

United States Patent

Holliday

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[54] **REFRACTORY HARD METAL
COMPOSITE CATHODE ALUMINUM
REDUCTION CELL**

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[51] Int. Cl. **C22d 3/12, C22d 3/02, B01k 3/06**

[58] Field of Search **206/67, 243-247,
206/291**

[56]

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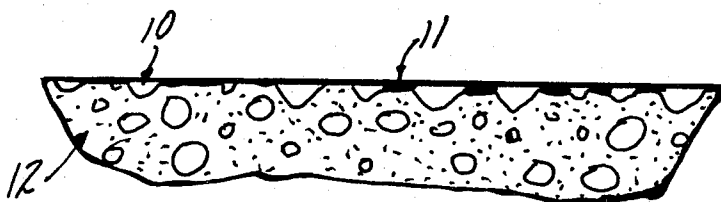
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[57]

ABSTRACT

The present invention is directed to cathodes of fused refractory hard metal alloy composited with certain bonding agents and their use, replacing the conventional carbon lining of an aluminum reduction cell.

15 Claims, 6 Drawing Figures



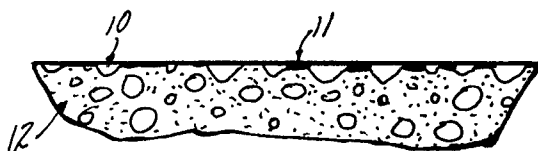


FIG-1

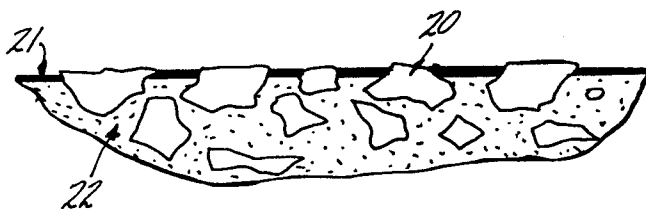


FIG-2

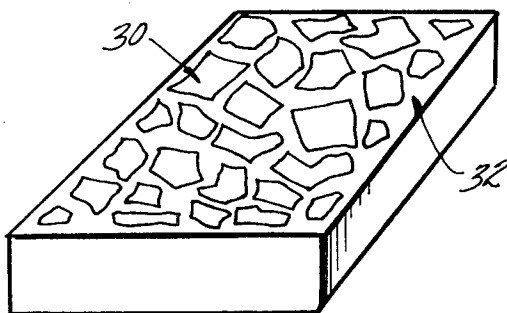


FIG-3

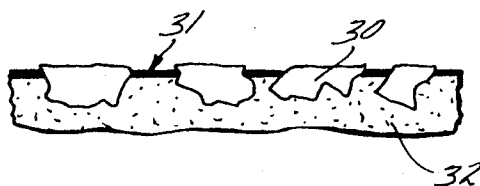


FIG-3A

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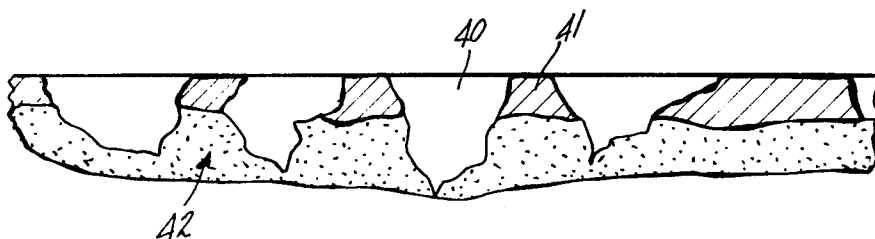


