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CATHODE CONSTRUCTION FOR ALUMINUM PRODUCTION

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FIG. 1

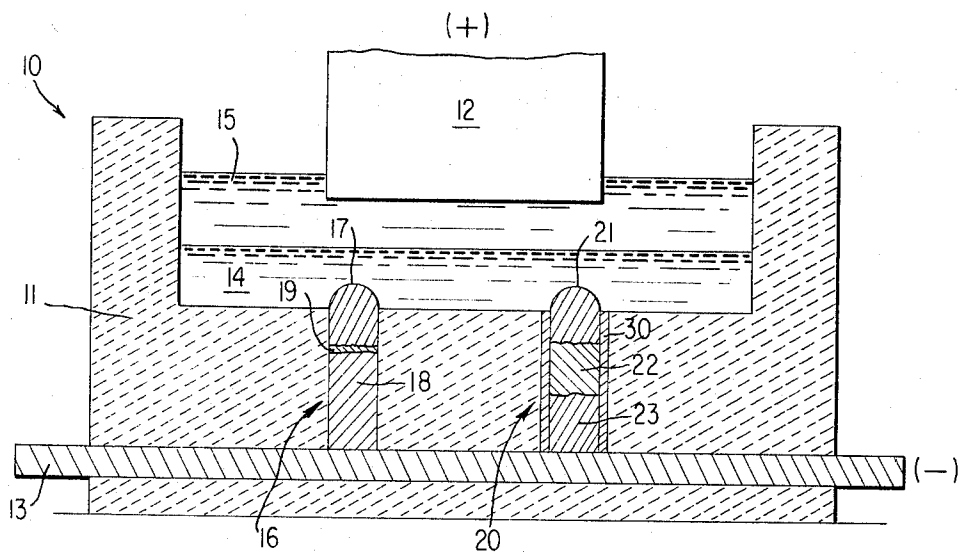
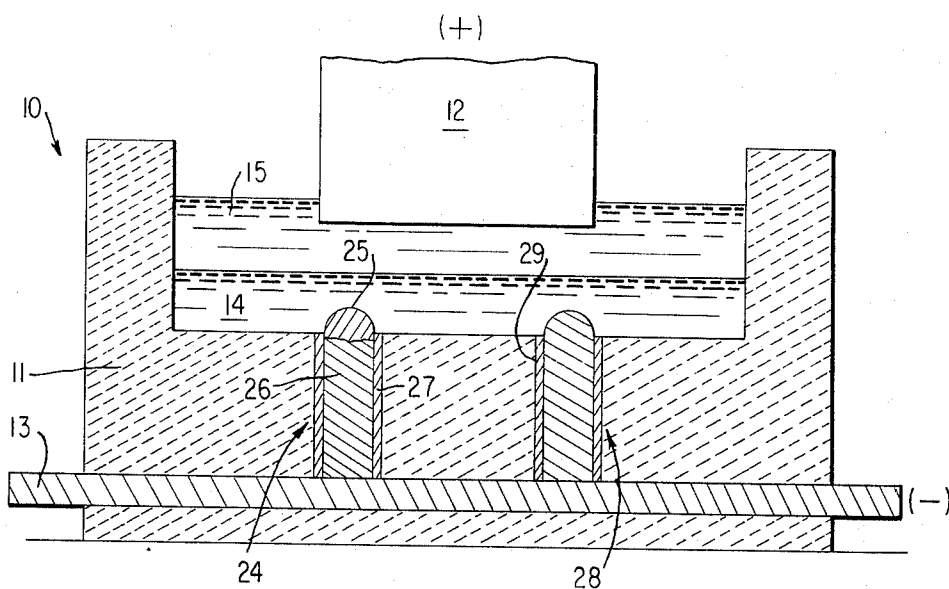


FIG. 2



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CATHODE CONSTRUCTION FOR ALUMINUM PRODUCTION

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This invention relates to improved electrode structures and more particularly to improved cathode structures finding significant utility in electrolytic cells used to reduce alumina to aluminum.

