JOURNAL OF MATERIALS SCIENCE **33** (1998) 3993–3997

Wettability of aluminium nitride by tin–aluminium melts

YU. V. NAIDICH, N. YU. TARANETS
Institute of Problems for Materials Science, Department 12, 3 Kryhzhanovsky street, 252142 Kiev-142, Ukraine
E-mail: naidich@ipms.kiev.ua

The wettability of aluminium nitride by Sn–Al melts was studied by the sessile drop method in a vaccum of 2×10^{-3} Pa at 1100 °C over the whole concentration region. The minimum interval on the contact-angle concentration dependence curve was observed at intermediate composition. For comparison, experiments were also performed on porous AlN. Wetting of porous nitride is worse than the dense nitride. The results have been analysed on the basis of the relation between wettability and the chemical interface reactivity in solid–liquid metal systems. © *1998 Kluwer Academic Publishers*

1. Introduction

The capillary and adhesive properties of metal melts in contact with different ceramics are of great interest. Wettability is a key factor for composite making technology, ceramics brazing, metal coating and corrosion processes [1]. Aluminium nitride is a promising material due to the combination of strength, high thermal conductivity and high electrical resistivity [2].

The wettability of AlN by pure metals has been investigated in a number of works [3–8] and in our previous work [9]. Most pure metals including tin, do not wet AlN; contact angles exceed 90°. However, aluminium wets AlN starting from a temperature of about 850 °C [9].

In order to be able to control capillary processes, it is important to investigate wettability by the alloys in which one of the components has high adhesive activity to the substrate. The purpose of the present work was to study the variation in the contact angle of Sn–Al melts on AlN with variation in the composition of the melt over the whole concentration region. The work of adhesion has been calculated on the basis of the recent data on surface tension of the Sn–Al melts [10].

2. Experimental procedure

The experimental apparatus used to measure the contact angle by the sessile drop method was described previously [1]. The main part of the apparatus is a horizontal resistance furnace consisting of an alumina tube heated externally by a molybdenum resistor. The furnace is connected to a vacuum system including a vane pump, and an oil diffusion pump. The system provides a vacuum of 10^{-3}–10^{-4} Pa. The apparatus is equipped with an optic and photo arrangement which makes it possible to receive the image of the sessile drop magnified approximately five to six times. Contact angles were measured with an accuracy of $\pm$ 1°–2°. The temperature was measured by a platinum–platinorhodium thermocouple located next to the drop. Experiments were performed at 1100 °C in a vacuum of 2×10^{-3}Pa.

The ceramic substrates were cylindrical plates with a diameter of 12 mm and a height of 3 mm. To produce them, AlN powder (Donetsk Plant of Chemical Substances) was used (Table I). The initial AlN powder contained about 1.5 wt% of adsorbed oxygen.

AlN substrates were produced by hot pressing in a graphite die. The residual porosity of the specimens was less than 1%. TEM observations showed that the samples were dense and composed of irregular-sized grains, ranging from 0.6–5μm. It was found that, at the AlN grain boundaries, there are solitary isolated pores with diameters of 0.1–0.2 μm and no continuous intergrain layers of other phases.

Experiments were also carried out on more porous AlN samples produced by sintering in a nitrogen medium. The residual porosity of these samples was about 15%, with a pore diameter of 1–6μm.

The hot-pressed AlN plates were darker in colour than sintered ones. Data for the wettability of porous ceramics are of practical interest (different kinds of ceramics are used technically).

Prior to the experiments, the ceramic substrates were ground and polished. The roughness ranged from $R_a \approx 0.01$–0.02μm for dense nitride samples. It was impossible to measure the roughness of porous samples, because of the surface porosity. The samples were cleaned in acetone and outgassed in vacuum at 800 °C for 30 min.

TABLE I Chemical composition (wt%) of the AlN powder

Al	N	Fe	Si	C
64.8	32.2	0.9	0.09	0.15

Aluminium (99.995% purity) and tin (99.999% purity) were used to prepare the alloys. Alloys were produced preliminarily by means of melting the components in a vacuum at 750 °C. The weight of the drops was about 0.5 g.

The change in contact angle was measured with time during isothermal exposure at 1100 °C. Simultaneously with the contact angle, the base diameter of the drop was measured. The contact angle was considered as final if it did not change more than 1°–2° during isothermal exposure of 15 min and the base diameter of the drop did not increase during this time.

