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Work of adhesion in ZrO_2–liquid metal systems

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Using the sessile drop technique for the measurement of contact angles, the work of adhesion of polycrystalline cubic ZrO_2 in contact with various liquid metals was determined. Based on these experimental values, a model for the evaluation of the work of adhesion is proposed. According to this model the wetting of ZrO_2 by the metals indium, tin, bismuth and lead is established by Van der Waals dispersion binding forces. For the transition metals silver, copper, nickel, cobalt and iron a chemical equilibrium bond between the liquid metal and the oxygen ion of the surface oxide is created at the interface. In this case the value of the work of adhesion is related to the enthalpy of formation of the oxide of the metal.

1. Introduction

The strength of the interface between ceramics and metals is an important consideration in such diverse fields as microelectronics, metal cutting by ceramic tools, biomedicine, engineering, and so on. The driving force for the formation of a ceramic–metal interface is the energy reduction when intimate contact is established between the ceramic and metal surfaces. The simplest description of the interaction between a ceramic and a metal is the work of adhesion, W_a, defined as the work needed to separate the unit area of the interface.

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

$$W_a = W_{a(\text{equil})} + W_{a(\text{non-equil})} \qquad (1)$$

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

$$W_{a(\text{equil})} = W_{a(\text{chem. equil})} + W_{a(\text{VDW})} \qquad (2)$$

In the case of a solid–liquid system, the term $W_{a(\text{chem. equil})}$ is the cohesive energy of the solid and the liquid phases due to establishment of chemical equilibrium bonds by mutual saturation of the free valences of the contacting surfaces. The second term, $W_{a(\text{VDW})}$, represents the energy of Van der Waals interaction (dispersion forces).

In this work, the thermodynamic adhesion of the ZrO_2–liquid metal systems was studied and a model for the evaluation of W_a proposed, which gives a good fit of the experimental data.

2. Bonding models

The adhesion of a ceramic–metal system is the subject of a variety of investigations. Three phenomenological models have been proposed to describe the experimental values of the work of adhesion of various ceramic–liquid metal systems.

According to MacDonald and Eberhart [2], a chemical bond between the liquid metal, Me, and the oxygen ion, O^{2-}, of the oxide surface is set up at specific oxygen sites at the interface, in addition to the Van der Waals bonds formed at the remaining sites. The energy of the chemical bond is assumed to be proportional to the standard Gibbs free energy, ΔG_F^0, of oxide formation of the metal at the temperature of the wetting experiment. Application of this model to Al_2O_3–liquid metal systems (silver, copper, nickel, cobalt, molybdenum, titanium) gives good agreement between calculated and experimental quantities. However, this model gives a high negative temperature coefficient for the work of adhesion, in disagreement with the experimental results.

According to Naidich [1], the non-equilibrium contribution to the work of adhesion is negligible for systems with positive value of the Gibbs free energy of the reaction, ΔG_R, between the liquid metal, Me, and the oxide, MO_n, ($Me + MO_n \rightarrow MeO_n + M$). For this sort of system and neglecting entropy contribution, Naidich [1] assumed that only the Van der Waals (VDW) interactions exist at the oxide–metal interface. The calculated $W_{a(\text{VDW})}$ values showed high deviations from experimental data, in particular for those metals with high melting point.

On the basis of the weaknesses of previous models, Chatain *et al.* [3] developed a model assuming that interactions at the interface of non-reactive ceramic–metal systems are essentially chemical. According to this model, two kinds of chemical bond are established: one between the liquid metal, Me, and the oxygen ion, O^{2-}, of the oxide, and the other one between the liquid metal, Me, and the metal of the oxide, M. The application of this model to Al_2O_3–liquid metal systems gives a good fit to the experimental data [3]. The basic notation, which led to the suggestion of this model, was that low values of W_a

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correspond to metals, Me, with repulsive interactions with the metal, M, of the ceramic, in contrast to the high values of W_a, which correspond to attractive forces between Me–M.

In the case of the ZrO_2–liquid metal systems, all the investigated metals have attractive interactions with the metal zirconium, but they show both low and high values of W_a. For this reason it is necessary to develop another model in order to describe the experimental data for these systems.

3. Experimental procedure and results

Direct measurement of the work of adhesion is not possible. An established method for studying the interfacial phenomena is that of a sessile drop of liquid metals lying on a substrate of the relevant solid ceramic. In this case the following equation holds [4]

$$W_a = \gamma_{LV}(1 + \cos\theta) \quad (3)$$

where γ_{LV} is the surface energy of liquid metal and θ the contact angle.

