

## Size Dependence of the Melting Temperature of Metallic Films: Two Possible Scenarios

V.M. Samsonov\*, N.Yu. Sdobnyakov†, A.G. Bembel, D.N. Sokolov, N.V. Novozhilov

Tver State University, 35, Sadovii Per., 170002 Tver, Russia

(Received 24 September 2013; published online 10 December 2013)

The size dependence was investigated of the melting temperature  $T_m$  of metallic films (tin and copper) on different substrate (amorphous carbon, another infusible metal), i.e. the dependence of  $T_m$  on the film thickness  $h$ . It was found that the effect of interfacial boundary can result in the growth of  $T_m$  for thin metallic films on the carbon substrate in comparison with the corresponding bulk value. For the metal 1 / metal 2 system the size dependence of  $T_m$  seems to be less pronounced and  $T_m$  decreases with decreasing thickness  $h$ .

**Keywords:** Thermodynamics, Metallic films, Carbon substrate, Size dependence of the melting temperature.

PACS numbers: 64.70.Nd, 65.80. – g

Size dependence of the melting temperature  $T_m$ , i.e. its dependence particle radius  $R$  in the case of a globular nanocluster and on the thickness  $h$  in the case of a film, is of great basic and practical interest in view of many actual and possible application in different technologies, including nanotechnology. In [1-6] we investigated the size dependence  $T_m(R)$ . The problem of  $T_m(h)$  dependence seems to be much more complicated as it involves the effect of the solid substrate on  $T_m$ .

In [7, 8] we carried out a thermodynamic analysis of the problem under consideration and next formulas:

$$\frac{\Delta T}{T_m^{(\infty)}} = \frac{2(\sigma_s - \sigma_l)}{\rho_l^{(\infty)} \lambda_m^{(\infty)} h}, \quad (1)$$

$$\frac{\Delta T}{T_m^{(\infty)}} = \frac{\sigma_s + \sigma_{ss'} - \sigma_l - \sigma_{ls'}}{\rho_l^{(\infty)} \lambda_m^{(\infty)} h} \quad (2)$$

were obtained for free and supported films respectively. In the above formulas  $\Delta T = T_m^{(\infty)} - T_m$  is the difference between the macroscopic melting temperature  $T_m^{(\infty)}$  and the melting temperature  $T_m$  of the film of thickness  $h$ ,  $\rho_l^{(\infty)}$  is the density (concentration of atoms) in the liquid phase,  $\lambda_m^{(\infty)}$  is the macroscopic value of the specific heat of melting,  $\sigma_s$  and  $\sigma_l$  are surface tensions of the solid substrate and melt, correspondingly,  $\sigma_{ss'}$  is the interfacial tension at the boundary between the crystalline area of the film and the substrate,  $\sigma_{ls'}$  is the interfacial tension at the melt-substrate boundary. Formula (1) coincides with an equation figuring in monograph [8].

Unfortunately, reliable values of  $\sigma_{ss'}$  and  $\sigma_{ls'}$ , quantities figuring in the right-hand side of equation (2) are as a rule, not known. Respectively, the reliable verification of this formula faces principal difficulties. For this reason, in [7, 8] the effect of the solid

substrate on  $\Delta T$  was taken into account a correction term added to the right-hand side of equation (1) and expressed vice the antiparticle potential  $\varphi(z)$  of the substrate. This potential may be defined as the energy of an atom of the film at the distance  $z$  from the substrate. So, extending equation (1) from the free film to the supported one, the difference of the energy of interaction should be added for the film in solid and liquid states:

$$\frac{\Delta T}{T_m^{(\infty)}} = \frac{1}{\rho_l^{(\infty)} \lambda_m^{(\infty)} h} \left[ 2(\sigma_s - \sigma_l) + (\rho_s^{(\infty)} - \rho_l^{(\infty)}) \int_a^h \varphi(z) dz \right] \quad (3)$$

Here  $a$  is the effective diameter of an atom in the film,  $\rho_s^{(\infty)}$  is the density of the solid phase (in  $\text{m}^{-3}$ ).

