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(54) Removal of alkali metals and alkaline earth metals from molten aluminium.

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Description

This invention relates to the removal of contaminant quantities of alkali metals and alkaline earth metals from molten aluminium by reaction with aluminium fluoride.

Molten aluminium withdrawn from electrolytic reduction cells contains small amounts of alkali metals such as lithium and sodium and alkaline earth metals such as magnesium and calcium. The presence of these contaminant alkali metals and alkaline earth metals is deleterious for various uses to which the primary metal may be put.

For example, in the production of magnesium-containing aluminium alloy sheet or plate, sodium in amounts of approximately 2 p.p.m. or more can cause "hot shortness" or edge cracking during hot rolling. The presence of trace quantities of lithium and/or sodium increases the rate of oxidation of molten aluminium. This increases the melt loss and generates a thick dross layer which can block casting machine nozzles and diminish metal fluidity. Therefore, economic and technical considerations require that these elements be removed as soon as possible after withdrawal of primary aluminium from the reduction cells to reduce the time period during which lithium- and/or sodium-containing molten aluminium is exposed to the atmosphere. Magnesium in small quantities is detrimental to electrical conductivity and should be removed from primary aluminium which is to be used for products in which this property is important.

Accordingly, it has been recognized as desirable to reduce the concentration of alkali metal and alkaline earth metal contaminants to 2 p.p.m. or preferably even less. Such removal is also desirable in other circumstances where aluminium or an aluminium-based alloy (the term "aluminium" being used herein broadly to embrace these alloys as well as pure aluminium metal) is contaminated with minor amounts of alkali metal and/or alkaline earth metal.

It is known that the content of dissolved alkali metals and/or alkaline earth metals can be reduced by bringing molten aluminium into contact with aluminium fluoride (AlF_3) (or a material containing it). The contaminant reacts with aluminium fluoride to form mixed compounds (e.g. cryolithionite compounds such as $3LiF.3NaF.2AlF_3$). Typically, aluminium fluoride in the form of solid particles is brought into contact with the molten aluminium. The treatment material may consist essentially of aluminium fluoride, or may be composed wholly or in part of alkali metal fluoaluminates which are solid at the temperature of the molten metal. An example of the latter type of material (useful for removal of lithium, magnesium, and calcium) is particulate sodium cryolite or lithium-free reduction cell electrolyte having a low ratio by weight of sodium fluoride to aluminium fluoride so as to contain aluminium fluoride in excess of the stoichiometric requirements of Na_3AlF_6 with a composition such that a major proportion remains solid at the treatment temperature, as is usually the case provided the aforementioned ratio remains within the range of 1.3—1.5. Indeed, it is not essential that the addition remain in solid form; a low (approximately 725°C) melting-temperature compound containing a large excess of AlF_3 (e.g. having a very low $NaF:AlF_3$ ratio by weight of 0.6—0.7) which melts on introduction to molten aluminium would be equally effective in removing alkali metals or alkaline earth metals. The active fluoride material may also contain inert material such as aluminium oxide, in a proportion even as high as 50% by weight, although 7—20% is the more usual aluminium oxide content of commercial aluminium fluoride.

Treatments with aluminium fluoride are considered advantageous for removal of alkali metals and alkaline earth metals, as compared with fluxing with chlorine gas or chlorine/inert gas mixtures, because the gas fluxing operations yield deleterious gaseous by-products and are otherwise inconvenient.

In prior treatments employing AlF_3, as described in U.S. Patents No. 3,305,351, No. 3,528,801, and No. 4,138,246, the molten aluminium was passed through a packed filter bed of solid particulate material containing aluminium fluoride, alone or in mixture with carbonaceous material, such as coke. In U.S. Patent No. 4,277,280 a similar effect is achieved by passing molten aluminium upwardly through a reactive bed of coarse granular AlF_3-containing material which is not a filter. However, the use of reactive beds or bed filters comprised of reactive materials has several disadvantages. A substantial proportion of the products of reaction of the alkali metal (Li, Na, Mg) with aluminium fluoride remains trapped on or within the reactive bed or associated filter material to cause premature plugging; electrolyte from the reduction cell, sludge and/or other solid or liquid impurities carried over with the molten metal from the electrolytic cell have the same effects. For similar reasons, a preferential metal path or "channel" can appear within the reactive bed and seriously reduce the alkali metal removal efficiency. The aluminium fluoride material is consumed during the treatment of molten metal and consequently the performance of a reactive bed is not constant during its service life.