In previous works, the contact angle and the work of adhesion in the systems ZrO_2–Cu, Ni, Co [4] and ZrO_2–Sn, Bi, Pb [5] have been determined. The systems ZrO_2–In, ZrO_2–Ag and ZrO_2–Fe were also investigated. The ceramic used was polycrystalline zirconia ZR23 (trade name of Friedrichsfeld Co., Germany) stabilized with 5 wt % CaO with a purity greater than 99%. The metals indium, silver and iron (Fa. Ventron GmbH, Germany) were of high purity (99.99%). The experiments were carried out under the same experimental arrangement and conditions as the previous systems, i.e. the samples were heated with an induction coil in a purified argon atmosphere [4, 5]. For each system and temperature, two to four experiments were carried out. Each experiment lasted about 20–30 min. Photographs of the sessile drop were obtained at 5 min intervals.

The results showed that the contact angle is time independent, decreases with increasing temperature and shows no wettability ($\theta > 90°$). The measured contact angles in the ZrO_2–liquid metal systems, together with data from the literature of the surface energies of the liquid metals indium, silver [6] and iron [6, 7] (Table I), were used for the calculation of the work of adhesion (Equation 3). All the measured and calculated quantities are listed in Table II.

The values of the work of adhesion of all the examined systems showed that W_a is a weak function of the temperature (mean value of the linear temperature coefficient $dW/dT = 4.15 \times 10^{-4}$ J m^{-2} K^{-1}). On the basis of this result, a value of W_a for each system was calculated at the mean temperature of the intervals where the experiments were carried out. Table III shows the temperature intervals, ΔT, the mean temperature, T_M, and the calculated values of contact angles, θ, and works of adhesion, W_a.

TABLE II Contact angle, θ, surface energy, γ_{LV}, and work of adhesion, W_a, in the ZrO_2–liquid metal systems

System	T (K)	θ (deg)	γ_{LV} (J m^{-2})	W_a (J m^{-2})
ZrO_2–In	523	149.19	0.552	0.078
	623	141.60	0.543	0.117
	763	138.54	0.530	0.133
ZrO_2–Ag	1373	121.67	0.891	0.423
	1473	120.46	0.876	0.432
	1573	117.77	0.861	0.460
	1673	116.56	0.846	0.468
ZrO_2–Fe	1823	115.55	1.821	1.036
	1873	110.83	1.808	1.165

TABLE III Contact angle, θ, and work of adhesion, W_a, at the mean temperature, T_M, in the ZrO_2–liquid metal systems

System	ΔT (K)	T_M (K)	θ (T_M) (deg)	W_a (T_M) (J m^{-2})
ZrO_2–In	523–763	640	142.81	0.110
ZrO_2–Sn	623–1073	850	152.20	0.060
ZrO_2–Bi	623–923	780	142.11	0.074
ZrO_2–Pb	673–973	820	137.37	0.116
ZrO_2–Ag	1373–1673	1520	119.13	0.446
ZrO_2–Cu	1473–1773	1620	119.68	0.635
ZrO_2–Ni	1740–1953	1830	119.37	0.879
ZrO_2–Co	1823–2043	1940	119.06	0.916
ZrO_2–Fe	1823–1873	1850	112.97	1.106

From the data of Table III it can be seen that the wetting of the ZrO_2 by the metals silver, copper, nickel, cobalt and iron is better than that caused by the metals indium, tin, bismuth and lead. This trend, observed also in the systems Al_2O_3–liquid metals [3, 8], UO_2–liquid metals [9] and SiO_2–liquid metals [10], leads to the assumption that the mechanism of the interaction at the interface ceramic–liquid metals is different for the two groups of metals.

4. Proposed model

Based on the experimental values of the work of adhesion of ZrO_2–liquid metal systems, a model for the evaluation of W_a is presented. The following assumptions hold.

1. The oxide surface structure is in the form proposed by Weyl [11], i.e. it consists of the ions O^{2-}, which are larger and with higher polarizability than the metal ions.

TABLE I Linear temperature functions of surface energies for liquid metals

Metal	Surface energy (J m^{-2})		Reference
In	$\gamma_{LV} = 0.560 - 0.09 \times 10^{-3}(T - T_m)$	$T > T_m = 429$ K	[6]
Ag	$\gamma_{LV} = 0.912 - 0.15 \times 10^{-3}(T - T_m)$	$T > T_m = 1234$ K	[6]
Fe	$\gamma_{LV} = 1.825 - 0.27 \times 10^{-3}(T - T_m)$	$T > T_m = 1809$ K	[6, 7]

2. The experimental data show that the work of adhesion is a weak function of temperature. From this observation it is concluded that the entropic contributions to W_a are negligible, therefore W_a can be expressed in terms of the enthalpic contributions.