Some of the samples were subsequently cross-sectioned and polished for investigation of the interface by scanning electron microscopy.

3. Results

Fig. 1 shows variation of the equilibrium contact angle with increasing of aluminium content in the melt at 1100 °C, for dense hot-pressed aluminium nitride. At this temperature, the contact angle of pure tin on aluminium nitride is 122° ± 2°. It was formed over 2–3 min and did not change after this time. Aluminium shows a different behaviour. The initial wetting angle is about 57° ± 2°, decreases with time to the final value of 39° ± 2°, after 30 min isothermal exposure.

Contact angles of the tin–aluminium melts show a time dependence in the contact with aluminium nitride. Fig. 2a shows the variation of the wetting angle, θ, and base diameter of the drop, d, with time, τ, for 40 at % Sn + 60 at % Al melt during isothermal exposure at 1100 °C. The forms of these curves, $\theta(\tau)$ and $d(\tau)$, are typical for all investigated Sn–Al alloys. For all melts, the isothermal exposure time required to form the final contact angle, was about 30 min.

The concentration dependence of the contact angle is characterized by a clearly expressed minimum in the interval 40–70 at % Al. The contact angle formed by melts in this region is about 19° less than the contact angle of the pure aluminium.

Investigation at the same temperature (1100 °C) for porous sintered AlN showed that, in the case of non-wetting metal (tin. in region of $\theta > 90°$), the value of the contact angle was near that for dense hot-pressed AlN. A higher value was observed for the contact angle measured on porous AlN in the case of wetting alloys ($\theta < 90°$). Porous AlN is wetted by aluminium with a contact angle of 48° ± 2°, but dense AlN is wetted by aluminium with the contact angle of 39 ° ± 2 °.

On the whole, wetting of porous AlN is worse than that of dense AlN (Fig. 3). The forms of the time dependences of $\theta(\tau)$ and $d(\tau)$ for porous AlN are similar to that for dense AlN (Fig. 2b). However, in this case, the isothermal exposure time required to reach

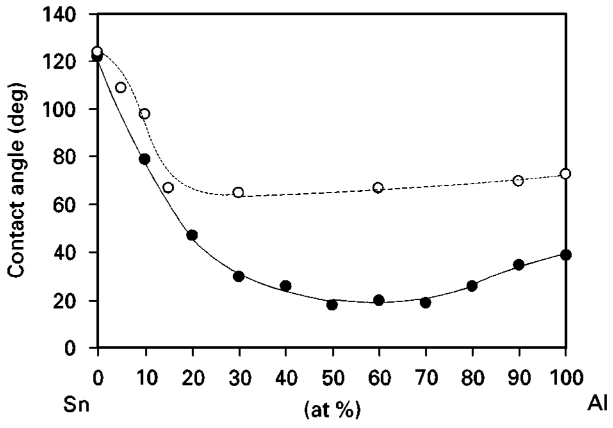

Figure 1 Concentration dependences of wetting by Sn–Al melts of (●) dense AlN and (○) Sapphire [14] at 1100 °C.

