Inert Anode/Cathode Program

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Evaluation of Wear Rates and Mechanisms of Titanium Diboride-Graphite Composite Materials Proposed for Use as Cathodes in Hall-Heroult Cells

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On the cover:

Aluminum reduction pots at the Pittsburgh Reduction Company's (Alcoa's) plant in 1889. Adapted from a photograph, courtesy of Alcoa.

EVALUATION OF WEAR RATES AND MECHANISMS
OF TITANIUM DIBORIDE-GRAPHITE COMPOSITE
MATERIALS PROPOSED FOR USE AS CATHODES
IN HALL-HEROULT CELLS

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SUMMARY

Titanium diboride (TiB_2)-containing materials have been under investigation for several years as candidates for stable cathodes in Hall-Heroult aluminum reduction cells. Carbon has recently been added as a filler to TiB_2 to reduce fabrication costs, permit the use of reduced amounts of lower cost TiB_2 , and improve the thermal shock resistance of the cathode block.

The purpose of this study was to measure the initial wear rates of TiB_2 -carbon-containing cathode materials (TiB_2 -G) under electrolytic conditions. Parameters evaluated included bath ratio, current density, and aluminum pad thickness. Two types of TiB_2 -G materials were supplied by the Great Lakes Carbon Company for evaluation. The materials differed in the concentration, size, and ways the separate TiB_2 and carbon phases were interconnected. These materials are undergoing long-term evaluations in full-size Hall-Heroult cells in a program sponsored by the Electric Power Research Institute (EPRI).

In order to measure initial wear rates, the tests were limited to 8 h. The prime wear mechanism of the TiB_2 -G is thought to be the reaction of aluminum metal and/or metallic sodium plus bath components with the carbon phase to form Al_4C_3 . The reaction product is then transported through the aluminum film that wets the cathode and into the bath. The wear rate of the TiB_2 -G cathode was estimated by measuring the build-up of Al_4C_3 in the bath. Since the solubilities of Ti and B in Al are low, and high in cryolite, the wear rate of the TiB_2 -G could be limited by either the rate of reaction of Al (or Na + cryolite) with graphite or the rate of diffusion of reactants and products through the intervening layer of Al that wets the TiB_2 -G cathode.

A cell and a sampling technique were developed to monitor Al_4C_3 build-up during transference cell operation. Based on Al_4C_3 accumulation rates observed in 8-h tests, extrapolated annual wear rates of TiB_2 -G under thin Al film conditions can be calculated. Linear extrapolation yields annual wear rates of 4.6 to 26 cm/yr. Parabolic extrapolation yields values of 0.18 to 0.67 cm wear in the first year's service. (Both extrapolations assume 50 vol% C in TiB_2 -G).

Micrographs of post-test TiB_2 -G specimens suggest that during short-term tests TiB_2 particles are loosened from the TiB_2 -G matrix and are removed from the active electrolysis surface as a slurry or suspended TiB_2 particles in liquid Al. Only in one test was evidence of Al_4C_3 found in the TiB_2 -G cathode reaction interface layer or in the frozen thin film of Al metal adhering to the cathode at the end of the test.

The equilibrium solubility of Al_4C_3 in Al metal is 0.36 mg Al_4C_3 /g Al (Dewing 1974). Transference cell test results indicated that about 13 mg of Al_4C_3 is produced per gram of Al metal. Since only limited evidence for Al_4C_3 could be found in the TiB_2 -G cathode reaction interface layer, the Al_4C_3 formed must be rapidly transported to the cryolite bath for dissolution and dispersion rather than persist as Al_4C_3 dissolved in Al metal.

An analytical method for determining the Al_4C_3 content in cryolite with lower detection limits than previously reported has been perfected. Details of the method and performance evaluation data are given in Appendix B of this report.

The thermal stability of Al_4C_3 in oxidizing and nonoxidizing atmospheres was determined in a thermal balance. In an argon atmosphere, Al_4C_3 was stable to at least 1100°C. In dry air, Al_4C_3 was stable up to approximately 650°C; above that, it readily reacted with O_2 to form Al_2O_3 and CO_2 . These results are presented in Appendix C of this report.

NOTE:

In tests completed after this report was written, the wear behavior of TiB_2 -G appeared to be diminished by the presence of a protective Al film that had been on the cathode at the start of the electrolysis tests. If a layer of Al is on the TiB_2 -G at the start of a 40-h electrolysis test, no attack of the cathode is observed. However, if the cathode is not protected by Al at the start of the test, TiB_2 particles are found to separate from the cathode, resulting in erosion of the cathode surface.

In the experiments covered in this report, cathode samples were not precoated with Al. The impact of no Al layer on cathode samples at the start of the tests, although not evaluated, could be significant. For example, if there were an effect of an Al layer on the cathodes tested in the experiments described in this report, it would be to reduce wear rates.

In review of this document, Great lakes Carbon staff indicated that the surfaces of the as-fabricated test specimens have higher concentrations of carbon than bulk. This higher concentration may contribute to the high initial wear rates measured in this study.

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INTRODUCTION

The Inert Anode/Cathode Program is being conducted by Pacific Northwest Laboratory (PNL)^(a) for the U.S. Department of Energy (DOE), Office of Industrial Programs (OIP). The purpose of the program is to develop long-lasting, energy-efficient anodes, cathodes, and ancillary sensor equipment for Hall-Heroult cells used by the aluminum industry. The program is divided into four tasks with the following objectives:

- Inert Anode Development - to improve the energy efficiency of Hall-Heroult cells by development of inert anodes.
- Cathode Material Evaluation - to confirm the chemical behavior of carbon-containing TiB_2 cathode materials (TiB_2-G) in the presence of molten cryolite and aluminum and to upgrade the analytical procedures for determining Al_4C_3 in cryolite.
- Stable Cathode Studies - to develop methods for retrofitting Hall-Heroult cells with TiB_2 -based cathode materials.
- Sensor Development - to devise sensors to control the chemistry of Hall-Heroult cells operated with stable anodes and cathodes.

The basic objective of the work discussed in this report was to determine the wear rate and wear mechanism of TiB_2-G as a replacement for carbon as the cathode material in a Hall-Heroult aluminum reduction cell. TiB_2-G is relatively inert to chemical attack by Hall-Heroult electrolyte (cryolite) and is "wetted" by molten aluminum, whereas carbon and graphite are not. Compared with carbon-based cathodes, swelling and erosion can be greatly reduced by using TiB_2-G .

A sufficiently low TiB_2-G wear rate and wetting of TiB_2-G by Al may lead to the use of dimensionally stable drained cathodes in Hall-Heroult cells.

(a) Operated for DOE by Battelle Memorial Institute under Contract DE-AC06-76RL0 1830.

Consequently, the anode/cathode distance of an operating cell could be reduced and more consistently controlled at an optimum spacing, which will lead to lower electrolyte "iR" loss and increased cell efficiency.

The addition of graphite to TiB_2 permits the use of smaller amounts of lower cost TiB_2 in the cathode, improves the thermal shock resistance of the cathode, and results in lower cost fabrication routes and the ability to fabricate more complex cathode shapes.