To prevent aluminium fluoride pyrohydrolysis and metal losses in reactive beds, it is preferable to keep aluminium fluoride always completely submerged in molten aluminium; but this requires a constant heating and fuel consumption, even when the installation is not operating, which adds to the cost of the treatment. Change of the composition of the metal treated through such a system is invariably associated with metal losses.

Also, during initial preheating of the AlF_3 bed, decomposition by pyrohydrolysis (i.e. reaction with water vapour in combustion products) tends to occur.

It is difficult to achieve effective contact between loose aluminium fluoride particles and molten aluminium metal. The reason for this is that, due to the high surface tension of molten aluminium and the small difference in density between aluminium fluoride powder and molten aluminium, AlF_3 powder will float on the surface of molten aluminium. Additionally aluminium fluoride powder is not easily wetted by molten aluminium, and is thermally very stable, i.e. it does not melt under atmospheric pressure, and it has a sublimation temperature of approximately 1,270°C, so that reaction between liquid-liquid or gas-liquid phases is impossible at the treatment temperature of molten aluminium (660°C—900°C). These physical characteristics explain the poor performances of previous attempts to introduce discrete particulate aluminium fluoride into molten aluminium.

It is possible to inject aluminium fluoride particles into molten aluminium in a jet of carrier gas, such as air or nitrogen, by means of an injection lance. Injection operations, however, have been found to require substantial periods of time, and there are safety hazards associated with the high gas pressure in the metal; in addition, use of air as the carrier gas can lead to excessive dross and oxide film formation.

It is also possible to make a large addition of aluminium fluoride powder to the bottom of an empty crucible before metal addition. However, it has been observed that the aluminium fluoride powder reacts preferentially with the cell electrolyte (which is invariably siphoned from the reduction cell along with the molten Al metal) to form a solid mass which remains attached to the crucible lining. Thus effective contact with the molten aluminium is prevented.

As will be understood from the foregoing discussion a substantial contact time is required for the efficient reaction between loose particulate AlF_3-containing material and alkali metal and alkaline earth metal contaminants in molten Al metal.

The method of the invention requires the addition of an appropriate charge of the treatment material (AlF_3 or AlF_3-containing material) to the molten Al metal under conditions which involve re-circulation of the treatment material within the molten metal while avoiding excessive disturbance of the molten metal surface, to hold down oxidation of the metal. In the method of the invention the treatment material is entrained in the molten aluminium by supplying the treatment material to a vortex generated in a body of the molten metal held within a container. The vortex generator also serves to generate upwardly spiralling currents in the molten metal in the region of the boundaries of the container to maintain prolonged contact of the particles of the treatment material with the molten metal. The circulation of the molten metal by vortex generation is continued for a sufficient length of time to reduce the alkali metal and alkaline earth metal content of the molten metal to a desired low value, after which the circulation is discontinued. Some of the reaction products, which are admixed with residual treatment material, will rise to the surface as a dross, from which the molten metal can be separated by dross skimming or metal siphoning or other conventional means. However the greater part tends to adhere to the crucible lining during the stirring process, whence it can be removed when the crucible is empty.

It is well known in metallurgical processes to introduce reactive materials into molten metal vortices, generated in vessels from which the molten metal is discharged as a continuous stream. In the present procedure generation of a vortex serves both as a means for bringing a finely powdered particulate material of relatively low bulk density into contact with molten metal and as a means for maintaining the particles of such material dispersed within said molten metal and in intimate contact therewith over an extended period until generation of the vortex is terminated.

The vortex is generated and maintained by using a rotating stirrer having a multi-bladed rotor immersed within a body of molten metal contained in a crucible and rotated about a vertical axis, with the blades pitched so that each blade has a major surface facing downwardly at an acute angle to the vertical. The impeller rotor is arranged in the crucible eccentrically with respect to the vertical centre line of the crucible.

The invention also provides apparatus for mixing particulate AlF_3 treatment material with molten aluminium, including a crucible for the molten metal, and an impeller or rotor having pitched blades and disposed eccentrically of the vertical centre line of the crucible, with various dimensional and positional relationships maintained within specified ranges or limits described below.

