

June 11, 1963

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REFRACTORY LINING FOR ALUMINA REDUCTION CELLS

Filed Oct. 20, 1959

3 Sheets-Sheet 1

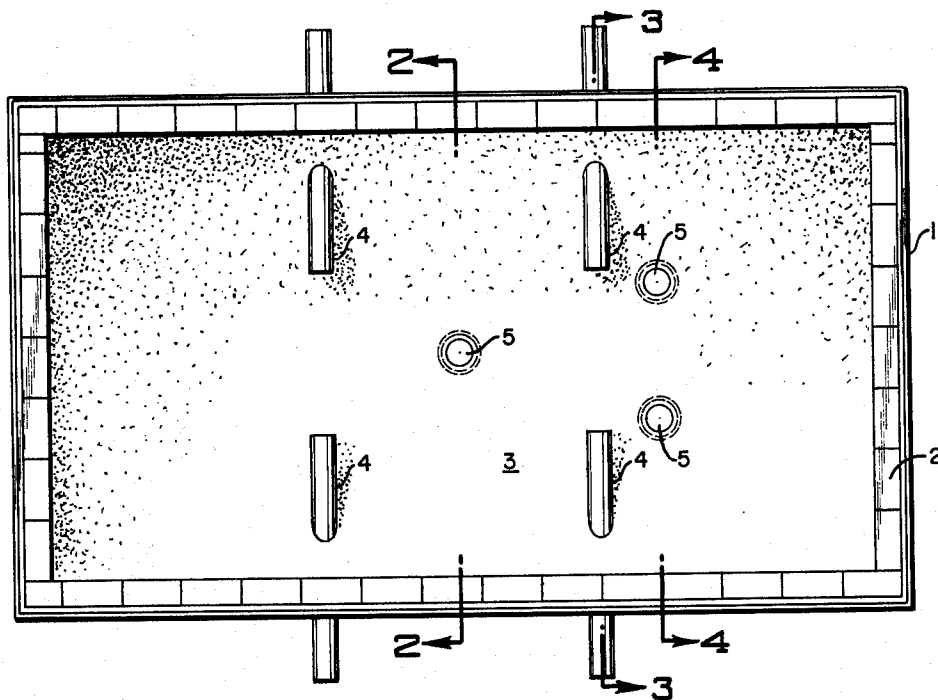


FIG. 1

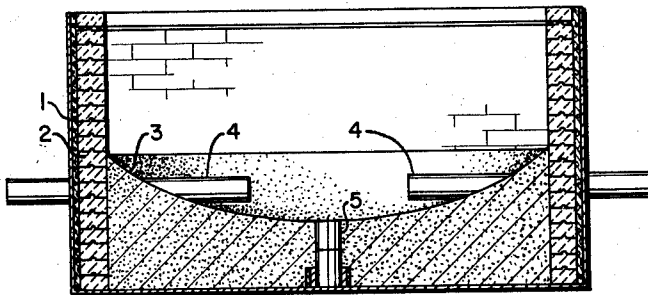


FIG. 2

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3 Sheets-Sheet 2

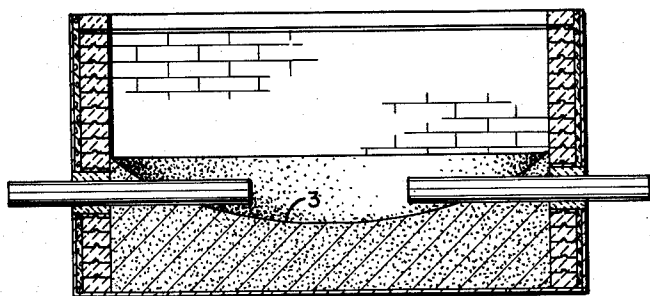


FIG. 3

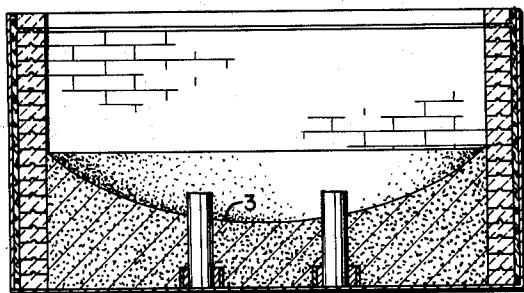


FIG. 4

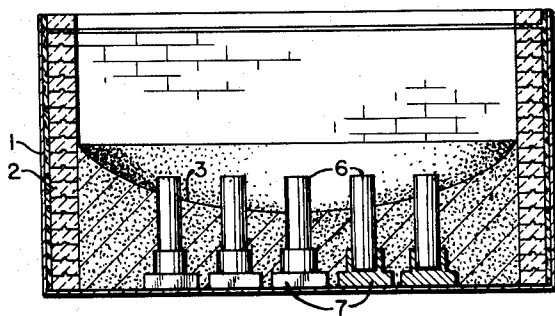


FIG. 5

