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Wetting and interfacial bonding in ionocovalent oxide-liquid metal systems

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Résumé. — A partir de différents modèles, nous discutons de la nature de la liaison interfaciale métal-oxyde ionocovalent. Les prédictions de ces modèles sont comparées aux résultats expérimentaux relatifs à la mouillabilité d'oxydes monocristallins par les métaux purs. Nous en concluons que la liaison métal-oxyde est de type chimique. Nous discutons ensuite de l'influence de l'addition d'oxygène ou de soluté métallique au métal, sur la mouillabilité des oxydes par celui-ci. Il apparaît que l'oxygène a deux effets : un effet de détérioration du mouillage aux basses températures lorsque l'oxygène est sous forme de film d'oxyde encapsulant le métal liquide, et un effet d'amélioration aux plus hautes températures lorsque l'oxygène est dissous dans le métal liquide. L'addition de solutés métalliques peut également améliorer le mouillage par adsorption ou par réaction à l'interface, du soluté avec l'oxyde.

Abstract. — The nature of the metal-ionocovalent oxide interfacial bond is discussed on the basis of different models. Predictions of these models compared to experimental results as regards the wettability of monocrystalline oxides by pure metals lead to the conclusion that interfacial bond is chemical even in non reactive systems. The influence of oxygen and of metallic additions to the metal on the wettability of the oxide is then discussed. Oxygen has two effects : a damage of the wettability at low temperatures when the oxide film covering the liquid metal is stable and an improvement of the wettability at higher temperatures when it is dissolved in the liquid metal. Metallic solutes can also greatly improve the wetting and the thermodynamic adhesion either by adsorption or reaction processes at the metal-oxide interface.

1. Introduction.

The interest shown in the energetics of ceramic-metal interfaces has grown with the development of new materials having better mechanical, thermal or electric properties. Many fields of material science are concerned :

- the joining of ceramics by brazing alloys can be performed only if the metal wets the ceramic properly [1, 2] ;

- in metal matrix composites reinforced with ceramic fibres, the degree of wettability of the ceramic by the liquid metal governs the conditions of the infiltration process : spontaneous infiltration or infiltration under low or high pressure [3, 4]. Moreover, the mechanical properties of these composite materials, particularly the fracture stress, depends to a large extent on the adhesion between metal and ceramic ;

- in other fields, metal-ceramic interfaces are

prepared for their inherent properties : in pyrometallurgy, they determine the chemical and thermal exchanges, while, in electronics, microelectronics or catalysis they regulate electronic charge transfers.

The energetics of liquid metal-ceramic interfaces can be characterized by two quantities :

- the contact angle, θ , of the liquid (L) on the solid (S) in vapour (V) described by Young's equation :

$$\cos \theta = (\sigma_{SV} - \sigma_{SL}) / \sigma_{LV} \quad (1)$$

where σ_{ij} is the interfacial tension between two phases ;

- the work of adhesion, W , which is the work per unit area which has to be provided to a system in order to create reversibly a solid-vapour surface and a liquid-vapour surface from a solid-liquid interface according to Dupré's relation :

$$W = \sigma_{SV} + \sigma_{LV} - \sigma_{SL} \quad (2)$$

By combining equations (1) and (2), W can be calculated from the contact angle and the liquid surface tension values :

$$W = \sigma_{LV}(1 + \cos \theta). \quad (3)$$

At high temperatures the surface tension of the liquid and the contact angle are generally measured by the sessile drop method [5]. More recently a tensiometric method adapted to the simultaneous measurement of the surface tension and the contact angle of a liquid in contact with a vertical rod or fibre ($100 \mu\text{m} \leq \varnothing \leq 5 \text{ mm}$) was developed [6].

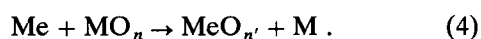
Experimental studies of the energetics of the liquid metal/ceramic interfaces performed in the years 1950-1960 highlighted major tendencies classifying ceramic-metal systems in systems where wetting of the ceramic by the liquid metal occurs, characterized by θ values much lower than 90° , and systems characterized by θ values much higher than 90° , called non-wetting systems. Unfortunately, for technological reasons, these experiments were performed using sintered polycrystalline ceramics. The impurities in these materials and their surface roughness gave rise to a wide dispersion in θ values and, consequently a dispersion in W values as much as one or two orders of magnitude.

The objective of this study is to discuss the features of the interfaces in ionocovalent oxide/liquid metal systems. As the ionocovalent oxides are the basic component of numerous ceramics a large amount of recent experimental and theoretical works on the oxide/metal interfaces was available.

This paper is divided into three parts. The first part discusses the nature of the metal-oxide interfacial bond on the basis of different models. The predictions of these models are compared to experimental results as regards the wettability of high purity monocrystalline alumina by pure metals. In the second part, the effect of oxygen on wettability and thermodynamic adhesion in metal/oxide systems is analysed. It is known that this impurity is always present, even in a ultra-high-vacuum chamber and that, even at partial pressure levels as low as 10^{-10} or 10^{-15} Pa, it can radically change the surface properties of the metal [5]. The last part of the paper deals with the influence of addition of metallic solutes in the metal on the metal-oxide interface.

