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Study of the Interaction between Liquid Aluminum and Silicon Nitride

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Abstract

The sessile drop method was used to determine the evolution as a function of time and temperature, under vacuum, of the contact angle θ of molten aluminum on two kinds of silicon nitride (SRBSN and CVD-SN). These results are discussed in terms of thermodynamic calculations (stability of a superficial metal oxide layer) coupled with morphological observations and characterization of the ceramic/metal interface. The limited interfacial corrosion and the formation of a protective dense aluminum nitride layer lead to the conclusion that silicon nitride is a good candidate as a corrosion resistant material for the handling or the melting of liquid aluminum.

Der Kontaktwinkel zwischen geschmolzenem Aluminium und zwei verschiedenen Siliziumnitriden (SRBSN und CVD-SN) wurde mit Hilfe der Tropfenmethode im Vakuum als Funktion der Zeit und Temperatur bestimmt. Die Ergebnisse werden bezüglich thermodynamischer Berechnungen (Stabilität einer Oberflächenmetalloxydschicht) zusammen mit morphologischen Beobachtungen und Charakterisierung der Keramik/Metall-Grenzfläche diskutiert. Aus der begrenzten Grenzflächenkorrosion und der Bildung einer schützenden, dichten Aluminiumnitridschicht kann geschlossen werden, daß Siliziumnitrid ein geeigneter Korrosionschutz beim Umgang mit geschmolzenem Aluminium ist.

L'évolution, sous vide, de l'angle de contact θ entre l'aluminium liquide et deux types de nitrure de silicium (SRBSN et CVD-SN) a été étudiée en fonction du temps et de la température par la méthode de la goutte sessile. Les résultats sont discutés sur la base de calculs thermodynamiques (stabilité de la couche superficielle d'oxyde métallique), couplés à des observations morphologiques et à la caractérisation de l'interface céramique/métal. La corrosion interfaciale, limitée par la formation d'une couche dense, protectrice, de nitrure d'aluminium, permet d'envisager l'utilisation du nitrure de silicium en temps que matériau résistant à la corrosion pour le maintien ou la fusion de l'aluminium liquide.

1 Introduction

The use of dipped heating elements for aluminum casting is not particularly widespread although this technique is industrially promising. Indeed, the aggressive environment leads to a significant corrosion of the protective tube which results in an insufficient and, above all, unpredictable lifetime. As part of the search for materials with greater compatibility with respect to molten aluminum, a study of the interaction of different non-oxide ceramics (AlN, SiC and Si_3N_4) in contact with liquid aluminum has been undertaken.

The results presented here concern the interactions between liquid aluminum and two kinds of silicon nitride, one obtained by reaction sintering (SRBSN) and the other by chemical vapor deposition (CVD-SN), respectively. After a short presentation of the materials and of the wettability equipment used to determine the contact angle θ, the observed influence of time and temperature on θ will be examined and discussed on the basis of the morphological observations and the ceramic/metal interface characterization.

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2 Experimental

In this work, 99·999% pure aluminum (Pechiney) was used. Just before the runs, in order to minimize the thickness of the superficial oxide layer, the metal was successively dipped for 2 h in a 10% NaOH solution and held for 5 min in a diluted HF solution.

The silicon nitride was either

—sintered reaction-bonded silicon nitride (SRBSN), a fully densified industrial product developed by ESK which contains free silicon (3·7 wt%), aluminum (0·67 wt%), iron (0·49 wt%), lanthanum (4·95 wt%) and oxygen (3 wt%), or

—pure silicon nitride obtained by chemical vapor deposition (CVD-SN). This material was deposited on SRBSN substrates, and obtained by the reaction of tetramethylsilane with ammonia in presence of hydrogen at 1125°C.[1]

The equipment used to determine the contact angle is composed of a graphite heating element, working under controlled atmosphere (non-oxidizing gas or vacuum) up to 1800°C, and of rotary and turbomolecular pumps that allow a minimum pressure of 10^{-6} Pa. The measurement system is based on a CCD camera coupled to a computer in order to have a precise, reliable and in real time numerization of the profile of the drop. The data are then computed by means of software developed in the laboratory, allowing a precision of $\pm 1°$ on the value of the contact angle.[2] A mass spectrometer enables the analysis of the residual gases (Fig. 1).