3. Physical interactions of the VDW type as well as chemical equilibrium bonds between the liquid metal and the ion O^{2-} act on the interface.

According to these assumptions, it is suggested that at the oxide–metal interface of the systems ZrO_2–In, Sn, Bi, Pb, only physical Van der Waals interactions exist. The low values of the work of adhesion (Table III) of these systems must be in good agreement with the expected values of VDW forces. For the ZrO_2–Ag, Cu, Ni, Co, Fe systems, which present high values of W_a (Table III), it is suggested that a chemical equilibrium bond between the liquid metal, Me, and the oxide ion, O^{2-}, of the surface oxide also takes place.

The expression of the dispersion interaction (VDW) between a pair consisting of a metal atom and an oxygen ion is given by the London equation

$$E = \frac{3}{2}\left(\frac{\alpha'_{Me}\alpha'_{O^{2-}}}{R^6}\right)\left(\frac{I_{Me}I_{O^{2-}}}{I_{Me} + I_{O^{2-}}}\right) \qquad (4)$$

where α' is the polarizability volume, I the ionization potential and R the distance between the centres of the interacting atoms/ions. It should be noticed that the other attractive forces, the orientation effect and the induction effect, are only important where permanent dipoles are present.

The ionization potential of the oxide ion, O^{2-}, is taken to be 88×10^{-19} J after Benjamin and Weaver [12], while the polarizability of the oxide ion is given by Pauling as 3.88×10^{-3} nm^3 [1]. The polarizability volume of the metal atom, α'_{Me}, is calculated from the expression

$$\alpha'_{Me} = \left(\frac{e^2 h^2}{4\pi^2 m_e^2 I^2}\right)\left(\frac{1}{4\pi\varepsilon_0}\right) \qquad (5)$$

If n atom/ion pairs interact at the ceramic–metal interface the energy, $W_{a(VDW)}$, is given by the relationship

$$W_{a(VDW)} = nE \qquad (6)$$

The number of bonds Me–O^{2-} was determined by calculating the number of the metal atoms per square metre and the number of O^{2-} per square metre (1.52×10^{-11} O^{2-} m^{-2}). Then, for a first approximation, the smallest of the two values was the number of bonds established at the ceramic–liquid metal interface.

The calculated values of the Van der Waals interaction energy are shown in Table IV. It can be seen that these values of $W_{a(VDW)}$ have an upper limit of about 0.5 J m^{-2} and they are in accordance with the low values of W_a in the systems ZrO_2–In, Sn, Bi, Pb, but a considerable deviation exists for the high values of W_a in the systems ZrO_2–Ag, Cu, Ni, Co, Fe (Fig. 1).

TABLE IV Calculated values of the energies of binding dispersion forces, $W_{a(VDW)}$

System	$W_{a(VDW)}$ (J m^{-2})
ZrO_2–In	0.222
ZrO_2–Sn	0.185
ZrO_2–Bi	0.096
ZrO_2–Pb	0.114
ZrO_2–Ag	0.306
ZrO_2–Cu	0.467
ZrO_2–Ni	0.525
ZrO_2–Co	0.516
ZrO_2–Fe	0.472

