FINAL TECHNICAL REPORT

Project Title	Wetted Cathodes for Low-Temperature Aluminum Smelting
Award Number	DE-FC07-00D13901
Project Period	June 15, 2000 through June 30, 2002
Date of Report	September 30, 2002
Report Author	Craig W. Brown
Award Recipient	Northwest Aluminum Technologies 3313 West 2 nd Street The Dalles, OR 97058
Subcontractors	Materials Modifications, Inc. (MMI)
Other Partners	PNNL, SINTEF
Contacts	Craig W. Brown, PhD Principal Investigator (206) 281-4550 cbrown@nwat.net Ray Roberts Project Director (541) 298-0801 arar@enternet.com.au
Project Team	John Yankeelov, Project Manager DOE Idaho

Acknowledgement

This material is based upon work supported by the U.S. Department of Energy under Award No. DE-FC07-00ID13901.

Disclaimer

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the Department of Energy.

Executive Summary

A low-temperature aluminum smelting process being developed differs from the Hall-Heroult process in several significant ways. The low-temperature process employs a more acidic electrolyte than cryolite, an alumina slurry, oxygen-generating metal anodes, and vertically suspended electrodes. Wetted and drained vertical cathodes are crucial to the new process. Such cathodes represent a significant portion of the capital costs projected for the new technology. Although studies exist of wetted cathode technology with Hall-Heoult cells, the differences make such a study desirable with the new process. This project is such a study.

In Phase 1, titanium diboride, zirconium diboride and composites of these with other materials were tested using a statistically useful test matrix. The materials were consolidated both by hot pressing and by a new method, plasma pressure compaction (P2C™). The materials were subject to controlled electrolysis tests under conditions of the low-temperature smelting process. Post-electrolysis characterizations included quantitative atomic analyses and electron microscopic examinations. These methods allowed evaluating the relative merits of the materials, and the mechanisms of their corrosion. Also, a few tests were performed to determine whether oxygen and carbon dioxide bathing vertically suspended cathodes exhibited different current efficiencies.

In Phase 2, additional composite materials were fabricated with P2C™, electrolysis tested, and subsequently characterized. The statistical test matrix was not used in this Phase. However, the materials were tested with electrolysis lasting both five and twenty hours.

The project demonstrated that good current efficiencies are obtained with the new process at this scale. All of the materials tested except for aluminum infiltrated aluminum nitride wetted well and gave comparable electrolysis voltages. Both hot pressing and P2C™ produce grain structures in the consolidated materials. Grain loss to the product metal is the dominant corrosion mechanism of these materials as cathodes. Grain loss is more of a problem with the composites than with pure materials. P2C™ consolidated materials performed well, and further development and scale-up of this emerging technology seems warranted.

Contributors Acknowledged

In part, this report contains excerpts, interpretations, tables, graphs, and micrographs taken from quarterly and monthly reports produced under the award by Materials Modification, Inc. (MMI), and Pacific Northwest National Laboratory (PNNL). The contributions of the following authors of these reports are hereby acknowledged:

Dr. T. S. Sudarshan, Dr. R. Radhakrishnan, Jeremy Abel and James Hutchins of MMI
Dr. Charles F. Windisch of PNNL

As required by DOE of participant national laboratories, Dr. Windisch has prepared a separate final report entitled "Final Report on Materials Characterization for the Wetted Cathodes for Low-Temperature Aluminum Smelting Program".

Table of Contents

Executive Summary	2
Contributors Acknowledged	3
Goals and Objectives	5
Accomplishments	5
Project Summary	6
Background	6
Two Phase project	7
Three activities	8
Experimental methods	8
Phase I materials	10
Raw materials	10
Consolidation	16
Phase I test matrix	18
Statistical quality of results	20
Statistical comparisons	30
Phase I microscopy	36
Phase II	40
Materials	41
Electrolysis tests	43
Phase II microscopy	45
Results with carbon anodes	45
Near-net shapes	46
Summary and discussion	49
Products	50
Publications	50
Presentations	50
Patents	51
References	51

Goals and Objectives

This project compared various materials, fabricated in several ways, for use as cathodes in a new low-temperature aluminum smelting process. A total of 18 distinct materials were fabricated. All but two of these were consolidated by hot pressing or P2C™. Most of the samples contained titanium diboride (TiB₂) as the predominant component. Composites of five other materials with TiB₂ were included in the program.

Once cathode specimens were fabricated, they were tested as cathodes in actual electrolysis. The low-temperature system conditions were used for these tests. In Phase I, a test matrix was employed that allowed statistical comparisons of the materials. In Phase II, this matrix was not used. Rather, materials were subject to electrolysis tests of two different durations.

Post-electrolysis characterizations gave information about the performance of the materials. The characterizations included atomic fluorescence and electron microscopy.

The low-temperature electrolysis tests used oxygen-generating metal anodes. A set of tests was performed, also, with carbon anodes. The goal of these tests was to determine if higher current efficiencies are obtained with vertical cathodes subjected to carbon dioxide rather than oxygen.

Another goal was to investigate the feasibility of producing near-net shape cathodes samples using P2C™.

Accomplishments

The project followed its plan and produced the data intended. One of the Phase I materials could not be machined to yield test cathodes, however, and another material was not tested with electrolysis. Thus 16 materials were tested as per the project plan. Of these, only two failed as viable cathode materials. The test data allowed a comparative evaluation of the remaining 14 materials.

The tests with carbon anodes yielded lower current efficiencies than is typical with the metal anodes. These results and the observed current efficiencies obtained in other tests [1] with metal anodes combine to support the feasibility of the low-temperature process.

Attempts were made to produce near-net shapes using P2C™. However, success was not achieved.

A detailed description of the project and its results follows.

Project Summary

Background

This project is part of a program of research and development of a low-temperature electrolysis (LTE) systems approach to aluminum smelting [1]. The system differs from the conventional Hall-Heroult approach in several ways. The LTE system incorporates dimensionally stable electrodes. The anodes are metal. Unlike carbon anodes, which react with the oxygen gas released from the alumina to form carbon dioxide, metal anodes are not consumed. The oxygen is thus released by the process. This is desirable, but actually requires more free energy than producing aluminum and carbon dioxide, since the reaction of carbon with oxygen releases free energy to the system.

This energy penalty is countered in the LTE system by keeping the anodes and cathodes closer together than is practically possible in a Hall-Heroult system. In order to do this, the cathodes must be wetted by the liquid aluminum produced on them, and the accumulating aluminum must be drained. This allows the location of the electrode surface to be known more precisely than in a conventional smelting cell, where the cathodes do not wet, and wherein a metal pad grows and can exhibit waves.

The metal anodes used do not survive in the Hall-Heroult electrolyte, which is close to cryolite in composition and typically at temperatures over 950°C. Thus the LTE system uses an electrolyte that is more acidic than cryolite, and which has a substantially lower melting temperature. With this, electrolysis can be conducted at temperatures below 800°C, reducing the anode corrosion rate.

The low-temperature electrolyte exhibits a reduced solubility for alumina, however, when compared to cryolite in the Hall-Heroult system. Thus the LTE system also employs a slurry of alumina. In this, some solid particles of alumina are kept in suspension at all times. Near the anode, where alumina is consumed, these dissolve as-needed to supplement diffusion of dissolved alumina from the bulk electrolyte.

It is necessary to keep the slurry particles from settling. The oxygen gas generated at the anodes is used to do this. Consequently, the bottom of the electrolysis cell is an anode, rather than a cathode as in the Hall-Heroult technology. In addition to this anode, additional anodes are employed. These reside in a vertical configuration above the bottom, interleaved with cathodes.

Because the LTE cell uses a bottom anode, and alternating cathodes and anodes that are suspended vertically above this bottom, the cathodes experience an environment that is different than in a Hall-Heroult cell. In the LTE system, product metal (liquid aluminum) is always draining down the wetted cathodes, and the product metal is bathed in oxygen bubbles and slurry particles.

Two Phase project

This project sought to answer several broad questions. A first question was whether electrolysis using oxygen-generating anodes beneath vertically suspended wetted cathodes produces lower current efficiency than electrolysis using carbon dioxide-generating carbon anodes beneath the cathodes. A second question was whether conductive ceramic materials, such as titanium diboride (TiB_2), were wet by liquid aluminum reproducibly and sufficiently to be good candidates for cathodes in the LTE system. A third was whether such materials would show undue degradation under the LTE conditions, especially with regard to the slurry electrolyte, product metal draining, and the oxygen evolved. Other questions were whether and, if so, how the relevant properties of such materials are effected by fabrication method.

The fabrication method questions are important because the cathode fabrication method can impact the capital cost of an LTE smelter. The primary method available is hot pressing (HP) of ceramics. This involves sintering under pressure at a high temperature. One of the project goals was to compare materials consolidated in this way to materials consolidated using an emerging technology, P2C™. The latter method derives the pressure to compact solid forms from powdered starting materials from a plasma condition created by flowing electrical current through the P2C™ apparatus. This method has the potential to yield smaller grain sizes, higher purity, and lower cost than HP.

The project comprised two Phases. Phase I involved two distinct parts. The minor part was undertaken to compare the performance of equivalent cathodes under LTE conditions using oxygen-generating anodes, and similar low-temperature slurry electrolyte conditions employing carbon dioxide-generating carbon anodes. This was done to ensure that, due to back reaction of the product aluminum, oxygen generation by the anodes did not yield decidedly low current efficiencies compared to CO_2 generation.

In the major portion of Phase I, nine different types of cathode specimens were prepared. One type used a commercial HP TiB_2 . The other eight were TiB_2 , zirconium diboride (ZrB_2), and composites of TiB_2 with two other ceramics. Each of these materials were prepared from characterized raw materials by both hot pressing and P2C™. Except for two of the materials which were dropped from the test matrix, four samples of each specimen type were tested under LTE conditions in a matrix of 16 tests in which each cathode specimen underwent four electrolysis tests. Thus a total of $7 \times 16 = 112$ LTE tests were conducted in this test matrix. The 4×4 test matrix for each material gave a sufficient number of replicate tests under a given condition to yield useful statistical comparisons of the materials' performances.

In Phase II, additional candidate materials for cathodes were surveyed. Because Phase I had demonstrated a high degree of reproducibility in the tests used, the extensive testing of the test matrix was not used in Phase II. Rather, the electrolysis testing in Phase II was meant to screen for catastrophic failures and other possible outstanding features of the materials screened. For most of the materials screened, two sample cathodes were employed. With the

first of these, electrolysis was maintained for five hours. With the second, electrolysis was maintained for twenty hours.

