

A REVIEW OF RHM CATHODE DEVELOPMENT

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Abstract

Reynolds Metals Company and the author have been involved in the development of Refractory Hard Metal (RHM) cathodes for reduction cells for over 35 years. The commercialization of wetted RHM cathodes is presently being pursued as a retrofit cell modification that could reduce specific energy requirements in the 15-20 percent range. The combination of RHM cathodes and inert anodes appears to offer the best possibility for major modifications to the Hall-Heroult process that could occur in the next two decades. This paper describes some past efforts to commercialize RHM cathodes and describes hurdles that must be overcome to realize this goal.

Introduction

Forty years ago The British Aluminium Company LTD. (BACO) observed that molten aluminum would wet titanium carbide and conceived that this and related compounds might be usable with advantage as cathode materials in the electrolytic reduction and refining of aluminum.

Reynolds Metals became aware of BACO French patent publications in 1955 and have been pursuing commercialization of titanium diboride (TiB_2), TiB_2 composites and other Refractory Hard Metal (RHM) materials as cathodes in Hall-Heroult process aluminum reduction cells since that time. There were time periods, especially in the early 1970s when there was little activity, but efforts were renewed with support from the U. S. Government and other organizations when energy-conservation became a major issue in the mid-1970s. Except for patent literature Reynolds has published very little in this RHM cathode development area.

Reynolds early work with RHM cathodes concentrated on the development of cylindrical elements (cathode bars) to contact the metal pad and provide a low electrical resistance path substituting for the carbon cathode block and steel collector bars. Following tests in production scale cells in the early 1960s, and failure to commercialize this use of RHM, the solid wetted cathode surfaces and reduced ACD operation concept has since been under investigation. During these efforts Reynolds developed, manufactured and patented RHM compositions.

Wetted solid cathodes remain one of the best possibilities for major reductions in energy requirement in Hall-Heroult process aluminum reduction cells. Wetted cathodes are especially promising as a retrofit modification for older high current density cells operating in areas of high power costs. In combination with inert anodes, they offer the best possibility for major modification to the process that has produced essentially all commercial purity primary aluminum for the past 105 years.

The Hall-Heroult electrolytic process as presently practiced is only about 40% energy efficient. A large fraction of the energy used in the reduction cell is expended as I-R drop in the 1.5-2.0 inch gap between the anode and cathode (ACD). Reductions in ACD in present cells generally result in no gain in energy efficiency because the current efficiency is reduced as the back reaction increases when the anode is moved closer to the mobile, uneven surface of the molten aluminum cathode.

The substitution of a solid wetted cathode surface for the molten aluminum cathode allows the ACD to be lowered without the adverse

effect on current efficiency. Titanium diboride and composites containing a major fraction of TiB_2 have appeared to be the best candidates for this solid wetted cathode. These materials have a low solubility in aluminum, have an excellent chemical resistance to the cell environment, good electrical conductivity, are wettable by aluminum and are favored over other possibilities by economic considerations. By adding graphite to form a TiB_2 -G composite, Great Lakes Research Corporation (GLRC) has developed a material that can be readily formed into complex shapes and that has demonstrated a good potential to survive and function over long term periods as a wetted cathode in reduction cells.

Reynolds is presently working jointly with DOE and GLRC to develop technology that could allow commercialization of a solid wetted cathode system using TiB_2 -G shapes manufactured by GLRC.

There are published comprehensive literature reviews on refractory hard metals and wetted reduction cell cathodes (1-3). This paper is not a comprehensive review of literature but instead concentrates on Reynolds developments and the history of Reynolds activities in researching this technology. History and developments by others in the industry are included so that major efforts made in the extended searches for commercialization of RHM cathodes might be related.

Historical Background and Early Approaches to Utilize RHM Cathodes

Patent applications in France by BACO alerted the industry to wettable RHM cathodes in 1954-55. By 1962 when C. E. Ransley, BACO, made a technical presentation at an International Symposium in New York, sponsored by the American Institute of Mining, Metallurgical and Petroleum Engineers, on the application of the refractory carbides and borides to aluminum reduction cells the industry had several extensive development efforts underway. Kaiser Aluminum and Chemical Corporation entered into a joint development program with BACO in 1956 that did not terminate until 1966. Even though Reynolds Metals acquired a controlling interest in BACO in the early 1960s, the confidentiality of the Kaiser-BACO agreement was honored. The Ransley presentation at the 1962 symposium preceded the issuance of the BACO basic U. S. RHM application patent by only a few weeks (4,5). A second presentation at the 1962 symposium by Norton Company reported on pilot scale (10 kA) testing of RHM cathode bars that was performed by Reynolds (6). Reynolds did not publish on early work on RHM cathodes, except for patents. There probably were major efforts by others in the industry that have not been reported in literature.

