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Wettability of non-reactive Cu/Si–Al–O–N systems

I. Experimental results

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Abstract

The purpose of this work was to study the evolution of ceramic/liquid metal interactions according to the ionocovalent nature of the anion–cation bond in the ceramic. In order to explore a wide ionicity scale, Si–Al–O–N systems were chosen, enabling variation in either the anion or the cation or both at the same time. The experimental work of adhesion, W_a, of pure liquid copper on seven compounds (oxides, nitrides and oxynitrides) was measured. Analysis (SEM, EDS and Auger) confirmed the non-reactivity of the systems studied. The values of contact angle, θ, and surface tension, σ_{lv}, have been obtained by the sessile drop method. There is no significant dependence on the nature of the substrate and satisfactory agreement with the literature data was found. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Contact angle; Cu; Sessile drop; Sialons; Wetting

Résumé

Le but de ce travail est d'étudier l'évolution de l'interaction céramique/métal liquide en fonction du caractère ionocovalent de la liaison anion–cation de la céramique. Pour explorer une large échelle d'ionicité, nous avons choisi d'évoluer dans le système Si–Al–O–N qui offre de nombreuses possibilités de changement de l'anion ou du cation, ou des deux simultanément. Nous avons mesuré le travail d'adhésion expérimental du cuivre liquide pur sur sept composés oxydes, nitrures et oxynitrures. Les analyses (MEB, EDS et Auger) confirment la non-réactivité des sytèmes étudiés. Les valeurs de l'angle de contact, θ et de la tension de surface, σ_{lv}, mesurées par la méthode de la goutte posée évoluent très peu avec la nature du substrat et concordent avec les résultats de la littérature. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The interaction of liquid metals with ceramic materials concerns various fields such as metallurgical studies, the fabrication and assembling of structures by welding or soldering, or the production of composite materials by impregnation. Whether one is attempting to minimise the corrosion or erosion of refractory materials or, on the contrary, to increase adhesion between the materials in contact, the understanding of interfacial phenomena and determination of the energy of adhesion are crucial. The study of wetting of metal/ceramic systems, leading to this energy of adhesion, leads to quantitative appraisal of the strength of the interaction between solid and liquid.

In the case of non-reactive systems, i.e. those not leading to the production of a third phase, various models have already been proposed.[1,2] Nevertheless, experimental verification has been limited to ionocovalent oxide type ceramics. In the present study, the investigation was extended to other types of ceramic materials and, in particular, to nitrides. Also, oxynitrides with one or two cations, such as AlON and SiAlON, are becoming increasingly popular in high technology applications: they are presently produced both on laboratory and industrial scales. In as much as these materials can constitute intermediary steps between oxides and nitrides, it was decided to consider systems based on silicon, aluminum, oxygen and nitrogen. The current study

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concerns specifically non-reactive wetting of molten copper on Si–Al–O–N systems.

2. Experimental

2.1. Choice of materials

2.1.1. Modification of the ceramic by anion change

In pseudo-binary Al_2O_3–AlN[3,4] phase diagrams, the γ'-AlON solid solution resulting from alumina carbonitridation[5] presents a wide range of compositions at temperatures below 1900°C. These intermediate phases between the oxide and the nitride are obtained by a progressive substitution of oxygen by nitrogen:

$$(1-x).Al_2O_3 + 3x.C + x.N_2 \xrightarrow{1600^\circ C} (1-2x).Al_2O_3$$

$$+ 2x.AlN + 3x.CO \xrightarrow{1850^\circ C} Al_{2-2x}O_{3-6x}N_{2x} + 3x.CO$$

Two γ'-AlONs were synthesised containing respectively 20 and 30% of aluminum nitride. The final composition of the spinel oxynitride, which can be written $Al_{(8+x)/3}O_{(4\text{-}x)}N_x$ ($x \in [0.22; 0.55]$), is related to the lattice parameter and can thus be established by X-ray diffraction. The four substrates chosen in the Al–O–N system are presented in Table 1.