Another activity in both Phases was to attempt producing net shapes using P2C™.

Three activities

The project activities broke into three areas. The first was preparation of the materials to be tested. The second was electrolysis tests with these materials. The third was post-electrolysis characterizations. Each area of activity employed specialized techniques. These are described in the Experimental methods sub-section to follow.

The fact that the second activity area is electrolysis testing is very important. Some wetting tests, such as sessile drop tests, are difficult to perform with relevance to actual electrolysis smelting conditions. For example, since aluminum oxidizes very readily, such tests must very carefully exclude oxidizing gases. The material being tested for wetting properties may also suffer in such tests. By using electrolysis, the actual wetting aided by the flux of the electrolyte is studied.

Experimental methods

Except for the commercial HP TiB₂, the raw materials were characterized prior to fabrication into test specimens. These characterizations included x-ray diffraction (XRD) analyses, particle size distributions with particle size analyzers, and electron microscopy. These supplemented the purity and other data provided by the suppliers of the raw materials.

Following the initial characterization, the raw materials were used to optimize the parameters for consolidation by P2C™. These parameters include consolidation temperature, pressure, and consolidation time. Following consolidation, the densities of the consolidated materials were compared to the theoretical density.

For Phase I, a minimum of six specimen cathodes of each type were then fabricated. For most Phase II materials, fewer samples were produced. The materials were produced in non-net shapes. Electro discharge machining (EDM) was used to yield the test cathodes from material blanks produced.

The specimens were then subjected to electrolysis tests. The tests were similar to laboratory tests described elsewhere [2], employing 500ml high-purity alumina crucibles to hold the electrolyte. Unlike the test apparatus described in [2], however, each test used three anodes. One was circular, covering the bottom of the crucible. The other two were square with the same cross-sectional area as the test cathodes. These two anodes were suspended vertically and parallel to the two faces of the cathode. Thus the cathode resided above a horizontal bottom anode and between two vertical anodes.

The electrical connections between the direct current (DC) electrolysis power bus and the anodes were made through risers of copper tubing insulated by high purity alumina sleeves. The voltage drop in these risers from electrolysis current is small, so voltage sensing connections were made to these at the riser/bus connection.

The electrical connections to the cathodes were more complicated. The square active surface of a cathode was connected to a section of riser made either from TiB_2 or the material of the specimen. This riser was shielded by a high purity alumina sheath, and extended above the electrolyte. This short riser section was then attached to a longer section of stainless steel rod that led to the DC bus. One voltage sensing connection was made at the stainless riser/bus connection. However, the voltage drop in the stainless steel from electrolysis current can be several hundred millivolts. Thus a second voltage sensing connection was made at the ceramic/stainless riser interface.

With these voltage sensing connections, then, the data included the voltage differences between 1) the bottom anode and the top of the stainless steel cathode riser, 2) the side anodes and the top of the stainless cathode riser, 3) the bottom anode and the TiB_2 /stainless cathode riser interface, and 4) the side anodes and the TiB_2 /stainless cathode riser interface.

The data acquisition used 12 bit A/D converters. For the voltage channels, a 0-10V scale was used. Thus on least significant bit was 0.0024V.

Two DC power supplies were used with the test stand to supply the electrolysis current. The negative terminals of these were common to the cathode bus. The positive terminal of one was attached to the bottom anode, while the positive terminal of the other was attached to the bus feeding the side anodes. During electrolysis, the supplies were operated in constant current mode, allowing the voltage to respond to the resistance of the current path.

The anodes used were all sintered and of the same composition. For Phase I, the bottom and side anodes used in a given test were kept together as a set throughout the test matrix. In Phase I, each set was used in four electrolysis tests.

At the completion of each electrolysis test, the electrodes were removed from the crucible, and the liquid contents dumped into a stainless steel pan. Once these froze, the product aluminum was separated from the electrolyte and weighed, yielding a % current efficiency based upon recovered aluminum. The frozen electrolyte was crushed, then riffled to produce samples for subsequent analysis.

After electrolysis testing, at least one cathode of each material was examined using optical and scanning electron microscopy. These post-electrolysis characterizations looked for several relevant characteristics. The first was contiguity of wetting by aluminum. Another was the phase and grain structure of the materials. A third was penetration of aluminum into the grain structure. A fourth was evidence of corrosion of the cathode materials.

Additional characterization involved quantitative spectroscopic analysis of the product aluminum and the electrolyte from each electrolysis test. The spectroscopic method was based on atomic fluorescence from samples excited in an inductively coupled plasma. The samples from the electrolysis work were digested in hydrochloric acid, and diluted to obtain the analytical samples. The analyses gave quantitative results for the weight percents of the relevant components: Sodium, aluminum, fluoride, and calcium for the electrolyte samples, nickel, iron, copper, and titanium or zirconium for the electrolyte and aluminum samples. Additional analyses of the electrolyte samples with a LECO analyzer yielded total oxygen content of the electrolyte samples.

All of these samples generated in Phase I were analyzed in duplicate. This allowed for verifying the quality of the analyses and of the sampling method.

Phase I materials

For Phase I, one consolidated material was purchased, eight were consolidated within the project, and seven of the nine materials were electrolysis tested and compared. The commercial material was HP TiB₂ produced by Ceradyne, of California. The chemistries of the eight fabricated materials were TiB₂, its composites with alumina (TiB₂-Al₂O₃) and zirconia (TiB₂-ZrO₂), and zirconium diboride (ZrB₂). Following characterization of the raw materials, these four materials were fabricated by both HP and P2C™ methods.

For the present report, the Phase I materials were assigned numbers, 1-9. These numbers, the material chemistry, and the material fabrication method are summarized in Table 1.

Table 1: Materials fabricated for Phase I

Material number	Chemistry	Fabrication method
1	TiB ₂	Commercial
2	TiB ₂	HP
3	TiB ₂	P2C
4	TiB ₂ -Al ₂ O ₃	HP
5	TiB ₂ -Al ₂ O ₃	P2C
6	TiB ₂ -ZrO ₂	HP
7	TiB ₂ -ZrO ₂	P2C
8	ZrB ₂	HP
9	ZrB ₂	P2C

Raw materials

Several vendors in the U.S were contacted to obtain information on the various available grades of TiB₂. Samples were procured from the sources in Table 2. This Table also lists the grades of

powders that were investigated. These powders were characterized by XRD, which showed only the presence of TiB_2 .

Table 2: Vendor sources and product information for Titanium Boride powders

Vendor	Grade	Particle Size	Wt% Ti	Wt% B	Wt% O	Wt% C	Wt% N
Advanced Ceramics Corp.	AC-6027	15 μm	67-69	27-31	0.366	0.467	0.055
Advanced Ceramics	HCT-30	14 μm	67-69	27-30	0.49	0.429	0.04
Advanced Refractory Technologies	TGF	11.3 μm	67.4	30.9	0.9	0.7	<0.2
Cerac Inc.	T-1150	15 μm	67-68	29-30	0.50	0.53	0.18

Figure 1: Particle size distribution data for grade AC-6027 from Advanced Ceramics Corporation, Cleveland, OH.

In order to verify the particle size and distribution for the powders, a HORIBA SA-3100 particle size analyzer was used. The results from the particle size analysis for grade AC 6027 (Advanced Ceramics Corporation) is shown as an example in Figure 1. The median particle size for this grade was 13.83 μm . The powders revealed a bimodal distribution which is beneficial for obtaining dense samples by consolidation. The corresponding surface area for this powder was 18.548 m^2/gm . The particle size data for all other grades were similar to those quoted by the vendors.

The aluminum oxide powders (Al_2O_3) were procured from Atlantic Equipment Engineers, Bergenfield, NJ. The manufacturer's specifications reported these to be submicron powders. They were characterized for particle size distribution using a laser scattering HORIBA LA-910 particle size analyzer. The results of the particle size distribution are presented in Figure 2. The median particle size was found to be 3.8 μm . The particle size analyzer does not have an ultrasonic dispersing facility and hence provides information only on the agglomerate particle size.

Figure 2: Particle size distribution of aluminum oxide powders used for the preparation of $\text{TiB}_2\text{-Al}_2\text{O}_3$ composite.

The ZrO_2 (3 mol% yttria stabilized) was procured from Stanford Materials Corporation, Aliso Viejo, CA. The ZrO_2 powders were extremely fine with a median particle size of $2.35\text{ }\mu\text{m}$. The results from the particle size analysis is given in Figure 3.

Figure 3: Particle size distribution for ZrO_2 powders used in the fabrication of TiB_2 - ZrO_2 composites.

ZrB_2 powders were procured from H.C. Starck, Newton, MA. The compositional analysis supplied by the manufacturer was as follows: Zr – 78.5%; B – 18.7%; C – 0.25%; O – 2.0 % and N – 0.25%. The powders are very fine with a mean measured particle size of $2.86\text{ }\mu\text{m}$.

XRD of TiB_2 , ZrB_2 , Al_2O_3 and ZrO_2 indicated the raw materials to be single phase powders with no second phases present. As verification, microscopy of the powders was also carried out and the micrographs are presented in Figures 4 through 7.

Figure 4: SEM micrograph of TiB₂ powders

Figure 5: SEM micrograph of ZrB₂ powders

Figure 6: SEM micrograph of Al₂O₃ powders

Figure 7: TEM micrograph of ZrO₂ powders

TiB₂, ZrB₂ and Al₂O₃ powders were in the micron size regime with an irregular particle size morphology while the ZrO₂ powders were nanocrystalline size (20 nm) with a irregular shape.

Consolidation

Several experiments were conducted to optimize the P2C™ parameters of temperature, time and pressure to obtain dense samples.

The first TiB₂ powder evaluated was grade TGF from ART. A 1" ID graphite die was used for consolidation. When a temperature of 1650°C was reached, melting and spurting of molten liquid from the dies was observed. The consolidation was interrupted and the sample was removed from the die after cooling, then examined. Melting was evident on the sample surface. The surface was characterized using EDAX (Energy Dispersive Analysis by X-Ray Diffraction) which revealed the presence of titanium and aluminum. The powders had possibly more titanium than required according to the TiB₂ stoichiometry. This excess titanium melted upon reaching its melting temperature and was forced out of the die due to applied pressure. Discussions with ART did not provide any further insight into the reason for melting or the presence of aluminum. It was pointed out by ART that an improved grade (SG) of titanium diboride has been developed.