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3 Sheets-Sheet 3

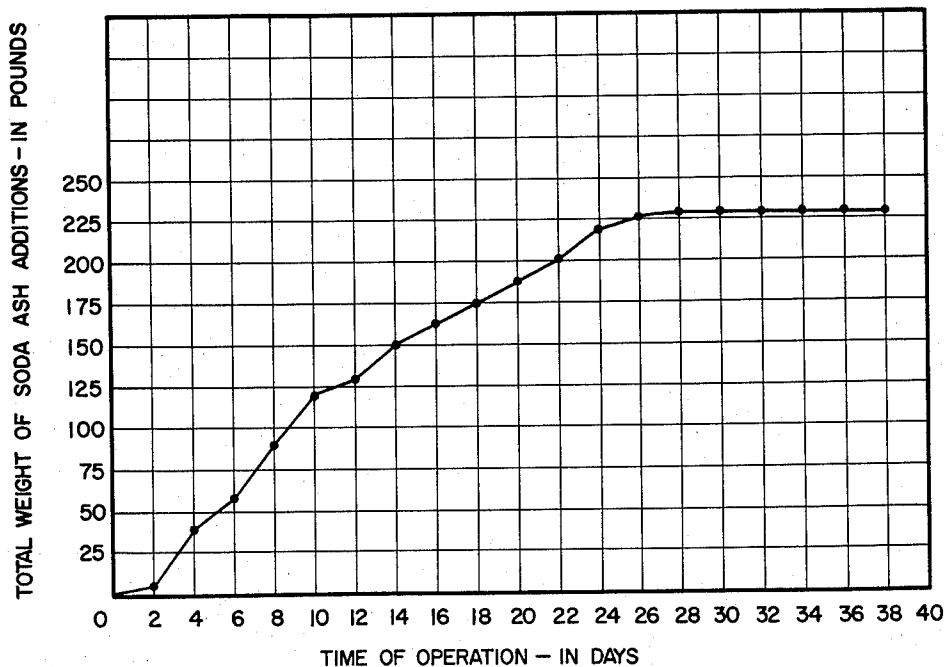
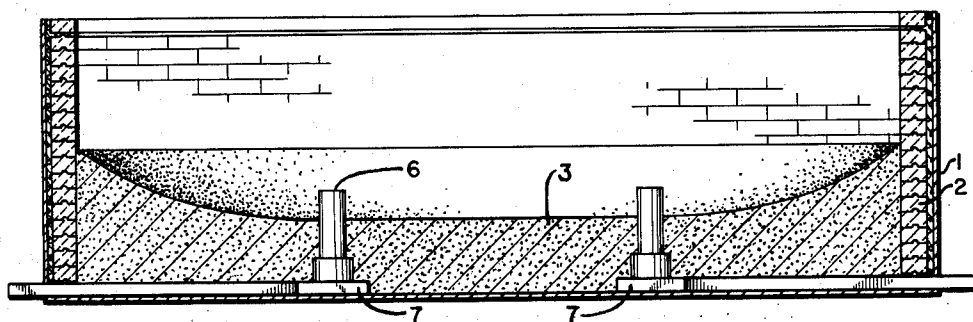


FIG. 7

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REFRACTORY LINING FOR ALUMINA
REDUCTION CELLS

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16 Claims. (Cl. 204-243)

The invention relates to refractory linings for electrolytic cells used in the production of aluminum, for aluminum melting furnaces and other purposes.

