Wetting and spreading of molten aluminium against AlN surfaces

C. TOY*, W.D. SCOTT
Department of Materials Science and Engineering, University of Washington, Seattle, WA 98195, USA

Wetting and spreading of molten aluminium against AlN substrates were investigated between 1100 and 1290 °C. The contact angles decreased linearly with time under isothermal conditions between 1100 and 1200 °C. The isothermal rate of spreading of molten aluminium against AlN substrates was constant between 1220 and 1290 °C and the rate increased exponentially with increasing temperature. Crystals of Al_4C_3 nucleated and grew on the substrate surface beneath the liquid. However, the formation of Al_4C_3 may not be solely responsible for the changes in contact angle and spreading. It is postulated that carbon contamination from the substrate and/or experimental equipment coupled with the low oxygen partial pressure of the chamber in the presence of graphite, were primarily responsible for the observed contact angle and spreading phenomena. The activation energy for the spreading process was $448 \, kJ \, mol^{-1}$, suggesting the presence of some chemical reaction at the interface. Carbon-rich aluminium may be initiating a continuous surface reaction with the AlN substrates by reducing the native oxide layer on the substrate surface.

1. Introduction

Aluminium nitride (AlN) is a hard refractory material which was considered for use as a high-temperature structural ceramic and refractory container for molten metals [1–3]. Oxidation of AlN into Al_2O_3 in air occurs at a significant rate above 1000 °C and this would limit its continuous use at high temperatures in oxidation atmospheres [4, 5]. On the other hand, AlN is stable up to 1400 °C in a vacuum, making it useful as a container for evaporation of metals in vacuum systems [6]. Recently, AlN has become an important ceramic substrate material in the electronics industry for thermal management [7]. Metallization of aluminium nitride with tin, aluminium, copper and other conductive metal alloys has been studied intensively for joining purposes [8]. AlN is also of interest for ceramic tile-faced lightweight armour applications [9].

AlN, and composites of AlN with other ceramic materials and metals, have been the subject of several recent studies. Formation of AlN/Al composites by directed metal nitridation [10], vacuum liquid metal infiltration [11], pressure metal infiltration [12] and nitrogen plasma-alloy reaction and spray deposition [13] have all been reported. AlN/Al composites prepared by pressure metal infiltration were shown to have superior thermal conductivity, tensile ductility and strength when compared to SiC/Al and Al_2O_3/Al composites [12]. Infiltration of AlN by aluminium in vacuum at 1220–1280 °C occurred with a relatively

high activation energy, suggesting a chemical interaction between aluminium and the AlN surface [11]. AlN/Al systems and interfacial reactions are therefore of interest for technological development of metallized substrates and composites.

Despite the fact that AlN was used as a crucible for molten aluminium in the past, there are only a few data in the literature with regard to wetting [8, 14–16]. Studies by Rhee [14] and Tomsia *et al.* [8], were at relatively low temperatures, up to 1000 °C, while Nicholas *et al.* [15] measured wetting up to 1140 °C. The results are somewhat contradictory: Rhee [14] reported a 90° contact angle at 850 °C, while Nicholas *et al.* [15] report the same angle at 950 °C. Tomsia *et al.* [8] measured a 140° contact angle at 900 °C. Fujii *et al.* [16] studied the contact angle time dependency of molten aluminium at 1100 °C against AlN substrates in the presence of various additives in AlN compositions. The initial contact angles were determined to be higher than 120° and stayed constant throughout the 2.5 h experiment duration when the AlN substrates contained the lowest amount of additive. The contact angle started to decrease, on the other hand, when the presence of additives was higher than 3%, reaching some new equilibrium value around 90° at 1100 °C. In the same study, the aluminium metal contact angle was also shown to decrease continuously from 115° to 95° at 1100 °C when the 40% carbon-containing AlN–C composite was used as a substrate. For both cases,

---

formation of Al_2O_3 crystals was reported at the AlN/Al interface.

The purpose of the present work was to measure the wetting and spreading of aluminium against AlN substrates in a temperature range above which pressureless infiltration of aluminium into the AlN preforms was shown to occur in a previous study [11].

