

The Wettability of Carbon/TiB₂ Composite Materials by Aluminum in Cryolite Melts

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Both pure TiB₂ and carbon/TiB₂ composites are potential cathode materials for aluminum reduction cells. An important requirement for this application is that the material be wetted by aluminum in cryolite melts. A sessile drop technique combined with X-ray radiography was used to measure the contact angle formed between aluminum and pure hot-pressed TiB₂, carbon/TiB₂ composite, graphite, and a carbonaceous cement in cryolite melts. Pure hot-pressed TiB₂ was found to be completely wetted by aluminum in cryolite melts. Graphite and the carbonaceous cement were nonwetted by aluminum in cryolite melts, the contact angles being in the range of 144 to 158 deg. The contact angle formed by aluminum on the carbon/TiB₂ composite in cryolite melts exhibited time dependency. It was proposed the time dependency was due to (1) removal of contamination from the composite surface and (2) removal of aluminum from the drop. The wettability of the composite material increased as the TiB₂ content increased.

I. INTRODUCTION

THE Hall-Heroult process for the production of aluminum is energy inefficient.^[1] This is due, in part, to the use of carbon cathode linings in the reduction cell construction. The properties of carbon, in particular, the nonwettability by aluminum, necessitate that the inter-polar gap in an aluminum reduction cell be maintained at 40 to 50 mm.^[2] This results in an ohmic voltage drop in the electrolyte of from 1.5 to 2.5 V, which represents between 30 to 40 pct of the total electrical energy consumption of the process.^[3,4]

The shortcomings of carbon have stimulated an extensive investigation into the possibility of replacing carbon cell linings with other materials.^[5] A candidate replacement material is carbon/TiB₂ composite.^[6,7] The major advantage of this material over carbon is that it can be wetted by aluminum. An aluminum reduction cell of a drained cathode design operating at a reduced anode-cathode distance, with attendant energy savings, may then be feasible. Previous studies, which were largely qualitative, have claimed TiB₂ is wetted by aluminum under aluminum conditions.^[2,5-8]

Rhee^[9] investigated the wettability of hot-pressed TiB₂ (98.5 pct of theoretical density) by liquid aluminum at 2×10^{-7} torr or less using the sessile drop technique. It was reported that the contact angle decreased with temperature from approximately 90 deg at 980 K to about 55 deg at 1110 K. Samsonov *et al.*^[10] studied the contact angle of Al on hot-pressed TiB₂ (porosity <6 pct) under vacuum by the sessile drop method and found a non-wetting contact angle of about 140 deg at 900 °C. At 1150 °C, a reduction in contact angle was observed over time, from an initial nonwetting angle of about 110 deg to a wetting angle of about 75 deg after 20 minutes. At 1250 °C, the contact angle decreased over time from an initial angle of about 70 deg to an angle of about 30 deg after 20 minutes. Both of these studies were conducted in the absence of cryolite melts.

Liao and Liu^[11] measured the contact angle of aluminum on hot-pressed TiB₂ and cathode carbon coated with a TiB₂ paste in cryolite-alumina melts. An X-ray radiographic sessile drop technique was used. The TiB₂ coating paste contained TiB₂ powder resin, pitch, and additives. Two pastes were used, (1) one containing 40 mass pct TiB₂ and (2) the other 60 mass pct TiB₂. They reported contact angle values for paste 1 of between 63 and 65 deg and for paste 2 of between 51 and 57 deg. The hot-pressed TiB₂ was found to be completely wetted by aluminum.

In the present study, the contact angles formed by aluminum on pure hot-pressed TiB₂, graphite, carbonaceous cement, and carbon/TiB₂ composites in the presence of cryolite melts were determined.

II. EXPERIMENTAL

The sessile drop technique incorporating X-ray imaging of the drop profile was used for contact angle measurements. The experimental apparatus has been described in detail previously;^[12] thus, only a brief outline is given.

The X-ray source was a medical-type tube (DYNAMAX*-type 60) with a tungsten anode. A split graphite resistor furnace containing molybdenum and INCONEL** radiation shields was used. The furnace at-

*DYNAMAX is a trademark of Latrobe Steel Company, Latrobe, PA.

