The Effect of Carbon on Wetting of Aluminum Oxide by Aluminum

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Vapor-deposited carbon films on sapphire enhance its wettability by high-purity aluminum. A reduction in the terminal contact angle of 30 deg, to a value of 31 deg, occurs at 1223 K under vacuum conditions. This effect is related to either the dissolution of carbon in aluminum or the formation of aluminum carbide. Etching of the sapphire by molten aluminum is greatly enhanced by the presence of carbon, as revealed by profilometry of substrates following removal of the aluminum sessile drops.

I. INTRODUCTION

NUMEROUS studies have shown that the contact angle of aluminum on aluminum oxide exceeds 90 deg at temperatures below 950 °C to 1000 °C.[1-12] This is due to the protective oxide film which forms on the molten aluminum and acts as a barrier to the formation of a true Al-substrate interface.[2,3,7,11-13] Since aluminum is such an attractive matrix material for metal-matrix composites, much work has centered on improved fabrication techniques.[14,15] Most of this effort has been aimed at improving the infiltration of molten aluminum into fiber preforms. In a recently published study, John and Hausner presented a technique to improve the wetting of aluminum oxide by aluminum whereby they applied thin carbon films to the oxide surface.[16] This approach has been studied in more detail in order to determine the mechanism of the contact angle reduction.

II. EXPERIMENTAL PROCEDURE AND MATERIALS

Sessile drops were formed by melting pellets (0.03 to 0.30 g) of 6N purity aluminum (Aesar: Johnson-Matthey, Inc., Seabrook, NH) in situ on various substrates. Wetting experiments were conducted on graphite, sapphire, and carbon-coated sapphire substrates.

The dense (1.74 g/cm^3), fine-grained graphite substrates were machined from 4.4-cm-diameter rods (ATJ grade from Union Carbide Corporation, Carbon Products Division, Cleveland, OH) and polished to a 5 micron finish with diamond paste yielding a disk approximately 3-mm thick. The average roughness of the finished surface as determined with a profilometer was 0.5 to 1.3 microns.

Sapphire disks (General Ruby and Sapphire Corporation, New Port Richey, FL), 1.7-cm in diameter and 0.3-cm thick, presented the (0001) surface. The average surface roughness of the sapphire was 0.03 microns.

Carbon films were deposited on the sapphire substrates by a vapor deposition process using a commercially available sample coating device (EFFA* carbon

coater, catalog no. 12560) which is used for scanning electron microscope (SEM) sample preparation. Films ranging from barely visible to dark brown were obtained by vaporizing carbon filaments in single or multiple passes ranging from 1 to 18 (Figure 1). Many techniques were used to characterize the resultant films. Profilometry, X-ray diffraction (XRD), SEM, X-ray photoelectron spectroscopy (XPS), and optical microscopy. Only the samples that had been subjected to 12 coating events revealed any crystalline structure when examined by Laue X-ray diffraction. Attempts to determine the thickness of the carbon films by depth profiling using Auger electron spectroscopy and XPS were unsuccessful due to charging during sputtering. Profilometer step height measurements of masked samples were more successful. No step height could be resolved on the 1 or 2 deposition event samples. The samples with three or more vaporization events exhibited similar step heights which ranged between 110 and 205 nm. In addition, the average roughness of the films was 20 to 30 nm, similar to that of the uncoated sapphire, and independent of the number of coating events. Morphological differences in the films could not be seen by either optical microscopy or SEM due to the extremely fine-grained nature of the deposits.