Two mechanisms have been proposed as the cause of wear of TiB_2 -G cathode materials: 1) cathodically produced Al may react with the carbon in TiB_2 -G to produce Al_4C_3 or 2) cathodically produced Na together with bath components may react with the carbon to produce Al_4C_3 . Prior to significant Al production in the cell, reaction 2 could predominate. Following the formation of an Al layer in the cathode, reaction 1 could predominate. The reaction products would be transported either by diffusion or convection through the intervening Al and/or cryolite layer. Upon reaching bulk cryolite bath, the Al_4C_3 readily dissolves and is dispersed. Once exposed to oxygen in the bath, Al_4C_3 is rapidly oxidized to Al_2O_3 . Therefore, in the current tests, oxygen (and traces of moisture) had to be rigorously excluded from the test environment to prevent loss of the Al_4C_3 reaction product.

In a drained cathode configuration, the thickness of the Al film coating on the TiB_2 -G will depend on, among other things, the slope of the cathode surface with respect to the horizontal. The steeper the slope, the thinner the Al coating should be. The thinner the Al film, the faster the rate of transport of Al_4C_3 through the Al film to the electrolyte. Since Al_4C_3 solubility in the electrolyte bath is greater than in molten Al and the rate-determining step for TiB_2 -G wear is hypothesized to be the transport step in the mechanism noted above, the overall observed rate of TiB_2 -G degradation should depend on the Al thickness, which is in turn controlled by the cathode surface slope.

In a commercial cell with carbon cathodes, very small concentrations of Al_4C_3 can be found in electrolyte bath samples. Bath and metal samples from a commercial cell were analyzed for Al_4C_3 content by Reynolds Aluminum for DOE with the following results: 0.0040 ± 0.0002 wt% Al_4C_3 in the bath and

<0.003 wt% in the metal. Because Al_4C_3 is easily destroyed by any oxidizing agent (O_2 in the air, even CO_2 and H_2O), the low concentrations of Al_4C_3 found in the bath samples are not surprising.

If a laboratory-scale cell were set up that rigorously excluded adventitious oxidants and if the anode reaction product were not oxidizing to any bath components, then the rate of wear of a $\text{TiB}_2\text{-G}$ cathode could be inferred from the rate of Al_4C_3 accumulation in the bath. Such a cell was designed and used in this work. This cell is referred to as a "transference cell" throughout this report. Samples from the bath were withdrawn from the cell periodically during electrolysis and analyzed for Al_4C_3 content using the analytical procedure discussed in this report. The slope of the curve generated by plotting Al_4C_3 content of the bath versus time of electrolysis is a measure of the $\text{TiB}_2\text{-G}$ degradation rate.

EXPERIMENTAL APPROACH

The cell design, test matrix, analytical technique, and sampling technique are discussed in this section.

CELL DESIGN

The design of the transference cell shown in Figure 1 evolved from a series of preliminary designs. The cryolitic bath was contained in a closed

FIGURE 1. Laboratory-Scale Transference Cell

aluminum oxide cell. Although a graphite crucible surrounds the cell, no graphite components were in contact with the bath. The final cell design excluded oxygen penetration and allowed electrolysis times up to 10 h. Initially, there was some concern that $\text{TiB}_2\text{-G}$ wear rates would be so low that extended electrolysis times would be needed to observe significant Al_4C_3 buildup in the bath. The results presented in this report show that at least initial rates of $\text{TiB}_2\text{-G}$ wear (and Al_4C_3 buildup) are well within detection capabilities.

TEST MATRIX

To verify the operation of the experimental approach and sampling technique, the cell was initially operated using a pure graphite cathode in a horizontal configuration. This test served as a baseline or worst-case example since the rate of Al_4C_3 buildup with a graphite cathode was expected (and observed) to be high.

Two types of $\text{TiB}_2\text{-G}$, Type A and Type B, were supplied by Great Lakes Carbon Corporation for testing. A "standard cryolite bath" (bath ratio = 1.07 by weight, saturated with Al_2O_3 and containing 5% CaF_2) was used in limiting slope configurations--horizontal and vertical. Both Type A and Type B materials were also tested in a cryolite bath with a ratio of 2.0 and were mounted in the vertical configuration. These latter tests were included to examine the possibility that high bath ratios, in which the equilibrium solubility of Al_4C_3 is much reduced, would lead to lower wear rates. Temperatures were $980^\circ \pm 15^\circ\text{C}$ for standard cryolite bath tests and $990^\circ \pm 10^\circ\text{C}$ for bath ratio = 2.0 tests.

ANALYTICAL TECHNIQUE

Typically, a 50-mg sample of cryolite containing Al_4C_3 was treated with aqueous NaOH at 100°C overnight in a stainless steel vessel evacuated to <0.1 torr. The methane produced by reaction of the carbide with water was manipulated in a calibrated gas sampling apparatus, and a known portion was eventually introduced to a gas chromatograph via a calibrated sample loop. The gas chromatograph used a 2-m-long 5-A molecular sieve column and a sensitive helium ionization detector. A standard gas mixture containing CH_4 was used to

calibrate the system. Conservatively, the detection limit was 0.001 wt% Al_4C_3 based on a 50-mg sample. Precision and accuracy were better than $\pm 10\%$ relative at the 0.1 wt% Al_4C_3 level. Further details can be found in Appendix B.

SAMPLING DURING ELECTROLYSIS

The molten bath was sampled by slowly lowering an alumina tube (6-mm inside diameter) down the chimney into the melt. The tube was flushed with argon until the end of it broke the cryolite surface; flushing was then stopped. The tube was inserted until the Al pool was contacted and then withdrawn from the melt. Capillary action was sufficient to ensure that a "core" sample of bath was obtained. The tube with the sample was allowed to cool under Ar in the upper portion of the chimney for a few minutes and was then removed from the chimney. The sample was easily removed from the alumina sampling tube by gentle tapping. Samples were stored in a desiccator until the analyses could be done.

Initial attempts to sample and analyze molten cryolite baths containing a known quantity of added Al_4C_3 or in cells operated with carbon cathodes gave very poor recoveries. It was found that rigorous exclusion of air was necessary to prevent loss of Al_4C_3 . The cell design shown in Figure 1, along with an Ar cover gas cleanup system, a liquid N_2 water trap, and heated Cu turnings, was developed to maintain the necessary low-oxygen partial pressure atmosphere.

The solubility of Al_4C_3 in cryolitic baths has been measured by several laboratories (Dewing 1969; Grjotheim, Naeuman, and Oye 1977; Odegard, Sterten, and Thonstad 1984). The data reveal a rather large dependence of Al_4C_3 solubility on bath ratio and only weak dependence on other parameters such as temperature, CaF_2 content, and Al_2O_3 content. The model developed by Odegard, Sterten, and Thonstad (1984) fits the observed Al_4C_3 solubility versus bath ratio data over the entire bath ratio investigated ($0.43 < \text{bath ratio} < 2.0$). This model suggests that the dissolution reaction is best described as:

This model and the data used to derive it indicate that Al_4C_3 has a maximum solubility at a bath ratio of 0.9. The equilibrium solubilities of Al_4C_3 in baths used in this study are about 1.1 wt% (bath ratio = 1.07) and 0.09 wt% (bath ratio = 2.0) as interpolated from Dewing's data (1969).