From the beginning of the aluminum industry to the present time, the metal has been produced in electrolytic cells or "pots" lined with carbon. The carbon linings are initially expensive and they are short-lived. The need for frequent repairs and replacement represents a significant maintenance and operating burden, and overhead costs are increased in direct proportion to the length and frequency of the periods when the pots must be shut down for lining work to be done. In spite of all this, none of the industry's experts has been able to discover any commercially feasible way of eliminating these burdens, and the production of aluminum has continued throughout the years seemingly wedded inseparably to the idea that carbon linings are indispensable.

Such linings constitute semi-permeable electrically conducting membranes. Molten salts from the electrolytic bath, particularly molten cryolite, seep through the carbon into the insulation beyond, where the freezing and growth of crystals create tremendous expansion forces. These forces are of such magnitude that unless the steel walls of the outer cell of the pot are stoutly braced they will bow outwardly. To resist these forces it is usual to brace the cell walls with large I-beams and/or massive concrete abutments. Such bracing increases the cost of construction, representing a further burden attributable to the use of a semi-permeable pot lining such as carbon. And even with such a massive system of bracing, experience in the United States has been that the useful life of a pot will not average much over three years.

Another problem encountered in the use of carbon linings has been the formation of aluminum carbide. This results in some loss of aluminum and it represents another cause of deterioration of the lining. Aluminum carbide has a lower electrical conductivity than the carbon, and where it is desired to pass electrical current through the membrane for the collection and removal of current from the cathode area, as is customary in fused salt cells and particularly in cells for the production of aluminum, the increase in electrical resistance brought about by carbide formation both within and on the surface of the carbon mass will in time cause such a loss of power as to seriously affect the economics of cell operation. The above and many other factors, the scientific reasons for which cannot even be conjectured, cause the cell to become economically inoperative in a relatively short period of time. In order to eliminate the need to pass electrical current through the carbon and so escape one deleterious effect of using a carbon lining, it has been proposed to use current collectors made of materials which have good electrical conductivity yet which are resistant to attack by constituents of the electrolytic bath, such as borides, nitrides and carbides of elements found in groups 4, 5 and 6 of the periodic table and particularly compounds of titanium and zirconium. However, current collectors made of these materials when used in conjunction with a carbon lining do not overcome the other disadvantages of such a lining nor eliminate the expansion problem. I have found that an alumina reduction cell, operated with titanium diboride current conductors extending into the aluminum metal layer in the bottom of the cell and so insulated with silicon nitride materials

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as to preclude flow of electricity within the carbon diaphragm, shows a rate of absorption of bath materials through the membrane with an attendant rate of increase of expansion forces at least equal to and possibly greater than has been found when electrical current is forced to flow downwardly through the carbon. Such conditions make it difficult to maintain intact for any appreciable length of time such brittle materials as borides, nitrides and carbides, by reason of the heaving, cracking and swelling of the cell components which cause shearing and cracking of current conductors made of such materials.

Thus it is the carbon lining itself which has all along been at the root of the several problems I have described. In the commercial production of aluminum the use of a carbon lining has seemed essential for a practical electrolytic cell operation. As an inevitable consequence, these problems have persisted to this day with only such alleviation as could be secured by improvements in structural details of pot construction, substitution of new types of current collectors and other expedients which have represented attempts to counteract the undesirable effects inherent in the use of the carbon linings. If the carbon lining itself could somehow be dispensed with in a manner which did not create other intolerable difficulties, perhaps the ideal answer would be at hand. But no such answer has been forthcoming, or at least none which has had any real practical merit, for the carbon lining is still with us.