2.1.2. Modification of both anion and cation of the ceramic

It is known that the β-Si_3N_4 lattice can form numerous solid solutions with oxides and nitrides[6] such as Al_2O_3 and AlN. This property enables the formation of β'-SiAlON by simultaneous substitution of Si by Al and of N by O (Table 2):

$$z\ AlN + z\ Al_2O_3 + (3-z)\ Si_3N_4 \rightarrow 3\ Si_{3-z}Al_zO_zN_{4-z}$$

(with $z \in [0; 2, 1]$)

This composition change occurs without any structural modification. The addition of up to 10% of yttria[7] enables the nitrides and the SiAlONs to be fully densified thanks to the formation of a silicon, aluminum and yttrium oxide rich intergranular glass. This phase also contains traces (< 0.2%) of carbon, iron and calcium.[7] Three silicon-containing materials were chosen in order to track the effect of the cation, and of both cation and anion, on the experimental values of the work of adhesion (Table 2). The EDS micronanalysis of the surface confirms that the β'-SiAlON contains almost 10 at.% of yttrium.

2.1.3. Choice of a non-reactive metal: the copper

The generally accepted thermodynamic criterion of reactivity in metal/oxide systems is the sign of the free energy ΔG^0_R of the redox reaction at the interface:

$$n\ MO_x + x\ Me \rightarrow x\ MeO_n + n\ M$$

with:

- Me liquid metal,
- M metallic cation of the ceramic.

In a reactive system ($\Delta G^0_R < 0$), the contact leads to the formation of a new compound which can favour adhesion by decreasing the free energy at the solid–liquid interface.

Oxygen leads to the formation of two copper oxides (Cu_2O and CuO) which are significantly less stable than silica and alumina: these can therefore not be reduced by the copper.

Table 1
Al–O–N substrates

Material	Al_2O_3-α	AlON-γ'		AlN
Origin	Desmarquest AF997	Alumina carbonitridation		HC Starck B
Densification	–	Hot Pressed: 1820°C, 30 MPa/1 h/10^5 Pa(N_2)		
Purity (%)	99.7	(20% AlN)	(30% AlN)	98
$d_{exp.}/d_{theo.}$ (%)	100	–	–	97

Table 2
Silicon containing substrates

Material	SiO_2	SiAlONβ'	Si_3N_4
Supplier	Quartz & Silice™, France	Goodfellow™, Great Britain	Goodfellow, Great Britain
Purity (%)	99 995	90	99.4 Si_3N_4-β
$d_{exp.}/d_{theo.}$ (%)	> 99 (glass)	> 99	97

The copper nitrides (Cu_3N, CuN_3 and CuN_6)[8] are not stable at high temperature. Reactions involving copper and nitrides can therefore be neglected.

The free enthalpies of solid solutions of the Si–Al–O–N system are not available in thermodynamic tables but have been calculated by Hillert et al.[9,10] These compounds are more stable than the copper oxides.

For the above reasons, it can be reasonably assumed that the copper/Si–Al–O–N ceramics systems are non-reactive.

The copper samples employed were cylinders of 5 mm diameter cut from a rod of 99.999% pure copper. The metallic impurities as specified by the supplier (Goodfellow) are given in Table 3.

2.2. Operating conditions

2.2.1. Sample preparation

Previous studies of wetting parameters have emphasised the major role played by the solid substrate surface roughness.[11] The main purpose of sample preparation was to obtain a reproducible smooth surface. Though the behaviour of the wetting triple line depends on the highest unevenness, the mean roughness (R_a) correctly represents the solid surface.[11]

After suitable levelling of the substrates, the mean roughness was decreased to less than 80 nm by manual polishing with diamond grinding wheels. The final grinder grade was better than Grit 1200 and the rotation speed roughly 450 rpm. Finally, the mean roughness of sintered substrates was found to be reproducible.

Prior to each experiment, the ceramic surfaces were chemically cleaned with acetone in an ultrasonic bath and heat treated at 1300°C in order to eliminate surface OH groups.[2] The copper was dipped in a molar solution of nitric acid and rinsed in water and ethanol successively.