The solidified drops and the substrates were sectioned, polished and examined by optical and scanning electron microscopy. The element distribution in the vicinity of the metal/ceramic interface was determined by means of an energy dispersive (EDX) or an electron probe microanalyzer (EPMA).

3 Results and Discussion

The sessile drop method, based on the observation of the profile of a drop lying on a plane surface, is commonly used[3] to determine the contact angle, θ, the liquid metal superficial tension, σ_{LV}, and the work of adhesion, W_a, parameters that characterize the liquid metal/ceramic interactions (Fig. 2). According to Young–Dupre's equations:

$$\sigma_{SV} - \sigma_{LV}\cos(\theta) - \sigma_{SL} = 0 \tag{1}$$

$$W_a = \sigma_{SV} + \sigma_{LV} - \sigma_{SL} \tag{2}$$

then:

$$W_a = \sigma_{LV}(1 + \cos\theta) \tag{3}$$

with σ_{SV} = solid/vapor superficial tension, σ_{LV} = liquid/vapor superficial energy, σ_{SL} = solid/liquid superficial tension, θ = contact angle and W_a = work of adhesion.

Although these equations are very often used, they are only valid if the system is thermodynamically stable, and if some precautions are taken (no chemical reaction, homogeneous temperature, good and reproductible surface roughness, etc.).

It should also be noted that θ is influenced by many parameters such as time, temperature, atmosphere, substrate roughness, etc.[4] Here, only the influence of time and temperature on θ will be studied, the other parameters being held as constant as possible.

3.1 Influence of temperature

Figure 3 shows that the dependence of θ on temperature is similar for both nitride substrates. Indeed, for a large range of temperature (from 660°C to 1000°C) the contact angle is constant ($\theta = 138° \pm 3°$ for SRBSN and $149° \pm 2°$ for CVD-SN). This behavior is due to the presence of an alumina layer at the surface of the drop, which prevents the

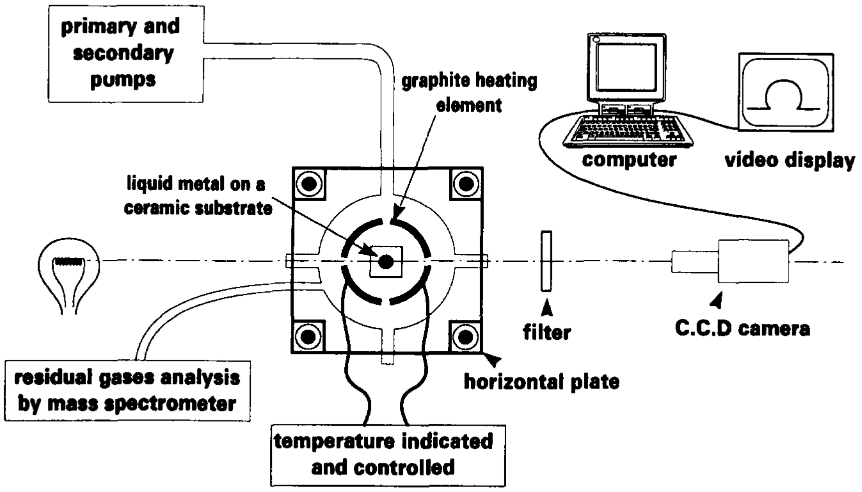

Fig. 1. Schematic representation of the wettability set-up.[2]

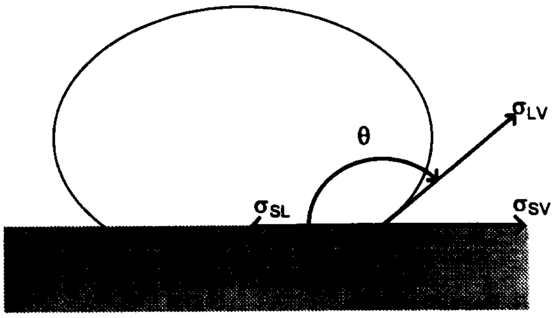

Fig. 2. Schematic representation of wetting parameters.

