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3,267,183

METHOD OF LINING AN ALUMINUM
ELECTROLYTIC CELL

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1 Claim. (Cl. 264—30)

This invention relates to the application of a refractory lining into a furnace or electrolytic cell of the type used for the preparation of aluminum, e.g., reduction or refining cell. More particularly, the invention relates to the application of an alumina-cryolite refractory lining therein.

Conventional electrolytic cells such as the type used for the preparation and production of aluminum typically employ rammed carbon bottom lining. Such cell lining are applied by disposing a powdered carbonaceous material onto the bottom shell of the electrolytic cell and ramming the powdered mixture into place to compress the carbonaceous material. Thereafter, the carbonaceous lining is fired in place prior to startup of the electrolytic cell.

The reason carbonaceous material has been selected for refractory linings of electrolytic cells is that the operation of conventional electrolytic cells requires a lining material which is electrically conductive and actually forms a part of the electrical system but also is resistant to molten aluminum and molten cryolite. With the discovery of suitable non-carbonaceous cathodic current conducting materials for use in electrolytic cells it was discovered that other refractory materials could be advantageously employed in such cells. Patents 3,028,324 to Ransley and 2,915,442 to Lewis disclose electrolytic cell designs employing refractory hard metal elements. In a copending application filed on this date in the name of A. C. Byrns, S.N. 271,210, an electrolytic cell prepared for use in the preparation of aluminum is disclosed which comprises refractory hard metal current conducting elements in combination with an alumina-cryolite bottom cell lining.

The present invention includes the production and application of an alumina-cryolite lining for use in electrolytic cells of the type described. According to one preferred embodiment of the invention, alumina and cryolite lining material is applied by first preparing a mixture of molten cryolite and alumina and casting the mixture into a desired form for use in the cell. The molten cryolite and alumina mixture can be cast into the form of blocks, and the shell of the cell thereafter lined with the blocks, or the lining can be formed in situ by casting the molten mixture into the cell bottom. An alternative embodiment is to place alumina material on the cell bottom and thereafter pour molten cryolite over the alumina material so as to penetrate and fill the pores of the alumina thereby forming an alumina-cryolite mixture and providing a hard, dense surface upon cooling and solidifying.

The refractory cell lining material according to the invention can be used to line the sides as well as the bottom of the cell. Thus, the alumina-cryolite refractory mixture can be used for lining the bottom, the bottom and sides or lining only the bottom and a portion of the sides. In all cases, however, the alumina-cryolite mixture should be used to line at least the bottom of the cell.

Material for electrolytic cell linings has been prepared containing at least 10% cryolite, the balance comprising alumina. Although advantages of the invention are obtained throughout a wide range of relative proportions of alumina and cryolite, the preferred range, according

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to the invention, involves a proportion of 20 to 75% cryolite, the balance alumina, with or without minor amounts of additives. In addition, the proportion of alumina and cryolite may vary within the lining itself from the molten material contacting surface to the containing shell structure of the electrolytic cell. Thus, the proportion of alumina may increase away from the molten material contacting surface with the higher concentration of cryolite appearing at the lining surface contacting the molten materials. Cryolite useful according to the invention generally includes all the alkali metal cryolites such as sodium or potassium cryolite and those chemical compounds generally regarded as having the formula $3XF \cdot AlF_3$ or X_3AlF_6 where X is an alkali metal. The alumina used is preferably Bayer alumina but may, of course, be any suitable form.

It has been found that molten material contacting the surface of the cell bottom lining is fused or sintered. Thus, in the cell beneath the molten constituents the alumina-cryolite refractory lining surface is a hard, dense material which is relatively impenetrable. Penetration of the molten material from the electrolytic cell into the lining is minimized and an additional advantage of the invention results from the fact that little of the aluminum or costly electrolyte additives will be lost through undue penetration of the lining. If, according to recent developments, a lithium additive is used in the electrolyte to improve cell operation, its loss into the lining will be minimized.

It may be desirable on occasion to include additives in the alumina-cryolite lining material for binders, etc. Among the additives which can be included are minor amounts of refractory oxides, such as titanium oxide or aluminates, such as calcium aluminate.

A refractory lining which can be made according to the invention may comprise a solidified alumina-cryolite mass. If the molten solution of alumina and cryolite is rapidly cooled the solidified product is a vitreous material comprising a supersaturated solution of alumina and cryolite. If the molten solution is cooled slowly some of the alumina will precipitate out of the alumina and cryolite solution and the refractory mass will comprise particles of alumina in a matrix of frozen alumina-cryolite solution.

