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Effect of temperature and surface roughness on the wettability of boron nitride by molten Al

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Abstract Reactive wetting of hexagonal BN by molten Al at 1073–1273 K was studied using an improved sessile drop method. The temperature and substrate surface roughness have a remarkable effect on the wetting behavior. Reasons for the large discrepancy in the final contact angles reported in the literature were addressed.

Introduction

Boron nitride (BN) is an intriguing ceramic because of its unique combination of properties such as low density, high melting point, high thermal conductivity and electrical resistivity, and good chemical stability at high temperatures. Therefore, it is generally used as a refractory material for high-purity alloy melting and crystal growth as well as a radiator substrate [1, 2]. Recently, it has also been used as reinforcement in aluminum matrix composite fabricated by pressureless infiltration [3], wherein the wettability of BN by molten Al plays a key role. One of the authors [4, 5] previously reported perfect wetting of hexagonal BN (*h*-BN) by molten Al at $T \geq 1273$ K and suggested, from the viewpoint of wetting, that *h*-BN might be the optimum ceramic material to be incorporated into an aluminum matrix. Other investigators [2, 6–10], however, reported much larger and quite scattered final stationary contact angles, as indicated in Table 1. The reasons for this significant scatter are not fully understood, although a reason concerning the different extents of the Al surface oxidation in different authors' work has been suggested [4]. The objective of this study is to probe into the possible reasons for these apparently different wetting results.

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Experimental procedure

The materials used in this study were high purity (99.99 wt.%) aluminum wire segments ($\phi = 3$ mm), weighing about 0.14–0.16 g, and sintered polycrystalline *h*-BN substrates with a purity over 99 wt.% and in dimensions of $20 \times 20 \times 5$ mm (produced by Kojundo Chemical Co., Saitama, Japan). The surfaces of the BN substrates were ground on No. 4000 silicon carbide sandpapers and polished by different micron-sized diamond pastes (6, 3, 1 and 0.25 μm). The polished substrates and the Al wire segments were then separately immersed in acetone and ultrasonically cleaned. Because of the soft nature of *h*-BN and some pores in the sintered samples, the surface roughness (Ra) of the substrates after the polishing and cleaning treatments is relatively large (Ra = 90–300 nm, depending on the extent of polishing) as measured by a surface profilometer (Dektek 3, Veeco Instrument, Inc., NY, USA; Scans were made in a distance of 2 mm at a speed of 80 μm/s and the average of the six values obtained at different positions was presented).

Table 1 Reported final stationary contact angles in the Al–BN system

θ (degree/after wetting time t (s)				Atmosphere	Reference
1073 K	1173 K	1273 K	1373 K		
–	–	–	<90 for h-BN < 60 for c-BN	Unknown	[8]
160	158	90	35	Vacuum	[9]
150/7200	136/7200	49/9000	–	Vacuum	[10]
140^a/3600	112^b/3600	72^c/1800	36^d/3600	Vacuum	[6,7]
–	130/3600	0/7200	0/~2000	Vacuum and He–3%H_2	[4]

^{a} 1070 K; ^{b} 1190 K; ^{c} 1290 K; ^{d} 1380 K

An improved sessile drop method, described in detail elsewhere [11, 12], was employed for the wetting experiments. The Al drops were formed by extruding the liquid through a small hole (ϕ = 1 mm) at the bottom of an alumina tube (in 99.6 wt.% purity) so as to remove the oxide film covering their surfaces. The wetting experiments were performed at 1073, 1173, and 1273 K, respectively, for 30 min in a purified Ar–3% H_2 atmosphere. The contact angles were measured from the drop profiles using an axisymmetric-drop-shape analysis (ADSA) program. After the experiments, the interfacial microstructures in selected samples were examined by an environmental scanning electron microscope (ESEM-2700, Nikon Co., Japan) with EDAX capability.

Results and discussion

Figure 1 shows the variation in contact angles with time and Fig. 2 gives the representative photographs showing this change. As indicated, the contact angles seem to be very sensitive to the temperature and substrate surface roughness. The initial contact angles at the testing temperatures are generally in the range of 120–140°. With the increase in time, the dynamic contact angle does not show an appreciable decrease at 1073 K but shows a moderate decrease at 1173 K and a remarkable decrease at 1273 K. Depending on the surface roughness, the final contact angles (after 30 min) at 1273 K obtained in this study are ~103° for Ra = 240 nm, ~84° for Ra = 138 nm, ~80° for Ra = 120 nm and ~62° for Ra = 94 nm, respectively.