The 1962 BACO patent claimed the use of RHM both as a drained cathode surface allowing energy savings through reduced anode-to-cathode distance (ACD) operation and as bars providing low resistance paths from the metal pad to the busbars.

In 1957 Norton Company furnished Reynolds hot pressed TiB_2 bars and suggested bar production costs of \$2-4/lb. Even with the low-cost power of this period savings could be projected at these bar costs if a three-year bar lifetime and 0.3 V cathode voltage drop could be achieved. By 1958 Reynolds had joint development efforts with Norton, National Carbon Company (Union Carbide) and Firth Sterling Company and were testing at 3 kA scale. Testing was expanded to 10 kA scale in 1959. U. S. Borax and Carborundum Company were also soon added as development partners.

Bottom-entry RHM cathode bars were combined by Reynolds with a non-carbon refractory cell lining. This cell lining, patented by Reynolds in 1963 (7), eliminated costs associated with the carbon cathode, and added economic incentive to the RHM bar approach. It further eliminates much of the carbon lining in which NaCN forms over the life of the cell. The lining could be simply metallurgical alumina or mixes of cryolitic salts and alumina. As described in the Norton paper presented in 1962, the RHM bars could be welded to steel to reduce the requirement for the RHM material. A full-scale cell (68 kA) with refractory lining and welded TiB₂ bottom-entry bars was tested by Reynolds in 1962.

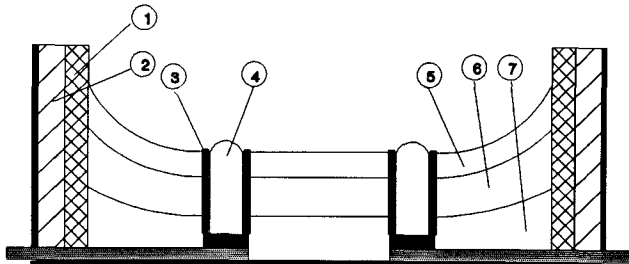


Figure 1: Schematic drawing of an aluminum reduction cell cathode with RHM collector bars and a refractory lining. 1: sidewall; 2: thermal insulation; 3: protective lining; 4: RHM bar; 5: fused layer of lining; 6: sintered layer; 7: loose alumina.

While the quality of RHM and especially TiB₂ hot-pressed and sintered bars improved by 1962 a crack and crack-propagation problem, associated with intergranular corrosion, remained a major problem. Good-quality, flaw-free, high-density TiB₂ would crack after about six months exposure to the reduction cell. While some cracking was tolerated and pilot-plant 10 kA cells were operated for up to 22 months, there were increases in electrical resistance and non-uniformity of current distribution. There was also chemical attack on TiB₂ within the refractory cell lining. Especially where there were high concentrations of sodium metal near the 880°C isotherm in the lining and where oxygen was also available, diameter reduction on TiB₂ bars was seen to limit lifetime independent of the problem of corrosion at grain boundaries and bar cracking. Reynolds patented bar sleeve protection and spray coatings to limit corrosion (8).

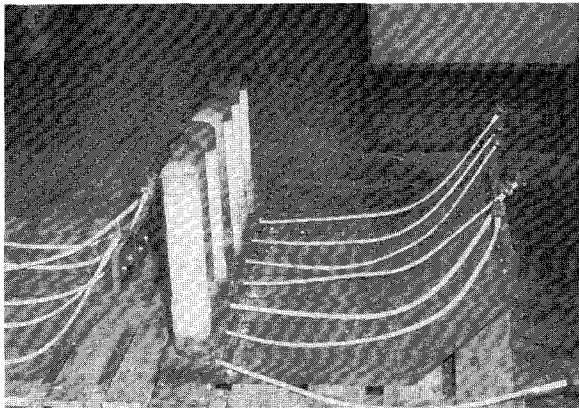


Figure 2: TiB₂ bar assemblies with spray coatings ready for installation in commercial-scale reduction cell.