2.2.2. Experimental parameters

The samples were first heated rapidly (20°C/min) under secondary vacuum (10^{-2} Pa) up to 950°C and maintained at this temperature for 15 min so that the graphite environment could establish reducing conditions for copper. Furthermore, oxidising species could thus be desorbed from insulators and furnace walls. The temperature was then rapidly increased to 1100°C and maintained for 1 h. Gas analysis was provided by a mass spectrometer and thermodynamic calculations indicated that the residual oxygen partial pressure was about 10^{-20} Pa. Under such conditions, the Sievert law predicts a high copper purity with no residual oxygen.[12] Earlier work, operated under vacuum with 1 g copper drops on alumina, gave a surface tension value of about 1283±15 mJ/m^2. This result, whose accuracy was estimated by the Student test with a confidence limit of 95%, indicates that the copper is effectively pure. Experiments also carried out with smaller drops weighing only 200 mg have shown that the contact angle did not depend on the drop size but their almost spherical shape prevents surface tension calculation.[13] Copper evaporation and its condensation on the furnace windows could be avoided by working under inert gas. Nitrogen was chosen in order to stabilise the nitrides without damaging the oxides. The metal evaporation was thus negligible (≈0.02 wt.%). Both contact angle and surface tension were stable for one hour and their variations are of the same order of magnitude as the measurement accuracy.

3. Results

The experimental results of contact angle, θ, surface tension, σ_{lv} and the Dupré energy of adhesion, W_a, are presented in Table 4. Values were obtained as follows.

The shapes of sessile drops of molten copper on employed substrates were analysed, the method being given in greater detail elsewhere.[13] In essence, drops of capillary length $\kappa^{-1}(=[\sigma_{lv}/\rho g]^{1/2})\approx 1$, where ρ is liquid density and g gravitational acceleration were observed in profile. Competition between capillary forces tending to render the drop spherical and gravitational forces flattening the liquid drop leads to a shape of decreasing radius of liquid/environment interface curvature as the meniscus approaches the solid surface. Analysis of this shape enables the evaluation of σ_{lv} and θ, W_a being obtained directly from the expression $W_a = \sigma_{lv}\cdot(1+\cos\theta)$.

Table 4
Experimental results

Substrate	θ (°)	σ_{lv} (mJ/m^2)	W_a (mJ/m^2)
Al_2O_3	150±1	1280±10	170±5
AlON-γ' (20% AlN)	150±1	1285±5	170±10
AlON-γ' (30% AlN)	147±1	1285±5	195±10
AlN	146±2	1285±15	190±15
SiO_2	148±2	1270±15	195±15
Si_3N_4	149±1	1290±10	185±15
SiAlON	150±2	1270±20	170±20

Table 3
Composition of copper impurities

Impurities	Al	Ag	Bi	Ca	Sn	Fe	Mg	Ni	Pb	Si
Concentration (ppm)	2	2	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1

In order to characterise the substrates from a mechanical point of view, the Wenzel[14] roughness coefficient (k), previously used by Johnson and Dettre,[15] was calculated according to the method of Hitchcock et al.[16]

When the ceramic belonged to the Al–O–N system, k was found to be lower than 1.05. The resulting error in contact angle was therefore less than 3°. This assessment led to the conclusion that the contact angle decreases when O is progressively substituted by N.

The ceramics containing silicon were smoother than the others. The roughness induced error was thus lower and the measured equilibrium contact angle did not significantly change from one substrate to another. Nevertheless, in spite of the very low values of the Wenzel coefficient (from 1.0001 to 1.0004), the delay before mechanical equilibrium was achieved could be greater than 20 min.

3.1. Samples observation after cooling

3.1.1. Optical observations

During cooling, defects appeared at the apex of most of the drops. As they had not been observed during the experiments, they could be due either to phenomena occurring during metal solidification or formation of a skin of different composition on the drop surface. This layer might result from the segregation of impurities less dense than the metal or of tensioactive agents, possibly oxidised by the atmosphere.

Independently of substrate nature, bubbles were observed at the interface. They were randomly distributed and occupied from 25 to 80% of the drop base area (Fig. 1a). Their size and number varied because of coalescence which led in some cases to a single bubble being present. Their origin might be ascribed to the thermal decomposition of ceramic intergranular phases. In every case, the value of the angle subtended between the bubble surface and the interface was close to 150° (Fig. 1b) and thus similar to the previously measured wetting angles.

