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METHOD OF TREATING ALUMINOUS METAL WITH
CARBON AND ALUMINUM FLUORIDE
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FIG. 1

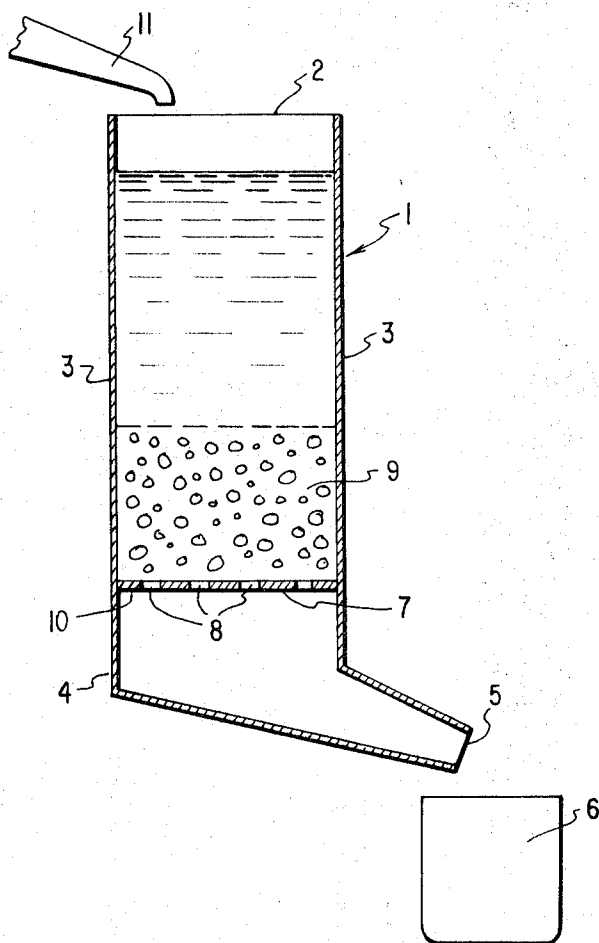
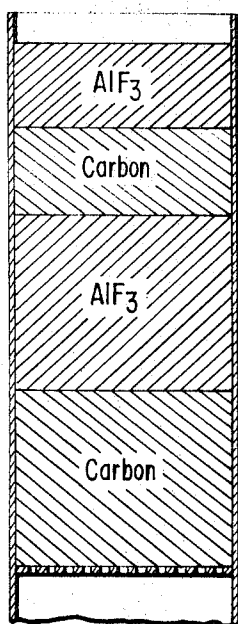


FIG. 2

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METHOD OF TREATING ALUMINOUS METAL WITH CARBON AND ALUMINUM FLUORIDE

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8 Claims

ABSTRACT OF THE DISCLOSURE

A method of treating liquid aluminous metal with a mixture of carbon and aluminum fluoride in solid condition.

Reference is made to prior copending application Ser. No. 346,625 (now U.S. Pat. 3,305,351).

This invention relates to the treatment of aluminous metal to remove trace amounts of alkali metals and magnesium. More particularly, the invention concerns the treatment of liquid aluminous metal with carbon and aluminum fluoride in solid condition.

It is known that very small amounts of lithium, of the order of 0.0005%, or even as little as 0.0003%, in dry annealed aluminum foil (over 99% aluminum) will cause the foil to corrode at an extremely rapid rate when the foil is stored under humid conditions. This phenomenon is known as "blue corrosion," and in humid weather may occur within a day where such lithium content is in the foil. The other alkali metals, such as sodium, produce hot shortness effects during hot working operations on aluminum alloys, especially alloys in which magnesium is a substantial alloying element. In aluminum coming from reduction cells, sodium and other alkali metals produce edge cracking. They are known to influence the formation of oxide films in solid state thermal reactions, and also to lower the electrical conductivity of the aluminum. Traces of magnesium should be held to a low upper limit in the case of condenser foil in particular, but are desirably held to a low upper limit for any type of foil. It is highly desirable, therefore, that the trace amounts of lithium, sodium, and magnesium be reduced substantially below the level at which they ordinarily occur in the aluminum as it comes from an electrolytic reduction cell, or as it may otherwise be obtained, for example, from melted scrap.