2. Pure metal/ionocovalent oxide interfaces.

Pure metals (Me)-ionocovalent oxide (MO_n) interfaces can be placed in two classes depending on the sign of the standard Gibbs' energy, ΔG°_R , of the oxido-reduction reaction between the two phases :



Specific wetting behaviour such as spreading kinetics and contact angle characterize each class :

In *non reactive* systems, with a positive value of ΔG°_R , the liquid metal spreads on the ceramic in less than one second and generally, at equilibrium, the contact angle value lies between 90° and 145° . Experimental data on the wettability of alumina by different molten metals non reactive with alumina are given in table I. They come from experiments performed in our laboratory, on sapphire, the surface roughness, Ra , of which is $0.01 \mu\text{m}$ or less. For such a Ra value, it has been shown [6] that the experimental advancing θ values cannot differ by more than 3° from the values of θ_Y , the thermodynamic contact angle given by Young's equation (1). This table gives typical values of the contact angle and the work of adhesion in non-reactive systems. The work of adhesion varies by half an order of magnitude from lead to nickel. It should be noted that even for metal-alumina systems with higher thermodynamic adhesion, the work of adhesion remains much lower than the cohesion energy of the metal, E_C ($E_C \approx 2 \sigma_{LV}$).

Table I. — *Experimental data on the wettability of alumina by different molten metals non reactive with alumina. σ_{LV} values are taken from reference [7].*

Metal	T (K)	θ ($^\circ$)	σ_{LV} (mJ.m^{-2})	W (mJ.m^{-2})	W $2 \sigma_{LV}$
Pb	1173	117 ± 3	392	214	0.27
Sn	1373	122 ± 2	478	225	0.24
Au	1373	139 ± 2	1 131	277	0.12
Cu	1373	131 ± 3	1 283	441	0.17
Al	1273	80 ± 3	814	955	0.59
Ni	1730	112 ± 2	1 782	1 114	0.31

In figure 1, the variation of contact angle of gold on sapphire is plotted as a function of temperature [8]. The slight linear decrease observed is typical of non-reactive metal-oxide systems for which the values of the contact angle temperature coefficient, $d\theta/dT$, are nearly zero but always negative, they lie between -0.01 and $-0.05^\circ \cdot \text{K}^{-1}$ [8]. The liquid-metal surface tensions slowly decrease as the temperature increases. Consequently the work of adhe-

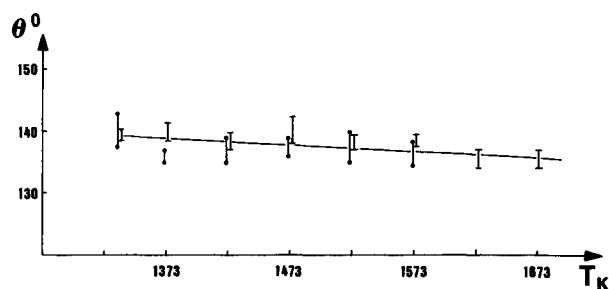


Fig. 1. — Variation of the contact angle of gold on sapphire as a function of the temperature [8].

sion temperature coefficient, dW/dT , is very small but always positive (from 0.05 to 0.5 $\text{mJ} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$ [8]).

In *reactive* systems, having a negative value of ΔG°_R , spreading of the liquid on the ceramic often occurs simultaneously with the formation of a new solid phase at the initial interface between the solid and the liquid. Contact angles much lower than 90° are typical of these systems. For example, contact angles are zero for titanium and zirconium on magnesia and 46° for aluminium on uranium dioxide [9]. In such systems, spreading kinetics are very different from those observed in non-reactive systems: reactive liquid metal requires a few minutes if not tens of minutes before spreading is completed. An increase in temperature generally speeds up the spreading process and can lead to a much greater decrease in θ value than that observed in non-reactive systems [9].

Several models were proposed to explain the wetting behaviour of liquid metals on oxides from the nature of the interfacial pure metal-oxide bond. In each model, experimental observations are made regarding the order of magnitude of the work of adhesion, W , and the differences between the values of W of several metals on a given oxide, as the work of adhesion quantifies the energy of the interfacial metal-oxide bond. From these observations, the authors attempt to define the nature of the interfacial metal-oxide bond and to propose an equation for calculating W .

The three models presented were proposed by McDonald and Eberhart in 1965 [10], by Naidich in 1981 [9] and by our team in 1986 [11]. They differ by the assumptions made concerning the nature of the bond at the metal-oxide interface. In the past, the impossibility of discussing the validity of the different models was linked to the wide dispersion of the experimental values of W (one to two orders of magnitude). Discussion is now possible on the basis of recent data on monocrystalline alumina/metal systems, the error on which is less than 20 %.