Summary

However, I have discovered that there is indeed a way to eliminate entirely the need for a carbon lining in the alumina reduction cell. This desirable result is accomplished by making a special kind of lining consisting essentially of 20 to 75% of a refractory oxide, the balance essentially cryolite, such lining defining a chamber to hold the molten contents of the cell and providing a surface disposed in contact with substantially the entire lower surface of said molten contents. By making such a lining consisting essentially of alumina and cryolite we will have in one sense a lining which chemically consists of the same elements as are contained in the electrolytic bath. Yet I have found that when that lining is properly formed, its heat transfer properties are such that, although the material is soluble in the molten cryolite of the bath, sufficient heat can be removed from the sides and bottom of the cell by exposure to surroundings to maintain a satisfactory thickness of refractory lining. Nevertheless, the heat flow is not so great as to interfere with maintaining the working areas of the cell at a proper operating temperature. My refractory lining according to one of its preferred embodiments consists of a refractory oxide crystallized from a molten solution of refractory oxide in fluoride salts and contained in a matrix of a frozen fluoride salt. For instance, with alumina and sodium cryolite, alumina is first dissolved in molten cryolite at a high temperature. The solution is then cooled. On rapid cooling the material can be made to solidify into a glassy-like material which is a super-saturated solution of alumina in cryolite. On slower cooling some of the alumina precipitates from the super-saturated solution in the form of alpha and beta alumina imbedded in a solid solution of alumina and cryolite. I have found that these materials can be compacted and sintered into a very strong refractory body at temperatures comparable to those existing in the bottom of alumina reduction cells. When this material is granulated or pulverized, tamped into a reduction cell in pulverulent form and the cell is then placed in normal operation, the refractory sinters or fuses in a region extending from the molten zone inwardly into the bulk of the refractory but usually

not throughout the refractory. The operating surface of the lining is in the form of a hard, dense, solid having a gray color. The color may vary from dark to light, being characteristically a bluish gray.

According to the first part of my discovery as described in the preceding paragraph, I believed it was essential to perform the preliminary steps of first dissolving the alumina in the molten cryolite, cooling, and granulating or pulverizing before tamping the material into place in the reduction cell. However, after a considerable period of testing and development work it later occurred to me to try using a loose powder mixture of alumina and cryolite which had not been subjected to treatment according to the preliminary steps I have described. I was surprised to discover that this loose powder mixture will create a satisfactory lining in situ through normal operation of the pot in the reduction of alumina. This simplification is obtained by tamping the loose powder mixture of the alumina and cryolite into the reduction cell, and then placing the cell in operation to cause the mixture to sinter in a region extending from the molten zone inwardly of the refractory. I found further that this procedure permits using a higher proportion of alumina to cryolite with additional economy due to the relatively lower cost of the former ingredient.

Description

It is desirable to utilize materials for the refractory which are similar to those normally present in the molten electrolyte so as to avoid contaminating the electrolyte. All known refractory oxides such as alumina, magnesia, titania, zirconia, silica, beryllia, etc., are soluble to a considerable extent in molten cryolite and thus can be used in the manufacture of the refractory as herein described. However, only alumina is a normal constituent of the cell and hence it is the preferred refractory oxide for alumina reduction cell lining refractory. The cryolite component of the refractory may be comprised of one or more alkali metals selected from the group comprising sodium, potassium, lithium, rubidium, and cesium. By cryolite I refer to the group of chemical compounds commonly written as $3XF \cdot AlF_3$ or X_3AlF_6 , where X designates an alkali metal selected from the group comprising sodium, potassium, lithium, rubidium, and cesium. Maintenance of the exact mole ratio of the formula is not necessary. Some excess of either XF or AlF_3 is permissible.