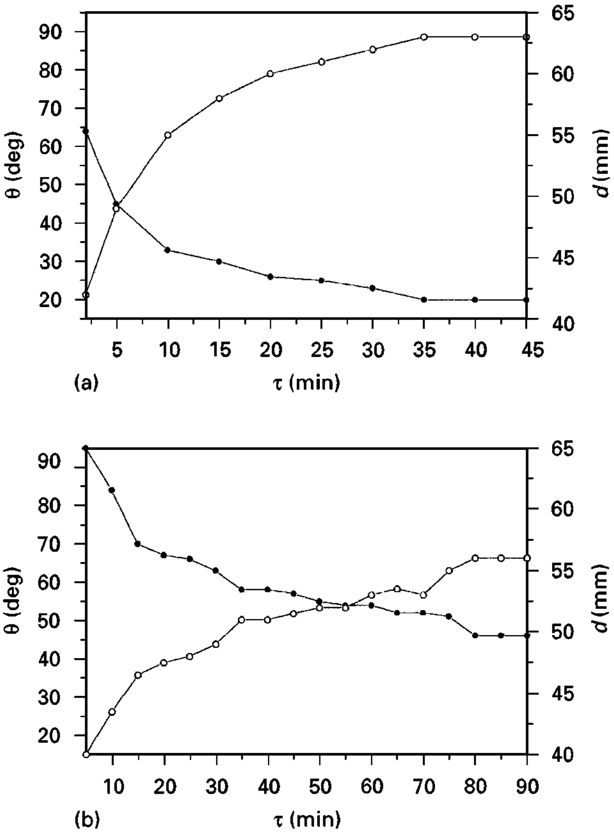

Figure 2 Variation of (●) contact angle, θ and (○) base diameter of the drop, d, with the time during isothermal exposure at 1100 °C for the melt composition 40 at % Sn + 60 at % Al, (a) for dense AlN, (b) for porous AlN. d was observed on the screen at a magnification of 5.5.

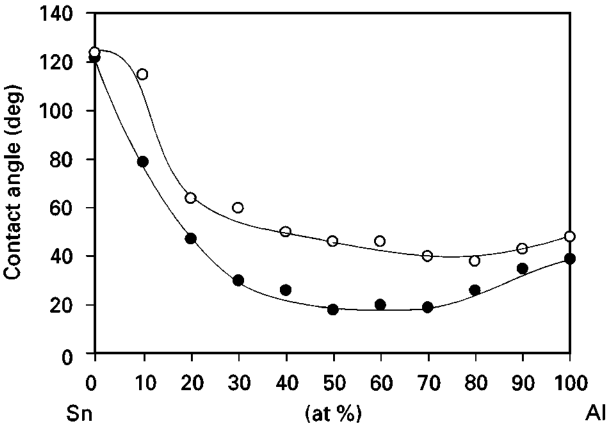

Figure 3 Concentration dependences for wetting by Sn–Al melts of (●) dense AlN and (○) porous AlN at 1100 °C.

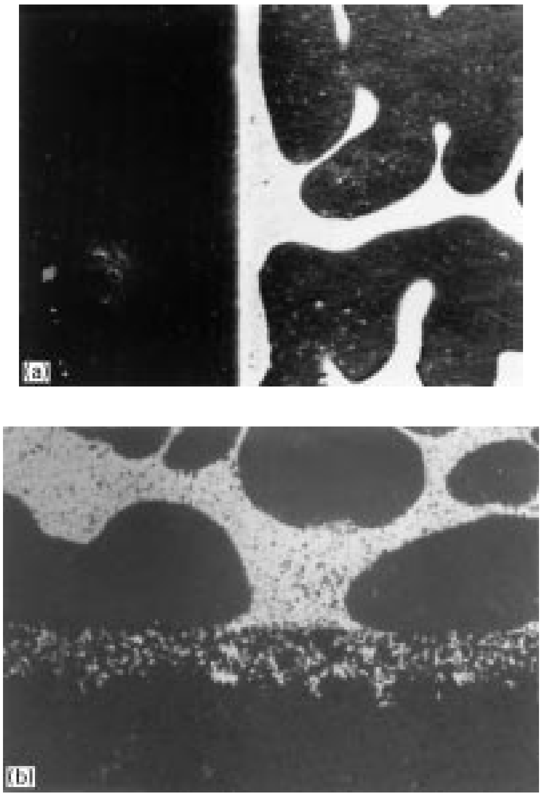

Figure 4 Microstructure of the interface for (a) dense AlN, × 540; (b) porous AlN, × 500.

the final contact angle was higher (30–80 min, depending on the melt composition). There was no clear dependence between increasing exposure time and increasing aluminium content in the melt. It should be noted that the melt with 10 at % aluminium content formed a stationary contact angle more rapidly.

The concentration dependence of the contact angle for porous AlN also passes through a minimum. However, it is expressed less clearly and is displaced somewhat to the pure aluminium side in comparison with dense AlN.

Scanning electron microscopy was performed on the two investigated types of AlN plates for melt composition 20 at % Sn + 80 at % Al. The results for both the hot-pressed and sintered nitrides showed the absence of any new intermediate chemical compound at the interface (Fig. 4a,b); for the porous ceramic substrate, a region of impregnation was observed. The thickness of this region was about 18μm.