3.1.2. Electronic microscopy and EDS analysis

No chemical contrast appeared at the drop apex using backscattered electron analysis. No layer could be observed at the interfaces on drop cross sections. Aluminum, silicon and yttrium were detected at the apex of a drop removed from a β-SiAlON substrate, but their concentration (≈1 wt.%) was close to the sensitivity threshold of the EDS detector. In all the other cases, copper was the only element detected in the metal phase. Whatever the system was, EDS analysis showed that the substrate did not contain copper and that the drops did not contain any cation from the ceramics. The topographical contrast was provided by secondary electrons and showed that the interfacial zone was frosted except under the bubbles.

3.1.3. Auger spectrometry analysis of interfaces

The analysis was operated on cross sections of the substrates and copper drops. Samples had been previously cleaned for several hours by ion etching. The measured compositions in the bulk of drops removed from different substrates (AlN, AlON and Si_3N_4) are given in Table 5.

In all cases, the high contamination by carbon could be due to the furnace environment which contained carbon oxides (CO and CO_2) and some hydrocarbon vapours

Table 5
Measured concentration of elements detected in copper drops

Substrate	Cu (at.%)	C (at.%)	O (at.%)	N (at.%)
AlN	73	15	6	6
AlON	55	30	7	8
Si_3N_4	75	12	7	6

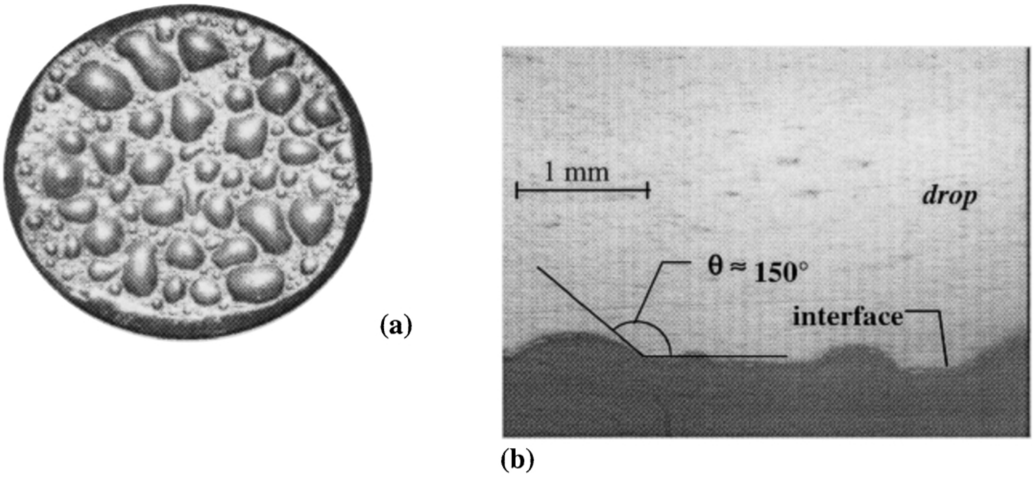

Fig. 1. Bubbles at the ceramic/metal interface after cooling: (a) drop base; (b) profile of interface.

coming from the vacuum system. Moreover, despite the care taken during sample preparation, some grains from the diamond tools or pull out from the ceramic substrates themselves could be trapped in the samples. The unevenness of the interface decreased the accuracy of localisation.

The concentration profile measured on a Cu/AlN cross section suggested that elements interdiffused up to a maximum distance of about 100 μm (Fig. 2).

However, no evidence of such a diffusion could be established. The overall analysis of the drops and the ceramics indicated that the materials were pure. On each side of the interfaces, the concentrations of oxygen and nitrogen were abnormal:

- the measured oxygen concentration in the copper (6.7 at.%) was much higher than its solubility at room temperature (<0.003 at.%). This could only be explained by the formation of Cu_2O[8] though no oxide was detected by the various means of investigation available (SEM, Raman spectroscopy). The oxygen concentration in the aluminum nitride (46.8 at.%) was also very high and corresponded to an oxynitride (γ-$Al_{23}O_{27}N_5$).
- The nitrogen concentration in AlN was lower than expected. Moreover, though it is not soluble in copper, the nitrogen concentration in this metal was abnormally high (6.6 at.%).

