

IntroductionUSE OF  $TiB_2$  CATHODE MATERIAL

## APPLICATION AND BENEFITS IN CONVENTIONAL VSS CELLS

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A low-cost proprietary  $TiB_2$  cathode material\* has been developed which circumvents the problems previously experienced in using  $TiB_2$  in aluminum smelting cells, i.e., chemical instability, poor thermal shock and impact resistance, attachment problems, and high cost. During the period 1981-83, the proprietary material was tested as a cathode lining in six Vertical Stud Soderberg (VSS) aluminum reduction cells at the Martin Marietta Aluminum plant, The Dalles, OR. The plant test has demonstrated that the material achieves excellent durability and longevity in commercial aluminum reduction cells, and can be utilized with no modification to conventional cell operating procedures. Current efficiency improvements and energy savings have been realized, and the rate of  $TiB_2$  loss indicates a potential 3-5 year life for the cathode material. Analysis of core samples taken from the experimental cathodes at The Dalles during temporary shutdown confirmed that the cathode lining was functioning as predicted.

\* Patents pending

Virtually all commercial aluminum is produced in Hall-Heroult design electrolytic cells. Power consumption for the process ranges from about 6 to 8.5 kWh/lb of aluminum produced, while the theoretical thermodynamic requirement is  $\sim 3.0$  kWh/lb (1). The long-term demand for aluminum is anticipated to rise as industry and consumers increase their use of this lightweight metal to reduce energy costs, for example, in transportation. Faced with growing demand and limited supplies of increasingly expensive electrical energy, the aluminum industry has strong incentive to develop a low-energy aluminum reduction cell.

In conventional electrolytic smelting, a significant portion of the "wasted" energy (the difference between theoretical and actual energy requirements) is due to the voltage drop across the resistive cryolite electrolyte bath in the interpolar space between the two electrodes. Reduction of the anode-cathode distance (ACD) in a conventional cell reduces the bath voltage loss, but, due to metal pad instabilities, the cell current efficiency decreases as the reaction products at both electrodes become intermixed. To reduce the ACD without concomitant loss in current efficiency, much work has been done to improve metal pad stability by controlling the cell magnetics. An alternate, more revolutionary, approach being investigated in the industry is the use of a solid aluminum-wetted cathode, such as  $TiB_2$ , from which the molten metal is continuously drained. Since in this latter method, the unstable metal pad is replaced with a thin film of aluminum, the ACD can be reduced without a loss of current efficiency.

Extensive industrial research has been carried out since the 1950's on the use of refractory hard materials (RHM) such as  $TiB_2$  for cathode lining applications (2).  $TiB_2$  is very slightly soluble in aluminum, highly conductive compared to cryolite, and most significantly, is wetted by molten aluminum. This property of wettability allows an aluminum film to be electrolytically deposited without the presence of an aluminum pad, because the molten metal skin effectively sticks to the surface instead of agglomerating into separate metal pools. Thus, new cell designs are possible, utilizing, for example, a sloped cathode so that the aluminum film runs off the surface continuously. Hence the ACD can be reduced from the normal 4-6 cm down to 1-3 cm without loss of current efficiency, permitting a 1.0-1.5 V decrease in cell voltage. High current efficiency is maintained because the aluminum film is tightly bound to the RHM surface and therefore has little tendency to intermix with the electrolyte and anode products. Moreover, the interaction between the magnetic field and the thin aluminum film is negligible by comparison with that associated with a full metal pad. Figure 1 illustrates two different cell design concepts in the patent literature for using  $TiB_2$  cathode material in a low-energy cell (LEC).

The two major technical problems arising during previous attempts to make a  $TiB_2$  surface on carbon/graphite blocks, from which the cathode is constructed, are lack of adhesion to the substrate and disintegration of  $TiB_2$  and  $TiB_2$  alloy structures. The generally accepted explanation for disintegration of these structures in aluminum cells is fluoride/molten metal attack and dissolution of oxide impurities segregated on the boundaries between individual  $TiB_2$  grains. The critical component delaying development of a practicable LEC has therefore been the failure to produce a low-cost, durable  $TiB_2$  cathode material.

TiB<sub>2</sub> Cathode Material Requirements

Several papers and patents (2) have documented the requirements for an ideal LEC cathode material. These specifications depend to a certain extent on the particular cell design, but the following properties represent the most important criteria that are commonly stipulated:

1. Wettability by molten aluminum
2. Good electrical conductivity
3. Low solubility and reactivity with molten aluminum and the cryolite-alumina bath
4. Reliable attachment to the underlying cathode substrate
5. Low cost
6. Easy fabrication into any desired shape
7. High resistance to mechanical wear and impact and thermal shock
8. Good resistance to high-temperature oxidation and corrosion by any reactive gases
9. Low thermal conductivity.

