Monatshefte für Chemie 137, 693–701 (2006)
DOI 10.1007/s00706-006-0471-7

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Physicochemical Modelling of Solid/Liquid Interfacial Phenomena

Alexey V. Koltsov[1], **Eduard V. Prihod'ko**[2], **Andrey S. Pashinkin**[3], and **Vladimir B. Koltsov**[3,*]

[1] Moscow State Steel and Alloys Institute, Moscow, Russia
[2] Nekrasov Institute of Ferrous Metallurgy, National Academy of Sciences of Ukraine, Dnepropetrovsk, Ukraine
[3] Moscow Institute of Electronic Engineering, Zelenograd, Russia

Received April 24, 2005; accepted (revised) October 12, 2005

Summary. The proposed modelling of solid/liquid interfacial phenomena consists in relating the main experimental parameter – contact angle θ for metals or alloys on different substrates to combinations of the interatomic interaction parameters of the phases in contact. Physically, these interatomic interaction parameters are analogous to the electronic density distribution in the first and second coordination spheres of the crystallographic lattice of the component, to the bond length, and to the electrochemical factors. The contact angle θ of some alloys on AlN substrates in the case of non-reactive or reactive wetting is calculated.

Keywords. Modelling; Contact angle; Interfaces; Nitrides.

Introduction

Aluminum nitride is a ceramic material with high thermal conductivity and low dielectric constant; therefore it is used widely in electronic applications, including emitting diodes, heat sinks, hybrid substrates, and semiconductor packages [1, 2]. Other applications for this material include passive barrier layers, high-temperature windows, and ceramic lightweight armours because of its low density [2].

In some applications, interfaces with liquid metals are involved, and it is thus important to investigate wetting and the interaction of AlN with liquid metals and alloys.

Wetting experiments of different substrates with liquid metals according to the sessile drop method allow a quantitative determination of spreading kinetics: change of contact angle θ, drop base diameter, and drop height during isothermal

---

* Corresponding author. E-mail: koltsow@yahoo.fr

holding until a steady contact angle is obtained [3, 4]. If a melt does not wet the substrate $\theta > 90°$, but if it wets $\theta < 90°$. It is well established that pure metals, such as Sn, In, Ga, Pb, Ge, Ag, Au, Cu, do not wet AlN ($\theta > 90°$) [3, 5]. An improvement of wetting may be realized by addition of Al into metals that do not wet AlN [6] or by addition of active elements as Ti, Zr, Hf, which react with AlN forming new and more wettable compounds at the interface [7].

The purpose of this work is to develop an approach assessing interfacial interactions between AlN and liquid metals based on the parameters of interatomic interaction in compounds and melts. *Prikhod'ko* [8–11] showed that the overall and partial characteristics of interatomic interaction inferred from physicochemical models for the structure of metallic and ionic melts carry "compressed" information about the compositional effects on the structure and properties of substances. Here, we demonstrate how physicochemical modelling can be used to analyze the wetting of AlN by metallic melts not only for non-reacting *Me*/AlN systems, but also for the cases of new compound formation at the interface due to chemical reaction between the metallic alloy and AlN.

Methods

The applied method is based on the periodic system of elements, and it represents the concept of the effective atomic charge. A modern interpretation of this method called "unpolarised ionic radii method" was given by *Prikhod'ko* [8–11]. The notion of "unpolarised ionic radii" r_i signifies the radii of isolated, non-reacting ions of the corresponding element. It may be added that according to its physical meaning the mentioned radii coincide with orbital radii of *Waber – Cromer – Bratsev* [12–14].

According to the classical theory of chemical structure it is assumed that the electron structure of a compound can be regarded as a result of individual pair interactions superimposing over one another. The combination of such interactions defines a molecular or crystalline compound as a chemical or structural entity. Developing a method for calculating the effective charges Z and the radii r_i of interacting atoms A and B as functions of distance d between them is crucial for such studies. In connection with this, a model of pair interatomic interaction was developed. According to this model, Z_A and Z_B are identified for a certain direction of an interaction, consisting of spherical ($Z_{i\ \min}$) and directional ($\Delta e/2$) components, *i.e.* $Z_A = Z_{A\ \min} + \Delta e/2$ and $Z_B = Z_{B\ \min} + \Delta e/2$ [8–11]. In order to identify such values, the following system of Eqs. (1)–(3) has to be solved for an assigned d, where $r_i^{Z_i}$ is the radius of an ion with charge Z; r_i and $\mathrm{tg}\alpha$ are constants tabulated for atoms of different components [8–11], while $Z_{A\ \min}$ and $Z_{B\ \min}$ are individual parameters for each pair of atoms calculated *a-priori* from such tabulated values, assuming that the interaction is purely ionic (*i.e.* assuming that $Z_A = -Z_B$ and that the contact is a point contact between spherical ions). The system of Eqs. (1)–(3) is solved using the method of step-by-step approximation (fitting Δe) which would make Eq. (1) true.

