Temperature dependence
of surface energy of solids

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The surface energy of a number of solid metals (In, Sn, Bi, Pb and Au) is determined in the temperature range $(0.6-1)T_s$ from the size dependence of melting temperature for small particles of these metals. A nonlinear decreasing of surface energy is established in the region of premelting temperatures that is attributed to the increase of the vacancy concentration. The obtained data are compared with available ones for massive samples.

The value of surface energy determines the character and course of capillary processes in multiphase systems. Its knowledge is especially important for prognosing the behaviour of highly disperse systems (powders, small particles, thin films) for which the surface component contribution into the total energy is substantial. At present a number of techniques have been developed for liquid metals which make it possible to obtain reliable information on their surface energy (σ_l) and its temperature dependence [1]. A quite different situation exists in determining the surface energy of a solid phase (σ_s). The known methods of finding σ_s (e.g., zero creep, multiphase equilibria, ion projector, solution heat measurements, etc.) produce a large error (up to 10 %) and do not permit to measure σ_s in a wide range of temperatures. The most developed method of zero creep is limited by the temperature range near the metal melting temperature. The value of σ_s is also affected by the absorption of gases under experimental conditions which can be hardly eliminated or unambiguously accounted for. Therefore the data available in the literature on the values of σ_s for metals are rather limited and insufficiently reliable. The information on the temperature dependence of metal surface energy in the solid state is mainly estimative and also contradictory [2], as the the existing techniques of determining σ_s does not permit to monitor reliably its changes with temperature.

At the same time these data are necessary to solve a wide range of scientific and practical problems. It is enough to mention the problem of stability of multilayer systems for which the surface and interphase energies are decisive. The wettability of solids with liquids, which is a problem of enormous practical importance, is also directly connected with the surface energy of solids and its temperature dependence.

In paper [3] it has been shown that σ_s and its temperature dependence in a wide range can be determined from the data on measurements of the small particle melting temperature as follows. In the triple point model the dependence of the melting temperature of free particles on their size is described by the expression

$$T_r = T_s(1 - 3\Delta\Omega / \lambda\rho\, r) \qquad (1)$$

where T_s and T_r are the melting temperatures of the solid sample and particle of radius r, respectively; λ is the melting heat; $\Delta\Omega$ is the surface energy variation when the particle melts, determined as $\Delta\Omega = \sigma_s - \sigma_\lambda(\rho_l/\rho_s)^{1/3}$ (here ρ_s and ρ_l are the densities of solid and liquid phases, respectively). It follows from (1) that the experimental dependence $T_r(r)$ makes it possible to determine the values of $\Delta\Omega$ at different temperatures and, if the temperature behavior of the liquid phase surface energy $\sigma_l(T)$ is known below T_s, σ_s can be found. Using this technique, the surface energy σ_s for tin has been found in paper [3] in the temperature

range of 400-500 K on the basis of experimental investigation of lowering of the island film melting temperature.

However, using the method of determining $\sigma_s(T)$ proposed in [3] one must take into account the following. Experimentally, the melting temperature is measured for islands of metals on different substrates (carbon, SiO, MoS_2, etc.); therefore such small particles cannot be considered to be free in the strict sense of the word. The melting temperature of small particles noticeably differs from the value in volume when their dimensions r ≤ 10 nm, i.e. when the surface energy itself and, hence, the value of $\Delta\Omega$ begin to depend on size, which is also ignored in [1]. As the liquid phase surface energy is known at T > Ts, and the value of σ_l must be known far below Ts down to temperatures (0.6 - 0.7) Ts in order to determine $\sigma_s(T)$, the legitimacy of linear extrapolation for finding σ_l becomes dubious.

