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A method for the calculation of interfacial energies in Al_2O_3 and ZrO_2/liquid-metal and liquid-alloy systems

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A method is proposed by which the interfacial energy, γ_{SL}, of polycrystalline solid oxides (Al_2O_3, ZrO_2) in contact with liquid metals and certain binary liquid alloys can be calculated from the values of the surface energy of the oxides, γ_{SV}, and the liquid metals or liquid alloys, γ_{LV}, respectively. According to this method, the interfacial energy depends on the geometric mean of surface interactions, $(\gamma_{SV}\,\gamma_{LV})^{1/2}$, the molar volumes, V, of the solid and liquid phases, and a parameter, K, which depends on the geometric details of the oxide surface defined by the ion sites in the oxide as well as the stoichiometry of the elements in the oxide and is given by the equation,

$$\gamma_{SL} = \left(K\frac{V_{metal}}{V_{oxide}} + 1\right)^{2/3} (\gamma_{SV}\,\gamma_{LV})^{1/2}$$

The method was verified using interfacial energy data obtained by measurements of the contact angle, θ, formed between the oxides and the liquid metals and liquid alloys with the sessile drop technique. A good agreement was observed between the calculated and the experimentally estimated values of γ_{SL} at the melting point of the metals and alloys.

1. Introduction

The interfacial properties between ceramics and liquid metals and liquid alloys are of importance in the development of joining techniques (brazing, diffusion welding) as well as in problems related to powder technology consolidation of two- or multi-phase composite materials by liquid-phase sintering. The wetting and bonding behaviour at the interface between two condensed phases (solid–liquid) in contact depends on the magnitude of the interfacial energy.

An established method to determine the interfacial energy in a solid–liquid–vapour system in thermodynamic equilibrium over a wide temperature range, is that of the sessile drop technique. In this case the following equation holds

$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV}\cos\theta \qquad (1)$$

where γ_{SV} and γ_{LV} are the surface energies of the solid and liquid phases, respectively, γ_{SL} is the interfacial energy of the solid–liquid and θ is the contact angle. If the values of the surface energy of the solid and liquid phases are known, the experimental determination of the contact angle allows calculation of the value of the interfacial energy.

The present work developed a theoretical treatment for the calculation of the interfacial energies between the solid oxides Al_2O_3 and ZrO_2 (CaO-stabilized) and liquid metals and certain liquid binary eutectic alloys at their melting point. The results are compared with interfacial energy values estimated from contact angle measurements in the same systems.

2. Theoretical treatment

The strength of the bond in a solid–liquid interface is given by the equation

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - W_a \qquad (2)$$

where W_a is the work of adhesion, defined as the work needed to separate an interface.

The work of adhesion between two phases in the general case can be written in the form [1]

$$W_a = W_{a\,(equil)} + W_{a\,(non\text{-}equil)} \qquad (3)$$

On the right-hand side of Equation 3, the magnitude of $W_{a\,(non\text{-}equil)}$ represents the amount of energy released when a reaction takes place at the interface. The magnitude of $W_{a\,(equil)}$ corresponds to non-reactive systems and can be divided in two separate terms.

$$W_{a\,(equil)} = W_{a\,(chem\text{-}equil)} + W_{a\,(VDW)} \qquad (4)$$

The term $W_{a\,(chem\text{-}equil)}$ is the cohesive energy of the

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solid and liquid phases due to the establishment of chemical equilibrium bonds by mutual saturation of the free valences of the contact surfaces. The second term, $W_{a\,(VDW)}$ represents the energy of Van der Waals interactions.

Based on Equation 2, Good and co-workers [2, 3] showed that the interfacial energy between the solid and liquid phases is given by

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2\phi\,(\gamma_{SV}\,\gamma_{LV})^{1/2} \qquad (5)$$

where ϕ is a function of the molecular properties of the two substances, and $(\gamma_{SV}\,\gamma_{LV})^{1/2}$ the geometric mean of the energies of interactions between molecules in the solid and the liquid, respectively.