$$r_A{}^{Z_A} + r_B{}^{Z_B} = d \tag{1}$$

$$\lg r_A{}^{Z_A} = \lg r_A - (Z_{A\ \min} + \Delta e/2)\mathrm{tg}\alpha_A \tag{2}$$

$$\lg r_B{}^{Z_B} = \lg r_B - (Z_{B\ \min} + \Delta e/2)\mathrm{tg}\alpha_B \tag{3}$$

The interpretation of chemical bonding rests on three ideas common to classical and quantum chemistry, and the simultaneous fulfilment of these is the aim of solving the system of equations discussed.

1. It is possible to calculate Z_i and $r_i^{Z_i}$ separately for every direction of the interatomic interaction in a molecule or a crystal. This permits, in particular, the assessment of anisotropy of the electron cloud of reacting atoms for interactions with the neighbours in the first and second coordination spheres of compounds.
2. The variation of the quantities Z_i and $r_i^{Z_i}$ is not discrete; they vary in accordance with d. The ionic component of the chemical bond, Z_{min}, for a certain pair of atoms is a constant while the directional component Δe varies. Positive values of Δe are (in the first approximation) a sign of metallic bond character (a donor bond), while negative values of Δe are a sign of covalency (an acceptor bond). Thus, an important general thesis of the theory of chemical bonding is used: there are no general values of charges and ion radii, but there are certain values of Z_i and $r_i^{Z_i}$ with respect to their particular bonding partners [8–11].
3. The method developed for calculating Δe, Z_{A}, and Z_{B} is based on the assumption that pair interatomic interaction can be interpreted in accordance with the diagram shown in Fig. 1. The condition required for any type of chemical bonding, *i.e.* a smooth joining of the electron density of the ionic shells of the bonding partners, is satisfied, and that joining is accompanied by a transition of a part of their valence electrons from atomic to bonding orbitals (into the shaded zone in Fig. 1). The position of point $\rho_{l\ \mathrm{min}}$ divides d into sections corresponding to the ion radii r_{A} and r_{B} which possess charges Z_{A} and Z_{B}. The condition $\rho_{l\ \mathrm{A}} = \rho_{l\ \mathrm{B}}$ is the metal chemistry analogue of the assumption that electronegativity of interacting ions evens out, and of the quantum-mechanical method of "sewing-up" of electron clouds of reactants.

In the model, ρ_{li} characterizes the "directional" charge density at a distance of $r_i^{Z_i}$ from the nucleus and, as was shown elsewhere [8–11], it can be obtained by the following formula (Eq. (4)).

$$\rho_{l\lim r_i^{Z+\Delta Z}\to r_i^{Z}} = \frac{\Delta Z}{r_i^{Z+\Delta Z} - r_i^{Z}} = \frac{0.434}{r_i^{Z} \cdot \mathrm{tg}\alpha} \tag{4}$$

