



Regular article

Effect of the interface energy on the pressure-induced superheating of metallic nanoparticles embedded in a matrix



M. Zhao, X. Yao, Y.F. Zhu *, Q. Jiang

Key Laboratory of Automobile Materials, Ministry of Education, School of Materials Science and Engineering, Jilin University, Changchun 130022, China

ARTICLE INFO

Article history:

Received 30 March 2017

Received in revised form 6 July 2017

Accepted 11 July 2017

Available online xxxx

Keywords:

Superheating

Nanocrystalline metal

Surface energy

Thermodynamics

ABSTRACT

The pressure-induced superheating of metallic nanoparticles embedded in a coherent or incoherent matrix was evaluated by considering the interface energy effect. As the size decreases, the superheating is weakened from the bulk value to zero for these two systems. Associated to the competing roles of different thermodynamic quantities, the weakening in the coherent system originates from the predominant lattice contraction and melting enthalpy reinforcement because of the negative interface energy, but that in the incoherent system results from the bulk modulus decline due to the positive interface energy. Our theoretical predictions are in agreement with available literature results.

© 2017 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

In materials science, considerable attention has been paid to the distinct mechanical, physical and chemical properties of nanoparticles (NPs) [1–9]. Among these properties, the melting depression $T_m(D)$ of NPs has been reported at small D because of the surface energy γ_{sv} , where T_m is the melting point, the subscript sv is the solid-vapor interface and D is the diameter of nanoparticles and wires or the thickness of nanofilms [10–14]. Similarly, attempts have been made to study the melting behavior of the coherent core/shell structures and nanostructured materials (NSs) [13,15]. Superheating and melting depression were respectively observed for the low- $T_m(\infty)$ core and NSs (∞ is the bulk size), attributed to the negative or positive interface energy γ_{ss} denoted as $T_m^Y(D)$ with the subscript ss being the solid-solid interface. In reference to the NP case [10,11], $T_m^Y(D)$ can be formulated as [13,15],

$$T_m^Y(D)/T_m(\infty) = \exp[-\delta(\alpha_{sv}-1)/(D/D_0-1)], \quad (1)$$

where α_{sv} is a physicochemical amount with $\alpha_{sv} = 2S_{vib}(\infty)/3R + 1$. S_{vib} is the atomic vibration entropy with $S_{vib}(\infty) \approx S_m(\infty)$, and R is the gas constant. $S_m(\infty) = H_m(\infty)/T_m(\infty)$, where H_m is the melting enthalpy [11,16]. $D_0 = 2(3-d)h$, where h is the atomic diameter, and d is the dimension with $d = 0$ for NPs; $d = 1$ for nanowires, and $d = 2$ for thin films. In the solid-solid interface structure, $\delta = 1/[1 + [\gamma_{sv}(T_\infty)/\gamma_{ss}(T_\infty) - 1]\alpha_{sv}]$. $\gamma_{sv}(T_\infty)$ or $\gamma_{ss}(T_\infty)$ is the surface or interface energy

of NPs, which can be given by $\gamma_{sv/ss}(T_\infty) = H(\infty) - T\Delta S(T_\infty)$ [17]. H and S here respectively denote the excess interface internal energy and the entropy associated with the solid-vapor or solid-solid interface. H is contributed from the difference in the atomic bonding state between the interface and the bulk with $H(\infty) = E_{cb}(\infty) - E_{csv/ss}(\infty)$, where E_c is the atomic cohesive energy. $\Delta S(T_\infty)$ can be given by the difference in the entropy of atoms between the solid-vapor (or solid-solid) interface and the bulk. Note that $\gamma_{sv}(T_\infty)$ or $\gamma_{ss}(T_\infty)$ is usually positive, because special energy is necessary to create a new dividing surface or interface [18]. If a coherent interface is formed by eliminating two surfaces, however, the negative interface energy may arise due to the decrease in the internal energy. Since the atomic bond at the coherent interface is usually positioned between the two crystals, and the interface energy will thus be negative for the crystal with low- $T_m(\infty)$, although it is positive for the other one with high- $T_m(\infty)$.