For "regular" interfaces for which intermolecular energies for pairs both of like and unlike molecules are of the same type [3], the value of ϕ is given by the equation

$$\phi = \frac{4(V_S\,V_L)^{1/3}}{(V_S^{1/3} + V_L^{1/3})^2} \qquad (6)$$

where V_S and V_L are the molar volumes of the solid and liquid phases, respectively. If V_S and V_L are not extremely different, ϕ is approximately unity. For interfaces that deviate from the definition of "regular', i.e. liquid fluorocarbon/water [2], ϕ becomes less than unity.

In systems of oxide ceramics in contact with liquid metals and liquid alloys, such as those studied in the present work, the type of bond at the interface is different from the type of bonds existing in the metallic phase or the phase of the ceramic. Furthermore, inserting in Equation 5 experimental values of γ_{SL}, γ_{SV} and γ_{LV} for the systems Al_2O_3 and ZrO_2/liquid-metals, it can be seen that the values of ϕ become less than unity, as expected.

For systems in which the same oxide is in contact with different metals, the value of ϕ increases with increasing melting point of the metal. This behaviour can be explained in association with Equation 4. In the case of liquid metals with high melting point, the term $W_{a\,(chem\text{-}equil)}$ in Equation 4 dominates and the contribution of $W_{a\,(VDW)}$ is small [4, 5]. From this observation, it is concluded that the bonds formed at the ceramic–metal interface are bonds between the atoms of oxygen of the oxide and the atoms of the liquid metal, as well as the atoms of the metal of the oxide with the atoms of the liquid metal. These two kinds of interfacial bonds show that the intermolecular energies, acting in pairs of atoms in the interface, approach the type of intermolecular energies in the oxide and the liquid metal. In the case of low melting point liquid metals and liquid alloys in contact with the same oxide, the term $W_{a\,(VDW)}$ in Equation 4 becomes significant and therefore the value of ϕ is reduced. For the same liquid metallic phase in contact with different oxides, particularly for high melting point metallic phases, the value of ϕ depends on the geometric details of the ceramic surface.

However, on the basis of the present analysis and using experimental results, it is concluded that in oxide ceramic/liquid-metal and liquid-alloy systems, it is possible to calculate the interfacial energy at the melting point of the metallic phases using a modified version of Equation 5. The modified equation contains the term of the geometric mean, $(\gamma_{SL}\,\gamma_{LV})^{1/2}$, and a coefficient which should depend not only on a gross description of the molar volumes of the phases in contact, but also on the geometric details of the surface of the solid defined by the ion sites in the oxide as well as the stoichiometry of the elements in the oxide. Accordingly, the following semi-empirical relation is proposed

$$\gamma_{SL} = \left(K\frac{V_{metal}}{V_{oxide}} + 1\right)^{2/3} (\gamma_{SV}\,\gamma_{LV})^{1/2} \qquad (7)$$

where K is the ratio of ionic radii in the oxide, multiplied by the ratio of the stoichiometry of the elements in the oxide, i.e. for the oxide Me_xO_y, $K = (R_O/R_{Me})(x/y)$ with R_O and R_{Me} the radii of the ions, and V_{metal}, V_{oxide} are the molar volumes of metal and oxide, respectively.

3. Results

For the calculations performed, the required temperature functions of the surface energies of the solid oxides Al_2O_3 [6] and ZrO_2 [7] and the liquid metals indium, silver, copper [8], tin, lead [9], bismuth [10] and nickel, cobalt and iron [8, 11] were taken from the literature. The surface energies of the binary liquid alloys Bi–Pb (44.5 wt %), Bi–Sn (42 wt %) and Sn–Pb (38.1 wt %) were calculated using the relation of ideal binary mixtures proposed by Belton and Evans [12]

$$\begin{aligned}\gamma_{LV,M} &= \gamma_{LV,1} + \frac{RT}{A}\ln\frac{x_1'}{x_1}\\ &= \gamma_{LV,2} + \frac{RT}{A}\ln\frac{x_2'}{x_2}\end{aligned} \qquad (8)$$

where $\gamma_{LV,M}$ and $\gamma_{LV,1}$, $\gamma_{LV,2}$ are the surface energies of the mixture and of each component, respectively, x and x' are the bulk and the surface mole fraction, respectively, and A is the mean molar surface area of the components (for two components, considering that $A \cong A_1 \cong A_2$, $A = (A_1 + A_2)/2$). The molar surface area of each component is calculated using Equation 9

$$A_i = 1.091\,N_0^{1/3}\left(\frac{M_i}{\rho_{L,i}}\right)^{2/3} \qquad (9)$$

where N_0 is the Avogadro number, M_i the molecular weight of the metal and $\rho_{L,i}$ the density of the liquid metal. The temperature dependence of $\rho_{L,i}$ is given by Allen [9].