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 imbedded within the carbon to establish the necessary electrical connection.

Recently an improvement has been made in such reduction pots. This improvement has been disclosed and described in the application of John L. Dewey, Serial No. 847, 594, filed October 29, 1959 now Patent No. 3,093,570. Briefly, this application teaches forming a pot lining from a refractory oxide and cryolite. An important factor in the successful operation of this improved pot is the structure of the cathode employed therein. It has been proposed, for example, to employ titanium diboride and other refractory hard metal compositions for the portions of such cathodes which contact the pad of molten aluminum; and techniques have been developed for substituting less costly and less fragile materials, such as high-purity iron, for part of the cathode and for protecting the iron and diboride from corrosive effects.

The present invention relates to a cathode structure for use in a similar environment, but constituting an improved composition, as well as the method for manufacturing the same.

In general, it may be said that the collector bar constructed in accordance with the present invention is composed partially or completely of cermets. Cermets as such are well known and are formed by a combination of a metal and a ceramic. They have been used as cutting agents, abrasion-resistant parts, protective coatings for heating elements, resistors, etc. The term is used to designate compositions of matter comprising at least one metal component and at least one ceramic component such as carbides, nitrides, borides, silicides and oxides. Cermets possess utility due mainly to their high resistance to wear, corrosion, oxidation and thermal impacts.

In accordance with the present invention, the ceramic component of the cermet may be constituted of a refractory hard metal. The term refractory hard metal is intended in the present circumstances to encompass the class of compounds of carbides, nitrides, borides and silicides of the transition metals of the fourth through the sixth groups. A preferred ceramic is titanium diboride. The combination of this diboride with aluminum provides a cermet which has been found to have extremely desirable properties for use in collector bars.

In general, the collector bars constructed in accordance with this invention have a higher concentration of the ceramic constituent of the cermet in the cap portion, that

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is, the portion of the bar that contacts the molten metal pad and a higher concentration of the metallic constituent in the stem portion of the collector bar that is to be joined to the cathode voltage supply bus. Such a collector bar combines the desirable properties of the refractory hard metals and the cermets made therefrom for reduction cell use. The use of a cermet section between the cap portion and the stem portion eliminates difficulties caused by differential thermal expansion between these portions. This cermet section may be very short, approaching a diffused junction, or may make up the entire stem portion of the collector. High thermal shock resistance is also provided. Such collector bars have the capability of bending under stress rather than breaking and offer lower electrical resistivity than a bar composed entirely of the diboride material. Additionally, simple casting or welding techniques may be used for joining the bar to an aluminum or copper conductor. Efficiency of cost is achieved due to the decreased use of high priced titanium diboride.

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:

FIGURE 1 is a semi-schematic cross sectional view of an electrolytic alumina reduction cell showing two embodiments of a collector bar in accordance with the present invention; and

FIGURE 2 is a view similar to FIGURE 1 showing still further embodiments of such collector bars.

In FIGURES 1 and 2 like numbers refer to like elements. The pot 10 includes the lining 11, the anode 12, the cathode voltage supply bus 13, the molten aluminum pad 14, and the bath materials 15. Referring for a moment to FIGURE 1, the collector bar 16 includes a cap portion 17 of titanium diboride and a stem portion 18 consisting of metal. Interposed between the cap portion 17 and the stem portion 18 is a junction made of cermet and identified at 19.

Relative to the collector bar 20, also shown in FIGURE 1, the cap portion 21 is of titanium diboride and the stem portion is composed of a section 22 of cermet material and a metal section 23. A protective shield in the form of a sleeve 30 surrounds the stem portion. This sleeve forms a corrosion resistant shield around the collector bar and may be made of silicon-nitrate bonded silicon-carbide.