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mosphere was flushed with argon gas which had been passed through a copper furnace at 450 °C to remove oxygen and dried with CaSO₄ desiccant. A quartz reaction tube contained the test crucible and isolated the furnace atmosphere. The specifications of the chemicals used to prepare the cryolite-alumina melts are given in Table I. The chemicals were dried at 120 °C for more than 2 hours before being mixed to the required composition. A standard melt composition of 8 mass pct (excess) AlF₃, 5 mass pct CaF₂, 3 mass pct Al₂O₃, balance cryolite was used for all tests. Batches of the mixed powders were fused using a graphite crucible and an induction furnace and then quenched on a large copper plate.

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Table I. Specifications of Chemicals

Chemical	Company	Specifications
Na ₃ AlF ₆	Alfa Products, Ward Hill, MA	97.6 pct (1.0 pct Al ₂ O ₃ -0.2 pct CaF ₂)
Al ₂ O ₃	J.T. Baker, Toronto, ON, Canada	reagent (99.1 pct)
AlF ₃	Alfa Products, Ward Hill, MA	(99.99 pct)
CaF ₂	Alfa Products, Ward Hill, MA	anhydrous (99.5 pct)
Al	Fischer, Ottawa, ON, Canada	certified
	Alfa Products, Ward Hill, MA	99.999 pct

The quenched material was crushed in a mortar and pestle to -5 mm. This provided a homogeneous electrolyte material (bath).

Contact angle measurements were conducted on pure hot-pressed TiB₂, carbon/TiB₂ composites of varying TiB₂ levels, graphite, and a carbonaceous cement. The compositions of the carbon/TiB₂ composites are shown in Table II. The samples were 19 or 14 mm in diameter. The hot-pressed TiB₂ samples were 6.8 mm in thickness, and all of the other samples were 5 mm in thickness. The surface of the samples was prepared using silicon carbide paper. The final finish was obtained with 600 grit paper.

The samples were glued to the bottom of a graphite crucible using the carbonaceous cement. An aluminum shot of nominal weight 0.55 ± 0.05 g was placed on top of the sample. Fifteen grams of the prepared electrolyte were added to the crucible. The crucible was placed into the reaction tube of the furnace, which was at the test temperature. The X-ray/TV system was used to monitor the heating and melting process. The bath was fully molten in typically 6 to 7 minutes. The time at which the bath was observed to be fully molten was designated time zero for the test. Radiographs were taken of the sessile drop as a function of time. The film exposure time was 10 seconds. The crucible was rotated 90° to assess drop symmetry. All tests were limited to less than 2 hours, as the fused silica reaction tubes were prone to failure at longer periods. The contact angles were determined from the radiographs using the method of Utigard and Toguri.^[13] At the completion of the test, the crucible was removed from the furnace and cooled in a stream of fanned air. The cooled crucibles were sectioned.

III. RESULTS AND DISCUSSION

In all tests, during the period of crucible heatup, the aluminum retained the original shape of the pellet, even when the temperature was above the melting point of aluminum. It appears that the thin adherent solid oxide film on the aluminum surface constrained any shape change. This phenomena is well documented in the literature.^[14] When the bath started to melt, the aluminum drop shape changed, presumably due to the removal of the oxide film from the surface of the aluminum by dis-

Table II. Carbon/TiB₂ Composite Samples (Mass Percent)

TiB ₂ powder	44.6	54.0	62.0	70.0
Carbon matrix	55.4	46.0	38.0	30.0

solution into the bath. The unconstrained liquid drop would then change its shape to that of lowest free surface energy. The behavior of the aluminum drop then became dependent upon the substrate material.

A. Graphite, Carbonaceous Cement, Hot-Pressed TiB₂

The contact angle values measured on the graphite, carbonaceous cement, and TiB₂ are given in Table III. The values given are those measured 30 minutes after reaching the test temperature. Contact angle (1) is an average of the contact angles measured on each side of the drop. Contact angle (2) is the value after rotation of the sample by 90 deg.

The graphite and carbonaceous cement were not wetted by the aluminum. The contact angles observed were obtuse, the averages being in the range of 144 to 158 deg. This was independent of temperature in the range of 980 °C to 1010 °C. Utigard^[12] reported contact angles of between 150 and 170 deg for aluminum on graphite in cryolite baths at various temperatures. A typical radiograph showing nonwetting between the aluminum and the graphite is given in Figure 1.

