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Solid-liquid interfacial energies in binary and pseudo-binary systems

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A simple thermodynamic model of the solid–liquid interface in binary systems is presented and used as a means of estimating the solid–liquid interfacial energy, γ_{SL}, in such systems. The model is extended to pseudo-binary systems such as transition metal carbide/liquid metal systems. In combination with wetting data the estimated γ_{SL} values can be used to estimate the surface energy of the solid, γ_{SV}. In most cases, estimated values of γ_{SL} and γ_{SV} are in good agreement with experimentally determined values.

1. Introduction

The interfacial energy between a solid and a liquid of different atomic composition is an important factor in such phenomena as the solidification of two-phase alloys and in commercially important processes such as liquid-phase sintering and directional solidification of eutectic composities.

Experimental determination of the interfacial energy is difficult and it is natural to attempt theoretical derivations of this property. Perhaps the most successful approach to this problem has been in the work of Eustathopoulos and coworkers in which the solid–liquid interfacial energies of a number of binary metal systems have been successfully estimated on the basis of thermodynamic considerations [1–3]. A simpler model has recently been presented by Miedema and Broeder [4].

Knowledge of the solid–liquid interfacial energy, γ_{SL}, in a binary system can also be of value in certain cases since it provides a means of measuring the solid–vapour surface energy, $\gamma_{SV'}$, of the solid using only a simple wetting experiment. Here, $\gamma_{SV'}$ refers to the surface in the presence of the vapour of the liquid. The wetting of a solid by a liquid sessile drop can be described by the Young equation

$$\gamma_{SV'} = \gamma_{SL} + \gamma_{LV} \cos\theta, \qquad (1)$$

where γ_{LV} is the surface energy of the liquid and θ the angle of contact of the drop. If γ_{SL} is known then $\gamma_{SV'}$ can be found by measurement of γ_{LV} and θ. For many binary systems γ_{LV} and θ are already available. In some cases where γ_{SL} is small compared to $\gamma_{LV} \cos\theta$ even a rough estimate of γ_{SL} will be sufficient to give a relatively accurate estimate of $\gamma_{SV'}$. In all cases a rough estimate of γ_{SL} will reveal its relative importance in the $\gamma_{SV'}$ estimate. If γ_{SL} cannot be estimated with sufficient accuracy then $\gamma_{SV'}$ (and γ_{SL}) must be determined experimentally by the rather involved method of multiphase equilibrium [5] or, where possible, by an alternative technique.

In the present work, a thermodynamic model is presented for the estimation of γ_{SL} in binary systems. The model, though developed independently, is similar to that of Eustathopoulos *et al.* By making certain approximations its use is extended to pseudo-binary systems such as those consisting of stable compounds in combination with liquid metals. This is exemplified by its application to systems of the transition metal carbides with metals such as cobalt, nickel and iron.

2. The model

A simplified model of the interface between a liquid, A, and a solid, B, in equilibrium is represented in Fig. 1. The solid contains an equilibrium content, $1 - X_2$ (molar fraction) of A atoms in solid solution while the liquid contains a fraction,

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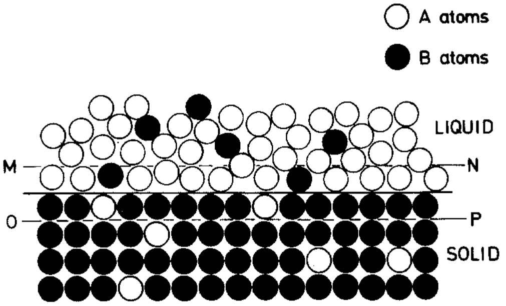

Figure 1 Schematic model of the solid–liquid interface.

X_1, of B atoms. A finite value of the interfacial energy exists because a region in the neighbourhood of the interface is disturbed from the bulk equilibrium states of both the solid and the liquid. The disturbance is both of the chemical composition and of the structure and these two will be treated as separate contributions in the model.