The melting behavior of low- $T_m(\infty)$ NPs embedded in a coherent or incoherent matrix (p/M) has also been investigated [19–23]. By experiments [24–28], at $D < 20$ nm, an obvious superheating is observed for the coherent structure, whereas the melting depression occurs for the incoherent case. At $D > 20$ nm, in contrast, a superheating was still observed for the coherent and incoherent structures [17,24,25,29,30] and evidenced clearly by a higher extrapolated T_m [25]. Since the superheating or melting depression of embedded NPs induced by $\gamma_{sv}(T_\infty)$ or $\gamma_{ss}(T_\infty)$ is remarkable at $D < 20$ nm but negligible at $D > 20$ nm [13,15,31–33], the superheating observed at $D > 20$ nm cannot be directly accounted by the interface energy effect [25,29]. With the nucleation theory or lower-bound melting temperature model [25,29], this behavior can be understood in terms of the build-up pressure or strain energy change effect on $T_m(D)$ of the embedded NPs denoted as T_m^P . It is therefore accepted that the roles by the interface energy and

* Corresponding author.
E-mail address: yfzhu@jlu.edu.cn (Y.F. Zhu).

build-up pressure effects are additive [25,30], which can be described with,

$$T_m(D) = T_m^Y(D) + T_m^P(D). \quad (2)$$

To work out $T_m(D)$ in Eq. (2), the size-dependence of $T_m^P(D)$ with D in the full size range from the nanometer regime to the bulk should be resolved.

According to the elastic energy calculation for a misfitting spherical NP based on the dislocation theory [34,35], Allen et al. [25] proposed that T_m^P of embedded NPs can be elucidated with,

$$T_m^P = 6G_M \left[2\delta_s \delta_f + \delta_f^2 \right] kT_m / \{ [1 + 4G_M/3K] H_m \}. \quad (3)$$

Here, $\delta_s = [\alpha_{Tp}^s - \alpha_{Tm}^s][T_m - T_f]$, and $\delta_f = f/3$. α_{Tp}^s is the thermal expansion coefficient, $T_f = 0.75T_m(\infty)$ is usually taken as the formation temperature of a matrix where the matrix is completely relaxed around the embedded nanoparticles [25], f is approximately 0.025 with the change in fractional volume during stress-free melting [25,29], and k is assumed to be unity as a factor to account for the effect of a free surface on the strain energy density [29]. K is the bulk modulus of the embedded particles, G is the shear modulus, the subscripts p and M denote atoms in the particles and matrix, and the subscript or superscript s denotes the solid state of embedded NPs. Using Eq. (3), T_m^P of the embedded bulk particles has been evaluated for the coherent In/Al (8 K) and incoherent Sn/C (6.4 K) structures [25,29] with $\alpha_{Tp}^s(T_m, \infty)$, $H_m(T_m, \infty)$ and $K(T_m, \infty)$. This is limited since T_m^P in the nanometer regime is still less considered, hindering our understanding to $T_m(D)$ with Eq. (2). Without any structure change on varying D , in fact, Eq. (3) derived from the dislocation theory should cover the full size range from the nanometer regime to the bulk [25,34,35]. It is therefore possible for us to resolve $T_m^P(D)$ as long as the size-dependent quantities $\alpha_{Tp}^s(T_m, D)$, $H_m(T_m, D)$ and $K(T_m, D)$ are known.

In the present work, to enhance our understanding to the melting behavior of the embedded NPs, the size-dependent superheating $T_m^P(D)$ with the coherent or incoherent structure will be investigated. The roles played by the size-dependent quantities $\alpha_{Tp}^s(T_m, D)$, $H_m(T_m, D)$ and $K(T_m, D)$ will be evaluated by considering the interface energy effect. Note that, the concept of superheating cited in literatures means heating above the thermodynamic transition temperature $[T_m(\infty)]$ to a region where the phase is metastable [17,24,25,29,30]. In the present work, this concept refers to a thermodynamic melting of the embedded NPs, which has also been illustrated in our early papers [15,31–33].