So, it is easy to show that for a particle in the form of a spherical segment of radius r forming the wetting angle Θ with the substrate, and under the assumption of angle Θ constancy during melting, the melting temperature is also determined by expression (1). However, in this case the melting particle volume is $\Phi(\Theta)$ times smaller than the volume of a free particle of the same radius $(\Phi(\Theta)=(2-3\cos\Theta+\cos^3\Theta)/3$ is the geometric factor). At $\Theta\rightarrow180°$ the volume of the particles melting on the substrate is close to the volume of free particles, and at $\Theta\rightarrow0$ for the same radius of curvature their volume tends to zero. Usually, for island metal films on amorphous neutral substrates $\Theta=(120-140)°$ [4]. In this case the influence of the substrate is insignificant, and therefore expression (1) can be used for analysis of experimental data on small particle melting in non-wettable substrates, as the particle radius determined from electron micrographs corresponds to their radius of curvature.

The error of determining the solid phase surface energy from the data on small particle melting connected with the difference of their surface energy from the value for solid samples (σ_∞) can be evaluated as:

$$\frac{\Delta\sigma_s}{\sigma_{s,\infty}} = \frac{\Delta\Omega_\infty}{\sigma_{l,\infty}} \frac{1-\Delta\Omega/\Delta\Omega_\infty}{1+\Delta\Omega_\infty/\sigma_{l,\infty}}$$

If we adopt $\Delta\Omega_\infty/\sigma_{l,\infty} \approx 0.15$ [6] and take into account that for small metal particles, e.g.

Pb, Ag, Au with the size of 3-5 nm the surface energy is ca. $0.9\sigma_\infty$ [5], then $\Delta\sigma_\sigma/\sigma_{s,\infty} \leq 1.5$ %. This is within the error of the existing methods of determining σ_s for solid samples.

The surface energy measurements of liquid Bi, In, Sn, Pb and Ga in a wide range of temperatures covering the region of the supercooled state ($\Delta T = Ts-T \leq 50$ K) indicate that the linear dependence $\sigma_l(T)$ remains also at T < Ts [7].

The legitimacy of linear extrapolation of $\sigma_l(T)$ in the region of supercooling down to $\Delta T \approx (0.3-0.4)Ts$ is confirmed by the following. Within the framework of the local configuration model taking into account the contribution of only the surface layer, the surface energy is determined via evaporation heat λ_f as follows [8,9]:

$$\sigma = \alpha\lambda_f = \alpha\left(\lambda_f^k + \int_T^{T_k} C_p\,dT\right) \qquad (2)$$

λ_f^k is the evaporation heat at boiling temperature T_k; α is the structure coefficient depending on the volume and surface coordinate numbers and the density of atoms in the volume and on the surface, C_p is the heat capacity at constant pressure. According to [10], coefficient α for the liquid phase weakly depends on the temperature and therefore it follows from (2) that

$$\partial\sigma_l/\partial T = -\alpha_l C_p^l \qquad (3)$$

i.e., the temperature coefficient of the liquid phase surface energy is proportional to its heat capacity. In paper [11] the heat capacities of supercooled drops of Hg, In, Sn and Bi were measured, according to which C_p^l slightly, by (3 to 5) %, increases at supercooling $\Delta T \approx (0.3-0.4)T_s$. Hence, it is legitimate to use the linear extrapolation for finding σ_l at $T \approx (0.6-0.7)T_s$ as well.