I have prepared such refractory lining materials containing between about 20% and about 75% alumina, the balance being sodium cryolite. Throughout this range the refractory appears to reveal the beneficial properties which make it suitable for the purposes of my invention. However, when considering the increase in beneficial properties of the refractory, such as crushing strength, obtained by increasing the alumina content of the refractory, a preferred range of composition is disclosed as being between the limits of about 40% and about 75% alumina. However, somewhat greater or lesser amounts of alumina will be found useful under some conditions of operation and should still show considerable advantage over the carbonaceous materials currently in use.

Tests performed with electrolytic cells lined with materials prepared according to my invention for the production of aluminum have shown that the invention produces other dividends in addition to eliminating shell deformation and the further difficulties encountered with carbon linings. One of these other dividends is an observed, but unexplained, increase in current efficiency. A second is that when my improved lining is used it becomes unnecessary to make additions of soda ash to the cell during the reduction process.

In the drawings:

FIG. 1 is a plan view of an electrolytic alumina reduction cell provided with a non-carbonaceous bottom lining according to my invention.

FIG. 2 is a vertical transverse sectional view taken on line 2—2 of FIG. 1.

FIG. 3 is a similar view on line 3—3 of FIG. 1.

FIG. 4 is a similar view on line 4—4 of FIG. 1.

FIG. 5 is a vertical transverse sectional view of a cell of modified construction.

FIG. 6 is a vertical longitudinal sectional view of the cell of FIG. 5.

FIG. 7 is a graph depicting a representative history of soda ash additions to a cell having a carbonaceous lining but otherwise generally similar to the cells of FIGS. 1-6, particularly in respect of utilizing the same type of current collector bars, i.e. bars made of TiB_2 .

In FIGS. 1-4, I have illustrated an alumina reduction cell consisting of a steel shell 1 provided with suitable refractory side walls 2 and a tamped bottom lining 3 made from a high melting mixture of alumina and cryolite according to my invention. Cathode current collector bars 4 and 5 of TiB_2 are used in this cell.

The cell shown in FIGS. 5 and 6 is of similar construction, as indicated by use of corresponding reference numbers, but the arrangement of the current collector bars is a little different. Here the bars 6 are mounted in cast aluminum slabs 7 for connection to the electrical bus bar system of the pot room.

Preparation of the Refractory Lining

As a specific example to disclose the practice of my invention according to one of its preferred embodiments I cite the following:

A powder mixture is prepared consisting of 50% by weight of natural Greenland cryolite and 50% by weight of Bayer process alumina. The two ingredients are thoroughly mixed together in powder form. The mixture is placed in an induction furnace and heated until melted or to approximately $1350^\circ C$. The molten mixture is quickly cooled by pouring it into water or onto a steel slab. The cooled material will be opaque and exhibit a glassy appearance. If the amount of alumina in the original mixture is increased to, say, 60%, a substantial amount of granular material will show in the glassy matrix, suggesting a faster rate of crystallization of alumina from this material of higher alumina content. The cooled material is now passed successively through jaw and roll crushers until 70% by weight of the granulated material will pass through a 30-mesh screen. In a representative example, I found that the largest size particles were about $\frac{1}{8}$ " with the following batch analysis:

Percent	Mesh
20	—100
20	50-100
30	30-50
25	16-30
5	+16

The crushed material is moistened with water and tamped into place to form the bottom of the pot as at 3 in FIGS. 2-6. In this representative example the thickness of the bottom was made about 10" at the center and sloping upwardly to extend somewhat up the sides of the pot as shown. In FIGS. 1-3, the boride collector bars 4 which enter from the sides of the pot are caulked with a material formed by mixing together 85 parts by weight of my refractory composition and 15 parts by weight of calcium aluminate, with the addition of water to the consistency suitable for making cast refractory walls. Aluminum pigs are placed into the line pot in sufficient quantity to yield a molten pad of aluminum covering the boride bars. Next the cell is heated internally with a compressed air-gas flame. When the aluminum has all melted, the gas burner is removed, the anode put into place, an electrical contact made with the aluminum and the current turned on. Then an electrolyte consisting in

this example of 92% Greenland cryolite and 8% fluor-spar is melted by the heat generated in the pot. The pot is now ready for operation.

