CATHODE FOR ALUMINUM PRODUCTION AND ELECTROLYTIC CELL

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ABSTRACT

The present invention provides an improved TiB₂ cathode for use in aluminum production cells for the electrolysis of alumina dissolved in a cryolite-based molten electrolyte and an improved electrolytic cell for producing aluminum. The cathode is a monolithic, porous, TiB₂ body having a continuous porosity and interconnected pores substantially throughout.
CATHODE FOR ALUMINUM PRODUCTION AND ELECTROLYTIC CELL

BACKGROUND OF THE INVENTION

[0001] The aluminum industry consumes a large amount of all electrical energy used by industry in the U.S. for the production of primary aluminum metal, i.e., metal derived from ore as distinct from recycled aluminum. Although the average U.S. energy consumption has been somewhat reduced in recent years, significant further savings appear possible only for smelters with technological improvements. Because the aluminum industry is very capital intensive, replacing current U.S. smelting facilities with new, low-energy reduction cells would be prohibitively expensive.

[0002] Moreover, aluminum is a vitally important and highly versatile material that is widely used throughout the United States and the world. The long-term demand for aluminum products is expected to increase as industry and consumers increase their use of this lightweight metal to reduce energy costs, e.g., those required to propel transportation systems. To maintain a competitive US position in the face of increasingly expensive electrical energy, labor costs and environmental restrictions, the aluminum industry has a strong incentive to develop a more energy-efficient process to produce primary aluminum at a lower cost.

[0003] For over 100 years, all primary aluminum has been produced commercially in Hall-Heroult (H-H) electrolysis. The conventional Hall-Heroult process involves the electrolyte decomposition of aluminum oxide dissolved in a molten cryolite bath. A carbon anode is consumed in the oxidation reaction that evolves CO₂ and CO, plus very environmentally objectionable fluorocarbons during an “anode effect”. Molten aluminum metal is reduced at the metal pad that serves as the cathode. However, because of electromagnetically induced waves in the liquid aluminum pad, combined with uneven oxidation of the carbon anode, a significant anode to cathode distance (ACD) (about 5 cm) must be maintained to avoid shorting. The contribution to the cell voltage resulting from this IR loss in the electrolyte constitutes an important expense in producing primary aluminum. Therefore, the industry has a need for a wettable, inert cathode which contacts the aluminum pad, but enters the cryolite to approach the anode. Deposition of aluminum onto this inert cathode then reduces the anode to cathode distance, thereby reducing the IR drop and cell voltage.

[0004] Producing aluminum by the conventional Hall-Heroult electrolytic cell process requires a large amount of energy and releases significant emissions of greenhouse and other detrimental gases. For decades, scientists and engineers have sought other methods for producing aluminum, but no viable alternative process that can reduce energy consumption, production costs, and the generation of greenhouse gases has been demonstrated.

[0005] The potential benefits of using electrically conductive titanium diboride (TiB₂) for an inert cathode have been long recognized. However, past attempts to apply dense TiB₂ cathodes to full-size reduction cells have resulted in short service lives. Because of residual sintering additives to facilitate their hot pressing fabrication, the materials are susceptible to intergranular penetration by molten aluminum, which eventually results in physical disintegration. Other material properties compound this problem: dense TiB₂ is brittle, thermal shock sensitive, cannot withstand mechanical impact, and may lack adequate wettability.

SUMMARY OF THE INVENTION

[0006] It is, therefore, a principal object of the present invention to provide an improved TiB₂ inert cathode for use in aluminum production cells for the electrolysis of aluminum dissolved in a cryolite-based molten electrolyte.

[0007] It is a still further object of the present invention to provide an improved electrolytic cell employing said cathode.

[0008] It is a still further object of the present invention to provide an improved cathode and cell, wherein the cathode is characterized by improved thermal shock resistance, good resistance to dissolution in cryolite or liquid aluminum, and good wettability toward molten aluminum.

[0009] Further objects and advantages of the present invention will appear herein.

[0010] In accordance with the present invention, an improved TiB₂ cathode is provided for use in aluminum production cells for the electrolysis of alumina dissolved in a cryolite-based molten electrolyte, which comprises a monolithic, porous, TiB₂ body having a continuous porosity and interconnected pores substantially throughout, prepared by compacting and possibly sintering at least one of titanium and titanium hydride powder to form or shape a porous preform, followed by boriding, at high temperature, said resulting porous body having improved thermal shock resistance and good wettability toward molten aluminum. The TiB₂ porous body desirably comprises compacted titanium powder reacted to form boride throughout. Also, desirably the porous TiB₂ body includes carbon intermixed therein prior to or following the boriding step, and possibly bonded thereto.

