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ELECTRODE

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FIG. 1a

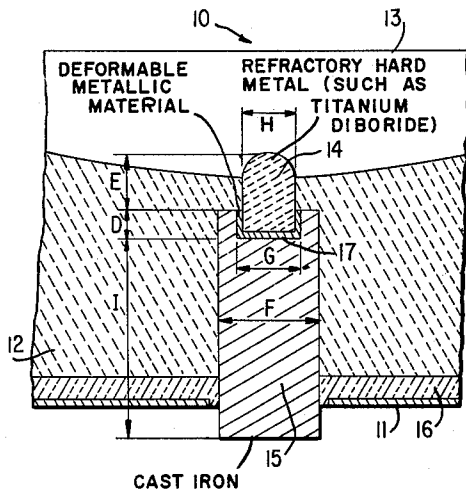


FIG. 1b

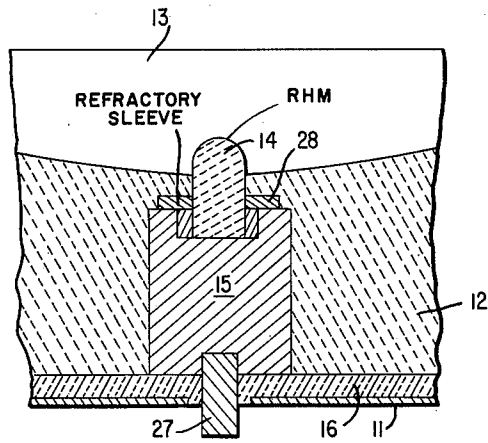


FIG. 2

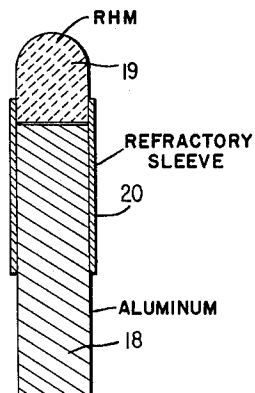


FIG. 3

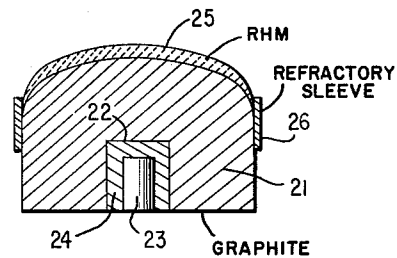
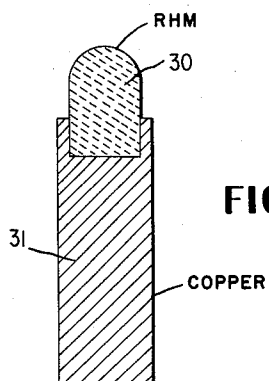


FIG. 4



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ELECTRODE

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This invention relates to an improved cathode structure and more particularly to a cathode structure finding significant utility in an electrolytic cell.

For many years it has been customary to obtain aluminum from alumina by a reduction process employing an electrolytic cell or pot. The pot includes a pot shell, usually constructed of mild steel, a suitable lining, typically carbon, for containing the molten bath constituents, and heat-insulating material between the shell and the lining. In addition, the conventional arrangement uses a carbon anode suspended within the cavity formed by the lining. The carbon lining and pad of molten aluminum overlying it function as the cathode and iron bars are embedded within the carbon to establish the necessary electrical connection.

A recent improvement in such electrolytic cells has been disclosed and claimed in the application of John L. Dewey, Serial No. 847,594, filed October 29, 1959, now U.S. Patent 3,093,570. Briefly, the patent teaches forming a pot lining from a refractory oxide and cryolite, and current collectors are suggested (for use with that type of lining) which are composed of materials such as borides, nitrides and carbides of elements found in groups 4, 5 and 6 of the Periodic Table. The present invention relates to cathode structures suitable for use in a similar environment, and particularly to improved techniques for joining a cap portion of such refractory hard metal materials to a stem portion of another material. These improved cathode structures are easy to manufacture, reliable in operation, and will accommodate high current densities therethrough with optimum resistance to corrosion and deterioration.

In accordance with the present invention, one embodiment provides an improved cathode structure for an electrolytic cell used for the reduction of dissolved alumina to molten aluminum. This cathode includes a collector bar having a stem portion which extends from the vicinity of the molten pad but is spaced therefrom, continues through the lining and protrudes from the pot shell. The stem portion has a generally centrally located socket therein on the end adjacent to the molten pad. A cap portion is supported in the socket and extends into contact with the molten pad. A deformable, substantially insoluble, metallic material at least partially fills the space between the cap portion and the socket, the metallic material being selected so as to wet the cap and stem portions and having a melting point which permits it to be molten, or at least softer than either the stem or the cap, at the operating temperature of the cell.