The next to be evaluated was grade HCT-30 from Advanced Ceramics Corporation. Consolidation was performed at 1800°C and 1900°C at 30 MPa for 10 minutes. The density of the sample consolidated at 1800°C was 76% and that consolidated at 1900°C was 84%. Similar results were obtained from the powders from Cerac, Inc.

Grade AC-6027 from Advanced Ceramics Corporation was the next grade of TiB₂ powder evaluated. Preliminary consolidation experiments were conducted using a 1" ID graphite die. Consolidation temperatures of 1800°C and 1900°C were evaluated with a consolidation time of 10 minutes. At a consolidation temperature of 1900°C, a pressure of 30 MPa and consolidation time of 10 minutes, densities of 96% were obtained. The conditions at 1900°C were repeated with a 2" diameter die. The consolidated sample density was 96% (theoretical).

Table 3 summarizes the results from the consolidation experiments performed with the various TiB₂ powders. Based on these results, grade AC-6027 from Advanced Ceramics Corporation was used for preparing all TiB₂-containing samples.

To prepare TiB₂ cathode samples for electrolysis tests, P2C™ consolidation was performed at 1900°C for 10 minutes in vacuum. 2" diameter disks were pressed from which plates measuring 1.3" x 1.3" x 0.125" (thick) were machined as test cathodes. Blanks measuring 3" x 2" x 0.5" were also fabricated from the TiB₂ powders. Rods machined from these blanks used in the electrolytic cells as the initial risers connecting the TiB₂ plates to the stainless steel risers and DC power source.

Table 3: Results from consolidation experiments

Vendor	Grade	Consolidation Conditions	Density	Remarks
Advanced Refractory Technologies	TGF	1800°C, 30 MPa, 10 min.	---	Melting was observed at temperatures > 1650°C
Advanced Ceramics Corporation	HCT-30	1800°C, 30 MPa, 10 min.	76%	
Advanced Ceramics Corporation	HCT-30	1900°C, 30 MPa, 10 min.	84%	
Cerac Inc.	T-1150	1800°C, 30 MPa, 10 min.	75%	
Cerac Inc.	T-1150	1900°C, 30 MPa, 10 min.	75%	
Advanced Ceramics Corporation	AC-6027	1800°C, 30 MPa, 10 min.	87%	
Advanced Ceramics Corporation	AC-6027	1900°C, 30 MPa, 10 min.	96%	

For the composite with alumina, TiB_2 were powders mixed and blended with 10 vol% Al_2O_3 powders and consolidated into 2" diameter disks. The P2C™ consolidation was performed at 1800°C for 10 minutes in vacuum of 10^{-2} torr. Similar conditions were used to consolidate blanks measuring 3" x 2" x 0.5". Plates and rods were machined from these disks and blanks, respectively.

For the $\text{TiB}_2\text{-ZrO}_2$ (10 vol%) composites, the P2C™ parameters were 1900°C for 10 minutes at 30 MPa. Rather than supply separate cathode squares and riser rods, the test specimens were machined as per the dimensions shown in Figure 7.

Figure 7: Schematic of test cathode with integrated riser.

The optimum P2C™ conditions for ZrB_2 were a consolidation temperature of 1500°C , a consolidation time of 10 minutes and a pressure of 30 MPa. These were machined into cathodes as per Figure 7.

The TiB_2 , $\text{TiB}_2\text{-Al}_2\text{O}_3$, $\text{TiB}_2\text{-ZrO}_2$ and ZrB_2 powders were hot pressed, also. TiB_2 , ZrB_2 and $\text{TiB}_2\text{-ZrO}_2$ powders were hot pressed for 1 hour at 1900°C and 30 MPa. $\text{TiB}_2\text{-Al}_2\text{O}_3$ powders were hot pressed at 1800°C for 1 hour and 30 MPa. Hot pressing was carried out in vacuum using graphite dies.

The hot pressed samples of TiB_2 , $\text{TiB}_2\text{-ZrO}_2$, $\text{TiB}_2\text{-Al}_2\text{O}_3$ and ZrB_2 were machined into test cathodes as per Figure 7. Hot pressed samples of $\text{TiB}_2\text{-ZrO}_2$ were difficult to machine due to insulating nature of ZrO_2 . During electro discharge machining, the cutting was interrupted at ZrO_2 and gave a very irregular cutting surface. Due to this difficulty, the decision was made to eliminate HP $\text{TiB}_2\text{-ZrO}_2$ from the test matrix.

In contrast to the difficult HP $\text{TiB}_2\text{-ZrO}_2$ material, the P2C™ $\text{TiB}_2\text{-ZrO}_2$ material was machined without much difficulty. The reason for this difference in behavior is not clear. However, it has been noted that P2C™ consolidated materials are easier to cut with diamond blades than are their HP counterparts. Perhaps the more uniform and small grain boundaries obtained with P2C™ compared with HP are responsible for this.

Phase I test matrix

Sample cathodes of Phase I materials were subjected to series of electrolysis tests. The test stand was described above. The side anode-to-cathode distances were nominally 1.75 cm, as

was the distance between the bottom anode and the bottom of the cathode. The electrolyte was about 45 mole% aluminum fluoride (AlF_3) and 55 mole% sodium fluoride (NaF). The electrolyte was treated prior to electrolysis to reduce contaminants and to saturate with dissolved alumina. The treated electrolyte was collected as a liquid and frozen, and then re-melted in the tests. Each test used 350g of the treated electrolyte. The electrolyte temperatures were maintained at $760^\circ\text{C} \pm 2^\circ\text{C}$ during electrolysis. The typical cell current was 10 A, and the electrolysis conducted for five hours. An additional 6 weight % of Alcoa A-152 calcined alumina was added to produce the slurry. During electrolysis, this same type of alumina was fed by hand every 20 minutes at a rate appropriate for 85% current efficiency.

For each test, the electrodes, alumina-sheathed thermocouple, and reference electrode were situated in a new, unused crucible. The 350 g of treated electrolyte and the alumina for the slurry were added, and heating with the furnace commenced. The electrodes were completely disconnected from the DC bus and power supplies during heat-up. Once the operating temperature was reached and remained stable for about 15 minutes, the electrodes were connected to the DC bus, and the electrolysis current was applied.

At the conclusion of the five hour electrolysis period, the current was shut off. The test cathode was then removed from the cell, photographed, and set aside to cool. The other components were also removed from the electrolyte and set aside. The anodes were also photographed. Finally, the electrolyte and product aluminum were poured from the crucible and cooled. The electrodes were cooled and held at room temperature for at least 12 hours before being used in any subsequent test.

For a given cathode material, four sample cathodes were introduced into the test matrix. These were identified as C1-C4 of that material. Four sets of three anodes, two side and one bottom anode, were identified as A1-A4 for that material. With these, sixteen electrolysis tests were conducted. These comprised four sets of four tests, and were given test set numbers 1-4. In test set one, the electrodes were given their first use, in test set 2 a second use, and so forth. Moreover, the anodes were rotated among the cathodes such that each cathode experienced each set of anodes.

The risers associated with a given electrode followed that electrode throughout the test matrix.

The test matrix for a given cathode material is specified as follows:

Test set	1	2	3	4
Cathode/anode combination	C1/A1	C1/A2	C1/A3	C1/A4
	C2/A2	C2/A3	C2/A4	C2/A1
	C3/A3	C3/A4	C3/A1	C3/A2
	C4/A4	C4/A1	C4/A2	C4/A3

Materials 1-7 were put through the test matrix. Material 8 was not, because of machining problems discussed above. Material 9 was not, because the tests with material 7 indicated no cost or performance advantages to using ZrB_2 instead of TiB_2 .

Statistical quality of results

During electrolysis tests, the following quantities were recorded:

V1	Voltage between cathode bus and bottom anode
V4	Voltage between cathode bus and side anodes
V7	Reference electrode voltage
V8	Voltage between cathode and bottom anode
T2	Temperature of electrolyte ($^{\circ}C$)
I3	Current through bottom anode (A)
I6	Current through side anodes (A)

Another voltage, called V'4, can be calculated as $V4 - (V1 - V8)$, and is the voltage between the cathode and the side anodes. The voltages V1 and V4 contain the voltage drop due to current through the stainless steel cathode riser section, whereas V8 and V'4 do not.

The power supplies determine stability of the currents. The set points for these currents were chosen to yield an overall current density in the cathodes tested of $0.4 \text{ A}\cdot\text{cm}^{-2}$, and a current density in the active anode surfaces of $0.18\text{-}0.20 \text{ A}\cdot\text{cm}^{-2}$.

An additional measured parameter associated with the electrolysis testing was the % current efficiency. This was determined from the mass of aluminum recovered, and is calculated as

$$\%CE = \frac{m_{Al}(g) \cdot 96,500(C \cdot eq^{-1}) \cdot 3(eq \cdot mol^{-1})}{d(h) \cdot 3600(s \cdot h^{-1}) \cdot A(C \cdot s^{-1}) \cdot 27(g \cdot mol^{-1})} \cdot 100\% \quad (1)$$

where $m_{Al}(g)$ is the mass of aluminum recovered in grams, $96,500(C \cdot eq^{-1})$ is the Faraday, 3 equivalents are required to yield one mole of aluminum, $d(h)$ is the electrolysis duration in hours, $A(C \cdot s^{-1})$ is the amperes (coulomb per second) of electrolysis current, and the formula weight of aluminum is $27(g \cdot mol^{-1})$.

Tables 4 – 10 summarize the voltages V1, V4, V8 and V'4 for the sixteen electrolysis tests of the test matrix for each of the seven materials. The values for these quantities are in volts, and are the time-averaged values measured during the five hours of electrolysis. The Tables also include the %CE obtained from each test. Also included are the averages of these five quantities for each test set within the matrix, and the overall averages of all sixteen tests for each material. For material 1, V8 was not recorded, so Table 4 has no values for V8 and V'4.

Table 4: Voltages and %CE for the electrolysis test matrix with Material 1.