Development of RHM compositions that were more crack-resistant became expensive as it was necessary to extend cell tests beyond six months to distinguish between state-of-the-art materials that were failing characteristically after 180 days of test and possible improved materials. The carbothermally produced TiB₂ powder had low-levels of carbon, oxygen and iron impurities and the concentration of these impurities at grain boundaries and subsequent intergranular penetration of reduction cell constituents including sodium and aluminum initiated slow developing cracks.

Development of composite and cermet materials was viewed as a means for overcoming the brittle and crack propagation problems with TiB₂ and other pure, dense RHM materials.

Reynolds developed and patented TiB₂-AlN-Al composition cermets (9) as well as graded cermets with the metal phase enriched away from the pure TiB₂ surface that contacted the metal pad in the reduction cell (10). More development work and tests were made with TiB₂-AlN composites. While this composite did alleviate some of the high purity requirements for the TiB₂, it did add electrical resistivity to bar components and did not completely eliminate the slow crack and crack propagation problems.

Reynolds pilot-scale (10-12 kA) testing of RHM bars and wetted drained cathodes ceased in 1970 not to be resumed for over 15 years.

The oil shortage crisis in 1973 and escalating power costs renewed interest in developing energy conservative processes. A very high purity non-carbothermic TiB₂ had been developed by Pittsburgh Plate Glass Corporation (PPG). The very fine grain structure and absence of impurity concentrations at grain boundaries indicated this would be a superior material in the reduction cell environment. A very important disadvantage was that manufacturing costs were high.

The PPG TiB₂ material, the Reynolds developed TiB₂-AlN composite and other TiB₂ materials under development by Kawecky Berylco, Inc. (KBI), and Carborundum were tested by Reynolds in the 1975-1982 time frame. These materials were tested in the form of plates and tiles, generally cemented, hot-pressed or otherwise fastened to a carbonaceous substrate for use as the surface for a drained cathode. Several tests of six months duration were performed in cells in reduction plants. Patents and a defensive patent publication by Reynolds illustrate some directions and efforts (11,12). Keeping tile or plates in place on the substrate proved to be a formidable task and efforts to solve this problem were never entirely successful. Also, a breakage problem remained with the RHM materials.

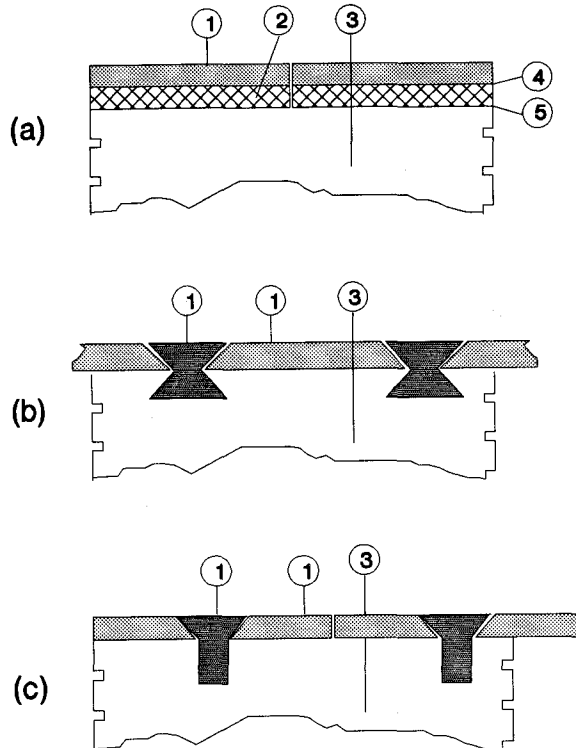


Figure 3: Schematic of configuration and methods to secure RHM tile to cathode block substrate. (a) hot pressed and/or cemented bond; (b) keyed fasteners; (c) pins or screws. 1: RHM; 2: carbon; 3: cathode block; 4: hot-pressed bond; 5: cemented bond.