The aluminum chunks and sapphire substrates were cleaned and degreased in an ultrasonic bath for 10 minutes each in trichloroethane and high-purity, liquid chromatography (HPLC) grade acetone. The graphite was cleaned in an ultrasonic bath after polishing. The carbon-coated sapphire substrates were stored in a vacuum oven until use and not subjected to any cleaning prior to the wetting experiment. The metal and substrate were dried in a hot air blast, inserted in the furnace, and outgassed at 250 °C in a vacuum of 1.3×10^{-2} Pa (10^{-4} torr) for 2 hours. Most of the sessile drop experiments were conducted in a graphite-lined furnace under medium (approximately 1.3×10^{-2} Pa or 10^{-4} torr) vacuum conditions. A few experiments were also run in this furnace under 1 liter/min flowing argon (oxygen-free grade from Linde Specialty Gas Division of Union Carbide). More details concerning this experimental apparatus are presented elsewhere.[12] Some experiments were also conducted in a quartz tube furnace system, which is diagramed in Figure 2. Since the porous graphite lining is eliminated
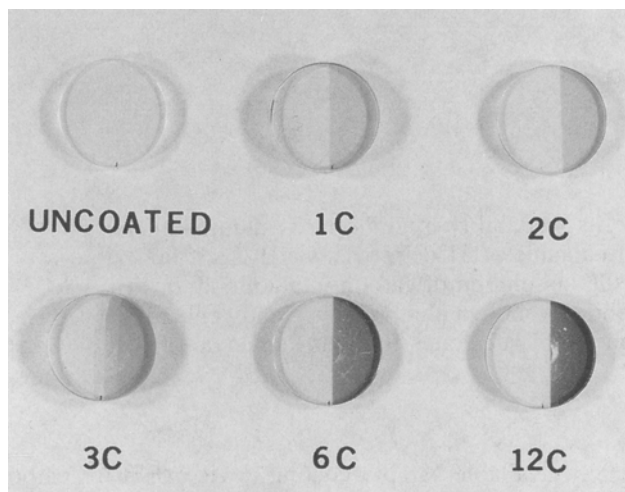
Fig. 1—The appearance of the vapor-deposited carbon films on sapphire. The labels "1C," "2C," etc. refer to the number of carbon deposition events.
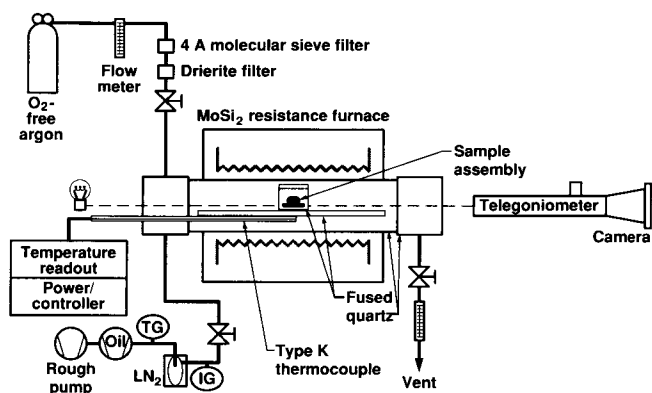

Fig. 2—Schematic diagram of the fused-quartz sessile drop apparatus.

in this apparatus, a much better vacuum (approximately 7 mPa) is attained at temperature.

III. RESULTS AND DISCUSSION

Selected contact angle results are summarized in Table I. The final contact angle of aluminum on sapphire at 950 °C is not significantly different from that of aluminum on graphite when the measurement is made in a graphite-lined furnace under vacuum conditions. Since the contact angle of aluminum on sapphire is the same under vacuum conditions in a silica tube furnace, the similarity is not due to an interaction of the carbon-saturated furnace atmosphere with the sapphire substrate.

Lower angles are achieved at 950 °C in a vacuum than under argon. This is true for aluminum on sapphire due to the rate of removal of a volatile suboxide which helps to remove the oxide film on aluminum and also the volatile product from the interaction of molten aluminum with the (0001) surface of sapphire.[3,4] In the case of Al on graphite, the same effect is observed, although the contact angle under flowing argon is much higher than that observed under vacuum. The higher contact angle observed for graphite compared to sapphire at 950 °C under flowing argon might be due to the formation of a thicker oxide film from the greater outgassing of the more porous graphite substrate during heatup. The same effect is observed for Al on the carbon-coated sapphire when one compares conditions to a flowing argon atmosphere.

The final contact angles observed for aluminum on sapphire include those of this study and values from this laboratory reported in an earlier study.[12] The contact angles observed for aluminum on graphite are compared to values cited in the literature in Table II.

There is general agreement between the contact angles cited in Table II, with the exception of the values determined under vacuum at 950 °C in the present study, which are significantly lower. There is also general agreement from these studies that the contact angle drops as temperature is raised. As stated earlier, the oxide film on the aluminum retards the reaction of molten aluminum with the substrate; consequently, vacuum conditions lead to lower contact angles by removing the oxide film which inhibits wetting as well as carbide formation.