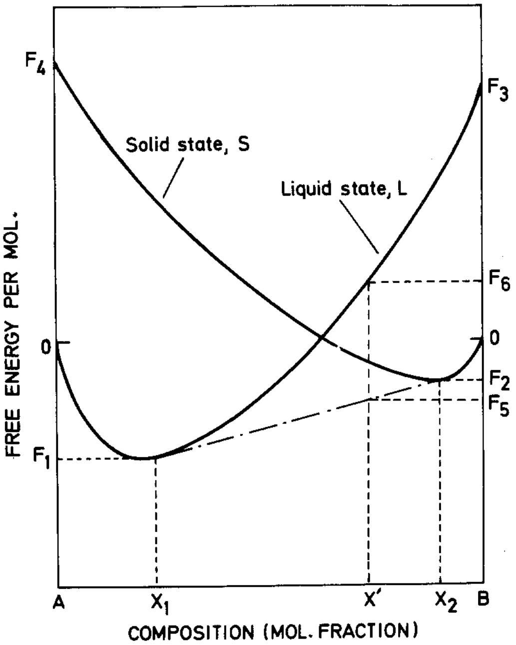

Figure 2 Free energy against composition diagram for the solid and liquid binary system B–A.

2.1. Chemical contribution

For the greatest simplicity the disturbed region can be considered to extend over only two atomic layers between the lines MN and OP (in Fig. 1). Within this region the chemical composition can be considered to be forced into a non-equilibrium value, X', lying between the equilibrium values X_1 and X_2. It is the excess free energy of this non-equilibrium composition, over that of the bulk solid and liquid states, that is taken to contribute to the interfacial energy. The magnitude of this excess energy can be estimated if the relationships between the free energy and composition are known. This is demonstrated in Fig. 2 in which the pure solid, B, and pure liquid, A, are taken arbitrarily as the standard states with zero free energy. The chemical contribution of the interface atoms to the interfacial energy is taken to be the difference between the equilibrium molar free energy, F_5, of the atoms in an equilibrium two-phase mixture and F_6, their energy when forced to exist together as a liquid of composition X'. The interfacial atoms are here assumed rather arbitrarily to exist in the liquid state whereas in reality they should be considered to be in a distinct state of their own. Such an interfacial state is necessarily difficult to define thermodynamically; for the purposes of calculation it is necessary to choose a well-defined state. The implications of the choice of the liquid state will be considered below in Section 2.2. in connection with the structure of the interface region.

Accepting for the moment the above choice, the chemical contribution to the interfacial energy per unit area, $\gamma_{SL(c)}$, becomes

$$\gamma_{SL(c)} = n(F_6 - F_5)/N, \qquad (2)$$

where N is Avogadro's number and n is the number of interface atoms per unit area, equal to the sum of the solid and liquid interface atoms, $n_S + n_L$. Assuming a simple cubic arrangement of atoms then

$$n_S = (N/V_S)^{2/3}, \qquad (3)$$

where V_S is the average molar volume of atoms in the solid. Assuming ideal behaviour then

$$\begin{aligned} V_S &= V_B X_2 + V_A(1 - X_2) \\ &= X_2 W_B/P_B + (1 - X_2)W_A/P_A, \qquad (4) \end{aligned}$$

where W_A, W_B, P_A and P_B are the atomic weights and densities of A and B respectively. Similarly

$$n_L = (N/V_L)^{2/3} \qquad (5)$$

and

$$V_L = X_1 W_B/P_B + (1 - X_1)W_A/P_A, \qquad (6)$$

where V_L is the average molar volume of atoms in the liquid. In Equation 4, P_A and P_B refer to the solid state while in Equation 6 they refer to the liquid state.

The values of F_5 and F_6 can be found knowing the effective composition of the interface region, X', and the free energy curves, F_S and F_L. Expressed in terms of the B atom concentration, the interface composition is given by

$$X' = (n_L X_1 + n_S X_2)/(n_L + n_S). \qquad (7)$$

In many of the binary systems to be considered here the free energy against composition curves are not known. In this case the values of X_1 and X_2 can be obtained from binary equilibrium diagrams. F_5 and F_6 can then be derived if F_3 and F_4 (see Fig. 2) are known, and if some simple functional form can be assumed for F_S and F_L. For example, following Kaufmann and Bernstein [6] produces the relations

$$F_L = F_3 X + RT\,[X \ln X + (1-X)\ln(1-X)] + L_L X(1-X) \qquad (8)$$

and

$$F_S = F_4(1-X) + RT[X \ln X + (1-X)\ln(1-X)] + L_S X(1-X) \qquad (9)$$

where L_L and L_S are constants, R is the gas constant and T is the temperature. Then

$$F_1 = F_3 X_1 + RT\,[X_1 \ln X_1 + (1-X_1)\ln(1-X_1)] + L_L X_1(1-X_1), \qquad (10)$$