In the accompanying drawings:

Fig. 1 is a simplified sectional plan view of an apparatus for performing the method of the invention, and

Fig. 2 is a vertical section on line 2—2 of Fig. 1.

In the drawings a cylindrical crucible 10 contains a body of molten aluminium 11. A separate lid 12 supports an eccentrically mounted impeller 14, driven by a motor 16. The impeller 14 has a shaft 18 which carries blades 20 for immersion in the molten aluminium body 11. The lid 12 also includes a duct 22 for supply of treatment material to the crucible; and an exhaust conduit 24 for exhausting fumes from the crucible. Typically, the crucible comprises a steel shell, with a refractory lining inert to molten aluminium. The lid 12 and associated items comprise a vortex generator assembly which may be transferred to permit the same stirring apparatus to be used to stir batches of molten metal contained in a series of different mobile crucibles.

For removal of contaminant alkali metals and/or alkaline earth metals from molten aluminium, the crucible 10 is charged with an appropriate quantity of molten Al metal. The lid 12 is then placed on the crucible to immerse the bladed portion of the impeller 14. Particulate treatment material comprising or consisting of aluminium fluoride (AlF_3), which is solid at the temperature of molten aluminium, is then fed by gravity through the duct 22. Rotation of the impeller should preferably be commenced before introduction of the treatment material (but may be commenced after such introduction) and maintains a stable vortex (indicated at 26 in Fig. 2) in the molten body 11. Generation of the vortex results in a combination of axial and radial flow components in the molten metal. The AlF_3 particles are drawn into the vortex and then circulated through the molten body along flow paths generally indicated at 28. It is not necessary to charge aluminium fluoride directly into the vortex, since the material will be rapidly moved thereto by the high rate of metal circulation at the melt surface.

Rotation of the impeller is continued, with maintenance of the vortex 26 and recirculation of the aluminium fluoride particles until there has been sufficient reaction between the aluminium fluoride and the dissolved contaminant alkali metals and/or alkaline earth metals to reduce the content of these contaminants in the melt to a desired low value. Typically, the time required to achieve this result is no more than about ten minutes, and indeed often substantially less than ten minutes. Compounds, such as cryolithionite compounds, produced by reaction of the contaminant alkali metals and alkaline earth metals with the aluminium fluoride, float on the surface of the molten body, and may be readily removed by skimming or other means when the rotation of the impeller is ended and the lid is lifted away from the crucible. The decontaminated molten metal may then be poured or otherwise withdrawn from the crucible.

By this method, it is possible to reduce the level of contaminants from a typical level of about 20 p.p.m. lithium and about 30—60 p.p.m. sodium to less than 1 p.p.m. within a period of ten minutes or less of continuous stirring with the impeller. Since some reduction in the levels of these contaminants occurs inherently during the performance of other steps commonly employed in handling molten aluminium, it is frequently possible to achieve satisfactory reduction in content of the contaminant metals, e.g. to 2 p.p.m. Li, with even shorter periods. Even though the aluminium fluoride may contain a proportion of alumina, the fluxing action of the fluoaluminate reaction product serves to remove the insoluble alumina. In fact, it is observed that the process of the invention has the incidental effect of removing inclusion-forming materials, such as aluminium carbide (Al_4C_3), which were present in the melt before treatment.

The optimum combination of axial and radial flow components for attaining a high mixing efficiency of the solid AlF_3 particles into the molten aluminium is achieved by appropriate disposition of the impeller relative to the crucible and/or by the dimensions and design of the impeller blade. To this end, the impeller comprises a plurality of equiangularly spaced, pitched blades 20 each having a major surface 20a that faces downwardly at an acute angle to the vertical. The axis of the impeller shaft is disposed eccentrically of the geometric axis of the crucible, and the direction of impeller rotation is such that the blade surfaces 20a are the leading surfaces of the blades, exerting a force having a downward component on the molten aluminium. In the drawing, θ designates the pitch angle of the blade surfaces 20a, *d* designates the overall diameter of the bladed portion of the impeller, *h* designates the height of the impeller blades, *x* designates the eccentricity of the impeller shaft, *y* designates the vertical distance from the bottom of the crucible interior to the midpoint of the impeller blades, *H* designates the vertical distance from the bottom of the crucible interior to the quiescent level of molten metal in the crucible, *D* is the internal diameter of the crucible, and the arrow *R* represents the direction of impeller rotation.