In their model of adhesion in oxide-metal systems [10], McDonald and Eberhart do not distinguish the *reactive* systems (with negative values of ΔG°_R (Eq. (4)) from the *non-reactive* systems ($\Delta G^\circ_R \geq 0$). They assume that the nature of the interfacial metal-oxide bonds depends on the sign of the standard Gibbs' energy ΔG°_F , of the metal oxidation reaction:



For Me metals having negative values of ΔG°_F , the authors assume that chemical bonds between Me atoms and O^{2-} oxygen ions of the oxide are set up at specific oxygen sites at the interface (n_c per oxide mole) in addition to Van der Waals bonds established at the remaining oxygen sites (n_p per oxide

mole). The energy of the chemical bond is assumed to be equal to $\Delta G^\circ_F/2$ and the energy of the physical bond (per oxygen site) is calculated as the metal atom-oxide ion pair interaction energy given by the expression:

$$E_{\text{VDW}} = -\frac{3}{2} \frac{\alpha_{\text{Me}} \alpha_{\text{O}^{2-}}}{R^6} \cdot \frac{I_{\text{Me}} I_{\text{O}^{2-}}}{I_{\text{Me}} + I_{\text{O}^{2-}}} \quad (6)$$

where α is the polarizability and I the first ionization potential of the metal, Me, or the oxide ion, O^{2-} , R is the internuclear distance between a metal atom and an oxide ion. Depending on the choice of R , $I_{\text{O}^{2-}}$ and n_p , the values of W_{VDW} , Van der Waals' interaction contribution to W , can change by a factor of two for a same system. Once these parameters have been fixed, the calculated values of W_{VDW} for different metal/oxide systems do not differ by more than 40 %. For example McDonald and Eberhart calculate W values for different metal/alumina systems equal to $500 \pm 150 \text{ mJ} \cdot \text{m}^{-2}$ [10] and Naidich found for metal/oxide systems W values of $350 \pm 150 \text{ mJ} \cdot \text{m}^{-2}$ [9]. For this reason, the expression proposed by McDonald and Eberhart for calculating W is written:

$$W = a - b \Delta G^\circ_F \quad (7)$$

where a and b are positive constants for a chosen oxide; a is the contribution of the $\text{Me}-\text{O}^{2-}$ Van der Waals interaction, to the work of adhesion ($a = -(n_p/\Omega_{\text{ox}}) E_{\text{VDW}}$) and b is equal to $n_c/2 \Omega_{\text{ox}}$, Ω_{ox} being the interfacial molar area of the oxide.

For metals having positive or zero values of ΔG°_F , the authors assume that the work of adhesion results only from Van der Waals bonds ($W = a$).

In figure 2 (curve a) the variation in the work of adhesion of different metals (characterized by ΔG°_F) on alumina as a function of ΔG°_F is schematically represented, as proposed by McDonald and

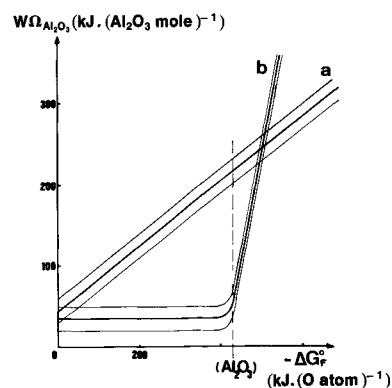


Fig. 2. — Schematic theoretical variations of the work of adhesion of Me- Al_2O_3 systems as a function of the standard Gibbs' energy of formation of the oxide MeO: (a) model of McDonald and Eberhart; (b) model of Naidich.

Eberhart. For this oxide, the authors proposed the existence of three oxygen sites per alumina mole, two *Van der Waals* sites and one *chemical* site. As the work of adhesion is calculated per alumina mole and ΔG°_F is referred to one oxygen atom, the slope of the (a) line, is equal to 1/2 ; the (a) line intercepts the Y-axis at $50 \pm 15 \text{ kJ. (alumina mole)}^{-1}$ which corresponds to about $20 \pm 5 \text{ kJ. (metal mole)}^{-1}$.

By proposing a chemical bond contribution to the thermodynamic adhesion proportional to the standard Gibbs' energy of formation of the metal oxide, McDonald and Eberhart assume that local but total breaking of the Me-Me bonds occurs in order to create Me-O bonds, even in *non-reactive* systems ($\Delta G^\circ_R \geq 0$). This means that the structure of the closest-to-oxide metallic monolayer would be imposed by the structure of the oxide surface. This seems to be highly improbable as the work of adhesion in the non-reactive systems is much lower than the cohesion energy of the liquid metal (see Tab. I). Moreover, as the entropy of the reaction (5) is negative, equation (7) would predict a high negative temperature coefficient for the work of adhesion, and this does not agree with experimental results in non-reactive systems ($dW/dT \geq 0$).

In figure 3, the selected experimental values of the work of adhesion, W , for different non-reactive metals on alumina [11] are plotted as a function of the standard Gibbs' energy of formation of each metal oxide. Metals with a positive ΔG°_F are reported at zero abscissa as proposed by McDonald and Eberhart. The points in figure 3 are widely dispersed and the linear correlation proposed by McDonald and Eberhart is not observed. Similar observations were recently made for silica/metal systems [12].

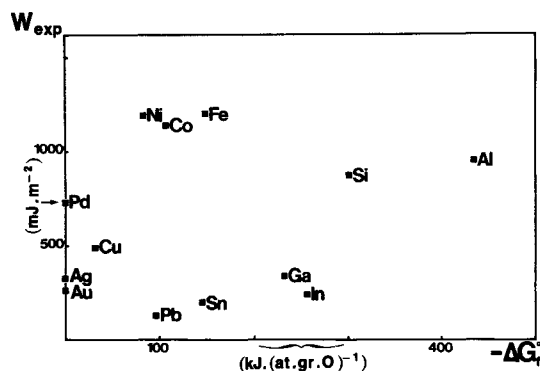


Fig. 3. — Experimental values of the work of adhesion for different non-reactive metals on alumina as a function of the standard Gibbs' energy of formation of each metal.