Another embodiment of the present invention provides an improved cathode structure in which the stem portion is made of aluminum and is directly bonded to the diboride cap portion within a refractory protective sleeve.

Still another embodiment of the present invention provides an improved cathode structure in which a graphite block stem portion is bonded to a cap portion of diboride, the block being provided with a steel rod conductor mounted thereto at the end opposite the diboride, and the rod providing electrical connection between the block and the cathode voltage supply.

A still further embodiment of the present invention provides an improved cathode structure in which a cop-

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per stem is cast around the lower end of a refractory hard metal cap portion.

For a better understanding of the invention and its objects, advantages and details, reference is now made to the present preferred embodiments of the invention which are shown, for purposes of illustration only, in the accompanying drawings.

In the drawings:

FIGURES 1A and 1B are fragmentary detailed cross-sectional views of electrode structures according to the present invention; and

FIGURES 2, 3 and 4 are alternate embodiments of the electrode structure constructed in accordance with this invention.

Referring first to FIGURE 1A, the pot 10 includes pot shell 11 and lining 12, defining a space 13 for containing the pad of molten aluminum. The collector bar constructed in accordance with the present invention includes a cap portion 14 and a stem portion 15. The cap portion 14 is made of a refractory hard metal, preferably titanium diboride. The term refractory hard metal is used in the present circumstances to encompass the carbides, nitrides, borides and silicides of the transition metals of the Fourth through the Sixth groups. The stem portion is massive and may be of cast iron which is known to be quite resistant to such an environment. It will be noted that one end of the stem portion 15 is adjacent to the molten pad, but spaced therefrom, and the stem extends through the lining 12. Any convenient means may be used for connecting the protruding portion of the stem to the cathode voltage supply. Thermal insulation 16 also serves to electrically insulate the stem portion 15 from the shell 11.

The top end of the stem portion 15, that is the end which is in the vicinity of the molten pad, has a generally centrally located socket therein for accommodating the cap portion 14. A deformable metallic material at least partially fills the space between the cap portion and the socket. As shown here, the cap portion 14 extends beyond the socket into contact with the metal pad. The metallic material 17 is a soft metal which wets both the cast iron and the titanium diboride and is not soluble in either to any damaging extent. It should be more compressible than the diboride under the conditions of use, and may conveniently be in a molten state at the cell operating temperatures. Examples of suitable metallic material are tin, zinc, copper, lead, silver, aluminum and alloys of these metals. Tin is preferred because it has a low melting point, but a high boiling point, and it is soft.

This improved cathode structure is fabricated by first casting the iron stem portion with the socket therein. Next, the iron stem portion is "tinned" by the alloy or pure metal to be used for the joint. The cap portion is then supported in the socket but spaced therefrom and the molten metallic material is cast in the annular space defined by this arrangement. Prior to the actual introduction of the metal used for the bonding of the cap portion 14 to the stem portion 15, the cap and stem portions are slowly preheated to casting temperature. After the insertion of the molten alloy, the assembly is slowly cooled to avoid thermal shock.

The preferred length of E is between eight and fourteen inches and the preferred length of D is between two and six inches. The length I is as great as necessary to reach the point decided upon for connection to the external bus. The stem portion 15 may extend to within about six inches of the pad-lining interface, in which case the cap portion 14 may be about twelve inches in length. Preferably, for every two inches of diameter of the cap portion, the surrounding stem portion is four to eight inches in diameter.

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In the illustrated embodiment, the stem portion, the cap portion and the socket defined in the former are of circular cross-section. However, instead of being a round bar of diameter H , the cap portion may be a long slab of thickness H , with height $E+D$ and length as desired. Then the cast iron is of thickness F with a suitable trough width G . In all cases, it should be noted that the size of the socket, and particularly the amount that G exceeds H , is such as to provide for any thermal expansion that may occur.

Referring to FIG. 1B where like numbers refer to like parts in FIG. 1A, the stem portion 15 of cast iron or graphite extends downwardly within the lining 12 flush to the insulating material 16 and carries a socket in the bottom thereof to accommodate a steel conducting rod 27. As shown, a refractory corrosion resistant sleeve 28 is mounted about the cap portion 14.