Direct evaluations of the uniparticle potential are possible for simplest modeling systems only, for example, for Lennard-Jones systems as well as for systems where both the substrate and the film are presented by metals or semiconductors not interacting chemically and non-soluble. In this connection the term of the substrate can be expressed as the difference between energies of adhesion of the film in liquid  $W_l$  and solid  $W_s$  states:

$$(\rho_s^{(\infty)} - \rho_l^{(\infty)}) \int_a^\infty \varphi(z) dz = W_l - W_s \approx W_l \left( 1 - \rho_s^{(\infty)} / \rho_l^{(\infty)} \right) \quad (4)$$

The energy of the adhesion of the liquid film will be approximately equal to the energy of the adhesion of liquid on the same substrate. Besides,  $W_l$  relates to the equilibrium contact angle  $\theta_e$  in accordance with the Dupre equation  $\cos \theta_e = 2W_a / W_c = W_a / \sigma_l$ , where  $W_c = 2\sigma_l$  is the cohesion energy. With respect of this equation (4) can be rewritten as

$$\frac{\Delta T}{T_m^{(\infty)}} = \left[ \frac{2(\sigma_s - \sigma_l) + \sigma_l \cos \theta_e \left( 1 - \rho_s^{(\infty)} / \rho_l^{(\infty)} \right)}{\rho_l^{(\infty)} \lambda_m^{(\infty)} h} \right]^{-1} \quad (5)$$

\* samsonoff@inbox.ru

† nsdobnyakov@mail.ru

Formula (5) predicts the increasing of  $\Delta T$  under effect of the substrate at  $\rho_s^{(\infty)} > \rho_l^{(\infty)}$  and the decreasing of this quantity for anomalous substance  $\rho_s^{(\infty)} < \rho_l^{(\infty)}$ . It is also worth to mention that formula (5) predicts the relationship between the size dependence of the melting temperature and the wetting conditions of the substrate by the melt corresponding to the substance of the film. Size dependence of the melting temperature of copper (upper curve) and tin (lower curve) films shown in Fig. 1 were calculated in frame of approximation (5) for two cases: (i) on a solid substrate presented by the same metal; (ii) on a carbon substrate. Experimental data used to calculate  $\Delta T$  are presented in Table 1. Evaluation of the contact angle  $\theta_e^{Me-Me}$  at the metal (s) – own melt was carried out on the basis of the Young equation with a autoadsorption term  $\Delta\sigma_{sa}$ :

$$\cos \theta_e = (\sigma_s - \sigma_{sl} + \Delta\sigma_{sa}) / \sigma_l, \quad (6)$$

where  $\sigma_{sl}$  is the interfacial tension at the metal (s) – own melt boundary. The term of the autoadsorption was taken from [18]:  $\Delta\sigma_{sa} = 0,203 \text{ J/m}^2$  for copper and  $\Delta\sigma_{sa} = 0,064 \text{ J/m}^2$  for tin, respectively.

According to Fig. 2, the forms of the size dependences of  $T_m$  for copper and tin on the carbon substrate are principally different. Obviously, the effect of the growth of the melting temperature under decreasing the film thickness result from a noticeable difference between the values of the surface tension of copper and carbon (see Table 1) as well as under effect of the interfacial boundary. Experimental results [19] of melting of tin nanocrystals on a carbon substrate and in a carbon matrix may be treated as an indirect confirmation of our model predicting the possibility of the growth of  $T_m$ . According to [19] the melting temperature was higher in the last case when the particles were completely surrounded by the matrix. There exist also experimental data on lead [20] and indium [21] nanoparticles in an aluminium matrix demonstrating the growth of the melting temperature with decreasing inclusions. So, an analogous effect for copper films seems to be also possible though it is not mentioned in scientific publications.

It is worth to mention a very high divergence of values of the surface tension of carbon: according to  $\sigma_C = 0,035 \div 2,560 \text{ J/m}^2$ . In this work we have used the value  $\sigma_C = 0,150 \text{ J/m}^2$  [13], which figures in literature most often. One can expect that growing  $\sigma_C$

will result in the growth of  $T_m$  with decreasing the film thickness not only for copper but for other metals as well. Such a sharp changing of the form of the size dependence can be observed not only for thermodynamic properties of thin films. For instance we observed [22] a similar behavior for the refraction index  $n$  of ethyl alcohol films on different substrate: the growth of  $n$  at increasing  $h$  was found on glass substrates and the fall of  $n$  on silicon ones.

For the contact between the film of an easily fusible metal (for example, tin) with difficultly fusible one (for example, copper) we predict the size dependence corresponding to decreasing  $T_m$  under decreasing  $h$  (Fig. 3) that can be explained by the high-energy nature of the substrate relative to the film (the substance of the substrate is characterized by higher value of the surface tension). The value  $\theta_e^{Sn-Cu} = 31^\circ$  of the Sn/Cu contact angle, used in calculations, was taken from [23].

It is also noteworthy that quit correct calculations of  $T_m$  for thin films should take into account the size dependence of the film surface tension, i.e., more exactly speaking, of its specific excess free energy  $\omega$ . The effect in question, i.e.  $\omega(h)$  dependence is analogous to the size dependence of the surface tension of small objects [24-31]. Besides, the size effect of the specific heat of melting should be taken into account. As for the size effect of  $\rho_l$ , it can be neglected as was justified in [32, 33].