The properties of the borides and carbides of the transition metals, particularly TiB<sub>2</sub>, make them especially suitable for use as cathodes in aluminum electrolysis cells (2). TiB<sub>2</sub> has a high melting point and hardness, good electrical and thermal conductivity, is wetted by molten aluminum metal, and, in its purest form, is resistant to the aluminum and cryolite bath. However, fabricated TiB<sub>2</sub> parts are brittle, sensitive to thermal shock, not easily attached to a carbon substrate, subject to chemical attack, and expensive. Thus, the early attempts to use hot-pressed TiB<sub>2</sub> tiles were thwarted by mechanical breakage, thermal shock, bath attack along oxide-rich grain boundaries, and attachment problems.

High-purity TiB<sub>2</sub> forms, and composites, made by addition of an oxide stabilizer (3,4) (such as AlN which forms stable oxynitrides), have been used recently (5) to improve the corrosion resistance of the material. Although beneficial, these measures do not address the problem of attaching TiB<sub>2</sub> to carbon over a very wide temperature range. A recent patent issued to Payne in 1978 (6) describes a method for bonding TiB<sub>2</sub> tiles to the carbon cell bottom in-situ during cell startup and operation by forming the adhesive bond as the temperature is gradually raised. This method avoids the detachment problem resulting from the difference in thermal expansion of TiB<sub>2</sub> and carbon during cell startup. However, these differences will cause debonding when the cell is shut down and restarted because the bond is irreversibly formed.

Another patent, assigned to Reynolds in 1982 (5), proposes the use of a tri-layer tile, comprising an intermediate bonding layer between an upper TiB<sub>2</sub>/AlN tile and a recessed graphite tile substrate. The bonding layer is present to accommodate thermal expansion mismatch by acting somewhat like a graded glass-to-metal joint. Even in this case, the bond to the carbon will degrade eventually due to molten metal wetting the lower surface of the TiB<sub>2</sub>/AlN tile.

None of these developments has led to a long-lived commercial TiB<sub>2</sub> cathode material, as evidenced by recent reports for the joint DOE/Kaiser Aluminum project on developing a drained TiB<sub>2</sub> cathode cell (7). The same series of problems has recurred time after time in unsuccessful attempts to operate a cell utilizing the TiB<sub>2</sub> materials available heretofore, viz. detachment from the carbon substrate, mechanical/thermal shock breakage, disintegration due to chemical attack, or overwhelming material costs.

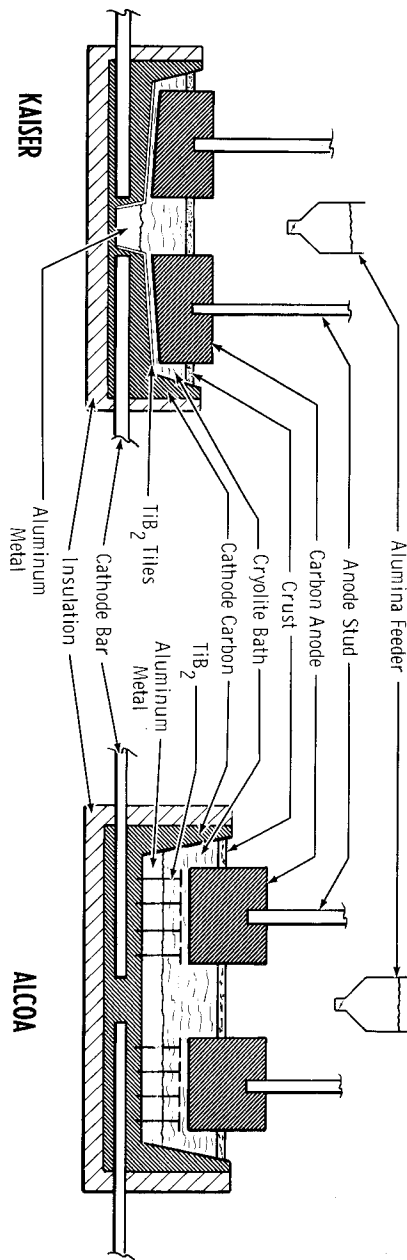


Figure 1. Patented Solid Cathode Reduction Cell Designs.

