Interfacial bonding, wettability and reactivity in metal/oxide systems

N. Eustathopoulos, B. Drevet

Classification
Physics Abstracts
68.10C — 68.22 — 73.40N

Interfacial bonding, wettability and reactivity in metal/oxide systems

N. Eustathopoulos ([1]) and B. Drevet ([2])

([1]) Laboratoire de Thermodynamique et Physico-chimie Métallurgiques, INP Grenoble, UA 29 CNRS, ENSEEG. B.P. 75, 38402 Saint Martin d'Hères Cedex, France
([2]) Section de Génie des Matériaux, CEA-DTA-CEREM-DEM, CENG. 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

Résumé. — La liaison interfaciale entre un métal pur non réactif et un oxyde iono-covalent (isolant) est généralement assurée par de faibles interactions de type physique (van der Waals) et chimique (états électroniques interfaciaux de faible densité). Par conséquent, un mauvais mouillage est observé, caractérisé par un angle de contact supérieur à 90°. Un moyen d'améliorer le mouillage est de rajouter, dans une matrice métallique, un soluté B capable de modifier favorablement l'interface métal/oxyde. Cet effet est obtenu *via* deux mécanismes, dépendant de la force des interactions entre le soluté B et l'oxygène dissous. Pour des interactions O-B modérées, l'interface côté liquide peut être modifiée par adsorption de clusters OB, l'oxygène provenant de la *dissolution* du substrat d'oxyde. Ce mécanisme entraîne une diminution de θ jusqu'à des valeurs de l'ordre de 60°. Pour de fortes interactions O-B, l'élément B peut conduire à la *précipitation* d'une nouvelle phase à l'interface. Lorsque ce produit possède un caractère partiellement métallique, le mouillage est amélioré de façon significative, un mouillage presque parfait pouvant être obtenu.

Abstract. — Pure non-reactive metals develop weak interactions with iono-covalent oxides (insulators) which can be both physical (van der Waals) and chemical (low density interfacial electronic states). As a result, non-wetting is generally observed, the contact angle being larger than 90 degrees. Improvement of wetting can be obtained by alloying the metal with a reactive solute B capable of modifying in a favourable sense the metal/oxide interface. This can be achieved *via* two mechanisms depending on the strength of the interactions between solute B and dissolved oxygen. For moderate O-B interactions, the solute B can modify the liquid-side of the interface by adsorption of OB clusters, the oxygen coming from the *dissolution* of the oxide substrate. This mechanism can lead to a decrease of θ down to $\approx$ 60°. For strong O-B interactions, the solute B can also lead to the *precipitation* at the solid-side of the interface of a new phase. When this new phase features metallic bonding, wetting can be strongly improved and nearly perfect wetting can be obtained.

1. Introduction.

Interfaces between ceramics and metals are of practical importance for the development of new strategic materials with better mechanical, thermal and electronic properties. Several fields of

materials science are concerned, e.g. metal/ceramic joining, metal matrix composites processing, microelectronic packaging or thin film technology. In many cases, the formation of the metal/ceramic interface involves liquid state processes for which wettability is a fundamental property.

The wettability is usually characterized by the angle θ formed at the liquid metal/ceramic/vapor triple line (Fig. 1). This angle is described by the well-known Young's equation :

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

where σ_{LV}, σ_{SV} and σ_{SL} are the interfacial energies between two phases (S = solid, L = liquid, V = vapor).
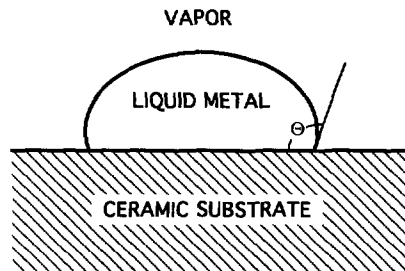

Fig. 1. — Definition of the contact angle of a liquid on a flat substrate.

The thermodynamic work of adhesion W defined as follows by Dupré :

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

is the work per unit area that must be performed to separate a solid-liquid interface to obtain a solid/vapor and a liquid/vapor interface. Combining equations (1) and (2), one obtains the Young-Dupré equation :

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

Thus, W can be calculated by measuring the contact angle between the liquid metal and the ceramic and by determining the surface tension of the metal. As σ_{LV} and σ_{SL} vary little with solidification of the metal, resulting measurements of W are roughly applicable both to liquid and solid states and can provide useful information on the mechanical behaviour of the metal/ceramic interface.

At elevated temperatures, the sessile drop method is generally used to determine θ and σ_{LV}. A drop of liquid metal is set on a flat substrate and its shape is recorded and used to compute the surface tension of the liquid metal, together with the contact angle. In practice, experiments are performed under high vacuum, inert or reducing atmosphere and substrates of controlled purity and roughness ($R_a < 20$ nm) are needed in order that the experimental θ does not differ from Young's angle (Eq. (1)) by more than 2°.

Interfaces between pure metals and ceramics are usually divided in two classes, i.e. non-reactive and reactive systems. As for the contents of our contribution, we shall first recall in the next section the wetting behaviour of *non-reactive* systems, previously described in [1, 2]. In other sections, we shall focus on *reactive* systems, with particular emphasis on the governing

parameters of wetting. Most of the results given in this paper concern oxide substrates but the developed concepts are excepted to be valid for other families of ceramics.

2. Wetting in non-reactive metal/iono-covalent oxide systems.

Non-reactive systems can be defined as systems for which reactivity consists in a slight dissolution of the ceramic substrate in the liquid metal, the maximum amount of dissolution being in the range of a few parts per million (ppm), i.e. on the order of the metallic impurity concentrations typically found in metals.

Both experimental and modelled results on contact angles and adhesion in non-reactive metal/iono-covalent oxide systems have been reviewed previously [1, 2]. Wetting is generally marginal or poor, as shown in table I, and W represents typically a few tens of percent of the work of cohesion W_c of the metal ($W_c \approx 2\,\sigma_{LV}$) (Tab. I). It has been proposed [3, 4] that *physical* (van der Waals) interactions between metal and oxide, resulting from dispersion forces [3] or from image forces [4], could account for these results. It also seems, from theoretical considerations [5-7], that even for non-reactive metal/oxide couples, *chemical* interactions localised at the interface are involved in the interfacial bond. On this basis, the following equation has been proposed for the work of adhesion of a metal M on an iono-covalent $M'O_n$ oxide [8, 9] :

$$W = -\frac{C}{N_a^{1/3} V_M^{2/3}}\left[\overline{\Delta H}^{\infty}_{O(M)} + \frac{1}{n}\,\overline{\Delta H}^{\infty}_{M'(M)}\right] \qquad (4)$$

where $\overline{\Delta H}^{\infty}_{O(M)}$ and $\overline{\Delta H}^{\infty}_{M'(M)}$ are the partial enthalpies of mixing at infinite dilution of oxygen and oxide metal M' in the metal M respectively. N_a is the Avogadro's number and V_M the molar volume of the liquid metal. C is an empirical constant equal to 0.2 for refractory oxides. Equation (4) gives good results for both alumina [9] and silica [10]. Thus, it seems that bonds at the non-reactive metal/iono-covalent oxide interface are stronger than van der Waals bonds. However, they are not strong enough to destroy the metallic bond in the neighbourhood of the interface and are responsible for the poor wetting observed in these systems.