For Sn–Pb alloy, the surface energy values calculated from Equation 8 agree satisfactorily with the experimental values given by Hoar and Melfort [13]. The binary alloys Bi–Pb [14], Bi–Sn [15] and Sn–Pb [16] show nearly linear dependence of the molar volume on the alloy composition and the deviation from linearity does not exceed 1%.

Table 1 contains all data needed to calculate the interfacial energies according to Equation 7.

TABLE I Some properties of (a) solid oxides and (b) liquid metals and liquid alloys needed for the calculation of the interfacial energies in oxide/liquid-metal and liquid alloy systems at the melting point of the liquid phases

(a)

Oxides	Surface energy $[\mathrm{J\,m^{-2}}]$	Ref.	Mean lin.expan. Coeff., α $[\mathrm{K^{-1}}]$	Molar volume, V_{293} (cm^3)	R_O/R_{Me}
Al_2O_3	$2.559-0.784 \times 10^{-3}T$ $0 \leqslant T \leqslant 2323$ K	[6]	8.1×10^{-6}	25.618	2.80
ZrO_2 (CaO stab.)	$1.428-0.431 \times 10^{-3}T$ $0 \leqslant T \leqslant 2890$ K	[7]	9.4×10^{-6}	20.219	1.715 CaO is under consideration

(b)

Liquid metals and alloys	T_m (K)	Surface energy for $T \geqslant T_m$ (J m^{-2})	Ref.	Molar volume at T_m (cm^3)
In	429	$0.560 - 0.09 \times 10^{-3}(T - T_m)$	[8]	16.33
Sn	505	$0.544 - 0.07 \times 10^{-3}(T - T_m)$	[9]	16.96
Bi	544	$0.372 - 0.09 \times 10^{-3}(T - T_m)$	[10]	20.75
Pb	600	$0.468 - 0.13 \times 10^{-3}(T - T_m)$	[9]	19.40
Ag	1234	$0.912 - 0.15 \times 10^{-3}(T - T_m)$	[8]	11.56
Cu	1356	$1.311 - 0.20 \times 10^{-3}(T - T_m)$	[8]	7.95
Ni	1726	$1.754 - 0.28 \times 10^{-3}(T - T_m)$	[8, 11]	7.56
Co	1768	$1.831 - 0.29 \times 10^{-3}(T - T_m)$	[8, 11]	7.68
Fe	1809	$1.825 - 0.27 \times 10^{-3}(T - T_m)$	[8, 11]	7.97
Bi – Pb	397	$0.415 - 0.09 \times 10^{-3}(T - T_m)$		19.73
Bi – Sn	412	$0.430 - 0.05 \times 10^{-3}(T - T_m)$		18.40
Sn – Pb	456	$0.525 - 0.09 \times 10^{-3}(T - T_m)$		17.45

The values of the interfacial energies used to verify the proposed method were taken from measurements of contact angle, θ.

The materials used for the experiments were polished discs of polycrystalline alumina (AL23) and zirconia (ZR23) (trade name, Friedrichsfeld Co., FRD) with a purity of > 99.5 wt % and $> 98\%$ (5 wt % CaO), respectively. The metals and the alloys used (Ventron GmbH, FRD) were of high purity.

All measurements were carried out in a purified argon atmosphere. The samples were heated in an induction furnace [17]. The temperature was measured using a thermocouple as well as by optical pyrometry with an accuracy of ± 10 K. For a given system and temperature, two to four experiments were carried out. Each experiment lasted for about 20–30 min. Photographs of the sessile drop were obtained at 5 min intervals. The contact angles were determined from the form of the liquid drop and using the tables of Bashfort and Adams [18]. The results show that contact angle is time-independent in all systems examined.