Material Formulation and Processing

Material Testing

Martin Marietta has developed a low-cost, durable TiB<sub>2</sub> cathode material, consisting principally of a phenolic resin, a furane resin precursor, curing agents, carbonaceous filler, carbonaceous additives, and RHM. This coating composition may be applied wet, directly to a carbon cathode substrate, and then cured and carbonized. The resulting relatively hard, tough surface layer consists of RHM imbedded in a largely non-graphitic and non-graphitizing matrix. The green mix also includes carbon fibers, which act as crack arrestors while the coating material undergoes shrinkage during cure and carbonization. Sufficient RHM is incorporated in the coating to ensure continuous aluminum wetting of the surface. Thus, the resultant composite material is an economic and effective means to obtain the advantages of RHM in cathodes, and eliminates the need for more costly TiB<sub>2</sub> tiles.

A family of coating compositions have been developed to accommodate different carbon substrates, coating thicknesses and aluminum wetting properties. Two typical formulations are given in Table I. All the percentages are by weight prior to mixing.

TABLE I. Typical Cathode Coating Compositions

	Composition 1 (wt%)	Composition 2 (wt%)
TiB <sub>2</sub> powder (-325 mesh)	36.0	37.5
Carbon cement solids	34.2	30.6
Mix liquid	19.7	29.6
Coke particles	10.1	----
1/4 in. carbon fiber	----	2.3

A 1/16-in. thick layer of mix is applied to the prepared surface of a carbon cathode block by trowel, and worked into the block surface. The layer is then built up to 3/8 in. thick, smoothed, and levelled. The coated block is then heated to 100°C at a rate of 25°C per hour, and held at this temperature for 3 hours. Heating is continued at 25°C per hour to 140°C, and the block is held at temperature 16 hours. It is then air cooled to room temperature.

The cured block is carbonized by heating to between 600°C and 1000°C over 24 hours in a protective coke bed to avoid oxidation, then cooled to below 200°C before removal from the coke bed. The integrity of the cured structure and substrate bond remain excellent after carbonization. No changes in cell construction or startup procedure were required for using the blocks coated with composite TiB<sub>2</sub> material.

A variety of cathode block materials, such as Kiowa Carbon, G.R. Stein, and Union Carbide amorphous and CFN grades have been successfully coated. Once carbonized, the TiB<sub>2</sub> coating material has a thermal expansion coefficient almost the same as that of the carbon block, thus eliminating the thermal cycling debonding problems inherent in hot-pressed TiB<sub>2</sub> tiles. Coating formulation changes were required to control the shrinkage of the material during the cure and bake steps, and thus prevent separation and/or damage of the underlying cathode block material.

Testing and scaleup of the cathode coating material involved both passive (or static) and dynamic (electrolysis) exposure tests. The development and evaluation process currently used for assessing materials and processing/formulation modifications comprises a series of sequential tests.

Wettability During Electrolysis

An inverted electrolysis cell, shown in Figure 2, is used for the initial wettability and bath penetration tests. Coatings containing as little as 10 weight percent TiB<sub>2</sub> were partially wet by the molten aluminum metal; at about 20 weight percent the coating was wetted over 90 percent of the surface. A content of 35 to 60 weight percent TiB<sub>2</sub> appeared optimal for achieving maximum wetting at minimum cost. Loss of coating integrity only begins at much higher TiB<sub>2</sub> percentages. Comparison of wettability data from the inverted electrolysis test and from metal pad immersion tests revealed that the coating material is more easily wetted by nascent aluminum generated during electrolysis than by a passive metal pad. This characteristic is a distinct advantage if the material is to be used in a drained cathode cell because these tests effectively show that it is more difficult to achieve aluminum wettability under a deep metal pad in a conventional reduction cell than in a drained cathode LEC.

Durability Under Molten Aluminum and Bath

Static exposure tests are used to assess various different formulations and types of candidate TiB<sub>2</sub> material as cathode linings for aluminum reduction cells. Samples of commercial hot-pressed TiB<sub>2</sub> tiles and proprietary carbon/TiB<sub>2</sub> composite materials were exposed to molten aluminum and molten cryolite bath for 7 to 30 days in externally heated retorts as shown in Figure 3. The samples were subsequently recovered, sectioned, analyzed, and evaluated for durability in the aluminum cell environment. Our significant findings were: 1) the very high-purity TiB<sub>2</sub> tile disintegrated below the aluminum metal line; 2) the stabilized TiB<sub>2</sub> alloy tile was undamaged but had debonded from the carbon cathode substrate; and 3) the various composite coating samples were undamaged below the aluminum metal line, but showed variable exfoliation cracks at the level of the cryolite bath. The exfoliation cracks virtually disappeared when carbon fiber was incorporated in the coating material.

