating of nano-sized particles, to the authors' knowledge, has seldom been proved by quantitative experimental measurements in the literature. In most previous studies, superheating was observed in metal–particle/metal–matrix systems with epitaxial particle/matrix interfaces, where the pressure effect is usually considered to be minor relative to the epitaxial interface effect [5–8]. It is difficult to distinguish the pressure effect from other effects in those superheating samples.

There is indeed some experimental evidence for the pressure effect on melting of metal particles embedded in a rigid matrix without an epitaxial particle/matrix interface. For example, superheating of up to 270 K was observed in encapsulated metal particles (Pb, Sn) in fullerene-like shells [18], which was attributed to the high pressure build-up in terms of atomistic simulations. A pressure-induced melting point elevation (but not superheating) was also observed in tin particles embedded in amorphous carbon films [19]. However, in these studies, no quantitative measurement was performed to verify the pressure effect.

Another important question remains unsettled as to whether the same pressure effect as in the bulk solids can be applied to the nanoparticle systems where surfaces and/or interfaces play a crucial role. To answer these questions, quantitative determination of pressure build-up in nanoparticles as well as its correlation to the melting point variation is crucial.

Determination of the pressure effect on melting point elevation in nanoparticle systems is difficult practically. To isolate the pressure effect from other influencing factors for the melting point variation of nanoparticles, one has to find a suitable system with the following conditions: (1) a rigid matrix or shell to sustain the pressure build-up without relaxation [20]; (2) a large TEC difference between the particle and the coating to ensure a large pressure build-up in the encapsulated nanoparticles that facilitates the pressure measurement; (3) formation of incoherent particle/matrix interfaces to exclude the possible interface effect on suppression of melt nucleation.

The objective of this work is to quantitatively determine the pressure effect on superheating in Al nanoparticles encapsulated in rigid Al$_2$O$_3$ shells by using in situ X-ray diffraction (XRD) analysis. There is a large TEC difference between Al$_2$O$_3$ (8.4 · 10$^{-6}$/K) [21] and Al (23.6 · 10$^{-6}$/K) [22]. Al$_2$O$_3$ is the stiffest and strongest oxide ceramics with a shear modulus of about 150 GPa [21]. Besides, the solubility of oxygen in Al is extremely small (<3 · 10$^{-5}$) [23] even at high temperatures close to the melting point of Al. All these properties facilitate the identification of the effect of pressure on the melting point of encapsulated Al nanoparticles. A preliminary study showed that Al nanoparticles encapsulated in Al$_2$O$_3$ shells can be superheated experimentally [24]. In this paper, we report a systematic investigation on the superheating behaviors of the encapsulated Al nanoparticles with different particle sizes and shell thicknesses, to reveal quantitatively the pressure effect on superheating for nanoparticles.

### 2. Experimental

Al nanoparticles were prepared by using active H$_2$ plasma evaporation and condensation. The nanoparticles were in situ passivated at room temperature before exposure to air (original sample). The passivated original Al nanoparticles were further oxidized in air at elevated temperatures. The original sample weight and the weight after oxidation were measured using a digital

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**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxidation temperature/time</th>
<th>$m_t/m_0$</th>
<th>$\Delta H_{m}(\text{Al/Al}_2\text{O}_3)$ (J/g)</th>
<th>$\Delta H_{m}(\text{Al}_2\text{O}<em>3)/\Delta H</em>{m}(\text{Al})$</th>
<th>$t/l$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>As-evaporated</td>
<td>1</td>
<td>286 ± 5</td>
<td>0.72 ± 0.01</td>
<td>0.09 ± 0.01</td>
</tr>
<tr>
<td>A</td>
<td>773 K/3 h + 873 K/1 h</td>
<td>1.45</td>
<td>88 ± 8</td>
<td>0.22 ± 0.02</td>
<td>0.53 ± 0.05</td>
</tr>
<tr>
<td>B</td>
<td>773 K/3 h + 873 K/3 h</td>
<td>1.51</td>
<td>68 ± 8</td>
<td>0.17 ± 0.02</td>
<td>0.66 ± 0.05</td>
</tr>
<tr>
<td>C</td>
<td>773 K/3 h + 873 K/6 h</td>
<td>1.60</td>
<td>56 ± 8</td>
<td>0.14 ± 0.02</td>
<td>0.76 ± 0.05</td>
</tr>
</tbody>
</table>