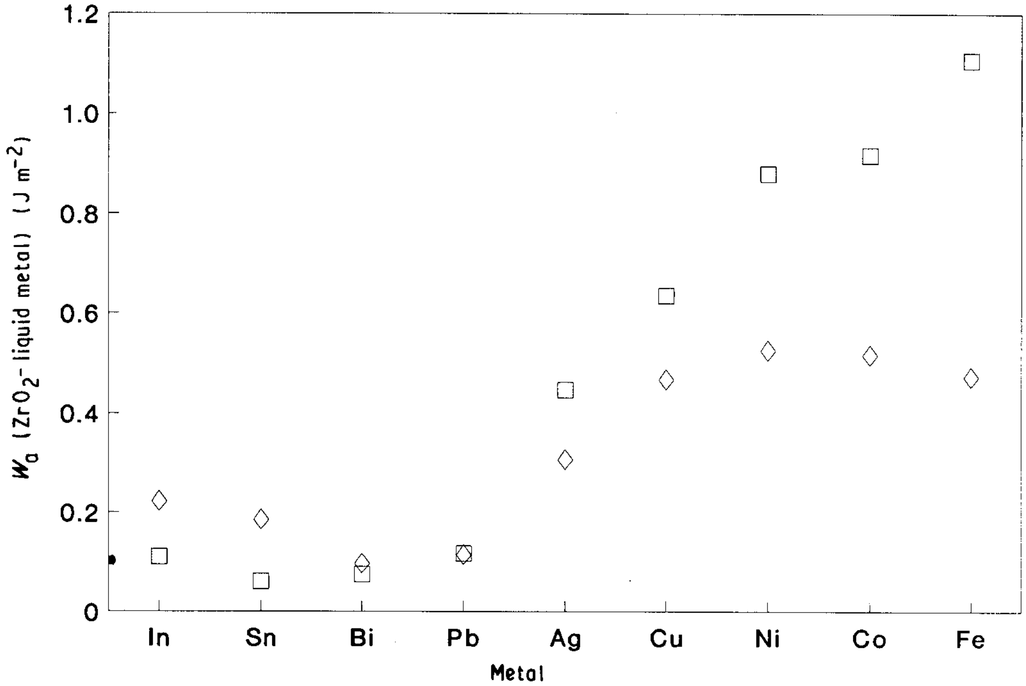

Figure 1 (□) Experimental values of the work of adhesion, W_a, and (◇) calculated values of the energies of binding dispersion forces, $W_{a(VDW)}$, in ZrO_2–liquid metal systems.

In the case of the metals silver, copper, nickel, cobalt and iron, a chemical bond between the atom of the liquid metal, Me, and the ion O^{2-} of the surface oxide, is developed. This assumption, based on the theoretical work of Johnson and Pepper [13], where a chemical covalent bond between the d-metals (silver, copper, nickel, iron) and the surface oxide is established. This does not mean that a new phase of oxide is formed at the interface. The strength of this bond should be proportional to the trend of the metal atom to be joined with the oxygen ion. Under these conditions the following linear equation between the work of adhesion, W_a, and the enthalpy of the formation, ΔH_f^0, of the oxide of the metal (Me–O, J/g-atom oxygen) is proposed

$$W_a = a + b(-\Delta H_f^0) \tag{7}$$

where the constant, a, represents the contribution of the Van der Waals (VDW) interactions.

Fig. 2 shows the dependence between the work of adhesion (Table III) and the enthalpy of formation of the oxide of the metal, taken from literature data [14],

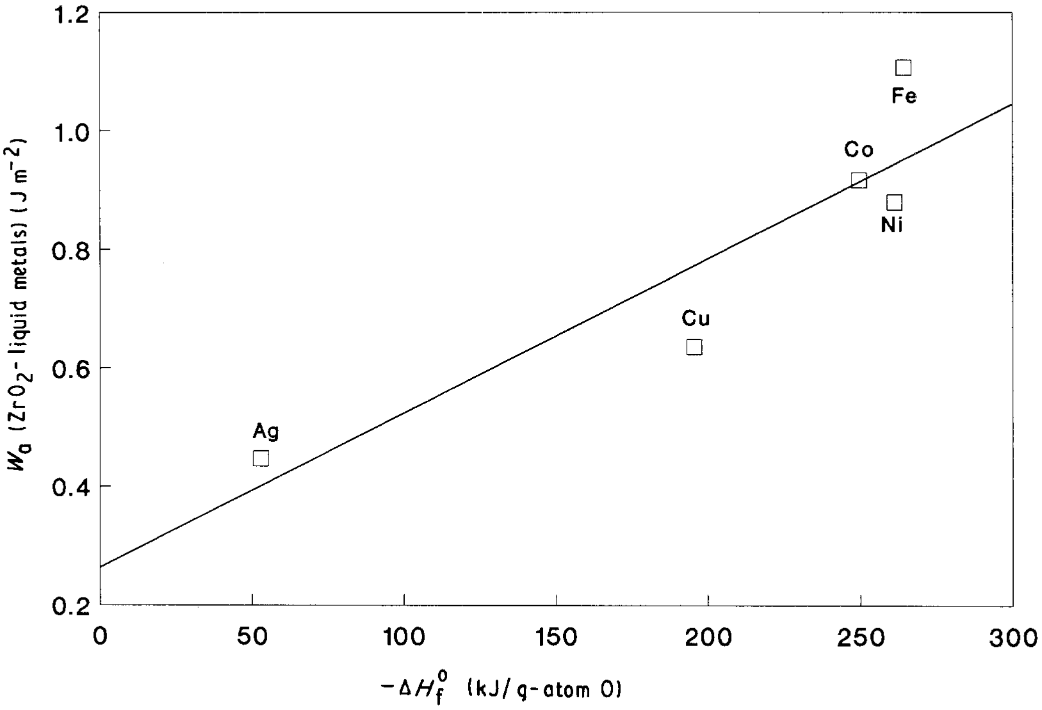

Figure 2 Experimental values of the work of adhesion, W_a, in ZrO_2–liquid metal systems as a function of the enthalpy of formation of the metal oxides, ΔH_f^0, (Me–O) per g-atom oxygen.