4. Discussion

Contact angle of pure aluminium on the AlN is much lower than that of pure tin. The level of the wettability in the system of the solid substrate with liquid metal depends on the chemical affinity of the metal melt to the components of the solid phase and this increases with increasing intensity of the chemical reaction at the interface [1]. The Sn–AlN system is characterized by the absence of chemical interaction at the interface. Tin does not form aluminides [11] and tin nitride is a very unstable compound which can only be with using special methods [2]. Therefore, tin does not wet aluminium nitride. Aluminium possesses a high chemical affinity to nitrogen. In this case, it is possible to stabilize the chemical bonds between aluminium from the melt and nitrogen from the solid substrate with the formation of aluminium nitride, which is a thermodynamically stable compound ($\Delta\ G^0_{298} - 287\,\mathrm{kJ/g}$ at N [12]). This results in good wettability of the substrate by the aluminium melt. Taking this into account, it is normal to expect a monotonic variation (decreasing) of the contact angle from tin to aluminium. However, the curve has a minimum in the region of intermediate concentration. This can be explained on the basis of a simple consideration. Recently, the surface tension of the Al–Sn melts was measured experimentally over the whole concentration region [10]. Fig. 5 shows the surface tension isotherm for Al–Sn melts at 1100 °C. It is characterized by the decreasing of the surface tension from aluminium to tin. Using these data, the work of adhesion can be calculated as

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

and the interfacial tension as

$$\sigma_{s-l} = \sigma_{s-v} - \sigma_{l-v}\cos\theta \tag{2}$$

The last parameter can be calculated with an accuracy of a constant (the surface tension of solid aluminium nitride). The results of the calculation are given in Fig. 6. The concentration dependence of the work of adhesion has no extremum and it is characterized by a continuous increase of W_a from tin (228 mJ m^{-2}) to aluminium (1422 mJ m^{-2}). The dependence for $\sigma_{s-l} - \sigma_{s-v}$ is also monotonic. Thus the extremum

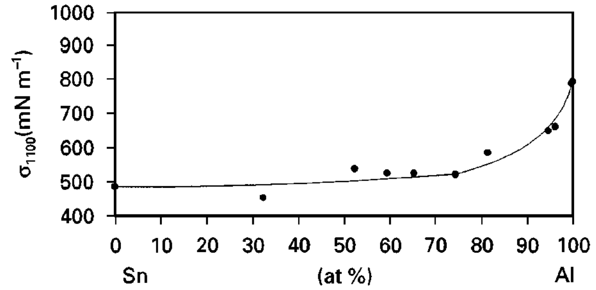

Figure 5 Concentration dependence of the surface tension of Sn–Al melts at 1100 °C [10].

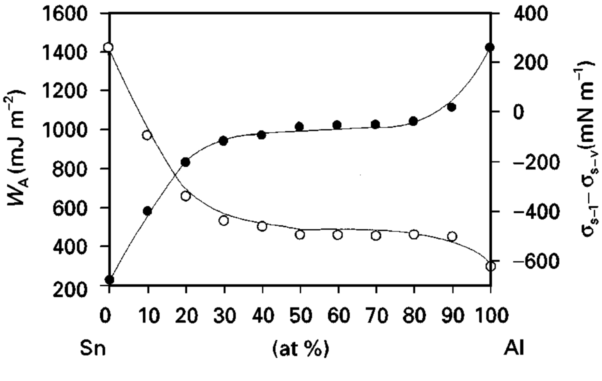

Figure 6 Variation of (●) the work of adhesion, W_a and (○) $\sigma_{s-l} - \sigma_{s-v}$ in the system Sn–Al melt–dense AlN at 1100 °C.

(minimum) of the concentration dependence of θ is conditioned as follows. As can be seen from the equation for the contact angle

$$\cos\theta = \frac{W_A}{\sigma_{l-v}} - 1 \tag{3}$$

Decrease of the contact angle from its value for pure tin is caused by an increase of the work of adhesion of the melt to the solid AlN with increase of the aluminium content in the melt. The decrease of the contact angle from that of pure aluminium arises from the lowering of the surface tension of the melt (tin has a lower surface tension). So these factors give an extremum (minimum) on the wetting isotherms. Qualitatively, the extremum of the concentration dependence for θ is predicted by theoretical calculations [13] for the liquid Al–Sn system.