Table I. — *Experimental data of θ and* W *for different non-reactive metals on sapphire under high vacuum or neutral gas* [38].

Metal	T (K)	θ (°)	W (mJ/m²)	W/W_c
Pb	1173	117	215	0 27
Sn	1373	122	225	0.24
Au	1373	139	275	0.12
Cu	1373	130	450	0.17
Ni	1730	112	1100	0 30

The influence of *charged defects* in the oxide on the metal/oxide adhesion and wetting has been recently studied by Chabert [11] for the gold/monocristalline TiO_{2-x} system. Decreasing the partial pressure of oxygen in the furnace by fifteen orders of magnitude, an increase of x from $x = 0$ to $x = 10^{-2}$ has been produced, leading to an increase of the electronic conductivity of the oxide by a factor 10^3. Despite these changes, no significant variation of θ has been observed, in disagreement with predictions of theoretical models [4].

2.1 INFLUENCE OF ALLOYING ELEMENTS. — The addition of an alloying element to the metal melt M can directly influence θ and W by adsorption to the liquid/solid interface or to the

liquid/vapor surface, leading respectively to a decrease of σ_{SL} and σ_{LV}. Interfacial adsorption improves both adhesion and wetting. Surface adsorption, on the other hand, always deteriorates adhesion and only improves wetting if θ is originally below 90°. These effects have been modelled by Li *et al.* [12], using the classical approximation of a monolayer surface. The model leads to the following expressions of the energies of adsorption of a solute B from the bulk liquid matrix M at S/L and L/V interfaces (noted E_{SL} and E_{LV} respectively) :

$$E_{SL} = E_{LV} + (W^M - W^B)\,\Omega_M \tag{5}$$

$$E_{LV} = (\sigma_{LV}^B - \sigma_{LV}^M)\,\Omega_M - m\lambda \tag{6}$$

where λ is the exchange energy of the M-B solution modelled as a regular solution, Ω_M the area occupied by a monolayer of one mole of M atoms ($\Omega_M \approx V_M^{2/3}$) and m a structural parameter roughly equal to 1/4 for liquid metals. A negative value of E means a reduction of the corresponding value of σ while a positive value of E means a negligible effect of the solute B on σ.

An example of this approach is found in Al-Sn alloys ($\lambda = 20$ kJ/mole, $\Omega \approx 5.5 \times 10^4$ m²/mole) on alumina at 1 273 K. Additions of Al ($\sigma_{LV} = 815$ mJ/m², $W = 955$ mJ/m²) to Sn ($\sigma_{LV} = 485$ mJ/m², $W = 220$ mJ/m²) have a negligible effect on the surface tension of Sn but induce a significant decrease in interfacial tension between Sn and alumina and, as a consequence, a decrease in θ. When Sn is the solute in Al, the surface tension of Al decreases but the interfacial tension between Al and alumina is not affected. Consequently, as it is less than 90°, the contact angle decreases again. These predictions agree well with the experimental results (Fig. 2) showing a minimum value of θ in the intermediate composition range [12].

2.2 INFLUENCE OF OXYGEN. — In all metal/ceramic systems, the role of oxygen is of particular interest as this element is present in most processes and because it influences the surface properties of many metals at partial pressures as low as 10^{-10} Pa [13]. The interaction of liquid
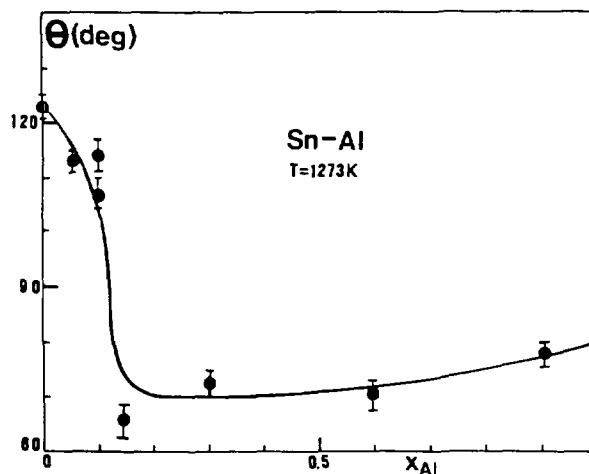

Fig. 2. — Contact angle isotherm of Sn-Al alloys on sapphire at $T = 1\,273$ K [12]. When Al is added to Sn, θ decreases because the solid/liquid interfacial energy σ_{sl} decreases. When Sn is added to Al, θ also decreases, but because the liquid/vapor surface energy σ_{lv} is decreased. As a result, the curve of contact angle *versus* composition passes through a minimum.

metals with oxygen results in the formation of either oxides, a tendency which predominates at low temperatures, or a single metallic phase containing dissolved oxygen.

Dissolution of oxygen increases the wettability of oxides by liquid metals even though the oxygen concentration may be as low as a few ppm [14] (see Fig. 3). To explain this phenomenon, Naidich [3] proposed that oxygen in solution in the metal associates with metal atoms to form clusters having a partially ionic character, which results in charge transfer from the metal to the oxygen atoms. These clusters can develop coulombian interactions with iono-covalent ceramics and, as a consequence, adsorb strongly at the metal/oxide interfaces (Fig. 4). It has recently be shown [15] that the beneficial effect of oxygen can be enhanced by adding to the metal M a solute B capable of developing strong solute-solute interactions with dissolved oxygen. The thermodynamic requirement for this is that $\varepsilon_O^B \ll 0$, ε_O^B being Wagner's first order interaction parameter, defined by :

$$\ln \gamma_O = \ln \gamma_{O(M)} + \varepsilon_O^B X_B + \cdot \tag{7}$$

where $\gamma_{O(M)}$ and γ_O are the activity coefficients of oxygen in pure M and in the M-B alloy, respectively, and X_B the molar fraction of B in M. The more highly negative ε_O^B is, the stronger the interaction is between B and O, and the greater is the interfacial activity of a cluster of O and B atoms. Examples of this effect are found in O and Cr clusters in Cu/Al$_2$O$_3$ [15], or O and Si clusters in Au/Al$_2$O$_3$ [16].