2. Experimental procedure

Wetting and spreading of molten aluminium was observed on fully dense translucent AlN substrates which were sintered using a CaC_2 additive [17]. They were specified to have a thermal conductivity of $180\ W\,m^{-1}K^{-1}$ and had one polished surface with average roughness less than $0.2\ \mu m$. Substrates $10\ mm \times 10\ mm \times 1\ mm$ and $25\ mm \times 6\ mm \times 1\ mm$ were used for wetting and spreading experiments, respectively. Substrates were cleaned in ethyl alcohol and dried at $60\,°C$ before use. Pre-purified aluminium (at least 99.99%) from the same lot was used in all experiments except in some of the wetting experiments in which ultra-high-purity aluminium with 99.9999% purity was used. The results were similar in both cases. The aluminium was also cleaned in alcohol and dried.

Wetting and spreading experiments were done in a furnace with a tungsten mesh heating element capable of $1800\,°C$ under inert gas and vacuum conditions. The furnace chamber was evacuated by a mechanical pump and maintained at less than $0.13\ Pa$ during vacuum experiments. In argon-atmosphere trials, the gas was passed through a molecular sieve and calcium sulphate for removal of H_2O, followed by hot copper turnings and titanium sponge for removal of oxygen. The AlN specimens were placed flat and level on some AlN bedding powder in a graphite crucible which was threaded to the end of a graphite tube. The graphite tube was long enough so that the upper portion extended into the cold zone of the furnace, thus avoiding damage to the heating element and contamination of the hot zone by aluminium vapour. A W5Re/W26Re thermocouple was used to measure the temperature at the outside of the graphite crucible. A digital optical pyrometer was also used to monitor the molten aluminium temperature through a quartz window in the top of the furnace.

For a wetting experiment, a piece of aluminium metal, weighing approximately 0.25 g, was placed on an AlN substrate. The same heating profile was applied in all experiments. On initial heating, a slight increase in chamber pressure was observed and therefore a pause in the heating was required to maintain the chamber pressure below $0.13\ Pa$. It usually took 35–40 min to reach the melting point of aluminium, after which the heating rate was increased to $20\,°C\ min^{-1}$. The system was held at a constant temperature for a specified time and it was then cooled to the solidification point of aluminium in about 10 min. After removal from the furnace, contact angles were measured with a 10x telescope fitted with a goniometer focused on the middle cross-section of the solidified sessile drop. Symmetry was confirmed for most of the drops, but if there was an asymmetry in
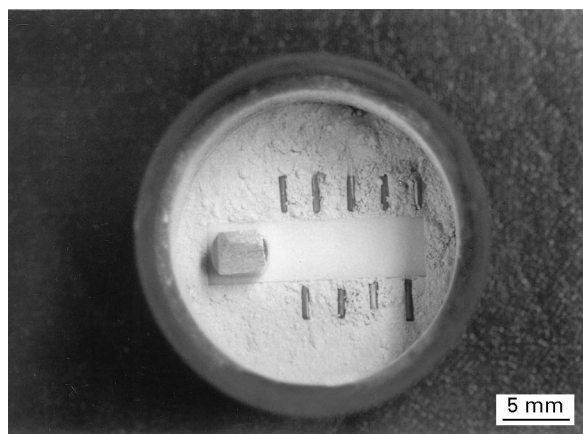

Figure 1 Experimental equipment for measuring the spreading rate of aluminium on an AlN substrate.
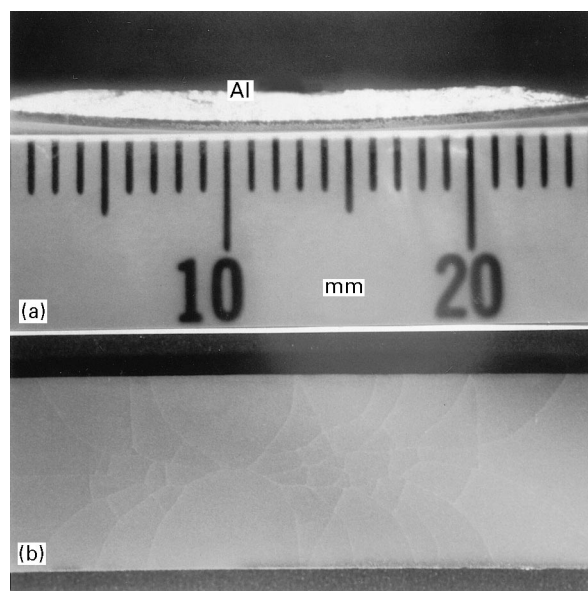

Figure 2 After spreading of aluminium on AlN at $1260\,°C$, (a) a highly bent substrate, and (b) crazing of the AlN bottom surface due to the thermal expansion mismatch, can be seen.

the sessile drop shape, an average value was recorded for the contact angle.