Li *et al.* [14] reported on the wettability of sapphire by Sn–Al alloys. It is interesting to compare these data with our results. The concentration dependence of the contact angle on aluminium oxide is similar to that for aluminium nitride (Fig. 1). The curve also has a minimum. However, the depth of the minimum is much less and it is displaced to the region of pure tin (about 15–25 at % Al). On the whole aluminium nitride is wetted better than aluminium oxide. This can be explained by taking into account the different ionicity of chemical bonds in the Al_2O_3 and AlN compounds. Aluminium nitride (a compound of A^{III} B^{V} type) should be considered as a substance having mainly covalent interatomic bonds with some ionicity. The weight of the ionic part can be evaluated. For a hypothetical molecule of AlN, according to Nekrasov's formula, the ionicity will be as follows

$$i = \frac{e.n._N - e.n._{Al}}{e.n._N + e.n._{Al}} \times 100\% \tag{4}$$

where *e.n.* is the electro-negativity of the atom [15, 16]. According to this formula, the calculated value of the bond ionicity for an AlN molecule is 12.6% (if Mulliken's values of electro-negativity are used) or 33% (if these values are taken from Pauling's data) [17].

Aluminium oxide is a more ionic compound. The same calculations for the Al_2O_3 molecule give an ionicity weight of 27% (with Mulliken's *e.n.* values) and of 36% (with Pauling's data for *e.n.*) [17]. The ionic part for the bonds in the crystal will be higher than that in the molecule [16, 18] (due to the increase of the coordination number by transition from molecule to crystal). Obviously, the difference between the ionic weight in the bonds for AlN and Al_2O_3 compounds will be more significant for crystals than for molecules (coordination numbers 4 and 6.6, respectively).

It should be noted that generally, at least for the same kind of substances, the increase in the ionicity value is accompanied by an increase in the thermodynamic stability of the compounds (the higher value for the free energy of formation). For these systems, $\Delta G^0_{298} = -287$ kJ/g. at N for AlN and it is much less than that of Al_2O_3 (-528 kJ/g. at O) [12, 19].

As a rule, the wetting of ionic compounds is worse than for covalent ones. Covalent compounds are wetted better by liquid metals.

Experiments revealed worse wettability of the porous AlN in comparison with dense AlN. This can be explained as follows. The influence of the porosity on the wettability can be considered by analogy with the influence of the surface roughness studied elsewhere [1, 20] on the basis of the Wenzel–Deryagin equation

$$\cos\theta = r\cos\theta_o \tag{5}$$

where θ and θ_o are contact angles of the liquid on rough and smooth surfaces, respectively, and r is the ratio of a real surface square to its image on the plane. According to this equation, in the region of wettability ($\theta < 90°$), roughness must cause the contact angle to decrease in comparison with the contact angle on a smooth surface. In the region of non-wettability ($\theta > 90°$), the contact angle on the rough surface would be higher. However, previous experiments [20] show an increase of the contact angle when the roughness increases for both regions ($\theta < 90°$; $\theta > 90°$).

According Naidich and Zhuravlyov [20], the contact angle of a tin–titanium melt on the smooth polished surface of silica glass ($R_a < 0.01\mu m$) is equal to 50.5°. This value increases for rough surfaces to 69°. This fact is explained by the fact that classical ideas do not take into account the direction of movement of a liquid when the equilibrium wetting angle is formed, namely, the advance of the liquid melt. During the advance, the spreading of the liquid on the rough surface will stop when the contact angle reaches the value of the equilibrium angle for a bump of the rough surface, inclined to the surface of the sample with an angle α (α is average angle of the inclination of the rough bumps [20]). Then the visible contact angle will be $\theta_o + \alpha$, i.e. it will increase. The angle α is about 10°–20° for real rough surfaces.

It can be supposed that porosity will influence the contact angle in the same way. Porosity increases the roughness of the surface and produces obstacles to the spreading of the liquid. Obviously, the slow kinetics for a porous substrates is explained by the necessity for the liquid melt to pass over porous obstacles.

5. Conclusion

Contact angles of Sn–Al alloys on an AlN substrate decrease from 122° for pure tin to about 20°, and then increase to 39° for pure aluminium.