There was a proliferation of patents on approaches to utilize RHM materials and shapes in reduction cells in this 1975-82 time frame. One noteworthy Alcoa approach was open RHM cylinders with molten aluminum, restrained from movement by its container, becoming the active cathode surface (13,14). The concept of the replaceable cathode element or module was also the subject of patents (15) as was "packed

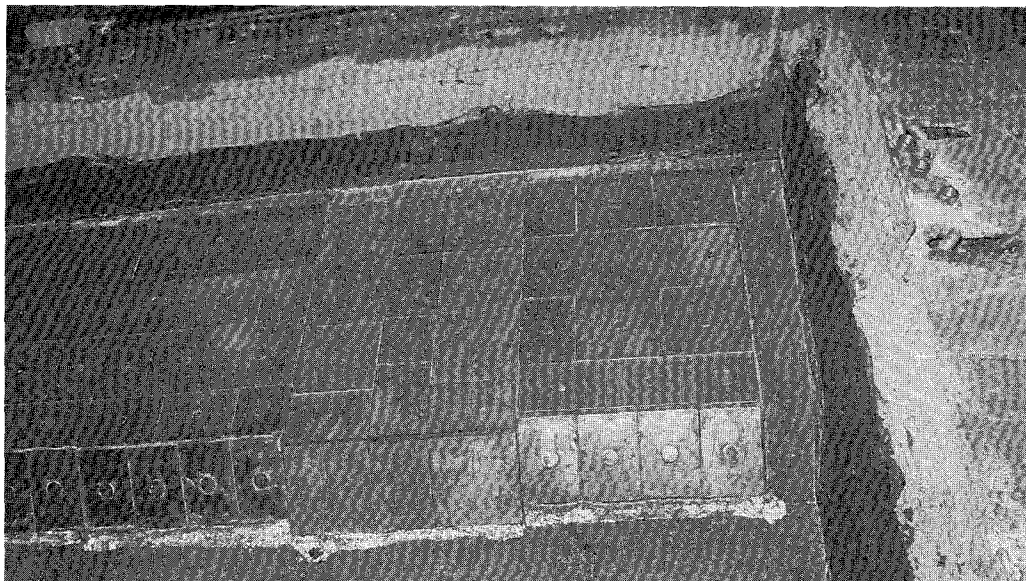


Figure 4: RHM tile fastened to carbon substrate with cement and screws to form drained cathode surface for commercial-scale cell test.

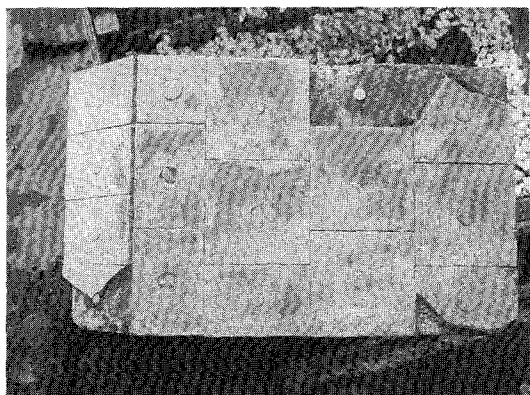


Figure 5: RHM tile after reduction cell test.

bed" metal pads and the placement of metal flow restrictors in the metal pad of cells (16,17).

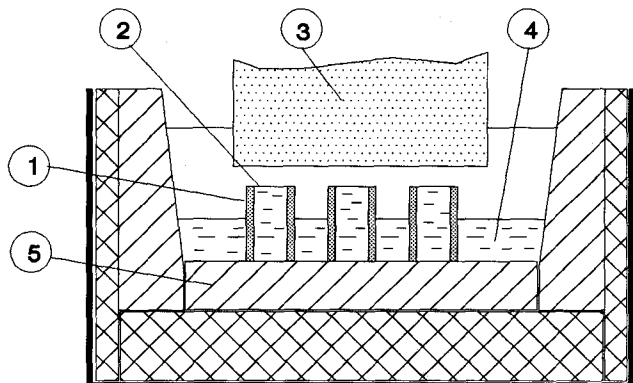


Figure 6: Schematic view of section of reduction cell with aluminum filled RHM cylinders providing cathode surface. 1: RHM cylinder; 2: aluminum cathode surface; 3: anode; 4: metal pad; 5: cathode block.

The status of the early development of reduced ACD, wetted cathode development was probably best described to the industry by Kaiser in 1983 when they summarized their DOE sponsored research at a meeting sponsored by the Aluminum Association in Washington, D.C.

The Kaiser-DOE-ERDA program as described in public records may be summarized as:

- 1975 - Bench Scale Evaluation of TiB_2 Materials
- 1976-77 - ERDA Sponsored Pilot Scale Tests of TiB_2 Cathodes (10-15 kA)
- 1978-82 - DOE sponsored Pilot Scale Tests (15-40 kA), Voltage Studies and Materials Characterization

In summary, the program did not demonstrate the power savings required to make the TiB_2 drained cathode retrofit systems that were tested economical. About 16% power savings was demonstrated compared with about 25% savings forecast. At this time \$30-40/lb was a good estimate for fabricated TiB_2 cathode modules with acknowledgements that very large volume production could reduce this cost. A TiB_2 cathode module lifetime of two years and a cell lifetime of about six years was estimated for the economic calculations.