In accordance with the invention, as particular or preferred features thereof, the following ranges of relationships and dimensions are observed in the design and disposition of an impeller of the illustrated type:

Relationship or dimension	Outside range	Preferred range
d/D	0.1—0.6	0.15—0.40
h/H	0.1—0.7	0.2—0.40
y	0.25H—0.75H	0.4H—0.6H
θ	above 0° and not more than 45°	30°—40°

The eccentricity, *x*, of the impeller shaft is usually in the range of 0.1—0.25D and more preferably in the range of 0.25—0.7 d. It is especially preferred to utilize three blades spaced 120° apart with a pitch angle of 30°—35°, and a ratio d/D of about 0.25. The impeller eccentricity, *x*, is mostly preferably 0.5 d.

The described impeller arrangement is advantageous in creating a stable vortex without use of vertical baffles, which would be impracticable in interchangeable transfer crucibles. The function of conventional baffles in generating vortices by maintaining a high rate of relative rotation between the impeller and the liquid is achieved with the present impeller arrangement by the combination of radial and axial flow components produced by the impeller.

Since blade pitch angles θ as large as 45° or more tend to cause splashing and surface waves, it is preferred to use a smaller pitch angle, such as 30°—35° to force the metal downwardly to drag the fluoride powder into the molten aluminium.

The requisite axial component of molten metal flow can be achieved by the use of an eccentrically located pitch-bladed impeller, in order to minimize metal waves and oscillations at the surface of the metal.

It is found that eccentric location of the impeller permits the crucible to be filled to a greater extent without risk of splashing during the stirring of metal in transfer crucibles of large size. The eccentric location of the impeller constitutes an important feature in accordance with the invention since it permits the treatment of a substantially larger batch of metal in a crucible of given size.

The minimum rate of rotation, for a given impeller, is that which will generate and maintain a stable vortex, while the maximum rotation rate is that above which air is ingested into the molten body being stirred. These values are determined by the impeller diameter *d*. The optimum rotation rate is that which produces a good vortex without causing excessive metal splashing and loss or being responsible for erosion of either the crucible refractory or impeller construction material. Referring to an impeller providing a d/D ratio within the preferred range of 0.15—0.40, it is at present preferred to operate such an impeller at a rotation rate of about 100 to about 300 r.p.m. However, rates of rotation outside this range may also be used, so long as they produce the desired vortex without excessive splashing. The use of an eccentrically disposed impeller having tilted or pitched blades rotated in the above-defined direction is found to be especially satisfactory in generating the stable vortex with a highly effective combination of axial and radial flow components for enhancing penetration of the solid aluminium fluoride particles into the molten metal.

During the treatment of molten aluminium with AlF_3 powder, alkali and alkaline earth metals react with AlF_3 to form mixed alkali cryolithionite compounds, e.g. $Na_5Al_3F_{14}$, Na_2LiAlF_6, and $Li_3Na_3Al_2F_{12}$. These compounds, having a relatively low melting point, can easily be agglomerated or stick to the crucible walls or float to the melt surface where they react with metal oxide or particles of cell electrolyte always present after the siphoning of electrolytic cells. During subsequent metal transfer by siphoning, most of these compounds will remain inside the crucible and are thus separated from the molten Al.

Although a high grade of AlF_3 is desirable for a fast reaction with alkali metal, a higher ratio of addition of AlF_3/Al could compensate for a lower-grade powder. Other mixtures which could be used are lower-grade AlF_3 (e.g. AlF_3 mixed with Al_2O_3) or electrolytic bath material containing a large excess of AlF_3 (i.e. Na_3AlF_6 with excess AlF_3).

By way of further illustration of the invention, reference may be made to the following examples:

Example 1

130 kilogram samples of 99.7% purity molten aluminium containing between about 20 and 25 p.p.m. Li were treated with solid AlF_3, ground to −35 mesh (−0.5 mm) particle size, using each of the following procedures:

A. 300 grams of AlF_3 particles delivered to the melt surface, without agitation.

B. 200 grams of AlF_3 particles delivered to the melt surface, with the melt agitated by a rotor rotating at 900 r.p.m.; without vortex generation.

C. 300 grams of AlF_3 particles injected into the melt below the surface through a graphite lance, using nitrogen as the carrier gas.