Referring to FIGURE 2, the collector bar 24 is composed of a cap portion 25 of titanium diboride and a stem portion 26 of cermet material. A protective corrosion resistant sleeve 27 similar to sleeve 30 in FIGURE 1 is provided as shown. The embodiment illustrated by collector bar 28 is entirely made of cermet material, the ceramic constituent of which is preferably graded as already discussed, and the protective sleeve 29 is similar to sleeve 27. All bars shown in these figures are mounted by any convenient means in electrical contact with bars 13, usually by casting or welding.

With particular reference to the collector bar 20 shown in FIGURE 1, there are at least two methods by which this collector bar may be made. According to the first method, the titanium diboride cap portion 21 is prepared by ordinary techniques, such as hot-pressing. Next, a mixture of titanium diboride grains and aluminum powder is placed in a mold with the titanium diboride cap and fired to approximately 1200° C. in a vacuum or inert atmosphere. In order to form a stem portion 22 which is graded from a high percentage of titanium diboride at the

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end to be joined to the cap portion to a low percentage thereof at the end to be joined to the aluminum section 23, the composition of the powder is graded from near-pure titanium diboride at the upper end to near-pure aluminum at the lower end. Finally, the aluminum end of the bar, section 23, can be joined to the lower end of the cermet section 22 by simple welding techniques to complete the collector bar.

The second and preferred method of manufacturing the collector bar 20 is as follows: A cold-pressed bar of titanium diboride with a density gradient is prepared by pressing powder with a particle size variation from one end to the other. The end of the bar that is to be the more dense is made, for example, from 30 percent 1-2 micron size particles and 70 percent 20-30 micron size particles and the percent of the small particles is increased substantially uniformly to 100 percent at the end where lower density is desired. Five percent cellulose (Methocel) binder is added for cold strength. The powder is cold-pressed in a mold at about 15,000 p.s.i. The pressed titanium diboride is then placed in a mold, of which the protective sleeve 30 may form a part, on top of a piece of dense titanium diboride which functions as the cap portion 21, and with the more dense end of the pressed piece downward. An aluminum slug approximately equal in weight to the pressed powder section is placed on top of this latter section and the assembly is heated in a furnace to approximately 1200° C. until the aluminum has drained downward into the pre-pressed diboride. The aluminum upon impregnating the cold-pressed titanium diboride piece will form the cermet and also wet the dense titanium diboride portion, joining the two together. Finally, the aluminum portion 23 of the bar is cast to the cermet and the furnace allowed to cool.

The collector bar 24 of FIGURE 2 may also be made in accordance with the methods outlined above, without the final step. By proper grading, the lower portion of the collector bar which joins the bus 13 has a high percentage of aluminum.

With regard to the collector bar 28 in FIGURE 2, either method outlined above may be employed. A separate cap portion is not required, however, and the final step may also be omitted. Again, the cap portion can be made to be highly concentrated in titanium diboride and the lower end contacting the bus 13 may be made to have a high concentration of aluminum.

Relative to collector bar 18 in FIGURE 1, the cap portion 17 of dense-pure titanium diboride is joined to the stem portion 18, rich in aluminum, by a diffused junction of cermet material by heating the cap and stem portions in contact with the cermet to a temperature between 1100 and 1500° C.

For the purpose of illustrating certain desirable properties of collector bars made in accordance with the invention, an aluminum-titanium diboride cermet was made by the following method:

A cold-pressed pellet of titanium diboride was made by mixing titanium diboride powder and a binder of Methocel in 95:5 proportions and pressing the mixture at 15,000 p.s.i. The resulting 1½" diameter by 1" long pellet was heated to remove moisture and then placed in an aluminum cup. The pellet and cup were heated to 1500° C. in a graphite crucible under an argon atmosphere to produce a pellet having grains of titanium diboride in a matrix of aluminum. It appeared that the cermet made in accordance with this procedure was approximately 50 percent aluminum. At a temperature of 1000° C. the sample did not slump or melt but was malleable, a hammer blow leaving an indentation in the sample. The cermet had an electrical resistivity of 9.7×10^{-6} ohm-cm. at 50° C. and 13.8×10^{-6} ohm-cm. at 250° C.