In conclusion, non-reactive solutes can improve wetting on iono-covalent oxide, but even in the most favourable cases, the contact angles remain above 60°. In principle, lower contact angles, which are needed in some cases (e.g. in the joining of ceramics by brazing alloys), can be expected using a reactive solute B. However, the central question is how to select B, no model of general acceptance being available relating wettability to reactivity. In the following sections, experimental results of reactive wetting will be reviewed in order to identify the governing thermodynamic and physico-chemical parameters.
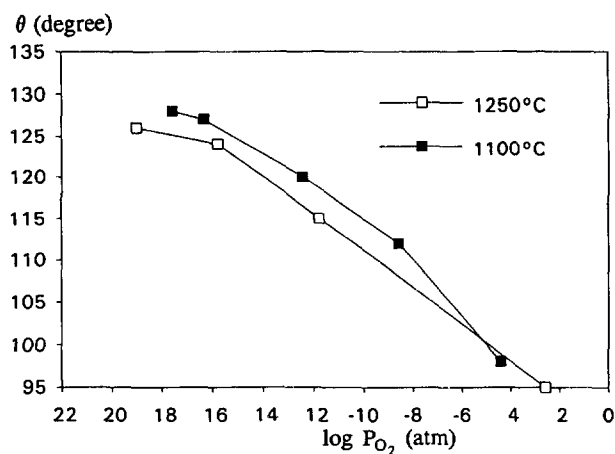

Fig. 3.

Fig. 4.

Fig. 3. — Variation of the contact angle with the oxygen partial pressure for the Cu/sapphire system. The orientation of the sapphire surface is 60° to the c-axis. From [14].
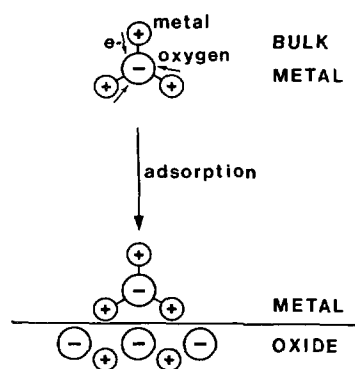
Fig. 4. — Adsorption of oxygen-metal clusters at a metal/oxide interface according to the model of Naidich [3].

3. Wetting in reactive metal/oxide systems.

3.1 EXPERIMENTAL RESULTS. — In pure metal/oxide systems, the oxido-reduction reaction is generally used to discuss reactivity [3, 17]. In order to simplify notations, we will now focus on the case of the reduction of alumina by a metal M with the formation of a MO oxide, according to a reaction of the type :

$$\frac{3}{2} (M) + \frac{1}{2} Al_2O_3 \Leftrightarrow \frac{3}{2} MO + (Al) . \tag{8}$$
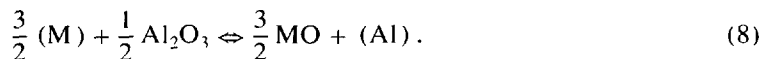
An approximate criterion for reactivity at the interface is that the standard Gibbs free energy change ΔG_R^0 of this reaction is negative, that is :

$$\Delta G_R^0 = \frac{3}{2} \Delta G_{MO}^0 - \frac{1}{2} \Delta G_{Al_2O_3}^0 < 0 \tag{9}$$

where ΔG_{MO}^0 and $\Delta G_{Al_2O_3}^0$ are the standard Gibbs free energies of formation of MO and Al_2O_3.

However, this criterion does not take interactions between the dissolved Al and the matrix M into account. Therefore, a better criterion is the degree of progress of the interfacial reaction (reaction (8)), α_{eq}, which can be obtained by calculating the equilibrium concentration of Al in liquid M, coming from the dissolution of Al_2O_3. α_{eq} is thus equal to the difference between final and initial (that is zero in our case) mole fraction of Al, X_{Al}. In the case $X_{Al} \ll 1$, the equilibrium X_{Al} for reaction (8) is written as follows (the detailed calculation is described in the Appendix) :

$$X_{Al} = \exp - \left(\frac{\Delta G_R^0 + \overline{\Delta H}_{Al(M)}^\infty}{RT} \right) = \exp - \left(\frac{\Delta G_R^*}{RT} \right) \tag{10}$$

where $\overline{\Delta H}_{Al(M)}^\infty$ is the partial enthalpy of mixing of Al at infinite dilution in M. Note that, as we will see in section 3.3, at moderate or high values of the quantity $\Delta G_R^*/RT$, the real reactivity consists in a simple dissolution of the oxide substrate in the liquid metal and not in an oxido-reduction reaction. Thus, the term $\Delta G_R^*/RT$ will not be used to quantify the real reactivity for a given system, but only to establish a rough scale of relative reactivity for different systems.

$\Delta G_R^*/RT$ is calculated for different pure metal/oxide systems, for which experimental values of contact angle are available. Working temperatures lie between 1 000 K and 2 200 K. For the non-reactive systems M/Al$_2$O$_3$ and M/SiO$_2$, that is systems for which $X_{Al(M)}$ or $X_{Si(M)}$ calculated by equation (10) are of the order of 10^{-6}, data respectively come from compilations of Chatain et al. [8] and Sangiorgi et al. [10]. Most of the results concerning reactive systems are taken from Naidich [18], also reported in his review [3]. For the others, references are specified in the caption of figure 5. Data of the standard Gibbs free energies of formation of oxides, needed for the calculation of ΔG_R^*(Eq. (10)), are provided by references [19-21]. Concerning the $\overline{\Delta H}_{M'(M)}^\infty$ data (M' being the metallic species of the oxide substrate), values calculated by Miedema [22] are used.

