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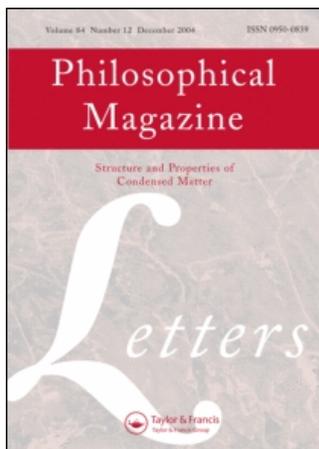
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## Explanation of the melting behaviour of embedded particles; equilibrium melting point elevation and superheating

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### ABSTRACT

The observed melting temperature of embedded particles can be either lower or higher than the bulk equilibrium melting point. Explanations for the observed melting-temperature elevation are still controversial and have been attributed either to an elevation caused by a strain energy effect and/or an interfacial energy effect, or to metastable superheating. Furthermore, there seems to be some confusion regarding the relationship between equilibrium melting-point elevation and the superheating effect. We suggest that the observed increase in melting temperature for embedded particles is caused by both an equilibrium melting-point elevation and a metastable superheating effect, and the two effects tend to be concurrent. An attempt has been made to clarify the two effects in the melting process of indium particles embedded in an aluminium matrix.

Embedded particles are found to melt at a temperature below or above the bulk equilibrium melting point (Allen *et al.* 1980, Rossouw and Donnelly 1985, Daeges *et al.* 1986, Saka *et al.* 1988, Koch *et al.* 1989, Zhang and Cantor 1991, Malhotra and Van Aken 1995, Sheng *et al.* 1996). Allen *et al.* (1980) and Malhotra and Van Aken (1995) reported that indium microcrystals embedded in an aluminium matrix melt at a higher temperature than the bulk melting point, and the strain energy upon melting was the major factor causing the observed elevation. Saka *et al.* (1988) explained the elevation on the basis of an interfacial energy difference between liquid particle–matrix and solid particle–matrix interfaces. It is notable that all these workers considered the observed melting temperature of the embedded particles to be the equilibrium melting point of these particles, rather than being associated with a metastable superheating effect.

Zhang and Cantor (1991) observed that indium and lead particles embedded in an aluminium matrix melt at temperatures 0–40 K higher than the corresponding bulk melting points. They claimed that the melting-temperature elevation was a superheating phenomenon caused by a kinetic difficulty of melt nucleation, rather than a thermodynamic equilibrium melting point elevation. Sheng *et al.* (1996) explained the similar melting behaviour of embedded lead particles on the basis of an equilibrium melting-point elevation; unfortunately, they confused the equilibrium melting-point elevation with the metastable superheating effect.

The idea of metastability, by definition, requires that there are states of higher free energy than the metastable state along all possible routes between the metastable

state and the stable state of a thermodynamic system (Ostwald 1910). Thus there should be free-energy barriers impeding the transformation of the metastable state into the stable state. Since the melting of solids invariably involves the formation of liquid nuclei and their growth (Christian 1965), at least two types of barrier may be involved in the metastability of superheated solids. The first is a free-energy barrier to liquid nuclei formation. For example, superheating has been realized in small silver single-crystal spheres coated with gold, a free-energy barrier to nuclei formation being introduced at the coherent Ag–Au interfaces (Daeges *et al.* 1986). The second is a free-energy barrier to liquid growth, which prevents the movement of molecules at a liquid–crystal interface from a crystal-like position to a liquid-like position. Substantial superheating has been observed in some network-forming materials which melt into viscous liquids with sluggish melting kinetics (Cormia *et al.* 1963, Uhlmann 1980). Thus the superheated solid is in a metastable state with respect to the stable liquid phase, just as the supercooled liquid is also in a metastable phase with respect to the crystalline state.

