Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 27 (2007) 3307–3310
www.elsevier.com/locate/jeurceramsoc

A general law for liquid metal-onto-ceramic wetting: An electrostatic approach

Diego Gómez-García *, Felipe Gutiérrez-Mora, Ángela Gallardo-López, Arturo Domínguez-Rodríguez

Departamento de Física de la Materia Condensada, Facultad de Física, Universidad de Sevilla, Apartado 1065, 41080 Sevilla, Spain

Available online 2 April 2007

Abstract

During the last decades, an intense research effort has been carried out to predict and model the equilibrium reactive wetting contact angle of liquid metals onto diverse ceramic surfaces. The experimental results display a large scattering, which has been attributed to several causes: degree of purity of the liquid metal, adsorption, chemical reactions along the liquid–solid interface, etc.

This work presents a model to explain such results. It considers as a basic tool the presence of an electrostatic field generated by the metal impurities-ceramic surface charge transfer. The addition of the corresponding electrostatic force to the Young–Dupré equilibrium equation modifies the equilibrium contact angle in ceramics–metals reactive wetting. The theoretical values are in excellent agreement with the reported values in the literature. Thus, charge transfer and the electrostatic effects associated to that transfer constitute a landmark for the comprehension of the equilibrium wetting angle in metal–ceramic systems.

Keywords: Interfaces; Wetting

1. Introduction

Metal–ceramic systems constitute a keystone in the emerging field of materials science of advanced materials due to the synergy of the outstanding electromagnetic properties of metals together with the excellent structural properties of ceramics. In order to co-sinter such challenging materials, liquid-phase sintering and infiltration of metals onto ceramic systems is a key objective to accomplish. At this point, a major drawback is the fact that most pure metals display obtuse contact angles on high melting point ceramics[1,2]; i.e. limited wetting of metals onto ceramic systems, which restricts potential applications such as brazing. Moreover, the equilibrium wetting angle is very well-reported to be quite sensitive to the presence of metal impurities in the liquid metal.[1] The equilibrium sessile-drop of liquid metal onto a ceramic surface, as well as the kinetics of the wetting process when a reactive element is added to the metal liquid to promote wetting, have been studied by several authors.[2,3] Two leading theories have been proposed to account for these phenomena. The first one,[2] known as reaction product control (RPC), states that wetting is controlled by reactions taking place at the interface. Enhanced wetting is just a consequence of local reactions happening when certain reactive impurities are added. This theory was severely criticized by Saitz et al.[3]; who gave an alternative explanation. According to these authors, wetting is controlled uniquely by the adsorption of some elements to the ceramic surface, so likely chemical reactions play no role in this phenomenon. The kinetics of wetting is then essentially controlled by the presence of a ridge at the front of the triple line of phase coexistence. A reanalysis of the RPC theory has been recently made by their authors,[4] with the corresponding reply to the facts pointed out by Saiz et al.

It is well known that wetting is critically affected by the presence of certain reactive elements, among them, titanium, vanadium, chromium, zirconium, niobium and hafnium have all shown to induce strong decrease in wetting angles. Although some chemical reactions have been proposed to take place with some of these elements, particularly titanium,[5] in other cases it has not been possible to identify clearly the reaction products.

A remarkable contribution has been provided by Swiler and Loehman,[6] who have applied improved molecular dynamics simulations applicable to wetting to model the

* Corresponding author.
E-mail address: dgomez@us.es (D. Gómez-García).

0955-2219/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.02.181

aluminium–alumina system. The method, known as embedded atom method (EAM), implies a coupling of an atom-density-potential embedding potential with a simple pair-wise potential to model the energy of a simple atom in the metal where each atom interacts with the overall electron gas as well as the atoms in its vicinity. This method has been demonstrated to be applicable to liquid metal–metal systems,[7] however, when facing up with metal–ceramic systems, a significant approach has revealed to be crucial: since metals have very large dielectric constants, the previously cited authors[6] propose that a surface charge is induced in the metal as a response to the partially ionic character of the surface in contact with it. This charge layer mirrors that of the ceramic, providing an additional attractive potential. The authors added such term to their simulation code and succeeded in reproducing the main features of the aluminium–alumina system. This work strongly suggests that electrostatic effects should play a key role when determining the equilibrium wetting angle of liquid metal–ceramics systems.