The hot-pressed TiB₂ samples were wetted by the aluminum immediately following the melting of the bath. The aluminum spread rapidly across the top of TiB₂ samples. In the initial tests (A), the measured contact angles were all approximately 26 deg. The aluminum had spread to and was confined by the wall of the crucible, as illustrated by the radiograph from Figure 2. Using samples of smaller diameter (B) placed in the center of the

Table III. Contact Angle Values

Sample	Temperature (°C)	Contact Angle (deg)		
		(at time = 30 min)		
		(1)	(2)	Average
Graphite	980	155	150	153
Graphite	1000	161	155	158
Graphite	1010	152	156	154
Carbon cement	980	141	147	144
Carbon cement	1010	144	148	146
Hot-pressed TiB ₂ (A)	980	24	28	26
Hot-pressed TiB ₂ (A)	980	27	25	26
Hot-pressed TiB ₂ (B)	980	0*	0*	0*
Hot-pressed TiB ₂ (B)	980	0*	0*	0*

*See Results and Discussion.

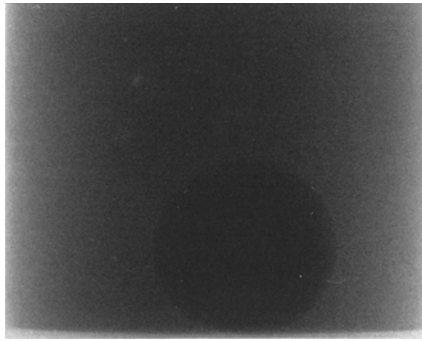


Fig. 1—Radiograph showing nonwetting of aluminum on graphite in a cryolite melt at 1000 °C; Magnification 3 times.

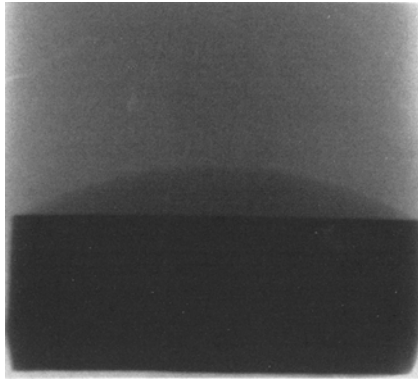


Fig. 2—Radiograph showing complete spreading of aluminum on hot-pressed TiB₂ in a cryolite melt at 1000 °C; Magnification 3 times.

crucible, with the outside of the sample well away from the crucible wall, the aluminum spread rapidly right across the top of the sample. Within a few seconds, the aluminum could not be visually discerned, and no contact angle could be measured. Subsequent sectioning of the crucibles revealed that the aluminum had spread across the top and down the sides of the sample, resulting in complete coverage of the sample by a film of aluminum. The pure TiB₂ samples were completely wetted by the aluminum, resulting in a contact angle of zero which is consistent with literature reports.^[2,5-8,11]

B. Carbon/TiB₂ Composite

The contact angle measurements for the carbon/TiB₂ composites are plotted in Figure 3. The values presented are an average of four contact angles measured at the drop periphery, each 90 deg apart. The plots in Figure 3 indicate that in all of the tests, the contact angle was time dependent. Two possible explanations for this time dependency are (1) removal of contaminants from the composite surface and (2) a reduction in the aluminum drop volume.

1. Surface contaminant removal

The results obtained in this and other studies^[11,12] suggest that pure TiB₂ is wetted and carbon nonwetted by aluminum in cryolite melts. The carbon/TiB₂ composite therefore consists of a wettable component in a non-wettable matrix. The contact angle is determined, in part, by the concentration of TiB₂ at the composite surface.