Referring to FIGURE 2, there is shown an alternate form of cathode structure which includes a stem portion 18 of aluminum and a diboride cap portion 19. The stem portion may be aluminum sweated to and enclosing individual diboride particles or a graded aggregate of such particles, the largest diameter of which particles may be as great as the stem diameter. These portions are bonded together by a unique process. The surface of cap portion 19 to which the stem 18 is to be joined is first prepared by bringing the diboride into contact with aluminum at about 1500°C ., thereby wetting the diboride surface with aluminum. Both the heating and subsequent cooling are carried out slowly to avoid thermal shock. Then aluminum stem portion is cast into the cavity formed adjacent the cap portion by the protective sleeve 20. The latter is a refractory material such as "Refrax" (a silicon nitride bonded silicon carbide), which may be joined to the cap portion in a manner known to the art, either before or after the wetting operation. If desired, the sleeve-cap combination may be inverted in a mold for receiving the aluminum in order that the cast stem will extend beyond the sleeve, as shown. The aluminum stem portion is connected to the external bus by any known means. This stem portion must be long enough and must be cooled sufficiently at the lower end to prevent melting thereof below the portion enclosed by the protective sleeve 20. If the temperature of the stem within the sleeve exceeds the melting point of aluminum, this will not have any deleterious effect upon the operation of the cathode provided a solid plug of aluminum remains at the lower end of the sleeve. Despite the fact that the bonding area may again become molten, the electrical continuity will persist.

The cathode structure shown in FIGURE 3 consists of a graphite block 21 which is of the general shape and dimensions of pre-baked cathode blocks of conventional design. It is provided with a groove 22 in the bottom surface thereof. A steel connecting rod 23 is mounted in this groove and then the rod is bonded to the graphite block by pouring molten cast iron 24 into the remaining portions of the groove, in accordance with known practice. The cap portion 25 is of a diboride material and the annular sleeve 26 is a refractory material.

One technique of forming the cathode structure of FIGURE 3 takes advantage of the fact that the diboride materials can be hot pressed in particulate form to produce a dense body. Consequently, the block 21 may be used as a male die member, and under heat and pressure a film of diboride material 25 can be bonded to the graphite block 21.

Referring to FIGURE 4, the stem portion 31 of copper is cast around the refractory hard metal cap portion 30. It is preferable to tin the contacting surface of the cap portion prior to the casting operation. This arrangement is particularly satisfactory since it substantially eliminates the necessity of a protective sleeve. It has been found that copper does not materially deteriorate

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in such use, even through metallic sodium is present in the lining. One preferred example of this construction employs a titanium diboride portion about 8 inches in length and 2 to 8 inches in diameter cast into the copper to a depth of approximately 4 inches. The copper casting then extends down into the cell lining where it is connected by any convenient means to the bus system.

The cathode structures of FIGURES 2, 3 and 4 are mounted within the reduction pot similarly to that illustrated in connection with FIGURE 1.

While present preferred embodiments of the invention have been illustrated and described, it will be recognized that the invention may be otherwise variously embodied and practiced within the scope of the following claims.

What is claimed is:

1. In an electrolytic cell for the reduction of dissolved alumina to molten aluminum, having a pot shell and shell lining to contain the bath constituents and the molten aluminum pad, a cathode structure comprising a collector bar having at least three distinct sections arranged substantially in axial alignment, including (a) a stem portion which terminates inwardly of the cell within said lining, at a position in the vicinity of said molten aluminum pad where the end of said stem portion is exposed to a temperature approaching the melting point of aluminum, said stem portion having a socket therein at the end adjacent to said molten pad, (b) refractory hard metal cap portion supported within said socket in spaced relation to said stem portion and extending out of said lining into contact with said molten pad, and (c) an intermediate portion of deformable metallic material at least partially filling the space between said cap portion and said socket to provide a resilient connection therebetween accommodating differences in the thermal expansion characteristics of said cap and stem portions, said metallic material being capable of wetting said cap and stem portions and having a melting point so as to be softer than said cap portion at the operating temperature of said cell.

2. An electrolytic cell according to claim 1, having a collector bar wherein said deformable metallic material consists essentially of a material selected from the group consisting of tin, zinc, copper, lead, silver, aluminum and alloys thereof.

3. An electrolytic cell according to claim 1, having a collector bar in which said stem portion is formed of cast iron and said deformable metallic material consists essentially of tin.