This work proposes a clear and simple model to account for a mechanism which allows the reactive elements to alter the equilibrium wetting angle of a metallic drop onto a ceramic surface.

2. Modelling and discussion

Let us consider a metallic drop at rest on a ceramic surface. According to the well-established Young–Dupré equation,[8] the static contact angle is given by:

$$\cos\,\theta_0 = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \tag{1}$$

where θ_0 is the equilibrium contact angle between the liquid sessile drop and the ceramic interface, γ_{sv}, γ_{lv} and γ_{sl} are the forces per unit area (surface tension) on the solid and liquid surfaces and on the solid–liquid interface, respectively. This equation is valid in conditions of static mechanical equilibrium. Our model introduces an additional electrostatic force at the liquid–vapour interface, whose origin is discussed afterwards. The force scheme is modified as displayed in Fig. 1. The electric force per unit area, denoted as f_E, is normal to the interface at the point of contact due to the metallic character of the drop, according to the general rule of electrostatics. Mechanical equilibrium requires the following equation to be satisfied:

$$\cos\,\theta = \cos\,\theta_0 + \frac{f_E}{\gamma_{lv}}\sin\,\theta \tag{2}$$

This equation represents the mechanical equilibrium condition for the forces parallel to the metallic drop–ceramic interface, and θ_0 is the contact angle between the liquid drop and the ceramic interface when no electrostatic force is present. Thus, it is possible to attain:

$$\cos\,\theta = \cos\,\theta_0 \frac{1 - \sqrt{1 - (1 + (f_E^2/\gamma_{lv}^2))(1 - (f_E^2/\gamma_{lv}^2\,\cos^2\,\theta_0))}}{1 + (f_E^2/\gamma_{lv}^2)} \tag{3}$$

Given the two solutions for $\cos\theta$ obtained from Eq. (2), the one displayed above is the only one which tends asymptotically to $\theta = 0$ when the ratio $f_E/\gamma_{lv} \to \infty$, so that complete wetting is expected when the electric force, being attractive, becomes intense enough. Let us admit θ_0 to be equal to 115° to allow a direct comparison with reported results for the titanium–copper–alumina system.[3] The contact angle from Eq. (3) is plotted versus the ratio f_E/γ_{lv} in Fig. 2, along with the reported values for the contact angle between a liquid metal copper and alumina as a function of the amount of titanium impurities dissolved in the liquid metal. The agreement is reasonably good despite the large scattering reported for very low wetting angles.

The origin of the electrostatic force altering the contact angle on wetting stems from the charge transfer from metal impurities in the ceramic surface. Such charge transfer takes place

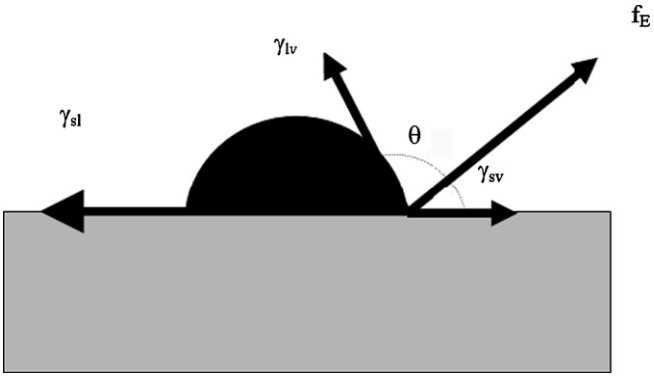

Fig. 1. Scheme of the applied forces on a sessile drop at mechanical equilibrium in the presence of an electrostatic force.