During the higher temperature wetting experiments, the sessile drop did not maintain a stable fixed position but it kept expanding towards the edges of the AlN substrates. An experiment was designed to measure spreading rates with different chamber conditions and temperatures. As shown in Fig. 1, molybdenum wires were placed as markers at 4 mm intervals along the edges of the substrate so that markers were offset 2 mm on opposite sides. An approximately 0.35 g piece of aluminium was placed at one end of the substrate. The chamber was evacuated to the desired pressure level and heated on a schedule similar to the wetting studies. At the peak constant temperature, spreading distance as a function of time was recorded by observing the advancing front of the drop through a window in the top of the furnace. The experiment was terminated when the aluminium covered the entire length of the AlN substrate. The final aluminium layer was about three times thicker than the substrate,

and thermal expansion mismatch on cooling caused the specimen to assume a concave curvature towards the aluminium side, as shown in Fig. 2. Although the substrate was badly cracked from tensile forces, it remained firmly attached to the aluminium.

3. Results and discussion

The effect of temperature on the contact angle of liquid aluminium on AlN is shown in Fig. 3. The contact angles are reported for 10 min soaking at a given temperature under vacuum conditions in a graphite crucible. The contact angles after 15 min soaking time are also reported in Fig. 3 for 1 atm Ar (graphite crucible) and in a vacuum with a molybdenum (graphite-free) environment. The contact angle becomes less than 90° above 1000 °C under ordinary vacuum conditions when the graphite is used. Under 0.1 MPa Ar, a 90° contact angle was not obtained until 1260 °C. At this same temperature under a vacuum with a molybdenum protective tube, the contact angle was 45°, while in the graphic tube environment it was 23°.

Although each AlN/Al study given in the literature was not carried out under similar conditions, comparison of our results to earlier studies can be made at particular points. Contact angles here are at least 50° higher at 900 °C than those reported by Rhee [14]. On the other hand, after 60 min holding time, our results for the same temperature are consistent with those of Tomsia *et al.* [8] and slightly higher than those observed by Nicholas *et al.* [15]. These differences are believed to result from the different sample preparation and furnace conditions used in each study. Rhee etched the aluminium in NaOH and HCl solutions to eliminate the thick oxide layer [14]. This was not done in the present study. In the present work, one aluminium sample was etched in HCl before the wetting experiment and the resulting contact angle was about 10° lower after 10 min at 1100 °C. Therefore, consistent with this observation, the change in slope between 1000 and 1100 °C in Fig. 3 can be attributed to the reduction of alumina skin on the molten aluminium surface. Similar slope changes were observed for Al_2O_3/Al [18] and Al/C [19] systems at 870 and 860 °C, respectively, and experiments with oxidized and clean aluminium materials indicated that the effects were due to the alumina skin on the aluminium surface. This hypothesis was also recently verified by others [20, 21].

Although change of contact angle as a function of temperature is a well established observation and is related to temperature-induced changes in the surface free energies of phases, the change in contact angle as a function of time at constant temperature is not very well understood. Under isothermal conditions, while equilibrium may be achieved after certain holding times for non-reactive systems, it may never be achieved for reactive systems. Particularly at high temperatures, compositions of solid and liquid may change continuously in the vicinity of the interface during an experiment and a reaction product may form between the liquid and solid.
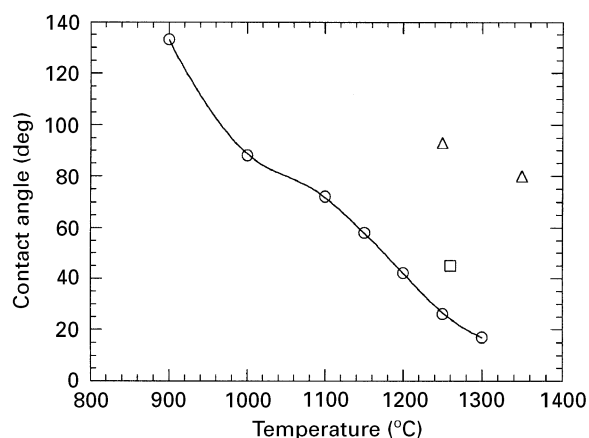