All these observations show that the model proposed by McDonald and Eberhart is not convenient to explain energetical properties in *non-reactive* metal-oxide systems. (The case of reactive systems

cannot be discussed as there is not a sufficient quantity of precise experimental data available.

In the model proposed in 1981 [9], Naidich separated the two cases of non-reactive and reactive metal-oxide systems. In non-reactive systems, only Van der Waals bonds are assumed at the metal-oxide interface. In reactive systems, chemical bonds are assumed to be established in addition to the Van der Waals' bonds.

Like McDonald and Eberhart, Naidich used the expression (6) to calculate the energy of the Van der Waals bonds, but differences in values of W_{VDW} calculated by these authors appears because they chose different values for the parameters of equation (6) and the number of Me-O^{2-} bonds per unit interfacial area. Values calculated by Naidich for different metal/ionocovalent oxide systems do not vary by more than 40 % and are in the range $350 \pm 150 \text{ mJ.m}^{-2}$.

In the case of reactive systems, Naidich assumed that the contribution of chemical bonds to the work of adhesion, W_{ch} , depends on the degree of progress, δ , of the reaction (4) :

$$W_{ch} = \int_0^{\delta_0} \frac{d(\Delta G_R)}{d\delta} d\delta \quad (8)$$

where δ_0 is δ at equilibrium and ΔG_R the Gibbs' energy of the reaction (4).

In figure 2, the curve (b) schematically represents the variation proposed by Naidich for the work of adhesion of different metals (determined by their ΔG°_F) on alumina as a function of ΔG°_F . For non-reactive systems (on the left of a region centered on the vertical X-axis line $\Delta G^\circ_F(\text{Al}_2\text{O}_3)$), W virtually does not change from the mean value of 350 mJ.m^{-2} calculated by Naidich which corresponds to $35 \text{ kJ. (alumina mole)}^{-1}$. As the value of ΔG°_F approaches $\Delta G^\circ_F(\text{Al}_2\text{O}_3)$ the reaction becomes possible due to the contribution of a negative free enthalpy of mixing of Al with the metal, and/or of MeO_n oxide with alumina, and the work of adhesion increases. When the reaction is total, the work of adhesion is proportional to ΔG°_F ; as W is reported per alumina mole the slope of the (b) line is 3.

Like the model proposed by McDonald and Eberhart, the validity of Naidich's model cannot be discussed for reactive systems due to lack of data. In the case of non-reactive systems, the experimental data of table I are compared with theoretical assumptions. It appears that the calculated values of W for metals like nickel or aluminium are largely underestimated. Moreover, the relative variations of the calculated values of W on alumina of the metals reported in table I ($\sim 40\%$ or less) do not agree with the experimental W values with discrepancies as high as 500 %.

These observations show that the Van der Waals

bonds are not sufficient to ensure the entire thermodynamic adhesion at the liquid metal-ionocovalent oxide interface. By comparing McDonald and Eberhart's model and Naidich's model it seems that bonds at the non-reactive metal/ionocovalent oxide interface are stronger than Van der Waals bonds, but remain weak enough not to destroy the metallic bond in the neighbourhood of the interface.

Regarding these two models and a series of recent experimental data on monocrystalline oxides we recently proposed a model for the thermodynamic adhesion for non-reactive liquid metal/oxide systems [11]. This leads to a semi-empirical equation for W based on the following assumptions :

— the bonds between metal and oxide metal are taken into account in addition to metal-oxide ion bonds classically considered by other authors ;

— these bonds are assumed to be chemical bonds located at the interface, and established without restructuring of the liquid metal ;

— finally, the energy of these bonds is identified with an enthalpy (and not with a Gibbs's energy) with a view to respecting the nearly zero variation in work of adhesion with temperature ;

The work of adhesion is then written :

$$W = - \frac{c}{N^{1/3} V_{Me}^{2/3}} \left[\overline{\Delta H}_{O(Me)}^{\infty} + \frac{1}{n} \overline{\Delta H}_{M(Me)}^{\infty} \right] \quad (9)$$

where c is a dimensionless parameter adjustable for each ionocovalent oxide, V_{Me} the molar volume of the metal, n the stoichiometric ratio of oxygen and metal ion in the oxide and $\overline{\Delta H}_{O(Me)}^{\infty}$ and $\overline{\Delta H}_{M(Me)}^{\infty}$ the enthalpies of mixing at infinite dilution of oxygen and M oxide metal in the metal Me. This relation (9) does not explicitly take into account Van der Waals interactions.