Experimental contact angles θ are represented in figure 5 as a function of the parameter $\Delta G_R^*/RT$ for a number of pure metal/oxide couples. We observe that an increase of $\Delta G_R^*/RT$ is correlated with an increase of θ. Moreover, at high values of $\Delta G_R^*/RT$, θ tends towards a limit, $\theta \approx 140°$, a value typical of noble metals (e.g. Au and Ag) on alumina and silica. In the same way, when $\Delta G_R^*/RT \to 0$, θ decreases steeply and perfect wetting can be reached (ex. Ti, Zr/MgO). A similar correlation between reactivity and wettability has already been observed by Naidich [3] and by Nicholas [17] using the function ΔG_R^0.
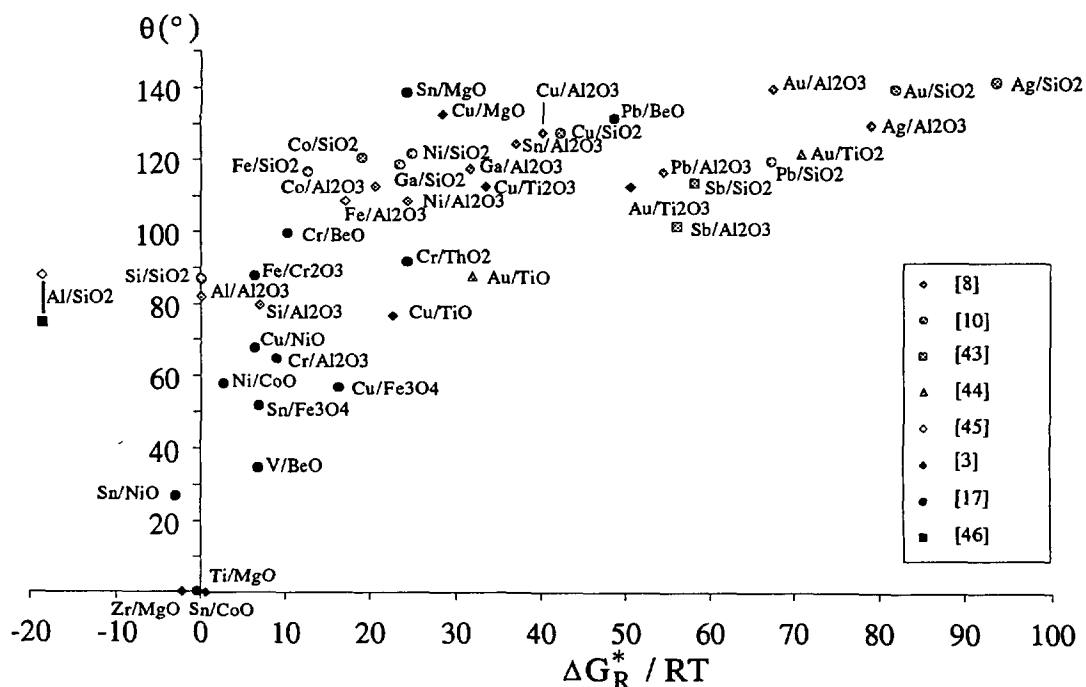
Fig. 5. — Experimental contact angles *versus* $\Delta G_R^*/RT$ for pure M/oxide systems. The reactivity increases from right to left.

However, the correlation of figure 5 presents some limitations, as can be seen from the great scatter of the $(\Delta G_R^*/RT, \theta)$ couples. Indeed, $\theta \approx 80°$ is obtained for highly reactive systems, such as Al/SiO$_2$ for which an intense reaction is observed experimentally, as well as for systems with a negligible reactivity, for example Al/Al$_2$O$_3$ and Si/Al$_2$O$_3$. In all cases, the work of adhesion W has a typical value of 900-1 000 mJ/m^2. Likewise, for $\Delta G_R^*/RT \approx 25$, contact angles lie between $\theta = 80°$ for Cu/TiO ($W = 1$ 600 mJ/m^2) and $\theta = 140°$ for Sn/MgO ($W = 150$ mJ/m^2). In the case of these two non-reactive couples, W varies by one order of magnitude. These comments on the absence of any simple relation between reactivity and wettability are also valid for other kinds of ceramics. A typical example is the reactive system Al/SiC, characterized by the same contact angle ($\theta \approx 55°$ at 1 373 K) than the Al-Si/SiC system, for which reactivity (Al$_4$C$_3$ precipitates at the interface) has been suppressed by presaturation of Al in Si [23].

Any model of reactive wetting should explain both the general tendency of improvement of wetting with reactivity and the strong scatter of results around the θ-$\Delta G_R^*/RT$ curve. In the next section, we will briefly present the different attempts of interpretation of reactive wetting.

3.2 ATTEMPTS OF THEORETICAL DESCRIPTION OF REACTIVE WETTING. — Despite some progress, reviewed by Laurent [23], there is at the present time no theory of general acceptance capable of describing satisfactorily reactive wetting, that is wetting followed by material transfer at the solid/liquid interface. According to Laurent, the smallest contact angle possible in a reactive system is given by :

$$\cos \theta_{min} = \cos \theta_0 - \frac{\Delta \sigma_i}{\sigma_{LV}} - \frac{\Delta G_i}{\sigma_{LV}} \qquad (11)$$

where θ_0 is the contact angle of the liquid on the substrate in the absence of any reaction. $\Delta\sigma_r$ takes into account the change in interfacial energies brought about by the interfacial reaction. ΔG_r is the change in free energy per unit area, released by the reaction of the material contained in the « immediate vicinity of the metal/substrate interface » [24].

Two different interpretations of reactive wetting exist, based (i) on the assumption that the predominant contribution is the Gibbs free energy term ΔG_r [3, 24, 25], i.e. a parameter related with the *intensity* of interfacial reactions, and (ii) on the assumption that the predominant contribution is the interface energy term $\Delta\sigma_r$ [26-28], i.e. a parameter related with the detailed *chemistry* and *structure* of interfacial reaction products.

3.2.1 *Models based on the ΔG_r term.* — This contribution to reactive wetting was first proposed by Aksay *et al.* [24] and by Naidich [3] who considered that the reaction between the liquid and a fresh, unreacted, solid surface at the periphery of the drop increases the driving force for wetting. Aksay *et al.* argued that, because the rate of interfacial reaction is maximum at the very first instants of contact between the liquid and the solid, the effect of the ΔG_r term is strongest during these early instants of contact. Thereafter, the interface becomes saturated in reaction products and the overall reaction is controlled by diffusion. Consequently, the reaction kinetics slow down and the contact angle would increase and gradually approach the equilibrium value (Fig. 6). Note that, in practice, such a dewetting would be difficult to observe as the triple line can be blocked by asperities (roughness) created by the reaction itself in the course of wetting.
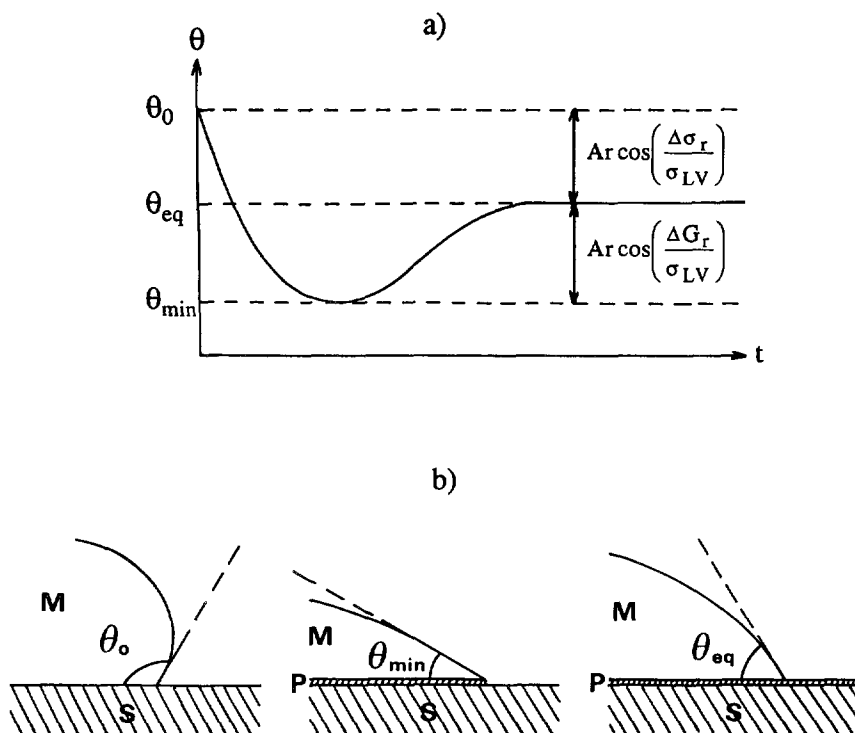

Fig. 6. — Schematic representation of the reactive wetting of a metal M on a solid S with the formation of a reaction product P according to the model of Aksay *et al.* [24]. a) Variation of the contact angle with time at a constant temperature. b) Corresponding contact angles in a sessile drop experiment.