Figure 3 Contact angle of aluminium on AlN substrates as a function of temperature after holding for (○) 10 and (△,□)15 min, in (△) 1 atm Ar, C, (○) vacuum, C, and (□) vacuum, Mo.
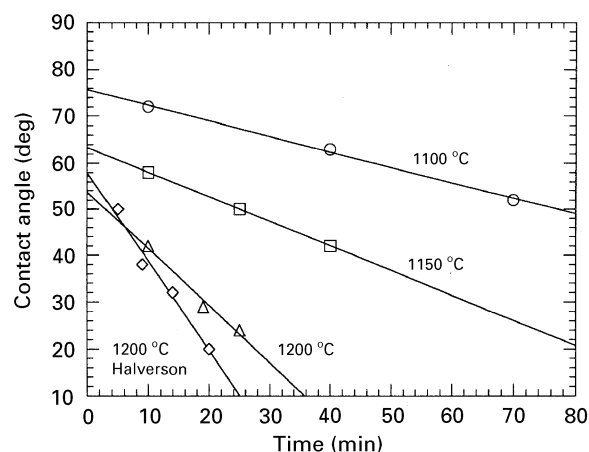

Figure 4 Change of the contact angles as a function of time under isothermal conditions.

Fig. 4 shows the contact angles for aluminium on AlN as a function of time for three different temperatures. We also included the measurements of Halverson [22] at 1200 °C. As is evident from the figure, the contact angle decreases linearly with time over this range. There is no theoretical justification for such linear behaviour if the system is at equilibrium. These results suggest that our system is apparently not reaching equilibrium within the conditions and the time period investigated. Owing to the high evaporation rate of molten aluminium above 1200 °C in vacuum, higher temperatures and longer holding times could not be studied.

Continuous decrease of contact angles as a function of time at constant temperature was also reported for the BN/Al system [23]. AlN and aluminium bond formation at the solid/liquid interface was shown to be responsible [24]. It was also shown that the contact angle slowly approached a constant value at temperatures below about 1100 °C, while complete wetting was obtained at 1196 °C. Tomsia [8] showed that the contact angle of aluminium on AlN decreased very slowly, changing from an obtuse to an acute angle after 7 h at 1000 °C under high vacuum conditions, and decreasing to 53° after 30 h. Although no reaction products were identified at the interface, the decrease

3245

of the contact angle with time at 1000 °C was thought to be caused by a slow reaction of aluminium with impurities in the AlN [8]. Our observations presented in Fig. 4, indicate a nearly linear decrease of the contact angles in the time/temperature range studied, similarly suggesting the presence of a continuous reaction at the interface.

Examination of the solid/liquid interface after removing the solidified aluminium drop with acid, disclosed the presence of small crystals at the interface, as shown in Fig. 5. X-ray diffraction analysis of the sample surface indicated that these crystals were Al_4C_3. It appears from the morphology of the crystal/substrate interface that Al_4C_3 crystals nucleate on the solid AlN surface and grow towards the liquid aluminium (Fig. 6). This morphology strongly indicates that the molten aluminium was contaminated with carbon during the wetting studies so that wetting and spreading were occurring with molten Al–C alloy rather than pure aluminium. It is not known whether Al_4C_3 forms at high temperature or precipitates during the cooling stage, because of the decreasing solubility limit of carbon in the molten aluminium.

There are several possibilities for the source of carbon contamination: the graphite crucible and tube, hydrocarbons back streaming from the pump oil, or the existence of the dissolved carbon in the AlN and/or aluminium metal. Experiments were conducted to identify the source of carbon. For example, the graphite crucible and tube were replaced with a molybdenum system, a liquid-nitrogen cold trap was used to stop hydrocarbon back-streaming and ultra-high-purity aluminium (99.9999%) was used in some wetting experiments. Despite all off these precautions, Al_4C_3 formation could not be avoided. When the AlN substrates were replaced with another type of AlN sintered with a different sintering aid, the amount of aluminium carbide was somewhat reduced, but not completely eliminated. All these trials indicated that the CaC_2 sintering additive in the substrates was the main source of carbon contamination.