In figure 4, the selected experimental values of the work of adhesion W , for different metals on alumina are plotted as a function of the quantity

$$Q = - (N^{1/3} V_{Me}^{-2/3}) \left(\overline{\Delta H}_{O(Me)}^{\infty} + \frac{2}{3} \overline{\Delta H}_{Al(Me)}^{\infty} \right)$$

which appears in expression (9). By linear correlation of the points in this figure, a value of 0.22 is obtained for the c parameter. The expression (9) written with reference to the work of adhesion of aluminium on alumina :

$$W_{Me} (N^{1/3} V_{Me}^{2/3}) = W_{Al} (N^{1/3} V_{Al}^{2/3}) + c \left(\overline{\Delta H}_{O(Me)}^{\infty} - \overline{\Delta H}_{O(Al)}^{\infty} + \frac{2}{3} \overline{\Delta H}_{Al(Me)}^{\infty} \right)$$

makes allowance for the respective weight of the three quantities : the molar volume of the metal and the energies of the metal-oxygen and metal-oxide metal bonds. By observing the translation of the points in figure 3, with respect to the straight line

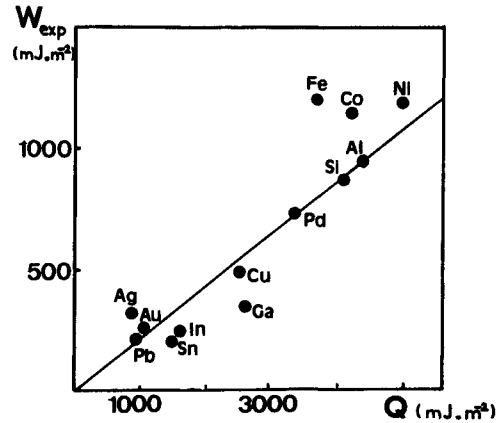


Fig. 4. — Experimental values of the work of adhesion of different metals on alumina as a function of :

$$Q = - (N^{1/3} V_{Me}^{2/3}) (\overline{\Delta H}_{O(Me)}^{\infty} + (2/3) (\overline{\Delta H}_{Al(Me)}^{\infty}))$$

going through zero and the Al point (Fig. 4) when equation (9) is applied instead of equation (7), we see quite clearly the effect of molar volume for high V_{Me} metals like lead, tin or indium and the effect of metal-oxide metal bonds specially for palladium, copper and the d-metals.

The validity of equation (9) was checked for other non-reactive metal-ionocovalent systems. The value of the c parameter was found to be 0.20 in metal/silica systems [12]. A constant value ($0.21 \pm 10\%$) seems to be convenient for numerous systems. It is then possible to make an a-priori estimation of the work of adhesion and the contact angle in non-reactive metal-ionocovalent systems [13]. From a fundamental point of view, the validity of equation (9) would assume that interactions at the interface in this kind of system are essentially chemical.

Metal/oxide interfaces were studied not just from the thermodynamic stand point. Theoretical work on the electronic structure of the interface was performed. Using a molecular orbital calculation Johnson and Pepper [14] showed that a chemical bond is established between d-metals and alumina. For sp metals on alumina, Hicter *et al.* [15] using an electronic band structure model, found that the metal-oxide adhesion results from an electron transfer from the liquid metal band to the conduction band of the oxide which was initially empty. The work of adhesion is calculated for IIB, IIIA, IVA and VA sp metals on alumina. Figure 5 shows that the relative magnitude and position of the calculated values of W agree with experimental measurements. The number of transferred electrons from the metal (shown in brackets for each metal in Fig. 5) is less than one : the metal is not oxidized, but the transferred charge is high enough to conclude that a chemical bond is formed between the metal and the oxide.

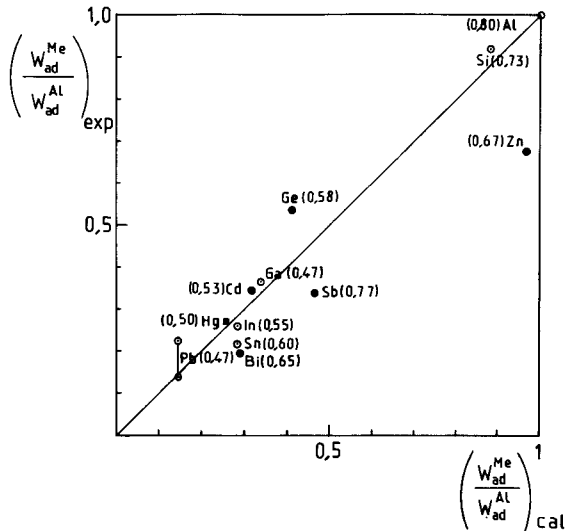


Fig. 5. — Calculated values of the ratio of the work of adhesion of different sp metals on alumina to the work of adhesion of aluminium on alumina as a function of the experimental ratio [15]. Between brackets are the calculated number of electrons transferred to alumina from each metal atom.

3. Effect of oxygen on oxide wettability by liquid metals.

In every apparatus for studying the wettability of solid by liquid metals, the presence of oxygen is detected. It is well known that this element, even in very small quantities (in good high vacuum apparatus, partial pressure of oxygen of 10^{-15} Pa can be reached) can radically change the properties of metals and ceramic surfaces.

3.1 DISSOLVED OXYGEN. — In some metals (generally with small negative values of ΔG_F°), the oxygen can be highly soluble. This is the case of silver, copper or d-metals.