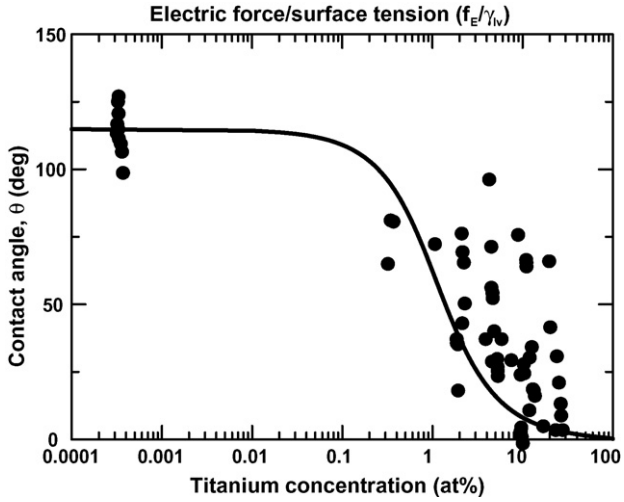

Fig. 2. Experimental outputs for the dependence of the wetting angle of a copper drop onto a surface of alumina or alumina-silver vs. the amount of titanium impurities within the liquid copper, according to the data collected by Saitz et al.[3] Titanium impurities can be ionised through the transfer of an electron to the alumina surface. That originates a separation of charge, and hence an electric field and an electric force. The theoretical prediction for the dependence of the contact wetting angle vs. the electric force (Eq. (2)) is plotted (top *x*-axis). The correlation between the theoretical law and experimental data is quite reasonable. Moreover, the electrostatic force is expected to be proportional to the amount of charged impurities (bottom *x*-axis).

as long as the ionization energy of the metal impurity is very close to the ceramic bandgap. In such a case, electron transfer may occur by means of tunnelling. This mechanism is similar to that proposed by Mott-Cabrera for low temperature oxidation of metals.[9] Although it may be argued that the potential barrier is too high for electron tunnelling to proceed, the negligible barrier length compensates such limitation.

A charge transfer mechanism is reported[10] to explain the adhesion work of liquid metals onto ceramic surfaces. Such adhesion work is linearly proportional to the bandgap of the ceramics. Concerning the particular case described in literature and displayed in Fig. 2, the alumina bandgap[11] is very close to 7 eV. First ionization energy of titanium, vanadium, chromium, zirconium, niobium and hafnium, the most reactive elements enhancing wetting, are given in Table 1. All values are in good agreement with the alumina bandgap, so that electron transfer may occur.

A major consequence of the electron transfer is the appearance of coulombian attractive forces, which are proportional to the amount of charged impurities. This fact is illustrated in Fig. 2: the bottom *x*-axis reports the titanium impurity concentration, impurities being expected to be charged. This charge is the result of the electron transfer from the titanium impurities to the ceramic layer contacting the liquid drop. The top *x*-axis reports a normalized version of the electrostatic force. The proportionality between them is evident.

Additional experimental support to the charge transfer statement has been given by Derby et al.[5] Making use of neutron reflection studies, these authors claim that reaction wetting of several liquid metals (with the addition of a certain amount of titanium) onto alumina is produced by segregation of a thin layer of titanium. This titanium segregation undergoes a localised redox reaction with the ceramic, which is just the consequence of the charge transfer mechanism described above. Similarly, molecular dynamics simulation studies in the aluminium–alumina system cited previously[6] have shown a partial oxidation of liquid aluminium and a partial reduction of the alumina surface which would induce a small layer of a suboxide.

The mechanism proposed thereon can be extended to systems other than metallic drops on alumina surface. A model physical system in which a similar mechanism seems to be operative is the one formed by nickel drops deposited onto an yttria tetragonal zirconia surface (YTZP). It is well-known that nickel shows a very poor wetting, if any, in such a system.[13] However, wetting takes place if an ionised form of nickel is deposited onto the same surface.[13] Such phenomenon can be explained quite easily: it is a reported fact that yttrium segregation takes place in many YTZP ceramic systems, producing an yttrium concentration in excess of the nominal one.[14] In consequence, a net surface charge exists on YTZP, leading an electric field emerging from the surface. Such electrostatic field is responsible for an electrostatic force to operate on cations. Such mechanism will induce an enhanced wetting to take place. This explanation accounts for the optimum wetting features of nickel oxide onto the YTZP surfaces.