In this application, the term "aluminous metal" refers to aluminum and to aluminum base alloys containing at least 50% by weight of aluminum.

In accordance with a first aspect of the present invention, it has been found that alkali metals and magnesium in trace amounts may be effectively removed from aluminous metal by passing the molten metal through a bed containing both carbon and aluminum fluoride in amounts effective to remove such trace metal content of the aluminum to the desired extent. Carbon in a wide variety of forms may be employed for this purpose, such forms including, for example, charcoal, graphite, coke, carbonized pitch, and granular resistor carbon (crushed anode butts from reduction cells).

The particle size of the carbon particles is chosen to provide sufficient surface area to enable the carbon to maintain effective contact with the liquid aluminum. At the same time, the particles should not be so small as to cause clogging of the filter bed. In general, a carbon particle size between about $\frac{3}{4}$ " and about $1\frac{1}{4}$ " has proved advantageous.

The aluminum fluoride particles may be in the form in

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which they come from a conventional converter, after separating out the fines, to provide an average particle size of typically about $\frac{1}{4}$ ". The cost of making the particles, by treating alumina particles with hydrofluoric acid gas, can be reduced by treating the alumina for a shorter period, thus forming aluminum fluoride only as a shell or coating around an inner core of alumina.

It has been found beneficial to provide a bed containing a substantial proportion of particles having an effective density not greater than that of the molten metal being treated. Thus, the use of charcoal or other forms of carbon which are less dense than molten aluminum offers the advantage of contributing a buoyancy factor to the bed which substantially eliminates any clogging tendency. The carbon in charcoal or baked pitch contains numerous residual voids from volatile products evolved during its preparation, which further lowers its effective density.

The proportion of aluminum fluoride may range from about 5% to about 90% by weight, preferably about 10–75%. The carbon and the aluminum fluoride can be brought together by physical mixing of the respective solid materials so that substantially uniform distribution results. Advantageously, however, the solid aluminum fluoride particles are admixed with pitch, the mixture is baked at elevated temperature for a period of time sufficient to carbonize the pitch in situ, and the resultant product is comminuted and screened to separate the desired range of particle size.

The pitch may be a suitable grade of coke oven or asphaltic pitch, of the type which customarily is used for making anodes, having a melting point between 50° and 55° C. The proportion of pitch to aluminum fluoride may range from 10% to about 90% by weight, depending upon the desired characteristics. Baking of the AlF_3 -pitch combination is carried out for about 18 to 36 hours, at a temperature between about 800° and 1200° C., preferably about 1000° C.

The combination of aluminum fluoride and carbonized pitch has proved effective in avoiding the clogging tendency of aluminum fluoride when used alone, and also in overcoming the normal friability of the aluminum fluoride particles.

Bed depth is also an important factor, and may range from about 12" to about 60", depending upon particle size and liquid aluminous metal flow rates. The flow rates are of the order of 200 to 2,000 pounds per minute.

In accordance with another aspect of the invention, particles of aluminum fluoride and particles of carbon are employed in alternate layers of appropriate depth. Where the alternate layers of aluminum fluoride and carbon are employed, the particle size range will be of the same order previously indicated. Total bed depth may range from about 36" to 60". The depths of individual bed segments may be equal, e.g. about 6" or 12", or an arrangement may be used in which the lower layers are 12" in depth, and upper layers are 6", or even 4".

The practices of the present invention make it possible to remove alkali metals and magnesium cheaply and effectively, and to eliminate the unsatisfactory and costly fluxing treatments involving heavy dosages of chlorine heretofore conventionally employed for this purpose.

It is believed that the action of the carbon is primarily an adsorption function. The action of the aluminum fluoride is believed to involve combination with lithium, sodium, and magnesium, respectively, to form complex double salts. Thus, for example, lithium reacts with the aluminum fluoride to form a lithium analogue of cryolite, or the lithium and the sodium can both react with the aluminum fluoride to form lithium-sodium-aluminum fluoride (cryolithionite, $3LiF \cdot 3NaF \cdot 2AlF_3$).