Microstructural examinations indicate that Al reacts with h-BN at $T \geq 1173$ K, forming a continuous layer of AlN at the interface (see Fig. 3) and liberating B, which reacts again with Al to form boride precipitates (according to the Al-B phase diagram, the precipitated phase is AlB_{12} at $T > 1258$ K and AlB_2 at $T < 1258$ K [4]). The wetting is promoted by this interfacial reaction. At $T = 1073$ K, the reaction is insignificant and the adhesion of Al to the BN surface is very weak. Thermodynamic calculations, however, indicate that the reaction of $3Al + 2BN = 2AlN + AlB_2$ is energetically favorable at 1073 K ($\Delta G_{r(1073\ K)} \approx -226.128$ KJ mol^{-1} [13]). In practice, this reaction does proceed at 1073 K, as observed by Lee et al. [3] in their fabrication of an AA6061/BN composite using the pressureless infiltration technique. It was insignificant here much likely because of the immediate formation of a thin oxide film on the aluminum surface after the liquid was extruded. The oxide film, even with a few tens of nanometers, may substantially inhibit an intimate contact of Al with BN at the interface. As having been demonstrated in many studies on the wetting in an Al-alumina system [12, 14–17], the Al surface oxidation and its effect on the wettability usually could not be eliminated at $T \leq 1173$ K; However, beyond this temperature, this effect turns to be minor or even negligible for the experiments conducted in high vacuum (>10^{-3} Pa) or in a reducing atmosphere due to an enhanced metal evaporation (which lowers the oxygen partial pressure around the Al drop) and the reaction between Al and alumina to form gaseous Al_2O. This is particularly true for the Al drops created by a dosing method as did in this work. On the other hand, as the reaction between Al and BN progresses, the solid–liquid–vapor triple line advances (see Fig.2 for an illustration). In this case, the oxide film, if still existing, can be easily destroyed by the triple line movement. Therefore, the large scatter in the reported final stationary contact angles obtained at $T \geq 1273$ K may not be simply attributed to the effect of the Al surface oxidation but to others.

With regard to the contact angles shown in Fig. 1, the effect of the substrate surface roughness on the wetting kinetics and the final contact angle is quite noticeable. Increasing surface roughness leads to larger final contact angles. This is not surprising since the spreading of Al could be easily pinned by a ridge or undercutting (e.g., pore) barrier at the triple junction. On the other hand, it was found that in all the samples tested at $T \geq 1173$ K, an extended reaction proceeded in front of the triple line, forming the same product