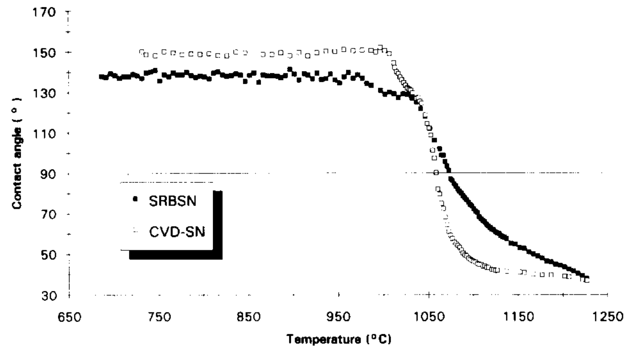

Fig. 3. Temperature dependence for contact angle of liquid aluminum on SRBSN (■) and CVD-SN (□).

liquid metal from spreading freely on the surface of the ceramic substrate.[5]

At about 1000°C, this superficial layer begins to decompose under the effect of the low oxygen pressure fixed by the CO/CO_2 and H_2/H_2O residual atmosphere of the furnace containing the graphite heating element. By simple thermodynamic calculations it is possible to check (Figs 4 and 5) that above around 1000°C and at a constant pressure of 10^{-3} Pa (which corresponds to the furnace total pressure during a run), the partial pressure ratios P_{CO_2}/P_{CO} and P_{H_2O}/P_{H_2} are low enough to induce the reduction of alumina in liquid aluminum. In this calculation, the reactions having the greatest probability to occur (i.e. having the highest conversion degree) under these experimental conditions were selected. This transformation was confirmed by the in-situ observation of the aspect of the metal drop: at this temperature, the drop, previously mat, becomes bright.

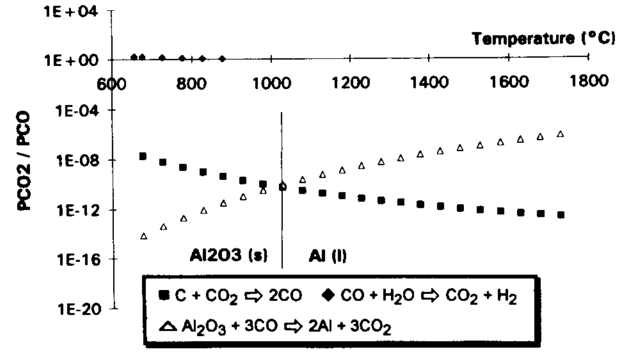

Fig. 4. Stability domain of Al_2O_3 as a function of the partial pressure ratio P_{CO_2}/P_{CO} and temperature.

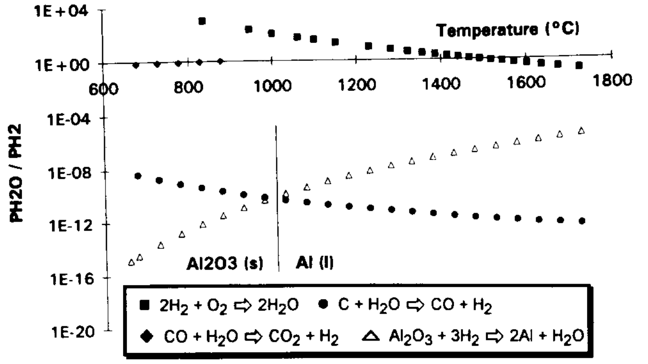

Fig. 5. Stability domain of Al_2O_3 as a function of the partial pressure ratio P_{H_2O}/P_{H_2} and temperature.

The complete disappearance of the superficial oxide film corresponds to the second break in the curves, at 1040 ± 3°C. Above this temperature, the drops spread quickly on the ceramic substrates until they reach their equilibrium state. In both cases, $\theta = 35° \pm 2°$ at the end of the run (1230°C). The transition temperatures (T_t) at which the metal becomes wetting (i.e. $\theta = 90°$) are 1060°C for CVD-SN and 1075°C for SRBSN, respectively. Moreover, as will be seen later, the slopes of the curves during this step are related to the reactivity of liquid aluminum with the substrates: the higher the value of the slope, the higher the reactivity.