It is also contemplated in accordance with this inven-

tion to employ a bed which is composed partly of carbon and aluminum fluoride, in amounts effective to remove the trace metal content of the aluminous metal to the desired extent, together with other filter bed constituents, such as alumina balls, which are essentially inert to the aluminous metal and are included for other reasons. Thus, for example, such inert constituents may be mixed with particles of carbon and particles of aluminum fluoride, or particles containing carbon and aluminum fluoride, or with both types of particles, or such additional constituents can be provided in a discrete layer or layers. It is preferable, however, not to mix alumina into the bed of carbon and aluminum fluoride, but, rather, to employ a discrete layer of alumina balls ahead of or behind such bed, in order to avoid fusion and subsequent channeling occasioned by interaction between the fluoride and alumina. It is to be emphasized, however, that, although the two systems are compatible to this extent, they are not equivalent in effect, the alumina balls performing essentially a physical filtering function whereas carbon and aluminum fluoride appear to constitute a chemically reactive bed in which filtration is only an incidental effect.

The form of aluminous metal which can be successfully treated in accordance with the invention include pure aluminum, e.g. 99+%, or alloy 1235, and various alloys, for example, those employed for electrolytic condenser foil, such as alloys 1188, 1193 and 1199. Other aluminum base alloys such as 2024 and 7075, may be effectively reduced in alkali metal content.

In the accompanying drawings:

FIG. 1 shows semi-schematically a form of apparatus suitable for the purposes of the invention;

FIG. 2 shows an embodiment of the invention having a bed composed of alternate layers of aluminum fluoride and carbon.

As shown in FIG. 1, the apparatus comprises a tubular shell 1, provided with an upper open end 2, side walls 3, and a lower end 4 terminating in a spout 5. A rigid partition 7 extends across an intermediate portion of the passage defined by the shell, to support a bed of particulate material 9. The partition 7 has a plurality of openings 8 through it, to allow passage of molten metal, and a fiber glass filter cloth 10 extends across and rests upon the partition 7, beneath the bed 9. The cloth 10 can be of any suitable mesh size for filtering molten aluminous metal (e.g. weaves No. 53 or 65 of Fibrous Glass Products Inc., Spokane, Wash.).

Molten aluminous metal is supplied from a source 11, such as, for example, a tapping crucible. The molten metal flows downward by gravity, passing through and in contact with the bed particles 9, whereby the amount of alkali metals and magnesium is substantially reduced.

The apparatus is preferably preheated prior to introduction of molten metal into it. Preheating is conveniently accomplished either by heating the bed directly as, for example, by means of a gas flame, until a temperature is reached at which the carbon ignites, or by induction heating to a dull cherry red appearance of adjacent steel portions of the apparatus. It is not ordinarily necessary, however, to achieve a bed temperature as high as that of the molten aluminous metal to be processed.

As will be seen from the examples to follow, the amount of trace elements in the form of alkali metals and magnesium following the treatment which remain in the aluminous metal will depend on the content prior to treatment, time of contact with the bed material, particle size and bed characteristics, and other factors. The degree of purity to be attained will depend upon the end use of the aluminous metal, which may be treated in the form in which it comes from the electrolytic reduction cell, or in any subsequent alloy form which does not interfere with the treatment. While it is possible, in accordance with the invention, to achieve limits whereby lithium is less than 0.0001%, sodium less than 0.0002%,

and magnesium, less than 0.0002%, for high purity metal, this degree of purity may not be needed. Thus, in the case of aluminous metal to be used in production of dry annealed foil of commercial purity, the treatment of the invention should be applied to reduce the lithium content to a level below 0.0003%, in order to avoid blue corrosion. In the case of sodium, it is more difficult to assign a practical upper limit, because traces of sodium in aluminum as it comes from the reduction cell tend to be reduced by subsequent melting. However, an upper limit of 0.0005% sodium will avoid hot shortness during subsequent hot working of aluminum-magnesium alloys, and can be readily achieved by the treatment of the invention. The upper limit of magnesium should be 0.001% in the case of aluminous metal to be used in the production of condenser foil, in order to avoid discoloration and related defects during high temperature annealing of the foil.