Coatings exposed in retorts for 30 days were compared with core samples taken from experimental VSS cell cathodes lined with carbon/TiB<sub>2</sub> composite that had been operating for between 100 and 300 days. The results correlated very closely, demonstrating the feasibility of evaluating materials for full-scale operation based on short-term static tests. Some care should be used in conducting and evaluating the retort test: 1) the molten liquid levels in the retort must be maintained during the test period, particularly during initial bath penetration of the carbon container; 2) the combined effects of molten aluminum metal and bath on the coating during the brief static retort exposure may prove more aggressive in some respects than prolonged full-scale use under a metal pad; 3) the molten metal in a closed system retort rapidly saturates with TiB<sub>2</sub>, whereas, in an operating cell, fresh metal is produced continually; therefore, more TiB<sub>2</sub> will dissolve from the coating on equilibrium solubility

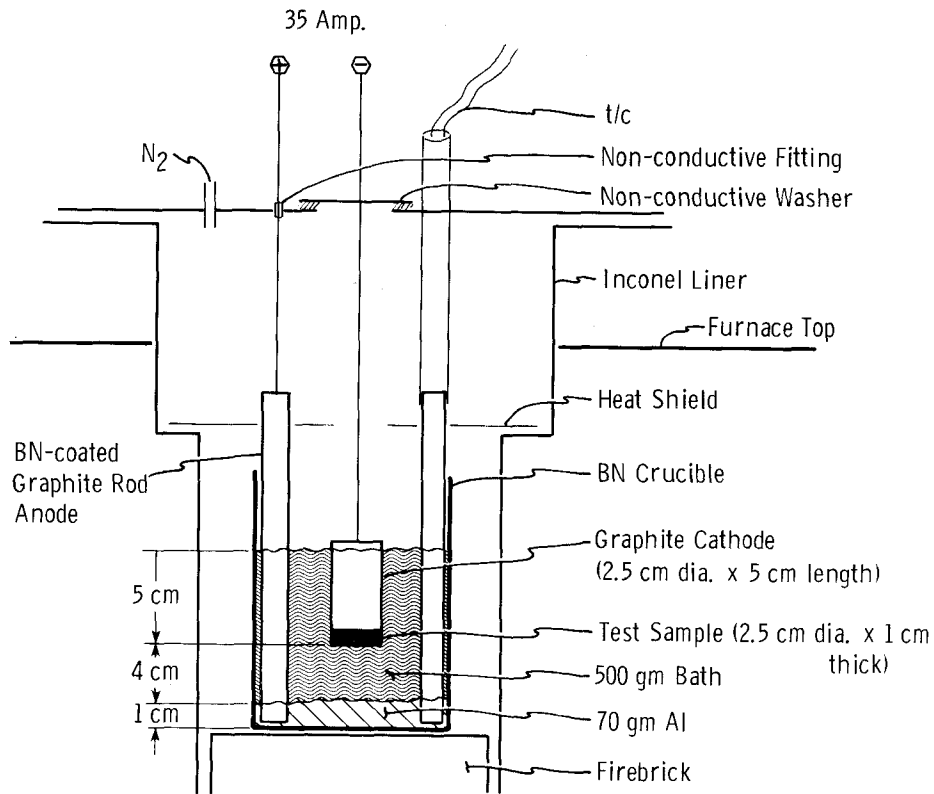


Figure 2. Inverted Electrolysis Test Cell.

