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Application of Wetting Theory to the Non-reactive Liquid Metal-Graphite Systems

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An attempt has been made to correlate the published contact angle data for graphite-liquid metal systems with the theory of liquid-solid wetting phenomena. To establish the reasonableness of the approach, the potential expression for dispersion interaction was employed for mercury, and the magnitude of the contribution from dispersion forces to the liquid surface energy of mercury, $\gamma_L{}^d$, was calculated to be 193 erg/cm². This compares favourably with the published experimental value of 200 erg/cm². Similarly the $\gamma_L{}^d$ values for liquid metals of known contact angle with graphite were calculated and subsequently substituted in a modified Young equation in order to calculate the respective values of Φ. The parameter, Φ, has been defined by Girifalco and Good as the ratio of adhesion and cohesion forces for any two phases in contact. The calculated values of Φ were observed to rise to a maximum for all metals in the same periodic group as carbon, which would be predicted for "chemically similar" phases.

1. Introduction

The erosion and wetting behaviour of liquid metals at a graphite-liquid metal interface are related phenomena of great interest. Present applications of graphite in the metals field is centred around container problems running from very large volume aluminium cells to quite specialised crucible materials for pure, exotic metals.

This paper attempts to survey the available literature for non-reactive liquid metal-graphite systems and to present what the authors feel is an interesting application of existing solid-liquid wetting theory to the data abstracted.

2. Calculations

The first two columns in table I show the published data for contact angle and liquid metal surface energy for non-reactive metal-graphite systems. It is these systems for which an attempt will be made to confirm the applicability of existing theories on wetting of solid surfaces.

In general, the wetting behaviour of a liquid on a solid surface depends on the relative attraction of the liquid molecules for the solid surface and for themselves. If the former exceeds the latter, wetting will occur. Girifalco and Good [1] defined the ratio for the free energies of adhesion and cohesion for two phases as follows:

$$\Phi = -\frac{\Delta F_{ab}}{(\Delta F_a \Delta F_b)^{1/2}} \qquad (1)$$

where: ΔF_{ab} is the free energy of adhesion for the interface between a and b per cm²; ΔF_a and ΔF_b are free energies per cm² of cohesion for phase a and phase b respectively.

By inspection it can be seen that the more "similar" phases a and b are, the more closely will Φ approach unity. Positive and negative deviation from unity can be visualised, that is, when the predominant binding forces within the separate phases are dissimilar, low values of Φ are expected. When reaction occurs between molecules forming the phases, the energy of adhesion is greater than the energy of cohesion, and $\Phi > 1$.

Subsequently [2], this concept ws incorporated into Young's equation for contact angle equi-

TABLE I Surface energy data for liquid metal-graphite systems.

Metal	Cos contact angle, cos θ	Metal surface energy* γ_L erg/cm^2	Calc. dispersion† contribution $\gamma_L{}^d$ erg/cm^2	$(\gamma_L{}^d/\gamma_L) \times 100$	Φ Theory‡	Φ Exp.§
Copper [9, 10]	− 0.643	311	120	38.6	1.06	0.30
Silver [9]	− 0.695	785	268	34.1	0.96	0.38
Gallium [11]	− 0.669	715	268	37.4	0.93	0.42
Germanium [9]	− 0.515	621	310	49.7	0.92	0.58
Indium [9]	− 0.602	515	108	21.0	0.94	0.43
Tin [9, 12]	− 0.407	506	121	23.9	1.07	0.64
Antimony [9]	− 0.643	361	117	32.4	0.94	0.33
Lead [9]	− 0.669	414	76	18.4	0.93	0.32
Bismuth [9]	− 0.695	348	90	25.8	0.96	0.27

*γ_L Selected as close as possible to temp. at which θ was measured.
†From equation 7 giving E_d, which is equal to $\gamma_L{}^d$ per atomic pair.
‡From equation 5.
§From rearrangement of equation 2, using $\gamma_S{}^d = 110$ erg/cm^2 + $\gamma_L{}^d$ calculated above.

librium as:

$$\cos\theta + 1 \simeq 2\,\Phi\,(\gamma_S{}^d/\gamma_L{}^d)^{1/2}\,. \qquad (2)$$

The main assumption being made is that the spreading pressure, π_e, is zero, which is reasonable if $\gamma_S < \gamma_L$ [3], and this probably is true for the non-wetting cases being considered. In equation 2, $\gamma_S{}^d$ and $\gamma_L{}^d$ are the surface free energies of the solid and liquid respectively.