As another example of the practice of my invention according to an embodiment which is to be preferred in normal operation of alumina reduction plants, I cite the following:

A powder mixture is prepared consisting of 25% by weight of natural Greenland cryolite and 75% by weight of Bayer process alumina. The two ingredients are thoroughly mixed together in powder form. The resulting powder mixture is then tamped in place in the bottom of an alumina reduction cell as at 3 in FIGS. 2-6. As before, aluminum pigs are placed into the lined pot in sufficient quantity to yield a molten pad of aluminum covering the boride bars. Next the cell is heated internally with a compressed air-gas flame. When the aluminum has all melted, the gas burner is removed, the anode put into place, an electrical contact made with the aluminum and the current turned on. Then an electrolyte consisting in this example of 92% Greenland cryolite and 8% fluor-spar is melted by the heat generated in the pot. The pot is now ready for operation.

It will be observed that when my invention is practiced according to the example last described, a further simplification has been achieved. Not only is the lining produced from a mixture consisting of the same alumina and the same cryolite which are used as ingredients of the electrolytic bath, but in addition the operation of the reduction cell is utilized as the very means for completing the formation of the lining.

Refractory and Sintering Properties

The refractory bottom remains quite hard and is capable of retaining for long periods of time essentially the form it has upon installation. I have found it necessary from the first day of operation to continually add aluminum fluoride to maintain the desired bath composition. This is a condition not usually reached in conventional cells during the first sixty to ninety days while bath material is being absorbed into the carbon and insulation. It thus appears that little bath material has been absorbed into the insulation of my pot. This is true not only with respect to the pre-fused refractory, but also with respect to the lining made from a loose mixture of powdered alumina and cryolite, i.e. without melting and crushing. The cryolite absorbed into the powdered mixture becomes a part of the refractory lining so that we have in each case a refractory lining consisting essentially of alumina and cryolite. Following a forty-four day run, a pot constructed and lined in the manner first described was so dismantled as to allow the cross section to be viewed. Underneath the frozen bath material, the refractory lining was found to be substantially in the same form or contour as when installed. The top one inch of the refractory was observed to be fused or sintered to a hard, dense, light gray solid. The inch of refractory directly under this first layer was almost white and was sintered or hardened. Underneath these two distinct layers there was no evidence of bath penetration and the refractory material was white and soft. The part that was not loose could be crumbled easily. Another pot lined in the manner last described was dismantled following a sixty-seven day run and the lining examined as before. The appearance and characteristics of this lining were substantially the same as those of the first lining.

The pre-fused refractory, with calcium aluminate as a binder, used around the collector bars 4, remained hard and crack-free and was not penetrated by bath or aluminum. Lining material formed by melting together the refractory oxide and cryolite has good low temperature sintering properties. The mechanism of sintering is not well understood. It seems possible that the strength obtained on sintering the powder compacts was due to

a growth of interlocking grains of alumina formed by precipitation of alpha and beta alumina from a super-saturated solid solution of alumina in cryolite. This material being composed only of crystalline alumina in a cryolite-alumina solid solution matrix has a very high resistance to penetration and chemical attack by molten aluminum. It therefore should be useful in furnaces used for the melting, storage and alloying of aluminum. In addition, the gas-free nature of the molten material as demonstrated by the absence of blow holes in the chilled material, which may be due to the fluxing action of the cryolite, should permit the preparation of low porosity brick and other shapes by pouring the molten material into suitable molds and allowing it to solidify. Also, the granulated material molded with or without additions of binder such as calcium aluminate, is useful as self-healing, impenetrable bottom and side walls for aluminum melting furnaces. Material made by crushing linings removed from pots which have seen service in the production of aluminum can be crushed and re-used in melting furnaces with or without such additions of binder to the crushed material. The sintering and other properties desirable for such uses have been found to be present in the case of both the pre-fused linings and those made from a loose mixture of powdered alumina and cryolite.