Scanning electron microscopy studies suggest that a

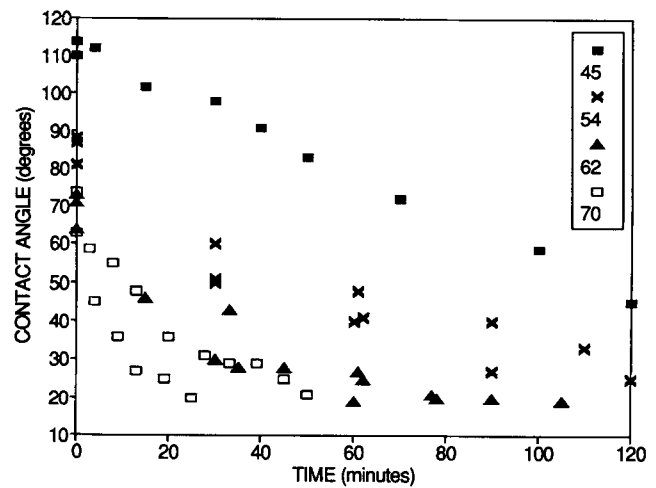


Fig. 3—Contact angle vs time for carbon/TiB₂ composites of various TiB₂ levels (mass pct) at 1000 °C.

carbon film is present on the surface of the carbon/TiB₂ composite. Such a film may play a role in the time dependency of the contact angle. The presence of a carbon film would lower the effective surface concentration of TiB₂. If the carbon film is removed, the wettability of the composite would increase. If this occurs as a function of time during the contact angle test, the measured contact angle will decrease over time.

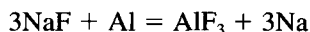
One possible mechanism for the removal of the carbon film from the TiB₂ particles is the formation and subsequent dissolution of aluminum carbide into the bath. This will increase the concentration of TiB₂ at the composite surface and, consequently, the wettability of the composite. The contact angle would decrease at a rate dependent upon the removal of the carbon through the Al₄C₃ formation and dissolution. Similarly, other contaminants at the composite surface which may affect wetting, such as oxides, may be removed by dissolution into the bath and so result in the time dependency of contact angle.

A reduction in contact angle due to this mechanism would result in the advance of the drop periphery. A decrease in contact angle and a corresponding advancement of the drop periphery, as revealed by inspection of the radiographs, was observed in tests carried out on these composites. Inspection of the sectioned crucibles revealed a yellow material on the carbon/TiB₂ composite surface adjacent to the aluminum drop periphery. This material was assumed to be Al₄C₃, which has a characteristic yellow color.^[2]

2. Aluminum removal

The time dependence of the contact angle may also be due to the removal of aluminum from the drop. Real surfaces generally exhibit contact angle hysteresis. There is a range of contact angles which are stable on the surface.^[15] The smallest of this range is termed the receding angle, Θ_r , and the largest the advancing angle, Θ_a . If the liquid is withdrawn from a drop initially at a contact angle greater than Θ_r , the contact angle will decrease, while the drop periphery remains stationary, until Θ_r is reached. If further liquid is withdrawn, the drop will no longer be stable, and the drop periphery will retreat to maintain the contact angle at Θ_r .

As the contact angle tests proceeded, the aluminum drop decreased in size, as shown by comparison of the radiographs in Figures 4(a) and (b). In this case, the drop volume decreased from about 204 to 65 mm³ over a period of 100 minutes, as calculated from the drop diameters. The loss of aluminum may be due to formation of sodium *via* the reaction



or by Al₄C₃ formation or by dissolution of aluminum into the bath. This loss of aluminum was also observed in cases where there was no wetting, suggesting loss by penetration into the substrate was not probable.

The contact angle decrease observed on the carbon/TiB₂ samples was characterized by an advancement of the aluminum drop periphery. This suggests that although removal of aluminum from the drop may have contributed to contact angle change, the dominant mechanism for the contact angle decrease was an increase in the substrate wettability *via* time-dependent removal of surface contamination.

C. Equilibrium Contact Angle and Complete Wetting

A decrease in contact angle over time and spreading of the aluminum were observed for all of the carbon/TiB₂ samples. The decrease in contact angle was more rapid the higher the TiB₂ content of the composite. This implies that the wettability of the composite increased as the TiB₂ content increased.

At the maximum test time, the contact angles were either still decreasing or had leveled out to a value of about 20 deg due to the confinement of the crucible walls. The final or equilibrium contact angles were therefore unknown. To assess if further reduction in the contact angles would occur, tests were conducted using samples of composite containing 62 and 70 mass pct TiB₂, of diameter smaller than the diameter of the crucible, as done with the hot-pressed TiB₂ samples.