Material	1					
Test Set	Cathode/Anode	V1	V4	V8	V'4	% CE
1	C1/A1	3.67	3.57	N/A	N/A	80.46
	C2/A2	3.65	3.54	N/A	N/A	86.20
	C3/A3	3.71	3.62	N/A	N/A	75.01
	C4/A4	3.49	3.41	N/A	N/A	77.89
	Test set average	3.63	3.53	N/A	N/A	79.89
2	C1/A2	3.87	3.76	N/A	N/A	89.73
	C2/A3	3.71	3.62	N/A	N/A	85.36
	C3/A4	3.61	3.53	N/A	N/A	90.98
	C4/A1	4.07	3.97	N/A	N/A	87.40
	Test set average	3.81	3.72	N/A	N/A	88.37
3	C1/A3	3.89	3.80	N/A	N/A	85.82
	C2/A4	4.26	4.18	N/A	N/A	87.33
	C3/A1	3.60	3.51	N/A	N/A	91.39
	C4/A2	4.22	4.12	N/A	N/A	87.91
	Test set average	3.99	3.90	N/A	N/A	88.11
4	C1/A4	4.10	4.02	N/A	N/A	90.92
	C2/A1	4.59	4.48	N/A	N/A	88.26
	C3/A2	3.69	3.60	N/A	N/A	89.55
	C4/A3	4.17	4.09	N/A	N/A	92.67
	Test set average	4.14	4.05	N/A	N/A	90.35
Material average		3.89	3.80	N/A	N/A	86.68

Table 5: Voltages and %CE for the electrolysis test matrix with Material 2.

Material	2					
Test Set	Cathode/Anode	V1	V4	V8	V'4	% CE
1	C1/A1	3.58	3.48	3.03	2.93	83.14
	C2/A2	3.53	3.44	3.04	2.94	83.46
	C3/A3	3.54	3.47	3.07	2.99	80.78
	C4/A4	3.49	3.41	3.04	2.97	80.43
	Test set average	3.54	3.45	3.05	2.96	81.95
2	C1/A2	3.56	3.47	3.03	2.94	90.13
	C2/A3	3.55	3.47	3.08	2.99	91.41
	C3/A4	3.48	3.42	2.98	2.92	91.35
	C4/A1	3.78	3.71	3.33	3.26	93.25
	Test set average	3.59	3.52	3.11	3.03	91.54
3	C1/A3	3.52	3.44	3.03	2.95	87.17
	C2/A4	3.54	3.46	3.03	2.95	94.84
	C3/A1	3.56	3.47	3.05	2.96	90.04
	C4/A2	3.78	3.69	3.24	3.15	90.78
	Test set average	3.60	3.51	3.09	3.00	90.71
4	C1/A4	3.59	3.48	3.00	2.90	96.22
	C2/A1	3.54	3.45	3.04	2.96	93.93
	C3/A2	3.54	3.46	3.00	2.92	94.02
	C4/A3	3.85	3.78	3.40	3.33	94.30
	Test set average	3.63	3.54	3.11	3.03	94.62
Material average		3.59	3.51	3.09	3.00	89.70

Table 6: Voltages and %CE for the electrolysis test matrix with Material 3.

Material	3					
Test Set	Cathode/Anode	V1	V4	V8	V'4	% CE
1	C1/A1	3.38	3.39	2.94	2.94	85.79
	C2/A2	3.39	3.33	2.94	2.88	83.63
	C3/A3	3.44	3.38	3.00	2.94	86.43
	C4/A4	3.37	3.48	2.86	2.97	91.35
	Test set average	3.40	3.40	2.93	2.93	86.80
2	C1/A2	3.42	3.35	2.97	2.90	96.22
	C2/A3	3.39	3.35	2.92	2.88	86.64
	C3/A4	3.43	3.38	2.98	2.93	92.91
	C4/A1	3.52	3.52	2.99	2.99	90.39
	Test set average	3.44	3.40	2.96	2.93	91.54
3	C1/A3	3.62	3.55	2.99	2.92	93.19
	C2/A4	3.46	3.42	2.89	2.85	85.42
	C3/A1	3.40	3.35	2.93	2.88	84.95
	C4/A2	3.60	3.55	3.06	3.01	82.09
	Test set average	3.52	3.46	2.97	2.91	86.41
4	C1/A4	3.49	3.48	2.95	2.93	89.80
	C2/A1	3.43	3.39	2.93	2.89	84.25
	C3/A2	3.46	3.40	2.96	2.90	87.10
	C4/A3	3.54	3.48	2.96	2.91	91.05
	Test set average	3.48	3.44	2.95	2.91	88.05
Material average		3.46	3.42	2.95	2.92	88.20

Table 7: Voltages and %CE for the electrolysis test matrix with Material 4.

Material	4					
Test Set	Cathode/Anode	V1	V4	V8	V'4	% CE
1	C1/A1	3.51	3.42	3.01	2.92	79.29
	C2/A2	3.52	3.42	2.98	2.88	83.12
	C3/A3	3.43	3.43	3.15	3.15	78.94
	C4/A4	3.51	3.42	3.05	2.96	94.91
	Test set average	3.49	3.42	3.05	2.98	84.06
2	C1/A2	3.75	3.67	3.01	2.93	93.13
	C2/A3	3.60	3.51	3.06	2.98	86.15
	C3/A4	3.53	3.43	3.17	3.08	90.40
	C4/A1	3.58	3.47	3.16	3.04	92.10
	Test set average	3.61	3.52	3.10	3.01	90.44
3	C1/A3	3.73	3.63	3.03	2.93	90.12
	C2/A4	3.50	3.43	2.97	2.90	88.51
	C3/A1	3.56	3.47	3.01	2.93	89.38
	C4/A2	3.76	3.66	3.61	3.51	88.07
	Test set average	3.64	3.55	3.16	3.07	89.02
4	C1/A4	3.56	3.45	2.99	2.88	88.99
	C2/A1	3.48	3.41	2.97	2.89	86.25
	C3/A2	3.69	3.60	2.96	2.87	92.61
	C4/A3	3.75	3.66	3.86	3.77	87.39
	Test set average	3.62	3.53	3.20	3.10	88.81
Material average		3.59	3.51	3.13	3.04	88.08

Table 8: Voltages and %CE for the electrolysis test matrix with Material 5.

Material	5					
Test Set	Cathode/Anode	V1	V4	V8	V'4	% CE
1	C1/A1	3.52	3.46	3.11	3.05	85.94
	C2/A2	3.54	3.47	3.01	2.95	89.95
	C3/A3	3.46	3.40	2.97	2.91	82.00
	C4/A4	3.53	3.46	3.01	2.93	87.00
	Test set average	3.51	3.45	3.02	2.96	86.22
2	C1/A2	3.69	3.63	3.02	2.96	89.95
	C2/A3	3.59	3.50	3.00	2.91	93.73
	C3/A4	3.75	3.68	3.03	2.96	89.70
	C4/A1	3.80	3.71	3.02	2.93	89.62
	Test set average	3.71	3.63	3.02	2.94	90.75
3	C1/A3	3.68	3.63	2.95	2.89	90.71
	C2/A4	3.61	3.53	3.04	2.97	88.28
	C3/A1	3.66	3.60	3.02	2.96	87.32
	C4/A2	3.70	3.63	3.03	2.95	90.49
	Test set average	3.66	3.60	3.01	2.94	89.20
4	C1/A4	3.59	3.53	2.95	2.88	89.18
	C2/A1	3.62	3.54	3.02	2.94	90.65
	C3/A2	3.67	3.59	3.03	2.95	90.82
	C4/A3	3.95	3.87	3.02	2.94	84.10
	Test set average	3.71	3.63	3.00	2.93	88.69
Material average		3.65	3.58	3.01	2.94	88.71

Table 9: Voltages and %CE for the electrolysis test matrix with Material 6.

Material	6					
Test Set	Cathode/Anode	V1	V4	V8	V'4	% CE
1	C1/A1	3.16	3.07	3.11	3.02	82.93
	C2/A2	3.16	3.07	3.11	3.02	85.49
	C3/A3	3.11	3.02	3.06	2.97	83.32
	C4/A4	3.14	3.05	3.08	2.99	83.76
	Test set average	3.14	3.05	3.09	3.00	83.87
2	C1/A2	3.10	3.00	3.05	2.95	89.86
	C2/A3	3.53	3.39	3.05	2.91	80.00
	C3/A4	3.62	3.53	3.09	3.00	85.00
	C4/A1	3.56	3.48	3.02	2.94	83.30
	Test set average	3.45	3.35	3.05	2.95	84.54
3	C1/A3	3.59	3.51	3.04	2.95	87.51
	C2/A4	3.32	3.44	2.87	2.99	89.31
	C3/A1	3.58	3.49	3.02	2.93	85.19
	C4/A2	3.80	3.71	3.09	3.00	86.30
	Test set average	3.57	3.54	3.00	2.97	87.08
4	C1/A4	3.70	3.59	3.10	3.00	83.43
	C2/A1	3.44	3.38	3.00	2.94	85.34
	C3/A2	3.78	3.69	3.14	3.04	85.15
	C4/A3	3.78	3.77	2.92	2.92	86.19
	Test set average	3.68	3.61	3.04	2.97	85.03
Material average		3.46	3.39	3.05	2.97	85.13

Table 10: Voltages and %CE for the electrolysis test matrix with Material 7.

Material	7					
Test Set	Cathode/Anode	V1	V4	V8	V'4	% CE
1	C1/A1	3.52	3.46	2.99	2.93	81.14
	C2/A2	3.54	3.45	3.02	2.93	85.30
	C3/A3	3.61	3.54	3.07	3.00	81.78
	C4/A4	3.53	3.53	2.96	2.96	75.07
	Test set average	3.55	3.50	3.01	2.96	80.82
2	C1/A2	3.75	3.69	3.05	2.99	60.26
	C2/A3	3.68	3.57	3.17	3.07	91.41
	C3/A4	3.72	3.64	3.13	3.05	93.18
	C4/A1	3.83	3.74	3.08	2.99	91.05
	Test set average	3.74	3.66	3.11	3.02	83.98
3	C1/A3	3.69	3.64	3.05	3.00	92.44
	C2/A4	3.63	3.60	3.04	3.01	89.57
	C3/A1	3.69	3.60	3.15	3.06	88.36
	C4/A2	3.78	3.64	3.11	2.97	88.51
	Test set average	3.70	3.62	3.08	3.01	89.72
4	C1/A4	3.54	3.46	2.98	2.90	93.85
	C2/A1	3.80	3.71	3.19	3.10	88.15
	C3/A2	3.64	3.57	3.10	3.03	88.84
	C4/A3	3.74	3.69	3.06	3.01	84.44
	Test set average	3.68	3.61	3.08	3.01	88.82
Material average		3.67	3.60	3.07	3.00	85.83

The quality of the electrolysis tests and the test materials is indicated by the variation of the measured quantities from one test to the next with a given material. Within the test matrix for a given material, there are four equivalent sets of four tests. Thus the standard deviations of these measured quantities across the four tests in a given set of tests indicate the quality and reproducibility of those four tests. The standard deviation of a quantity is best expressed in relation to the average value of that quantity, thus as a percent relative standard deviation (%RSD). This is the standard deviation divided by the average times 100%. The %RSDs obtained in Phase I of the test set averages in Tables 4 – 10 are summarized in Table 11.