In the present study, contact angles were further reduced by vapor depositing carbon films on sapphire substrates. The variation in observed contact angle with time is summarized in Table III.

Initial contact angles were very variable, probably due to differences in structure and thickness of the oxide film that formed during the ramp to 950 °C.[12] The time required for the contact angles to attain a stable value ranged

Table I. Summary of Contact Angles of High-Purity Aluminum on Selected Substrates*

Substrate	Furnace	Atmosphere (deg)	Final Contact Angle	
			800 °C	950 °C
Sapphire	graphite	vacuum	123	63, 59
	graphite	argon	100	82, 84, 83
	silica	vacuum	139	62
	silica	argon	141	—
Graphite	graphite	vacuum	169	54, 57
	graphite	argon	164	128
C-coated sapphire**	graphite	vacuum	—	43
	graphite	argon	—	79
	silica	vacuum	144	36, 38

*Direct readings after more than 20 hours at temperature.
**Three vapor deposition events.

Table II. The Final Contact Angle of Aluminum on Graphite

Substrate	Contact angle (deg) 800 °C	950 °C	1000 °C	Atmosphere	Time (h)	Reference
Graphite	169	55.5	—	10^{-4} torr	>20	this study
	164	128	—	argon		
Graphite	140	—	72	hydrogen	1	17
Vitreous carbon	150	—	110	argon	0.5	13
Vitreous carbon	125	—	65	10^{-6} torr	1.5	13
	144	124	105	10^{-5} torr	1	18
Diamond	—	—	75	10^{-3} torr	2	19
Pyrographite	100	—	80	10^{-5} torr	2	9

Table III. Summary of Contact Angle Measurements at 950 °C in Vacuo

Run No.	Run Order	No. C Deposition Events	Mass Al Drop (g)	Time (h) 0	0.33	0.50	0.75	1.0	1.5	2.0	2.5	3.0	19	24
1	1	0	0.269	78	74	74	74	74	75	74	73	73	64	63
2	13	0	0.256	124	91	89	89	89	87	86	85	84	71	71
3	3	1	0.290	144	119	100	86	75	68	68	68	68	68	65
4	4	2	0.319	156	141	135	129	121	110	98	89	77	56	60
5	9	2	0.027	71	58	59	58	56	55	54	54	53	44	43
6	2	3	0.168	155	149	140	128	119	100	90	84	71	44	43
7	5	6	0.207	160	151	145	136	132	123	114	104	99	39	39
8	10	6	0.028	76	67	62	57	55	51	46	46	45	38	35
9	11	9	0.027	84	80	80	76	73	67	63	60	57	31	31
10	14	9	0.029	161	140	127	118	113	93	78	64	55	42	42
11	8	12	0.123	154	150	147	131	123	112	106	103	100	64	53
12	12	18	0.028	150	110	94	75	67	65	65	65	65	61	61
13	7	graphite substrate	0.150	157	131	125	119	108	96	90	88	87	63	54
14	6	graphite substrate	0.169	163	—	143	137	126	98	94	89	—	60	57

from 1 hour to greater than 3 hours. The contact angle kinetics are presented for selected experiments in Figure 3. Interestingly, small drops with carbon coatings that yielded low final contact angles (runs 5 and 8) dropped below 90 deg by the time the furnace reached 950 °C ("time 0"), whereas the larger drops required several hours to do so.

The lightest carbon application, 1 carbon deposition event (1C), did not significantly reduce the final contact angle relative to uncoated sapphire (60 and 65 compared to 63 and 71 deg). Two carbon deposition events did succeed in reducing the final contact angle significantly but only when a small sessile drop was used. The combination of 3 carbon deposition events (3C) and a relatively large sessile drop produced an identical, low final contact angle of 43 deg. Drop size had a much smaller effect when 6 carbon deposition events were applied to the sapphire. The lowest value, 31 deg, was obtained for 9 deposition events (9C). Interestingly, 12 or 18 deposition events resulted in contact angles of 53 and 61 deg, comparable to the values of 54 and 57 deg obtained on graphite substrates.