2. Model

Thanks to the above discussion on the T_m^P equation derived from the dislocation theory [34,35], the $T_m^P(D)$ expression in Eq. (2) can be obtained by imposing the size effect on the quantities in Eq. (3), which can be shown as,

$$T_m^P(D) = 6G_M(\infty) \times \left[2\delta_s(D)\delta_f + \delta_f^2 \right] kT_m(\infty) / \{ [1 + 4G_M(\infty)/3K(T, D)] H_m(T_m, D) \}, \quad (4)$$

where $\delta_s(D) = [\alpha_{Tp}^s(T, D) - \alpha_{Tm}^s(T, \infty)][T_m(\infty) - T_f]$. In reference to our previous studies on NSs or the core/shell structures [13,15], $T_m^P(D)$ can be resolved by considering the positive or negative interface energy effect.

Because of the proportional relationships with $\alpha_T \propto E_c^{-1}$ and $H_m \propto E_c$ [13], one has $\alpha_{Tp}^s(T, D)/\alpha_{Tp}^s(T, \infty) = E_c(\infty)/E_c(D)$ and $H_m(T_m, D)/H_m(T_m, \infty) = E_c(D)/E_c(\infty)$. $E_c(D)$ can be given by $E_c(D)/E_c(\infty) = T_m(D)/T_m(\infty)$ with $T_m(D)$ taken from Eq. (1) as the first order. In thermophysics, K is proportional to the Young's modulus Y . Based on our studies on $Y(T, D)$

of NPs or NSs [36,37], $K(T, D)$ of the embedded NPs at $T = T_m(D)$ is formulated as $K(T_m, D) = \{K(T_m, \infty)E_c(D)/E_c(\infty) + K(0, \infty)[1 - E_c(\infty)/E_c(D)]\} \{h_p(\infty)^3 \varepsilon(D)/[h_p(D)^3 \varepsilon(\infty)]\}$. Thus, $K(T, D)$ is related to E_c , ε and h_p with ε being the bond energy. For the coherent interface, $\varepsilon(D)/\varepsilon(\infty) = E_c(D)/E_c(\infty)$. $h_p(D)$ is contracted at the interface because of the elastic restriction from the matrix with small $h_M(\infty)$. Geometrically, the atomic number of NPs at the outmost surface layer is $6D^2/h^2$, whereas the total atomic number of the entire crystal is $(D/h)^3$. Then, $h_p(D)/h_p(\infty) = \{6Z_{sv}h_M(\infty) + 6(Z_b - Z_{sv})h_p(\infty) + 2Z_b[D - 6h_p(\infty)]\}/(DZ_b)$, where Z is the coordination number, and the subscript b denotes atoms in the bulk; $Z_b = 12$ and $Z_{sv} = 9$ for face-centered cubic (FCC) crystals and $Z_b = 8$ and $Z_{sv} = 6$ for body-centered cubic (BCC) ones. For the incoherent structure, $\varepsilon(D)/\varepsilon(\infty) = [E_c(D)/E_c(\infty)]/[6(Z_{ss}/Z_b - 1)h(\infty)/D + 1]$ and $h_p(D)/h_p(\infty) = 1 + h_p/(3D)$, where Z_{ss} is 11 for FCC crystals and 7 for BCC ones [36].