RESULTS AND DISCUSSION

MATERIALS EXAMINED

Two types of TiB_2 -G were supplied by Great Lakes Carbon for evaluation; they were designated Types A and B by Great Lakes. The processes for manufacturing these materials have not been disclosed by Great Lakes. Micrographs of the materials are shown in Figure 2. The graphite phase, which is black in the micrographs, appears to be more continuous in the Type A material than in the Type B material. Porosity is also dark in the micrographs. The TiB_2 phase in the Type B material appears more continuous than in the Type A material. The large TiB_2 particles, which appear to be agglomerates of finer particles, are finer in the Type A material than in the Type B material. The agglomerates appear more uniform in size in the Type A material than in the Type B material. No effort was made to measure the relative concentrations of the graphite, the TiB_2 , the porosity, or the degree of graphitization in the materials.

MATERIALS TESTING

In addition to material being evaluated in the transference cell tests, samples were soaked in cryolite for 48 h at 960°C without an applied voltage to determine the effect of cryolite alone on material performance. The results of the transference cell test will be described first, followed by the soak test results.

TRANSFERENCE CELL RESULTS

Tests were conducted to determine the effect of material type, current density, bath ratio, sample position (either vertical or horizontal) on wear rate. A photograph of a cathode and test cell is shown in Figure 3. Results are summarized in Table 1. Rates are reported in terms of the amount of carbon lost from the surface of the sample ($\text{mgC}/\text{cm}^2\text{-h}$) and carbon thickness lost per year (cm/yr). For the latter calculation, it was assumed that the TiB_2 -G was 50 vol% TiB_2 and that the carbon was lost uniformly from the surface. Lower volume fractions of carbon would increase the calculated wear rate proportionately.

a) Type A

b) Type B

FIGURE 2. Microstructure of TiB_2 -G in the As-Received Condition

FIGURE 3. Example of $\text{TiB}_2\text{-G}$ Cathode Tested in the Vertical Configuration. The Al pool anode is at the bottom of the cell.

TABLE 1. Summary of Results of Successful Transference Cell Tests of TiB_2 Materials

Test	Material	Horizontal or Vertical	Bath Ratio	Area, cm ²	Current Density, A/cm ²	Wear Rate			
						Linear Extrapolation		Parabolic Extrapolation	
						mgC/cm ² -h	cm/yr*	mgC/Cm ² -h ^{1/2}	cm/yr*
EB-23	TiB ₂ -G-A	H	1.07	2.3	1.3	2.51	20	7.58	0.63
EB-25	TiB ₂ -G-A	V	1.07	9.8	0.8	1.22-0.89	9.5-7.0	3.53-4.49	0.29-0.37
EB-30	TiB ₂ -G-A	V	2.00	10.0	0.8	0.83	6.5	2.78	0.23
EB-17	TiB ₂ -G-B	V	1.07	13.9	1.04	0.98	7.6	3.31	0.28
EB-24	TiB ₂ -G-B	V	1.07	9.8	0.8	0.65	5.1	2.78-3.10	0.23-0.26
EB-19	TiB ₂ -G-B	H	1.07	2.3	1.3	3.13	24.0	3.63	0.30
EB-29	TiB ₂ -G-B	H	1.07	2.3	0.87	1.9-0.8	15-6.3	4.17	0.35
EB-27	TiB ₂ -G-B	V	2.00	10.0	1.2	0.54	4.2	1.92	0.16

* Assumes TiB₂-G is 50 vol% C.

It is readily apparent that both Type A and Type B TiB₂-G tested in the horizontal configuration exhibited higher wear rates than when tested in the vertical configuration. There is some evidence from post-test photomicrographs that electrolysis was not completely confined to the exposed horizontal surface. If this was the case, then the true current density was less than that given in Table 1 and corresponding wear rates are less than those tabulated. In Test EB-19 (Type B TiB₂-G in horizontal configuration), other problems occurred that increased the uncertainty of the calculated wear rate. This particular test is discussed later in this section.

The results of a typical successful test (EB-17) are summarized in Figure 4. If a linear model is assumed, the slope of the fitted straight line (0.054 g Al₄C₃/h) can be used to calculate wear rate by the following equation:

$$\frac{0.054 \text{ g Al}_4\text{C}_3}{\text{h}} \times \frac{36 \text{ g C}}{144 \text{ g Al}_4\text{C}_3} \times \frac{1}{13.9 \text{ cm}^2} \times \frac{10^3 \text{ mg}}{\text{g}} = 0.97 \text{ mg C/cm}^2\text{-h}$$

FIGURE 4. Aluminum Carbide Content of Bath as a Function of Electrolysis Time for Test EB-17

Extrapolating this wear rate to 1 year, the following annual wear rate is predicted:

$$\frac{0.97 \text{ mg C}}{\text{cm}^2\text{-h}} \times \frac{24 \text{ h}}{\text{day}} \times \frac{365 \text{ day}}{\text{yr}} \times \frac{10^{-3} \text{ g}}{\text{mg}} = 8.54 \text{ g C/cm}^2\text{-yr}$$

Using the density of graphite = 2.25 g/cm^3 , a linear wear rate of 3.80 cm C/yr can be calculated. Finally, if the $\text{TiB}_2\text{-G}$ specimen is 50 vol% carbon, the wear rate of the $\text{TiB}_2\text{-G}$ surface is 7.6 cm/yr . If the $\text{TiB}_2\text{-G}$ specimen is 25 vol% carbon rather than 50 vol%, the $\text{TiB}_2\text{-G}$ wear rate is 15.2 cm/yr . For comparison purposes throughout this report, 50 vol% carbon is used in all calculations.

These calculations represent the initial recession rate of carbon only. Whether the sample surface erodes at the same rate as the carbon depends on the integrity of the TiB_2 network remaining as the carbon is removed. If the TiB_2 network does maintain its structural integrity as carbon is removed, Al_4C_3 formation would be at progressively deeper layers away from the original cathode surface. The Al_4C_3 would have to diffuse through a thicker and thicker layer of Al/TiB_2 in order to disperse in the bath. Such a situation would lead to a diffusion limited wear rate and, thus, a parabolic Al_4C_3 accumulation rate would be predicted. That is, a diffusion-controlled model predicts that a plot of wt Al_4C_3 in bath versus $\sqrt{\text{time}}$ should be linear. The transference cell data were fitted to this model and results are included as the last two columns in Table 1. Overall, the statistical "goodness-of-fit" favors neither the linear nor parabolic model. Note that the last column of Table 1 represents the wear calculated for the first year of exposure. Figure 5 depicts behavior observed in several of the successful tests. In these cases, parabolic curve fits were somewhat better than linear fits.

Figure 6 summarizes a partially successful test (Test EB-19). Post-test examination of the cell revealed that the crucible cracked sometime during the test. Access of aluminum to the graphite crucible resulted in additional Al_4C_3 formation. The Al_4C_3 results suggest anomalously high formation rates after the 2-h sample was taken. The wear rate of the TiB_2 -G specimen used in this test, based on the few initial data points, is given in Table 1.