[0011] The electrolytic cell for producing aluminum by electrolyzing alumina dissolved in a cryolite-based molten electrolyte includes an anode and said cathode in contact with the aluminum product. The cathode contacts the liquid aluminum pad and is immersed in the electrolyte. The anode and cathode face each other and are spaced from each other, desirably with a spacing of less than 2 cm.

[0012] Other features and advantages of the present invention will appear hereinbelow.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The present invention will be more readily understood from a consideration of the accompanying, illustrative drawings, wherein:

[0014] FIG. 1 is a partly schematic partial view of an electrolytic aluminum production cell of the present invention, including an improved TiB₂ cathode of the present invention;

[0015] FIG. 2 is a further, schematic partial view of a cell comprising vertical interlaced inert anodes and inert cathodes; and

[0016] FIG. 3 is a cross-sectional greatly enlarged micrograph of a boride-coated titanium slab, such coating of particles employed as a porous TiB₂ cathode of the present invention.

DETAILED DESCRIPTION OF P Е D EMBODIMENTS

[0017] The present invention provides an improved TiB₂ cathode which may have virtually any desired shape or
configuration and which is relatively tough, inexpensive, pure, conductive, wettable towards molten aluminum and essentially inert so that it does not readily dissolve under operating conditions. Moreover, the TiB₂ cathode is a monolithic, porous, TiB₂ body having a continuous porosity and interconnected pores substantially throughout. 

In accordance with the present invention, one fabricates the present porous TiB₂ cathode by compaction and perhaps at least partial sintering of titanium powder and/or titanium hydride powder into the desired net shapes followed by boriding the porous powder preforms in a second step at high temperature, for example, at 1100-1200° C. to allow complete or substantial conversion of the preforms into the desired, final TiB₂ bodies in a relatively simple, convenient and inexpensive manner.

Today, a significant portion of the electrical energy consumed in aluminum smelting is spent on the voltage drop across the resistive cryolite electrolyte bath between the anode, which is generally carbon, and the agitated aluminum pad cathode. Decreasing the anode-cathode distance (ACD) in a conventional H-H cell reduces the cell voltage, but introduces metal pad instability, increases the incidence of shorting, and results in a loss in current efficiency. The potential benefits of introducing a dimensionally stable, wefted cathode to bridge a significant fraction of the ACD have been known for several decades. Aluminum producers in Europe, Asia, and North America have undertaken research related to development of this “inert cathode”. In the United States, significant efforts have been expended to develop an essentially inert cathode, which would contact the aluminum pad and rise above it into the cryolite bath. Ideally, the cathodically reduced aluminum would wet this inert cathode and support the flow of the deposited liquid aluminum to the underlying aluminum pad. Dense bodies of hot pressed TiB₂ and TiB₄—graphite are being pursued as the materials of choice for wettable cathodes, because of their relatively high electrical conductivity, good chemical stability in both aluminum and the cryolite bath, as well as good wettability by aluminum. Sane et al., U.S. Pat. No. 4,544,457, have described a thin porous sheath to cover a dense underlying inert cathode. This sheath serves to hold a thin layer of liquid aluminum which contacts the underlying dense inert cathode. However, after decades of experimentation around the world, the effectiveness of candidate inert cathodes is still unsatisfactory. Attempts to retrofit dense TiB₂ and TiB₄ composite materials as inert cathodes have been thwarted by high costs, marginal TiB₂ purity (impurities introduced by sintering additives), poor thermal and mechanical shock resistance, intergranular attack, and an attachment problem. Also, the impure, dense, experimental TiB₂-graphite cathodes still exhibit excessive dissolution into the liquid aluminum pad, leading to unsatisfactory contaminant levels in the metal produced.