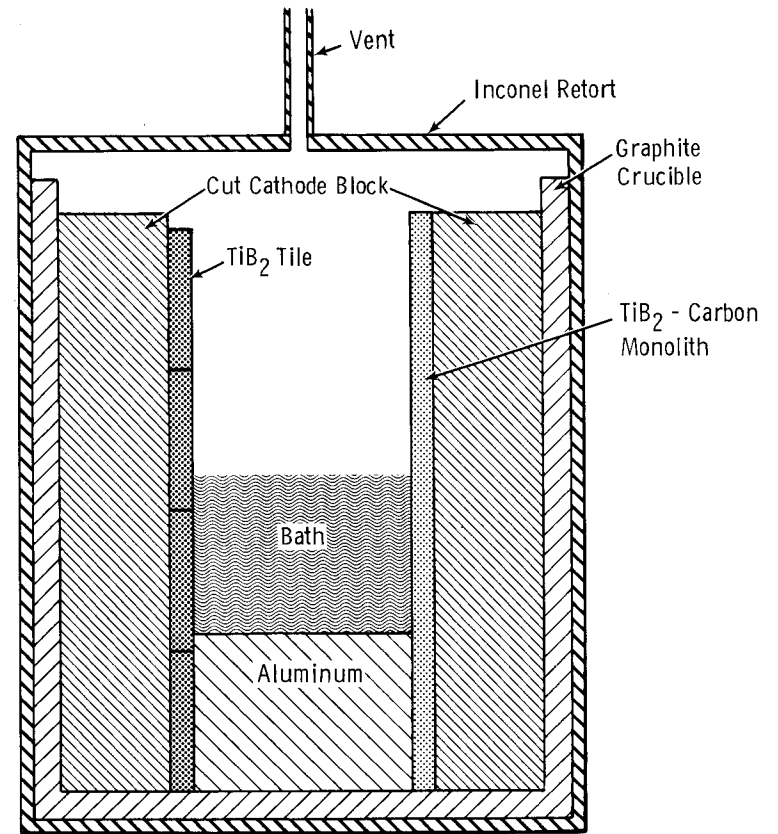


Figure 3. Static Exposure Test Apparatus

grounds in actual cell operation. Tests are in progress in the static retort tester to evaluate the effect of a regular tapping cycle.

Pilot Cell Exposure and Electrolysis Testing

Long-term exposure testing of cathode materials under electrolysis conditions is not feasible in bench-scale test cells. A 1500 A externally heated pilot electrolysis cell is therefore used to evaluate  $TiB_2$  materials under continuous electrolysis for periods up to 3 weeks. The pilot cell (Figure 4) was equipped with automatic temperature control, anode-cathode distance control, alumina feed equipment, and a remote alarm system to permit unattended operation. Use of a replaceable, internally weighted cathode block facilitated the rapid exchange of test cathodes while the cell was operating.

Cathode materials were tested under a 1-in. thick metal pad and in a drained cathode configuration. Two metal wells were cut in the bottom of the cell cavity - one for collecting the aluminum metal (which could be emptied regularly) and the other for exposing test samples to a pad of molten metal. Certain areas of the bottom liner were thus used for metal exposure while the remainder was lined with samples exposed to bath. The operating life of the cell liner was approximately 4 months. At that time, the cell was shut down and the test samples were recovered for analysis.

Results of the pilot cell exposure, in both the static and dynamic configurations, were consistent with those from the retort tests. Figure 6 shows some typical cross sections of cathode samples held under a metal pad during pilot cell operation. In all cases, the coated cathode surface remained covered with a thin film of metal even after the cathode was inverted during removal from the cell. The continuously wetted surface is shown in the enlarged section of the aluminum/coating interface.

The absence of muck on the coated cathode surface in Figure 5 is characteristic of all the coated cathodes tested under electrolysis. By contrast, the uncoated carbon surfaces were consistently found to have a partial covering of muck. We also observed that any aluminum metal remaining in the uncoated 1-in. deep cavity of a metal pad cathode was always separated from the cathode carbon by a thin film of frozen bath material. On a carbon cathode surface, the bath material preferentially wets the surface; on a  $TiB_2$  cathode, molten aluminum expels the bath and wets the cathode instead. Hence, there is little tendency for muck, a bath-rich material, to attach itself to the surface of a  $TiB_2$  cathode; rather, it is easily swept upwards for dissolution in the bath. Plant experience with the  $TiB_2$ -coated cathodes confirms that these cells tend to run "cleaner" than cells with conventional carbon linings. It is particularly important for the cathode surface to be muck free in a drained cathode LEC with its reduced anode-cathode distance. The present data indicate that  $TiB_2$ -coated cathodes reduce mucking and thereby increase current efficiency in conventional cells. Thus, there will be little tendency for muck to form or settle on a drained cathode surface.

Plant Tests

Six commercial VSS cells with  $TiB_2$ -coated cathodes were installed in the Martin Marietta Aluminum smelter at The Dalles, OR, in late 1981 and early 1982. This full-scale plant test of the cathode coating was designed to determine whether:

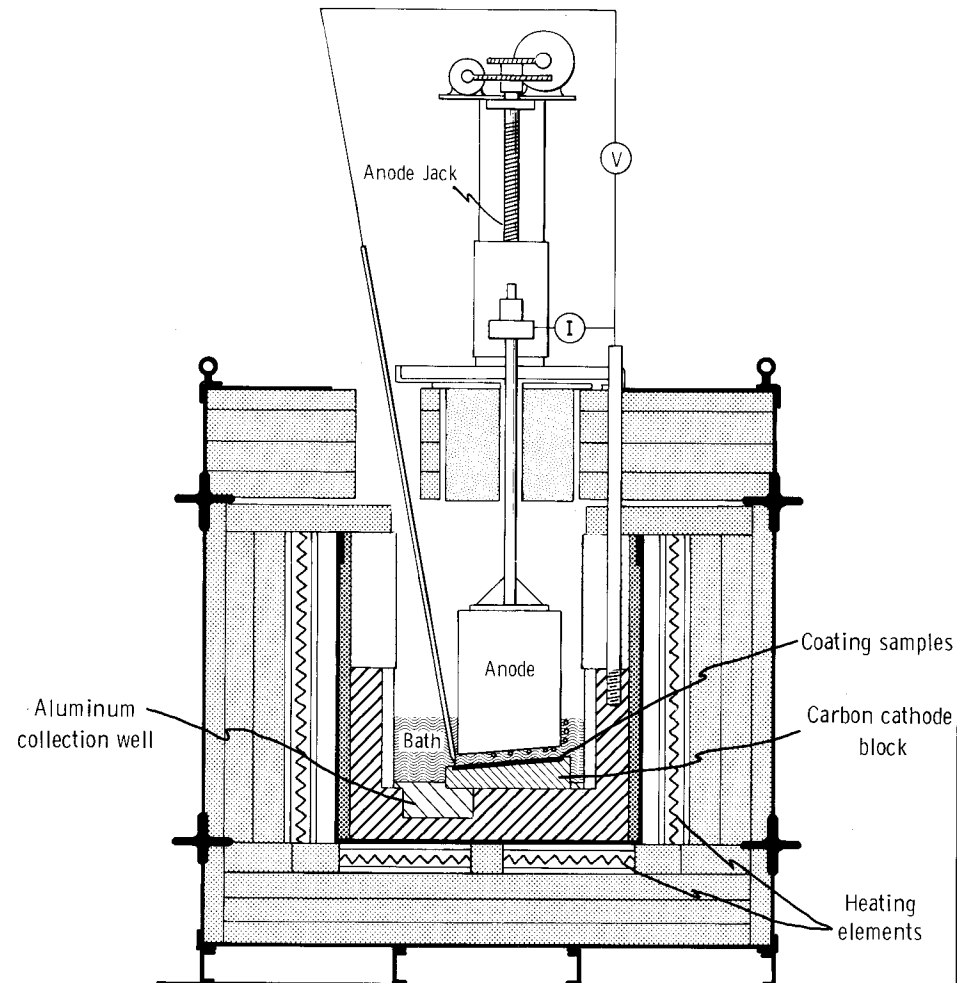


Figure 4. 1500 Ampere Pilot Electrolysis Cell.

1. The coating can be applied in a plant environment
2. The coated cells can be started using conventional procedures
3. The coating is durable under operating cell conditions
4. The coating is wettable in commercial use
5. The coating has an acceptable projected life
6. The coating reduces cell mucking
7. The coating has no adverse effects on cell performance
8. The use of the coating in conventional cells results in energy savings or reduced operating costs.

By the end of 1982, it was clear that all of these criteria had been met.

Cathode blocks, coated using the direct spreading techniques described earlier, were used to reline six 105-kA VSS aluminum reduction cells. The only deviation from standard reline and cell startup procedures was to wire brush the excess cathode-ram material from the coated block surface prior to cathode installation in the potroom. No difficulties were encountered in the coke bake startup of the first four test cells or the hot metal startup of the final two.

A production curtailment in June 1982 necessitated the shutdown of a potroom containing three of the test cells. Core samples were taken from two of the coated cathodes before the cells were moved and restarted in another room. Two of the coated test cells were restarted after being out of service for approximately 2 months; another had been out of service for 8 months. No difficulties were experienced in restarting the cells, and performance continued as before the planned shutdown. This demonstrated ability of the cathode coating material to withstand shutdown and restart without sustaining any apparent damage greatly enhances the flexibility and usefulness of the coating material in a plant environment.

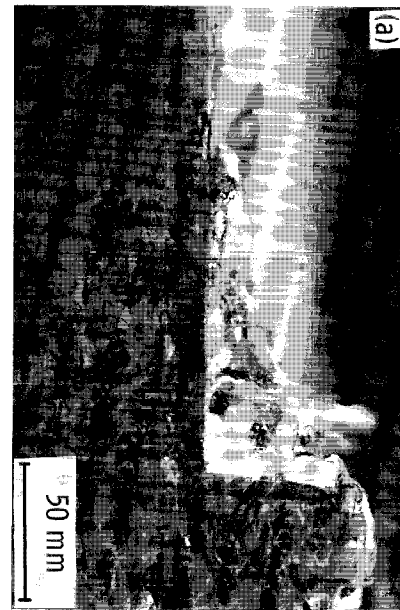
The cathode core samples provided an opportunity to examine two different coating materials which had been in service for 310 days and 109 days, respectively. Cross-section photographs and EDS elemental maps across the coating/aluminum and coating/substrate interfaces are given in Figures 6 and 7, respectively. The sections show that a strong bond was maintained between the cathode coating and underlying cathode block even after 310 days of electrolysis in the aluminum cell environment. Moreover, the thin pad of aluminum, left after complete tapdown, can be seen still tenaciously wetting the surface of the coating. The measured decrease in apparent coating thickness was consistent with the coating life estimated from measured Ti loss rate in the metal pad (see below). Extensive scanning electron microscope (SEM) analysis for islands of  $TiB_2$  in the aluminum metal adjacent to the coating did not reveal any significant disintegration or loss of  $TiB_2$  beyond the solubility limit. The measured  $TiB_2$  loss from the coating appears to be almost exclusively due to dissolution and not erosion.