However, major difficulties lie in the calculation of the ΔG_r term. Indeed, the coupling conditions of the time-dependent interfacial reaction with the kinetics of wetting are unknown. As a consequence, a rigorous calculation of the thickness of the reaction zone in « the immediate vicinity of the interface » is still not possible and choices differing by a factor 10 have been made [3, 24, 25]. Clearly, such calculations can only provide order of magnitude estimates of ΔG_r.

Despite these difficulties, Naidich [3] performed calculations of ΔG_r assuming that the « reactive » interface consists of two monolayers, one at the liquid-side of the interface, the other at the solid-side. Supposing that chemical equilibrium in this region is reached rapidly, ΔG_r is estimated by :

$$\Delta G_r = \int_0^{\alpha_{eq}} \Delta G_R \, d\alpha \tag{12}$$

where α and α_{eq} are respectively the current and equilibrium degrees of progress of the reaction and ΔG_R the Gibbs free energy of the reaction per unit area. Using this model, Naidich calculated ΔG_r for some M/oxide reactive systems like Sn/NiO, Ti/MgO and Zr/MgO (but also Ti/C, Zr/C, Si/C..) and found that the calculated values of W agree, within a factor two, with the experimental ones [3]. It has been concluded that ΔG_r represents the predominant contribution to reactive wetting and that an *intense reaction* is required to obtain a good wetting of a liquid on a solid [29, 30]. Thus, neglecting the $\Delta\sigma_r$ term, this model provides an explicit relation between wettability and reactivity (Eqs. (11) and (12)), relation which seems to confirm the empirical correlation of figure 5.

However, using such a purely energetical model, it is not possible to explain neither the differences of θ observed for a same $\Delta G_R^*/RT$ value (for example between Sn/MgO and Cu/TiO), nor, on the contrary, the fact that wettability is similar in systems with a very different reactivity (for example Al/SiO$_2$ and Si/Al$_2$O$_3$). Moreover, from the Al/SiO$_2$ example but also from results on the Fe/SiC system [31], in which wettability is rather poor ($\theta \approx 70°$) despite a great reactivity (a reaction zone of several hundreds of microns is formed in a few minutes), it appears that the occurrence of an intense reaction is not a *sufficient* condition to obtain a good wettability, i.e. $\theta \ll 90°$. This condition is neither *necessary*, is clearly shown by results given in table II for some metal/metal or metal/ceramic combinations without any significant reactivity (for example, in the case of the metallic systems given in this table, solubility of Fe in liquid Pb and Ag is less than 100 ppm). In these examples, the good wetting observed is due to the establishment of strong chemical bonds at the interface between the metal and the substrate : bonds of metallic type (for example in Pb/Fe) or covalent type (for instance in Si/SiC).

Table II. — *Examples of good wetting obtained for liquid/solid systems with a negligible reactivity.*

T (K)	Liquid	Solid	θ(°)	Reference
1273	Pb	α-Fe	32	[39]
1240	Ag	α-Fe	40	[40]
1690	Si	SiC	34	[3,41]
1100	Al	TiN	45	[42]

3.2.2 *Models based on the $\Delta\sigma_r$ term.* — In order to appreciate the relative importance of ΔG_r and $\Delta\sigma_r$ terms, two series of experiments were recently carried out, in which each of these two terms was successively kept constant. In the first series, the wetting of a CuPd-Ti alloy of

fixed composition has been studied on three oxide substrates of different thermodynamic stability (aliumina, mullite and silica) [32]. In these systems, Ti reacts with all oxides leading to the same interfacial product (Ti_2O_3) but reactivity, as evidenced by the thickness of the Ti_2O_3 layer, differed from one oxide to other by one to two orders of magnitude. Despite this great difference, wettability on the three substrates is nearly the same (Tab. III). In another discriminant experiment, the inverse situation has been obtained, i.e. a change of interfacial chemistry occurs at a fixed value of the Gibbs free energy of the metal/ceramic reaction. Adding Ti to NiPd alloys placed on alumina substrates, a series of wetting transitions is observed at particular values X_{Ti}^*, with a change in the type of Ti-oxide formed at the interface (Fig. 7) [33]. Since when $X_{Ti} = X_{Ti}^*$ the thermodynamic driving forces for the interfacial reactions are the same, the change $\Delta\theta$ can only be explained by a change in $\Delta\sigma_r$.

From these two studies and other experiments (on Cu-Ti/Al_2O_3 [26] and NiPd-Ti/C [27]), it has been concluded that at least in metal/ceramic systems with a weak or moderate reactivity, the predominant contribution to reactive wetting is the term $\Delta\sigma_r$, reflecting interface energy

Table III. — *Wettability and interfacial chemistry of* CuPd-Ti ($X_{Ti} = 0.15$)/*oxide sessile drop experiments* [32].

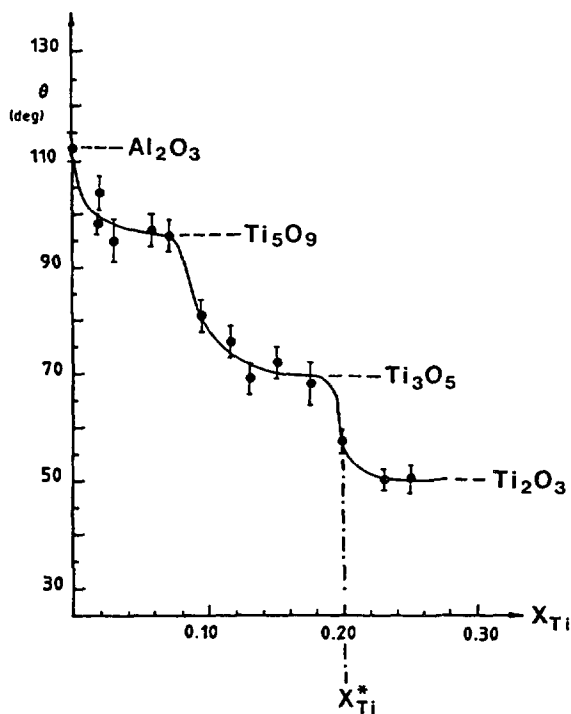| substrate	θ (°)	interfacial product	thickness (μm)
alumina	34	Ti_2O_3	≈ 0.5
mullite	32	Ti_2O_3	≈ 1
silica	35	Ti_2O_3	≈ 10