FIG - 4

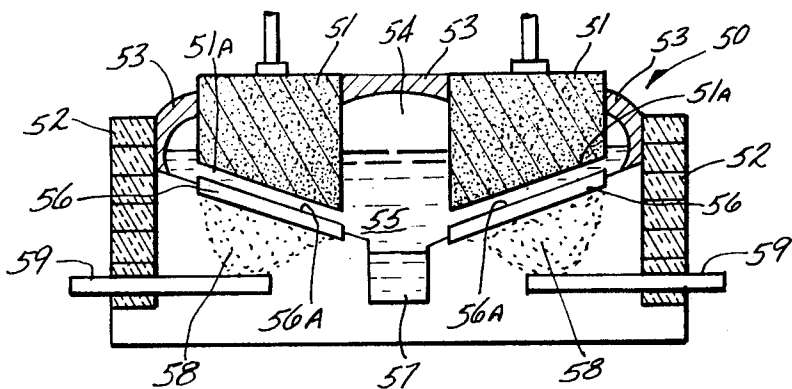


FIG - 5

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REFRACTORY HARD METAL COMPOSITE CATHODE ALUMINUM REDUCTION CELL

Application of refractory hard metals such as TiB_2 -TiC alloys in aluminum reduction cells has been previously considered to require "structural members" such as rods, bars, etc. Successful use of such members requires bodies having high-strength and high density. Such bodies have been previously considered to be fabricable only by hot-pressing.

It has proved extremely difficult to achieve the necessary high level of mechanical properties in conjunction with the stringent control of chemical composition essential for avoiding specific severe forms of corrosion.

Such materials have previously been considered for use in reduction cells, but only in the form of self-bonded, hot-pressed shapes. Application has been restricted because of the difficulty and expense involved in fabricating such shapes to meet the necessary stringent mechanical and composition requirements. See French Pat. No. 1,311,473.

According to the present invention it has been found that cathodes made of fused refractory hard metal composited with certain bonding agents can be used to replace the conventional carbon lining of an aluminum reduction cell.

Such composite cathodes combine the advantages of conventional carbon linings (structural integrity and relative cheapness) with specific basic property improvements conferred by the presence of a refractory hard metal phase. These improvements are (1) wettability by molten aluminum, (2) low overvoltage for aluminum deposition from cryolite, (3) extremely low solubility in molten aluminum-cryolite systems, (4) freedom from penetration by aluminum-cryolite, when prepared in such a way as to minimize deleterious impurity effects and (5) good electrical conductivity.

The requirements of composition control are met in the present invention by employing refractory hard metals, preferably TiB_2 -TiC alloys, which have been purified by arc melting under controlled conditions, as described in my copending application, Ser. No. 822,705, filed May 7, 1969. The amount of TiC in the alloy may vary over a wide range, for example, from 10 to 50 percent by weight.

This combination of properties makes it possible to use such composites as solid monolithic cathodes on which Al ions may be deposited directly. If the aluminum is allowed to run off as it deposits and is collected in a suitable receptacle in the cell, then many disadvantages of the Hall cell system are by-passed.

The cathodes of the present invention make possible an enormous improvement in the performance of reduction cells. Specifically, a 50 percent reduction in anode-cathode distance is feasible when the molten aluminum pool which now functions as cathode is replaced by a solid, wettable cathode block. Such a reduction in anode-to-cathode distance proportionately reduces the interelectrode voltage drop. The voltage savings may be utilized to obtain an increase of approximately 40 percent in current density, with an equivalent increase in output of metal from the cell.

Refractory hard metals and alloys prepared in this way may be used as "structural members," if desired, but the particular purpose of the present invention is to reveal their application in the form of composite bodies. For this purpose it is no longer necessary to consider large, self-bonded structural shapes of high mechanical integrity. Instead, fractured lumps, pieces and even small particles of refractory hard metal alloys may be employed. The refractory hard metals may be composited with bonding agents, such as graphite with pitch or other carbonaceous binders. For such use, adherence to strict specifications for mechanical strength and impact strength is no longer necessary since mechanical support is provided by the carbon, or other electrically conducting matrix. The process of fabricating the composite bodies may be similar to that for manufacture of carbon anodes, both in technique and in costs.

Thus, particulate refractory hard material ranging from pass 100 mesh to above 4 mesh on the Tyler screen system may be prepared by casting, for example, an alloy of TiB_2 with 40 per-

cent TiC in arc furnaces of known construction equipped to directly produce the desired range of particle sizes by suitably dispersing and chilling the melt.

The resulting particulate grog may then be blended with graphite powder of the same general particle size distribution range in conventional mixing apparatus.

The proportion of carbon or graphite to refractory hard metal grog can vary widely, over the range 2 to 50 volume percent refractory hard metal. When the size of the RHM particles and the graphite or carbon particles is essentially the same, it can be shown that the percentage of exposed RHM surface area in the resulting carbon-bonded composite equals the volume percentage of the refractory hard metal component. To minimize material costs, the proportion of RHM to carbon should be the minimum needed to impart the desired electrochemical properties to the composite.