The mechanism and model presented in this paper can certainly be a crucial issue for wetting to be favoured during metal–ceramic sintering through the addition of the suitable metal impurity. It is not opposed to the RPC model since nothing is said about the kinetics of the wetting process, which is very likely to be controlled by a mechanism such as that pictured in the 'PRC' model. Our model explains the ultimate mechanism at the equilibrium sessile drops as well as the origin of the possible chemical reactions which may occur. From a basic viewpoint it represents an essential term to be added for an accurate analysis of equilibrium contact angles in metal–ceramic systems.

Table 1
First ionization energies for reactive elements enhancing wetting, according to data reported in the literature[12]

Element	First ionization energy (eV)
Ti	6.85
V	6.78
Cr	6.80
Zr	6.70
Nb	6.80
Hf	6.86

All of the present values are close to 7 eV.

3. Conclusions

Equilibrium contact angles in liquid metal–ceramic systems have been explained in terms of the electrostatic force originated as a result of charge transfer process at the metal–ceramic interface. Our model explains qualitatively and quantitatively the wetting results in systems reported in the literature, and gives an insight into the mechanism operating when impurities are added to the liquid.

Acknowledgements

This research work has been supported by the Spanish "Ministerio de Ciencia y Tecnología" through the CICYT project "MAT2003-04199-C02-02. We thank Dr. N. García from the Spanish "Instituto de Sistemas Pequeños y Nanotecnologías", CSIC-Spain for fruitful discussion.

References

1. Wynblatt, P., The effects of interfacial segregation on wetting in solid metal-on-metal and metal-on-ceramic systems. *Acta Mater.*, 2000, **48**, 4439–4447.
2. Eusthatopoulos, N., Nicholas, M. and Drevet, B., Wettability at high temperatures. *Pergamon Materials Series*, *Vol 3*. Pergamon, Oxford, 1999.
3. Saitz, E., Cannon, R. and Tompsia, A. P., Reactive spreading: adsorption, ridging and compound formation. *Acta Mater.*, 2000, **48**, 4449–4462.
4. Eusthatopoulos, N., Progress in Understanding and modeling the reactive wetting of metals and ceramics. *Curr. Opin. Solid State Mater. Sci.*, 2005, **9**, 152–160.
5. Derby, B., Xiao, P. and Webster, J., Neutron reflection studies of titanium segregation to metal–ceramic interfaces. *Physica B*, 1998, 304–309.
6. Swiler, T. P. and Loeham, R. E., Molecular dynamics simulations of reactive wetting in metal–ceramic systems. *Acta Mater.*, 2000, **48**, 4419–4424.
7. Daw, M. S., Foiles, S. M. and Baskes, M. I., The embedded-atom method: a review of theory and applications. *Mater. Sci. Rep.*, 1993, **7–8**, 251–310.
8. De Gennes, P. G., Wetting: statics and dynamics. Part I. *Rev. Mod. Phys.*, 1985, **57**(3), 827–869.

9. Cabrera, N. and Mott, N. F., Theory of oxidation in metals. *Rep. Progr. Phys.*, 1948, **12**, 163–195.
10. Li, J. G. and Hausner, H., Wetting and adhesion in silicon/ceramics systems. *Mater. Lett.*, 1992, **14**, 329–332.
11. Strehlow, W. H. and Cook, E. L., *J. Phys. Chem. Ref. Data*, 1973, **2**, 163.
12. Huheey, J. E., Keiter, E. A. and Keiter, R. L., *Inorganic Chemistry: Principles of Structure and Reactivity* (*4th ed.*). HarperCollins, New York, USA, 1993.
13. Morales-Rodríguez, A., Gómez-García, D., García-Gañán, C., Zapata-Solvas, E. and Domínguez-Rodríguez, A., The role of metal–ceramic interfaces on the high temperature mechanical response of nanostructured nickel-yttria tetragonal zirconia polycrystals (Ni-YTZP). *J. Mater. Sci.*, 2006, **41**, 5190–5193.
14. Flewit, P. and Wild, R., *Grain Boundaries: Their Microstructure and Chemistry*. John Wiley & Sons, Chichester, United Kingdom, 2001.