The effect of dissolved oxygen in liquid metal on the wettability of oxide by this metal is relatively well known. As an example the experiments performed by Gallois [16] on liquid silver/alumina system are presented. In this system, no oxide or mixed oxide is formed with silver as the oxygen content in this metal increases. Figure 6 shows the variation at 1 253 K of the contact angle of silver on

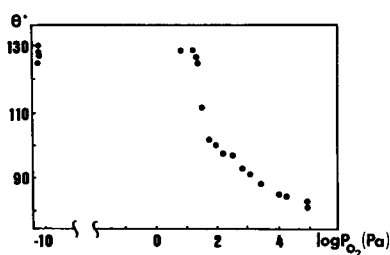


Fig. 6. — Effect of dissolved oxygen in molten silver on the wettability of sapphire by this metal at 1 253 K [16].

sapphire as a function of the partial pressure of oxygen, i.e., the oxygen content in silver. It is seen that when enough oxygen is present in the melt, the contact angle drastically decreases from values much higher than 90° to values of about 90° . Similar results were obtained for Ag/SiO₂ [17] and Cu/Al₂O₃ [18] systems.

Naidich [9] explained these results with a model in which the oxygen in solution in the metal melt would create Me²⁺ - O²⁻ clusters with the metal atoms in its vicinity. Such clusters would adsorb all the greater at the metal surface since the metal has a higher affinity for oxygen. Moreover, they would adsorb to a greater extent at the metal-oxide interface due to an additional force, the electrostatic attraction between Me²⁺ cations of the cluster and O²⁻ anions emerging from the oxide surface (see Fig. 7). Consequently, the solid-liquid interfacial tension decreases more rapidly than the surface tension of the metal melt decreases to the extent that the contact angle decreases and the work of adhesion increases.

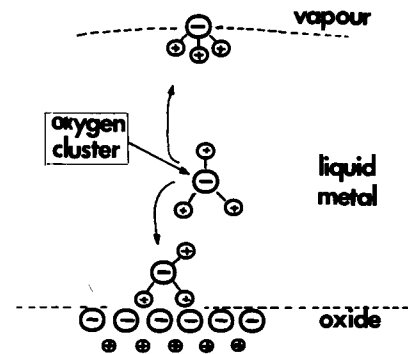


Fig. 7. — Adsorption of oxygen-metal clusters at the metal-vapour and metal-oxide interface according to the model of Naidich [9].

3.2 OXIDE FILM. — If the case of oxygen dissolved in the metal melt and its influence on the wettability of oxide was investigated, the effect of the oxide film covering the liquid metal was not accurately studied.

Metals with high oxygen affinity do not generally dissolve oxygen but form a solid oxide with it. This is the case of aluminium which, at low temperature, is covered with a more or less compact layer of alumina. The wetting of ceramics by this metal gives rise to a number of difficulties related to the inhibition of aluminium-ceramic interface development.

In figure 8, curve (a) represents the schematic variation of the contact angle of aluminium on alumina as a function of temperature. Such a curve, showing a sharp decrease in θ around 1 150 K, was obtained by different authors when they performed their experiment in a classic 10^{-3} Pa high vacuum, in

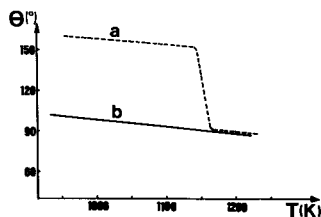


Fig. 8. — Schematic variation of the contact angle of aluminium on alumina as a function of temperature : (a) $p_T = 10^{-3}$ Pa. An oxide film covers the metal up to about 1150 K ; (b) $p_T = 10^{-5}$ Pa. The oxide film disappears from melting temperature of aluminium.

which the oxygen partial pressure is generally more than 10^{-6} Pa. The slight linear decrease in the contact angle with temperature typically obtained in non-reactive metal-oxide systems (see Fig. 1) is highlighted from the melting temperature working only in the thermodynamic conditions of non-oxidation ($P_{O_2} \leq 10^{-44}$ Pa at 973 K) [19] or in dynamic vacuum conditions so that the alumina film evaporates [20] (Fig. 8, curve b). The oxide film at low temperature, by inhibiting the contact between the liquid metal with the solid, induces the same high θ values of aluminium on different ceramics as SiC, C or Al_2O_3 [21]. On curve of type (a), the true contact angle is measured as soon the sharp decrease in θ occurs, characteristic of the oxide film disappearance. Assuming a constant value for σ_{LV} (experiments showed that apparent surface tension of liquid aluminium covered by an oxide layer differs by less than 20 % from the surface tension of the free metal [20, 22]) the disappearance of the oxide film corresponds to a one order of magnitude increase in the work of adhesion of the liquid on the ceramic, due to the decrease in θ .

