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 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 (TiB₂), TiB₂ composites and other Refractory Hard Metal (RH M) 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 1982, literature on Reynolds has published very little in this RH M cathode development area.

Reynolds early work with RH M 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 RH M, the solid wetted cathode surfaces and reduced ACD operation concept has since been under investigation. During these efforts, Reynolds developed, manufactured and patented RH M 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 great deal of the energy used in the process is expended as I-R drops 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 TiB₂ 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 TiB₂-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 TiB₂-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 RH M cathodes might be related.

Historical Background and Early Approaches to Utilize RH M Cathodes

Patent applications in France by BACO alerted the industry to wettable RH M 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 through 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. RH M 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 RH M cathode bars that was performed by Reynolds (6). Reynolds did not publish on early work on RH M 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 RH M 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 tubulars.

In 1957 Norton Company furnished Reynolds hot pressed TiB₂ 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 eliminated much of the carbon lining in which NaCl forms over the life of the cell. The lining could be simply metallurgical alumina or mixes of cryotitic 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.

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 compositions. 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 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 Kaweck 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 1: Schematic drawing of an aluminum reduction cell cathode with RHM collector bars and a refractory lining. 1: sidewall; 2: thermal insulation; 3: protective sleeve; 4: RHM bar; 5: fused layer of lining; 6: sintered layer; 7: loose alumina.](image1)

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 882°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.](image2)

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 carbothermically 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.

![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.](image3)

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 thin 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..."