The porous, net-shaped, essentially inert TiB₂ cathode of the present invention is tougher, less expensive, purer and more wettable than TiB₂ cathodes heretofore. Relative to the enhanced wettability for a porous body, reference should be made to K. P. Trumble, "Spontaneous Infiltration of Non-Cylindrical Porosity: Close-Packed Spheres", Acta Mater. 46 (1998) p. 2363. Because of the ability of the pores and interfaces to blunt crack propagation, the porous TiB₂ cathode of the present invention will lessen the brittleness and poor thermal shock resistance associated with current dense TiB₂ cathodes. Furthermore, the TiB₂ cathodes of the present invention can be easily and desirably impregnated with carbon or other powders (prior to or following boriding) to form a TiB₂ composite cathode where desired. For example, zirconium and hafnium can be included if desired. The boride diffusion coating on titanium of the present invention is normally a mixture of mono- and di-borides.

Alternatively, titanium hydride can be used at least in part, or other transition metals combined therein, in forming the preform compact prior to boriding. Volatile binders may be included, and other desirable additives admixed therein prior to the formation of the TiB₂ bodies.

The porous TiB₂ bodies of the present invention are readily prepared. First, a porous, net shape preform is prepared from titanium or titanium hydride powder, for example, by cold pressing by powder metallurgy. Alternatively, the titanium powder could be sprayed to form a desired porous shape or placed cold into a mold and sintered, to achieve a porous sintered preform.

The foregoing preform is then reacted at elevated temperature, as by chemical vapor deposition (CVD) or pack cementation, both of which are well known to form a conversion coating of titanium boride wherein each titanium particle is essentially converted to TiB₂. The halide-activated pack cementation method constitutes an in situ generated CVD technique suited to grow a wide variety of diffusion coatings on a wide variety of metals and alloys. The parts to be coated are placed in a closed retort and buried in a mixture of powders comprising a source for the element(s) to be deposited, a small amount of a halide salt, and a majority of inert filler. At high temperature, the halide salt melts and reacts with the boride coating element to generate volatile halide species, which diffuse in the gas phase through the pack and react with the substrate to deposit the boride coating element resulting in the growth of a diffusion (conversion) layer at all exposed surfaces of any part. This conversion coating technology can be readily applied to the porous titanium body after compressing titanium powder into a porous green body, followed by reactive boriding to produce a net-shape but porous TiB₂ cathode, either absent of residual titanium or containing some unreacted titanium at the cores of the powder particles.

A dense diffusion coating of TiB₂ and TiB (~20 microns thick) can be grown on dense titanium by pack cementation in 12 hours at 1150° C. The rate of thickening or growth of such a boride conversion coating is limited by diffusion of boron through the product boride layer. Thus, virtually no gradient in gas composition exists in the gas phase. Although a 20 μm coating on dense titanium is too thin for extended service in contact with aluminum and cryolite, boriding a porous titanium preform with continuous porosity to any virtually desired depth can be achieved, e.g., 1 to 2 cm depth or greater if desired, and such a coating can be readily formed for each powder particle of the porous preform of the present invention. A micrograph of a boride coating on dense titanium is shown in FIG. 3, with base titanium 10 coated by TiB₂ plus TiB borides 12, wherein such borides are employed as the TiB₂ cathode of the present invention.

In accordance with the present invention, the TiB₂ bodies have interconnected pores throughout. These are present in the preform so that the boron-halide vapor can diffuse readily into the interior of the preform for conversion of each titanium particle to TiB₂, and the pores are also present in the final product.

Moreover, the resultant porous TiB₂ bodies have high wettability towards molten aluminum, which is inher-
ently enhanced by the porosity of the bodies. In addition, while dense TiB₂ material is very brittle and sensitive to thermal shock, the porous TiB₂ of the present invention is less sensitive in these regards and represents a considerable improvement. In addition, the pure TiB₂ bodies of the present invention have desirable limited solubility in molten aluminum and cryolite-alumina bath. The particle diameter is not sufficiently small to contribute an important capillarity effect to the solubility.

[0027] In addition, the present invention obtains significant advantages in cell operation. The improved TiB₂ cathode of the present invention achieves a significant reduction in cell energy consumption, thereby improving the efficiency of the electrolysis process. This is attributed to the smaller AC current in the H-H current, resulting in significant energy savings, reduced cost, reduced heating in the cell, and reduced air pollution at the electric power plant. It is estimated that a 15-20% reduction in cell voltage can be obtained in accordance with the present invention, corresponding to a potential savings of about 4 to 5 cents per pound of aluminum, which is quite significant.