Although we observed Al_4C_3 formation in all wetting experiments, the continuous change of contact angle was only observed under vacuum with the graphite tube conditions. Based on this observation, it is certain that formation of Al_4C_3 is not solely responsible for the continuous change of contact angle, and some other mechanism is operating. We suggest that the amount of carbon dissolved in molten aluminium can enhance the wettability and result in spreading in the following way. The solubility limit of carbon in molten aluminium can vary depending on the experimental conditions. It has been reported that more carbon is soluble in molten aluminium under vacuum than in the 0.1 MPa inert gas atmosphere [25]. Therefore, the presence of more carbon in the case of vacuum and very low oxygen partial pressure may activate the aluminium metal for some type of continuous surface reaction. Naidich [20] has shown that addition of oxygen to molten metal can enhance the wetting behaviour in the case of oxide surfaces. The similar situation, i.e. addition of carbon into the molten aluminium under low oxygen partial pressure,
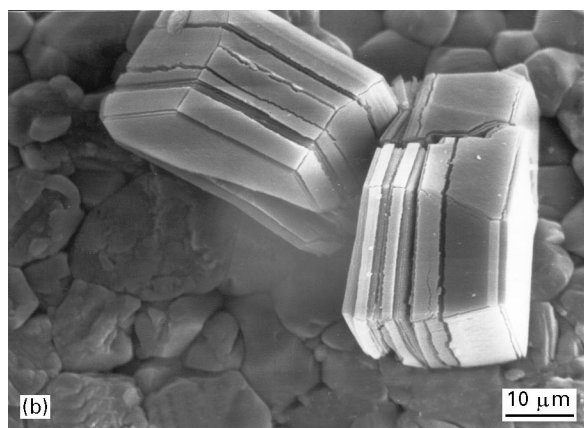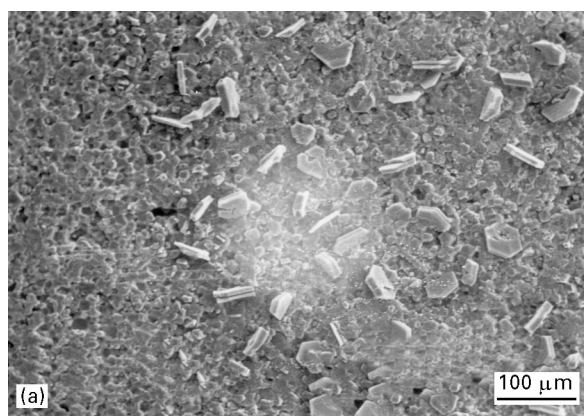

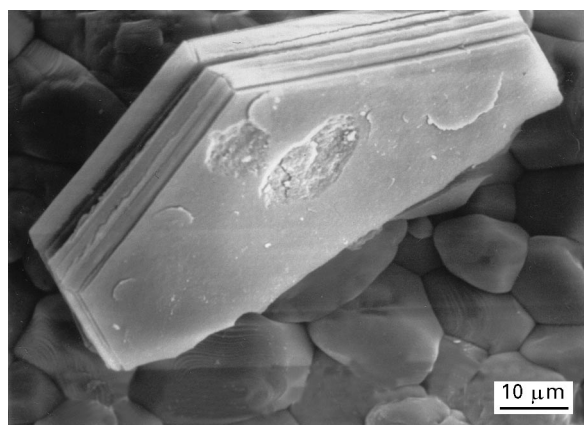Figure 5 (a,b) Al/AlN interface after the removal of aluminium metal.

Figure 6 A growing Al_4C_3 crystal exposed at the solid/liquid interface, by etching away the aluminium in HCl.

may be responsible for the enhancement of wettability of the nitride. It has been shown that the wetting of Al_2O_3 by liquid aluminium can be improved considerably by the presence of an extremely thin carbon layer at the interface [26, 27]. Analysis of the gas composition with a mass spectrometer during wetting of Al_2O_3 showed that enhanced wetting was associated with an increased concentration of hydrocarbons, carbon monoxide and carbon dioxide [26]. Furthermore, the presence of a carbon film on the alumina surface was shown to increase the etching of the alumina surface by molten aluminium [27], suggesting a strong interaction between the two phases. The AlN surface
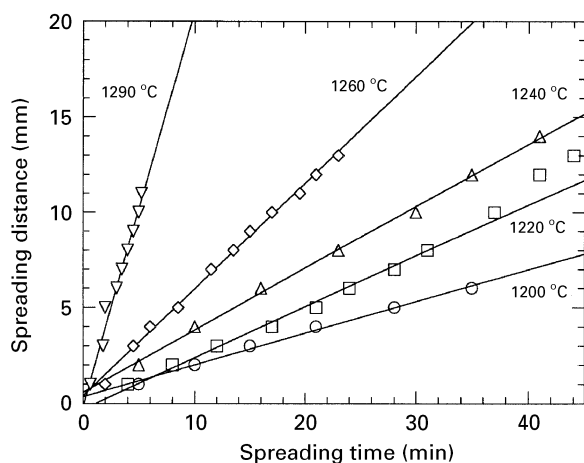
Figure 7 The spreading distance as a function of holding time for several temperatures.