Figs 1 and 2 show the temperature dependence of the contact angle for the systems Al_2O_3/tin, cobalt [6], bismuth, lead, copper, nickel [19], indium, silver, nickel, iron, Bi–Pb, Bi–Sn, Sn–Pb and ZrO_2/copper, nickel, cobalt [20], tin, bismuth, lead [21], indium, silver, iron, Bi–Pb, Bi–Sn, Sn–Pb, respectively. The literature data refer to the same experimental conditions, i.e. oxides and furnace atmosphere.

After each wetting experiment, removal of the cooled solid drop from the ceramic surface (by pushing the drop) was attempted. No adherence was observed at the interface between the ceramics and the metals or alloys, except in the Al_2O_3/Ni system where a strong force was needed to remove the nickel drop

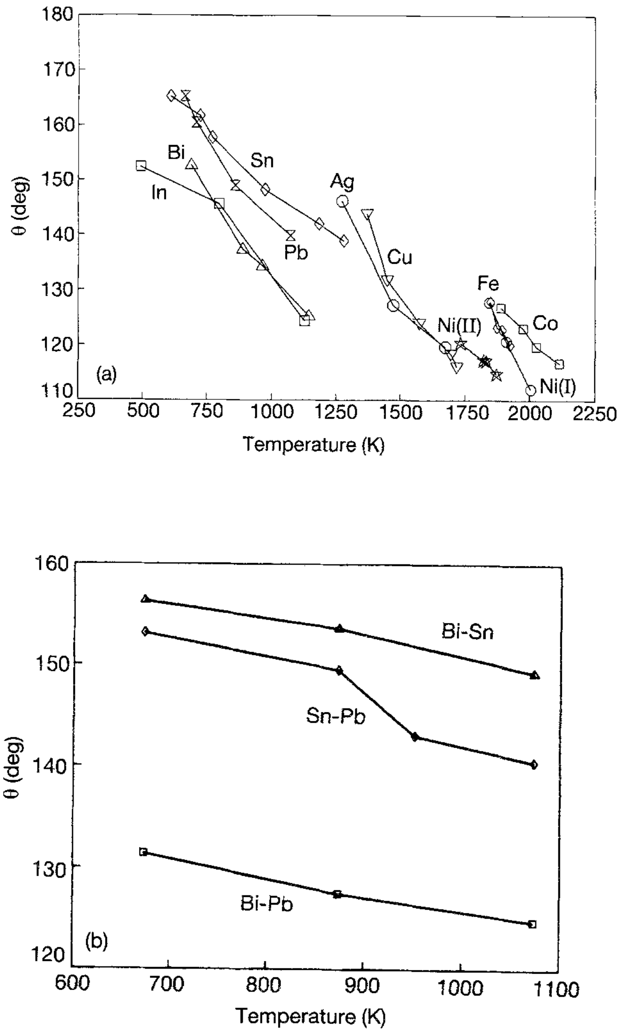

Figure 1 Temperature effect on the contact angles formed by (a) liquid tin, cobalt [6], bismuth, lead, copper, nickel(I) [19], indium, silver, nickel(II), iron, and (b) Bi–Pb, Bi–Sn and Sn–Pb on Al_2O_3.