3.2 Influence of time

The results, corresponding to the runs at 900°C and 1075°C, have been plotted in Fig. 6, as they are representative of the isothermal behavior of the ceramic substrates. For the one hour runs at 900°C, since the superficial oxide layer is not reduced, the drop is held in a non-equilibrium state. The corresponding contact angle, constant with time (in both cases, $\theta = 153° \pm 3°$), is representative of strongly non-wetting systems.

At 1075°C, the oxide is reduced during the temperature ramp. Therefore, during the 1 h dwell time, the real $Si_3N_4/Al_{(l)}$ contact is observed. The angle, initially high due to the presence of the oxide layer, decreases quickly, especially for CVD-SN, and then tends toward a limit value representative of the

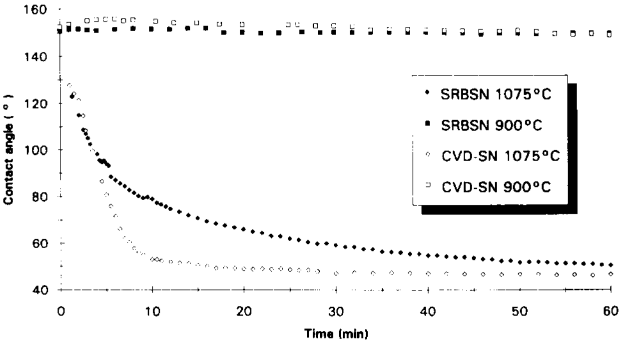

Fig. 6. Isothermal behavior of the contact angle of liquid aluminum at 900°C (■, SRBSN and □, CVD-SN) and at 1075°C (◆, SRBSN and ◇, CVD-SN).

equilibrium angle of the system Si_3N_4/Al at this temperature ($\theta = 48° \pm 3$). In the case of the pure silicon nitride this value is reached after only 30 min, while in the case of the SRBSN material the contact angle still decreases slightly at the end of the one hour test. Here again, the value of the slope of the curves is directly correlated to the reactivity of the ceramic/metal systems.

3.3 Characterization of the ceramic/metal interface

Although the evolution of the contact angle is almost similar for both silicon nitride substrates, the characterization of the ceramic/metal interfaces has revealed that the reactivity of the pure and of the unpure ceramics are very different.

Indeed, in the case of the SRBSN ceramic, and for the non-isothermal run corresponding to Fig. 3, the optical observations of the interface made after the run, reveal only a limited internal attack of the substrate by the aluminum (Fig. 7). However, the composition map of this region (Fig. 8) indicates the presence of a 6-μm thick layer containing aluminum, nitrogen, silicon and oxygen. In addition, the presence of these elements within the metal drop proves that some dissolution of the ceramic in the metal has occurred.

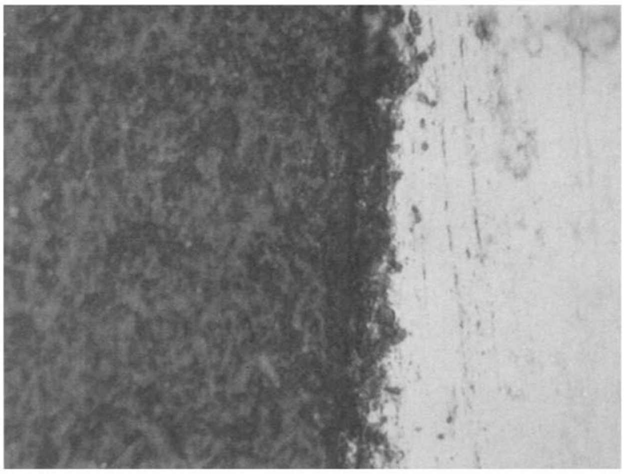

Fig. 7. Optical microscope observation (×900) of the SRBSN/$Al_{(l)}$ interface after the non-isothermal test.