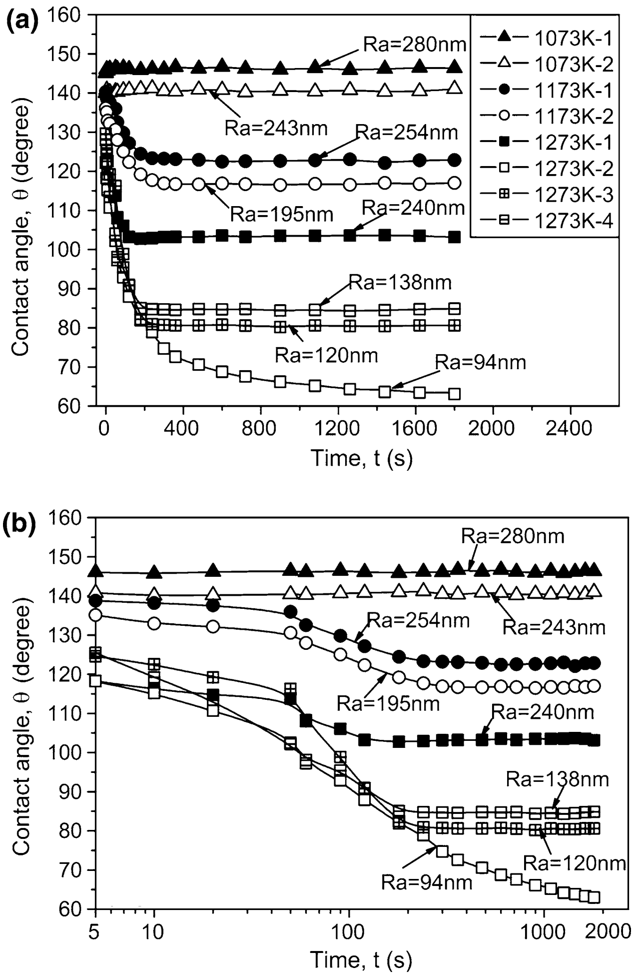

Fig. 1 Variation in contact angle with time for Al on different roughness of BN surfaces at 1073–1273 K plotted on (**a**) linear and (**b**) logarithmic timescales

(i.e., AlN) as that beneath the Al drop. Such a reaction is most likely induced by molten Al infiltration through the porous substrate surface, although either the Al diffusion to or evaporation and then condensation ahead of the triple line may also play a role. The configuration at the solid–liquid–vapor triple junction thus changed from the initial BN–Al–vapor to the final AlN–Al–vapor, as schematically shown in Fig. 4a. According to the viewpoint of Eustathopoulos [18, 19] that the wetting in a reactive system is determined by the final interfacial chemistry at the triple line, the final stationary contact angles should be close to those for Al on AlN provided that the surface roughness does not exert an influence on the wettability, which are generally in the range of 40–60° at 1273–1373 K [9, 20–23]. The larger final contact angles at $T > 1223$ K listed in Table 1, on the other hand, may result from the effect of the substrate surface roughness as demonstrated in this study (note that the reaction also increased the roughness at and the triple junction).

It seems quite strange that the final zero-degree contact angle could be produced in the Al–BN system, as previously reported by one of the authors [4]. One possible explanation is that the reaction product layer has never extended to the free surface beyond the triple line during the reactive wetting (this needs the spreading rate of Al on the BN surface should be always larger than or at least comparable to the reaction rate and the AlN formation rate). In this case, a critical configuration like Fig. 4b and a corresponding dynamic contact angle (θ_d) following

$$\cos\theta_d = \frac{\sigma_{sv} - \sigma_{pl}}{\sigma_{lv}} \quad (1)$$

could be derived, where σ_{sv} denotes the surface energy of BN beyond the triple line, σ_{pl} denotes the interfacial energy between Al and the reaction product AlN, and σ_{lv} denotes the surface tension of liquid Al (assuming the librated B does not change the surface tension of

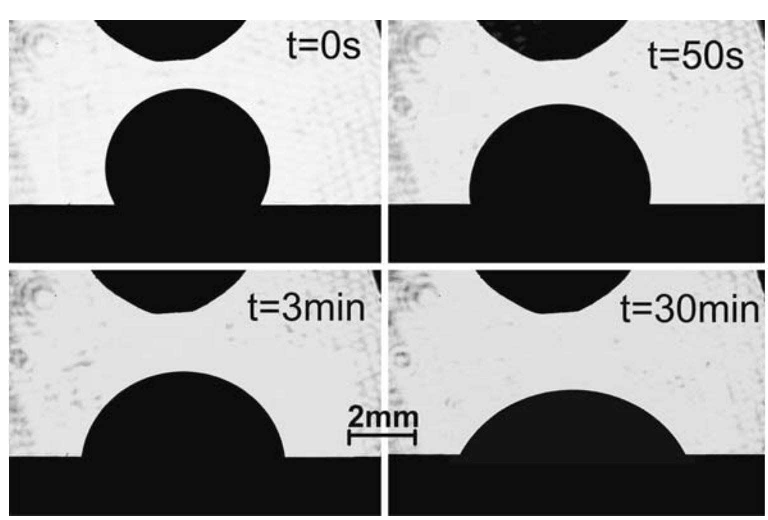

Fig. 2 Representative photographs showing the changes in the Al drop shape and contact angle with time ($T = 1273$ K and Ra = 94 nm)