Fig. 7. — Wetting transitions observed at particular values of the molar fraction of Ti for the reactive NiPd-Ti/alumina system at $T = 1\,523$ K. Each plateau corresponds to a particular Ti oxide identified at the interface by microprobe analysis. From [33].

change during the reaction, rather than the transient ΔG_r term. Accordingly, an interfacial reaction could be a way to modify *in situ* the metal/ceramic interface. In practice, to exploit interfacial reactions as a means of promoting wetting without causing massive reactions between the metal and the ceramic, one can alloy a non-reactive base metal with controlled quantities of reactive solute additions, leading to the optimum relation between wettability and reactivity. Let us thus consider, at a given temperature, a reactive solute B dissolved in a non-reactive matrix M on an oxide substrate, for instance an alumina substrate. The chemical interaction in this system can be described by the dissolution of alumina in the alloy [26, 34] :

$$Al_2O_3 \Leftrightarrow 2\,(Al) + 3\,(O) \tag{13}$$

possibly followed by the precipitation of a B oxide at the interface, for example :

$$2\,(B) + 3\,(O) \Leftrightarrow B_2O_3 \,. \tag{14}$$

For small values of the mole fractions of B and Al, the equilibrium mole fraction of dissolved oxygen X_O^D for reaction (13) (the superscript D stands for dissolution) will be given by the equation :

$$X_O^D = K \exp\left(-\frac{3}{5}\,\varepsilon_O^B\,X_B\right) \tag{15}$$

where K is a constant [34] and ε_O^B Wagner's first-order interaction parameter between the O and B solutes defined by equation (7). If $\varepsilon_O^B < 0$, for sufficiently high values of X_B, X_O^D increases rapidly : strong O-B interactions will promote alumina dissolution in the melt, as expected (curves D in Fig. 8).
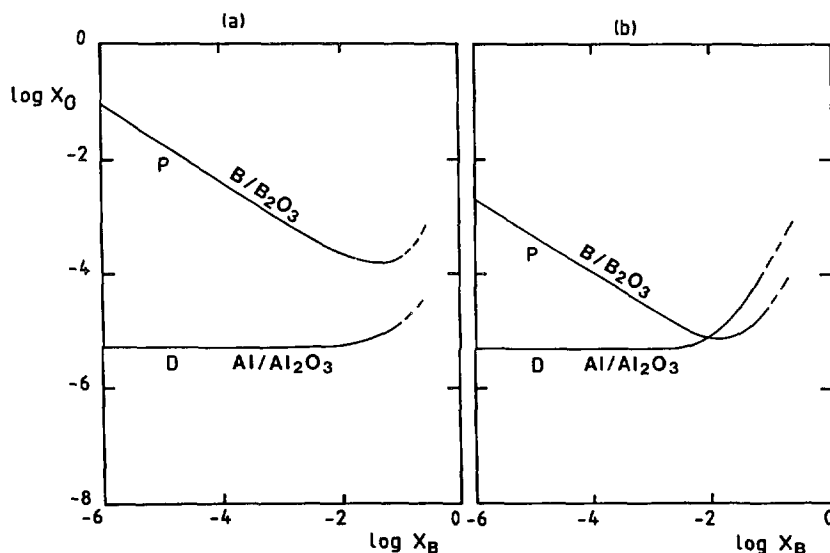

Fig. 8. — Thermodynamics of matrix M-solute B/Al_2O_3 systems ($\varepsilon_O^B < 0$). Curve D gives the logarithm of the mole fraction of oxygen from stoichiometric dissolution of alumina in MB alloys as a function of log X_B. Curve P describes logarithmically the variation of X_O in equilibrium with B_2O_3 as a function of X_B. a) Only dissolution of alumina in the melt occurs. This is the case of Ni-Cr alloys at $T = 1\,773$ K [47]. b) The solute B reduces alumina on the right of the intersection point of the two curves. This occurs for Ni-Ti at $T = 1\,773$ K [34, 48].

Moreover, a solute B satisfying the condition $\varepsilon_O^B \ll 0$ can also lead to precipitation of an oxide B_2O_3 by reaction with the excess oxygen in the alloy. The mole fraction of dissolved oxygen in equilibrium with the B_2O_3 precipitate (reaction (14)), denoted X_O^P, is given by :

$$X_O^P = K' \, X_B^{-2/3} \exp(- \varepsilon_O^B X_B) \tag{16}$$

where K' is a constant [34]. When $X_B \to 0$, X_O^P varies as $X_B^{-2/3}$, i.e. it is a decreasing function of X_B. However, for $\varepsilon_O^B \ll 0$, at higher X_B values, the exponential term in equation (16) predominates and X_O^P increases rapidly with increasing X_B (curves P in Fig. 8). Thus, in both cases of dissolution and precipitation, the concentration of dissolved oxygen increases above a certain value of X_B.

If for the same value of X_B the inequality $X_O^D > X_O^P$ is verified, the solute B will reduce the alumina, forming B_2O_3.

$$Al_2O_3 + 2(B) \Leftrightarrow B_2O_3 + 2(Al) . \tag{17}$$
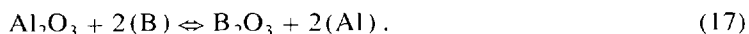
This condition is verified for the Ni-Ti alloy, interactions between oxygen and titanium solutes being very strong ($\varepsilon_O^{Ti} = -100$), but not for the Ni-Cr alloy ($\varepsilon_O^{Cr} \approx -25$). Indeed, additions of Cr up to 20 at.% in Ni do not lead to the formation of a chromium oxide : the only effect of Cr in this matrix is to increase the dissolution of alumina in the alloy. As shown in figure 9, Cr additions in Ni considerably decrease the contact angle of Ni on alumina. The influence of chromium would result from two effects :

i) an increased concentration of dissolved oxygen due to interfacial reactions, i.e. an increased concentration of OM clusters which can be adsorbed at the metal/oxide interface ;

ii) an increased adsorption capability of the OCr clusters as compared with the ONi clusters. Indeed, as chromium is more electropositive than nickel, the charge transfer from chromium to oxygen (or, in other terms, the degree of ionicity of OCr clusters) would be greater than in the case of nickel.
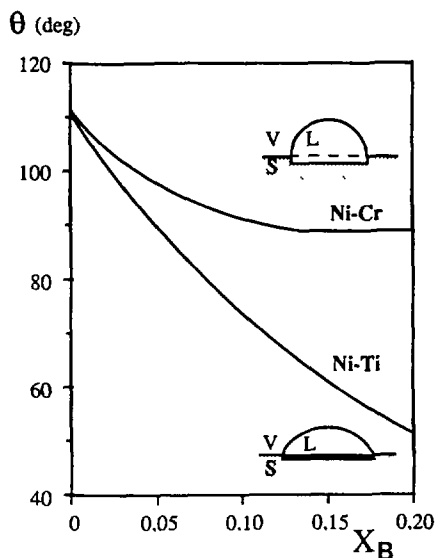

Fig. 9. — Contact angles of Ni-based alloys on alumina as a function of Cr or Ti mole fraction for Ni-Cr [47] (simple dissolution of alumina) and Ni-Ti [34, 48] (dissolution + precipitation of a Ti oxide) at 1 773 K.

