# Carbon/$TiB_2$ Composites for Aluminum Reduction Cells

Arthur V. Cooke, Larry G. Boxall, Dennis C. Nagle, W. Mark Buchta
Martin Marietta Laboratories/Comalco Ltd.
1450 South Rolling Road
Baltimore, Maryland 21227

## Introduction

Over the past few years the combined effects of recession, escalating power costs, and low metal prices have pushed the U.S. aluminum industry into a precarious position, unable to compete with foreign imports. In order to retain a competitive position, a new energy efficient and less labor intensive process must be developed for producing primary metal.

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 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. To reduce the ACD without loss in current efficiency, a revolutionary approach being investigated in the industry is the use of a solid aluminum-wetted cathode, such as $TiB_2$. Here, the unstable metal pad cathode is replaced with a solid cathode wetted by a thin film of aluminum.

Extensive industrial research has been carried out since the 1950s on the use of refractory hard materials (RHM), such as $TiB_2$, for cathode lining applications.[1] $TiB_2$ has very low solubility in aluminum, is highly conductive, and most significantly, is wetted by molten aluminum. This property allows an aluminum film to be electrolytically deposited without the presence of an aluminum pad. Thus, new cell designs are possible, utilizing, for example, a sloped cathode so that the aluminum film runs off the surface continuously. The interaction between the magnetic field and the thin aluminum film is negligible, thus enabling increased energy efficiency and operating stability in the cell.

The two major problems with prior attempts to make a $TiB_2$ surface on carbon/graphite blocks, (from which the cathode is constructed) were lack of adhesion to the substrate and disintegration due to poor chemical resistance.

Disintegration of $TiB_2$ has been associated with fluoride/molten metal attack of oxide impurities on the boundaries between individual $TiB_2$ grains. Furthermore, fabricated $TiB_2$ parts are brittle, sensitive to thermal shock, not easily attached to a carbon substrate, and expensive. High-purity $TiB_2$ forms, and ceramic $TiB_2$ composites, have been used recently[2] to improve the corrosion resistance of the material. Although beneficial, these measures do not address the problem of attaching $TiB_2$ to carbon over a wide temperature range. This $TiB_2$ materials problem has been the critical element delaying the development of a practicable low energy cell (LEC).

## Combining the Properties of Carbon and $TiB_2$

A carbon/$TiB_2$ composite approach has been successfully used at Martin Marietta Laboratories to combine the aluminum wetting properties of $TiB_2$ and the proven durability of carbon in the cell environment. This new material has circumvented the shortcomings of the prior art by employing a particular specification of $TiB_2$ powder and a unique carbon matrix. The carbon matrix is chosen for granulometry compatible with the required cure and bake procedures, while the types of carbon solids and binder phase are blended in such a way as to provide the most chemically and physically rugged mix of hard and soft carbons.[3] A wet mixture is prepared consisting principally of a phenolic resin, a furane resin precursor, curing agents, carbonaceous filler and additives, and $TiB_2$. 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 $TiB_2$ 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 $TiB_2$ 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 $TiB_2$ in cathodes, and eliminates the need for more costly $TiB_2$ tiles.

## Materials Testing

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

An inverted electrolysis cell, shown in Figure 1, is used for the initial wettability and bath penetration tests. A coating composition containing 35-60 wt.% $TiB_2$ appeared optimal for achieving maximum wetting at minimum cost.

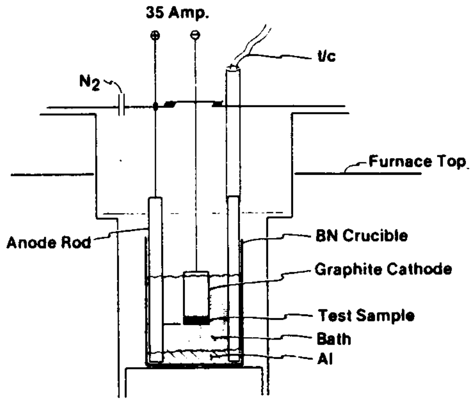


Figure 1. Inverted Electrolysis Test Cell

Static exposure tests are used to assess different coating formulations and types of candidate $TiB_2$ material as cathode linings for aluminum reduction cells. Following exposure for up to 1 month in heated retorts, a high-purity $TiB_2$ tile disintegrated below the aluminum metal line, a stabilized $TiB_2$ alloy tile was undamaged but had debonded, while the various composite coating samples were intact below the aluminum metal line. The composites showed variable exfoliation cracks at the level of the cryolite bath, but these were virtually eliminated when carbon fibers were incorporated into the formulation.

A 1500 Ampere externally heated pilot electrolysis cell was used to evaluate $TiB_2$ materials under continuous electrolysis for periods up to 3 weeks. Cathode materials were electrolysis tested under a 1" thick metal pad and in a drained cathode configuration. The exposure results under electrolysis were consistent with those from the retort tests. 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 absence of muck (undissolved alumina in frozen cryolite bath) on the composite surface was characteristic of all the coated cathodes tested under electrolysis. By contrast, uncoated carbon surfaces were consistently found to have a partial covering of muck. On a conventional cathode surface , bath material preferentially wets the carbon; on a $TiB_2$ cathode, molten aluminum expels the bath and wets the cathode instead. Hence, there is little tendency for muck, to attach itself to the surface of a $TiB_2$ cathode.

## Plant Tests

A total of 20 commercial VSS cells with $TiB_2$ coated cathodes were installed in the Martin Marietta smelters in the Pacific Northwest between 1981 and 1984. One of these smelters is now owned by Commonwealth Aluminum. These full-scale plant tests of the cathode coating were designed to determine whether:

1. Cells could be coated with the $TiB_2$/carbon material in a plant environment and then started by conventional methods.
2. The coating was wettable and has an acceptable projected life in commercial use.
3. The coating reduces cell mucking and has no adverse effects on cell performance.
4. The use of the coating in conventional cells results in energy savings or reduced operating costs.

By the end of 1984, it was clear that all of these criteria had been met. Extensive monitoring of test and control cells has demonstrated an average 2.5% energy efficiency improvement in the coated test cells. A 5- to 7-year life is predicted depending upon the $TiB_2$ type and the original coating thickness, and improved cell stability and easier operation is reported by the cell room workers.

A \$1-4 x $10^6$ annual cost saving is estimated for a typical smelter using coated cathodes. No capital investment beyond the coating cost, or changes in operating procedures are required to implement this technology. However, of greater long term importance, the carbon/$TiB_2$ composite opens the way to a new generation low energy cell capable of an order of magnitude greater savings. In addition, the durability and refractory properties of this material offer numerous opportunities in other metal processing systems, both on earth and in space.

## Acknowledgements


The authors wish to thank Comalco Ltd. for permission to publish this work and gratefully acknowledge the support and assistance of Martin Marietta Aluminum (now Commonwealth Aluminum) management and plant personnel in this project. We are indebted to the Bonneville Power Administration for financial assistance during the detailed plant monitoring phase of the project.


## References


1. K. Billehang, and H.A. Oye, "Inert Cathodes for Aluminum Electrolysis in Hall-Heroult Cells," Aluminium, 56 (1980) pp. 642-648 and pp. 713-717.
2. H.I. Kaplan, et al., "Cathodes for Alumina Reduction Cells," U.S. Patent No. 4,333,813 (1982).
3. D. Dumas, and C.J. Michel, "Low Resistivity Carbon Products for Cell Linings," 111th AIME Annual Meeting, Dallas (1982).