Two tests, EB-27 and EB-30, were done with a cryolitic bath ratio of 2.0 and are the only tests in which the amount of Al_4C_3 found in bath samples exceeded the equilibrium solubility values. The calculated Al_4C_3 saturation values were 0.166 g and 0.152 g for EB-27 and EB-30, respectively. All tests other than EB-27 and EB-30 were done with acidic cryolitic baths (bath ratio = 1.07). All samples obtained from these tests had Al_4C_3 concentrations at least a factor of five less than saturation.

At a bath ratio of 2.0, the equilibrium solubility of Al_4C_3 is a factor of about 12 less than at a bath ratio of 1.07. During the relatively short duration of these tests, saturation was not reached in the tests with bath ratios of 1.07.

FIGURE 5. Aluminum Carbide Content of Bath as a Function of Electrolysis Time for EB-25

Within the time frame of the high bath ratio tests, the cryolite reached saturation in Al_4C_3 . As additional Al_4C_3 was formed by the reaction of Al with carbon, resulting Al_4C_3 particles may have formed in the bath. The higher-than-saturation values of Al_4C_3 found in several samples indicate that both truly dissolved and suspended particles of Al_4C_3 were probably included in the samples. The wear mechanism proposed for TiB_2 -G in this study suggests that the rate of formation of Al_4C_3 is not impeded by the presence of previously formed Al_4C_3 in the bath.

FIGURE 6. Aluminum Carbide Content of Bath as a Function of Electrolysis Time for EB-19

An alternative way of presenting these data is to estimate the amount of Al_4C_3 produced as a fraction of the electrolytically produced Al. If 100% current efficiency for Al production is assumed, the "current inefficiency" due to formation of Al_4C_3 from the primary product (Al metal) can be calculated. For the graphite cathode specimen in the horizontal configuration (Test EB-14), a ratio of 80 mg Al_4C_3 /g Al produced was calculated.

For TiB_2 -G specimens under thin film conditions, that is, an exposed vertical surface, a current inefficiency of 13 ± 4 (SD) mg Al_4C_3 /g Al was estimated. This estimated current inefficiency does not correlate with current density or bath ratio. Within the accuracy of the experimental data, it appears that the initial wear rate of TiB_2 -G under thin film conditions is strongly correlated to the amount of Al metal deposited on it.

During system testing, a graphite specimen was used as a horizontal cathode in the transference cell. This test provided baseline data for the rate of Al_4C_3 formation at cathodic graphite not under thick Al pad conditions. Since molten Al does not wet graphite, simultaneous exposure of the graphite to liquid Al and molten cryolite took place. The calculated wear rate was 78 cm/yr. The Al_4C_3 content of samples taken during the graphite test is graphically displayed in Figure 7 as a function of time up to 5 h. The test was discontinued after 7 h. Al_4C_3 build-up in the bath was linear with time.

The linear wear rate of carbon under thick pad conditions is known to be about two orders of magnitude less than the value quoted above. This high value is attributed to concomitant production of Al and Na at the high current density used in this test (3 A/cm^2). Metallic sodium is known to intercalate and weaken graphitic structures leading to accelerated wear. It is not known whether the wear rate would have been reduced if the cell had been operated at a more typical value of about 1 A/cm^2 .

METALLOGRAPHIC ANALYSIS

Both types of TiB_2 -G were soak tested in cryolite for 48 h. After the soak tests, the specimens were sectioned with frozen baths and polished for metallographic analysis and scanning electron microscope (SEM) analysis of the reaction zone. Results of the analyses are described below.

FIGURE 7. Aluminum Carbide Content of Bath as a Function of Electrolysis Time for Test EB-14

Type B Material

Optical micrographs revealed evidence of some dissolution of the cathode material in the cryolite bath (Figure 8). Attack by the cryolite was more evident in the SEM micrographs (Figure 9). The formation of a scale on the $\text{TiB}_2\text{-G}$ as well as particles within the bath material can be seen in the SEM micrographs.

Elemental analysis showed that the bright particles in the cryolite were highly Ti enriched (Figure 9c). The morphology of these particles is different from that of the TiB_2 particles in the original $\text{TiB}_2\text{-G}$. There was a lower

FIGURE 8. Optical Micrograph of Type B TiB₂-G
After Soak Test in Cryolite

level of Ti in the scale (reaction product layer between the bath and cathode) compared with the unreacted cathode material. The boron analysis was inconclusive but tended to show low levels in both the scale and the bath. The TiB₂ appears to be dissolving, and a Ti-rich phase is forming in the bath that has a higher Ti concentration than the TiB₂-G itself.

Based on these elemental maps, the carbon matrix did not exhibit evidence of attack. The elemental map showed little difference between carbon in the scale or in the matrix (Figure 9d). Overlapping the elemental maps of Al and C did not show the presence of Al₄C₃.

The Na, Al, O, and Si maps were all similar. All showed the penetration of cryolite into the TiB₂-G matrix (Figure 9e). The high silicon content comes from the quartz crucible used in the test. The bath material migrated through the pores and interstices in the TiB₂-G. Evidence of bath was found up to

a) SEM Micrograph of TiB₂-G After Soak Test in Cryolite

b) Backscattered Electron Micrograph of Scale Region

FIGURE 9. Elemental Maps of Type B TiB₂-G After Soak Testing in Cryolite

c) Ti Elemental Map of Scale Region

d) C Elemental Map of Scale Region

FIGURE 9. (contd)

e) Al Elemental Map of Scale Region (Si, Na, O maps are similar)

f) F Elemental Map of Scale Region

FIGURE 9. (contd)

0.25 mm from the original interface. Fluorine, in general, behaved similarly to Na except that occasional high concentrations of F were found (Figure 9f). These tended to be concentrated in the scale. The explanation for this high fluorine concentration is not known.

Based on the above analysis, the cryolite penetrated the TiB_2 -G through the porous network. Concurrently, it was dissolving (reacting with) the TiB_2 to form some complex Ti/cryolite mixture in the scale. Some of the titanium apparently reprecipitated, probably upon cooling, in the bath near the scale. These precipitates had a different morphology than the original TiB_2 and were highly Ti enriched.

Type A Material

The general appearance of the reaction zone in Type A material after a cryolite soak was similar to that in Type B. Backscattered electron micrographs, which reveal compositional variations, show an apparent bilayer scale (Figure 10). The outer scale may be somewhat atypical and may be due to the

FIGURE 10. Backscattered Electron Micrograph Showing Compositional Variation in Reaction Zone of Type A Material

indentation at the point examined, allowing bath material to be trapped near the TiB_2 -G surface. An enlargement of the scale adjacent to the TiB_2 -G is shown in Figure 11.

Elemental mapping clearly showed the bright band to be highly Ti rich (Figure 12). This band is analogous to the isolated particles seen on the edge of the scale in Type B material. There was also a much lower concentration of Ti in the scale. The Ti-rich band could be pure Ti since a boron map showed no boron present in this band (Figure 13). It is suggested that boron is lost due to the reaction of TiB_2 with cryolite and subsequent loss of volatile reaction product BF_3 . Hence, boron is lost from the bath.