The estimated life for the cathode coating used in The Dalles' test cells is 3-5 years, determined by dividing the total weight of  $TiB_2$  contained in the coating by the average daily loss of  $TiB_2$  in the metal tapped from the cell (based on increase in Ti content beyond the plant average). The effective  $TiB_2$  content in the metal (calculated from the total titanium analysis in the pad) was slightly higher ( 0.0015%) than that predicted from the published  $TiB_2$  solubility data (8) and varies with

$$\log K_{sp} = 5.22 - \frac{1.62 \times 10^4}{T(k)}$$

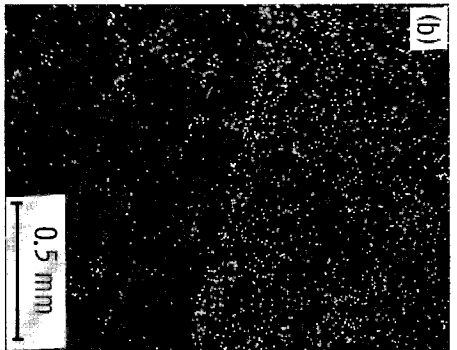
Figure 5. Cross section of cathodes after electrolysis tests in aluminum pilot cell.

(a) Conventional carbon cathode  
 (b) Carbon/ $TiB_2$  coated cathode  
 (c) Enlargement of interface between cathode coating and frozen aluminum

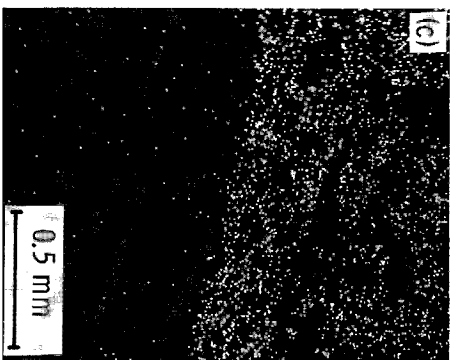




SEM

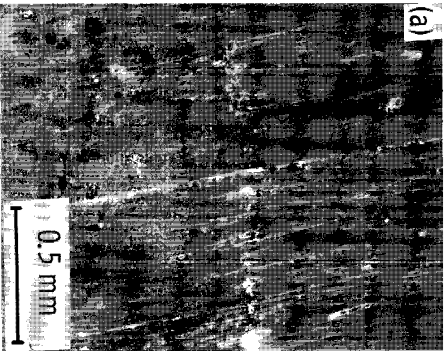


Aluminum Distribution

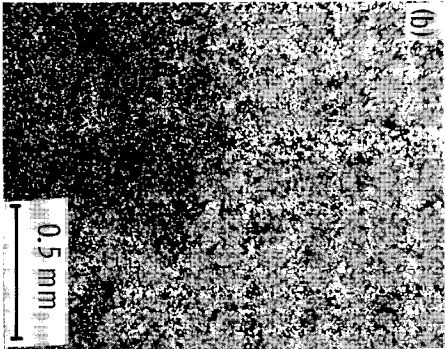


Titanium Distribution

Figure 7. SEM photograph and EDS maps across the interface between  $TiB_2$  coating material (top) and cathode block (bottom) in a core sample taken from the coated cathode of a conventional cell after 109 days of operation.



SEM



Aluminum Distribution



Titanium Distribution

Figure 6. SEM photograph and EDS maps across the interface between the aluminum pad (top) and  $TiB_2$  coating material (bottom) in a core sample taken from the coated cathode of a conventional cell after 109 days of operation.

temperature as anticipated. The Ti/B ratio is not stoichiometric in the metal pad since boron is continuously and irreversibly lost to the bath and in the cell fumes. Typical Ti and B levels in the test cell metal pads were 0.0075-0.0110% and 0.0012-0.0018%, respectively, compared to plant average values of 0.0035-0.0060% and 0.0006-0.0010%, respectively. The plant average Ti values were subtracted from the test cell values to obtain the contribution attributable to the coating. The coating life calculation assumes a uniform loss across the entire coated surface. This assumption appears to be valid since there has been no evidence of any lack of uniformity in wear rate even after approximately 700 days operation in the longest running test cell.