$m_0$: original sample weight, $m_t$: weight after oxidation, $\Delta H_{m}(\text{Al})$: literature value (in terms of J/g) of the melting enthalpy for pure Al.
From the TEM images and the SAED pattern that only for most particles the oxide shell is hardly identifiable to 80 nm. While in a few particles the oxide shell is seen, approximately spherical with a mean diameter of about 200 nm. Samples for TEM and HRTEM observations were prepared by dispersing the nanoparticles in ethanol by sonication and then dropping on to a carbon-coated copper grid.

XRD measurements at room temperature were carried out on a Bruker D8 Discover X-ray diffractometer with Cu Kα radiation. The X-ray wavelengths λKα1 (=1.540562 Å) and λKα2 (=1.544390 Å) were selected using a Goebel mirror. The divergence, scattering and receiving slits were chosen with the widths of 1, 1 and 0.1 mm, respectively. Measurements of 0–20 scans for the samples were made in the reflection mode with a step of 20 = 0.1° and a counting time of 1 s for qualitative analysis, and a step of 20 = 0.02° and a counting time of 3 s were used for quantitative analysis. A standard SiO2 sample provided a measurement of the instrumental broadening. The peak separation method was used to separate neighboring Al and Al2O3 peaks.

In situ XRD experiments were conducted on the same diffractometer with a high-temperature attachment. A platinum thermocouple was used to monitor the sample temperature, of which the accuracy is ±1 K. A step size of 0.02° and counting time of 3–5 s were used, depending on the diffraction intensity of the samples. All experiments at high temperatures were carried out under vacuum conditions (2 × 10⁻³ Pa). The sample was heated to each temperature at a heating rate of 18 K/min and held for 5 min before collecting the XRD profiles of four Bragg reflection peaks of Al, (1 1 1), (2 0 0), (2 2 0), and (3 1 1), respectively.

3. Results and discussion

3.1. Structure characterization

As shown in Fig. 1, the as-evaporated particles are approximately spherical with a mean diameter of about 80 nm. While in a few particles the oxide shell is seen, for most particles the oxide shell is hardly identifiable from the TEM images and the SAED pattern that only shows a single face-centred cubic Al phase. Typical morphology and the corresponding SAED pattern for the oxidized sample are shown in Fig. 2. After oxidation, particles are still rough spheres and oxide shells are clearly visible for most particles. The corresponding SAED pattern clearly shows the presence of γ-Al2O3 phase. Crystalline γ-Al2O3 was formed during the oxidation treatment at elevated temperatures, either via the crystallization of the amorphous Al2O3 or the direct reaction of Al with O2. From the HRTEM observations (Fig. 3), one can see that an amorphous Al2O3 shell of about 5 nm thick was found on particles in the original sample, which was formed in the passivation process, similar to that reported previously [25,26]. For the oxidized samples, much thicker oxide shells were formed and the Al core was well encapsulated in the Al2O3 shell. For sample B, the average shell thickness is about 18 nm.

From the electron diffraction patterns and the HRTEM observations of the oxidized Al nanoparticles, no crystallographic orientation relationship was noticed between the Al core and the γ-Al2O3 shell. Although epitaxial relationships were observed in planar Al/α-Al2O3 interface in the literature [27,28], in the present case it is unlikely to form a coherent or semi-coherent Al/γ-Al2O3 interface on the nanometer-sized spherical Al core due to the large lattice mismatch between Al and γ-Al2O3. Observations of a large number of particles indicated that the Al/γ-Al2O3 interfaces are random without an epitaxial relationship. The Al/γ-Al2O3 interfaces are mostly curved and no sharp edged particles with strong facets were observed by HRTEM, as shown in Fig. 3(c).