The fact that the forecast power savings were not achieved in test programs was attributed to the increase in the anode off-gas content of the electrolyte when ACD was reduced. Only a 40% reduction in voltage drop in the electrolyte was noted when ACD was reduced 65% (from 4.5 to 1.6 cm).

From about 1983 to at least through 1987, Alcan International Ltd. and Eltech Systems Ltd. were engaged in the development of RHM cathodes and non-carbon cell linings. Three papers presented at the 1987 TMS-AIME annual meeting described their cathode technology and presented results of their testing program (18-20). There have been many patents issued on these cathode systems. This technology concentrates on non-carbon, recyclable cell bottoms and RHM cathode leads (not wetted drained cathodes). There was some commercial cell scale testing in 1986-88.

The Cathode Bar Concept

Several major projects in the 1950s and early 1960s aimed at commercialization of RHM cathode bars that conducted current from the metal pad to cathode busbar connectors and reduced the electrical resistivity of the cathode. The RHM cathode bars were primarily TiB_2 , although especially BACO experimented with titanium carbide. Zirconium diboride appeared to be at least the technical equivalent of TiB_2 but was rejected because it was more expensive.

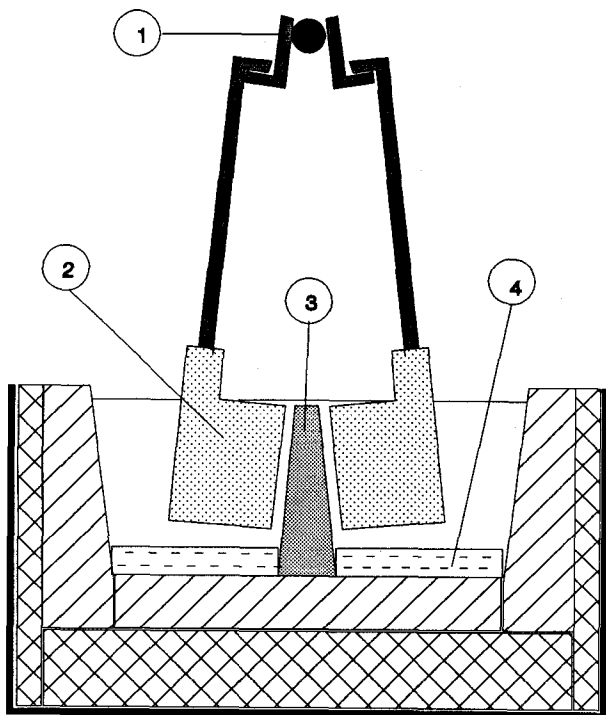


Figure 7: Schematic view of section of reduction cell used by Kaiser of DOE sponsored testing featuring a near vertical wetted cathode surface. 1: anode pivot mechanism; 2: anode; 3: RHM cathode assembly; 4: metal.

Tests in commercial size (around 50 kA) and pilot scale (10-15 kA) reduction cells were operated with:

- "Candle stick bars" that extended into the metal pad and terminated several inches into the carbon cathode block.
- Top-entry bars where the cathode bus of the cell was elevated between the anode bus in prebaked cells and the bars extended through the crust cover and bath between the anodes to conduct the metal pad.
- Bottom-entry bars that contacted the metal pad and removed the carbon cathode from the electrical circuit. Reynolds used a non-carbonaceous cell liner with experimental bottom-entry bars.
- Side-entry bars that contacted the metal pad and exited through the cell sidewall.

The cathode bars manufactured in this period were hot-pressed or formed under pressure and sintered (with and without sintering aides such as CrB₂). Three inch diameter bars became the size commonly used in Reynolds tests and each bar normally conducted about 3 kA. Cathode voltage drop in 10-12 kA test cells was reduced to as low as 0.18 V with 3 inch diameter bars conducting 2.5 to 3 kA each. Magnetic disturbances become a significant factor when bar currents were increased. One Reynolds 10 kA cell with a single vertical cathode bar in the center of the cell introduced severe magnetically induced metal pad instability to the pilot test.