To explore Eq. (1), $\gamma_{sv}(T, \infty)$ or $\gamma_{ss}(T, \infty)$ should be known. Due to the coordination imperfection at the surface, the surface energy is positive [18], which was measured as $\gamma_{sv}(T, \infty) = 760 + 4.77T_m(\infty)/h_p^2$ [38]. When the interface is coherent, $\gamma_{ss}(T, \infty)$ can be obtained using the aforesaid $\gamma_{ss}(T, \infty)$ expression. $E_{cb} = Z_b \varepsilon_b/2$; E_{css} is related to the bonding state of atoms at the interface with $E_{css} = [Z_{ss} \varepsilon_{ss} + (Z_b - Z_{ss}) \varepsilon_b]/2$. Hence, $H(\infty) = Z_{ss}(\varepsilon_b - \varepsilon_{ss})/2$. At $T = T_m$, $\Delta S(T_m, \infty) = S_b(T_m, \infty) - S_{ss}(T_m, \infty)$ with $S_{ss}(T_m, \infty) = Z_{ss}[S_b(T_m, \infty) - S_{ss}(T_m, \infty)]/Z_b$. $\gamma_{ss}(T, \infty)$ is largely dependent on the $H(\infty)$ term. If $\varepsilon_{ss} > \varepsilon_b$, $\gamma_{ss}(T, \infty)$ is negative. Otherwise, it will be positive. Upon the incoherent case, $\gamma_{ss}(T_m, \infty)$ will be positive because of the weak coordination imperfection, which can be conveniently calculated with $\gamma_{ss}(T_m, \infty) = 4h_p S_{vib}(\infty) H_m(\infty)/(3V_s R)$ [5], where V_s is the molar volume and the averaged values of h_p , S_{vib} , H_m and V_s are taken between the NPs and substrate. The negative or positive interface energies for some coherent or incoherent p/M structures are found in Table 1. Note that γ_{ss} might be affected by the entropy contribution of the mixed (alloyed) interface layer between particle and matrix [39–41]. Considered that the incoherent structures discussed in this work are immiscible systems, the effect of mixture entropy at the interface should be insignificant [17], neglected as the first order approximation.

3. Results and discussion

Fig. 1 shows the $T_m(D)$ curves of the metallic NPs ($d = 0$) or films ($d = 2$) embedded in the coherent matrix with (A) Pb/Cu, (B) Ag/Ni, (C) In/Al and (D) Pb/Al and in the incoherent matrix with (E) Al/Al₂O₃, (F) Fe/Al₂O₃, (G) Au/SiO₂ and (H) Sn/C considering Eqs. (1), (3) and (4). The superheating of $T_m(D)$ is observed in (A)–(D), while $T_m(D)$ declines as D decreases with $T_m(D) < T_m(\infty)$ at $D < 20$ nm in (E)–(H). In (A)–(H), $T_m(D)$ is slightly higher than $T_m(\infty)$ at $D > 20$ nm. The experimental, simulation and theoretical results available in literatures are shown for comparison, and good agreement can be found between them.

In view of Eq. (2), the change in $T_m(D)$ of the embedded NPs is contributed from $\Delta T_m^Y(D)$ and $T_m^P(D)$ with $\Delta T_m^Y(D) = T_m^Y(D) - T_m(\infty)$. To illustrate this, the $\Delta T_m^Y(D)$ and $T_m^P(D)$ curves considering Eqs. (1) and (4) are shown in Fig. 2 for the (A) coherent In/Al structure and (B) incoherent Sn/C structure. In (A), $\Delta T_m^Y(D)$ is positive, suggesting the superheating in the coherent structure. In (B), $\Delta T_m^Y(D)$ is negative, meaning the melting depression in the incoherent structure. In (A) and (B), $\Delta T_m^Y(D)$ tends to be zero at $D > 20$ nm. In contrast, $T_m^P(D) > 0$ at any D in (A) and (B), while it abruptly decreases to zero at approximately $D < 5$ nm. This infers that the superheating or melting depression dominates melting of embedded NPs at $D < 20$ nm, while the slight superheating at $D > 20$ nm observed in experiments should be originated from the build-up pressure or strain energy change.

The superheating of $T_m^Y(D)$ for NPs embedded in the metallic matrix originates from the negative interface energy, attributed to the strong bonding nature at the coherent interface. The melting depression of $T_m^Y(D)$ is relevant to the positive interface energy because of the bond disorder at the incoherent interface. A key role of the negative or

Download English Version:

<https://daneshyari.com/en/article/5443169>

Download Persian Version:

<https://daneshyari.com/article/5443169>

[Daneshyari.com](https://daneshyari.com)