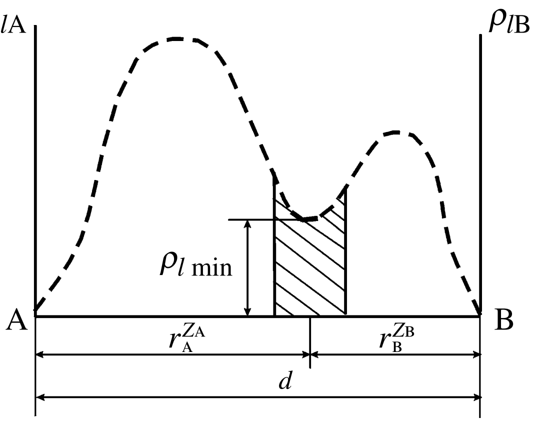

Fig. 1. Diagram of a directional intratomic interaction

Prikhod'ko [8–11] established that for this approach, the effective charges in the first and the second coordination spheres, *i.e.* Z^x and Z^y, are specifically related to each other for some types of crystallographic lattices (body centred cubic lattice: $4Z^x = Z^y$; face centred cubic lattice: $12Z^x = Z^y$; hexagonal lattice: $18Z^x = 11Z^y$). In the case of a multicomponent system the left and right parts of these relations are interpreted with considering the probability of forming all possible types of chemical bonding. The value of parameter Z^y is an integral characteristic of interatomic interaction in the examined system that permits to consider this value as a chemical equivalent of composition. It characterizes the composition of the corresponding substance and carries information on the effective charges of the constituent components with allowance made for the formation of different directed bonds. The d parameter characterizes the average length of these bonds; $\mathrm{tg}\alpha$ characterizes the chemical properties of the set of components.

The analysis of interatomic interaction on the solid/liquid interface allows to conclude that the use of the differences in the parameters of melts and substrates ensures sufficiently good fit for experimental data on contact angles θ (the main experimental parameter of the process in question).

Using the differences given by Eq. (5), one can take into account the detailed chemistry of the interacting phases with a minimum number of fitting parameters, which is essential for assessing the reliability of the model [15–19].

$$\begin{aligned} \Delta Z^y &= Z^y_{\text{melt}} - Z^y_{\text{substrate}} \\ \Delta d &= d_{\text{melt}} - d_{\text{substrate}} \\ \Delta \mathrm{tg}\alpha &= \mathrm{tg}\alpha_{\text{melt}} - \mathrm{tg}\alpha_{\text{substrate}} \end{aligned} \tag{5}$$

Results and Discussion

For modelling of the wetting of AlN substrates by liquid metals and alloys we used more than 50 experimental results obtained by sessile drop technique on wetting under high vacuum of different nitrides by melts of simple substances for systems without any chemical reaction at the interface [5, 20–31]. The chemical interaction of the melt with the substrate can provide an important variation of chemical composition of the melt and formation of new compounds at the interface that change completely chemical and structural properties of the interface. Thus, the formation of a new interfacial compound suggests the change of the parameters of interatomic interaction in the contact zone and, consequently, the change of the contact angle.

Table 1 lists the structural characteristics for crystalline compounds which will be considered below.

Table 1. Model parameters of interatomic interaction in crystalline compounds

Compound	Z^y/e	d/nm	$\mathrm{tg}\alpha$	Compound	Z^y/e	d/nm	$\mathrm{tg}\alpha$
AlN	1.057	0.2035	0.143	$ZrN_{1.0}$	1.585	0.2467	0.102
Si_3N_4	1.367	0.1702	0.1133	$TiN_{1.0}$	1.457	0.2277	0.1075

Table 2. Model parameters of interatomic interaction in molten metals

Melt	Z^y/e	d/nm	tgα	Melt	Z^y/e	d/nm	tgα
Al	0.641	0.3294	0.145	Ge	1.25	0.2446	0.08
Si	1.098	0.2087	0.091	Pd	1.03997	0.3164	0.096
Fe	1.136	0.28274	0.088	Ag	1.162	0.3321	0.086
Co	1.0306	0.25723	0.097	In	0.943	0.3725	0.106
Ni	0.9256	0.28611	0.108	Sn	1.379	0.3029	0.073
Cu	0.847	0.29284	0.118	Au	1.851	0.3314	0.054
Ga	0.68	0.3702	0.147	Pb	1.481	0.3433	0.067

Analogous data for metallic melts are summarized in Table 2.