Note that for a solute B, the thermodynamic requirements for both i) and ii) effects are the same, i.e. $\varepsilon_O^B < 0$.

In the $Ni-Ti/Al_2O_3$ system, due to strong O-Ti interactions, OTi clusters in Ni must be very tensioactive at metal/oxide interfaces. However, in this case, one must also take into account the effect on wettability of the formation of a continuous Ti_2O_3 layer at the nickel/alumina interface by reduction of alumina. Currently, it is generally accepted that the more metallic in character an oxide is, the more it will be wetted by molten metals [3, 17]. This effect clearly appears in the results of table IV, concerning non-reactive Cu/oxide systems, the metallic-like oxide TiO being more wettable than an iono-covalent oxide like Al_2O_3. Thus, in the $Ni-Ti/Al_2O_3$ system, the replacement of Al_2O_3 by the semi-metallic oxide Ti_2O_3 must increase W and decrease θ. The combination of these two effects, i.e. (a) adsorption of OTi clusters at the *liquid-side* of the interface and (b) formation of a semi-metallic oxide such as Ti_2O_3 at the *solid-side* of the interface can explain the strong decrease in contact angle caused by Ti additions in Ni (Fig. 9).

Table IV. — *Contact angle and work of adhesion of copper on different oxides at* $T = 1\ 423$ K [3].

Oxide	Conduction type	θ (°)	W (mJ/m²)
Al_2O_3	insulator	128	460
Ti_2O_3	semi-metallic	113	740
$TiO_{1.14}$	metallic	82	1460
$TiO_{0.86}$	metallic	72	1650

This influence of Ti is even greater in the case of Cu-Ti alloys on alumina [26, 30] where, due to the higher thermodynamic activity of Ti, the metallic-like TiO oxide is formed at the interface. In that case, wetting becomes nearly perfect (Fig. 10, curve 2), as opposed to the $Cu-Ti/Y_2O_3$ system [30] (Fig. 10, curve 1) where only dissolution of Y_2O_3 into Cu-Ti alloys occurs, producing a significant but limited decrease of θ (from 140° to 80°).

Unlike the effect of Ti additions, adding Ca to Al on Al_2O_3 or SiO_2 substrates has no effect on wetting, in spite of the formation of CaO at the interface [35]. Indeed, the iono-covalent substrate is now replaced by an oxide of the same type.

3.3 INTERPRETATION OF RESULTS ON PURE M/OXIDE SYSTEMS. — Based on the conclusion that the predominant contribution to reactive wetting is the $\Delta\sigma_1$ term, three kinds of behaviour can be distinguished on the curve of figure 5 :

1) For $\Delta G_R^*/RT \gg 0$, that is typically for values of 20 or more, M/oxide couples can be considered, with regard to wettability, as non-reactive systems (i.e. $\Delta\sigma_1 \approx 0$). In that case, the work of adhesion W is ensured by metal/oxide interactions localized at the interface and for iono-covalent oxides can be described by equation (4). The scatter $\Delta\theta$ at a given $\Delta G_R^*/RT$ is essentially due to the variation of the bonding character of the substrates, between insulating oxides and oxides for which cohesion is provided by partially metallic bonds. This explains the dispersion between $\theta = 139°$ for Sn/MgO and $\theta = 77°$ for Cu/TiO or $\theta = 88°$ for Au/TiO.

2) For positive but low values of $\Delta G_R^*/RT$ (of the order of 10), the corresponding contact angles lie between 60° and 100°. A typical example is Cu/NiO ($\theta = 68°$ at 1 473 K). From data
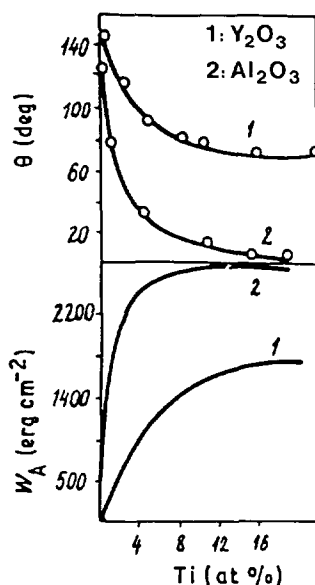
Fig. 10. — Wetting and work of adhesion of Cu-Ti melts on Y_2O_3 and Al_2O_3 at $T = 1\ 423$ K from [30]. Reactivity consists in a simple dissolution of the oxide substrate in the first case, and in a dissolution + precipitation of a Ti oxide at the interface in the second case.

of table V relative to this system and the value $r_O^{Ni} \approx -7$ [36], thermodynamic calculations performed at equilibrium lead to the following value of the molar fraction of oxygen coming from the dissolution of NiO :

$$X_O^D = X_{Ni}^D = 1.5 \times 10^{-2}$$

X_O^D is not high enough to produce precipitation of the copper oxide Cu_2O ($X_O^P \approx 4 \times 10^{-2}$). Thus, the only possible effect in the Cu/NiO system is the adsorption of dissolved oxygen. This adsorption leads to a much lower contact angle than for the Cu/Al_2O_3 system [14] (Fig. 3) for the same value of X_0 (68° against 100°). This can be explained by an increased adsorption capability of ONi clusters with respect to OCu clusters, as indicated by the negative value of r_O^{Ni}.

Wettability in systems like Sn/Fe_3O_4 ($r_O^{Fe} \approx -50$ [36]), Cu/Fe_3O_4 ($r_O^{Fe} \approx -540$ [36]) or Fe/Cr_2O_3 ($r_O^{Cr} \approx -10$ [37]) can be interpreted in the same way. Moreover, the positions of the Al/Al_2O_3 and Si/Al_2O_3 systems in figure 5 suggest that these couples, considered previously as non-reactive systems [8], fall into the same category, in spite of the very low solubility of oxygen in Al and Si respectively.