After addition and blending of pitch or other form of binder is carried out, the resulting blend can be cold pressed into green bodies. These bodies may then be sintered using, for example, conditions similar to those adopted in preparing anode carbon blocks for the Hall process. In essence, the conditions provide for a gradual increase of temperature over an extended time period until a maximum near $1,100^\circ C$ is reached. This brake is followed by a slow cool.

The method of fabricating composites of this type is, of course, not restricted to a blending-sintering type operation. Hot-pressing of an arc melted refractory hard metal alloy-carbon mixture may be employed. Alternately, an alloy of refractory hard metal with carbon can be produced directly in the arc furnace. Further, hot isostatic compaction can be used in apparatus conventional for this process.

The resulting carbon-RHM composites show a particularly desirable combination of properties. The refractory hard metal component functions as an equipotential surface on which deposition of aluminum ions occurs preferentially, i.e., the refractory hard metal forms the electrochemically active part of the composite system. The carbon matrix provides mechanical support for the wettable RHM surface, and in addition, permits electricity to be conducted from the RHM dominated surface to current collector bars such as are now used with conventional carbon linings.

It is postulated that the carbon fraction of the surface of the composite electrode becomes protected by an aluminum carbide layer. The high overvoltage for aluminum and sodium deposition and the inherent high electrical resistivity of the aluminum carbide cooperate to make it immune from further deterioration by aluminum or sodium once a protective layer forms. This aluminum carbide layer functions somewhat like the corrosion resisting oxide films on stainless alloys.

The invention will be better understood from referring to the drawings.

FIG. 1 is a schematic view showing the refractory hard metal-carbon-composite.

FIG. 2 is a view of another embodiment of the invention showing large chunks of refractory hard metal.

FIG. 3 is a perspective view of another embodiment of the invention and FIG. 3A is a typical section through FIG. 3.

FIG. 4 is a view of another embodiment of the invention.

FIG. 5 is a sectional view of an electrolyte cell according to the present invention.

The system of the present invention is depicted in FIG. 1. RHM fused-cast purified alloy particulate grog, having an electrochemically active surface is shown at 10. The surface layer 11, believed to be of Al_4C_3 , makes this region electrochemically inert and stable with respect to aluminum-cryolite. The supporting and conducting carbon matrix is shown at 12.

It is not necessary that composites be formed using only particles of RHM grog. In another embodiment of the invention shown in FIG. 2, large chunks of RHM alloy 20, ranging from one-fourth inch to several inches average diameter, may be embedded in a supporting carbon matrix.

In another type of composite shown in FIG. 3 and 3A, large chunks 30 of RHM alloy are cast to develop at least one reasonably flat side, and set in a conducting matrix to form a flagstone type surface. The surface layer 31 is shown in FIG. 3A.

It is not necessary that choice for the supporting matrix be restricted to carbon and graphite. Indeed, aluminum carbide may be used as a filler material. This is particularly suitable when relatively large chunks of RHM alloy are used in the flagstone type cathode. Moreover, either pure Al_4C_3 , old reacted reduction cell linings, or Al_4C_3 -NaF- AlF_3 mixture may be used.

Preferably, as shown in FIG. 4, a cathode of this type will consist basically of three components: (1) relatively large chunks of arc-melted RHM alloy 40, (2) a powdered filler 41 such as Al_4C_3 or similar material between the refractory hard metal chunks and, (3) a lower conductive layer 42, preferably carbon or graphite, forming a substrate layer providing electrical contact between the RHM surface and current collector bars of the cell.

A three-component composite of this type would be fabricated, for example, by cold-pressing followed by sintering, conditions being chosen to promote formation of a solid bond between aluminum carbide particles and between aluminum carbide and carbon.

It is also possible to achieve a satisfactory filler for a composite cathode by using aluminum carbide alloyed with materials such as TiC by arc welding.

Such a fusion process yields a mixed valency semi-conductor with a much higher electrical conductivity than aluminum carbide. In this case, use of a third component such as carbon is superfluous, and may be dispensed with.

In addition to carbon and aluminum carbide, other materials of the refractory hard metal class such as TiC and TiN or their alloys are also suitable for bonding the electrochemically active solid fused chunks of RHM alloy.