Taking into account the superheating effect, the observed melting temperature  $T_m$  of a crystal, either in the bulk or in the form of free or embedded particles, can be written (Peppiatt and Sambles 1975, Couchman and Jesser 1977a,b, Spiller 1982, Rossouw and Donnelly 1985) as

$$T_m = T_0 + \Delta T_s, \quad (1)$$

where  $T_0$  is the equilibrium melting point of the crystal and  $\Delta T_s$  is the temperature elevation caused by the superheating effect, which can be either zero or positive. Most metals are found to melt on heating at the equilibrium melting point with no superheating effect, that is  $\Delta T_s = 0$ . The conventional explanation to this melting phenomenon is that most liquid metals effectively wet their own solids, that is

$$\gamma_{sl} + \gamma_{lv} \leq \gamma_{sv}, \quad (2)$$

where  $\gamma_{sl}$ ,  $\gamma_{lv}$  and  $\gamma_{sv}$  are interfacial energies of the solid–liquid, liquid–vapour and solid–vapour interfaces respectively (Christian 1965). For a wetting angle  $\theta = 0$ , no free-energy barrier exists for the nucleation of liquid, and no superheating is needed for melt nucleation.

For small embedded particles, the equilibrium melting point  $T_0^p$  is different from  $T_0$ , the equilibrium melting point of the bulk counterpart. The Gibbs free-energy change  $\Delta G$  associated with the melting of embedded spherical particles is given (Porter and Easterling 1988) as

$$\Delta G = \frac{4}{3}\pi r^3 \left( \frac{L}{T_0} (T_0 - T) + \Delta E \right) + 4\pi r^2 (\gamma_{lm} - \gamma_{sm}), \quad (3)$$

where  $L$  is the latent heat of fusion per unit volume,  $r$  is the radius of the particle,  $\Delta E$  is the strain energy per unit volume resulting from the difference between the coefficients of thermal expansion and volume change upon melting, and  $\gamma_{lm}$  and  $\gamma_{sm}$  are interfacial energies of the liquid particle–matrix and solid particle–matrix interfaces respectively. The interfacial energy contribution is the well known Gibbs–Thomson effect for finite-size particles (Porter and Easterling 1988). Since the free-energy change  $\Delta G$  is zero for an equilibrium melting process, an expression for the equilibrium melting point  $T_0^p$  for the embedded particles can be calculated from eqn. (3) to be

$$T_0^p = T_0 \left( 1 + \frac{\Delta E}{L} + \frac{3(\gamma_{lm} - \gamma_{sm})}{rL} \right). \quad (4)$$

Thus, eqn. (2) can be changed to

$$T_m^p = T_0^p + \Delta T_s = T_0 \left( 1 + \frac{\Delta E}{L} + \frac{3(\gamma_{lm} - \gamma_{sm})}{rL} \right) + \Delta T_s, \quad (5)$$

where  $T_m^p$  is the observed melting temperature of the particles. From this we can see that the difference between the observed melting temperature  $T_m^p$  and the bulk equilibrium melting point  $T_0$  that is the observed melting-temperature elevation, is determined by three effects: the strain energy effect, the interfacial energy effect and the superheating effect.

In the following, we discuss the relationship between the equilibrium melting-point elevation and the metastable superheating effect in the melting process of embedded particles. As eqn. (2) is often valid for metals surrounded by their own vapour, superheating is negligible for bulk metals. However, for embedded metal particles, especially when the dispersion of particles is obtained through rapid quenching techniques, and the particles sizes are in the range of a few nanometres, there is often an epitaxial relationship between the particle and the matrix (Rossouw and Donnelly 1985, Saka *et al.* 1988, Zhang and Cantor 1991, Sheng *et al.* 1996). The solid particle–matrix interfaces may assume a coherent or semicoherent boundary structure, and the corresponding interfacial energy  $\gamma_{sm}$  may be very low, even lower than  $\gamma_{lm}$ , the interfacial energy of the liquid particle–matrix interface. For example, Zhang and Cantor (1990) have calculated the difference between the interfacial energy to be  $\gamma_{lm} - \gamma_{sm} = 0.0267 \text{ J m}^{-2}$ . If  $\gamma_{lm} > \gamma_{sm}$  is valid, then the interfacial energy effect will result in an equilibrium melting-point elevation according to eqn. (4). Also, eqn. (2) will no longer be valid, and there exists an inverse relationship of  $\gamma_{sl} + \gamma_{lm} > \gamma_{sm}$ . The inverse relationship will give rise to a free-energy barrier for melt nucleation and makes the superheating effect possible. So, if the difference between  $\gamma_{lm}$  and  $\gamma_{sm}$  is favourable for equilibrium melting-point elevation, it is also favourable for the metastable superheating, that is the two effects tend to be concurrent.