The most general expression from which Φ may be evaluated is:

$$\Phi = \frac{4r_1\,r_2}{(r_1 + r_2)^2}\left[\frac{\sum A_{12}}{(\sum A_{11}\,\sum A_{22})^{1/2}}\right], \qquad (3)$$

where the A terms are attraction constants in a Lennard-Jones potential expression, r terms are molecular radii and V terms are molar volumes. If the inter-molecular forces are of the following type:

$A = A_{\text{dispersion}} + A_{\text{induction}} + A_{\text{dipole}}$, Φ is shown to be:

$$\Phi = \frac{4(V_1V_2)^{1/3}}{(V_1{}^{1/3} + V_2{}^{1/3})^2}\left\{\frac{\frac{3}{4}\,\alpha_1\alpha_2\,\frac{2I_1I_2}{I_1 + I_2} + \alpha_1\mu_2{}^2 + \mu_2\mu_1{}^2 + \frac{2}{3}\,\frac{(\mu_1\mu_2)^2}{\mathrm{K}T}}{\left[\left(\frac{3}{4}\,\alpha_1{}^2\,I_1 + 2\alpha_1\mu_1{}^2 + \frac{2}{3}\,\frac{\mu_1{}^4}{\mathrm{K}T}\right)\left(\frac{3}{4}\,\alpha_2{}^2\,I_2 + 2\alpha_2\mu_2{}^2 + \frac{2}{3}\,\frac{\mu_2{}^4}{\mathrm{K}T}\right)\right]^{1/2}}\right\} \qquad (4)$$

where, α terms are polarisabilities, μ terms are dipole moments, I terms are ionisation potentials, K is the Boltzmann constant and T is temperature. The difficulty in applying this expression (equation 4) in equation 2 is obvious, except if we consider only the data collected to graphite-metal systems. Here, the μ terms in equation 4 become zero, and Φ reduces to:

$$\Phi = \frac{4(V_1V_2)^{1/3}}{(V_1{}^{1/3} + V_2{}^{1/3})^2}\left[\frac{2\,(I_1I_2)^{1/2}}{I_1 + I_2}\right]. \qquad (5)$$

Fowkes [4] later extended this treatment to include the case of cohesive forces of unlike type. He proposed that the surface tension of a liquid could be expressed as the sum of all intermolecular forces acting at the surface layer of liquid, and that these forces would be independent. For example, for a saturated hydrocarbon: $\gamma_L = \gamma_L{}^d$ since dispersion forces are the only attractive forces operating, while for a liquid metal: $\gamma_L = \gamma_L{}^m + \gamma_L{}^d$ since there exist in this case metallic and dispersion forces. Applying this concept to the Young equation, assuming $\Phi = 1$:

$$\gamma_L\,(1 + \cos\theta) = 2\,(\gamma_L{}^d\,\gamma_S{}^d)^{1/2}\,. \qquad (6)$$

The dispersion forces arise from the interaction of fluctuating electric dipoles with an induced dipole and therefore will contribute to cohesion in all materials, but their magnitude will depend on the type of material. The advantage of equation 6 is the use of $\gamma_S{}^d$ as opposed to γ_S since the latter is quite difficult to define. Experimentally, the contribution of $\gamma_L{}^d$ to γ_L for mercury [5] has been found to be 41 % of γ_L, or 200 erg/cm^2. The temperature coefficient of $\gamma_L{}^d$ is not known, but in hydrocarbons this can be estimated since γ_L increases as the fourth power of the density. Work on these systems [6] suggests the temperature contribution is minor.

In order to demonstrate the feasibility of predicting wetting behaviour for graphite-liquid systems, an attempt was made to correlate the non-reactive, liquid metal data from the literature with the theory. According to equation 2, a plot of cos θ versus $1/\sqrt{\gamma_L{}^d}$ will be linear if Φ is constant. Such a plot was found to be decidedly non-linear (fig. 1), so that Φ must be considered further, and the theory of Fowkes is not applicable in this case. Equation 5 predicts values of Φ for liquid metals on graphite ranging from 0.92 to 1.07 (see table I). However, Pitzer [7] suggests that equation 5 is inadequate since it does not consider the possibility of more than one electron being promoted to the continuum, and therefore (I) should be replaced by a term perhaps twice as large for the many-electron system.

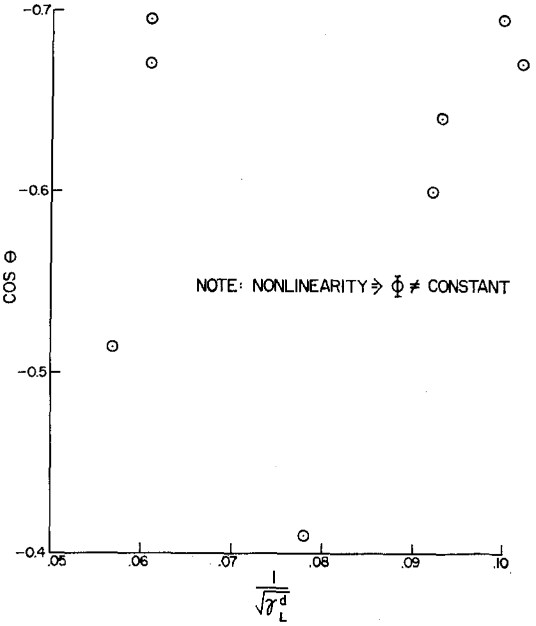

Figure 1 Cosine θ versus $1/\sqrt{\gamma_L{}^d}$ for liquid metals on graphite, where $1/\sqrt{\gamma_L{}^d}$ has units of cm/ergs$^{1/2}$.