Even though the solubility of carbon in liquid aluminum at 950 °C is expected to be very low,[20] aluminum samples were analyzed to determine differences in carbon content. Quenched sessile drops were carefully removed from their substrates with a diamond wafering saw. These samples were then analyzed for carbon con-

tent using a LECO* carbon analyzer. The aluminum pel-

*LECO is a trademark of Leco Corporation, St. Louis, MI.

let starting material registered 0.01 wt pct carbon, which is at the limit of detection. Due to the small sample size (0.1 g or less), there was too much uncertainty in the
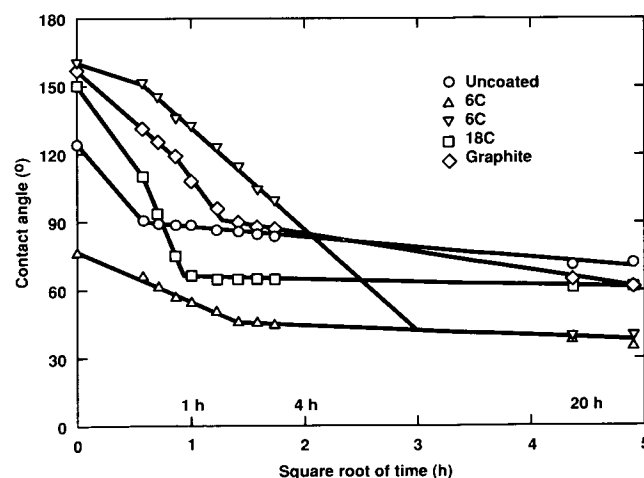

Fig. 3—Change in contact angle of aluminum on various substrates with time at 950 °C in a medium vacuum. The labels "1C," "2C," etc. refer to the number of carbon deposition events.

sessile drop analyses for the samples exposed to the carbon films, which registered less than 0.01 pct. Consequently, calculations were undertaken to determine the amount of carbon that would be taken up by the aluminum drop, assuming that all of the film in contact with the drop participated. Average drop diameters were determined from etch lines on the quenched samples. Starting aluminum masses were used in the calculations, although the sessile drops typically lost 0.5 wt pct during the experiments. The mass of carbon deposited on the sapphire substrate was scaled to the number of deposition events from a measurement for an 18-event deposition. The results of these calculations are presented in Table IV.

The final contact angle is plotted against added carbon concentration in Figure 4. For sessile drops with added carbon contents below 125 ppm, the aluminum/sapphire interface as viewed through the sapphire has shiny patches when viewed in reflected light, suggestive of a clean Al-Al_2O_3 interface (Figure 5(a)). For higher carbon contents, the interface has a dull appearance (Figure 5(b)), and the final contact angle is close to that of Al on graphite (Figure 4, labeled "Heavy LS Interfacial Deposition"). In yet other cases, there is a dull interface cut by bright channels (Figure 5(c)). The aluminum sessile drops were removed with a 50 pct NaOH solution, allowing the liquid/solid (LS) interface to be examined by SEM and XRD. Figure 6 shows two examples of the exposed

(a) 6 C-Run 8

(b) 18 C-Run 12

Table IV. Calculated Carbon
Contents of the Aluminum Sessile Drops

Run Number	Mass Al (g)	Added Carbon Content (ppm)	Number of Carbon Deposition Events
1	0.2692	0	0
3	0.2896	6	1
4	0.3193	15	2
5	0.0273	39	2
6	0.1682	35	3
7	0.2074	65	6
8	0.0278	123	6
9	0.0265	243	9
10	0.0288	171	9
11	0.1233	133	12
12	0.0280	237	18