Figure 8 Arrhenius plot to determine the activation energy for spreading, $\Delta H = 448 \text{ kJ mol}^{-1}$.

may also contain a small amount of native oxide from exposure to air. Therefore, the continuous change in contact angle is associated with the reaction of molten aluminium containing carbon with the native alumina layer on the AlN substrates during the wetting and spreading.

As the contact angle decreases with time at a fixed temperature, the area of the solid–liquid interface increases. The rate of advancement of a molten drop was studied in the experimental arrangement shown in Fig. 1. After reaching the constant experimental temperature, the spreading rate of the drop was recorded along the AlN substrate. Fig. 7 shows the spreading distance as a function of spreading time and temperature. Spreading rates were determined from the slope of each line. The spreading rate was constant along the full length of AlN substrates at temperatures between 1220 and 1290 °C. At 1200 °C the spreading rate decreased after 35 min and only the linear portion of the data is shown in Fig. 7 for the 1200 °C curve. When argon was passed through the chamber to maintain 1330 Pa (10 torr) chamber pressure, the spreading rate was significantly reduced and also changed from the linearity observed under vacuum conditions. Spreading experiments were only reproducible in the case of the graphite crucible and tube under vacuum above 1200 °C. No spreading was observed when the graphite was replaced with molybdenum. This suggests that the oxygen partial pressure influences the observed spreading. All these observations show that the chamber pressure and temperature have a major effect on the rate of spreading. An Arrhenius plot of the spreading rate versus reciprocal temperature is given in Fig. 8, from which the activation energy was determined to be 448 kJ mol⁻¹. This high activation energy indicates that spreading is not a simple viscosity-controlled phenomenon but is a chemical reaction process, as is suggested above for the wetting experiments. The exact nature of the chemical reaction is not known, but we suspect that it is activated by the presence of carbon at the interface and/or in the molten aluminium above 1100 °C. We also suspect that the high vaporization rate of aluminium may also contribute to the continuous spreading by evaporation and conden-
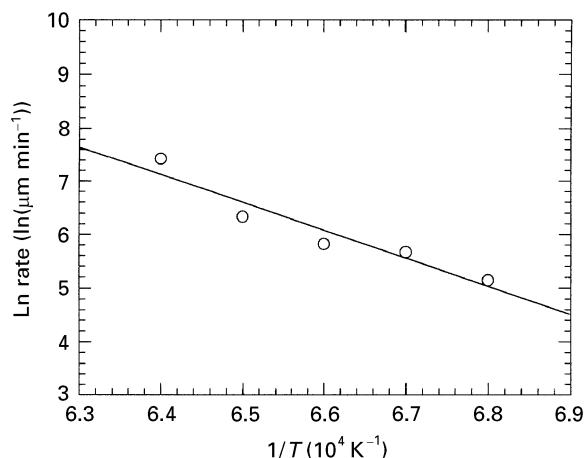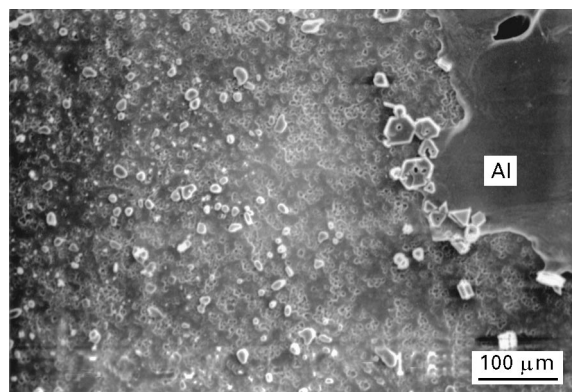

Figure 9 The spreading edge of aluminium on AlN substrate, showing the presence of aluminium droplets at the head of the periphery and Al_4C_3 crystal at the solid/liquid interface after the solidification shrinkage of molten aluminium.

sation because small aluminium droplets were also observed ahead of the periphery as shown in Fig. 9.

