

Carbon Chemistry of Carbon/TiB₂ Composites

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Introduction

Because of current high energy costs and labor costs, and the low price of competing imported aluminum, the U.S. primary aluminum business can only remain onshore if new processes are developed which are less labor and power intensive than the present Hall-Heroult cell. One of the most promising of the emerging technologies involves the use of aluminum wettable ceramics, such as TiB₂ in place of carbon.¹

Aluminum smelting cell cathodes typically comprise an insulated steel shell, lined with large carbon blocks that are connected electrically to the cathode bus. The advantages of the ceramic compound, TiB₂, as a cathode material for new cell designs, have been recognized since before 1950, and are well documented.² However, all previous attempts to use TiB₂ have been thwarted by materials problems, such as, chemical deterioration, brittle ceramic properties, difficulties in adhesion to the cell lining, and high cost.

Composite Cathode Materials

Potential Advantages of Composites

In concept, at least, composite technology can be applied to produce a material with more or less of the properties of each of the constituents. Thus, for example, a composite of carbon and TiB₂ has the potential to overcome all of the shortcomings of prior art single phase TiB₂ bodies. Adhesion to a carbon substrate presents no problem if the coefficient of thermal expansion of the composite and its chemistry are close to that of carbon. Chemical attack is avoided if the composite acquires more of the chemical durability of carbon, and the vulnerable TiB₂-TiB₂ grain boundaries are replaced with C-TiB₂ boundaries. Finally, the physical properties are enhanced if the ceramic powder is imbedded in a carbon matrix, because the material will then acquire the rugged properties of refractory carbon.

Previous Attempts to Develop Composites

A number of two phase (TiB₂/X) ceramics have been developed that have good chemical resistance, but fail to address the problems of adhesion, cost, and inherent fragility. TiB₂/carbon composites have also been prepared, but these failed in service either catastrophically, or through rapid carbon loss. In general, the matrix for these materials was predominantly soft carbon, comprising pitches, cokes, anthracite and the like.

Development Of A Novel Carbon Matrix.

Carbon Type versus Refractory Performance in the Aluminum Cell

Traditionally, soft carbons have been used to the exclusion of almost any other material in the manufacture of carbon electrodes.³ In use, the carbon slowly graphitizes in contact with the molten aluminum⁴, and becomes increasingly susceptible to mechanical attrition, and chemical erosion through aluminum carbide formation. Cathodes that are wholly graphitic fail much faster for these same reasons.

Hard carbons have never been applied to cathode manufacture, if one applies the strictest definition as meaning non-graphitizable. On the other hand, calcined anthracite has many of the attributes of a hard material and is the commonest raw material for this application. The anthracitic cathode is wear-resistant and only "carbides" slowly, but has lower electrical conductivity and is prone to attack and disruption by sodium, which is co-deposited with the aluminum.⁶

Alternative carbon types have not been seriously considered for Hall cell electrodes because the material choice has always been dominated by considerations of short cathode life, tonnages used in relining and consequent high replacement costs.

Selection of Carbon Types

To realize the benefits obtainable separately from hard and soft carbons, a mix of the two was chosen for the composite, and optimized for use in the aluminum cell environment. In addition, carbon black and carbon fibers were incorporated.

The granulometry of the solid carbon components of the mix was tailored to the TiB_2 powder sizing since this is critical to the performance of the composite cathode. In practice, different sieve fractions of graphite were blended with carbon black to achieve maximum dry density. This had the added advantage of ensuring that the TiB_2 particles were locked into the structure by carbon particles.

A mixture of solid and liquid resin binders was used to prepare the hard carbon matrix. This technique was found to minimize the total binder content required for structural integrity while retaining sufficient liquid to wet the solids and to bond to the substrate.

The heat treatment cycle used to cure the resin was developed as a compromise between adequate reaction rate, minimum volatile loss, product quality and time. Marked quality improvements were observed when provision was made for volatile release in the binder, and when carbon fibers were incorporated to arrest cracks that developed during heat treatment.

Results In Service

The material was bench-tested and pilot-tested in the laboratory, and plant trials have been running since mid-1981. Samples from the pilot cell, and from autopsied production cells, demonstrated the value of the composite approach since the material was clearly wetted by molten aluminum, even with very small volume fractions of TiB_2 . The durability of the material was also remarkable and was strongly influenced by the amount of fiber in the mix. Conventional cathode carbon is worn away at 1-2 cm/yr², whereas the thickness reduction of the composite, calculated from Ti and B analyses in the aluminum pad, was an order of magnitude less. Studies of the coating wear mechanism have shown that the data is inconsistent with control by carbon loss, since the rate of loss and its temperature dependence are different for composites with different TiB_2 specifications, even though the carbon type is the same. Pending further autopsy work, it is thought that the coating loss is controlled by the TiB_2 dissolution parameters and that the carbon is only attacked following localized TiB_2 depletion.

Conclusions

It has been proven that TiB_2 can be incorporated into a special carbon matrix to produce a tough, economical, aluminum wettable refractory. In service, the composite is always covered with molten aluminum which demands special attention to the blend of carbon types used in the matrix. Wear rate studies have shown that coating loss is controlled by slow TiB_2 dissolution and not by the rate of carbon loss.

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References

1. L.G. Boxall, A.V. Cooke, and H.W. Hayden, " TiB_2 Cathode Material: Application in Conventional VSS Cells," J. of Metals, 36 (November 1984), pp. 35-39.
2. A.V. Cooke, L.G. Boxall, D.C. Nagle, and W.M. Buchta, "Carbon/ TiB_2 Composites for Aluminum Reduction Cells," Proceedings of the 17th Biennial Conference on Carbon, Lexington, Kentucky, 1985.
3. C.L. Mantell, "Carbon and Graphite Handbook," R.E. Krieger Publishing Co., NY, 1979, p. 234.
4. J. Waddington, title in Extractive Metallurgy of Aluminum, Vol. 2, ed. G. Gerard, Interscience Publishers, New York, 1963, p. 435.
5. K. Grjotheim, R. Naeumann, H.A. Øye, "Formation of Aluminum Carbide in the Presence of Cryolite Melts," TMS AIME, Light Metals, vol. 1, 1977, pp. 233-242.
6. E.W. Dewing, "The Reaction of Sodium with Non-Graphite Carbon; Reaction Occurring in the Linings of Aluminum Reduction Cells," Trans. Metall. Soc. AIME, Dec. 1963, 227, pp. 1328-34.
7. E.A. Hollingshead, J.A. Brown, "Rate of Solution of Carbon in Molten Aluminum Under a Cryolite Melt," TMS AIME, Light Metals, 1982, ed. J.E. Andersen, p. 625-634.