(c) 6 C-Run 7

Fig. 5 — The Al-Al_2O_3 interface of quenched sessile drops as viewed through the sapphire substrate: (a) 6C = run 8; (b) 18C = run 12; and (c) 6C = run 7.
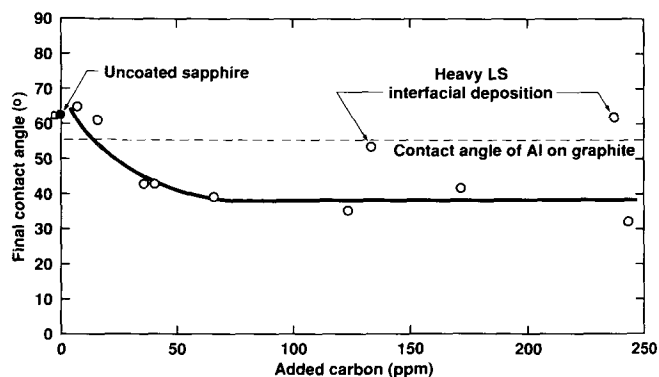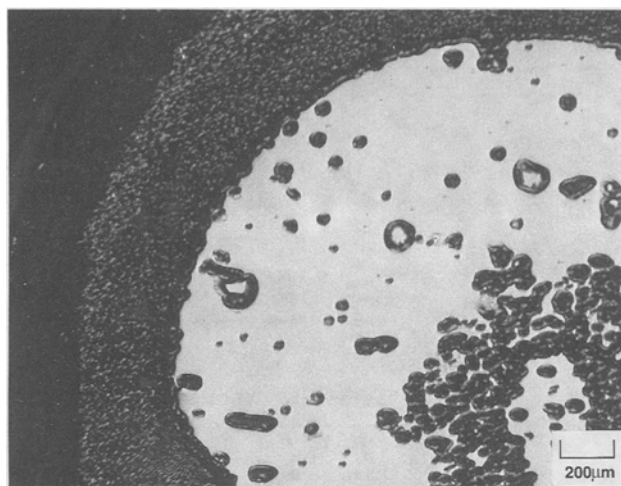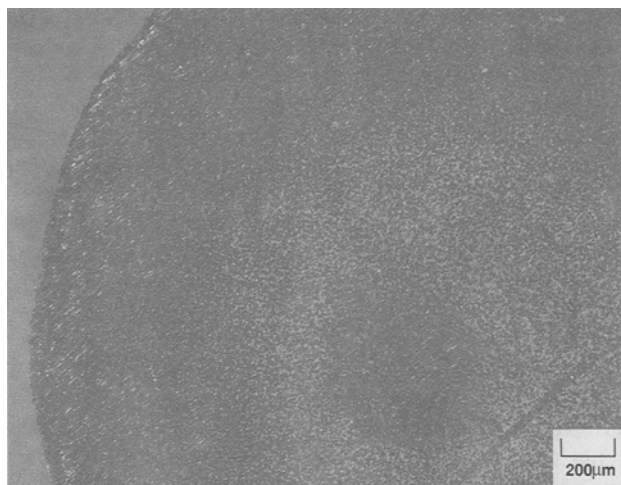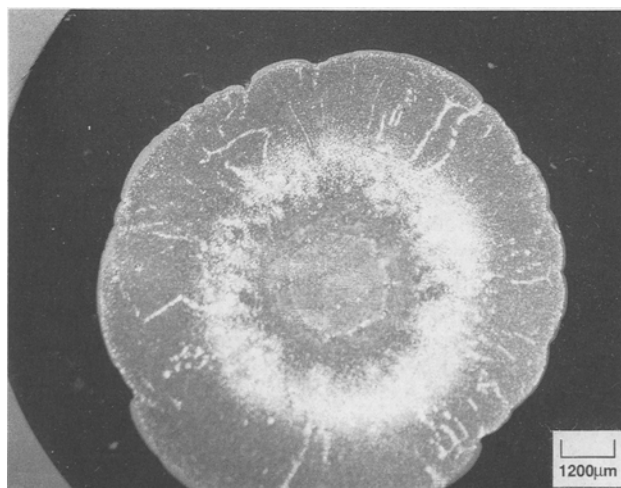