The carbon elemental map showed little effect on the carbon phase. The carbon is relatively uniform in the Ti-rich band as well as in the scale and matrix. The cryolite is apparently only attacking the TiB_2 .

Sodium, aluminum, and silicon had similar elemental maps; they generally occur in the same phase. There appeared to be somewhat less penetration of the bath into the matrix in Type A material than in Type B, which was somewhat

FIGURE 11. Enlargement of Scale Region Shown in Figure 10

FIGURE 12. Ti Elemental Map Showing High Ti Concentration with Light Band at Edge of Scale (TiB_2 matrix is at far right)

FIGURE 13. B Elemental Map. B is only observed in the TiB_2 matrix at the far right.

surprising since Type A material seems to have more porosity. Within the scale regions, regions of higher sodium concentration indicated that several different cryolytic phases formed.

METALLOGRAPHIC AND SEM ANALYSIS OF TiB_2 -G TESTED IN A TRANSFERENCE CELL

Horizontal Cathodes

Figure 14a shows a cross section of the Al typically deposited on a horizontal TiB_2 -G specimen (EB-16). This specimen is Type A TiB_2 -G subjected to 4-1/2 h of electrolysis. In Figure 14b, the enlargement of Region A in Figure 14a shows that the Al is separated from the TiB_2 -G substrate. Cryolite was observed clinging to the Al. Cryolite had also penetrated into the TiB_2 -G. In fact, traces of cryolite were observed near the center of the TiB_2 -G specimen. There was no evidence of aluminum carbide at the interface. The needle-like phase in the Al contained significant Ti and Zr. The Zr could have come from the ceramic cement used in mounting the test specimen. There was only a small amount of this phase in the deposited Al.

Evidence of bath penetration along the sides of the cathode was clearly observed. Backscattered electron images show that the gray needle-like phase near the TiB_2 -G is rich in Al. Elemental maps of Al, C, and O indicated that it is aluminum oxide and not aluminum carbide. Cryolite bath was evident in the interstices between the oxide particles as well as in the TiB_2 -G matrix, as shown by the elemental Na map. The oxide phase was also found at the bottom of the cathode in Region C. The oxide phase was also present in the region of the Al/bath interface. It probably formed during the cooling of the bath. This oxide phase was rarely observed after a soak test.

In Test EB-19, interfacial interactions were similar to those in Test EB-16 except that Al appears to have flowed down the sides and down a crack in the center of the TiB_2 -G (Figures 15 and 16). It is not certain whether the Al flowed in a molten state down the sides of the cathode or whether it formed in situ on the sides during the electrochemical reaction. Figure 16 shows a higher magnification of Region A in Figure 15. TiB_2 particles are imbedded in the Al. The aluminum oxide particles are present near the Al/bath interface. The Zr-Ti-rich phase was also present in the deposited Al.

a) Cross section

b) Enlargement of Region A

FIGURE 14. Al Deposited on Type A TiB_2 -G Cathode in Test EB-16

FIGURE 15. Cross Section of Al Deposited on TiB_2 -G Cathode in Test EB-19

FIGURE 16. Magnification of Region A in Figure 15

In Region B, the Al had penetrated into the TiB_2 -G matrix (Figure 17). The aluminum oxide particles formed near the Al. These particles were never seen within the TiB_2 -G even though bath was present within the cathode material. In neither Region A nor B is there evidence for an aluminum carbide phase.

The deposited Al adhered to the TiB_2 -G substrate in Test EB-18 much better than in the others discussed (Figure 18). However, bath material was always evident in the TiB_2 -G matrix at every region. Figure 19 shows a higher magnification of Region A in Figure 18 in which TiB_2 particles (very light gray) are imbedded in the Al (white area). These TiB_2 particles could have become

FIGURE 17. Magnification of Region B in Figure 15

FIGURE 18. Cross Section of Al Deposited on TiB_2 -G Cathode in Test EB-18

FIGURE 19. Magnification of Region A in Figure 18

mechanically dislodged from the $\text{TiB}_2\text{-G}$ as the aluminum carbide was formed by the reaction of Al with carbon in the $\text{TiB}_2\text{-G}$ matrix. The aluminum oxide (gray needle-like structure) phase was again present near the Al. The oxide phase was never present between the $\text{TiB}_2\text{-G}$ and the Al.

Vertical Cathodes

In the EB-26 test (Figure 20), there appears to be no interaction between the Al and the TiB_2 particles. Rather, the Al replaced the original carbonaceous matrix. As a result, there was an adherent layer of Al on the cathode.

As on the other cathodes tested, the Al formed or flowed along the sides of the cathodes. The appearance of the interface at Region B was very similar to that at the bottom surface of the cathode in Figures 21 and 22. The needle-like aluminum oxide particles were also present in the frozen bath near the Al layer.

Test conditions for EB-26 consisted of 8 h of electrolysis in a bath with a bath ratio = 2.0 using Type A $\text{TiB}_2\text{-G}$. Al_4C_3 results obtained from samples taken during electrolysis were erratic due to sampling difficulties and are not reported.

Micrographs of the cathode reaction layer from Test EB-20 are shown in Figures 23 and 24. In Test EB-20, a Type B specimen was subjected to electrolysis at 1 A/cm^2 for 1-1/2 h. The test was terminated due to failure of the cathode lead connection; therefore, test results are not included in Table 1. As in previous examples, there appears to be a multitude of discrete TiB_2 particles suspended in the electrolytically formed Al. In Figure 24, one can see what may be an Al_4C_3 phase between the $\text{TiB}_2\text{-G}$ and the Al/ TiB_2 surface layer. This is the only evidence for a reaction product, which might be Al_4C_3 . The composition of this phase was not analyzed using microprobe techniques.

FIGURE 20. Type B Cathode Tested in the Vertical Position in Test EB-26

FIGURE 21. Magnification of Region A in Figure 20

FIGURE 22. Magnification of Region B in Figure 20

FIGURE 23. Cross Section of Al Deposited on $\text{TiB}_2\text{-G}$ in Test EB-20. An Al_4C_3 phase may be present at region A.

FIGURE 24. Higher Magnification of Reaction Area Shown in Figure 23. Phase at reaction interface between $\text{TiB}_2\text{-G}$ and Al may be Al_4C_3 .

FIGURE 24. Higher Magnification of Reaction Area Shown in Figure 23. Phase at reaction interface between TiB_2 and Al may be Al_4C_3 .

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APPENDIX A

TRANSFERENCE CELL DATA

APPENDIX A

TRANSFERENCE CELL DATATABLE A.1. Aluminum Carbide Content of Samples from Graphite Cathode Test^(a)

<u>Elapsed Time, h</u>	<u>Al₄C₃ Found, wt%</u>	<u>Sample Location</u>
2	0.038	Composite of whole core sample
2.5	0.098	Composite of whole core sample
3	0.057	Composite of whole core sample
3.8	0.097	Top portion of core
3.8	0.085	Middle portion of core
3.8	0.097	Bottom portion of core
4.75	0.092	Top portion of core
4.75	0.102	Middle portion of core
4.75	0.119	Bottom portion of core
End of test (cold samples)		
	0.120	From anode area
	0.137	From cathode area
	0.45	From anode area with Al needles included

(a) Initial mass of cryolite bath = 860 g; current density = 3.0 A/cm².