Taking into account the above considerations, this paper determines the surface energy in solid phase for In, Sn, Bi, Pb and Au in a wide range of temperatures (Figs.1,2). For these results of investigating melting of small particles of the indicated metals were used [12-19]. Besides the melting temperature, in these works there was measured sufficiently reliably the corresponding size of the particles (methods of electronography and transmission electron microscopy, dark-field microscopy, in situ
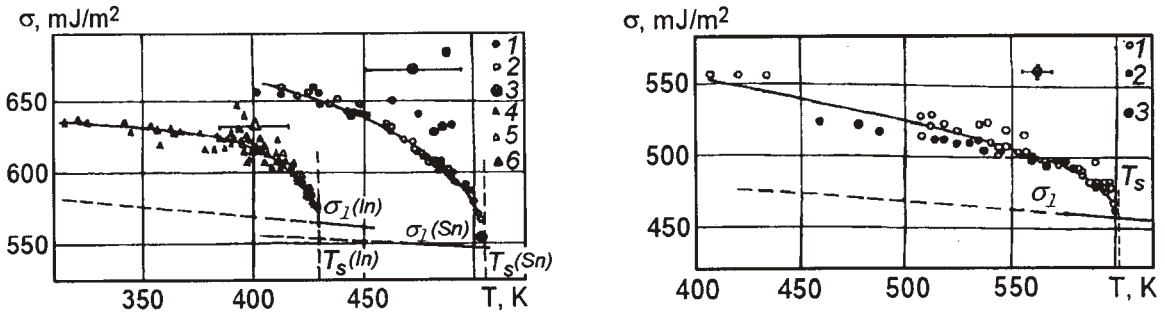
Fig.1. Temperature dependence of surface energy for In, Sn (a) (from Tr(r) data; 1 — [19], 2 — [12], 4 — [13], 5 — [14], 3,6 — σ_s from creep [20]) and for Pb (b) (from T$_r$(r) data; 1 — [14], 2 — [19], 3 — σ_s from creep [20]). Dashed line — extrapolation of σ_l(T) values.

measurements of the particle evaporation rate). The surface energy values for metals in the liquid phase are taken from [1].

When determining the surface energy in the solid phase from the lowering melting temperature of small particles it is necessary to keep in mind the following. Usually, small particles in island films at premelting temperatures are monocrystal ones and possess an equilibrium form according to the Wulff's condition

$$\left(\sum_i \sigma_i / h_i \right)_v = \min,$$

where σ_i is the surface energy of the i-th face, and h_i is the distance along the perpendicular from this face to the center of mass. Therefore the value of σ_s in expression (1) is the surface energy averaged over all faces. Only in the case of fcc crystals the habit can be composed of one face only (111), possessing the minimum surface energy. And according to microscopy data, such single-crystal particles have a round form

close to a spherical one. In the case of crystals of other systems only most densely packed faces cannot compose a closed form.

It should be noted that for all metals except Bi the results of σ_s calculations from the data of T$_r$(r) measurements by different authors are in good agreement between themselves within the error determined by the accuracy of the particle melting temperature and particle size measurements and this error not exceeding 3 %. For Bi the discrepancy between the values of σ_s is observed taken from data for T$_r$(r) in paper [17] and [18,19], reaching 10 % in the entire temperature range (Fig. 2a). It is impossible to prefer one result or another, as the authors [17,19] do not give data on the initial state of bismuth microcrystallites. At the same time it is known that the crystallite shape can influence its melting temperature. So, according to [18], the transition from the nearly spherical to the lamellar shape of the particles at equal surface-to-volume ratio is accompanied by melting
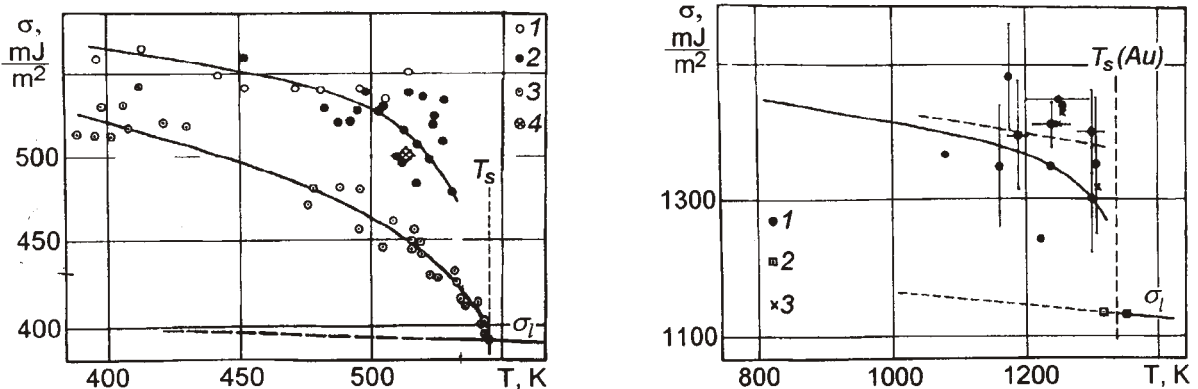