Fig. 4 — The effect of the amount of deposited carbon on the wetting of (0001) sapphire by aluminum. The label "LS" refers to the liquid/solid interface.
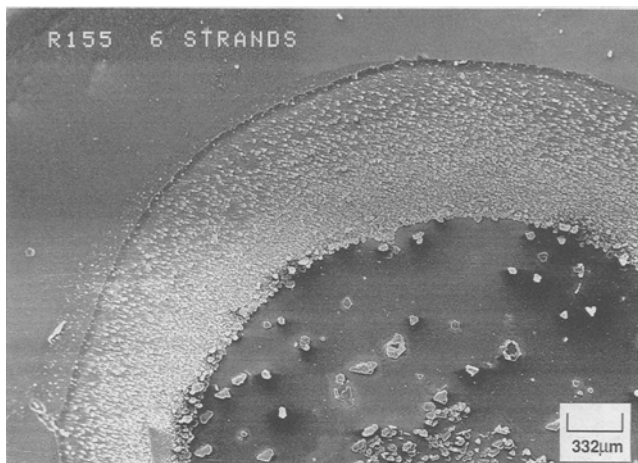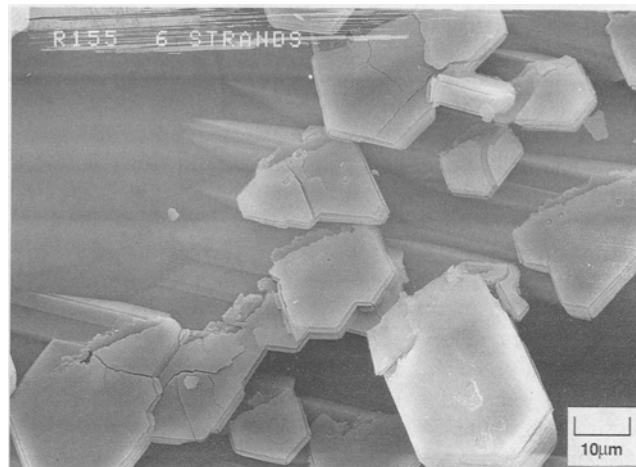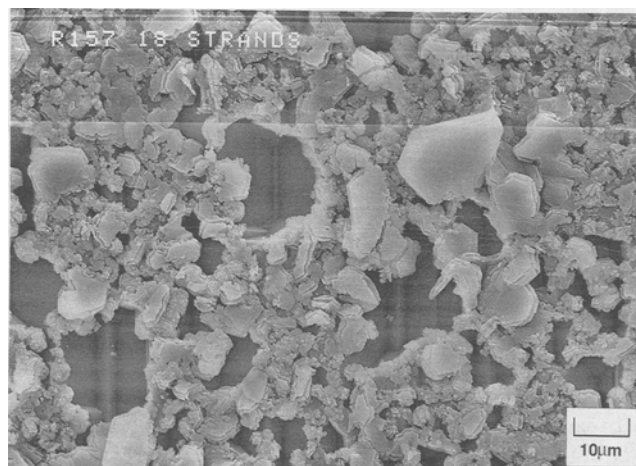
(a)

(b)

(c)

(d)

Fig. 6—The appearance of the Al-Al$_2$O$_3$ interface following removal of the Al drop; (a) and (b) sapphire with 6 deposition events and (c) and (d) sapphire with 18 deposition events.

LS interface. In Figure 6(a), the etched surface of sapphire is decorated with crystals; XRD and EDX analyses of the surface only revealed alpha alumina. In Figure 6(b), a second interfacial phase is observed in the nearly complete interfacial layer. This second phase has a corroded appearance and does not have the distinctive yellow color of aluminum carbide.[23] Furthermore, XRD of reacted surfaces from runs 1, 8, and 11 showed no evidence of Al$_4$C$_3$. While Al$_4$C$_3$ is water soluble, it has been shown to survive the attack of a 10 pct NaOH solution.[29] The interfacial phases in Figure 6(b) are therefore believed to be alpha alumina crystals and the remnants of the vapor-deposited carbon film that ceased to dissolve in the molten aluminum when the point of saturation was reached.

John and Hausner[16] attributed the reduction in contact angle they observed with carbon-coated sapphire to carbide formation. Al$_4$C$_3$ is the thermodynamically favored phase when solid carbon and aluminum are brought in contact at this temperature. Eustathopoulos et al.[13] also noted that molten aluminum should wet carbon at its melting point (660 °C), since the reaction to form Al$_4$C$_3$ is thermodynamically favored. In this study, the greatest reduction in contact angle was realized without direct

evidence of a carbide phase. An alternate explanation is that the contact angle decrease is related to the dissolution of carbon in aluminum, which agrees with the influence of droplet mass on α on low coating numbers.