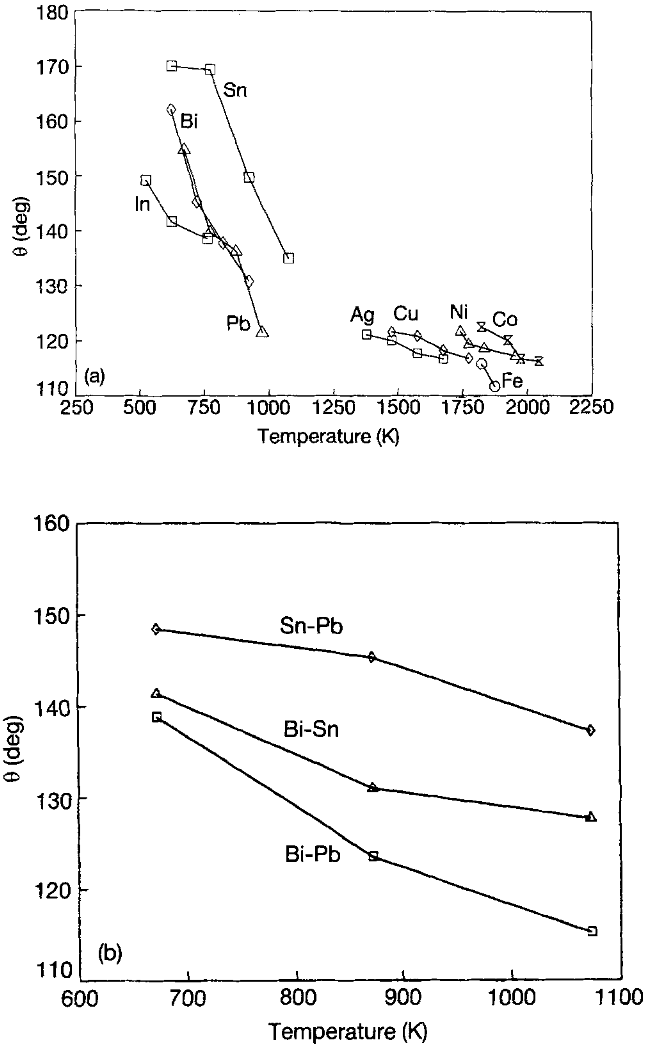

Figure 2 Temperature effect on the contact angles formed by (a) liquid copper, nickel, cobalt [20], tin, bismuth, lead [21], indium, silver, iron and (b) Bi–Pb, Bi–Sn and Sn–Pb on ZrO_2.

TABLE II Linear temperature functions of the interfacial energy, γ_{SL}, in Al_2O_3/ and ZrO_2/liquid-metal and liquid-alloy systems (from sessile drop experiments) and calculated interfacial energy values, γ_{SL}, at the melting point of the liquid phases (from Equation 7)

System	Interfacial energy (J m^{-2})	
	γ_{SL} from experiments $\gamma_{SL,T_m} + \left(\frac{d\gamma_{SL}}{dT}\right)(T - T_m)$	γ_{SL} calculated at T_m (Equation 7)
Al_2O_3/In	$2.750 - 1.117 \times 10^{-3}(T - 429)$	2.654
Al_2O_3/Sn	$2.710 - 1.014 \times 10^{-3}(T - 505)$	2.626
Al_2O_3/Bi	$2.492 - 1.083 \times 10^{-3}(T - 544)$	2.385
Al_2O_3/Pb	$2.552 - 1.112 \times 10^{-3}(T - 600)$	2.556
Al_2O_3/Ag	$2.359 - 1.620 \times 10^{-3}(T - 1234)$	2.424
Al_2O_3/Cu	$2.528 - 2.141 \times 10^{-3}(T - 1356)$	2.419
Al_2O_3/Ni	$2.105 - 1.947 \times 10^{-3}(T - 1726)$	2.458
	$2.641 - 3.778 \times 10^{-3}(T - 1726)$	
Al_2O_3/Co	$2.463 - 2.301 \times 10^{-3}(T - 1768)$	2.491
Al_2O_3/Fe	$2.391 - 3.873 \times 10^{-3}(T - 1809)$	2.485
Al_2O_3/Bi – Pb	$2.542 - 0.922 \times 10^{-3}(T - 397)$	2.525
Al_2O_3/Bi – Sn	$2.645 - 0.885 \times 10^{-3}(T - 412)$	2.474
Al_2O_3/Sn – Pb	$2.705 - 1.012 \times 10^{-3}(T - 456)$	2.641
ZrO_2/In	$1.741 - 0.747 \times 10^{-3}(T - 429)$	1.742
ZrO_2/Sn	$1.805 - 0.821 \times 10^{-3}(T - 505)$	1.724
ZrO_2/Bi	$1.567 - 0.844 \times 10^{-3}(T - 544)$	1.565
ZrO_2/Pb	$1.629 - 1.045 \times 10^{-3}(T - 600)$	1.678
ZrO_2/Ag	$1.409 - 0.743 \times 10^{-3}(T - 1234)$	1.595
ZrO_2/Cu	$1.591 - 0.898 \times 10^{-3}(T - 1356)$	1.595
ZrO_2/Ni	$1.603 - 1.124 \times 10^{-3}(T - 1726)$	1.624
ZrO_2/Co	$1.719 - 1.524 \times 10^{-3}(T - 1768)$	1.647
ZrO_2/Fe	$1.473 - 3.260 \times 10^{-3}(T - 1809)$	1.643
ZrO_2/Bi – Pb	$1.675 - 0.788 \times 10^{-3}(T - 397)$	1.657
ZrO_2/Bi – Sn	$1.626 - 0.642 \times 10^{-3}(T - 412)$	1.624
ZrO_2/Sn – Pb	$1.712 - 0.642 \times 10^{-3}(T - 456)$	1.733