The following examples illustrate the practice of the several aspects of the invention, but are not to be regarded as limiting:

EXAMPLE 1

Particles made from a carbon-AlF₃ mixture

A mixture was prepared of 2,000 lbs. of AlF₃, particle size up to 1/2", and a low-melting (50-55° C.) coke oven pitch, in the proportion of 75% AlF₃:25% pitch, by weight. The mixture was placed in a wooden box 10 feet long, 12" deep and 18" wide and baked at 1000° C. for 28 hours, 10 hours by direct fire, and then comminuted in a jaw crusher. The resultant particles were screened to a particle size range of 1/4" to 3/4", and placed in a 12" diameter, 48" long steel tube having 1/2" diameter drainage holes and a fiber glass screen in the bottom (cf. FIG. 1), to provide a bed depth of 36". Molten aluminum from a tapping crucible was poured through the preheated bed into 1500 lb. pig molds, at a flow rate of about 1,000 lbs. per minute. Three pigs were cast.

The average reduction in contaminants was as follows:

	Na	Ca	Li	Mg
Metal from crucible, percent ---	0.0049	0.0004	0.0004	0.0011
Filtered metal pigs, percent.....	<0.0002	<0.0002	<0.0002	0.0002

EXAMPLE 2

Aluminum fluoride-charcoal mixture

Particles of aluminum fluoride (89% AlF₃), total 325 lbs., average size 1/4", were mixed with 445 lbs. of lump charcoal, bulk density 16 lbs. per cu. ft., to form a bed 23" deep, which was then preheated. A total of 7,000 lbs. reduction cell aluminum was poured through the bed at a rate of about 700 lbs. per minute. The reduction in contaminant metal content was as follows:

Sample	Mg	Li	Ca	Na
Before filtration.....	0.0006	0.00023	0.0001	0.0048
After filtration.....	0.0001	0.00015	0.0001	0.0001

EXAMPLE 3

Charcoal admixed with carbon-AlF₃ particles

475 lbs. of an aluminum fluoride-carbonized pitch mixture, prepared as described in Example 1, particle size 1/8" to 1/2", were admixed with 255 lbs. of lump charcoal, bulk density 16 lbs. per cu. ft. to form a bed 32" deep, which was then preheated. About 7,000 lbs. of reduction cell aluminum were poured through the bed at a rate between 500 and 700 lbs. per minute. Analyses of the feed metal showed: Mg 0.0006%, Na 0.0048%, Ca 0.0005% and Li 0.00023%. After treatment, analysis indicated that these metal impurities were reduced to 0.0002%, 0.0001%, 0.0001% and 0.00015%, respectively.

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EXAMPLE 4

Alternate layers of aluminum fluoride and carbon

A bed was prepared of alternate layers of aluminum fluoride particles, and particles of resistor carbon (crushed reduction cell anode butts). The particle size of the former was about $\frac{1}{2}$ ", while that of the carbon was $\frac{3}{4}$ " to $1\frac{1}{4}$ ". The layers were arranged as shown in FIG. 2 of the drawings, the lower layers being 12" deep, and the upper layers 6" each in depth. A feed of reduction cell metal supplied to the bed analyzed: Mg 0.0015%, Na 0.0041%, Li 0.0006%, and Ca 0.0004%. After treatment, the pig analyzed: Mg less than 0.0005%; Na 0.0003%; Li less than 0.0002%; and Ca 0.0002%. The flow rate of molten metal through the bed averaged about 350 pounds per minute.

What is claimed is:

1. Method of treating aluminous metal which comprises passing the aluminous metal in liquid form through a bed of particulate material comprising a mixture of carbon and aluminum fluoride in amounts effective to lower the alkali metal content thereof.

2. The method of claim 1 in which the flow rate of said liquid aluminous metal through the bed is from about 200 to about 2,000 pounds per minute.

3. The method of claim 1 in which the proportion of aluminum fluoride in the bed ranges from about 5% to about 90% by weight.

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4. The method of claim 1 in which the bed contains carbon particles mixed with particles of aluminum fluoride.

5. The method of claim 4 in which said carbon particles range in size substantially from about $\frac{3}{4}$ " to about $1\frac{1}{4}$ ".

6. The method of claim 1 in which the bed contains carbon in the form of charcoal.

7. The method of claim 1 in which the bed contains particles individually composed essentially of aluminum fluoride and carbon.

8. The method of claim 1 in which the bed contains charcoal particles mixed with particles individually composed essentially of aluminum fluoride and carbonized pitch.

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