$$F_2 = F_4(1-X_2) + RT\,[X_2 \ln X_2 + (1-X_2) \times \ln(1-X_2)] + L_S X_2(1-X_2) \qquad (11)$$

and

$$F_6 = F_3 X' + RT\,[X' \ln X' + (1-X')\ln(1-X')] + L_L X'(1-X'). \qquad (12)$$

Also, differentiating Equations 8 and 9, gives

$$\mathrm{d}F_L/\mathrm{d}X = F_3 + RT \ln X_1 - \ln(1-X_1) + L_L(1-2X_1), \qquad (13)$$

(at $X = X_1$),

and

$$\mathrm{d}F_S/\mathrm{d}X = -F_4 + RT \ln X_2 - \ln(1-X_2) + L_S(1-2X_2), \qquad (14)$$

(at $X = X_2$).

For two-phase equilibrium it is known that

$$\mathrm{d}F_L/\mathrm{d}X = \mathrm{d}F_S/\mathrm{d}X = \frac{F_2 - F_1}{X_2 - X_1} = \frac{F_2 - F_5}{X_2 - X'} \qquad (15)$$

(for $X = X_1$ and $X = X_2$).

Equations 10 to 15 are a set of simultaneous equations that can be solved to obtain F_5 and F_6 in terms of F_3, F_4, X_1, X_2, and X'. F_3 is the free energy of melting of the solid B and to a good approximation can be written as

$$F_3 = H_B(1 - T/T_B), \qquad (16)$$

where H_B is the latent heat of melting and T_B the temperature of melting of B. F_4 is the free energy of melting of A when A, in its solid form, is isomorphous with B. Often, the heat of melting of A, H_A, will be known only for A in some other solid form. If so, the free energy of transition between the two solid states must also be known.

The solution of the above equations is easily carried out with the aid of a computer, but manual calculation is rather tedious. For many systems of interest the above equations can be simplified. For example, if the solubility of A in the solid B is small then $X_2 \approx 1$ and $F_2 \approx 0$. Furthermore, if F_4 is reasonably high its value does not affect the results of the calculations significantly. In such systems, $\gamma_{SL(c)}$ can be estimated knowing only X_1 and F_3.

A further simplification also arises if the solubility of B in A is also low for then both $\mathrm{d}F_L/\mathrm{d}X$ (at $X = X_1$) and F_5 approach zero giving

$$\gamma_{SL(c)} = nF_6/N \qquad (17)$$

with

$$F_6 = F_3(X')^2 + RT[X' \ln X' + (1-X')\ln(1-X')] - RT \ln X_1\,[X'(1-X')]. \qquad (18)$$

It can be seen that in systems of this type X' is relatively insensitive to changes in X_1 and therefore $\gamma_{SL(c)}$ is directly proportional to $-\ln X_1$.

2.2. Structural contribution

A solid–liquid interface is disturbed structurally with respect to both the solid and liquid state. The structural disturbance leads to a finite interfacial energy between a pure solid and its melt as well as between a solid and a chemically different liquid. In the latter case the structural and chemical contributions are added.

In the present model the structural contribution is considered to be equal to the interfacial energy between the pure solid, B, and its melt. This assumption is primarily one of convenience since values of γ_{SL} for pure substances are relatively accessible. This, together with the assumption of the previous section that the interface bi-layer is in the liquid state, implies that the interfacial energy derives from:

(a) a liquid–liquid interface between two structurally similar but chemically different phases (between MN and OP in Fig. 1); (b) a solid–liquid interface between a solid and a liquid with the same composition (interface OP).

The interfacial energy in the binary system is then given by

$$\gamma_{SL} = \gamma_{SL(B)} + \gamma_{SL(c)}. \qquad (19)$$

Experimentally measured values of $\gamma_{SL(B)}$ are available in a few cases. Alternatively, estimates such as that of Miedema and Broeder [4] or that of Miller and Chadwick [7] lead to relatively reliable values. A direct knowledge of $\gamma_{SL(B)}$ is not always necessary if wetting data exists for the liquid A on the solid B and if the liquid surface energy is known; recalling the Young equation (Equation 1) and combining it with Equation 19 yields

$$\gamma_{SV(B)'} = \gamma_{SL(B)} + \gamma_{SL(c)} + \gamma_{LV(A)} \cos\theta. \qquad (20)$$