[0028] FIG. 1 is a schematic representation of the electrolytic cell 18 of the present invention, including the TiB₂ cathode 20 with interconnected pores 22 therein, with anode 26 thereof spaced from the cathode. Molten electrolyte 28 is provided, with the anode and cathode immersed therein. The cathode is immersed in a pool of molten aluminum 30 and is supported by the floor of the hearth 24.

[0029] FIG. 2 is a schematic representation of an alternative electrolytic cell 38 of the present invention showing an interleaved or interdigitated sequence of vertical inert anodes and inert cathodes. The TiB₂ cathodes 40 of the present invention with interconnected pores 42 therein are positioned on the floor of the hearth 44 with the interleaved anodes 46 spaced therefrom. Molten electrolyte 48 is provided, with anodes and cathodes immersed therein. The cathodes are immersed in a pool of molten aluminum 50. Reference should be made to U.S. Pat. No. 5,279,715 by LaCamera et al. relative to interleaved or interdigitated inert anode and inert cathode cells.

[0030] FIG. 3 is a scanning electron micrograph of the cross-section of a boride coating on a dense titanium slab, reacted using a pack cementation process at 1150°C for 12 hours. The TiB₂ external coating 12 and an internal TiB product 11 are grown on the titanium substrate 10.

[0031] It is to be understood that the invention is not limited to the illustrations described and shown herein, which are deemed to be merely illustrative of the best modes of carrying out the invention, and which are susceptible to modification of form, size, arrangement of parts and details of operation. The invention rather is intended to encompass all such modifications which are within its spirit and scope as defined by the claims.

What is claimed is:

1. An improved TiB₂ cathode for use in aluminum production cells for the electrolysis of alumina dissolved in a cryolite-based molten electrolyte, which comprises:
   a. a monolithic, porous, TiB₂ body having a continuous porosity and interconnected pores substantially throughout, prepared by compacting at least one of titanium and titanium hydride powder to form a porous preform, followed by sintering, said body having improved thermal shock resistance and good wettability towards molten aluminum.
   2. An improved TiB₂ according to claim 1, wherein the powder is sintered at least in part.
   3. An improved TiB₂ according to claim 1, wherein said body composes compacted powder reacted to form a TiB₂ body throughout.
   4. An improved TiB₂ according to claim 1, wherein said porous TiB₂ body includes carbon intermixed therein.
   5. An improved TiB₂ according to claim 4, wherein the carbon is at least in part bonded to the compacted powder.
   6. An improved TiB₂ according to claim 1, wherein the TiB₂ body is a composite material.
   7. An improved TiB₂ according to claim 1, wherein each titanium particle is essentially converted to TiB₂.
   8. An improved electrolytic cell for producing aluminum by electrolyzing alumina dissolved in a cryolite-based electrolyte, comprising an anode and a cathode in contact with the aluminum product, wherein:
      said cathode comprises a monolithic, porous, TiB₂ body having a continuous porosity and interconnected pores substantially throughout, prepared by compacting at least one of titanium and titanium hydride powder to form a porous preform, followed by sintering, said body having improved thermal shock resistance and good wettability towards molten aluminum.
   9. An improved electrolytic cell according to claim 8, wherein said cathode is immersed in said electrolyte and in contact with the liquid aluminum pad.
   10. An improved electrolytic cell according to claim 9, wherein the anode and cathode face each other and are spaced closer to each other than the usual AC current density for the carbon anode and aluminum pad cathode.
   11. An improved electrolytic cell according to claim 8, wherein each titanium particle is essentially converted to TiB₂.
   12. An improved electrolytic cell according to claim 8, wherein said porous body comprises compacted powder reacted to form a TiB₂ body throughout.
   13. An improved electrolytic cell according to claim 8, wherein said porous TiB₂ body includes carbon intermixed therein.
   14. An improved electrolytic cell according to claim 13, wherein said carbon is at least in part bonded to the compacted powder.
   15. An improved electrolytic cell according to claim 13, wherein said carbon is intermixed following sintering.
   16. An improved electrolytic cell according to claim 15, wherein said carbon is intermixed following sintering.
   17. An improved electrolytic cell according to claim 9, wherein the anode is a carbon anode.
   18. An improved electrolytic cell according to claim 9, wherein the cell comprises interdigitated vertical inert anodes and inert cathodes.
   19. An improved electrolytic cell according to claim 9, wherein the TiB₂ body is a composite material.