Table 11: % relative standard deviations of quantities measured in electrolysis tests for the seven materials tested in Phase 1. The values for each test set are for the four tests comprising that set.

Test set	Quantity	Material						
		1	2	3	4	5	6	7
1	V1	2.3%	0.9%	0.8%	1.1%	0.9%	0.7%	1.0%
	V4	2.2%	0.8%	1.6%	0.0%	0.9%	0.7%	1.1%
	V8		0.5%	1.7%	2.2%	1.7%	0.7%	1.4%
	V'4		0.8%	1.1%	3.5%	1.8%	0.7%	1.0%
	%CE	5.2%	1.7%	3.3%	7.7%	3.3%	1.2%	4.6%
2	V1	4.6%	3.1%	1.4%	2.3%	2.1%	6.1%	1.5%
	V4	4.5%	3.2%	2.1%	2.6%	2.2%	6.2%	1.7%
	V8		4.3%	1.0%	2.2%	0.4%	0.8%	1.6%
	V'4		4.5%	1.5%	1.9%	0.8%	1.1%	1.2%
	%CE	2.4%	1.2%	3.8%	2.9%	1.9%	4.2%	16.3%
3	V1	6.7%	2.9%	2.6%	3.1%	0.9%	4.8%	1.5%
	V4	6.9%	2.9%	2.5%	2.8%	1.0%	2.9%	0.6%
	V8		2.8%	2.1%	8.2%	1.2%	2.7%	1.4%
	V'4		2.8%	2.0%	8.3%	1.1%	1.1%	1.1%
	%CE	2.3%	3.0%	4.8%	0.9%	1.6%	1.8%	1.8%
4	V1	7.7%	3.6%	1.2%	2.9%	3.8%	3.8%	2.7%
	V4	7.8%	3.9%	1.3%	2.9%	3.8%	4.0%	2.8%
	V8		5.4%	0.5%	12.1%	1.1%	2.8%	2.4%
	V'4		5.8%	0.6%	12.4%	0.9%	1.7%	2.4%
	%CE	1.8%	1.0%	3.0%	2.7%	3.1%	1.2%	3.8%

During test with the commercial Ceradyne material, material 1, the experimental set-up did not yet incorporate the voltage sensing between the ceramic cathode riser and the stainless steel riser. Thus values of V8 and V'4 were not obtained with this material. For most materials and test sets, the RSDs of voltages are pretty much comparable. The largest discrepancy in the RSD is for material 4. In this material in run sets 3 and 4, the fourth cathode of the four exhibited an unusually high V8 value, which is not explained. In general, the RSDs are small

enough that student t-tests using these populations are a good test for comparing populations, thus cathode materials.

The analytical data for the electrolyte and product metal samples was also analyzed in terms of standard deviations. Of the various analytes, the most relevant are titanium (Ti) and zirconium (Zr). Without exception, Zr was not detected in electrolyte samples. With few exceptions, Ti was not detected in the electrolyte samples, and was just above detection limit in the few exceptional cases. Thus the present report will focus upon Ti (or Zr) in the aluminum recovered. This data is important for it tells of the propensity for intergranular corrosion of the cathode materials to yield grain loss into the product metal.

Table 12: % relative standard deviations of Ti (Zr for material 7) contamination of duplicate metal samples taken in Phase I.

Test set	Material						
	1	2	3	4	5	6	7
1	9.7%	41.8%	26.3%	2.1%	25.7%	49.8%	11.2%
	23.5%	20.9%	24.4%	24.5%	14.3%	12.9%	4.5%
	0.7%	26.0%	5.9%	4.3%	5.6%	4.6%	4.9%
	12.0%	15.9%	47.5%	47.6%	4.0%	7.5%	35.9%
2	49.5%	31.5%	71.4%	70.7%	1.6%	11.5%	16.8%
	51.7%	7.6%	28.1%	57.9%	11.6%	37.7%	24.7%
	22.0%	16.2%	15.6%	5.6%	6.2%	15.8%	19.7%
	44.1%	10.0%	48.0%	40.0%	14.4%	67.9%	1.1%
3	23.9%	34.8%	90.8%	13.8%	38.5%	18.5%	36.2%
	10.5%	22.7%	47.4%	55.6%	23.9%	5.7%	33.8%
	10.8%	4.2%	22.4%	15.4%	7.0%	44.4%	24.2%
	9.6%	10.2%	73.0%	7.2%	8.0%	40.0%	0.0%
4	51.5%	47.4%	36.5%	13.8%	28.7%	14.3%	22.6%
	13.3%	26.3%	33.3%	13.2%	17.3%	55.8%	3.6%
	35.4%	33.3%	68.4%	32.1%	3.8%	15.6%	4.7%
	26.1%	15.8%	43.3%	22.9%	6.7%	50.0%	15.9%

The %RSD of the duplicate analyses of product metal samples for Ti, or Zr with material 7, appear in Table 12. These values vary widely and are often fairly large. This does not indicate poor analyses. It does indicate that the nature of the Ti (Zr) contamination is from particles that have dislodged from the cathode material into the product metal. In such cases, the number of particles in one of the duplicate metal samples is different than in the other of the duplicates.

The interpretation that the fairly high %RSDs in Table 12 are due to inhomogeneous contamination by cathode material particles is supported by the values in Table 13. This Table contains the %RSD of the analyses of the same duplicate product metal samples as led to the

values in Table 12. However, the analyte for the results in Table 13 was copper from the anodes. Copper reports to the product aluminum by dissolution into the electrolyte, diffusion, and mass transfer. Most of the values in Table 13 are below 5%. It is typical for analytical laboratories to consider this a high precision for duplicate analyses. The results in Table 13, then, are particularly good, since they reflect the combined effects of both product metal sampling and the elemental analysis.

Table 13: % relative standard deviations of copper contamination of duplicate metal samples taken in Phase I.

Test set	Material						
	1	2	3	4	5	6	7
1	1.2%	3.1%	0.0%	1.3%	0.9%	0.7%	2.9%
	1.6%	0.0%	1.1%	2.1%	2.0%	0.8%	3.9%
	1.4%	0.9%	0.9%	3.0%	1.9%	2.7%	2.3%
	5.4%	1.1%	0.7%	0.8%	2.0%	0.8%	3.0%
2	4.4%	4.8%	0.0%	3.7%	1.3%	1.3%	0.3%
	1.6%	1.2%	4.0%	1.3%	0.3%	1.7%	3.4%
	2.4%	1.7%	2.3%	4.6%	1.3%	1.5%	4.4%
	0.5%	1.0%	0.9%	15.5%	0.0%	7.7%	0.0%
3	2.9%	0.0%	1.7%	2.2%	3.7%	0.5%	3.7%
	5.1%	3.3%	1.7%	1.4%	0.8%	0.3%	2.7%
	0.3%	1.2%	1.7%	1.3%	0.0%	5.0%	1.5%
	0.9%	2.9%	1.2%	2.6%	1.3%	0.0%	1.7%
4	0.9%	1.3%	0.4%	1.2%	1.1%	1.8%	7.9%
	0.6%	5.5%	0.3%	0.1%	1.2%	32.9%	5.8%
	12.6%	0.2%	1.4%	2.4%	0.0%	1.3%	0.2%
	5.6%	2.1%	1.5%	1.1%	0.3%	2.4%	2.2%

Statistical comparisons

Student t-tests were used to compare the performance of the various materials during the electrolysis tests. Given the structure of the test matrix, a variety of populations were readily compared.

With each of the Phase 1 materials that underwent electrolysis testing, the measurements made for the first test set were compared to those for test sets 2-4, those in set 2 compared to those in sets 3 and 4, and those of set 3 compared to those of 4. It was anticipated that the first test sets might prove to be different from the others because the electrodes were new and unused in the first test sets.

The results of these comparisons for material 1 are summarized in Table 14. Only voltages V1 and V4 are used with this material, since V8 was not recorded. The results are for one-tailed paired average t-tests with assumed zero difference of the means and 95% confidence intervals. Since each population contains four samples, each test exhibits 3 degrees of freedom. The table columns show the two test sets compared, the quantity used for comparison, whether the test indicates a difference between populations (y) or not (n), and which population average is larger.

Table 14: Student t-test comparisons of electrolysis data for different test sets with cathode material 1.

Test sets	Quantity	Difference y/n?	Which mean >
1/2	V1	n	2>1
	V4	n	2>1
	%CE	y	2>1
1/3	V1	n	3>1
	V4	n	3>1
	%CE	y	3>1
1/4	V1	y	4>1
	V4	y	4>1
	%CE	y	4>1
2/3	V1	n	3>2
	V4	n	3>2
	%CE	n	2>3
2/4	V1	n	4>2
	V4	n	4>2
	%CE	n	4>2
3/4	V1	n	4>3
	V4	n	4>3
	%CE	n	4>3

For this material (Ceradyne HP TiB₂), there is no indication that voltages vary significantly between test sets, except between sets 1 and 4. However, current efficiency is lower in test set 1 than the other sets. This is presumably because the cathode samples must be wet initially in test set 1, whereas sets 2-4 start with wetted cathodes.

Similar t-tests comparing test sets for the other two pure TiB₂ materials showed the same voltage trend, and the first test set voltages were not distinguished from those of sets 2-4. However, the other materials (ie, composites and ZrB₂) all showed voltage differences

between test sets 1 and the remaining test sets. Additionally, most of the materials showed current efficiency differences between test sets 1 and the remaining test sets.