For pure metals, $\gamma_{SL}/\gamma_{SS} \approx 0.45$ [7] and $\gamma_{SS}/\gamma_{SV} \approx 0.33$ [8], where γ_{SS} is the grain boundary energy, then $\gamma_{SL} \approx 0.15\ \gamma_{SV}$. A similar estimate is obtained using the empirical relationship, $\gamma_{SV} \approx 1.18\ \gamma_{LV}$ [8], and the relationship for pure metals $\gamma_{SL} \approx 0.2\ \gamma_{LV}$ [4], so $\gamma_{SL} \approx 0.17\ \gamma_{SV}$. Taking $\gamma_{SL(B)} \approx 0.16\ \gamma_{SV(B)}$ and neglecting the difference between γ_{SV} and $\gamma_{SV'}$, Equation (20) becomes

$$\gamma_{SL(B)} = (\gamma_{SL(c)} + \gamma_{LV(A)}\cos\theta)/5.25. \qquad (21)$$

As well as providing an estimate of $\gamma_{SL(B)}$ and consequently γ_{SL} for the binary system, this approach gives a value for $\gamma_{SV(B)'}$. Strictly, the relationships between $\gamma_{SL(B)}$ and $\gamma_{SV(B)}$ used above refer to the melting point of B, and should be adjusted to the temperature of the estimate. Usually, however, the temperature effect is relatively small and an adjustment not warranted. Frequently, $\gamma_{SV'}$ is significantly lower than γ_{SV} due to the adsorption of liquid atoms. The neglect of this effect in the above leads to an underestimation of the derived value of $\gamma_{SL(B)}$ and $\gamma_{SV(B)'}$.

3. Extension of the model to pseudo-binary systems

In many multi-component systems a liquid can exist in equilibrium with a stable solid compound such that their phase relationships can be described by a pseudo-binary phase diagram. Examples are refractory oxides and carbides in contact with liquid metals. Transition metal carbides, such as TiC, WC and TaC, form pseudo-binary eutectic systems with such metals as Fe, Co and Ni [9]. The present model can be extended to such systems if it is assumed that the compound retains its stoichiometry and that its molecules can be treated as a single species. In most cases it will be found that the liquid-phase atoms have negligible solubility in the solid and so the simplified version of the model will be applicable requiring only knowledge of X_1 and F_3.

In calculating the numbers, n_S and n_L, of B molecules and A atoms per unit area of interface, account must be taken of the number of atoms in the B molecules. It will be assumed here that the effective area of a molecule at the interace A_B, is equivalent to b times the average area of the atoms in the molecule, where b is the number of atoms in the molecule. Thus

$$A_B = b(V_B/Nb)^{2/3} \qquad (22)$$

where V_B is the molar volume of the compound B. With this definition the *effective* molar volume, V_S, in the equation

$$n_S = (N/V_S)^{2/3} \qquad (23)$$

becomes

$$V_S = X_2 V_B b^{1/2} + (1-X_2)V_A, \qquad (24)$$

and similarly V_L, in the equation

$$n_L = (N/V_L)^{2/3} \qquad (25)$$

becomes

$$V_L = X_1 V_B b^{1/2} + (1-X_1)V_A. \qquad (26)$$

For most systems of this type, thermodynamic data is incomplete. The pseudo-binary phase diagrams are often known; for example, for the carbide/metal systems, they have been collected by Frey and Helleck [9] and Nazaré and Ondracek [10]. Data for the latent heats of melting of compounds such as the carbides, however, are rare. Nazaré and Ondracek [10] have demonstrated a relationship between the heat of melting and the melting point temperature of cubic ionic solids:

TABLE I Estimation of the interfacial energy of selected binary systems

System (B–A)	T (K)	H_B (J mol^{-1})	T_B (K)	F_4 (J mol^{-1})	Compositions (molar fraction) X_1	X_2	$\gamma_{SL(c)}$ (J m^{-2})	$\gamma_{SL(B)}$ (J m^{-2})	γ_{SL} estimated (J m^{-2})	γ_{SL} experimental (J m^{-2})
Al–Sn	623	10 740	933	2000	0.075	0.99975	0.069	0.158 [12]	0.227	0.250 [12]
Cu–Pb	1000	13 042	1356	n.r.	0.06	1	0.103	0.236 [13]	0.339	0.410 [13]
Fe–Cu	1473	15 200	1809	1119 [6]	0.06	0.93	0.143	0.300 [2]	0.443	0.465 [14]
Co–Cu	1473	15 500	1766	2864 [6]	0.09	0.89	0.100	0.305*	0.405	
W–Cu	1773	35 000	3670	n.r.	0.01	1	0.610	0.520*	1.130	0.980
W–Ni	1773	35 000	3670	n.r.	0.45	1	0.195	0.520*	0.715	
C–Cu	1773	104 500	4500	n.r.	0.00003	1	3.060	0.870*	3.930	
C–Ni	1773	104 500	4500	n.r.	0.105	1	1.250	0.870*	2.120	

n.r. indicates values not required for the calculation.

* indicates values estimated from Equation 28.

TABLE II Interfacial energies and solid surface energies of binary systems estimated with $\gamma_{SL(c)}$ and wetting data

System (B–A)	T (K)	$\gamma_{SL(c)}$ (J m^{-2})	$\gamma_{LV(A)}$ (J m^{-2})	θ (°)	$\gamma_{LV} \cos\theta$ (J m^{-2})	γ_{SL} estimated (J m^{-2})	$\gamma_{SV(B)}'$ estimated (J m^{-2})
W–Cu	1773	0.610	1200	2 [15]	1.199	0.955	2.154
C–Cu	1773	3.060	1200	120 [16]	– 0.600	3.530	2.930
C–Ni	1773	1.250	1680	90 [17]	0	1.490	1.490

$$H_B \approx 25 T_B, \tag{27}$$

where H_B is measured in J mol^{-1} and T_B is measured in K, and suggest that this can be extended to the carbides. Values of $\gamma_{SL(B)}$, the structural contribution to γ_{SL}, are also not available for such compounds and again recourse has to be made to some form of empirical relationship. For example, a relationship between $\gamma_{SL(B)}$ and the melting point is sought, for example, similar to that observed between γ_{SV} and the melting point [11]

$$\gamma_{SL(B)} = kT_B/V_B^{2/3}, \tag{28}$$

where k is an empirical constant. For those pure metals for which experimental values of γ_{SL} are known, the value of k lies between 5×10^{-4} and 8×10^{-4} (for T_B in K and $\gamma_{SL(B)}$ in J m^{-2}). Recalling the definition expressed in Equation 22, the corresponding relationship for a compound would be

$$\gamma_{SL(B)} = kT_B/b(V_B/b)^{2/3}. \tag{29}$$

If wetting data exists for the liquid A on the compound B then γ_{SL} can be determined without direct knowledge of $\gamma_{SL(B)}$ by the alternative method described in the previous section, using Equation 21.

4. Application to specific systems

In Tables I–IV the results of the calculation of γ_{SL} for a number of metallic binary systems and pseudo-binary systems are summarized. The Tables also include data used for the calculations. Where specific references are not given the data were either taken from standard reference works or are estimates based on values from several sources.

Table I gives the interfacial energies of a number of binary systems selected either because experimental values exist for comparison or because they are of some interest in materials science. For some of the systems the value of $\gamma_{SL(B)}$ was estimated using Equation 28 with a value of $k = 6.5 \times 10^{-4}$. The estimated value of $\gamma_{SL(B)}$ for carbon must be considered unreliable because of uncertainty in the melting point temperature. In general, the agreement between the estimated γ_{SL} and available experimental values is seen to be satisfactory. In Table II, the estimates are repeated for three of the systems using

TABLE III Estimation of the interfacial energy, γ_{SL}, of pseudo-binary systems

System (B–A)	T (K)	T_B (K)	Compositions (molar fraction) X_1	X_2	$\gamma_{SL(c)}$ (J m^{-2})	$\gamma_{SL(B)}$* (J m^{-2})	γ_{SL} estimated (J m^{-2})	γ_{SL} experimental (J m^{-2})
TiC–Fe	1773	3340	0.19	1	0.260	0.320	0.580	
TiC–Co	1773	3340	0.10	1	0.295	0.320	0.615	0.505 [18]
TiC–Ni	1773	3340	0.17	1	0.265	0.320	0.585	
ZrC–Co	1773	3690	0.06	1	0.275	0.300	0.575	
HfC–Co	1773	4225	0.05	1	0.410	0.350	0.760	0.385 [19]
VC–Co	1773	2970	0.17	1	0.230	0.310	0.540	0.465 [19]
NbC–Co	1773	3870	0.075	1	0.365	0.350	0.715	0.480 [19]
TaC–Co	1773	4270	0.05	1	0.470	0.385	0.855	0.670 to 1.150 [18]
WC–Co	1723	2980	0.23	1	0.215	0.280	0.495	> 0.575 [18]
TiC–Cu	1373	3340	(10^{-6})†	1	1.700	0.320	2.020	
WC–Cu	1373	2980	(10^{-4})†	1	1.050	0.280	1.330	
UC–U	1773	2560	0.042	0.96	0.195	0.205	0.400	0.138 [20]