Table V. — *Thermochemical data at $T = 1\ 473$ K relative to the* Cu/NiO *system.*

reaction	Gibbs free energy (kJ)	reference
$(Ni) + \frac{1}{2}[O_2] \Leftrightarrow \langle NiO \rangle$	$\Delta G_f^0 = -111$	[20]
$2(Cu) + \frac{1}{2}[O_2] \Leftrightarrow \langle Cu_2O \rangle$	$\Delta G_f^0 = -60$	[19]
$(Ni) \Leftrightarrow (Ni)_{Cu}$	$\overline{\Delta G}_{Ni(Cu)}^{E\infty} = +12\ 5$	[20]
$\frac{1}{2}[O_2] \Leftrightarrow (O)_{Cu}$	$\overline{\Delta G}_{O(Cu)}^{E\infty} = -19$	[43]

3) For values of $\Delta G_R^*/RT$ close to zero or negative, reaction produces a new phase at the interface. Nevertheless, wettability will depend on the bonding character of this interfacial layer and two cases can be distinguished :

• the first case corresponds to the replacement at the interface of an iono-covalent oxide by another of the same type. For this kind of systems, no important improvement of wetting is expected. Al on SiO_2 provides an example of intense reactivity, involving the reduction of SiO_2 to form Al_2O_3 at the interface, and a slight liquid enrichment in Si. As the iono-covalent oxide SiO_2 is replaced by an oxide of the same type, the contact angle of Al on SiO_2 ($\theta \approx 80 \pm 5°$ at 1 073 K) is therefore close to that of Al on Al_2O_3. The same explanation is valid for the Al-Ca on Al_2O_3 or SiO_2 systems previously mentioned, for which Ca additions do not improve wetting because the interfacial product (CaO) has roughly the same bonding character than the substrate ;

• the second case corresponds to the replacement at the interface of an iono-covalent oxide by a metallic one. A typical example of this situation is Ti/MgO [3]. Liquid titanium can dissolve a large quantity of oxygen (a few at.% O) and form a metallic-like oxide, such as TiO, even solid solutions of Ti with high oxygen contents. The perfect wetting observed for this system (Fig. 5) can be explained by the double *in situ* modification of the interface : the adsorption of oxygen at the liquid-side and the formation of a metallic-bonded phase at the solid-side.

These features can also explain the excellent wetting obtained for Sn on NiO or CoO (Fig. 5). The reduction of these substrates by liquid Sn is possible and the amount of dissolved Ni or Co produced by this reaction is greater than that needed to precipitate the intermetallics Ni_3Sn or Co_3Sn_2 at the temperature of the experiment.

4. Conclusion.

For systems with weak or moderate reactivity, the governing parameter of reactive wetting appears to be the term reflecting interfacial energy change $\Delta\sigma_i$, rather than the transient Gibbs free energy term ΔG_r. However, the importance — and even the predominance — of this last term must not be excluded in some cases, for instance when an intense reaction strongly localized at the triple line occurs.

Pure metal/oxide systems can be divided into three categories :

i) in systems for which $\Delta G_R^*/RT \gg 0$ (typically greater than 20), θ is about 120°. Weak metal/oxide bonds are localized at the sharp interface and the work of adhesion can be described by equation (4) ;

ii) in systems characterized by $\Delta G_R^*/RT \approx 10$, an improvement of wetting is obtained with regard to the preceding case ($\theta \approx 80°$), due to the effect of adsorbed oxygen at the interface, produced by the dissolution of the oxide substrate. This effect is greatly enhanced by the formation of metal-oxygen clusters ;

iii) when $\Delta G_R^*/RT \leqslant 0$, both dissolution of the oxide substrate and precipitation of a new phase occur. Wetting will depend on the nature of this interfacial layer : for iono-covalent compounds, a case ii) behaviour will be observed whereas for metallic compounds (metallic-like oxides or intermetallics), nearly perfect wetting can be expected.

In order to produce a strong improvement of wetting of a non-reactive metal by an alloying element B, two conditions have to be satisfied :

i) the thermodynamic parameter ε_O^B must be very negative. Then, the solute B can modify both liquid and solid sides of the interface, forming at the liquid-side an adsorption layer rich in OB clusters and at the solid-side a new phase ;

ii) this new phase must be at least partially metallic-bonded.

It is noted that, although this work focused on oxide substrates, some of these concepts can be applied to other kinds of ceramics. For example, the contact angle of copper on a covalent carbide such as B_4C is very high (136° [3]), while it is only a few tens of degrees on metallic-like carbides such as chromium or molybdenum carbides [3]. However, metallicity is not the only criterion for good wettability of non-oxide ceramics. Indeed, good wetting has been observed for some metals on covalent ceramics, for instance for liquid silicon (which is a metal) on silicon carbide (Tab. II).

Despite the significant improvements in our knowledge of physico-chemical and energetical properties of metal/ceramic interfaces gained in the past 10 years, further experimental and theoretical work is needed, especially for the non-reactive and very reactive couples : for the non-reactive metal/ceramic systems, because a physical description of the interface at an atomic level is still missing, and for the very reactive systems in order to evidence experimentally and to model theoretically the transient contribution to the wetting driving force, ΔG_i, predicted by general considerations.

Appendix.

The thermodynamic equilibrium condition for reaction (8) is written as follows :

$$\Delta G_R^0 + RT \ln a_{Al} = 0 \qquad (A.1)$$

where a_{Al} is the thermodynamic activity of Al in the liquid, a_M supposed equal to unity. Assuming that the melt is a regular solution, the activity coefficient of Al, γ_{Al}, is given by :

$$RT \ln \gamma_{Al} = \overline{\Delta H}_{Al(M)} \qquad (A.2)$$

$\overline{\Delta H}_{Al(M)}$ being the partial enthalpy of mixing of Al in M. From relations (A.1) and (A.2), the equilibrium mole fraction of Al becomes :

$$X_{Al} = \exp - \left(\frac{\Delta G_R^0 + \overline{\Delta H}_{Al(M)}}{RT} \right) = \exp - \left(\frac{\Delta G_R^*}{RT} \right) . \qquad (A.3)$$

In this equation, $\overline{\Delta H}_{Al(M)}$ depends normally on X_{Al}.

$$\overline{\Delta H}_{Al(M)} = \lambda (1 - X_{Al})^2 = \overline{\Delta H}_{Al(M)}^\infty (1 - X_{Al})^2 \qquad (A.4)$$

For small X_{Al}, $\overline{\Delta H}_{Al(M)}$ is thus constant and equal to its value at infinite dilution of Al in M (Henry's law). $\overline{\Delta H}_{Al(M)}^\infty$ is used in our calculations, which can in consequence only provide a rough estimate of reactivity. Indeed, when $\Delta G_R^* \to 0$ then $X_{Al} \to 1$ and the hypothesis $a_M = 1$ is no more valid. Moreover, the replacement of $\overline{\Delta H}_{Al(M)}$ by $\overline{\Delta H}_{Al(M)}^\infty$ leads to an overestimation of $|\overline{\Delta H}_{Al(M)}|$ and an underestimation of ΔG_R^* for negative $\overline{\Delta H}_{Al(M)}$, in that case, reactivity is over-estimated.

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