from some solid substrates. Metallographic observations showed irregularities at alumina/nickel interface. However, it has been shown that the presence of elevated oxygen concentration in the nickel metal gives rise to the formation of a thin layer of spinel at the Al_2O_3/Ni interface [22] that disappears at elevated temperatures. These activities at the interface may possibly cause the deviation in the contact angle values near to the melting point of nickel found by two different experiments as shown in Fig. 1.

The measured contact angle values together with the values of the surface energies of solid oxides and liquid metals and liquid alloys taken from their linear temperature functions (Table I), allow the calculation of the interfacial energy for each temperature in the examined systems using Equation 1. The metal vapour existing in the furnace atmosphere, does not have a significant influence on the surface energy of solid oxides and therefore can be neglected [6, 7].

From the existing data as has been shown in previous works [6, 7, 19, 21], the interfacial energy for each system can be given as a linear temperature function with negative slope ($d\gamma_{SL}/dT < 0$). The required value of γ_{SL} in order to verify the calculated value from Equation 7 for each system, is estimated by linear extrapolation to the melting point of the metals or alloys. Table II shows the linear temperature functions of the interfacial energies in the systems examined, obtained from sessile drop experiments and the calculated ones as resulting from Equation 7 at the melting point of the liquid phases.

Figs 3 and 4 show the calculated values of the γ_{SL} versus the experimentally estimated ones in Al_2O_3 and ZrO_2/liquid-metal and liquid-alloy systems, respectively. In the Al_2O_3/Ni system the value of γ_{SL} is a mean value of the interfacial energy at the melting point of nickel, obtained from the equations shown in Table II. A good agreement is observed between the calculated and the experimentally estimated values at the melting point of the metals and the alloys for non-reactive systems.

From a practical point of view, the magnitude of the contact angle between ceramics and liquid metals is of interest for the technologies of joining and powder metallurgy preparation of multiphase materials. The contact angle is indicative of good ($\theta < 90°$) or poor ($\theta > 90°$) wetting and apparently of the strength of the bond at the interface between the different phases.

The contact angle, θ, at the melting point of the liquid metals and liquid alloys for the systems examined is calculated from a rearranged form of Equation 1

$$\theta = \arccos \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \qquad (10)$$