Fig.2. Temperature dependence of surface energy for Bi (a) (from Tr(r) data; 1 — [19], 2 — [18], 3 — [17], 4 — σs from creep [20]) and Au (b) (solid line — σ_s from T$_r$(r) data [15,16]; 1 — σ_s from creep [20]; 2,3 — data on small particle evaporation [15] and [23], respectively). Dashed line — extrapolation of σ_l(T) values.

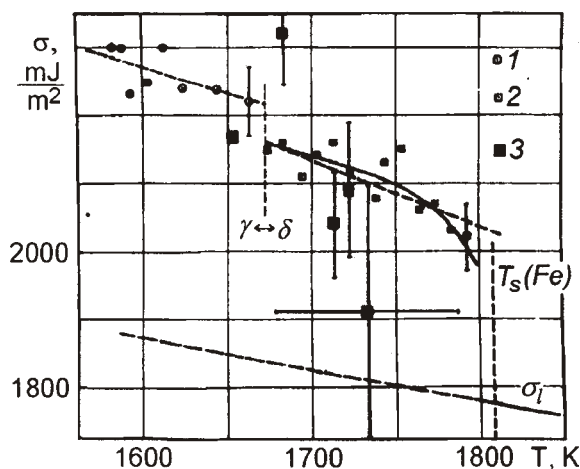Fig.3. Temperature dependence of surface energy for Fe (1,2 — from wetting hysteresis [6], 3 — σ_s values from creep [20]).

Fig.4. $|\partial\sigma/\partial T|$ vs temperature for indium.

temperature variation. Among the metals studied bismuth is the most prone to lamellar growth of condensates, which is the probable cause of different $T_r(r)$ in papers [17,19] and, hence, the calculated values of σ_s.

Figures 1 and 2 also present the values of σ_s for corresponding metals obtained by different techniques on solid samples [20]. The values of the surface energy for the solid samples agree with the data of this work at corresponding temperatures. This is clearly seen for the example of gold (Fig. 2b) for which the literature data are most abundant.

As the temperature approaches T_s the non-linear decrease of σ_s obtained for In, Sn, Bi, Pb and Au probably has a general character. This is supported by the results of paper [6] where the surface energy of iron (carbonyl iron grade B-3 purified by zone melting) has been determined in a wide range of temperatures (1583-1793 K) by the method of solid surface deformation during wetting determined by measuring the wetting hysteresis and metalographically. The authors in [6] have approximated the obtained data by a linear function in the entire temperature range (dashed line in Fig. 3). However, taking into account the results of the present paper, the dependence $\sigma_s(T)$ for Fe at $T{\to}T_s$ within the measurement error limit can be represented by a nonlinear function (solid line in Fig. 3).