Analysis of the results for AlN in contact with molten metals in the case of non-reactive wetting demonstrates that the contact angle θ is fitted sufficiently well (correlation coefficient $r = 0.8$) by Eq. (6) where T is the temperature (K).

$$\theta = 37.85 - 41.286 \cdot \Delta Z^y + 452.438 \cdot \Delta d - 1002.565 \cdot \Delta \mathrm{tg}\alpha - 1.183 \cdot 10^{-2} \cdot T \quad (6)$$

The correlation between experimental and calculated values of the contact angle may be improved somewhat increasing the number of correlation parameters, that is, examining separately model parameters of the substrate and the melt (Eq. (7)).

$$\begin{aligned}\theta = {} & 1129.74 - 200.307 \cdot Z^y{}_{\mathrm{substrate}} - 1169.22 \cdot d_{\mathrm{substrate}} - 2106.08 \cdot \mathrm{tg}\alpha_{\mathrm{substrate}} \\ & - 101.568 \cdot Z^y{}_{\mathrm{melt}} + 70.75 \cdot d_{\mathrm{melt}} - 1647.64 \cdot \mathrm{tg}\alpha_{\mathrm{melt}} - 1.238 \cdot 10^{-2} \cdot T \qquad (7)\end{aligned}$$

The correlation coefficient r for the experimentally determined and calculated properties by Eq. (7) is better than 0.83.

The experimental values of the contact angle and the values, calculated by Eq. (7) are shown in the Table 3.

From the comparison of calculated data with experimental ones obtained by different authors, this method allows to describe sufficiently well the interaction of

Table 3. The calculated and experimental contact angles of some melts of pure elements on AlN substrate

System	T/K	$\theta_{\mathrm{calc}}/^\circ$	$\theta_{\mathrm{exp}}/^\circ$
Al/AlN	1123	84	70 [5]
Al/AlN	1150	84	84 [22]
Fe/AlN	1873	116	123 [20]
Ni/AlN	1753	105	98 [20]
Ni/AlN	1873	104	92 [20]
Ga/AlN	1273	78	97 [20]
Ge/AlN	1273	122	113 [20]
Pd/AlN	1848	114	108 [20]
Ag/AlN	1273	127	134 [5, 21]
Sn/AlN	515	134	129 [5, 23]
In/AlN	958	120	123 [5, 23]
Pb/AlN	1023	130	137 [22]

Table 4. The experimental and calculated contact angles in combination with integral parameters of interatomic interaction of different liquid alloys on AlN substrate

Melt	Z^y/e	d/nm	tgα	T/K	$\theta_{\mathrm{calc}}/^\circ$	$\theta_{\mathrm{exp}}/^\circ$
Ag – 39.7 at.% Cu	1.157	0.31513	0.0987	1123	107	
Ni – 4.8 wt.% Cr	1.0807	0.28435	0.1057	1833	92	101 [30]
Ni – 24.7 wt.% Cr	1.5629	0.28149	0.0967	1833	58	73 [30]
Ge – 20 at.% Al	1.4289	0.25098	0.0952	1373	76	70 [31]
Ge – 50 at.% Al	1.4112	0.26125	0.118	1373	43	32 [31]
Ni – 10 at.% Si	1.1247	0.26953	0.1063	1623	88	
Ni – 50 at.% Si	1.5179	0.24049	0.0995	1623	58	

melts with AlN substrate. Note that such high precision of the calculated values is possible only at the absence of oxidation of the drop and the surface of substrate as well as of strong chemical interaction of the melt with the substrate. For example, at low temperatures in Al/AlN system the high values of contact angle are observed ($\theta \sim 125^\circ$ at $T = 970$ K [22] and $T = 1023$ K [5]) because of slow deoxidation kinetics of Al drop and AlN surface [3].

Using Eq. (7) and parameters of interatomic interaction for any melt, the contact angles of these melts on AlN substrate were estimated (Table 4). The good correlation of the calculated values of the contact angle with its experimental values confirms the high precision of this calculation method (Table 4).

The presented method may also be used for the calculation of contact angles for such systems consisting of a liquid drop and a substrate, where chemical reactions take place at the interface, which reduce to the formation of a new phase. In this case it is necessary to take into account the existing experimental data of wetting of this phase layer by different metals and alloys and to calculate not the contact angle of melts on the initial substrate, but the contact angle of melts on the layer of the new interfacial phase which is in direct contact with the liquid alloy. Thus, the calculated contact angle of the melt on the original substrate is the initial contact angle (the first contact angle determined at initial contact of the liquid drop with the substrate), and the calculated contact angle of the melt on the new interfacial phase is the last, stationary contact angle. In this calculation we neglect any spreading kinetics of the drop on the substrate, but we can determine the initial and the steady contact angles. Note, that such elements as Ti, Zr, Hf are active enough in most systems, that's why the formation of new interfacial layer occurs during the first minutes or even seconds of the experiment. The change of composition or stoichiometry of the interfacial layer results in a change of the model parameters of interatomic interaction and, therefore, it may be also estimated by the presented model. Evidently, this method of modelling must be closely connected to the experiment, as it is necessary to determine the chemical nature of interfacial layer, wetted by a drop.