Side-entry tests were in part an expedient to monitor for the development of cracks in cathode bars at Reynolds. Ultrasonic testing was performed on bars as they functioned in operating test cells.

Titanium diboride cathode bars produced around 1960 had the following typical properties:

Electrical Resistivity (micro-ohm-cm)	
25°C	17
1000°C	85
Density (g/cm ³)	4.3 (95% theoretical)
Coeff. of Thermal Expansion (RT to 1000°C)	8.1 x 10 ⁻⁶ /°C

As described in the previous section of this paper, there were large scale development efforts in the 1980s by Alcan and Eltech to commercialize bottom-entry RHM conductors in conjunction with non-carbon cell linings.

Drained Cathodes Concept

The "basic" RHM cathode patent issued to C. E. Ransley in 1962 (U.S. Patent 3,028,324) described reduced ACD as an advantage of operating with an inclined drained wetted cathode.

This concept has been aptly demonstrated by many experimenters. Reynolds demonstrated the advantage of the wettable cathode surface in 1967 by operating one drained cathode 10 kA cell with a wettable cathode surface and one identical cell but without a wettable cathode surface. These two cells were operated at a very high anode current density of 11 amp/in² (1.7 amp/cm²) and at reduced ACD.

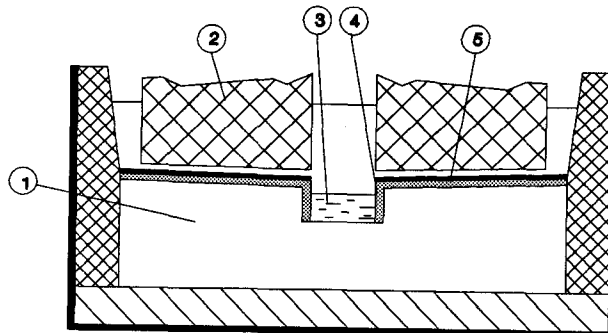


Figure 8: Schematic view of reduction cell with wetted and drained cathode surface and tapping well. 1: carbon cathode block; 2: anode; 3: metal; 4: RHM coated surface; 5: aluminum coating on wetted-drained cathode surface.

	Wetted Cathode	Un-wetted Cathode
Anode Current Density, amp/cm ²	1.7	1.7
Current Efficiency, %	85%	47%
Cell Volts	5.0	5.3
Cathode Voltage Drop	0.25	0.38
Anode-Cathode Distance, cm	3.0	3.8

There was some grounding of the anode to the cathode in the cell with the un-wetted carbon cathode surface. This cathode was "flooded" and operated with a conventional metal pad after one month's operation in the drained mode. With a conventional metal pad, a current efficiency of 86% was maintained at the same 3.8 cm anode-cathode spacing while operating at 5.35 volts at 1.7 amp/cm² anode current density.

Cathode Surfaces With Thick Wettable Coatings

A United States patent issued in 1968 to R. A. Lewis and R. D. Hildebrandt and assigned to Kaiser claimed a RHM-carbon composite surface operating as a drained cathode in a reduction cell (21).

At the 1984 annual TMS-AIME meeting, Martin Marietta Aluminum described a TiB₂-carbon coating that had been tested in plant cells operating with a conventional metal pad (22). A paste containing TiB₂, carbonaceous materials and other agents was applied in about a one centimeter thick layer to a carbon cathode substrate and then cured. A Martin Marietta paper presented at the 1985 TMS-AIME meeting reported on a larger plant test in similar reduction cells and reported benefits attributed to a cleaner cathode surface and improved cathode current distribution (23).

Since acquisition of this Martin-Marietta technology by Comalco, development of this coating has continued. It has been reported that significant commercial-scale cell testing of drained cathodes has been underway in Australia.

TiB₂-G Cathode Components

Great Lakes Research Corporation developed two proprietary titanium diboride-graphite products during a program started in early

1980 to develop stable cathode components for aluminum reduction cells.