The temperature dependence of the solid phase surface energy in the premelting region can be explained taking into account the rela-
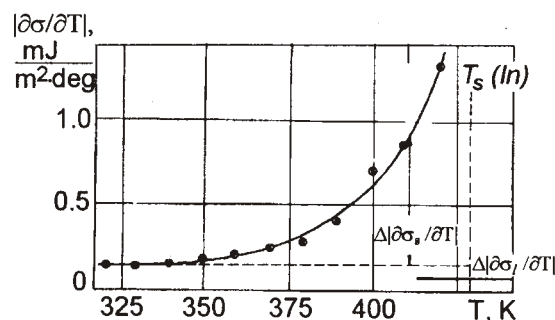
tion between the coefficient $\partial\sigma_s/\partial T$ and the heat capacity C_p. According to the obtained data, the temperature coefficient of the surface energy $\partial\sigma_s/\partial T$ increases in modulus at $T{\to}T_s$ (Fig. 4). On the other hand, it is known [21] that approximately the same range of temperatures has a nonlinear increment caused by the increased concentration of vacancies, so $\Delta C_p{=}c_f \varepsilon_f^2 /kT^2$ (here ε_f is the energy of vacancy creation and $c_f{=}A\exp(-\varepsilon_f/kT)$ is their concentration). Therefore the increment of the temperature coefficient $\Delta|\partial\sigma_s/\partial T|$, and hence the nonlinearity $\sigma_s(T)$ in the premelting region is probably the consequence of increased concentration of vacancies. Therefore the energy of vacancy creation ε_f can be determined by substituting the obtained values in coordinates «$\ln T^2 \Delta|\partial\sigma_s/\partial T| - 1/T$». The values of ε_f obtained in this way are 0.65, 0.55 and 0.45 eV for In, Sn and Pb, respectively, and agree well with the values of ε_f from other measurements (e.g. for Pb $\varepsilon_f{\approx}0.48$ eV by the variation of C_p^s at premelting temperatures and 0.46 eV at dilatometry [21]). We can obtain the same results if we use the data from paper [22] which within the framework of the electron theory of the surface energy of metals shows that the decrease in σ_s caused by the presence of vacancies is proportional to their concentration

$$\Delta\sigma_s /\sigma_s = - (1 + \gamma - g\beta) c_f \qquad (4)$$

(γ,g and β are the coefficients depending on the metal type). Assuming the dependence $\sigma_s(T)$ in the premelting region to be caused by the increased concentration of vacancies and representing the results in coordinates «$\ln T^2 \Delta|\partial\sigma_s/\partial T| - 1/T$» we can determine the
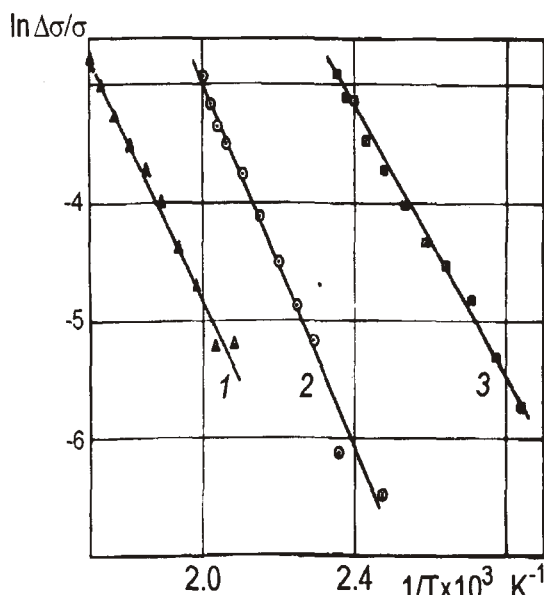
Fig.5. Logarithm of surface energy variation caused by increased vacancy concentration vs neverse temperature (1 — Pb, 2 — Sn, 3 — Bi).

values of ε_f. Figure 5 shows the indicated dependences for In, Sn and Pb which yield the values of ε_f equal to 0.5, 0.62 and 0.6 eV, respectively.

Thus, using the data on the size dependence of the small particle melting temperature it is possible to follow up the temperature dependence of the solid phase surface energy in a wide temperature range. The obtained nonlinear decrease of $\sigma_s(T)$ in the premelting region is related to the corresponding increment of vacancy concentration. These data have made it possible to evaluate the values of vacancy creation energies within the framework of the model of local configuration approximation. They agree with the available values of ε_f obtained by the independent experimental methods.

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