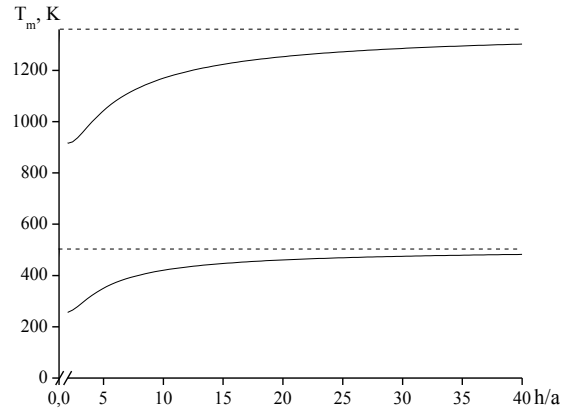
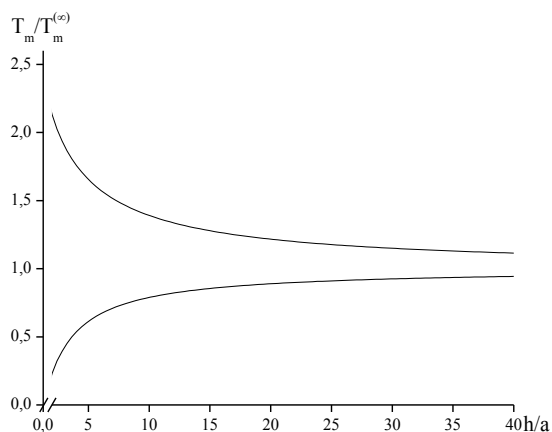


Fig. 1 – Size dependence of the melting temperature for copper (upper curve) and tin (lower curve) films on the same metal under assumption on a primary skin-layer existence of the thickness  $\delta = 1 \text{ nm}$  (the dotted line corresponds to the macroscopic value of  $T_m$ )

Table 1 — Experimental data on physical quantities for copper and tin used to calculate  $\Delta T$

Substance	$T_m^{(\infty)}$ , K	$\rho_s^{(\infty)} \cdot 10^{-5}$	$\rho_l^{(\infty)} \cdot 10^{-5}$	$\lambda_m^{(\infty)}$ , J·mol <sup>-1</sup>	$\theta_e^{Me-Me}$ , degree
		mol·m <sup>-3</sup>			
Cu	1358 [10]	1,320 [10]	1,250 [10]	13050 [10]	16
Sn	505 [11]	0,605 [11]	0,588 [11]	7080 [11]	15
C	–	1,915 [11]	–	–	–
Substance	$a$ , 10 <sup>-10</sup> m	$\sigma_s$	$\sigma_l$	$\sigma_{sl}$ , J·m <sup>-2</sup>	$\theta_e^{Me-C}$ , degree
		J·m <sup>-2</sup>			
Cu	2,335	1,720 [11]	1,354 [11]	0,217 [14]	140 [16]
Sn	3,160	0,673 [12]	0,544 [12]	0,084 [15]	153 [17]
C	–	0,150 [13]	–	–	–

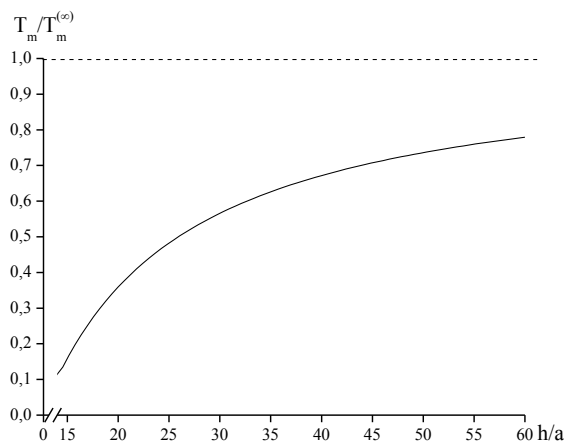


**Fig. 2** – Size dependences of the melting temperature of copper (upper curve) and tin (lower curve) films on the carbon substrate

Unfortunately the available experimental data even on the  $T_m(h)$  dependence are rather scanty to verify all the hypotheses put forward in this work and, in particular, our conclusion on the possibility of the qualitatively different behavior of the  $T_m(h)$  dependence.