Based on the performance up to the end of 1982, we make the following general observations on the differences in performance of the six coated cathode test cells and the rest of the plant:

1. The cathodes tended to run cleaner and recover from upsets more rapidly, particularly with respect to ledge mobility and poor muck adhesion,
2. The coated cathode collector bar current distribution was more uniform,
3. The coated cathode voltage drop was lower
4. The test cell current efficiency was significantly higher,
5. The specific energy consumption of the tests cells in 1982 was lower than the plant average by approximately 0.23 kWh per pound of aluminum produced,
6. The metal grades and cast house operations were not affected by the coated cathodes,
7. The coated cells were easier to operate and were well accepted by the plant personnel.

#### Conclusions

A low-cost  $TiB_2$  cathode coating with good durability and operational benefits has been demonstrated in conventional VSS aluminum reduction cells. Cells can be retrofitted with the cathode coating and started up without any major disruptions in plant routine. Shutdown and restart of the coated cathodes have no apparent detrimental effect on the  $TiB_2$  coating. Based on the projected coating life of 3-5 years, and the lower processing costs of coating compared to hot pressing, the  $TiB_2$ /carbon composite is clearly an economically viable cathode material suitable for use in future drained cathode low-energy cells and present day cells with deep metal pads.

This plant test was originally undertaken primarily to demonstrate a viable  $TiB_2$  cathode material of adequate longevity and durability for drained cathode cells. Secondary results indicate that significant benefits can be gained from the use of a  $TiB_2$ /carbon surface in conventional Hall-Heroult cells. These improvements include facilitated cell operation, and better current and energy efficiency. Calculations for return on investment indicate that the present payoff period for the Dalles cells appears to be approximately half of the anticipated coating life. The economic benefits will improve substantially if any increase in overall cathode life is realized. An extension in service life of just one year would more than pay for the coating since the expensive and disruptive relining is done less frequently. A complete covering with molten aluminum is expected to protect the bottom from attack by the aggressive bath and muck constituents. Increased longevity is therefore anticipated in the

coated cells since the  $TiB_2$  surface is covered exclusively by aluminum for a greater proportion of the time than a conventional carbon surface.

The lack of an economic, durable  $TiB_2$  cathode material has been a major obstacle in past attempts to develop a low-energy cell that can be readily retrofitted into existing smelter facilities. Our new cathode coating material appears to be the key to the development of a viable LEC.

#### Future

Improved coating formulations and processing techniques are presently being tested in another 14-cell plant test at the Martin Marietta Aluminum Goldendale, WA, smelter as a joint project with the Bonneville Power Administration. The results of this test will be published in the near future. Materials specification tests are continuing to optimize the trade-off between coating quality and material cost.

#### Acknowledgement

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#### References

1. Grjotheim, K., Thonstad, J., Matiašovský, K., and Malinovsky, M., "Energy Efficiency and Bath Composition in Aluminum Electrolysis," *Aluminium*, 49, 12 (1973) pp. 803-807.
2. Billehang, K., and Oye, H.A., "Inert Cathodes for Aluminum Electrolysis in Hall-Heroult Cells," *Aluminium*, 56 (1980) pp. 642-648 and pp. 713-717.
3. Long, G., and Foster, L.M., "Aluminum Nitride, A Refractory for Aluminum to 2000°C," *Journal of American Ceramic Society*, 42, 2 (1959) pp. 53-59.
4. McCauley, J.W., and Corbin, N.D., "Phase Relations and Reaction Sintering of Transparent Cubic Aluminum Oxynitride Spinel (ALON)," *Journal of American Ceramic Society* 62, 9-10 (1979) pp. 476-479.
5. Kaplan, H.I., et al., "Cathodes for Alumina Reduction Cells," U.S. Patent No. 4,333,813 (1982).
6. Payne, J.R., "Bonding of Refractory Hard Metal," U.S. Patent No. 4,093,524 (1978).
7. Kaiser Aluminum and Chemical Corporation, "Energy Savings Through the Use of an Improved Aluminum Reduction Cell Cathode," DOE Contract DE-AC)#-76CS 40215.
8. Finch, N.J., "The Mutual Solubilities of Titanium and Boron in Pure Aluminum," *Met. Trans.*, 3 (1972) pp. 2709-2711.