TABLE A.2. Results from Test EB-17(a)

<u>Electrolysis Time, h</u>	<u>Al₄C₃ Found, g</u>	<u>Portion of Sample Core Analyzed</u>
0.25	0.0013	Middle
1.25	0.063	Top
1.25	0.088	Bottom
2	0.043	Composite
3	0.118	Composite
4	0.281	Composite
5	0.273	Composite
6	0.309	Composite
7	0.391	Composite

(a) TiB₂-G, Type B, vertical configuration; 779-g standard bath; exposed area = 13.9 cm²; current density = 1.04 A/cm². These data are shown graphically in Figure 3 of the main text.

TABLE A.3. Results from Test EB-19^(a)

<u>Electrolysis Time</u>	<u>Al₄C₃ Found, g</u>
15 min	0.011
37 min	0.0053
1 h	0.049
2 h	0.051
3 h	0.278 ^(b)
4 h	0.554
5 h	1.18
6 h	1.37

-
- (a) TiB₂-G, Type B, horizontal configuration; 1069-g standard bath; exposed area = 2.3 cm²; current density = 1.3 A/cm²; composite samples. These data are shown graphically in Figure 5 of the main text.
- (b) The rate of Al₄C₃ formation after the 2-h sample increased dramatically. The alumina test crucible probably cracked sometime after the 2-h sample, which exposed cell contents to the graphite outer cell.

TABLE A.4. Results from Test EB-23^(a)

<u>Electrolysis Time, h</u>	<u>Al₄C₃ Found, g</u>
1	0.068
2	0.082
3	0.126
4	0.118
5	0.180
6	0.173

(a) TiB₂-G, Type A, horizontal configuration; 223-g standard bath; exposed area = 2.3 cm²; current density = 1.3 A/cm²; composite samples. These data are shown graphically in Figure A.1.

TABLE A.5. Results from Test EB-24^(a)

<u>Electrolysis Time</u>	<u>Al₄C₃ Found, g</u>
35 min	0.006
1.5 h	0.163
2.5 h	0.224
3.75 h	0.206
4 h 40 min	0.264
6 h 40 min	0.232

(a) TiB₂-G, Type B, vertical configuration; 249-g standard bath; exposed area = 9.8 cm²; current density = 0.80 A/cm²; composite samples. These data are shown graphically in Figure A.2.

FIGURE A.1. Al_4C_3 Content of Bath as a Function of Electrolysis Time for Test EB-23

FIGURE A.2. Al_4C_3 Content of Bath as a Function of Electrolysis Time for Test EB-24

TABLE A.6. Results from Test EB-25(a)

<u>Electrolysis Time</u>	<u>Al₄C₃ Found, g</u>
35 min	0.14
2 h 25 min	0.29
4 h 25 min	0.36
6 h 25 min	0.43

- (a) TiB₂-G, Type A, vertical configuration; 169-g standard bath; exposed area = 10 cm²; current density = 0.80 A/cm²; composite samples. These data are shown graphically in Figure 5 of the main text. Data points form a straight line after the first point. The calculated wear rate is based on the slope of the curve after the obvious initial transient higher wear rate.

TABLE A.7. Results from Test EB-27(a)

<u>Electrolysis Time, h</u>	<u>Al₄C₃ Found (g)</u>
0.5	0.080
1.5	0.051
2.5	0.0385
4.25	0.100
5.5	0.131
6	0.104
6.75	0.129
7.25	0.177

- (a) TiB₂-G, Type B, vertical configuration; 184-g cryolite bath with bath ratio = 2.0; exposed area = 10 cm²; current density = 1.2 A/cm²; composite samples. These data are shown graphically in Figure A.3.

FIGURE A.3. Aluminum Carbide Content of Bath as a Function of Electrolysis Time for Test EB-27

TABLE A.8. Results from Test EB-30(a)

Electrolysis Time	Al_4C_3 Found (g)
1.5 h	0.118
2 h 35 min	0.162
3.5 h	0.199
4 h	0.250
6.5 h	0.282

(a) TiB_2 -G, Type A, vertical configuration; 169-g cryolite bath with bath ratio = 2.0; exposed area = 10 cm^2 ; current density = 0.8 A/cm^2 ; composite samples. These data are shown graphically in Figure A.4.

FIGURE A.4. Aluminum Carbide Content of Bath as a Function of Electrolysis Time for Test EB-30

TABLE A.9. Results from Test EB-29(a)

Electrolysis Time	Al ₄ C ₃ Found (g)
25 min	0.0005
55 min	0.046
1 h 55 min	0.0787
3 h 35 min	0.0673
4 h	0.0715
4 h 55 min	0.0684
5 h 55 min	0.104

(a) TiB₂-G, Type B, horizontal configuration; 174 g standard bath; exposed area = 2.3 cm^2 ; current density = 0.87 A/cm^2 ; composite samples. These data are shown graphically in Figure A.5.

FIGURE A.5. Aluminum Carbide Content of Bath as a Function of Electrolysis Time for Test EB-29

FIGURE A.5. Aluminum Carbide Content of Bath as a Function of Electrolysis Time for Test EB-59

APPENDIX B

A1C₃ ANALYSIS

APPENDIX B

Al₄C₃ ANALYSIS

BACKGROUND

Al₄C₃ reacts with sodium hydroxide to produce methane as follows:
 $\text{Al}_4\text{C}_3 + 4 \text{NaOH} + 4\text{H}_2\text{O} \rightarrow 4\text{NaAlO}_2 + \text{CH}_4$. The CH₄ from this reaction was analyzed with a Varian Aerograph gas chromatograph (GC) with helium ionization detectors and a 6-ft 5-A molecular sieve column. This GC is operated with a vacuum system to minimize introduction of air into the gas sampling system.

Equipment

1. Reaction Vessel - ~200-mL volume with a port for addition of NaOH, vacuum tight, and volume calibrated.
2. Vacuum System and Associated Gas Traps - volumes receiving gas from the sample must be calibrated.
3. Manometers - for pressure data in torr, MKS Baratron-1000 torr + 10 torr manometers.
4. Gas Chromatograph with Sampling Valve - 0.25 mL and 5 mL Varian Aerograph with helium ionization detectors and 6-ft 5-A molecular sieve column (also a 10-ft Poropak Q column).
5. Sand Bath with Temperature Controller - to immerse and heat reaction vessel plus thermocouples to read temperatures in the sand bath.
6. Helium Glove Box
7. Dry Ice, Trap, and Dewar - removal of water vapor.
8. Helium Tank and Regulator

Chemicals

1. Al_4C_3 aluminum carbide, Aldrich, Lot #3311BJ was used for calibration.
2. Greenland cryolite.
3. Aluminum.
4. Hall cell bath mixture: 3000 g Greenland cryolite, 480 g AlF_3 , 480 g Al_2O_3 , and 165 g CaF_2 blended for 48 h in a V-blender.
5. Reagent-grade 2 M NaOH.