The results of these tests are given in Figure 5. The measured contact angles showed a decrease over time similar to that observed in tests with samples of larger diameter, until a contact angle of about 45 deg. This contact angle corresponded to the aluminum having spread to the edges of the smaller sample. This angle is higher than the 20 deg observed for the larger diameter samples, as the same amount of aluminum was used in all tests. The contact angle continued to decrease. At a contact angle of about 8 deg, the point of contact between

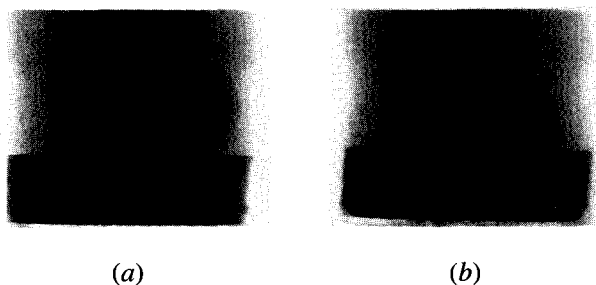


Fig. 4—Radiograph of aluminum on graphite in a cryolite melt at 1000 °C; Magnification 1.8 times. (a) Test time = zero and (b) test time = 100 min.

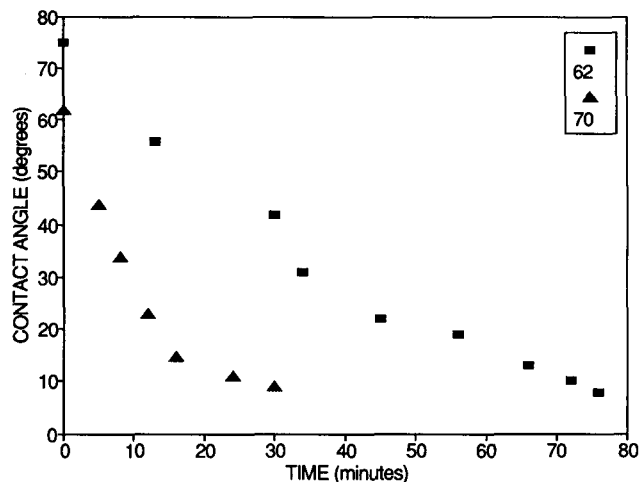


Fig. 5—Contact angle vs time for carbon/TiB₂ composites (small diameter samples) containing 62 and 70 mass pct TiB₂ at 1000 °C.

the aluminum and the composite surface could no longer be resolved. Examination of the sectioned crucibles revealed that the aluminum had spread completely over the top and down the sides of the composite surface. This indicates that these carbon/TiB₂ samples were completely wetted by aluminum, *i.e.*, a contact angle of zero.

Similar tests were not conducted on the carbon/TiB₂ composites containing 45 and 54 mass pct TiB₂ due to the constraint on the maximum test time. The equilibrium contact angle formed by aluminum on these composites was therefore not determined, and it is uncertain whether they would achieve complete wetting given sufficient time.

Liao and Liu^[11] measured the contact angles formed between aluminum and carbon/TiB₂ composite materials in cryolite melts. The composites they studied contained 40 and 60 mass pct TiB₂. They did not report the contact angle as a function of time or refer to any time dependency for the contact angles. Their technique was similar to that used in the present study. However, in the present study, the radiograph exposure time was 10 seconds, whereas Liao and Liu used an exposure time of 8 minutes. The sensitivity of a technique that employs such a long exposure time may be questionable.

IV. CONCLUSIONS

From the present study, the following conclusions are made:

1. Graphite and a carbonaceous cement were not wetted by aluminum in cryolite melts. The average contact angles were in the range of 144 to 158 deg and were independent of temperature in the range studied (980 °C to 1010 °C).
2. Hot-pressed TiB₂ was found to be completely wetted, contact angle of zero, by aluminum in a cryolite melt at 980 °C.
3. The contact angle formed by aluminum on carbon/TiB₂ composites in cryolite melts at 1000 °C exhibited time dependency. It was proposed the time dependency was due to (1) removal of contamination from the

composite surface, and (2) removal of aluminum from the drop.

4. The wettability of the carbon/TiB₂ composite by aluminum in cryolite melts at 1000 °C increased as the TiB₂ content increased. Complete wetting, contact angle of zero, was observed within 90 minutes on composites containing 62 and 70 mass pct TiB₂.

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