The concentration dependence of the wettability passes a minimum at intermediate concentrations.

The work of adhesion increases continuously from tin to aluminium due to the interphase active role of the aluminium in the melt, thus lowering interfacial tension. The surface activity of the tin results in a decrease of contact angle of the melt in the region where it reaches the aluminium concentration.

Comparative experiments made for porous AlN (about 15% porosity) showed it to have worse wettability than dense AlN. The value of the discrepancy in contact angles is about 10°–20°, depending on the melt composition. This difference is explained by the fact that porosity (about 15%) increases the roughness of the sample structure and produces obstacles to the spreading of the melt.

Tin–aluminium melts can be used as adhesive-active solder and binder metal for brazing of aluminium nitride, or for making composite materials with AlN as their base.

Acknowledgement

This work was supported by the International Association for the Promotion of Cooperation with Scientists from the Independent States of the former Soviet Union (Project N INTAS-94-352). The authors thank Professor N. Eustathopoulos (Institut National Polytechnique de Grenoble, France) and Dr A. Vasylyev (Institute for Materials Science Problems, Kiev, Ukraine) for help in making the SEM analyses of the samples.

References

1. YU. V. NAIDICH, "Kontactniye yavleniya v metallicheskih rasplavach" (Naukova dumka, Kiev, 1972) (in Russian).
2. G. V. SAMSONOV, O. P. KULIK and V. S. POLISCHUK, "Poluchenie i metody analiza nitridov" (Naukova dumka, Kiev, 1978) (in Russian).
3. S. RHEE, *J. Am. Ceram. Soc.* **53** (1970) 426.
4. *Idem*, *ibid.* **53** (1970) 639.
5. J. LABBE and G. BRANDY, *Rev. Int. Hautes Temp. Refract.* **26** (1990) 121.
6. A. TOMSIA, J. PASK and R. LOEHMAN, *Ceram. Eng. Sci. Proc.* **20** (1989) 1631.
7. M. TRONTELJ and D. KOLAR, *J. Am. Ceram. Soc.* **61** (1972) 204.
8. M. NICHOLAS, D. MORTIMER, L. JONES and R. CRISPIN, *J. Mater. Sci.* **25** (1990) 2679.
9. YU. V. NAIDICH and N. YU. TARANETS, in "Proceedings of the International Conference of High Temperature Capillarity", edited by N. Eustathopoulos (Institute of Inorganic Chemistry Slovac Academy of Sciences, Bratislava, 1994) p. 138.
10. V. I. NIZHENKO and YU. I. SMIRNOV, *Rasplavy* **1** (1995) 3.
11. V. S. SYNELNIKOVA, V. A. PODYORGYN and V. N. RECHKIN, "Aluminides" (Naukova dumka, Kiev, 1965) (in Russian).
12. I. S. KULIKOV, "Thermodynamika karbidov i nitridov" (Metallurgiya, Chelyabinsk, 1983) (in Russian).
13. J. G. LI, L. COUDURIER and N. EUSTATHOPOULOS, *J. Mater. Sci.* **24** (1989) 1109.
14. J. G. LI, D. CHATAIN, L. COUDURIER and N. EUSTATHOPOULOS, *ibid.* **7** (1988) 961.
15. V. V. NEKRASOV, "Osnovy obschey chimi i", Vol. 2 (Chimiya, Moskva, 1973) (in Russian).
16. S. S. BATSANOV, "Electrootritsatelnost elementov i himicheskaya svyas" (AN SSSR, Novosybirsk, 1962) (in Russian).
17. F. COTTON and G. WILKINSON, "Advanced inorganic chemistry", Vol. 1 (Interscience, New York, 1966).
18. C. A. COULSON, L. B. REDEI and D. STOCKER, *Proc. R. Soc. A* **270** (1962) 357.
19. G. V. SAMSONOV, "Physico-chimicheskive svoystva okislov" (Metallurgiya, Moskva, 1978).
20. YU. V. NAIDICH and V. S. ZHURAVLYOV, in "Poverhnostniye vavleniya v rasplavah i obrazuyuschihsya na nih tverdyh phazah" (Kab-balk. kn. izd-vo, Nalchik, 1965) p. 245 (in Russian).

Received 6 December 1996
and accepted 22 April 1998