In contrast, comparisons among the last three test sets failed almost exclusively to show differences, either in voltages or in current efficiencies. The only exceptions were with V1 for material 7, test sets 2 and 3, and material 3, test sets 2 and 4. Relaxing the criteria for detecting differences, either by decreasing the confidence interval a few percent, or using two-tailed t-tests, resulted in these statistical differences also vanishing. Consequently, for comparing the electrolysis data of different materials using V1, V4, and current efficiency, only test sets 2-4 were used.

The results of these comparisons appear in Table 15. These used two-sided t-tests of paired means and 95% confidence intervals. These results are particularly useful for comparing material 1 to the other materials, since only V1 and V4, and not V8 were recorded for material 1. The most striking result is that material 1 exhibited a statistically different voltage for test sets 2-4 than all of the other materials. Indeed, it turns out it had the highest voltages of any materials. From this, it seems that the materials consolidated specifically for the present project performed better, with lower electrolysis voltage, than the commercial material.

Materials 2-7 were also compared using V8, which excludes voltage drop in the stainless steel cathode riser sections. These results appear in Table 16. The table also includes the average value of V8 for each material over all tests, and the differences in the average between the materials compared. The evaluation of the meaning of these results appears in the Summary and discussion sub-section to follow.

The Phase I materials were also compared with respect to the product metal contamination. Table 17 presents the duplicate-average weight percentage contamination by Ti (Zr for material 7) for all 112 tests in the test matrix.

Given the masses of aluminum recovered in each test, the results in Table 16 were converted to grams of Ti (Zr) lost to the product metal. The averages for these for each test set are shown in Table 18.

Table 15: V1, V4 and current efficiency t-test comparisons of Phase 1 materials using test sets 2-4 only.

Quantity	Materials Compared	Difference y/n?	Materials Compared	Difference y/n?
V1 V4 %CE	1/2	y y y	3/4	y y n
V1 V4 %CE	1/3	y y n	3/5	y y n
V1 V4 %CE	1/4	y y n	3/6	n n y
V1 V4 %CE	1/5	y y n	3/7	y y n
V1 V4 %CE	1/6	y y y	4/5	y y n
V1 V4 %CE	1/7	y y n	4/6	n n y
V1 V4 %CE	2/3	y y y	4/7	y y n
V1 V4 %CE	2/4	n n y	5/6	y n y
V1 V4 %CE	2/5	y y y	5/7	n n n
V1 V4 %CE	2/6	n n y	6/7	n n n
V1 V4 %CE	2/7	y y n		

Table 16: V8 t-test comparisons of Phase 1 materials using all test sets. The table also shows the average V8 voltages of each material, and the differences of these for the materials compared.

Materials compared a/b	Different y/n?	Voltages and difference		
		a	b	b-a
2/3	y	3.087	2.954	-0.133
2/4	n	3.087	3.125	0.038
2/5	y	3.087	3.013	-0.074
2/6	n	3.087	3.047	-0.040
2/7	n	3.087	3.070	-0.017
$\frac{3}{4}$	y	2.954	3.125	0.171
3/5	y	2.954	3.013	0.059
3/6	y	2.954	3.047	0.093
3/7	y	2.954	3.070	0.116
4/5	n	3.125	3.013	-0.112
4/6	n	3.125	3.047	-0.078
4/7	n	3.125	3.070	-0.055
5/6	n	3.013	3.047	0.034
5/7	y	3.013	3.070	0.057
6/7	n	3.047	3.070	0.023

Table 17: Ti contamination (wt%) of product metal (Zr for material 7) for all 112 tests of the Phase I test matrix. The values are averages of duplicates.

Test set	Test designation	Material						
		1	2	3	4	5	6	7(Zr)
1	C1/A1	0.216	0.169	0.177	0.146	0.119	0.154	0.667
	C2/A2	0.272	0.180	0.238	0.216	0.116	0.198	1.266
	C3/A3	0.506	0.118	0.110	0.786	0.306	0.165	0.505
	C4/A4	0.275	0.148	0.397	0.159	0.177	0.186	1.304
2	C1/A2	0.050	0.073	0.098	0.130	0.127	0.026	0.304
	C2/A3	0.029	0.060	0.032	0.038	0.086	0.663	0.174
	C3/A4	0.103	0.037	0.032	0.224	0.193	0.019	0.069
	C4/A1	0.056	0.070	0.089	0.065	0.157	0.125	0.221
3	C1/A3	0.036	0.068	0.033	0.062	0.096	0.041	0.035
	C2/A4	0.019	0.044	0.010	0.068	0.071	0.133	0.077
	C3/A1	0.037	0.036	0.076	0.104	0.071	0.036	0.066
	C4/A2	0.068	0.025	0.056	0.069	0.082	0.060	0.082
4	C1/A4	0.066	0.029	0.032	0.178	0.072	0.039	0.016
	C2/A1	0.015	0.010	0.012	0.316	0.052	0.226	0.042
	C2/A2	0.050	0.003	0.038	0.224	0.053	0.087	0.064
	C4/A3	0.046	0.019	0.030	0.042	0.134	0.056	0.063

Table 18: Averages of mass, in grams, of Ti or Zr lost to the product aluminum in the test sets of Phase I.

Test set	Material						
	1	2	3	4	5	6	7(Zr)
1	0.045	0.022	0.032	0.046	0.027	0.026	0.134
2	0.010	0.010	0.009	0.018	0.022	0.030	0.027
3	0.006	0.007	0.006	0.012	0.012	0.011	0.010
4	0.007	0.002	0.004	0.030	0.012	0.016	0.007

Since Zr has a higher formula weight ($91.2 \text{ g}\cdot\text{mol}^{-1}$) than Ti ($47.9 \text{ g}\cdot\text{mol}^{-1}$), it was also instructive to convert the values in Table 16 to test set averages of atom percent contamination. These results are in Table 19.

Table 19: Averages of atom percent contamination of product aluminum by cathode material Ti or Zr for the test sets of Phase I.

Run set	Material						
	1	2	3	4	5	6	7
1	0.179%	0.086%	0.130%	0.184%	0.101%	0.099%	0.277%
2	0.033%	0.034%	0.035%	0.064%	0.079%	0.117%	0.057%
3	0.022%	0.024%	0.024%	0.043%	0.045%	0.038%	0.019%
4	0.025%	0.008%	0.016%	0.107%	0.044%	0.057%	0.014%

The atom percentages can be compared by test set for each material. The results of these comparisons are in Table 20.

Table 20: Results of two-sided paired means t-tests comparing atom% contamination of product metal by Ti or Zr between test sets of Phase I materials. Entries of y indicate a difference with a 95% confidence interval.

Test sets	Material						
	1	2	3	4	5	6	7
1/2	y	y	n	n	n	n	y
1/3	y	y	n	n	n	y	y
1/4	y	y	y	n	n	n	y
2/3	n	n	n	n	n	n	n
2/4	n	y	n	n	n	n	n
3/4	n	y	n	n	n	n	n

Phase I microscopy

Eleven Phase I cathode samples were investigated using scanning electron microscopy (SEM). Three of these were blanks, unused in electrolysis testing. The others all underwent electrolysis testing. One of these, which was the commercial HP TiB₂, had been used in tests outside of the

test matrix, and is not discussed further here. The remaining seven represent the seven materials used in the test matrix.

The ten samples discussed are listed in Table 21. The Table indicates an ID number for the SEM sample, the electrolysis history, the material ID number used in this report, and two columns describing the material. The materials of ID numbers 11-13 are discussed under Phase II.

Table 21: Phase I cathode samples examined using SEM. Those not used in electrolysis were blanks. Those used in electrolysis went through the test matrix.

ID number	Electrolysis	Material	Material chemistry	Fabrication method
1	n	4	TiB ₂ -Al ₂ O ₃	P2C
2	n	2	TiB ₂	P2C
3	n	2	TiB ₂	P2C
4	y	1	TiB ₂	commercial HP
6	y	2	TiB ₂	P2C
7	y	4	TiB ₂ -Al ₂ O ₃	P2C
8	y	6	TiB ₂ -ZrO ₂	P2C
9	y	3	TiB ₂	HP
10	y	7	ZrB ₂	HP
14	y	5	TiB ₂ -Al ₂ O ₃	HP

The first notable finding from the microscopy was that all of the materials wetted with aluminum produced during electrolysis. An example is shown in Figure 8. This Figure shows the Al layer over its thinnest region on the sample, cathode ID number 6. The top of the Al layer is about 17.4 mm from the bottom of the cathode. The picture shows the top, approximately 6.8 mm length, of this layer. Below the region shown, i.e. between 10.6-mm mark and the bottom of the cathode, the Al is thicker and there are clearly no breaks in the Al layer. As shown in Figure 8, sixteen images were taken to illustrate the Al layer over its "thin" region (join B-to-B, C-to-C, etc.). In this region the layer is approximately 30 μ m thick on average, but is as thin as 10 μ m in some regions and thickens to about 65 μ m near the 10.6-mm mark. Two important observations are noted: (1) There are no "breaks" in the Al. The Al layer is intact over its full length. In some regions, a few grains of the TiB₂ matrix have loosened and are "floating" in the Al layer but the Al is still apparently unbroken by these grains. (2) The Al appears to wet the TiB₂, as well as any loose grains, down to at least 1- μ m scale.

The hypothesis used to explain the %RSDs of Ti contamination in Table 12 is supported by these observations. The images of Figure 8 show only the aluminum still left on the cathode sample after removal from the electrolysis cell, while the majority of the aluminum produced was recovered separately from the cathode. However, that grains of cathode material are found in the residual layer on the cathode indicates that grains are the source of product metal

contamination. This observation also indicates that the distribution of such grains may not be truly homogeneous and could produce the statistical results in Table 12.

Figure 8: A micrograph of a TiB_2 cathode, consolidated by P2C™, following use in the Phase I test matrix.

The micrographs yielded insight into the mechanism of the grain-loss corrosion. Figure 9 contains four SEM micrographs of the same cathode as in Figure 8. The locations of the micrographs are indicated by reference to the optical image adjacent to them. There are several similarities between this cathode and the other cathodes analyzed. These include: the intergranular attack of the TiB_2 matrix to a depth of about one layer of grains (C, D); and the observation of a metallic phase that contained anode components (e.g. Fe) along grain boundaries in the Al metal coating (see lighter phase in Al coating in B).

