ON THE QUESTION OF THE MAGNITUDE OF THE INTERPHASE SURFACE ENERGY OF METALS AT THE CRYSTAL-MELT BOUNDARY

1960

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

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ON THE QUESTION OF THE MAGNITUDE OF THE INTERPHASE SURFACE ENERGY OF METALS AT THE CRYSTAL-MELT BOUNDARY

(Presented by Academician A. N. Frumkin, 30 X 1959)

The free surface energy σ_{12} of a one-component system at the solid body—melt boundary is of great importance in the process of crystallization from the melt. There is a single work (1) in which an attempt is made at a theoretical calculation of σ_{12} for metals. In calculating σ_{12}, Skapski (1) uses Dupré' s formula, taking in it the work of adhesion to be equal to twice the value of the surface tension of the liquid phase at the boundary with its own saturated vapor. However, the latter quantity is, undoubtedly, less than the work of complete removal of the liquid from the surface of the solid body. Therefore the results obtained by Skapski are clearly overestimated.

In the present work we give a simple method for estimating the interphase surface energy of metals at the polycrystal—melt boundary.

According to the thermodynamic theory of capillarity developed by Gibbs, the excess free surface energy of the transition layer separating two phases with volumes v' and v'' is determined by the expression

$$F_S = F - w'v' - w''v'', \tag{1}$$

where w' and w'' are the free energies per unit volume of the homogeneous phases (far from the dividing surface); F is the free energy of the entire system.

The excess free energy per unit area of the phase boundary is called the surface free energy

$$\sigma_{12} = F_S/S, \tag{2}$$

where S is the area of the dividing surface.

It is known that in the liquid phase (melt) there is no long-range order. Therefore, for a crystalline face in contact with the melt, formula (2) for σ_{12} can be written (2) as:

$$\sigma_{12} = \sum_{k=0}^{\infty} \left(F_S^{(k)} - F'_v \right) n_S^{(k)} + \int_{r_0}^{\infty} [w(z) - w''] \, dz, \tag{3}$$

where $F_S^{(k)}$ and $n_S^{(k)}$ are, respectively, the total free energy of one particle inside the solid phase and the number of particles per 1 cm^2 of a plane located at a distance $r = kr_0$ from the crystalline face bordering the melt (r_0 is the interplanar spacing).

If it is assumed that short-range order is preserved in the melt and that the density of the liquid phase at the melting temperature differs from the density of the crystal at the same temperature by $p\%$, then at the surface of the crystalline face in contact with the melt, n_S particles have the same number of nearest neighbors as inside the crystal, and $\Delta n_S = \frac{2}{3} p n_S$ particles each have Δf missing neighbors.

Taking the zeroth approximation and assuming $w(z) = w''$, we have

$$\sigma_{12} = (F_S^{(0)} - F'_v) n_S + (F_S - F'_v) \Delta n_S. \tag{4}$$

Obviously,

$$F_S^{(0)} - F'_v = \frac{Q}{f_{kv}} \Delta f, \tag{5}$$

since at the crystal–melt boundary each particle among the number n_S has Δf weakened bonds, each by the amount Q/f_{kv}, where Q is the heat of fusion per particle, and f_{kv} is the volume coordination number.

The second term in (4), according to (^{3,4}), will be

$$(F_S - F'_v) \Delta n_S = {}^2/_3 \, p \sigma(hkl), \tag{6}$$

where $\sigma(hkl)$ is the surface tension of the metal face under consideration at the melting temperature.

Substituting (5) and (6) into (4), we finally obtain the following formula for the interphase surface energy of the face (hkl)—melt:

$$\sigma_{12}(hkl) = \frac{\Delta f}{f_{kv}} (hkl) \, n_S(hkl) Q + \frac{2}{3} p \sigma(hkl). \tag{7}$$

In view of the fact that in a crystal of the cubic system there are 6 faces (100), 12 faces (110), and 8 faces (111), it is obvious that for an arbitrary section of a polycrystal we obtain the following value of the surface energy at the polycrystal—melt boundary:

$$\bar{\sigma}_{12} = \frac{6\sigma_{12}(100) + 12\sigma_{12}(110) + 8\sigma_{12}(111)}{26}. \tag{8}$$

In Table 1 we give the results of calculating $\bar{\sigma}_{12}$ for some metals of face-centered cubic structure and experimental values of the surface tension of liquid metals at the melting temperature. The experimental values Q were taken from (^{5}), p from (^{1}), and in the absence of the latter in (^{1}) $p = 3\%$ was assumed.

Table 1

Results of calculating $\bar{\sigma}_{12}$ by formula (8)

Metal	$n_{(100)} \cdot 10^{-14}$	$Q \cdot 10^{+13}$, erg/atom	Melting temp., °K	P, %	σ, erg/cm^2	σ_{12}, erg/cm^2, calc.	σ_{12}, erg/cm^2, exp.
Ag	11.1	1.88	1234	4.5	923	119	126
Au	11.0	2.17	1336	5.2	1120	145	132
Cu	14.6	2.16	1356	4.1	1154	170	177
Pb	7.62	0.718	600	3.4	461	35.4	33
Al	11.5	1.74	933	3.0	860	95.0	93
Pt	12.0	3.66	2047	6.9	1819	288	240
β-Ni	16.2	3.00	1725	3.0	1735	223	–
β-Co	16.0	2.68	1763	3.0	1936	217	–

The values of $\bar{\sigma}_{12}$ calculated by us from formula (8) agree satisfactorily with the experimental results given in (^{6}).

It is seen from Table 1 that the interphase tension of metals at the polycrystal–melt boundary amounts to approximately 8–15% of the surface tension of metals at the melting temperature.

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Received
7 V 1959

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