The reduction in contact angle ceases when the carbon addition reaches a level of approximately 60 ppm (Figure 4). As discussed earlier, the measured background level of carbon in the source of aluminum used for the sessile drop experiments is below the 100 ppm limit of detection. The total carbon content for the limit of contact angle reduction is therefore between 60 and 160 ppm carbon. This level falls between values of the solubility of carbon in aluminum extrapolated from high temperature (5 ppm,[21] 200 ppm[23]) and is higher than the recently published value of 6 ppm at 960 °C.[28]

Similar contact angle effects have been reported for sessile drop experiments of metals undersaturated with respect to oxygen.[24,25] Contact angles were observed to fall as the oxygen partial pressure, pO_2, in their experiments was increased, up until the equilibrium value for the specific metal/metal oxide system was reached. Further increase in pO_2 failed to result in additional reduction in the contact angle. Both Cu and Ag sessile drops

on sapphire exhibited this behavior. They reasoned that the migration of solute (in this case, oxygen) to the LS interface was driven by the formation of a spinel-type compound, since chemisorption of oxygen on the aluminum oxide surface was not energetically favorable. Beruto et al.[26] explained a reduction in the LS interfacial energy (γLS) of iron alloys on alumina by the adsorption of the more electropositive (than iron) alloying element at the LS interface. They further stated that a rapid decrease in interfacial tension (and, consequently, contact angle) proceeds as soon as a monolayer of the electropositive element is completed. Further bulk reaction does not significantly affect the contact angle. The theoretical foundation for the contact angle reduction that occurs when the initial liquid is not saturated with a component of the solid phase has been presented by Aksay et al.[27]

The reason for the reduction in contact angle in the present study is unclear. It could stem either from a process of carbon dissolution and adsorption at the Al-Al$_2$O$_3$ interface or be driven by the formation of aluminum carbide. No evidence of carbide formation was obtained, however. In those cases where the contact angle did not fall to the level of the lowest values (Figure 4), it is possible that the aluminum reached saturation before the carbon film was lifted from the sapphire surface. Even partial removal of the carbon film accompanied by the formation of cracks is sufficient to allow the aluminum to form an interface with sapphire, leading to low contact angles (Figure 5(c)). The residual carbon presumably possesses a surface energy comparable to graphite, and an intermediate static condition is attained.

In addition to the diminution of the contact angle, etching of the sapphire substrate along the vapor-LS interface (VLS) is also enhanced by the presence of the carbon film. Profilometry of the sapphire surface following removal of the aluminum drop by a NaOH solution revealed a maximum etch depth of 2.9 microns after 24 hours for the uncoated sapphire and 13.0 microns for the sapphire that received 6 carbon coats. The attack of sapphire by molten aluminum at the VLS interface is well documented.[2,4,7,9,10,12,13] Since such attack is limited by the removal of gaseous Al$_2$O as a reaction product,[4] the reduction in contact angle caused by the carbon probably promotes the attack lowering the metallostatic head of the sessile drop.

IV. CONCLUSIONS

The sessile drop technique has been used to study the effect of vapor-deposited carbon films on the wetting of sapphire by molten, high-purity aluminum. The terminal contact angle (after 24 hours) of aluminum on uncoated (0001) sapphire at 1223 K and 1.3×10^{-2} Pa (10^{-4} torr) was determined to be approximately 61 deg. Contact angles as low as 31 deg were obtained on carbon-coated sapphire. This represents a reduction of 30 deg from uncoated sapphire. Terminal contact angles on high-density graphite substrates in the range of 56 deg were determined for these experimental conditions.

When the level of carbon added by the carbon films exceeded 0.012 at. pct (60 ppm), no further reduction in

terminal contact angle was realized. At added carbon levels exceeding 0.028 at. pct (125 ppm), terminal contact angles approached values of either 35 or 56 deg. The aluminum-sapphire interface was devoid of carbon or appeared to have remnants of the carbon film broken by channels filled with aluminum when the contact angle was low. The cases with high contact angles had a uniform, low-reflectivity appearance, suggestive of an undisturbed carbon layer. No direct evidence of a carbide phase was obtained. The interpretation of this wetting behavior is that contact angle reduction is driven by the dissolution of carbon in the molten aluminum or the formation of aluminum carbide, or both.

The extent of substrate etching is enhanced by the presence of the carbon films. The depth of the outermost etch ring measured by profilometry is more than four times greater for carbon-coated samples. The metallostatic head is believed to control the reaction by opposing the removal of the volatile aluminum suboxide reaction product.[4] Lower contact angles, as observed with the carbon-coated samples, translate to lower metallostatic heads at the drop perimeter and more extensive etching.

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