Other micrographs revealed penetration of both Al and Al-fluorides along grain boundaries. The presence of the fluorides indicates penetration by the electrolyte, presumably prior to wetting.

Given the test matrix, such fluorides would have to penetrate before electrolysis in the first-of-four test sets, and remain in the grain boundaries throughout the testing program.

Figure 9: SEM micrographs of the cathode in Figure 8.

The addition of Al_2O_3 or ZrO_2 to produce composites worsened the intergranular attack. For example, the surface of the cathode ID number 7 was significantly more attacked than in pure TiB_2 samples. Several layers of grains were loosened from the matrix. This contrasts the performance of cathode ID 6, where only the very top layer of grains was affected. The mode of attack appears to be intergranular corrosion with the grains being loosened from the matrix while retaining much of their original geometric shape. These observations correlate with the analytical results of product metal purity. There, the composite exhibited persistent high levels of Ti contamination through all four of the test sets, whereas the contamination dropped significantly from the first to the fourth test set with pure TiB_2 .

Higher magnification images of the Al/Cathode interface revealed part of the mechanism for intergranular attack in this composite. This cathode material has a phase of aluminum oxide, presumably Al_2O_3 , distributed through it. However, the oxide is missing in the intergranular

region where Al metal has penetrated. Moreover, deeper in the cathode but still near the surface, the Al_2O_3 regions are partly eroded. Energy dispersive spectroscopic (EDS) analysis revealed that the phase that (apparently) had once been Al_2O_3 contained much less oxygen than in the stoichiometric Al_2O_3 (as measured in regions further from the surface) as well as varying amounts of F, Na, and Ti.

Clearly, there is some reaction that contributes to the deterioration of the Al_2O_3 phase near the surface of this cathode material. As the phase reacts, the grains loosen, Al or electrolyte penetrates the cathode, and additional Al_2O_3 phase dissolves. It is likely that this mechanism involves cathodic reduction of the Al_2O_3 phase during cell operation, although it is unclear what roles the Al metal layer and the electrolyte play in this process.

The case with the ZrO_2 composite was similar, and presents an additional complication. This arises because Zr is only slightly less noble than Al at temperatures over 705°C . At lower temperatures, it is more noble. Thus at some temperatures possible in LTE systems, penetration of the Al can cause reduction of the ZrO_2 , leaving Al_2O_3 and Zr contamination in the product metal.

With the HP materials, the grains dislodged from the cathodes were larger than with the P2C™ compacted materials. This is consistent with the smaller grain boundaries produced with P2C™. The HP ZrB_2 behaved quite similarly to the HP TiB_2 , as the analytical results of the product metal also indicate.

The only material used in Phase I electrolysis testing that showed damage beyond the intergranular corrosion was the HP $\text{TiB}_2\text{-Al}_2\text{O}_3$ composite. The cathode sample ID number 14 showed cracking. The bottom of this sample showed several cracks that extended hundreds of microns up into the cathode. Al metal was detected in these cracks indicating that they were present during electrolysis testing.

Phase II

In Phase II, six additional composite materials, three with 90 vol% TiB_2 and three with 97.5 vol% TiB_2 , were consolidated with P2C™ and screened for performance under LTE conditions. An additional TiB_2 material was produced in a proprietary way utilizing P2C™. An attempt was made to produce a TiB_2 surface on a Ti substrate. A final material, Al infiltrated AlN (Al/AlN) was tested. This material was produced by SINTEF of Trondheim, Norway. Thus the Phase II effort subjected nine additional materials to LTE conditions, yielding a project total of 19 materials.

Another emphasis in Phase II was to expose commercial HP TiB_2 and the six additional composites to LTE tests of 20 continuous hours or more. The materials in Phase I each experience a cumulative 20 hours of LTE testing, but in four separate tests, with cooling and re-heating cycles.

The only difference between the LTE test method for the 20 and 40 hour tests and the 5 hour tests was that product metal was periodically removed from the cathodes during the longer

tests. This was done in a proprietary way, and yielded aluminum samples representative of different time intervals during the tests. With these, the contamination by Ti was evaluated against time of continuous electrolysis.

Materials

The materials studied in Phase II are summarized in Table 22. This is similar to Table 1. However, where applicable, it also includes the cathode sample ID number for post-electrolysis microscopy, as in Table 21. All of the materials in Table 22 were subjected to LTE conditions.

Table 22: Non-commercial materials tested in Phase II. The ratios specified in the Chemistry column are volume % TiB₂:other compound.

Material number	Chemistry	Fabrication method	Microscopy ID number
10a	TiB ₂ -B ₄ C (97.5:2.5)	P2C	15
10b	TiB ₂ -B ₄ C (90:10)	P2C	16
11a	TiB ₂ -BN (97.5:2.5)	P2C	17
11b	TiB ₂ -BN (90:10)	P2C	18
12a	TiB ₂ -TiC (97.5:2.5)	P2C	19
12b	TiB ₂ -TiC (90:10)	P2C	20
13	TiB ₂	proprietary surface rxn SINTEF	
14	TiB ₂ /Ti		
15	Al/AlN		

It had been anticipated that the ZrB₂ analogues of materials 10a-12b might also be fabricated. However, Phase I demonstrated no cost or performance benefit from ZrB₂ over TiB₂, so these materials were not pursued.

Material 1, the commercial HP TiB₂, also contributed to the cathode samples for Phase II. In particular, the microscopy samples with ID numbers 11-13 underwent LTE test lasting 67.6 hours, 40 hours and 20 hours, respectively. Another cathode of this material, not submitted for microscopy, was also tested for 40 hours.

For this Phase, TiB₂ powders were procured from Advanced Ceramics Corporation. The compositional details are:

Ti : 67-69 wt%
B : 27-31 wt%
O : 0.366 wt%
C : 0.467 wt%
N : 0.055 wt%

Average particle size (D₅₀) : 15.6 μm

For materials 10a and 10b, B₄C powders were procured from H.C. Starck, Newton, MA. Compositional details for the B₄C powders are as follows:

B – 75.65 wt%
C – 22.12 wt%
N – 0.51 wt%
O – 1.23 wt%
Fe – 215 ppm
Si – 370 ppm
Average particle size (D₅₀) – 0.92 μm

Although the B₄C powders were reported to be submicron by the manufacturer, the powders had a bi-modal distribution when characterized for particle size distribution using a laser scattering HORIBA LA-910 particle size analyzer. The results of the particle size distribution are presented in Figure 10.

Figure 10: Particle size and distribution of B₄C powder (H.C. Starck).

Specifications and characterizations were not supplied for the BN powders used. The TiC powders were procured from Atlantic Equipment Engineers, with the following specifications:

Total Carbon:	19.50
Free Carbon:	0.130
Oxygen:	0.200
Average particle size:	44μm

TiB₂ powders were mixed with 2.5 vol% and 10 vol% of B₄C powders. The powders were blended in a ball mill for a period of 4 hours to ensure homogeneous mixing. Blended powder compositions were consolidated using plasma pressure compaction (P2C™) into rectangular tiles measuring 3.1" x 2.3" x 0.3" (thick). The tiles were consolidated at 1900°C and 30 MPa for 10 minutes. The density of consolidated samples was measured to be 98.5% of theoretical using Archimedes method. This density was later verified with a gas pycnometer. Sample cathodes were machined from the tiles.

Similar procedures were used for the other four composites, although the consolidation times and/or temperatures differed. For instance, the consolidation time for the TiB₂-BN (97.5:2.5) composite was 18 minutes. Displacement of the ram was observed even after 10 minutes indicating that consolidation was still in progress. When the displacement of the ram ceased, samples were slowly cooled to room temperature and removed from the dies. This composition was 99% of theoretical density as measured using Archimedes method. Overall, the average density of the TiB₂-BN composites was 97% theoretical as determined with a gas pycnometer.

At 13 minutes, the consolidation times of the TiC composites were lower, as were the consolidation temperatures, than for the BN composites. These samples also showed a low propensity to bond to the graphite dies, allowing more used per die. The average densities of the consolidated samples was 96.5% theoretical using a gas pycnometer.

Electrolysis tests

If possible, materials 10a-15 were all tested for five hours and 20 hours under the LTE conditions used in Phase I. Materials 14 and 15 either did not survive, or performed quite badly and will not be discussed further. Material 1 from Phase I was also tested within the project in two 20 hours tests, one 40 hour. A sample of material 1 from another test program, which experienced 67.5 hours of electrolysis, was also examined microscopically, but will not be discussed further.

Table 23: Electrolysis test data for the five hour Phase II LTE tests.

Material	V1	V4	V8	%CE	wt% Ti	atom % Ti	Compare
10a	3.532	3.425	3.006	85.72	0.165	0.093	worse
10b	3.614	3.516	3.194	79.54	0.484	0.273	worse
11a	3.474	3.472	3.467	88.38	0.189	0.107	worse
11b	3.569	3.490	3.071	82.44	0.071	0.040	better
12a	3.533	3.447	3.015	89.29	0.091	0.051	better
12b	3.561	3.467	3.023	88.29	0.412	0.232	worse
13	3.743	3.556	3.153	86.35	0.172	0.097	worse*
13	3.776	3.663	3.166	89.70	0.042	0.024	better
13	3.690	3.541	3.124	92.21	0.051	0.029	better
13	3.745	3.512	3.129	90.80	0.023	0.013	better

*about the same as the Phase I, test set 1 average for P2C™ TiB₂, 0.086 atom % Ti.

Table 23 summarizes the most relevant electrolysis test data for the five hour tests. The last column compares the atom % Ti with the average test set 1 average from Phase 1 for the P2C™ consolidated TiB₂, material 2. Material 2 was the best performer in this regard of all Phase I materials. Thus if the atom % is greater than 0.0864 %, the material is worse in this regard, and otherwise it is better.

Since all of these materials performed reasonably well in these five hours tests, fresh specimens were also tested for 20 hours. The electrolysis results are summarized in Table 24. This Table also includes the results for the 40 and 20 hour tests with material 1. Since several Al samples were collected and analyzed for each test, the range of contamination by Ti is indicated by giving the maximum and minimum atom % Ti for each test. The voltage V8 was not monitored in all of the tests.

Table 24: Summary of LTE test data for longer tests conducted during Phase II.