The same abnormalities were observed in the Cu/AlON and Cu/Si_3N_4 systems.

4. Discussion

The experimental results (Table 4) of the present work showed that the contact angle of pure liquid copper on the Si–Al–O–N ceramics studied did not significantly depend on the nature of the substrate. The work of adhesion is on average close to 185±15 mJ/m^2. These results were comparable to literature data (Table 6). When the substrates were AlN[17,18] or oxides,[19–21] for which bibliography data are abundant, the agreement was satisfactory. However, the difference between our values of contact angles and those of the literature was as high as 15° when the substrate was Si_3N_4 based.

The discrepancies may be attributed to three possible causes:

- the means of drop observation and of reproduction of its image, as well as the angle calculation technique;[22,23]
- the substrate mean roughness, when it was reported, was between 0.15 and 0.35 μm,[17,24] which is much higher than the R_a values (≈0.08 μm) obtained in this work;
- the purity of both the metal and the ceramic, as well as the inertness of the atmosphere, have an influence on interfacial energies.

Oxygen and easily oxidisable metallic impurities such as aluminium, silicon and magnesium are likely to segregate on the copper surface and thus may decrease the liquid interfacial free energies and the contact angle.[17,20]

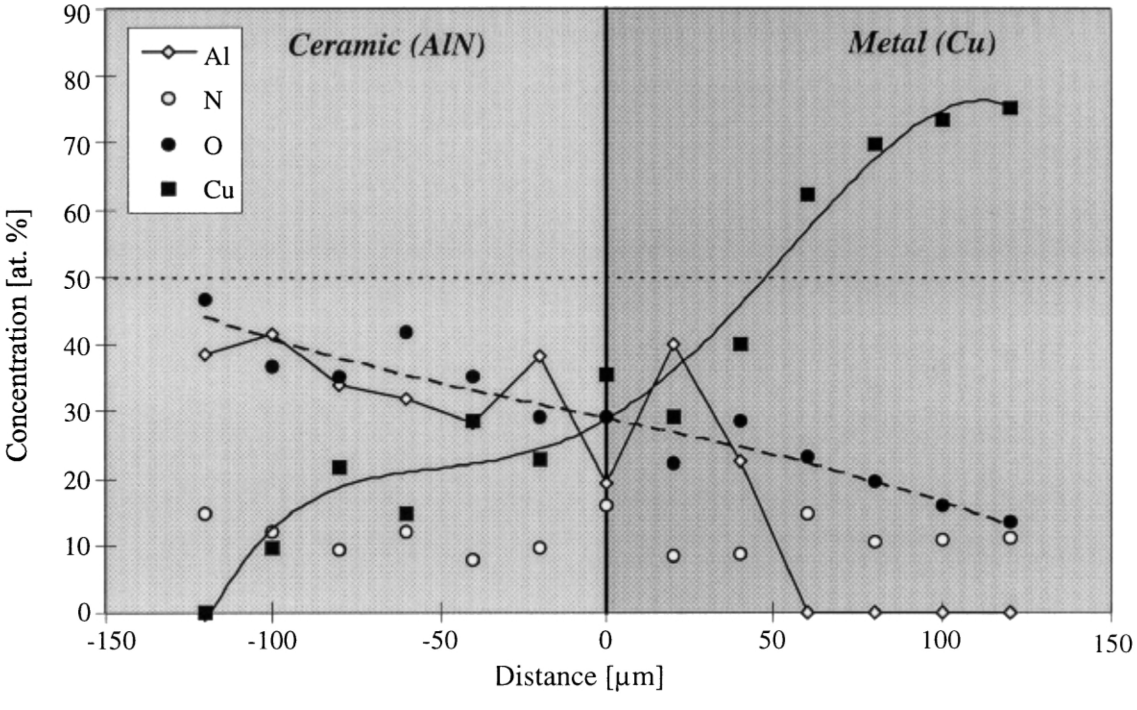

Fig. 2. Concentration profile at Cu/AlN interface.