Procedure

1. A weighed sample (~50 mg) is placed in the reaction vessel, sealed, and evacuated of gas.
2. About 10 mL of 2 M NaOH is introduced to sample in reaction vessel, the 10 mL water is added to rinse the valve.
3. Reaction vessel is immersed into a sand bath and heated overnight to ~100°C so that the reaction is complete.
4. The reaction vessel is removed from the sand bath and temperature equilibrated back to room temperature.
5. The trap volume is well evacuated and filled with helium, which is used to backfill^(a) the reaction vessel. A reduced pressure (~20 mL at 150 torr) of helium was used for the cryolite bath samples for backfilling the vessels. If the sample was aluminum, atmospheric pressure of helium was required for backfilling to overcome the hydrogen pressure.

(a) Backfilling is necessary to clear the valves from the vessel to the trap to insure equilibration of gas pressures between trap and vessel.

6. The trap is re-evacuated and isolated, then the reaction vessel is expanded to the trap and pressure equilibrated. The gas in the trap is then isolated from the reaction vessel (hence, a known portion is taken).
7. The trap is immersed in dry ice to remove water vapor.
8. The gas in the trap is expanded into the volume calibrated portions of the vacuum system, then to the Toepler Pump, which is used to mix and concentrate the gas in volume calibrated parts of the vacuum system. If Al metal is analyzed for Al_4C_3 , the pressures from the vessel will be too high for the Toepler pump mixing and may be analyzed directly.
9. Gas is analyzed via the GC to give the proportion of the total gas that is methane. The GC is calibrated with various pressures of a standardized gas mixture.
10. Calculations are made using the ideal gas law:

$$n = \frac{PV}{RT} \text{ moles total gas}$$

and the portion of the gas that is CH_4

$$\frac{\%}{100} \text{ or ppm} \times 10^{-6} \times \text{moles total gas}(n)$$

Once the moles of CH_4 is determined, Al_4C_3 content is back calculated from the chemical equation.

TABLE B.1. Reproducibility of Al_4C_3 Standard Mixtures (a-c)

Al_4C_3 , wt%	Analysis Date	Al_4C_3 by Analysis, wt%	Reproducibility, (c) Average $\pm$ SD	Comments
1.0334 in cryolite	8-14-85	0.799	0.811 $\pm$ 8.5%	
	8-16-85	0.845		
	8-16-85	0.815		
	8-20-85	0.819		
	8-20-85	0.805		
	12-31-85	0.922		
	1-03-86	0.814		
	1-10-86	0.774		
	2-05-86	0.867		
	2-05-86	0.654		
0.10337 in cryolite	1-25-86	0.0472	set for a week	Reaction vessel
	1-25-86	0.0717		Reaction vessel
	1-27-86	0.0988	0.0621 $\pm$ 28.9%	Mixed 1.0334% mixture with cryolite. Did not mix well on roller mill.
	1-30-86	0.0534		
	2-03-86	0.0586		
	2-06-86	0.0519		
	2-06-86	0.0530		
0.01229 in cryolite	1-25-86	0.0088	0.00972 $\pm$ 15.2%	Mixed 1.0334% mixture with cryolite. Mixed well on roller mill.
	1-25-86	0.0114		
	1-27-86	0.0105		
	2-03-86	0.0082		
0.9995 in aluminum	8-01-85	0.666	0.00674 $\pm$ 1.6%	Analysis may be low due to short reaction time.
	8-01-85	0.681		
100% Al_4C_3	9-29-85	81.0	72.8% $\pm$ 7.5%	
	7-29-85	69.4		
	7-30-85	70.1		
	7-30-85	70.7		

- (a) The purest Al_4C_3 material available was Aldrich, Lot 3311 BJ, which was estimated to be 80% to 85% Al_4C_3 by x-ray diffraction.
- (b) Stated weight percents are uncorrected for Al_4C_3 purity.
- (c) Standards are less reproducible than samples as they are particulate mixtures rather than solution mixtures.

TABLE B.2. Reproducibility of Hall Cell Bath Samples

Sample ID	Analysis Date	Al ₄ C ₃ by Analysis, wt%	Reproducibility, Average $\pm$ SD	Comments
EB-1T	9-05-85	0.300	0.316 $\pm$ 7.2%	
EB-1T	9-09-85	0.332		
EB-1B	9-05-85	0.169	0.168 $\pm$ 1.3%	
EB-1B	9-09-85	0.166		
EB-10, #3	1-13-86	0.470	0.434 $\pm$ 11.7%	
Inside	1-15-86	0.398		
Middle	--	--		
EB-10, #3	1-14-86	0.351	0.407 $\pm$ 25.6%	
Inside	1-14-86	0.342		
Bottom	1-13-86	0.527		
EB-10, #4	1-16-86	0.574	0.577 $\pm$ 0.7%	
EB-10, #4	1-16-86	0.580		
EB-11, #2	1-29-86	0.0120		
Inside	1-31-86	0.0122		
Middle	--	--		
EB-11, #3	1-30-86	0.0083	0.0084 $\pm$ 0.8%	
Inside	1-31-86	0.0084		
Middle	--	--		

TABLE B.3. Background Levels of Al₄C₃

Hall Cell Component ^(a)	Analysis Date	Al ₄ C ₃ by Analysis, wt%	Average Al ₄ C ₃	Comments
Cryolite	8-13-85	0.0013	~0.0002	0.0017 - omitted from average, considered a flyer
	8-20-85	0.0017		
	8-20-85	0.0002		
	8-26-85	<0.0002		
	8-26-85	<0.0002		
	8-30-86	<0.0002		
	8-30-86	<0.0002		
Cryolite bath mixture	3-05-86	0.0002		
Al ribbon	3-05-86	0.0018		
Al button	3-05-86	0.0023		

APPENDIX C

THERMAL STABILITY OF ALUMINUM CARBIDE

APPENDIX C

THERMAL STABILITY OF ALUMINUM CARBIDE

Thermogravimetric analysis (TGA) and mass spectroscopy (MS) were used to define the thermal stability limit and degradation products of Al_4C_3 . Nitrogen, argon, and dry air atmospheres were used.

In both N_2 and argon atmospheres, no significant weight change ($<0.1\%$) of neat Al_4C_3 is observed up to 1100°C . Thus, Al_4C_3 is stable in nonoxidizing atmosphere up to at least 1100°C .

In dry air, Al_4C_3 sample weights began increasing at about 650°C . The rate of decomposition appears to increase as temperatures increase up to about 1050°C . Based on the assumed decomposition reaction:

approximately 50% of the original Al_4C_3 decomposed during the test. Total time at temperature above 650°C was 2 1/2 h. Mass spectra taken at 30-s intervals during this experiment showed two obvious CO_2 release peaks--one at approximately 700°C and the other at approximately 1000°C . The higher temperature CO_2 release peak represented approximately twice as much CO_2 as the 700°C peak. A completely satisfactory explanation for this observed two-step CO_2 release is not available.