From the XRD profiles for the original and the oxidized samples at ambient temperature (Fig. 4), one can see that diffraction peaks of Al2O3 are not visible in the original sample, while are obvious in the oxidized sample. The apparent peak broadening of Al in the
oxidized sample indicates ultrafine size of Al cores, which can be quantitatively determined from the peak broadening according to the Scherrer and Wilson method [29]. For sample B, the average Al core size determined from the XRD peak broadening is about 37 nm, which is close to that from TEM observations (40 nm).

The relative shell/core ratio is defined as $t/r$, where $t$ is the shell thickness and $r$ is the core radius. For the sample containing both Al and Al$_2$O$_3$ (original sample and the oxidized samples), the melting enthalpy of Al measured from the DSC curve (in terms of J/g) should be proportional to the mass fraction of Al in the sample. Note that the melting enthalpy is normally defined per mole; while in the followed calculations Eqs. (1) and (2), we use the value defined per gram to facilitate calculation. Assuming that the particles are spheres and the size effect on melting enthalpy can be neglected, the relative shell/core ratio of each sample can be estimated by

$$\left(1 + \frac{t}{r}\right)^{3} = 1 + \frac{\rho_{\text{Al}}}{\rho_{\text{Al}_{2}\text{O}_{3}}} \left(\frac{\Delta H_{m}(\text{Al})}{\Delta H_{m}(\text{Al}/\text{Al}_{2}\text{O}_{3})} - 1\right), \quad (1)$$

where $\rho_{\text{Al}}$ and $\rho_{\text{Al}_{2}\text{O}_{3}}$ are the densities of Al and Al$_2$O$_3$, respectively, $\Delta H_{m}(\text{Al})$ is the literature value of melting enthalpy for pure Al (in terms of J/g), and $\Delta H_{m}(\text{Al}/\text{Al}_{2}\text{O}_{3})$ denotes the melting enthalpy measured from DSC curves for the original and the oxidized samples (in terms of J/g). With available data for $\rho_{\text{Al}}$, $\Delta H_{m}(\text{Al})$ and $\rho_{\text{Al}_{2}\text{O}_{3}}$ [21, 22], $t/r$ of each sample can be estimated from the corresponding $\Delta H_{m}(\text{Al}/\text{Al}_{2}\text{O}_{3})$ values measured from DSC experiments. The results are listed in Table 1. Similarly we have

$$\left(\frac{r}{r_0}\right)^{3} = \frac{\Delta H_{m}^{0}(\text{Al}/\text{Al}_{2}\text{O}_{3})}{\Delta H_{m}^{0}(\text{Al}/\text{Al}_{2}\text{O}_{3})} \cdot \frac{m_{t}}{m_{0}}, \quad (2)$$

where $r_0$ and $r_t$ are the average Al core radius for the original and the oxidized sample, respectively, $m_{0}$ and $m_t$ are the original sample weight and the sample weight after oxidation, respectively, and $\Delta H_{m}^{0}(\text{Al}/\text{Al}_{2}\text{O}_{3})$ and $\Delta H_{m}^{0}(\text{Al}/\text{Al}_{2}\text{O}_{3})$ denote the melting enthalpy measured from DSC curves for the original sample and the oxidized samples, respectively. With the measured values of $m_t/m_0$ (as listed in Table 1), and the average Al diameter for the original sample ($2r_0$) determined by XRD, the average Al core diameter ($D = 2r_t$) and the average shell thickness for the oxidized samples can be estimated by Eqs. (2) and (1).
Fig. 5 demonstrates the determined results of the average Al core diameter ($D_{Al}$) and the average shell thickness ($t_{Al_2O_3}$) for the original and the oxidized samples, in comparison with the results from the XRD, TEM and HRTEM measurements. Clearly, the results from different experiments are rather consistent, confirming that the average core size decreased and the average shell thickness increased markedly after oxidation.