During 1985 and 1986 GLRC and RMC cooperated in a cost-shared program with the Mellon Institute's Center for Metals Production (on R&D Application Center sponsored by the Electric Power Research Institute (EPRI). In this study GLRC TiB_2-G cathode formulations in the form of plates and cylinders were exposed to reduction cell electrolyte and the molten aluminum in a Reynolds cell for periods of up to ten months (24). Post test evaluation of the exposed samples led to the following reported observations and conclusions (in part):

- "All of the exposed TiB_2-G components developed a thin "skin layer" about one-millimeter thick. This layer was present on portions of the surface that were exposed to metal as well as those exposed to electrolyte. Scanning Electron Microscopy (SEM) indicated the presence of primarily titanium diboride in this layer with substantial aluminum penetration. It appears this layer protected the material below.
- Samples were all wetted by aluminum.
- There was no apparent thermal shock breakage as a result of hot TiB_2-G sample exchange.
- In summary, the results of medium-term commercial cell testing of GLRC TiB_2-G materials to date indicate that these materials have good potential to survive and function over long term periods in the harsh environment of reduction-cells."

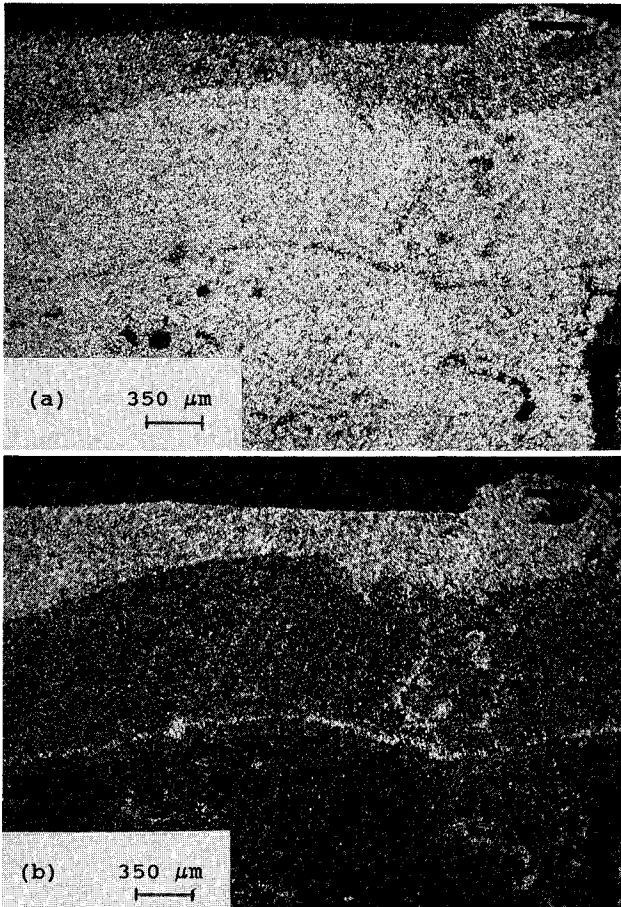


Figure 9: SEM images of polished surface of reduction cell exposed TiB_2-G specimen showing Al enriched outer skin. (a) Ti dot map; (b) Al dot map.

A paper presented at the 1987 annual TMS-AIME meeting described this GLRC approach to TiB_2 cathode technology and describes the 1985-1986 commercial scale testing in more detail (25).

Development of this GLRC TiB_2-G material and the use of this material in replaceable wettable cathode elements in reduction cells continued in the 1987-1990 period under cost shared programs with GLRC, RMC and the Department of Energy (DOE). Pilot reduction cell tests were conducted with 6 and 10 inch diameter mushroom shapes operating as wetted-drained cathodes (26). Conclusions from this test included:

- The material had excellent thermal shock properties.
- Acceptable wear rates were demonstrated.

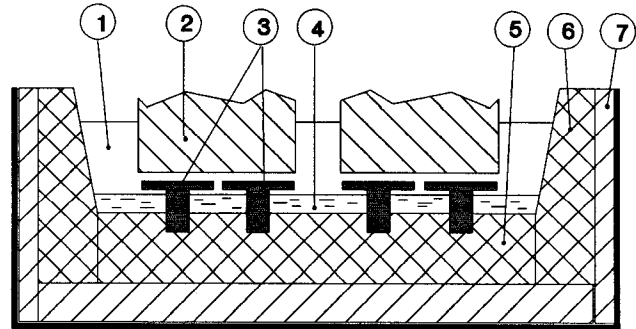


Figure 10: Schematic view of reduction cell with replaceable, wetted TiB_2-G cathode elements. 1: electrolyte; 2: anode; 3: TiB_2-G cathode elements; 4: metal pad; 5: cathode block; 6: sidewalls; 7: thermal insulation.