Control of Electromagnetically Induced Metal Pad Rotation

For large pots at say 80,000 amperes and over, it may be desirable to maintain an essentially downward flow of the electrical current. The preferred method of obtaining this downward direction of the current is to extend the current collectors upwardly into the metal pad from the bottom. This arrangement provides the downward flow of current and also provides obstructions, or baffles as it were, which tend to hinder the rotation of the metal pad due to the electromagnetic forces without completely stopping such rotation. It can readily be shown from the known laws of mass and heat transfer, the diffusion of ions and particles, etc., and the known facts of the chemical changes during passage of electrical current through the electrolyte that a complete cessation of the rotation of the metal pad would be disadvantageous to the operation of the cell, particularly by causing an increase in the concentration overpotential in the region of the cathode. The rate of rotation of the metal pad may, by trial and error in the placing of upwardly extending collector bars, be tailored to a desired value for any particular size pot. Both the number and location of the bars extending upwardly into the metal pad, and where necessary those extending in from the side, may be changed to make desired changes in the rate of rotation and in the flow lines or lines of constant velocity, that is, the flow pattern of the rotating metal, in pots of any particular design.

Current Efficiency

Comparative tests have revealed that a significant increase in current efficiency can be secured with the use of my refractory lining. The results of these tests are here summarized:

Pot No.	Lining material	Collector bar material	Length of test, days	Current efficiency, percent
1	Carbon	Steel	38	79.3
2	do	do	68	82.1
3	do	TiB ₂	74	81.3
4	My refractory ¹	TiB ₂	44	88.8
5	do ¹	TiB ₂	23	90.8
6	do	TiB ₂	67	90.8
7	do	TiB ₂	28	90.6

¹ Pre-fused.

The data given in the above table show that current efficiency averaged about 9 percent higher in four cells provided with my refractory lining than has been normal in comparable cells with carbon linings. In pot No. 3, collector bars of TiB_2 were used in conjunction with a carbon lining. Thus a comparison of the current efficiency of this pot with that of pots Nos. 4 through 7, in which collector bars of the same material were used in conjunction with my refractory lining, can be made without regard to the effect of the use of the boride bars. This comparison would indicate that the increase in current efficiency is to be attributed primarily, if not entirely, to the use of my improved lining composition.

Soda Ash Additions

Soda ash was added to carbon-lined cells to replace sodium that is preferentially absorbed out of cryolite by the carbon linings. The cells without carbon linings did not require soda ash additions. The correct bath ratio, i.e.

$$\frac{\text{Wt. percent NaF}}{\text{Wt. percent } AlF_3}$$

was easier to maintain in these refractory-lined cells because of this property.

FIG. 7 shows the total amount of soda ash additions required to maintain the correct bath ratio over a period of 38 days in the operation of a representative cell having a conventional carbon lining. It has been found that sodium-rich bath material is absorbed preferentially by a carbon lining whether or not current is collected through the lining, thus requiring the soda ash additions for replacement of the material lost from the bath through such absorption. With the use of my invention the need to make such additions to the bath is completely eliminated.

Heaving, Cracking and Swelling

The expansion forces which are characteristics of carbon-lined pots are not noticeable when my improved refractory lining is used.

In conclusion, my invention provides a solution to the principal problems which have for so long been inseparably associated with the production of aluminum in carbon-lined pots; makes available a refractory of excellent sintering properties which will neither contaminate the bath or deplete it through absorption or selective penetration of the lining; yields a surprising and valuable increase in current efficiency; eliminates the need for soda ash additions to the bath; facilitates the use of collector bars of fragile materials which otherwise can be sheared off by movements of the cell lining; avoids the destructive expansion forces which produce heaving, cracking and swelling and shorten the service life of the pots; and makes it possible to dispense with the costly strengthening members heretofore required to resist such deformations.

The terms and expressions which I have employed are used in a descriptive and not a limiting sense, and I have no intention of excluding such equivalents of the invention described as fall within the scope of the claims.