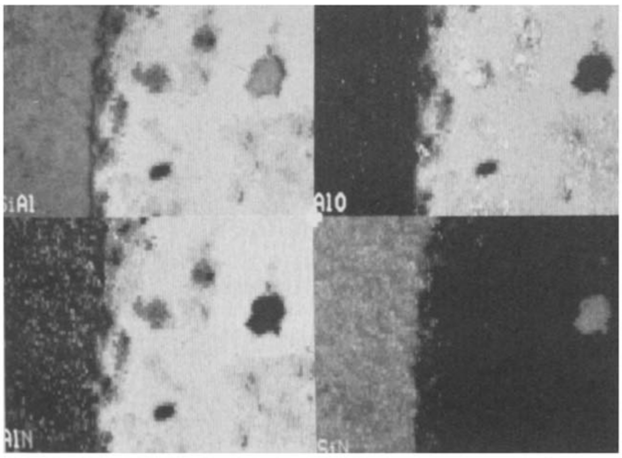

Fig. 8. Elemental maps (EDX) of the SRBSN/Al interface after the non-isothermal test (×1500). The individual maps show the element distribution of Si + Al, Al + O, Al + N and Si + N, respectively.

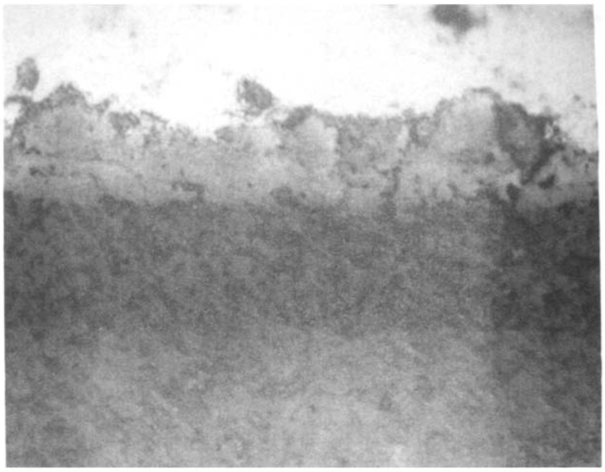

Fig. 9. Optical microscope observation (×900) of the CVD-SN/$Al_{(l)}$ interface after the non-isothermal test.

In the case of pure silicon nitride (CVD-SN), a thicker dense reaction zone (15 μm) located at the surface of the CVD coating is observed by optical microscopy (Fig. 9). The EPMA analysis (Fig. 10) reveals that it is only composed of aluminum and nitrogen. Therefore, in good agreement with previous works,[6-9] the formation of a dense protective aluminum nitride intermediate layer between the substrate and the metal is revealed. In the absence of significant contents of silicon and nitrogen in the metal drop, it is possible to conclude that this layer prevents the dissolution of the ceramic subs-

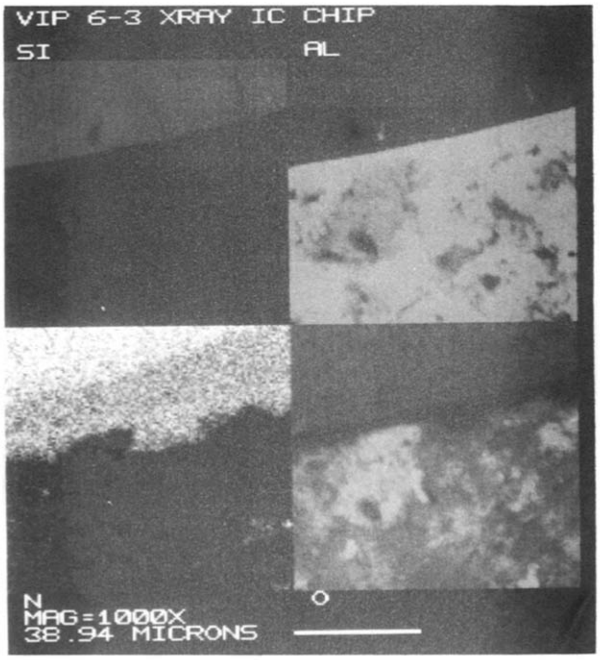

Fig. 10. Elemental maps (EPMA) of the CVD-SN/$Al_{(l)}$ interface after the non-isothermal test. The individual maps show the element distribution of Si, Al, N and O respectively.