### 3.2. Melting and superheating measurements

In situ XRD experiments were conducted to study the melting behavior of the oxidized samples. For comparison, a bulk Al sample with coarse grains (grain size $>$100 μm) and the original sample were also tested. Fig. 6 collects in situ XRD profiles of Al (1 1 1) peak for sample B heated to various temperatures. The diffraction intensity of Al (1 1 1) peak reduces gradually as the temperature rises, especially in the vicinity of the equilibrium melting point of Al ($T_0 = 933$ K). It was expected that the Al diffraction line would disappear around this temperature if no superheating exists. However, an evident Al (1 1 1) profile with a substantial intensity (about 40% of the intensity at room temperature) still exists at 934 K. Even at 948 K, 15 K above $T_0$, the diffraction peak is clearly visible. The observation indicates some Al crystals in the sample can be retained above $T_0$, i.e. the Al crystals are superheated at least by 15 K beyond $T_0$. At 953 K, the (1 1 1) peak starts to disappear.

Fig. 7 shows variations of integrated intensities of Al (1 1 1), (2 0 0), (2 2 0) and (3 1 1) diffraction peaks with temperature for the original sample and the oxidized samples A, B and C. For the original sample, the integrated intensities of these diffraction peaks reduce gradually with an increase of temperature due to thermal scatterings. When the temperature approaches $T_0$, the intensities decline rapidly at about 10 K below $T_0$ and tend to zero at $T_0$. It suggests a pre-melting process occurred at about 10 K below $T_0$, which can be understood in terms of the small particle sizes and insufficient constraint of the thin amorphous Al$_2$O$_3$ shell. For the oxidized samples, the diffraction intensities begin to decrease markedly at similar temperatures, indicating the pre-melting in some particles without effective constraint. However, the intensities do not drop to zero at $T_0$. From the relative intensities at $T_0$, one can speculate that a considerable portion (approximately 20–40%) of the Al particles remain in crystalline state at the equilibrium bulk melting point of Al. The intensity gradually
diminishes at about 7, 15 and 10 K beyond $T_0$ for samples A, B and C, respectively. With consideration of the XRD resolution and the substantial holding time scale at elevated temperatures above $T_0$ we believe that a considerable number of Al nanoparticles have been superheated in these samples. After cooling down the superheated sample (sample B) to room temperature, the sample was reheated, and the superheating phenomenon could be reproduced in the second heating, as demonstrated in Fig. 7(d).

3.3. Determination of pressure

To understand the origin of the observed superheating in the encapsulated Al nanoparticles, we determined the pressure build-up on the Al nanoparticles according to the thermal expansion behavior around the melting point. Estimation of the overpressure on the Al cores can be performed via the in situ measurement of the lattice spacing $d$ at elevated temperatures in terms of [29],

$$d_{hkl} = \lambda / 2 \sin \theta_{hkl},$$

where $d_{hkl}$ is the lattice spacing of $(h k l)$ crystallographic plane, $2 \theta_{hkl}$ is the XRD intensity centroid position, which was calibrated by an external standard method using a pure Si polycrystal, and $\lambda$ is the X-ray wavelength. Fig. 8 shows the lattice spacing of Al (1 1 1) plane ($d_{111}$) as a function of temperature for all samples. It is obvious that the lattice spacing values of the five different samples are approximately identical from room temperature to about 800 K. The thermal expansion coefficients of the samples derived from the temperature dependence of the lattice spacing are consistent with the literature data in this temperature range [30]. When the temperature approaches $T_0$ more closely, no difference can be identified in the lattice spacing values between the original sample and the bulk Al. However, a pronounced difference appears in the superheated samples, as shown in Fig. 8. The lattice spacing values of the superheated samples are obviously smaller than those in the original sample when the temperature exceeds 880 K, and the slope of the temperature dependence of $d_{111}$ is much smaller than those for the bulk and the original samples. It means the thermal expansion coefficient of Al lattice is lower in the superheated samples around the equilibrium melting point. Measurements on other crystallographic planes showed similar behaviors.