For the prediction of contact angles in systems AlN/liquid alloy, where a chemical reaction takes place at the interface, we also used experimental data of wetting of AlN and other nitrides [20–31] by pure metals which are in accordance with Eq. (7). As an example for the description of reactive wetting we will make the calculation of the contact angle in the system Ag–Zr/AlN. The wetting of an

AlN substrate by Ag alloys containing 0.5–3.0 at.% Zr was explored rather in detail in the work [32]. The authors of this work determined that at 970°C in vacuum at the interface of AlN with all alloys of Ag, containing 0.5, 1, and 3 at.% Zr, a thin (300–500 nm) continuous layer of zirconium nitride ZrN_{1-y} is formed, which is responsible for the improvement of wetting in the system [32].

The initial contact angle θ_0 measured by transferred drop method of the Ag–Zr alloy on AlN substrate is almost 100°. Note that in reactive systems the classical sessile drop technique does not allow to determine the initial contact angle because of the interaction of metal sample with substrate at heating before its complete melting. This interaction leads to a chemical and structural modification of the interface and, consequently, to the change of the contact angle.

The Eq. (7) for Ag–Zr alloy on AlN substrate gives $\theta_0 = 125°$. The calculated value of the initial contact angle seems to be close to the real initial contact angle in this system (calculated value of θ_0 is close to the contact angle of pure Ag on AlN, which is slightly modified by the presence of some percent of Zr). Thus, the measured initial contact angle can be underestimated because of the rapid Zr adsorption on AlN [32] or the presence of the oxide layer on AlN surface [6]; the contact angle of silver on zirconia is about 100° [32].

For the calculation of the steady contact angle in the system Ag–Zr/AlN we used model parameters of phases that are in contact (interfacial reaction product ZrN or $(Zr,Ag,Al)_6N$ and Ag–Zr alloys). Note that in this case the change of composition of the melt as consequence of chemical reaction can be also neglected because of the very small thickness of the reaction product layer, which blocks the interaction of the melt with the AlN substrate (the diffusion coefficient of N in ZrN is very low, $\sim 10^{-19}\,m^2/s$ at 1000°C) [32]. The steady contact angle of Ag–Zr alloys calculated on corresponding interfacial reaction products [32] in comparison with experimental θ values is given in Table 5.

As shown in Table 5, the predicted and the experimental contact angles for the system Ag–Zr/AlN are well correlated. The difference between the calculated and the experimental θ values for an Ag-1 at.% Zr alloy on an AlN substrate is evidently related to the non-stoichiometry of the ZrN_{1-y} interfacial layer (the lower the nitrogen content in ZrN_{1-y}, the better the wetting of this compound by metallic melts). Note, that the correlation between calculated and experimental values of the

Table 5. Experimental and calculated stationary contact angles of Ag–Zr alloys on AlN substrate at 970°C

Alloy	Interfacial layer	Interaction parameters of interfacial layer			$\theta_{calc}/°$	$\theta_{exp}/°$
		Z^y/e	d/nm	tgα		
Ag – 0.5 at.% Zr	ZrN	1.585	0.2467	0.102	56	50 [32]
Ag – 0.5 at.% Zr	$ZrN_{0.82}$	1.606	0.25423	0.0992	49	
Ag – 1 at.% Zr	ZrN	1.585	0.2467	0.102	55	25–30 [32]
Ag – 0.5 at.% Zr	$ZrN_{0.82}$	1.606	0.25423	0.0992	48	
Ag – 3 at.% Zr	$(Zr,Ag,Al)_6N^*$	1.515	0.31185	0.082	30	25–30 [32]

* 55Zr-26, 5Ag-2, 3Al-16, 2N (at. %) [32]

contact angle can be improved by using the real model parameters of the formed interfacial product layer (precise chemical composition and stoichiometry of the interfacial layer). However, in many cases the experimental determination of the precise chemical composition of the interfacial layer is difficult.