4. Conclusion
Wetting and spreading of molten aluminium against an AlN substrate indicate non-equilibrium conditions under vacuum and low oxygen partial pressure above 1100 °C. Formation of Al_4C_3 crystals at the liquid/solid interface was found for all the experimental conditions considered. However, Al_4C_3 formation is not primarily responsible for the presence of non-equilibrium conditions. Contact angle decrease and spreading were linear with time under isothermal conditions. The activation energy of the spreading process was high, 448 kJ mol⁻¹, suggesting that a chemical interaction between Al–C alloy and AlN substrate, other than the formation of Al_4C_3, is primarily responsible for the continuous contact angle change and the spreading process.

References

1. M. BILLY and J. MEXMAIN, *Sprechsall* **118** (1985) 245.
2. G. LONG and L. M. FOSTER, *J. Am. Ceram. Soc.* **42** (1959) 53.
3. *Idem, J.Am. Ceram. Soc. Bull.* **40** (1961) 423.
4. V. A. LAVRENK and A. F. ALEXEEV, *Ceram. Int.* **9** (1983) 80.
5. K. M. TAYLOR and C. LENIE, *J. Electrochem. Soc.* **107** (1960) 308.
6. G. LONG and L. M. FOSTER, *Ceram. Bull.* **40** (1961) 423.
7. W. WERDECKER and F. ALDINGER, *IEEE Trans. Compos. Manufac. Technol.* **7** (1984) 399
8. A. P. TOMSIA, J. A. PASK and R. E. LOEHMAN, *Ceram. Eng. Sci. Proc.* **10** (1989) 1631.
9. E. SAVRUN, C. Y. TAN and J. ROBINSON, in "Proceedings of the 22nd SAMPE Technical Conference", Boston, MA, edited by D. Michelooe *et al.* (The Society for the Advancement of Material and Process Engineering, Covina, CA, 1990) p. 619.
10. H. SCHOLZ and P. GREIL, *J. Mater. Sci.* **26** (1991) 669.
11. C. TOY and W. D. SCOTT, *J. Am. Ceram. Soc.* **73** (1990) 97.
12. S. LAI and D. D. L. CHUNG, *J. Mater. Sci.* **29** (1994) 3128.
13. A. INOUE, K. NOSAKI, B. G. KIM, T. YAMAGUCHI and T. MASUMOTO, *ibid.* **28** (1993), 4398.
14. S. K. RHEE, *J. Am. Ceram. Soc.* **53** (1970) 386.
15. G. NICHOLAS, D. A. MORTIMER, L. M. JONES and R. M. CRISPIN, *J. Mater. Sci.* **25** (1990) 2679.
16. H. FUJII, H. NAKAE and K. OKADA, *Metall. Trans.* **24A** (1993) 1391.
17. Y. KUROKAWA, K. UTSUMI and H. TAKAMIZAWA, *J. Am. Ceram. Soc.* **71** (1988) 588.
18. J. J. BRENNAN and J. A. PASK, *ibid.* **51** (1968) 569.
19. N. EUSTATHOPOULOS, J. D. JOUD, P. DESRE and J. M. HICTER, *J. Mater. Sci.* **9** (1974) 1233.
20. J. V. NAIDICH, *Progr. Surface Memb. Sci.* **14** (1981), 354.
21. L. MOURADOFF, A. L. DURAND, J. DESMAISON, J. C. LABBE, O. GRISOT and R. REZAKHANLOU, *J. Eur. Ceram. Soc.* **13** (1994) 323.
22. D. C. HALVERSON, private communication, unpublished study, 1990.
23. X. M. XUE, J. T. WANG and M. X. QUAN, *J. Mater. Sci.* **26** (1991) 6391.
24. *Idem, Mater. Sci. Eng. A* **132** (1991) 277.
25. L. F. MONDOLFO, "Aluminium Alloys; Structure and Properties" (Butterworth, London, 1976) p. 236.
26. H. JOHN and H. HAUSNER, *Int. J. High Technol. Ceram.* **2** (1986) 73.
27. D. A. WEIRAUCH and W. J. KRAFICK, *Metall. Trans.* **21A** (1990) 1745.