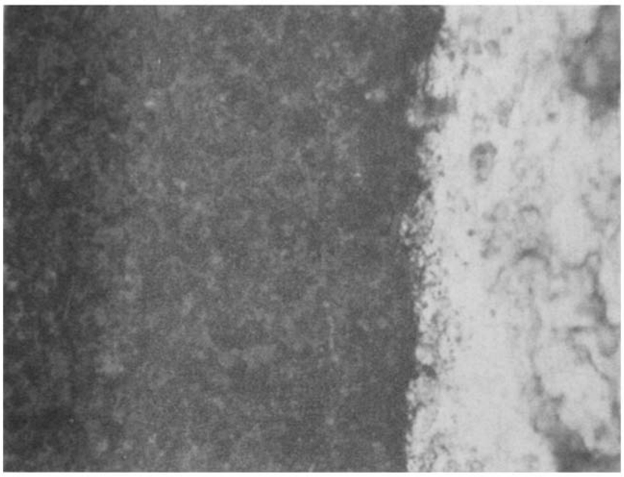

Fig. 11. Optical microscope observation (×900) of the SRBSN/$Al_{(l)}$ interface after the isothermal run at 1075°C.

trate.[10,11] Therefore the oxygen present in the aluminum comes from the oxidation of the metal drop.

In the case of the isothermal tests at 900°C (corresponding to the curves shown in Fig. 6), the drop stays strongly non-wetting, and the liquid metal does not penetrate the ceramic substrates, which are not corroded at all.

At 1075°C (Fig. 6), the aluminum reacts only slightly with the substrates. In the case of SRBSN, the depth of penetration of Al in the ceramic is less than 5 μm (Fig. 11), even in the middle of the sample, where the attack is always greater. In fact, the most important sign of this attack is the increase of the roughness of the ceramic surface, as can be seen in Fig. 11.

For the CVD-SN substrate, although the protective layer is much thinner (less than 1 μm) than in the non-isothermal run, it plays a protective role. Indeed the ceramic underneath is unchanged, even if it has become rough and cracked in some places (Fig. 12).

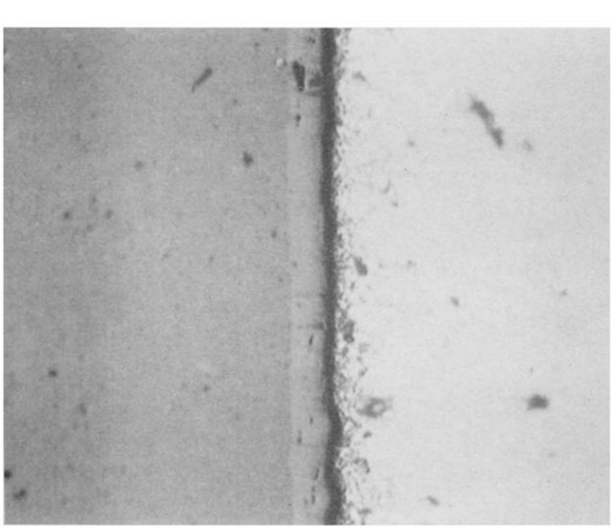

Fig. 12. Optical microscope observation (×360) of the CVD-SN/$Al_{(l)}$ interface after the isothermal run at 1075°C.

4 Conclusion

In the present work, the influence of three parameters on the contact angle in the system $Si_3N_4/Al_{(l)}$ is studied: the temperature, the time of contact and the purity of the ceramic substrate.

At temperatures below 1000°C, the aluminum drop is held in a non-equilibrium state due to the strong alumina layer present on surface. This layer exists even if the initial metal is carefully chemically treated before the tests, because of the oxygen partial pressure characteristic for this particular furnace having a graphite heating element. However, above 1000°C, this oxide layer is reduced and the real $Si_3N_4/Al_{(l)}$ contact can be studied.

The results indicate that the evolution of the contact angle is similar for both nitrides, but that the interfacial reactions are influenced by their composition. For the purer silicon nitride (CVD-SN), the formation of a dense and highly protective intermediate aluminum nitride layer is observed. In the case of the SRBSN, containing sintering aids, the EDX analysis revealed the presence of a reaction zone a few microns thick containing not only aluminum and nitrogen, but also silicon and oxygen. Nevertheless, in both cases, the interaction is limited. Therefore, thanks to these wetting tests, and to complementary 'dipped finger tests' which are underway, it is possible to conclude that silicon nitride, pure or not, is a good candidate as a corrosion-resistant material for the handling or the melting of liquid aluminum.

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