The main point here is that Al_4C_3 readily decomposes in air (oxygen) at Hall-Heroult cell operating temperatures. Dissolved and solvated carbide in cryolite is probably even more susceptible to attack by oxidants. The fact that rigorous exclusion of oxygen and water vapor was necessary to prevent loss of carbide in transference cell tests is consistent with the results obtained from TGA-MS.

APPENDIX D

ANALYSIS OF A TiB₂-G CATHODE USING XPS AND AES

APPENDIX D

ANALYSIS OF A TiB₂-G CATHODE USING XPS AND AES

A cathode was fabricated from Type A provided by Great Lakes Carbon. The exact composition of the TiB₂-G was not provided by Great Lakes. The cathode was fabricated for use in an experimental Hall-Heroult cell to determine the behavior of this material under polarized conditions. A molybdenum rod was used as the cathode lead, and the method of connecting the rod to the TiB₂-G was also tested in this experiment. The cathode measured 2 in. long, 1 in. wide, and 0.29 in. thick. The cell was operated at a cathode current density of 1.1 A/cm² in a electrolyte solution having a bath ratio of 1.07. The cathode was placed in the cell in a vertical position. The experiment was run for 6 h and the bath was maintained at alumina saturation.

The cathode was removed from the cell at the completion of the experiment. The surface of the cathode had a thin green layer of an unknown material in several places. These areas were suspected to be an aluminum carbide phase, which would indicate degradation of the cathode material. The cathode sample was analyzed using x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) to determine the composition of the light green areas. The XPS and AES techniques can provide elemental identification within a surface layer approximately 3 nm thick. The area analyzed with XPS was approximately 4 mm in diameter. The optimum spatial resolution of the AES instrumentation used for this work was 0.8 μ m.

The AES technique uses a primary electron beam (2 to 10 KeV) that is focused onto the solid surface, creating a core electron vacancy. Relaxation of the electronic structure involving two other electron energy levels leads to emission of Auger electrons. The energies and intensities of the emitted Auger electrons are measured. Elements are identified through their characteristic spectra. The intensities of specific Auger electron spectral peaks can be used to semiquantitatively determine concentrations on the surface.

The XPS technique impinges x-ray photons (in this case, Mg K) on the solid surface to be analyzed, and causes photoelectrons to be emitted. The energy and intensity of these photoelectrons are then carefully analyzed. Elements on the sample surface are identified through their characteristic spectra. The relative intensities of the peaks allow semiquantitative concentration determinations. Minor shifts in the energies of the photoelectron spectral peaks are used to obtain much of the chemical valence state information.

The accuracy of the XPS and AES concentration calculations are not trivial to determine without standards and is currently being disputed in the literature. Typical reported accuracies for the sort of calculation done here are $\pm 30\%$. Better accuracies can only be assured with the use in known concentration standards with chemical matrices similar to that of the specific samples being examined. The precision of the measurements (i.e., the reproducibility) is considerably better, with values of $\pm 10\%$ typical for samples of this type. Detection limits are also not trivial to calculate since they are determined by intrinsic elemental sensitivity factors, instrument characteristics, signal-to-noise ratios in the specific spectral region, and will also be influenced by the sample itself. Thus, the detection limits which vary from element to element, may vary from sample to sample, and even from one spectra to the next on a given sample. Typical detection limits range a few tenths of a percent to a few percent.

Sputter-etching consists of hitting the sample with a beam of argon ions. The ion beam has sufficient energy to remove layers of atoms from the sample surface. AES and/or XPS data can then be taken, and the elemental concentrations can be monitored as a function of depth. In this manner, depth profile information may be obtained.

EXPERIMENTAL

The sample had been cut to the appropriate size for analysis using an oil-cooled saw. Sequential ultra-sonic rinses in acetone and methanol were required to remove the oil from the sample. The sample surface was very porous, and serious outgassing occurred when the sample was put into the

analysis chamber. Therefore, the sample had to be pumped on overnight before analyzing so that acceptable pressures could be maintained in the high vacuum system.

All spectra were obtained using a Physical Electronics 560 spectrometer equipped with a double-pass cylindrical mirror analyzer. For the XPS data, a 15-KeV 300-W MgK x-ray source (1253.6 eV) was used. The spectrometer was calibrated so that the Cu $2p_{3/2}$ line appeared at 932.4 eV and the Au $4f_{7/2}$ line at 83.8 eV. Charge referencing was made to the adventitious C 1s line at 284.6 eV. A pass energy of 100 eV was used for the survey data. The AES data was taken using a 5-KeV primary electron beam and beam currents of 0.03 to 0.05 A.

RESULTS AND DISCUSSION

Table D.1 shows the results of the XPS elemental analysis both on and off the green area. An ND entry indicates that the elements was not detected. A number of parenthesis means that while a peak was found in the proper location for that element, the magnitude of the peak was not much above the background level (these values provide a rough indication of the detection limits for that element). The symbol "Tr" indicates that a trace amount of that element was observed.

It was difficult to determine the significance of the composition differences seen in the two areas since it appeared that components from the melt were present in large quantities in both areas. There appeared to be slight evidence from the Auger data that some of the C found in the green might be in

TABLE D.1. XPS Compositional Analysis for TiB_2 -G Cathode Sample

Location	Relative Composition, at.%												
	C	O	Na	Ca	Ti	F	N	Al	Si	S	Cl	B	Li
Green Area	25	34	15	(0.5)	(0.2)	7.7	ND	14	0.5	0.4	0.8	1.7	Tr
Off Green	15	41	8.8	(0.5)	(0.2)	10	(0.5)	20	0.7	0.4	0.4	2.2	Tr

the form of a carbide, but it was difficult to positively identify due to the large graphite or hydrocarbon signal. It was felt that by sputter-etching a better determination of the composition of the green area might be possible if the melt layer could be removed.

Most of the carbon was removed both on and off the green area after approximately 100 Angstroms of material had been removed, and what carbon remained appeared to be graphite or hydrocarbon. Therefore, it does not appear that the green area contained significant amounts of aluminum carbide. Furthermore, the aluminum data was consistent with an oxide form in all spectra, both on and off the green area. After approximately 300 Angstroms of sputtering, the major difference on and off the green areas was that relatively more F and Na, and less aluminum oxide was seen away from the green area. The green appears to consist of "cleaner" aluminum oxide and is free from melt components. This is consistent with the observation that the green area appears visually to be located beneath the surface crust deposited from the melt onto the cathode.

The ion beam was focused so that a small area within the green region could be rapidly sputtered. After about 1500 Angstroms of material was removed, the surface consisted primarily of aluminum oxide, with very small amounts of carbon, fluorine, and sodium remaining. After about 2500 Å (total) was removed, more fluorine was visible on the surface, and some silicon was evident. After visual inspection of the sample, it was determined that the green layer had been sputtered through.

CONCLUSIONS

The results of the study that aluminum carbide was not present on the surface of the cathode material. The composition of the green layer of interest is indicated in Table D.1. It should be noted that these values are qualitative as calibration against standards was not possible.

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