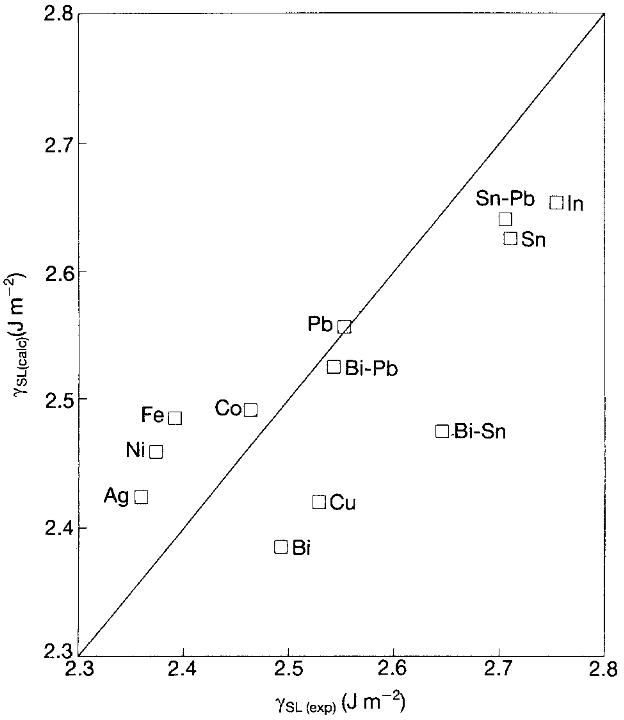

Figure 3 Correlation between calculated and experimentally estimated values of the interfacial energies, γ_{SL}, in Al_2O_3/liquid-metal and liquid-alloy systems at the melting point of the liquid phases.

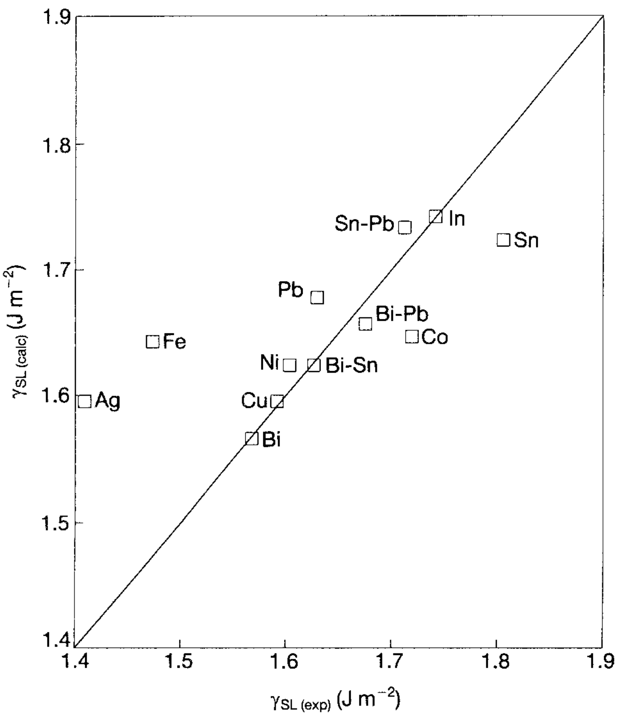

Figure 4 Correlation between calculated and experimentally estimated values of the interfacial energies, γ_{SL}, in ZrO_2/liquid-metal and liquid-alloy systems at the melting point of the liquid phases.

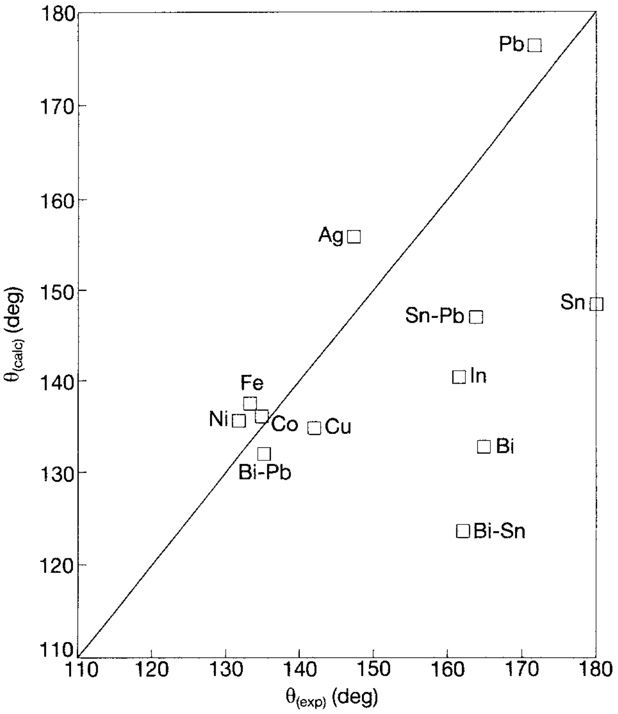

Figure 5 Correlation between calculated and experimentally estimated values of contact angle, θ, in Al_2O_3/liquid-metal and liquid-alloy systems at the melting point of the liquid phases.