## REFERENCES

- V.M. Samsonov, O.A. Malkov, *Russian Metallurgy (Metally)* **2**, 71 (2005).
- V.M. Samsonov, V.V. Dronnikov, O.A. Malkov, *Russ. J. Phys. Chem.* **78** No 7, 1203 (2004).
- V.M. Samsonov, O.A. Malkov, *Central Eur. J. Phys.* **2** No 1, 90 (2004).
- N.Yu. Sdobnyakov et. al, *Bulletin of the Russian Academy of Sciences: Physics* **72** No 10, 1371 (2008).
- N.Yu. Sdobnyakov et. al, *Rasplavy* **5**, 88 (2012).
- N.Yu. Sdobnyakov et. al, *Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques* **5**, 109 (2011).
- V.M. Samsonov, M.V. Samsonov, *Book of Abstracts OMA-11.* **2**, 153 (Rostov na Donu: 2008).
- V.M. Samsonov, N.Yu. Sdobnyakov, A.G. Bembel, D.N. Sokolov, *Physiko-khimicheskie Aspekti Izucheniya Klasterov, Nanostruktur i Nanomaterialov* **4**, 257 (2012).
- N.T. Gladkikh et al, *Surface Diffusion and Spreading* (Moscow: Nauka: 1969).
- H.Y. Kai, *Nanocrystalline Materials. A study of their Preparation and Characterization: PhD Thesis* (Netherlands. Amsterdam: Universiteit van Amsterdam: 1993).
- Physical Quantities. Handbook* (Ed. I.S. Grigořev, E.Z. Meilikhov) (Moscow: Energoatomizdat: 1991).
- V. Missol, *Surface Energy of the Phase Interface in Metals* (Moscow: Metallurgy: 1978).
- N.T. Gladkikh et al, *Adhesion of Melts and Brazing Materials* **19**, 36 (1987).
- R.M. Digilov et al, *The Physics of Metals and Metallography* **41** No 5, 979 (1976).
- L.F. Mondolfo, N.L. Parisi, G.J. Kardys, *Mater. Sci. Eng.* **68** No 2, 249 (1985).
- V.I. Kostikov, G.V. Belov, *Hydrodynamics of the Porous Graphite* (Moscow: Metallurgy: 1988).
- N.T. Gladkikh et al, *Surface Phenomena and Phase*



**Fig. 3** – Size dependences of the melting temperature of Sn/Cu system

This work was supported by the Russian Foundation for Basic Research (projects № 12-03-31593, №13-03-00119).

*Transitions in Condensed Films* (Kharkov: 2004).

- V.M. Yakovlev, A.I. Krestev, *J. Tech. Phys. Lett.* **24** No 3, 201 (1998).
- G.L. Allen, W.W. Gile, W.A. Jesser, *Acta Metallurgica* **28** No 12, 1695 (1980).
- L. Graback, J. Bohr, *Phys. Rev. Lett.* **64** No 8, 934 (1990).
- D.L. Zhang, B. Cantor, *Acta Metallurgica et Materialia.* **39** No 7, 1595 (1991).
- D.A. Kim et al, *Physiko-khimicheskie Aspekti Izucheniya Klasterov, Nanostruktur i Nanomaterialov* **4**, 122 (2012).
- M.P. Dokhov, *J. Tech. Phys. Lett.* **22**, No 12, 25 (1996).
- N.Yu. Sdobnyakov, *Size Dependence of the Surface Tension of Nanoparticles and the Problem of Thermodynamic Stability. PhD Thesis* (Tver: TSU: 2003).
- V.M. Samsonov, A.N. Bazulev, N.Yu. Sdobnyakov, *Chemistry and Computer Simulaton. Butlerov Communications* **10**, 267 (2002).
- A.N. Bazulev, V.M. Samsonov, N.Yu. Sdobnyakov, *RJPC A* **76**, 11, 1872 (2002).
- N.Yu. Sdobnyakov, V.M. Samsonov, *Izvestiya VUZov: Khimiya i Khimicheskaya Tekhnologiya* **46**, 5, 90 (2003).
- V.M. Samsonov, A.N. Bazulev, N.Yu. Sdobnyakov, *Russian Journal of Physical Chemistry* **77** Suppl 1, 158 (2003).
- V.M. Samsonov, N.Yu. Sdobnyakov, A.N. Bazulev, *Doklady RAS* **389** No 2, 211 (2003).
- N.Yu. Sdobnyakov et al, *Kondensirovannii Sredi i Mezhfaznie Granici* **9** No 2, 156 (2007).
- N.Yu. Sdobnyakov et al, *Kondensirovannii Sredi i Mezhfaznie Granici* **9** No 3, 250 (2007).
- M.I. Alymov, M.Kh. Shorokhov, *Russian Metallurgy (Metally)* **2**, 29 (1999).
- M.I. Alymov et al, *Russian Metallurgy (Metally)* **3**, 95 (2009).