Interfaces have been thought to play an important role in the melting process of solids (Couchman and Jesser 1977a,b, Cahn 1986); however, the interfacial energies of the liquid particle–matrix and the solid particle–matrix interfaces are often unavailable and further, since superheating and equilibrium melting-point elevation are inclined to be concurrent effects, it is very difficult to separate the two effects.

In the following, an attempt will be made to clarify the superheating effect and equilibrium melting-point elevation in the melting process of indium particles embedded in an aluminium matrix obtained through rapid quenching. The Al–In system is chosen because there have been many investigations on the melting behaviour of this system, and the necessary data are available. Malhotra and Van Aken (1995) have calculated the equilibrium melting-temperature elevation caused by the strain energy effect by a method similar to that used by Allen *et al.* (1980). The calculated equilibrium melting-temperature elevation caused by the strain energy effect in indium particles embedded in aluminium is about 6.4 K, which is close to the experimental result that the melting temperature of micrometre-sized indium particles (for such particles the interfacial effect is negligible) in aluminium is 4 K higher than the bulk equilibrium melting point (Malhotra and Van Aken 1995). So,

according to eqn. (4), the equilibrium melting point  $T_0^p$  (K) of indium particles, with a radius  $r$  (in metres) can be written as

$$T_0^p(r) = 436.2 + \frac{6.44 \times 10^{-6}(\gamma_{lm} - \gamma_{sm})}{r}, \quad (6)$$

where the bulk melting point of indium has been taken as 429.8 K (Smithells 1976), the term for the strain energy effect as 6.4 K (Malhotra and Van Aken 1995), and the latent heat  $L$  of fusion as  $2.00 \times 10^5$  kJ m<sup>-3</sup> (Allen *et al.* 1986). From the above equation we can see that the interfacial energy difference  $\gamma_{lm} - \gamma_{sm}$  is a crucial factor dominating the equilibrium melting-temperature elevation of embedded particles, especially when the particle radii are somewhere in the range of a few nanometres.

With the interfacial energy difference  $\gamma_{lm} - \gamma_{sm} = 0.0267$  J m<sup>-2</sup> (Zhang and Cantor 1990), the equilibrium melting temperature of indium particles with a radius of 5 nm in an aluminium matrix can be calculated to be 471 K. Saka *et al.* (1988) reported that the melting temperature of indium particles with a radius of 5 nm in aluminium is as high as 473 K. Zhang and Cantor (1991) and Sheng *et al.* (1996) also reported the melting temperature of In particles embedded in an aluminium matrix to be as high as 470 K. The calculated equilibrium melting point of the indium particles nearly coincides with the observed melting temperature. So, there is actually no superheating at all. This may explain why most workers are successful in attributing the observed melting-temperature elevation of embedded indium particles only to the equilibrium melting-point elevation. It should be noted that the reliability of the above evaluation of the equilibrium melting-point elevation is strongly dependent on the interfacial energy difference (Zhang and Cantor 1990, 1991, Malhotra and Van Aken 1995).

In conclusion, we have pointed out that the observed melting-temperature elevation in embedded particles is caused by both an equilibrium melting-point elevation and a metastable superheating effect, and the two effects tend to be concurrent. An attempt has been made to clarify the two effects in the melting process of indium particles embedded in an aluminium matrix.

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