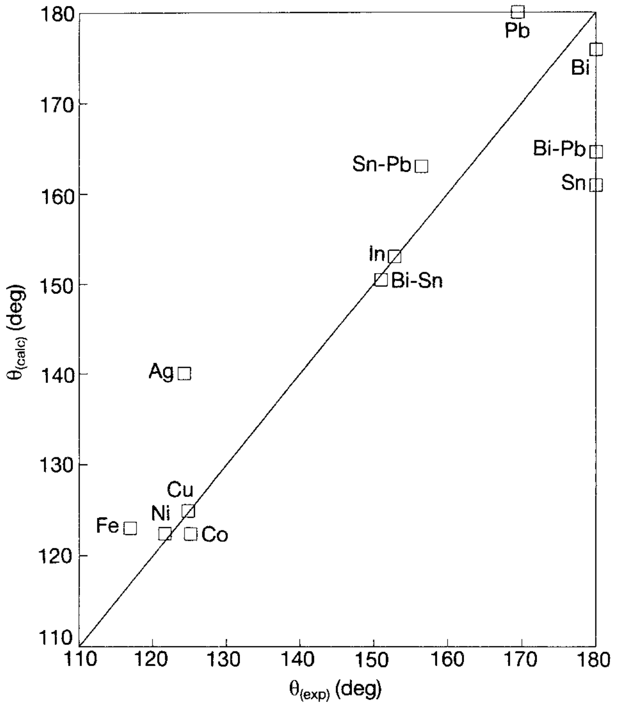

Figure 6 Correlation between calculated and experimentally estimated values of contact angle, θ, in ZrO_2/liquid-metal and liquid-alloy systems at the melting point of the liquid phases.

In Figs 5 and 6, the calculated values of $\theta(\gamma_{SL,\,(calc)}$ from Table II) versus the experimentally estimated ones ($\gamma_{SL,\,(exp)}$ from Table II) at the melting point of the liquid phases, are plotted for the systems Al_2O_3 and ZrO_2/liquid metals and liquid alloys, respectively. In both cases, the values of γ_{SV} and γ_{LV} are taken from Table I.

From Figs 5 and 6 it is observed that in all systems examined the calculated contact angles, as well as the experimentally estimated ones generally decrease when the melting point of the metallic phase increases. The scattering of the contact angles varies in several systems, especially when a low melting point metallic phase is involved and becomes significant particularly for certain Al_2O_3/liquid-metal and liquid-alloy systems (Fig. 5). This is dealing with the difference of $\gamma_{SV} - \gamma_{SL}$ (Equation 10) which is of the same order of magnitude as the value of the surface energy of the liquid metallic phases. Thus, a small change of the value of $\gamma_{SV} - \gamma_{SL}$ or γ_{LV}, possibly due to a small content of impurities in metallic phases, results in a significant variation in the experimentally estimated values of contact angle. Systems with metallic phases with high surface energy values (high melting point metals) present good agreement in θ.

In conclusion, in all systems studied, both the calculated and the experimentally determined values of the contact angles show poor wetting between the oxides and the liquid metals and liquid alloys ($\theta > 90°$).

4. Conclusion

The treatment discussed above shows that it is possible to estimate the interfacial energy of the solid oxides Al_2O_3 and ZrO_2 in contact with liquid metals and certain liquid binary alloys at the melting point of the melting phases. The proposed equation

$$\gamma_{SL} = \left(K\frac{V_{\text{metal}}}{V_{\text{oxide}}} + 1\right)^{2/3} (\gamma_{SV}\,\gamma_{LV})^{1/2}$$

gives values of the interfacial energy which are generally in good agreement with those obtained experimentally through measurements of the contact angle by the sessile drop technique, and then extrapolated to the melting point of the metallic phases.

The contact angle values at the melting point of the metallic phase, obtained from the calculated values of the interfacial energies, show no wetting ($\theta > 90°$) of the oxides by either liquid metals or liquid alloys. Contact angles decrease with increasing melting point of the metallic phase. These results are in accordance with the experimental data of contact angles.

The agreement between the calculated and the experimentally estimated values of the contact angle in most of the systems examined is good, especially in those systems where a high surface energy (high melting point) metallic phase is involved.

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