*estimated from Equation 29.
†no reliable values available.

TABLE IV Interfacial energies and solid surface energies in pseudo-binary systems estimated with $\gamma_{SL(c)}$ and wetting data

System (B–A)	T (K)	$\gamma_{SL(c)}$ (J m^{-2})	$\gamma_{LV(A)}$ (J m^{-2})	θ (°)	$\gamma_{LV}\cos\theta$ (J m^{-2})	$\gamma_{SV(B)}'$ estimated (J m^{-2})	γ_{SL} estimated (J m^{-2})
TiC–Fe	1773	0.260	1.850	30	1.600	2.215	0.615
TiC–Co	1773	0.295	1.850	30	1.600	2.255	0.655
TiC–Ni	1773	0.265	1.700	20	1.595	2.215	0.620
ZrC–Co	1773	0.275	1.850	35	1.515	2.130	0.615
HfC–Co	1773	0.410	1.850	35	1.515	2.290	0.775
VC–Co	1773	0.230	1.850	10	1.820	2.440	0.620
NbC–Co	1773	0.365	1.850	11.5	1.815	2.595	0.780
TaC–Co	1773	0.470	1.850	10	1.820	2.725	0.905
WC–Co	1723	0.215	1.850	0	> 1.850	> 2.460	> 0.610
TiC–Cu	1373	1.700	1.350	110	– 0.460	1.475	1.935
WC–Cu	1373	1.050	1.350	20	1.425	2.945	1.520
UC–U	1773	0.195	1.030 [20]	50 [20]	0.410	0.720	0.310

the alternative method of Equation 21. For the W–Cu system the result is consistent with the estimate of Table I. Furthermore, a reasonable value of $\gamma_{SV(B)}'$, the surface energy of tungsten, is obtained.

Calculations of γ_{SL} for a number of pseudobinary carbide/metal systems are given in Table III. In general, the agreement with experimental values is good. In Table IV the alternative method of estimation using Equation 21 is presented for the same systems. It should be noted that there is very close agreement between the two estimates indicating self-consistency between them. Furthermore, values obtained for the surface energies of the carbides TiC, VC, NbC, HfC and TaC are in good agreement with earlier experimental values [18, 19].

In carbide/copper systems the solubility of the carbide in the copper, X_1, is extremely low and no reliable values exist. The estimate obtained for γ_{SL} is obviously dependent on the value chosen for X_1, as is shown by inspection of Equation 17. This is demonstrated more clearly in Table V, which shows the effect of the chosen X_1 on γ_{SL} in the TiC–Cu system. The estimated value of $\gamma_{SV(B)}'$ using Equation 21 is also sensitive to the choice of X_1. To obtain a value of $\gamma_{SV(B)}'$ consistent with that obtained with the other TiC systems it is necessary to assume a solubility as low as $X_1 = 10^{-8}$ for TiC in liquid copper.

5. Conclusions

Reasonable estimates of the solid–liquid interfacial energy in binary and pseudo-binary systems can be made on the basis of a simple thermodynamic model of the interface. The estimate can often be used in combination with wetting data to obtain an estimate of the surface energy of solids.

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TABLE V Effect of the assumed solubility of TiC in Cu on the estimated interfacial energy and solid surface energy

System (B–A)	Assumed solubility X_1 (molar fraction)	$\gamma_{SL(c)}$ (J m^{-2})	$\gamma_{SV(B)}'$ estimated (J m^{-2})	γ_{SL} estimated (J m^{-2})
TiC–Cu	10^{-2}	0.560	0.120	0.580
(at 1373 K)	10^{-4}	1.120	0.785	1.245
	10^{-6}	1.700	1.475	1.935
	10^{-8}	2.280	2.165	2.625

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