Upon installation of the refractory material into a cell structure as a lining therefor, the molten material contacting surface of the lining is present as a hard, dense, relatively impenetrable layer. If the molten solution of alumina and cryolite is cast into the form of blocks of desired configuration, the blocks can then be used to line the bottom of the cell structure. The blocks can be "cemented" together by additional alumina-cryolite material or through the use of calcium aluminate or other binder substances. The entire molten material contacting surface can thereafter be sealed by pouring molten cryolite or additional molten alumina-cryolite mixture over the lining, if desired. Alternatively, as discussed above, the molten alumina-cryolite mixture can be cast in place in the cell bottom, forming a refractory lining therefor in situ. It is also understood that the molten alumina-cryolite solution can be cast into bottom lining in forms outside the cell, and after cooling the solidified nonporous mass can be placed in the cell or furnace for use in lieu of casting the mixture in place in the cell structure.

An additional technique which can be used instead of forming a molten cryolite-alumina mixture is to place the alumina into a desired form, either as blocks or as powder disposed in the bottom of the cell, and thereafter pour enough molten cryolite or molten alumina-cryolite mixture onto the alumina mass to fill all the voids and

form a lining of an alumina-cryolite mixture with a dense surface. The alumina powder can be compacted in the cell bottom by tamping or ramming in the manner that present-day carbon linings are installed. After compaction molten cryolite or refractory mixture can be poured over the surface to form an alumina-cryolite mixture.

It is understood that wherever cryolite is used herein, previously used or "spent" bath material which comprises a mixture of alumina and cryolite, can be used instead. This has the additional advantage of avoiding the necessity of subjecting the spent bath material to a cryolite recovery process, yet still allows full reuse of spent bath. Spent bath material itself, as stated, comprises a mixture of alumina and cryolite and other substances in relatively minor amounts. Similarly, spent or used lining material can be used for the alumina component of refractory mixture. It is economically desirable to employ larger proportions of alumina than cryolite in the lining.

An additional advantage accrues from practice of the invention by virtue of the fact that spent lining material can also be reused either as cell feed or to produce additional lining for the cells. Thus, when it is desired to cease cell operation to replace structural components, etc., the lining which comprises a mixture of alumina and cryolite can be readily processed, e.g., ground to suitable size, for cell feed or can be utilized in the production of new lining material.

The following examples are provided to illustrate various embodiments of the invention:

A heating vessel is filled with spent bath material comprising 90% sodium cryolite, 6% alumina and 4% fluorspar. The vessel is heated to melt the bath material and preheated Bayer process alumina is introduced into the molten bath. The composition is adjusted so that the resulting alumina-cryolite mixture contains 35% cryolite and 65% alumina. The molten refractory mixture is poured into refractory block forms and cooled. The term "cooling" as used in the specification and claims includes all techniques which result in a lowering of the temperature and solidification of the refractory mixture. Thus, cooling can either be accelerated or the mixture can merely be allowed to cool by exposure to lower ambient temperatures. The blocks of alumina and cryolite are glassy in appearance with only minute amounts of alumina particles scattered throughout a matrix of alumina-cryolite solution. The blocks are placed in the bottom of the electrolytic cell to form a lining therefor. Additional molten cryolite-alumina mixture is poured over the refractory blocks to cement the blocks together and fill the cracks and voids between blocks. In this way a hard, dense lining for the electrolytic cell is produced, which is substantially impervious to the molten material penetration by electrolyte and aluminum.

If a cell design is employed wherein the cathodic current conducting elements are extended through the bottom into the cell chamber, they can be placed in position and

alumina-cryolite refractory blocks or powder material disposed around the elements to line the bottom of the cell. The elements can be preheated prior to sealing the surface of the refractory blocks or densifying the refractory powder with additional molten cryolite-alumina material or binder.

In another example of the practice according to the invention Bayer process alumina in powdered form is deposited on the bottom of the cell wherein it is compacted into a lining of the desired thickness. Molten cryolite is then poured over the alumina lining wherein it penetrates the voids and mixes with the alumina. Some of the alumina is dissolved into the cryolite. Upon cooling, a cell lining is produced wherein the cryolite concentration decreases from the molten material contacting surface downward to the containing shell structure of the electrolytic cell.

According to still another embodiment of the invention an electrolytic cell lining is produced by forming a molten mixture of cryolite and alumina in a heated vessel in the proportion of 50% alumina and 50% cryolite. The molten material is heated until substantial dissolution of the alumina occurs and a supersaturated solution is formed. The molten cryolite and alumina mixture is then poured into the shell structure of the electrolytic cell and cast in place within the shell body. When the refractory mixture is cooled, some of the alumina precipitates out of solution and the result is refractory lining comprising tiny granules of Al_2O_3 dispersed in a matrix of solidified alumina-cryolite solution.

It is apparent that various changes and modifications in the invention may be made without departing from the spirit thereof. Accordingly, the scope of the invention should be limited only by the appended claim, wherein what is claimed is:

A method of making a lining for use in an electrolytic cell for the preparation of aluminum, comprising disposing alumina in the bottom of an electrolytic cell, applying molten cryolite onto the surface of the alumina so as to penetrate said alumina and form a cryolite-alumina solution at least at the surface thereof, and cooling said alumina-cryolite solution so as to form a hardened bottom lining surface for said electrolytic cell.

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