4. An electrolytic cell according to claim 1, having a collector bar in which said stem portion is formed of graphite.

5. In an electrolytic cell for the production of aluminum, having a pot shell and shell lining to contain the bath constituents and a pad of molten aluminum, a cathode structure comprising a collector bar having an aluminum stem portion which terminates inwardly of the cell within said lining, at a position in the vicinity of said molten aluminum pad where the end of said stem portion is exposed to a temperature approaching the melting point of aluminum, with a refractory hard metal cap portion connected in abutting relation to said stem portion at the inner terminal end thereof, said cap portion protruding out of said lining into contact with the molten pad; and a refractory sleeve surrounding said stem portion along the inner terminal end thereof and overlapping the juncture between the cap and stem portions, said sleeve being adapted to contain and support the part of said stem portion which becomes softened during operation of the cell, the length of said sleeve being sufficient that a solid plug of aluminum fills at least the outer end of the sleeve so as to block egress of molten aluminum from the sleeve and prevent disruption of the electrical connection between said cap and stem portions of the collector bar even when the

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inner end of said stem portion becomes softened substantially to the point of melting.

6. In an electrolytic cell for the production of aluminum, having a pot shell and shell lining to contain the bath constituents and a pad of molten aluminum, a cathode structure comprising a collector bar having a stem portion which terminates inwardly of the cell adjacent the pad of molten aluminum and extends outwardly through at least a part of said lining for connection to a cathode voltage supply exterior to said pot shell, said stem portion including a graphite block, and a refractory hard metal cap portion integrally joined to said block adjacent the inner terminal end thereof to form a pad-contacting element of the bar, said cap portion being comparatively small in relation to the thickness of said block.

7. Apparatus according to claim 6, further comprising a corrosion resistant refractory sleeve surrounding a portion of said block and sealing the peripheral area defined by the bonding of said cap portion to said block.

8. In an electrolytic cell for the production of aluminum, having a pot shell and shell lining to contain the bath constituents and a pad of molten aluminum, a cathode structure comprising a collector bar having a stem portion which terminates inwardly of the cell within said lining at a position adjacent the pad of molten aluminum, said stem portion having a socket therein at the end adjacent said molten pad, and a cap portion cast into said socket and extending out of said lining into contact with the molten pad, said cap portion consisting essentially of refractory hard metal and said stem portion consisting essentially of copper.

9. In an electrolytic cell for the production of aluminum, having a pot shell and shell lining to contain the bath constituents and a pad of molten aluminum, an improved cathode structure comprising a collector bar having at least three distinct sections arranged substantially in axial alignment, all of which are disposed at least partially within said lining, including (a) a stem portion which terminates inwardly within said lining closely adjacent the pad of molten aluminum, at a position where the end of said stem portion is exposed to a

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temperature approaching the melting point of aluminum, (b) a refractory hard metal cap portion disposed in spaced relation to said stem portion adjacent the inner terminal end thereof and extending out of said lining into contact with the aluminum pad, and (c) an intermediate portion of deformable metallic material disposed between said cap and stem portions to join said portions in electrically conductive relationship, said metallic material being softer than the cap portion under operating conditions of the cell, and the thickness of said intermediate portion being sufficient to provide a resilient connection accommodating differences in the thermal expansion characteristics of said cap and stem portions.

10. In an electrolytic cell for the production of aluminum, having a pot shell and shell lining to contain the bath constituents and a pad of molten aluminum, a cathode structure comprising a collector bar which extends outward of the cell for connection to the cathode voltage supply of the cell, said collector bar including a graphite block which terminates inwardly of the cell adjacent the pad of molten aluminum, and a layer of refractory hard metal bonded to said block, covering the inner terminal end thereof and disposed in contact with the molten pad, the thickness of said layer being substantially less than the thickness of said block.

References Cited in the file of this patent

UNITED STATES PATENTS

2,593,751	Grolee	Apr. 22, 1952
2,797,460	Whitfield	July 2, 1957
2,806,272	Craver	Sept. 17, 1957
2,846,388	Morel	Aug. 5, 1958
2,866,743	Schmitt	Dec. 30, 1958
2,915,442	Lewis	Dec. 1, 1959
3,028,324	Ransley	Apr. 3, 1962

FOREIGN PATENTS

902,611	France	Dec. 22, 1944
462,364	Italy	Mar. 13, 1951
784,696	Great Britain	Oct. 16, 1957
802,905	Great Britain	Oct. 15, 1958