Conclusions

The analysis of the dependence of contact angles on parameters of interatomic interaction, relating physicochemical properties of compounds to their electronic structure, shows the possibility to describe the complex interaction metal melt/ceramic substrate as a single system, where the change of the composition of one component leads to a change of the interaction in the contact zone and causes a change of the contact angle. The obtained results permit to conclude that the presented method of physicochemical modelling allows to describe the process of interaction between liquid and crystal not only in the case of non-reactive wetting, but also in the case of reactive wetting, when the layer of a new compound forms at the interface which also causes a change of composition of the liquid.

References

[1] Davis RF, Einfeldt S, Preble EA, Roskowski AM, Reitmeier ZJ, Miraglia PQ (2003) Acta Mater **51**: 5961

[2] Ambacher O (1998) J Phys D: J Appl Phys **31**: 2653

[3] Eustathopoulos N, Nicholas M, Drevet B (1999) In: Wettability at high temperatures, vol 3. Pergamon, Oxford, pp 282–291

[4] Popel SI (1994) In: Superficial phenomena in melts, Metallurgiya, Moscow, pp 273–321

[5] Naidich YuV, Taranets N (1995) Wetting of aluminium nitride by liquid metals. In: Eustathopoulos N (ed) Proc Int Conf High Temp Capillarity, Reproprint Bratislava, Smolenice Castle, p 138

[6] Rosazza Prin G, Baffie T, Jeymond M, Eustathopoulos N (2001) Mater Sci Eng **A298**: 34

[7] Loehman RE, Tomsia AP (1992) Acta Metall Mater **40**: 75

[8] Prihod'ko EV (1996) Met Phys Adv Tech **15**: 1221

[9] Prikhod'ko EV (1995) In: Effectiveness of Combined Doping of steels and alloys, Naukova Dumka, Kiev, p 18

[10] Prihod'ko EV (1995) In: Metallochemistry of multicomponent systems, Metallurgiya, Moscow, p 18

[11] Prihod'ko EV (1973) In: The system nonpolarising ionic radii and its using for analysis of structure and properties of substances, Naukova Dumka, Kiev, pp 5–62

[12] Waber JT, Cromer DT (1965) J Chem Phys **42**: 4116

[13] Allen CI, Waber JT (1968) J Chem Phys **48**: 5021

[14] Bratsev VF (1966) In: The table of atomic wave functions, Nauka, Moscow, pp 1–104

[15] Prihod'ko EV, Moroz VF (2000) Functional materials **7**: 867

[16] Prihod'ko EV, Moroz VF (2002) Inorganic Materials **38**: 507

[17] Prihod'ko EV, Sidorenko KY, Koltsov VB (1988) Zh Fiz Khim **62**: 62

[18] Prihod'ko EV, Garmash LI (1992) Izv RAN Series – metals **1**: 59

[19] Prihod'ko EV, Petrov AF (1995) Functional Materials **7**: 108

[20] Taranets NYu, Naidich YuV (1996) Powder Met **5**: 74

[21] Rhee SK (1970) J Amer Ceram Soc **53**: 639

[22] Rhee SK (1970) J Amer Ceram Soc **53**: 386

[23] Tomsia AP, Pask JA, Loehman RE (1989) Ceram Eng Sci Proc **10**: 1631
[24] Ljungberg L, Warren R (1989) Ceram Eng Sci Proc **10**: 1655
[25] Nicholas MG, Mortimer DA, Jones LM, Crispin RM (1990) J Mater Sci **25**: 2679
[26] Allen BC, Kingery WD (1959) Trans Met Soc AIME **215**: 30
[27] Naka M, Kubo M, Okamoto I (1987) J Mater Sci Lett **6**: 965
[28] Kotsch H (1967) Neue Hütte **12**: 350
[29] Xiao P, Derby B (1996) Acta Mater **44**: 307
[30] Panasyuk AD, Belich AB (1982) Powder Met **4**: 79
[31] Taranets NY, Nizhenko VI, Poluyanskaya VV, Naidich Yu V (2002) Acta Mater **50**: 5147
[32] Koltsov A, Hodaj F, Eustathopoulos N, Dezellus A, Plaindoux P (2003) Scripta Mater **48**: 351