Clearly, there is no restriction on the size of composite shapes other than that imposed by size limits of apparatus needed for fabrication. For example, blocks may be fabricated in sizes of conventional bricks. Bonding of such bricks can be accomplished by means of conventional carbon pastes like those now used in reduction cells.

Also, a part of this invention is a reduction cell designed particularly suitable for using the composite cathodes of the type hereinbefore described.

As shown in FIG. 5 such a reduction furnace shown generally at 50 may comprise one or more carbon anodes such as 51 and roof or enclosure 53. A cell gas space 54 is found above the electrolyte 55. The RHM composite dry cathodes 56 are placed below the lower surface 51A of the anodes.

The sloped electrode surfaces 56A permit run-off of aluminum into accumulating chamber 57 and directional flow of anode gas to gas space 54.

The carbon supporting matrix for the RHM composite is shown at 58. The steel cathode current collector bars 59 are embedded into insulation 52 and supporting matrix 58.

As shown in FIG. 5, the composite cathodes may be used in cells where the molten aluminum is drained from the sloping surface 56A as it is deposited, and accumulated in collection chamber 57 within the cell. The required slope of the wettable refractory hard metal surface is not large; a gradient of 1° to 10° is normally all that is needed to secure adequate removal of molten aluminum as it deposits. Obviously, however, a steeper slope can be used, such as the one shown in FIG. 5.

Such a design has the advantage of using an anode system identical to that presently used in present commercially operated prebake cells.

The composite cathode materials of this invention are not limited to installations in a near horizontal position. In one embodiment of the invention, composite cathodes may be ap-

propriately shaped for use in a vertical arrangement, either in cells using conventional cryolitic electrolytes, or in cells for electrolytic reduction of aluminum chloride.

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

What is claimed is:

1. A process for producing aluminum comprising providing an electrolyte in a cell with aluminum dissolved therein, providing at least one anode in said cell, providing at least one cathode in said cell, said cathode comprising refractory hard metal imbedded in an electrically conductive matrix said matrix selected from the group consisting of aluminum carbide and an arc melted material comprising aluminum carbide and titanium carbide wherein the particles of said hard metal are relatively larger than the particles of said matrix, passing electrical current between said anode and said cathode causing said alumina to react yielding aluminum ions, said aluminum ions depositing directly on said cathode.
2. A process according to claim 1 in which metallic aluminum runs off said cathode and is collected at a point other than at said cathode.
3. A process according to claim 2 in which said aluminum flows by gravity from said cathode to a separate collection receptacle within said cell.
4. A process according to claim 1 wherein said refractory hard metal comprises an arc melted material comprising titanium boride and titanium carbide.
5. A process according to claim 1 wherein said matrix comprises aluminum carbide.
6. A process according to claim 1 wherein said refractory hard metal is at least 0.25 inch average diameter.
7. A process according to claim 1 wherein said matrix comprises an arc melted material comprising aluminum carbide and titanium carbide.
8. Apparatus for producing aluminum comprising means for confining a molten electrolyte containing alumina, at least one anode contacting said electrolyte, at least one cathode contacting said electrolyte, said cathode comprising a composite of refractory hard metal imbedded in an electrically conductive matrix said matrix selected from the group consisting of aluminum carbide and an arc melted material comprising aluminum carbide and titanium carbide wherein the particles of said hard material are relatively larger than the particles of said matrix, means for causing electrical current flow between said anode and said cathode whereby aluminum ions are deposited on said cathode.
9. Apparatus according to claim 8 in which means are provided for continually removing and collecting metallic aluminum from said cathode.
10. Apparatus according to claim 9 in which the means for removing aluminum from said cathode is means which support said cathode on an incline.
11. Apparatus according to claim 8 in which said means for collecting is a chamber within said cell.
12. An apparatus according to claim 8 wherein said refractory hard metal comprises an arc melted material comprising titanium boride and titanium carbide.
13. An apparatus according to claim 8 wherein said matrix comprises aluminum carbide.
14. An apparatus according to claim 8 wherein said refractory hard metal is at least 0.25 inch average diameter.
15. An apparatus according to claim 8 wherein said matrix comprises an arc melted material comprising aluminum carbide and titanium carbide.

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