Table 6
Comparison of experimental values with literature data

	Experiments at 1100°C		Literature			
Substrate	Atmosphere	θ (%)	Temperature (°C)	Atmosphere	θ (°)	Reference
AlN	Vacuum	149±1	1100	Vacuum	140–157	17,18
	N_2	148±2	1100	N_2 (1 ppm O_2)	145	18
Al_2O_3	Vacuum/N_2	150±1	1100	Vacuum	155–170	19,20
AlON (20% AlN)	N_2	147±1	–	–	–	–
AlON (30% AlN)	N_2	150±1	–	–	–	–
SiO_2	–	–	1100	Vacuum	145	22
SiO_2 (glass)	Vacuum/N_2	148±2	1100	–	148	20
Si_3N_4	N_2	149±1	1100	Vacuum	131–144	22,23
SiAlON	Vacuum	149±1	1100	Ar (15 ppm O_2)	133–140	27
	N_2	150±2				

Copper oxides can form intermediate phases such as $CuAlO_2$ or $CuAl_2O_4$ which favour the adhesion of copper to alumina and aluminum nitride.[18] The contact angle of such systems is thus decreased to less than 40° by oxygen.[25]

The nature of intergranular phases must also be taken into account. They can result from either the oxidation of ceramics containing nitrogen from the environment or from reactions between the major phase (or solid solution) and the sintering aids. Their influence on the corrosion resistance of Si_3N_4 based ceramics has already been emphasised.[26] Generally, such phases modify, at least locally, the surface free energy of ceramics and lead to a contact angle which differs from the value obtained on the pure material (if it exists). In the case of Si_3N_4 and β-SiAlON,[27] the discrepancy between our result and literature data could be due to the difference in nature, composition and quantity of the intergranular phase. However, literature data are not necessarily more reliable than ours. As the operating conditions (i.e. metal purity and substrate smoothness) were carefully established, the values of contact angles were considered.

Nevertheless, electron spectrometry analysis at the interface could not completely rule out the dissolution of the ceramic components into the metal. Earlier thermodynamic calculations[28] have shown that aluminum from alumina could dissolve into copper until its molar fraction was about 1.8×10^{-17}. The hypothesis of a non-reactive systems allows a low range dissolution of the substrate in the metal until the concentration is of the order of magnitude of the ppm, which corresponds to the quantity of impurities in a "pure" metal.[29]

5. Conclusion

In order to establish the influence of the ionic nature of substrates on the interactions with metals, the sessile drop method was used to establish the work of adhesion of seven copper/Si–Al–O–N ceramic systems. The composition of the substrates was chosen in order to move between oxides and nitrides and thus explore a wide ionicity scale. The choice of copper as a non-reactive metal was based on thermodynamic criteria. Operating conditions enabled the performance accurate measurements of contact angle and surface tension: substrate smoothness, absence of oxygen in both metal and atmosphere, limitation of metal evaporation and long isothermal dwell. Under such conditions, metal weight losses were lower than 0.5% after 1 h at 1100°C and the surface tension values were on average about 1285±20 mJ/m^2. This mean value was in agreement with the value generally accepted for pure copper (i.e. 1283 mJ/m^2). Values of contact angle did not significantly depend on substrate nature and were comparable to literature data except for silicon nitride based ceramics. The discrepancy was attributed to the difference in composition either in the major phase or in the intergranular one. Some bubbles were nearly always observed at the interface. Their origin is briefly discussed in the present work but could not be elucidated with certainty. Nevertheless, interface analysis showed that the ceramic dissolution in the metal was low enough to be consistent with the hypothesis of non-reactivity of the systems studied.

The experimental values of the contact angle of liquid copper on the ceramics of the Si–Al–O–N system studied were on average 148°±5°. This result led to the conclusion that the work of adhesion of copper on these ceramics does not significantly depend on substrate nature and that its mean value is 185±15 mJ/m^2.

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