

Methods of Producing TiB_2 /Carbon Composites for Aluminum Cell Cathodes

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Introduction

It has been known since the early 1950's that the use of refractory hard materials (RHM), such as TiB_2 , in aluminum reduction cell cathodes would result in dramatic performance benefits. However, previous attempts to implement this technology have failed due to the instability, fragile nature and high cost of these materials.

Martin Marietta Laboratories has developed a carbon/ TiB_2 composite which can be applied to the cathode blocks of an aluminum cell using a variety of methods.^{1,2,3} A particular technique may be preferred depending on time, equipment, cost and manpower constraints.

Coating Method

The composite coating consists of TiB_2 powder, graphite aggregate, carbon fiber and a carbon cement system which comprises a mixture of resins and carbon powders. The carbon matrix requires a granulometry that is compatible with subsequent heat treatments while providing acceptable density.

The solid components are blended under mild heat (30-40°C) to thoroughly homogenize before adding the liquid resin component. Total mixing times range from 30-50 minutes. A sigma-blade or double planetary mixer with wide blade tolerances is used to avoid altering the original granulometry.

The wet mix may be applied either to individual cathode blocks or to complete, rebuilt cathodes depending on plant requirements. Individual blocks are prepared by defining the coating area and depth with disposable aluminum strips attached to the sides of the blocks or with a removable assembly which can be transferred from block to block. The blocks are preheated to 30-50°C then coated with the carbon/ TiB_2 composition using regular spackling or cement tools.

Depending on block type, an intermediate coating layer, consisting of conventional carbon

cement modified with a graphite addition, may have to be applied to accommodate the coating shrinkage during heat treatment. The carbon granulometry of the matrix may also be changed to adjust the total shrinkage. Figure 1 shows how a strongly bonded coating with excessive shrinkage can cause block fracture.

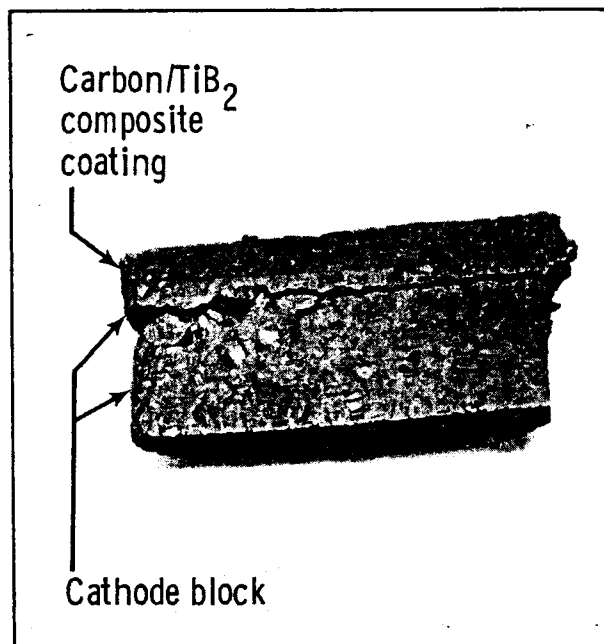


Figure 1. Example of Block Fracture Caused By Excessive Coating Shrinkage

The coated blocks undergo a 24 hour, low-temperature (170°C maximum) cure, then a high temperature (650°-1000°C) bake. Cure oven construction may be kept relatively simple (e.g., a large hood containing several individually controlled infrared heating elements). After curing, the coating is quite hard and the coated blocks may be stored indefinitely until baking.

For baking, the coated blocks are placed in steel containers, covered with a protective coke bed, and baked using existing plant equipment such as homogenizing furnaces. Once baked, the blocks may be handled without further precautions during cell relining procedures.

The coating composition may also be applied to an entire cathode after it has been rebuilt. In this case, volatile release from the cathode ramming paste can cause debonding, so the cathode surface is specially roughened to develop a stronger mechanical bond. Inverted aluminum channel, nailed into the ram slots between blocks, is used for depth guides and cathode preheating is achieved with propane-fired heaters. Experienced personnel can mix and apply the coating for an entire cathode within 4-6 hours.

More sophisticated curing and baking equipment is required for in-situ application since the heating unit must rest on the cathode shell to distribute heat over the entire cathode area. With a combined cure and bake furnace, the total heat treatment can be continuous and several cells can be prepared for start-up in a fraction of the time required when coating individual blocks.

Cast Plates

Instead of applying the carbon/TiB₂ composite directly to cathode blocks, the material may be used to fabricate plates. Product quality is enhanced by mixing under heat and vacuum to reduce the liquid content and increase the density. The mix is then spread into steel molds, but because of the increased viscosity, a vibratory screed is used to level the material. Steel weights are placed on top of the castings to prevent warpage during cure. Large infrared or convection ovens may be used to cure a number of plates which are then packed in a coke bed and baked to 650-1000°C. Again, the heat treatments are relatively simple and do not require custom built equipment.

After baking, the plates are attached to the cathode blocks using a conventional carbon cement and may be used to cover individual blocks or an entire, installed cathode. Plate fabrication can be performed in special facilities to ensure the sort of quality control that is hard to achieve in the plant.

Hot Pressed Tiles

Carbon/TiB₂ composite tiles can also be fabricated in a hot pressing operation.⁴ The pressing composition consists essentially of the solid components of the coating and casting material together with selected low melting resins. The components are blended in a ball mill, with precautions to ensure that the fibers are adequately dispersed throughout the mixture.

Hot-pressing is performed at 140-170°C and 3000-5000 psi for 5-20 minutes. The size and thickness of the tile can be varied depending on mold dimensions, amount of material placed in the mold, press capacity, etc.

Instead of dispersing the TiB₂ throughout the tile, it can be concentrated in the top surface using a bi-layer process. A base mixture comprising essentially carbonaceous materials is placed in the mold followed by a layer of the carbon/TiB₂ composite material. Thus, tiles may be fabricated with a TiB₂-rich composition in the top layer, to increase the TiB₂ surface concentration without additional cost.

After pressing, the tiles are baked in much the same way as the cast plates, then attached to the cathode blocks with carbon cement.

Hot pressing offers the same advantages as cast tiles but is much faster because the 24 hour cure is replaced by one of 5-20 minutes. The equipment is more expensive but less manpower and physical effort are required.

Conclusions

All of the described techniques are effective means of achieving a carbon/TiB₂ composite cathode surface. The versatility of the system allows a particular method to be chosen based on the specific plant requirements and capabilities.

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