I claim:

1. An alumina reduction cell having an interior lining defining a chamber to hold the molten contents of the cell and providing a surface disposed in contact with substantially the entire lower surface of said molten contents, said cell lining consisting essentially of 20 to 75% of a refractory oxide, the balance essentially cryolite.

2. An alumina reduction cell having an interior lining defining a chamber to hold the molten contents of the cell and providing a surface disposed in contact with substantially the entire lower surface of said molten contents, said cell lining consisting essentially of 20 to 75% of a refractory oxide, the balance essentially a cryolite comprising an alkali metal.

3. An alumina reduction cell having an interior lining defining a chamber to hold the molten contents of the cell and providing a surface disposed in contact with substantially the entire lower surface of said molten contents, said cell lining consisting essentially of 20 to 75% of a refractory oxide, the balance essentially a cryolite of the general composition X_3AlF_6 where X designates at least one alkali metal selected from the group comprising sodium, potassium, lithium, rubidium and cesium.

4. An alumina reduction cell having an interior lining defining a chamber to hold the molten contents of the cell and providing a surface disposed in contact with substantially the entire lower surface of said molten contents, said cell lining consisting essentially of 20 to 75% alumina, the balance essentially cryolite.

5. An alumina reduction cell having an interior lining defining a chamber to hold the molten contents of the cell and providing a surface disposed in contact with substantially the entire lower surface of said molten contents, said cell lining consisting essentially of 40 to 75% alumina, the balance essentially a cryolite comprising an alkali metal.

6. An alumina reduction cell having an interior lining defining a chamber to hold the molten contents of the cell and providing a surface disposed in contact with substantially the entire lower surface of said molten contents, said cell lining consisting essentially of 40 to 75% alumina, the balance essentially a cryolite of the general composition X_3AlF_6 where X designates at least one alkali metal selected from the group comprising sodium, potassium, lithium, rubidium and cesium.

7. An alumina reduction cell having an interior lining defining a chamber to hold the molten contents of the cell and providing a surface disposed in contact with substantially the entire lower surface of said molten contents, said cell lining consisting essentially of 40 to 75% Bayer process alumina, the balance essentially cryolite.

8. A lining for an aluminum cell comprising a pulverulent mixture comprised of 20 to 75% alumina, balance essentially cryolite, the operating surface of which is a fused layer of the same in the form of a hard dense, solid.

9. The method of making a lining for an alumina reduction cell which comprises the steps of preparing a molten solution of 20 to 75% of a refractory oxide in cryolite, cooling the molten mixture to produce a solid slution of the oxide in the cryolite, granulating the solid mixture and forming a refractory body from the granulated mixture.

10. The method according to claim 9 in which the forming of the refractory body from the granulated mixture comprises the steps of tamping the granulated mixture into a reduction cell and then placing the cell in operation to cause the mixture to sinter in a region extending from the molten zone inwardly of the refractory.

11. The method according to claim 9 in which the forming of the refractory body from the granulated mixture comprises the step of molding the mixture into the form of the refractory body.

12. The method according to claim 11 in which the molding step is performed with the addition of a binder.

13. The method of making a refractory body for use as a bath-contacting bottom lining in an alumina reduction cell which comprises the steps of preparing a molten solution of 20 to 75% of a refractory oxide in cryolite, and casting the molten mixture into desired form.

14. The method of forming a refractory lining in an alumina reduction cell which comprises the steps of preparing a mixture consisting essentially of 20 to 75% alumina, the balance essentially cryolite, in the form of powder, placing the mixture into a reduction cell and then putting the cell in operation to cause the mixture to sinter in a region extending from the molten zone inwardly of the refractory.

15. The method of making a refractory material which consists of preparing a refractory lining according to

claim 14, removing the lining from the cell following its operation to sinter the mixture, and crushing the lining.

16. The method of making a refractory body which comprises performing the steps according to claim 15, and the further steps of molding the crushed material into the form of the refractory body and sintering it. 5

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