3.3 DISSOLVED OXYGEN AND OXIDE FILM. — At constant oxygen partial pressure, numerous liquid metals are in equilibrium with one of their oxides at low temperature and dissolve oxygen over a wide range at high temperature. A study of the wettability of ceramic by such metals as a function of temperature can provide surprising results, differing widely from the slight and linear decrease which should be observed as in figure 1. As an example, in figure 9, the variation in contact angle of tin on sapphire is presented as a function of temperature between 873 K and 1523 K. This result is obtained from experiments performed by Rivollet *et al.* [8] under one atmosphere of helium with an oxygen partial pressure of 10^{-16} Pa. This curve shows three ranges : at low temperature, high θ values are induced by the SnO_2 film around melted tin ; when the temperature increases, the oxide film is dissolved in tin and enough oxygen is present in the melt to be active at the metal/oxide interface, the contact angle de-

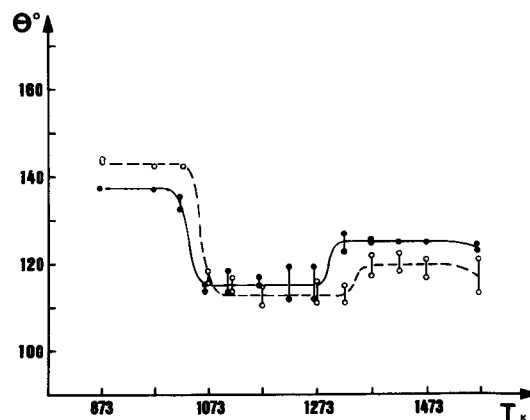


Fig. 9. — Contact angle *versus* temperature at constant partial pressure of oxygen ($\approx 10^{-6}$ Pa) for tin on sapphire [8].

creases to a value lower than the value for the pure tin/alumina system. This value is reached when the temperature is again increased as the solubility of oxygen decreases and oxygen desorbs from the interface. At high temperature, the *normal* wetting behaviour of non-reactive pure metal/oxide system is observed.

In this section, it has been shown that non-metallic impurities such as oxygen, can change quite considerably the wettability of stable stoichiometric oxide by liquid metals by acting on the liquid phase from the vapour phase. The above results clearly show that the experimental conditions in wettability experiments in metal-ceramic systems, and particularly the oxygen partial pressure, have to be strictly controlled. An additional reason is that a lot of ceramics are very sensitive to oxygen which can change their surface composition [23] (as in non-stoichiometric oxides) or produce oxide films (like SiO_2 on SiC or Si_3N_4 [24]).

4. Effect of metallic solutes on metal/oxide interfaces.

In the past, rules for improving the wettability of an oxide by an A metal by allowing a B metallic element have been defined. They result from the models for pure metal/oxide adhesion described in the second section of this paper.

McDonald and Eberhart [10] proposed that, as a rule, the wettability would be improved if the affinity of the B element for oxygen is greater than the affinity of the A matrix element ($\Delta G_F(B) > \Delta G_F(A)$). Some results on metal/oxide systems agree with this rule but a lot of examples show that this condition is not sufficient ; indeed the addition of tin in copper did not change the contact angle of copper on sapphire [25] although $\Delta G_F(Sn)$ and $\Delta G_F(Cu)$ are respectively (-140) and (-32 kJ. (at.gr.0) $^{-1}$) at 1423 K. The same observations were made as copper was added to

silver on alumina [26] or as iron was added to palladium on alumina [27].

According to his model for pure metal/oxide interface, Naidich concluded that only the B metallic solute, which reduces the oxide, would induce a decrease in the contact angle of the A metal on the oxide [2, 9]. Spectacular decreases in the contact angles of copper, silver, tin or gallium on alumina were observed when a small amount of titanium was added to these metals and had reduced alumina to titanium oxides [9]. As an example, in figure 10, the variation in the contact angle of Cu-Ti and Au-Ti alloys on alumina is plotted as a function of the titanium concentration in alloy. These results agree with Naidich's rule. Nevertheless, a gradual but significant decrease in the contact angle (several tens of degrees) was observed with solutes which do not reduce the oxide to their own oxide at the interface. This occurs when aluminium is added to copper or tin on sapphire [25] or silicon to gold on sapphire [28]. Figure 11 shows, as an example, the case of the Al-Sn/Al₂O₃ system [29].

A simple model was proposed to explain the effect of the non-reactive B metallic solutes (for which ΔG°_R is positive) on the wettability of A pure metal/oxide systems [25]. In this model the A-B alloy was assumed to be a regular solution and the liquid-vapour surface and the solid-liquid interface were limited to a monolayer. Calculations of statistical thermodynamics led to the following expressions for the slopes of the surface tension of the liquid and the oxide/liquid interfacial tension at infinite dilution of the B solute in the A matrix :

$$(d\sigma_{LV}/dx_B)_{x_B \rightarrow 0} = \frac{RT}{\Omega} \left[1 - \exp\left(-\frac{E_{LV}^\infty}{RT}\right) \right] \quad (10a)$$

$$(d\sigma_{SL}/dx_B)_{x_B \rightarrow 0} = \frac{RT}{\Omega} \left[1 - \exp\left(-\frac{E_{SL}^\infty}{RT}\right) \right] \quad (10b)$$

with

$$E_{LV}^\infty = (\sigma_{LV}^B - \sigma_{LV}^A) \Omega - m\lambda \quad (11a)$$

$$E_{SL}^\infty = E_{LV}^\infty - (W^B - W^A) \Omega \quad (11b)$$

where E_{LV}^∞ is the energy of adsorption in the surface monolayer of a B solute atom infinitely diluted in A metal. This equation of E_{LV}^∞ is similar to Guggenheim's equation for binary solutions [30]. It is expressed as a function of the difference in surface tension of the B and A pure metals, σ_{LV}^B and σ_{LV}^A , the surface molar area of the AB alloy, Ω , ($\Omega \sim V_{Me}^{2/3}$), the molar exchange energy of the AB solution, λ estimated from enthalpy of mixing data, and a structural parameter m (m is 0.25 for liquid metals). In the expression of E_{SL}^∞ an additional term appears, which is the difference between the work of adhesion of the A and B pure metals. It should be noted that negative values of E^∞ lead to