The properties of this cermet are distinctly different from either aluminum or titanium diboride. For example, the electrical resistivity of a titanium diboride pellet

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pressed in the manner described above and then baked at 1500° C. without impregnation with aluminum was 209×10^{-6} ohm-cm. at 250° C. and the electrical resistivity of pure aluminum is 3.8×10^{-6} ohm-cm. at 250° C. In addition, aluminum melts at 660° C. and pure titanium diboride is not malleable but instead is very hard and brittle. As stated above, the cermet did not melt at 1000° C. but was malleable at this temperature.

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. An electrolytic cell for the production of aluminum, including a cathode construction comprising a collector bar having a surface adapted for contact with the molten contents of the cell and a stem portion adapted for connection to a cathode voltage supply, said stem portion of the collector bar comprising a section of cermet material having a metal component and containing a refractory hard metal ceramic constituent, said metal component being distributed substantially throughout the cermet, the proportion of said refractory hard metal constituent relative to the metal component of the cermet being graded lengthwise of that section.

2. Apparatus according to claim 1, wherein said contact surface of the collector bar is provided by a cap portion which consists principally of refractory hard metal, and that section of said stem portion adjoining the cap portion is composed of the cermet material.

3. Apparatus according to claim 1 wherein said contact surface of the collector bar is provided by a cap portion which consists essentially of refractory hard metal and said stem portion consists essentially of the cermet material, the ceramic constituent of said cermet being in greater concentration adjacent said cap portion than at the opposite end of the stem portion.

4. An electrolytic cell for the production of aluminum, including a cathode structure comprising a composite collector bar including a cap portion having a surface adapted for contact with the molten contents of the cell and a stem portion adapted for connection to a cathode voltage supply, said stem portion having a metallic section joined to said cap portion by an intermediate section consisting essentially of cermet material having a refractory hard metal ceramic constituent, the proportion of said refractory hard metal constituent being graded from a relatively high concentration adjacent said cap portion to a lower concentration adjacent the metallic section, and said cap portion consisting essentially of refractory hard metal.

5. An electrolytic cell according to claim 4, wherein the metallic section of said stem portion consists of the metallic constituent of said cermet.

6. An electrolytic cell according to claim 4, wherein the ceramic constituent of said cermet is titanium diboride and the metallic constituent is aluminum.

7. An electrolytic cell for the production of aluminum, including a cathode construction comprising a composite collector bar having a refractory hard metal cap portion providing a surface adapted for contact with the molten contents of the cell and a stem portion adapted for connection to a cathode voltage supply, at least that section of the stem portion adjoining said cap portion consisting essentially of a malleable cermet material having approximately equal quantities of a metal component and refractory hard metal as the ceramic constituent, the cermet having a greater proportion of said metal component relative to its ceramic constituent than the refractory hard metal cap portion is capable of absorbing by contact with molten aluminum.

8. An electrolytic cell according to claim 7, in which the ceramic constituent of said cermet material includes titanium diboride.

9. An electrolytic cell for the production of aluminum, including a cathode construction comprising a collector

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bar having a surface adapted for contact with the molten contents of the cell and a stem portion adapted for connection to a cathode voltage supply, said collector bar consisting essentially of a cermet material having a metal component and refractory hard metal as the ceramic constituent, the proportion of said refractory hard metal constituent relative to the metal component of the cermet being graded lengthwise of the collector bar, that portion of the collector bar providing said contact surface having a high concentration of the refractory hard metal constituent, at least a part of said stem portion comprising a more malleable section of the collector bar having a higher concentration of said metal component than the aforesaid contact portion of the collector bar.

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References Cited by the Examiner

UNITED STATES PATENTS

2,904,863	9/1959	Schmid	22—202
3,009,870	11/1961	Helling et al.	203—243
3,028,324	4/1962	Ransley	204—294
3,161,579	12/1964	Henry et al.	204—243
3,186,044	6/1965	Ransley	22—202

FOREIGN PATENTS

868,031	2/1953	Germany.
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