Material	Hrs	V1	V4	V8	%CE	Ti in Al (atom %)	
						max	min
1	40.0	3.57	3.505		93.4	0.190	0.003
1	40.0	3.74	2.350		96.5	0.056	0.002
1	20.0	3.45	3.375	2.894	93.9	0.104	0.008
10a	20.0	3.55	3.465	3.030	87.2	0.024	0.013
10b	20.0	3.50	3.678	2.994	87.1	0.072	0.018
11a	20.0	3.53	3.454	3.003	90.2	0.027	0.011
11b	20.0	3.30	3.489	3.030	83.6	0.076	0.022
12a	20.0	4.27	4.412		87.1	0.086	0.020
12b	20.0	3.57	3.493	2.974	90.3	0.074	0.019
13	23.6	3.59	3.479	3.089	81.7	0.019	0.012

It is clear from Table 24 that the current efficiencies dropped about 5% using the composites rather than the commercial HP TiB₂. Also, the minimum contamination levels were greater with the composites. These facts indicate that the composites are less likely to be good cathode materials than HP TiB₂.

The way the Ti contamination dropped with time in the tests with material 1 is shown in Figure 11. This Figure displays the wt% Ti contamination versus Al sample # during these tests. The samples were roughly evenly spaced in time, so this plot roughly shows the decrease in contamination with time.

Figure 11: The decrease of product metal contamination by Ti from commercial HP TiB₂ cathodes with sample #.

Phase II microscopy

The composites followed the pattern of the Phase I composites. Having the composite components exacerbated grain loss.

It was noted with samples of material I in this Phase that corrosion of the material is worse in the risers than in the active cathodes. This indicates that the electrolyte and aluminum protect the material from airburn.

Results with carbon anodes

Early in the project, anodes for the 10A cell were machined from anode carbon obtained from the Goldendale, WA smelter. At that point in time, the experimental cell of the test matrix, with a bottom anode and two side anodes and low anode current densities, had not been statistically verified. So these were tested using the same low-temperature electrolysis (LTE) conditions used for many tests prior to this project with metal anodes, using only a bottom anode.

Thus the cell temperature was held at 760°C, the current density in the anode was 0.5 A/cm², a 10wt% excess of undissolved alumina was maintained, the anode was on the bottom of the cell with the TiB₂ cathode suspended above it, and electrolysis performed for five hours. The cathodes in these tests also were of a different design than those used in the Phase I and Phase II cathode tests. In particular, these cathodes were 1" x 4" x 1/4" thick rectangles of material 1. They were attached to a stainless steel riser by using nuts and bolts through holes machined near one end. Only about 1/3-1/2 of their length was under the electrolyte, and there was no alumina shielding the TiB₂ "riser" section. Three tests were conducted with the addition of oxygen gas bubbled from near anode such that the bubbles bathed the cathode. Three tests were conducted with no such gas bubbling.

The two main indicators of cell performance in these tests were the electrolysis voltage V_1 and the current efficiency (CE) determined from aluminum recovered. Statistical tests were performed to compare the two sets of tests. At a 95% confidence level, no difference was found between them. This indicates that the oxygen does not reduce CE by back reaction with aluminum on the suspended cathodes.

The average CEs obtained for the two sets of tests were 73% without oxygen and 65% with. The variances were large enough that these results were not statistically different. It is worth noting that both of these values are lower than the CEs obtained typically with oxygen-generating metal anodes and the rectangular cathodes, in the range 85% - 90%. Moreover, many of the current efficiencies obtained in the test matrix exceeded those obtained with the carbon anodes.

With the carbon anodes, the CO_2 gas bubbles released are large and relatively infrequent compared to the small O_2 bubbles generated by metal anodes. Perhaps the hydrodynamic conditions produced with the relatively large bubbles have a greater impact on current efficiencies with vertically suspended cathodes than does the gas composition.

Near-net shapes

Another project activity was to fabricate net shape TiB_2 pieces. For this purpose a “lollipop” design was chosen for the cathodes. A suitable die was also designed for fabricating these shapes by plasma pressure compaction. The shape of the die shown in Figure 12 was chosen to minimize current loss through the die.

Figure 12. Graphite die for compacting net shape TiB_2 cathodes.

The first set of dies fabricated were 1" in height. Dies were made from two commercially available grades of carbon, EK-90 and Carbone 2020. These dies failed at load levels of < 5 MPa and temperatures of 1200°C. The height of the dies were increased to 2 inches to provide more strength to the die during compaction. These dies also failed, but at a higher loads (10 MPa). A carbon-carbon composite material capable of withstanding pressures up to 50 MPa was fabricated. The thickness of this die was only 1' inch due to the manufacturing limitations associated with the forming of C-C composites. Although the carbon-carbon dies worked the best, full density was not achieved as this die cracked at the higher temperature (1700°C).

All the dies broke in relatively the same location, at the very bottom of the 0.35-inch section. This indicated some amount of structural non-uniformity. Therefore a Finite Element Analysis (F.E.A) was performed on the designs. This revealed the presence of a large stress concentration at the location. Due to the odd shape, the applied pressure does not get evenly distributed throughout the die causing large stresses to build up at specific locations.

In studying different design options, it became apparent that the thicker die walls tended to reduce the stress concentration. The maximum size of the die is limited however by the size of the ram (5" dia) and the inner diameter of the heat shield in the P2C™ machine. The first design has a maximum length of 5 ½ inches. As a result the wall thickness cannot be changed. Upon evaluating different shapes for the outer walls, it seems that a circular disk with the "lollipop" shape in the center produces the least amount of maximum stress under loading conditions normally used during consolidation (Figure 13).

This die design appears to be the best of all examined. The maximum stress reduces from 31.1 to 19.9 psi. As the applied pressure is increased, the difference in maximum stress between the two cases increases considerably. With a 1000 psi pressure applied to the inner walls of the dies, the difference in maximum stress between these two cases is approximately 1,100psi.

Despite these efforts, however, successful consolidation with these dies was not achieved.

Figure 13. F.E.A. of Circular Die. 10 psi pressure applied to inner surface.

Summary and discussion

The Al/AlN and the TiB₂ layer on a Ti substrate proved not to be adequate as cathode materials. All of the other materials tested might still be considered candidate materials.

All of the Phase I materials performed well with respect to wetting by product metal, and current efficiency. Table 25 summarizes the %CE obtained for each averaged over all test sets, and averaged over the last three test sets. Material 2, the P2C™ TiB₂ appeared best overall based solely on the %CE obtained in these tests. Based on the product metal contamination results in Table 19, it also performed as well or better than any of the materials tested. This includes material 3, which was HP TiB₂ using the same raw material as material 2.

Table 25: Average %CE of Phase 1 materials.

Material	1	2	3	4	5	6	7
Test sets 1-4	86.68	89.70	88.20	88.08	88.71	85.13	85.83
Test sets 2-4	88.94	92.29	88.67	89.43	89.55	85.55	87.50

Inspection of Table 23 indicates that the Phase II materials also give good current efficiencies. Material 13, which is similar to material 2, seemed to be a good performer in single five hours tests, but did not perform the best in 20 hour tests with respect to current efficiency. As Table 24 indicates, overall the best performance in Phase II came from the commercial HP TiB₂.

Table 16 indicates, material 2 performed about as well as all of the Phase 1 materials with respect to electrolysis voltage. Although Table 16 indicates differences in the average voltages among these materials, the differences are very small except for the worst case, that of material 4.

The measured electrolysis voltage differences probably do not reflect the material resistivities. For example, the measured resistivities of materials 2, 3, and 13 (from Phase II) are, respectively, 19 micro ohm/cm, 55 micro ohm/cm, and 43 micro ohm/cm. Thus material 2 exhibits the highest conductivity of these three materials, yet its average voltage in Table 16 is greater than that of material 3.

It is stressed that the voltage differences are very small. That t-tests find differences reflects the small variances in the data sets. The voltage obtained in a full sized LTE cell will depend on many factors, including cathode design. Based only on voltage, all of the materials tested are comparable.

With respect to product metal purity, the composite materials produced more contamination than the pure TiB₂ or ZrB₂ materials. As stated before, materials 2 and 3 performed best in Phase I. The commercial HP TiB₂ gave the superior long-test performance in Phase II.

Microscopy showed that the composites were more susceptible to grain loss than the pure materials. This accounts for the metal purity results.

Based upon these results, pure TiB_2 remains the material of choice for wetted cathodes. The P2C™ method gave good materials, and warrants further development and scale-up. The corrosion of these materials seems tied to the existence of grain boundaries and to the presence of impurities, whether added (as with the composites) or introduced with the raw materials or fabrication process. Once electrolyte or aluminum penetrates grain boundaries, reaction with the impurities hastens grain loosening and loss.

Products

Note: Copies of the publications and presentations are incorporated as separate documents attached to this report. The names of the files containing these documents are given in square brackets following the individual citations.

Publications

Craig Brown, "Next Generation Vertical Electrode Cells", *Journal of the Minerals, Metals and Materials Society* (Volume 53, Number 5, May 2001), pp. 39-42.
[JOM-0105-39.pdf]

Presentations

Craig Brown, *Wetted Cathodes for Low-Temperature Aluminum Smelting*, OIT Aluminum Portfolio Group Annual Review Meeting, Lexington, KY, October 17, 2001.
[NAT-10-17-01.pdf]

Craig Brown, *Next Generation Vertical Electrode Cells*, Invited paper, inert anode session, TMS 2001, 130th annual meeting, New Orleans, LA, February 2001.
[NAT-TMS2001.pdf]

Craig Brown, Invited panel member, inert anode session, TMS 2001, 130th annual meeting, New Orleans, LA, February 2001. Associated publication: L. Edwards, N. Richards, and H. Kvande, "Inert Anodes and Other New Al Technologies--The Benefits, Challenges and Impact on Present Technology," *Journal of the Minerals, Metals and Materials Society* (Volume 50, Number 5, May 1998), pp. 48 - 50.
[JOM-0105-48.pdf]

Patents

Craig W. Brown, *Cathode for a Hall-Heroult Type Electrolytic Cell for Producing Aluminum*, Application no 10/126,068, April 22, 2002.

Craig W. Brown, *Cathode for Aluminum Producing Electrolytic Cell*, Application no 10/126,104, April 22, 2002.

References

- [1] Craig Brown, *Journal of the Minerals, Metals and Materials Society* (Volume 53, Number 5, May 2001), pp. 39-42.
- [2] Craig W. Brown, *Light Metals 2000* (2000), pp. 391-395.