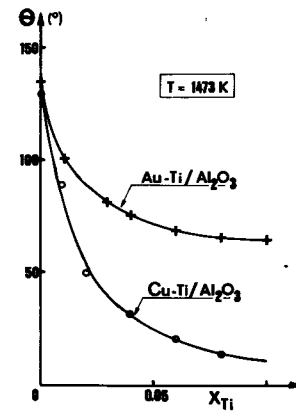


Fig. 10. — Contact angles versus molar fraction of titanium for Cu-Ti and Au-Ti alloys on alumina [9].

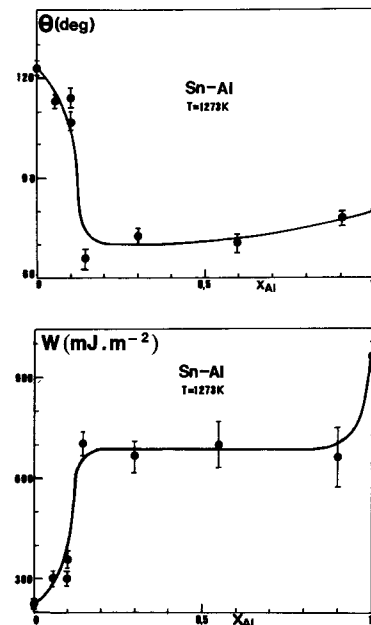


Fig. 11.— Contact angle and work of adhesion isotherms of Sn-Al alloys on sapphire [29].

very negative values of $(d\sigma/dx)$ while positive values of E^∞ lead to slightly positive values of $(d\sigma/dx)$. By introducing equations (10) in the expression of the work of adhesion (2) and the contact angle (3), the change in W and θ values can be calculated as small quantities of B in A are added. It is to be noted that (dW/dx_B) and $(d\theta/dx_B)$ values essentially depend on relative surface tensions and works of adhesion of the pure A and B metals, as the absolute values of these quantities are generally greater than the volumic mixing term, $m\lambda$.

This model was used in order to classify AB alloy/oxide systems as a function of the relative values of the adsorption energies E_{LV}^∞ and E_{SL}^∞ [25]. As an example the Sn-Al/Al₂O₃ system (cf. data in Tab. II) is placed in the class of systems satisfying

Table II. — Calculation of liquid-vapour and liquid-solid adsorption energies E^∞ of a solute B at infinite dilution into the metal matrix A.

	σ_{LV} (mJ.m ⁻²)	Ω (10 ⁴ m ² .(mole) ⁻¹)	W (mJ.m ⁻²)	λ	$E_{LV}(B(A))$	$E_{SL}(B(A))$
					(kJ.(mole) ⁻¹)	
<u>A or B</u>						
Al	815	4.75	955			
Sn	485	6.45	220			
A-B					+ 13.5	- 28.0
Sn-Al		} 5.60		} 20.0		
Al-Sn						- 23.5

the inequalities $E_{SL}^\infty(B(A)) < 0 < E_{LV}^\infty(B(A))$. Additions of aluminium to tin would have a negligible effect on the surface tension of tin but would induce a significant decrease in interfacial tension between tin and alumina. Consequently, the contact angle would decrease and the work of adhesion would increase. When tin is the solute in aluminium the surface tension of aluminium would decrease but the interfacial tension between aluminium and alumina would not be affected. Consequently, the work of adhesion should decrease and, as it is less than 90°, the contact angle should slightly decrease. These predictions agree well with the experimental results (Fig. 11) showing a minimum value of the contact angle in intermediate composition range.

The effect of reactivity, in terms of formation of a new phase at the interface in alloy/oxide systems, is not clearly understood. Of course, numerous metal-ceramic systems (for example the Cu-Ti/Al₂O₃ system shown in Fig. 10) agree with the assumption of Naidich considering that a chemical reaction between the two phases is a sufficient condition to improve the wetting. But, in some experiments [1], additions of metals which react with the ceramic, do not any influence the contact angle. It seems, as Nicholas suggested, that the structure and the chemi-

stry, at microscopic scale, of the product grown at the interface would also influence the wettability.

Except for these general propositions, the part played by a reaction in the energetics of the metal/ceramic interfaces has not been clearly explained. This subject remains wide open and needs new wetting experimental investigations associated with accurate characterisation of the interfaces. From the theoretical standpoint, modelling of the reactive wetting should take into account both the thermodynamics and kinetics of the interfacial reaction.

The results given in this paper concern the interfaces formed between molten metals and ionocovalent oxides below 1800 K. At higher temperature and under low oxygen partial pressure atmosphere, the surface structure of these oxides becomes deficient in oxygen which would promote adhesion and wettability [31]. Additional work is needed in order to quantify the effect of the non-stoichiometry of the ceramic on the energetic properties of oxide (or carbide)-metal interfaces.

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