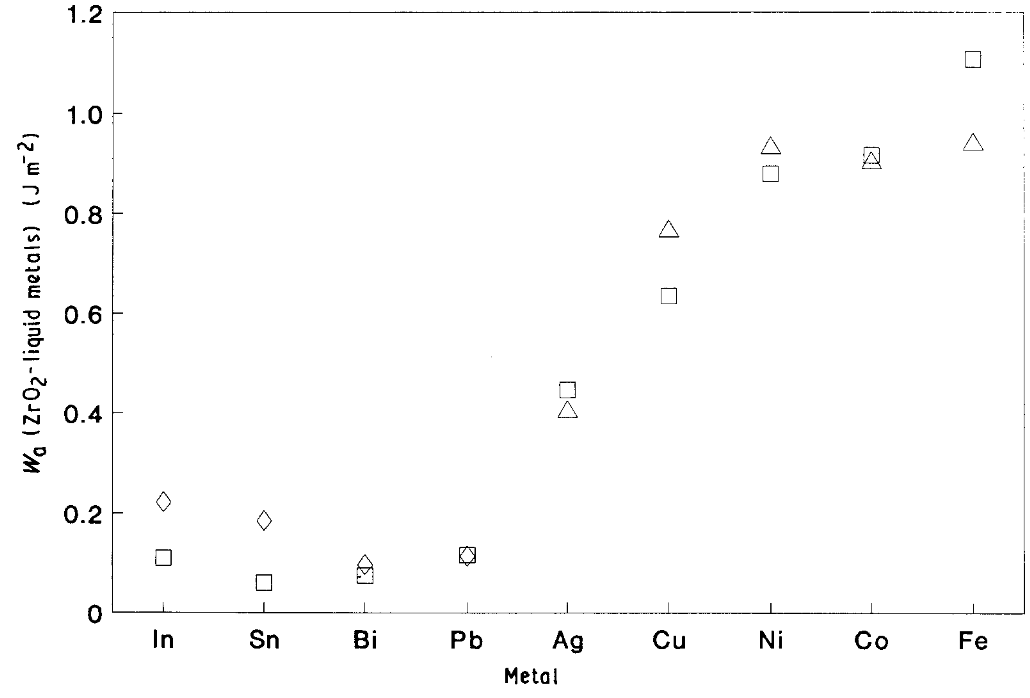

Figure 3 (□) Experimental and (◇, △) calculated values of the work of adhesion, W_a, in ZrO_2–liquid metal systems. (◇) VDW, (△) $-\Delta H_f^0$.

for the ZrO_2–liquid metal systems. The proposed linear relationship between W_a and ΔH_f^0 correlates well with the experimental data for the investigated systems. The resulting equation is given as

$$W_a = 0.263 + 2.607 \times 10^{-6}(-\Delta H_f^0)\ \mathrm{J\,m^{-2}} \quad (8)$$

The value of constant a, given as 0.263 $\mathrm{J\,m^{-2}}$, is related to the lower limit of the values $W_{a(\mathrm{VDW})}$ obtained from Table IV for the d-metals.

In Fig. 3 the calculated values of the work of adhesion, W_a (Equations 6 and 8) together with the experimental values for each ZrO_2–liquid metal system, are depicted. The agreement between calculated and experimental values shows (Fig. 3) that the proposed model, which combines the physical interactions (VDW) and the chemical bonds at the interface, is a good approach for the evaluation of the work of adhesion in the ZrO_2–liquid metal systems.

5. Conclusion

The experimental values of work of adhesion, W_a, obtained by sessile drop experiments for various ZrO_2–liquid metal systems are used to propose a model for the evaluation of W_a. This model is based on the assumption that the interaction at the ceramic–metal interface take place in two different ways, i.e. (a) by physical Van der Waals forces only, and (b) by also establishing a chemical bond.

According to this model, the values of W_a of the ZrO_2–liquid In, Sn, Bi, Pb systems are given by the London equation, which describes the energy of binding dispersion forces (VDW). For the ZrO_2–liquid Ag, Cu, Ni, Co, Fe, the value of W_a is given by the equation $W_a = 0.263 + 2.607 \times 10^{-6}(-\Delta H_f^0)\ \mathrm{J\,m^{-2}}$. The proposed model gives good agreement between calculated and experimental quantities.

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