Samples of TiB_2-G manufactured by each of two GLRC processes were recovered intact after up to 15 months exposure in commercial cells (27). Thermal shock testing results demonstrated that a six inch diameter mushroom shape could be inserted without preheating into an operating commercial cell without breakage.

Autopsies of test samples exposed for up to 15 months in cells confirmed previously expressed opinions about erosion of the TiB_2-G cathode shapes. The TiB_2 matrix was apparently gradually dissolved and eroded away by molten aluminum that penetrated into the bulk porosity of the fabricated shape. The penetration was limited to an outer 1.0-1.5 mm thick zone and progressed deeper into the body only as loose material was removed from the exterior edges. There was some evidence of porosity development by aluminum penetration into the bulk matrix (28).

Additional economic analyses based upon the 1981-90 cell tests of materials, and model studies performed by Reynolds continue to show cost savings potential for commercial utilization of this retrofit technology. Continued improvements in TiB_2-G processing efficiencies and reductions in materials costs at large production levels is expected to benefit the projected economics.

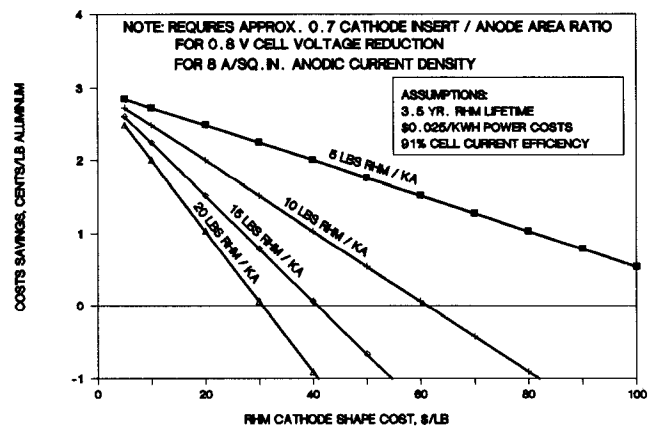


Figure 11: Economics of RHM cathode elements in retrofit application.

The evaluation of TiB₂-G cathode elements continues in the 1990-1992 time period with Reynolds and GLRC cost-sharing with the U. S. Department of Energy under the Steel and Aluminum Energy Conservation and Technology Competitiveness Act of 1988. Two commercial-scale cells with replaceable cathode elements are to be constructed and operated for one year in the reduced ACD-wetted cathode mode under this agreement.

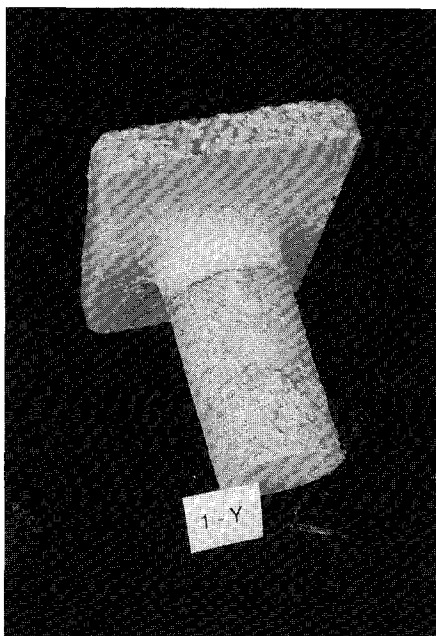


Figure 12: TiB₂-G cathode element (top flat surface is 6.5 in. x 9.5 in. and stem is 3 in. diameter).

Conclusions

For this wetted cathode retrofit technology to become commercially viable, the following hurdles must be overcome:

- The TiB₂-G material that has shown promise in recent tests must be proven as a complete wetted cathode system in an industrial environment.
- Energy savings must justify the cost of the TiB₂-G cathode elements and other costs necessary to implement the retrofit and operation of the modified process.
- The cathode elements must be proven durable as the wetted, drained cathode in the cell environment and yet be efficient in material usage.
- The manufacturing process for the TiB₂-G cathode elements must be proven to be low-cost with quality control at high-volume production ensuring the projected economics.
- Thermal insulation systems for the cell must be capable of maintaining proper heat balance at reduced power inputs. This may require improved sidewall materials and non-conventional placement of thermal insulation for the sides and tops of cells.
- Engineering packages and modified cell operation procedures must be developed to ensure that the cathode elements will survive in a commercial potline.

Other technologies seeking commercialization of wetted drained cathodes have similar goals and hurdles.

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