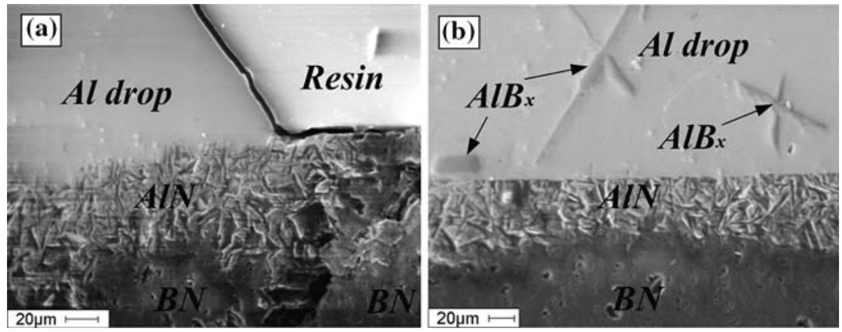

Fig. 3 Interfacial microstructures in the sample tested at 1273 K: (**a**) formation of reaction product at the solid–liquid–vapor triple line and (**b**) formation of boride precipitates in the Al drop

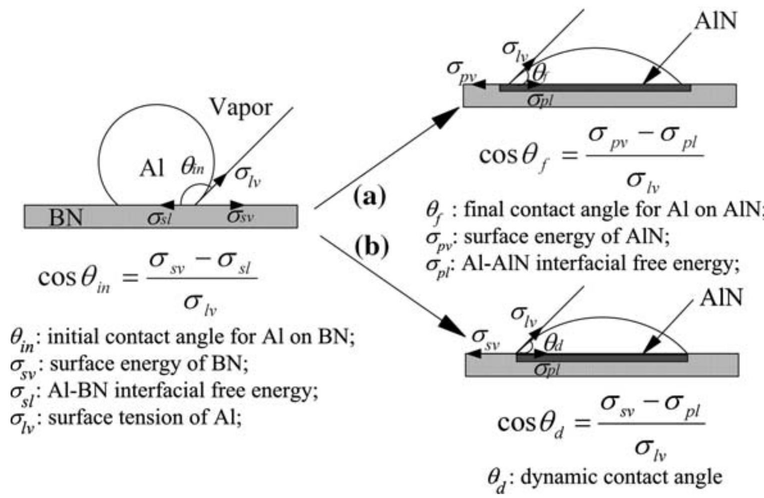

Fig. 4 Two possible configurations for the development of the contact angles for Al on the BN substrates: (**a**) the reaction preceding the wetting at the triple junction, and (**b**) the reaction lagging or progressing at the same rate as the wetting at the triple junction

molten Al). Providing $\sigma_{sv} >> \sigma_{pl}$ and $\sigma_{sv} > \sigma_{lv}$, the contact angle will decrease to zero degree in the end. In other words, this possibility needs both the thermodynamic (interfacial energies) and kinetics conditions to be satisfied. Such a configuration (Fig. 4b), however, was thought to be metastable [18, 19].

Another possibility is that AlN is essentially perfectly wetted by molten Al. If so, it might be reasonable for the final stationary contact angle for molten Al on the BN surface to be zero. In fact, a close-to-zero-degree contact angle for Al on the AlN substrate was reported by Naidich and Taranets [21] at a temperature approaching 1473 K in a vacuum about 2×10^{-3} Pa. The much higher contact angles reported by others for Al on AlN might be affected by experimental conditions such as Al and/or AlN surface oxidation and substrate surface roughness. Prin et al. [23] demonstrated that the Al and/or AlN surface oxidation is incident and plays a significant role in deteriorating the wettability.

Summary

In summary, we have examined the wettability of hexagonal BN by molten Al at 1073–1273 K using an improved sessile drop method. The results show that both the temperature and substrate surface roughness have a remarkable effect on the wetting behavior. The initial contact angles for Al on BN are generally in the range of 120–140°. At $T < 1173$ K, because of the Al surface oxidation, the contact angle does not show a time-dependent decreasing behavior, whereas at $T > 1173$ K, the interfacial reaction between Al and BN leads to a considerable decrease in the dynamic contact angle, and the final contact angle strongly depends on the substrate surface roughness. At high temperatures, in the case of a reaction preceding wetting in front of the triple line, the final contact angles, in principle, should be close to those for Al on AlN, i.e., the reaction product at the Al–BN interface. The *intrinsic* wettability of AlN by molten Al, on the other hand, might be perfect, i.e., the stationary contact angle is zero degree at $T \geq 1273$ K, provided without any influence of surface oxidation and roughness.

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