Fig. 8 shows the lattice spacing of Al (1 1 1) plane ($d_{111}$) as a function of temperature for all samples. It is obvious that the lattice spacing values of the five different samples are approximately identical from room temperature to about 800 K. The thermal expansion coefficients of the samples derived from the temperature dependence of the lattice spacing are consistent with the literature data in this temperature range [30]. When the temperature approaches $T_0$ more closely, no difference can be identified in the lattice spacing values between the original sample and the bulk Al. However, a pronounced difference appears in the superheated samples, as shown in Fig. 8. The lattice spacing values of the superheated samples are obviously smaller than those in the original sample when the temperature exceeds 880 K, and the slope of the temperature dependence of $d_{111}$ is much smaller than those for the bulk and the original samples. It means the thermal expansion coefficient of Al lattice is lower in the superheated samples around the equilibrium melting point. Measurements on other crystallographic planes showed similar behaviors.

The reduced thermal expansion coefficient of Al lattice in the superheated samples is an indication of pressure build-up on the nm-sized Al core. Based on a simple elastic consideration, the pressure build-up on the Al core at $T_0$ in the superheated samples can be determined by

$$P = K_{Al}(d_b - d_s)/d_s,$$

where $d_s$ is the lattice spacing measured at $T_0$ or the superheated samples, $d_b$ is the corresponding bulk value measured at the same temperature, $K_{Al}$ is the bulk modulus of Al. The calculated pressures from the XRD mea-

### Table 2

Estimated overpressure ($P$) at $T_0$ and the melting point elevation based on Clausius–Clapeyron equation ($\Delta T_P$) as well as the superheating measured from in situ XRD ($\Delta T_{meas}$) for samples A, B and C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$P$ (GPa) $(T = T_0)$</th>
<th>$\Delta T_P$ (K)</th>
<th>$\Delta T_{meas}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1 1 1)</td>
<td>(2 0 0)</td>
<td>(2 2 0)</td>
</tr>
<tr>
<td>A</td>
<td>0.11</td>
<td>0.12</td>
<td>0.13</td>
</tr>
<tr>
<td>B</td>
<td>0.25</td>
<td>0.23</td>
<td>0.26</td>
</tr>
<tr>
<td>C</td>
<td>0.18</td>
<td>0.17</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Fig. 8. (a) Temperature dependence of lattice spacing $d_{111}$ of Al (1 1 1) plane for different samples as indicated. $d_{111}(RT)$: $d$ of (1 1 1) plane determined at room temperature. (b) Expanded version of the high temperature part of the graph shown in (a).
Table 3
Parameters used in the calculation of the pressure by using the shell model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>K (Al)</td>
<td>76 GPa</td>
<td>[22]</td>
</tr>
<tr>
<td>ν (Al2O3)</td>
<td>0.27</td>
<td>[21]</td>
</tr>
<tr>
<td>μ (Al2O3)</td>
<td>150 GPa</td>
<td>[21]</td>
</tr>
<tr>
<td>γAl</td>
<td>23.6 × 10^{-6}/K</td>
<td>[22]</td>
</tr>
<tr>
<td>γAl2O3</td>
<td>8.4 × 10^{-6}/K</td>
<td>[21]</td>
</tr>
<tr>
<td>ΔV(Al)</td>
<td>6%</td>
<td>[22]</td>
</tr>
</tbody>
</table>

The pressure on the Al cores results from the different thermal expansion coefficients between the shell and the core upon heating. According to the shell model proposed previously [31,32], the overpressure on the Al core encapsulated by the γ-Al2O3 shell can be calculated by using

$$ P = \frac{4\mu}{2r + (1 - \nu)\Delta r + 2\nu} \cdot \frac{\delta}{\kappa}, $$