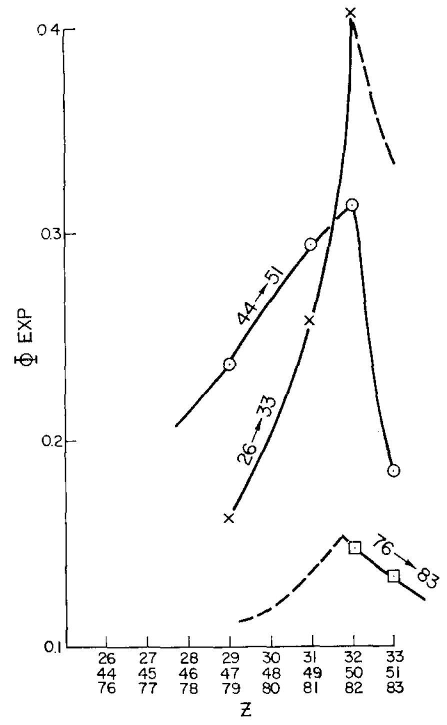

Figure 2 Φ_{exp} versus atomic number (Z) for metals on graphite.

Examination of equation 2 shows that Φ may be obtained from existing experimental data if $\gamma_L{}^d$ can be estimated. The potential expression for dispersion interaction (E_d) is:

$$E_d = -\frac{3}{4} h \nu_0 \frac{\alpha^2}{r^6} \qquad (7)$$

where, h is Planck's constant, ν is the frequency of oscillation of the charge distribution in the atom taken as $\sim 10^{14}$/sec, α is the polarisability taken as $\sim 3 \times 10^{-24}$ cm^3 for Hg by analogy with similar systems [8], and r is the dispersion interaction range taken as the atomic radius.

For the case of mercury this leads to $\gamma_L{}^d = 193$ erg/cm^2 compared to the experimental value of 200 erg/cm^2. This agreement with the experimental value is sufficiently encouraging to use this type of calculation to determine the approximate contribution of $\gamma_L{}^d$ to γ_L for the metals in table I.

Equation 2 was then used to calculate the experimental value of Φ for the several metal-graphite systems reported in the literature. These data are presented in table I and fig. 2. It was mentioned earlier that as the liquid and solid phases become more "similar", the value of Φ more closely approaches unity, it is therefore interesting to note in fig. 2 that the plot of Φ_{exp}

versus Z (atomic number) peaks, for the row of elements where Z is 44 to 51 has a maximum at $Z = 50$, the Periodic Group IVA member. This is the group containing carbon and therefore represents the similarity within the group of elements. The dotted extrapolations of the curves for elements with $Z = 26$ to 33 and 76 to 83 represent the anticipated values of Φ_{exp} inferred from the behaviour of the curve for Z in the range 44 to 51 and the actual shape of the "leading" and "trailing" experimental portions of the incomplete curves. Sufficient data to complete all three curves are unavailable to the authors. The difference in Φ for adjacent liquid metal atoms, $\Delta\Phi$, appears to decrease as the period number increases, and $\Delta\Phi$ for atoms in the sixth period reaches its minimum value, probably owing to the interposition of the filled 4*f* shell which increases the shielding effect of the inner electronic shells.

3. Conclusions

Analysis of data from the literature on the wetting properties of various non-reactive liquid metal-graphite systems led to the following conclusions:

(*a*) For the liquid metals considered, the classical dispersion equation leads to reasonable values of $\gamma_L{}^d$ when applied to a form of the Young equation, modified to include the parameter Φ, the ratio of attraction terms between the liquid and solid phases.

(*b*) Φ was found to increase in value towards a maximum in any particular period of the Periodic Table as the liquid metal in question approached column IVA, containing carbon.

This behaviour (fig. 2) corroborates the fundamental definition of Φ, in that it should increase to unity for the case of identical binding forces acting in and between the liquid and solid phases present.

The practical implication in this work is that a mathematically simplified energetic approach to the prediction of wetting properties of dissimilar elements has been applied to non-reactive graphite-liquid metal systems with consistent and reasonable results. To what extent this approach may be applicable to industrially important systems (Hall cells, graphite-molten slag and steel production, high temperature crucibles) which are much more complex, is not known. However some encouragement is obtained from results on the simpler systems reported herein.

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