(5)

where μ is the shear modulus of the shell, K is the bulk modulus of the core, ν is the Poisson’s ratio for the shell, δ is the misfit parameter, which is defined as ΔTΔx, where ΔT is the temperature difference, and Δx is the TEC difference between Al and Al2O3, and

$$ G = \frac{2r^3 + (r + t)^3}{2[(r + t)^3 - r^3]}, $$

(6)

is a geometrical factor. Here in this model, the excess volume of the interface was not taken into account. By using parameters from the literature as listed in Table 3, we calculated the pressure as a function of the relative shell/core ratio (t/r). For sample B, the pressure derived from the shell model is about 0.36 GPa, which agrees reasonably well with the measured pressure from the temperature dependence of d (0.25 ± 0.03 GPa). The slight difference may originate from the experimental measurement error of the pressure and the approximation in calculation.

3.4. The pressure effect on superheating

To understand the origin of the observed superheating for the encapsulated Al nanoparticles, one should consider two effects: the interface effect and the pressure effect. As presented above, the HRTEM observations confirmed that the Al/Al2O3 interfaces are incoherent without epitaxial relationship in the oxidized samples. Therefore the epitaxial interface effect on superheating can be excluded in the present case. It has been reported that formation of a surface oxide layer (PbO) may reduce the surface energy and thereby suppress the surface melting of Pb [33]. However, in the present case, such an effect (formation of an oxide layer to suppress surface melting) is insufficient to rationalize the observed superheating, because only the coherent/semi-coherent interface may favor a superheating. Besides, no superheating was observed for the original sample in which oxide layers were already formed. It is also worth noting that for Pb nanoparticles embedded in SiO2 and Al2O3 [34,35], no superheating was reported, which may be attributed to the defective structure of the interfaces in those samples.

Based on classic thermodynamic analysis, the pressure effect on the melting point for bulk solids can be derived by using the Clausius–Clapeyron equation [36]

$$ \frac{dP}{dT} = \frac{\Delta V}{\Delta L} \cdot \frac{T}{L}, $$

(7)

where P is the pressure, T is the absolute temperature, L is the latent heat of fusion and ΔV is the relative volume change. With the pressure measured on the Al core for the superheated samples, the melting temperature elevation can be calculated in terms of Eq. (7). It is interesting to note that the calculated results are well in agreement with the measured superheating from the in situ XRD experiments for the three superheated samples, as listed in Table 2. The agreement between the measured superheating and the melting point elevation derived from the classical thermodynamics (Clausius–Clapeyron equation) in the present samples verifies that the observed superheating in the present case is a pressure-induced phenomenon in which the epitaxial interface effect on suppressed melting nucleation can be excluded. The pressure effect on melting point in the present nanoparticle system seems to follow the same rule for bulk solids.

4. Summary

The melting and superheating behavior was studied for Al nanoparticles encapsulated in Al2O3 shells without epitaxial interfaces. By using in situ XRD, we measured simultaneously the melting temperature and the thermal expansion behavior of the encapsulated particles. Experimental results revealed that the encapsulated Al nanoparticles with different particle sizes can be superheated to 7–15 K beyond the bulk equilibrium melting point of Al, accompanied with a suppressed thermal expansion behavior. A value for the pressure build-up on the Al core due to the constraint of the rigid Al2O3 shell of up to 0.25 GPa was derived from the temperature dependence of lattice spacing for the superheated samples. The correlation between the measured pressure and the observed superheating validated that the observed superheating is a pressure-induced phenomenon following the Clausius–Clapeyron relation. It was demonstrated with
convincing experimental evidence that substantial superheating can be achieved by a pressure build-up even without confinement of epitaxial interfaces for a metal/ceramic system.

Acknowledgement

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