D. 200 grams of AlF_3 particles injected as in C, but with the melt agitated by a rotor (positioned above the lance outlet) rotating at 900 r.p.m.

E. 200 grams (E-1) and 300 grams (E-2) of AlF_3 particles delivered to the melt surface while a stable vortex is generated and maintained in the melt, by a stirrer rotating at 225 r.p.m., in accordance with the present method.

In a further procedure (F), no AlF_3 was used, but the melt was agitated (without creation of a vortex) by a rotor rotating at 900 r.p.m. Results were as follows:

	Li (p.p.m.) remaining after treatment time of:				
Procedure	0 min. (start)	3 min.	6 min.	9 min.	12 min.
A	24	14	9	6	4
B	22	10	7	5	3
C	23	9	4	2	1
D	15	7	2	1	1
E-1	20	2	2	1	1
E-2	24	3	2	1	1
F	22	16	14	12	11

The procedures embodying the present method (E-1 and E-2) achieved significantly more rapid reduction in lithium content than any other procedures, and the lithium level reached after nine minutes (1 p.p.m.) with the procedures of the present method was equalled only by the procedure (D) involving combined use of injection and agitation, wherein the initial level of lithium contamination was much lower.

The dimensions and disposition of the impeller stirrer in this example are as follows:—

The impeller diameter, d, was 12.5 cms and the impeller was a four-bladed impeller having a blade height of 8.8 cms, with the blades inclined at an angle of 35°.

The diameter of the crucible was 50 cms and the values of H and x were respectively 37.5 cms and d/2.

Example 2

Using equipment of the type illustrated in the drawing, including a cylindrical crucible having an internal diameter of about 160 cms with a nominal capacity of about 4500 kg of molten aluminium, a series of quantities of molten aluminium contaminated with lithium and sodium were treated in accordance with the present method. In each instance, the crucible was filled to a depth of 100 cms with the molten aluminium, and AlF_3 powder at the rate of about 1.7 kg per metric tonne of aluminium was supplied to the molten aluminium surface. A pitched-bladed impeller having a blade height of 25 cms and diameter of 45 cms was immersed in the molten aluminium with an eccentricity of 20—30 cms (preferably 22.5 cms) with the centre of the impeller blades 37.5 cms above the crucible bottom, such that the top edges of the blades were located halfway between the top of the melt and the crucible bottom (the blades thus being disposed entirely within the lower half of the molten metal body); the impeller was rotated, in each case, for 10 minutes at a rate of between about 130 and about 135 r.p.m. to create and maintain a stable vortex. The mode of addition of AlF_3 particles, and the molten metal temperature, were varied from test to test. Results of twenty successive tests were as follows:

	Lithium (p.p.m.)			Sodium (p.p.m.)			
Addition mode of AlF_3 to metal surface**	Start	After 10 min.	% Removed	Start	After 10 min.	% Removed	Metal temperature (°C)
a	19.9	0.9	95	63	<1	∼100%	743
a	16.2	1.1	93	43	<1	∼100%	780
b	19.7	0.5	97	42	<1	∼100%	705
b	18.1	1.0	94	35	<1	∼100%	765
b	18.5	0.4	98	33	<1	∼100%	735
b	20.6	0.8	96	47	<1	∼100%	720
b	15.4	0.3	98	39	<1	∼100%	722
b	15.7	0.9	94	39	<1	∼100%	720
b	14.9	1.3	91	44	<1	∼100%	800
b	12.1	1.4	88	31	<1	∼100%	725
b	21.0	0.5	98	61	<1	∼100%	730
c	16.5	1.2	93	28	<1	∼100%	745
d	21.2	1.0	95	48	<1	∼100%	785
d	19.8	2.4	88	58	1	∼100%	870
e	17.7	1.7	90	32	<1	∼100%	810
f	16.7	1.2	93	41	<1	∼100%	*
f	17.6	1.6	91	42	<1	∼100%	*
g	6.8	0.8	88	7	<1	∼100%	*
g	13.2	2.3	83	43	2	∼100%	*
g	16.8	1.7	90	35	<1	∼95%	*

* not measured

** a—50% of AlF_3 added at start, 50% added after 1 minute of impeller operation
b—33% added at start, 33% after 30 seconds, 33% after 1 minute of impeller operation
c—continuous feed for 1.5 minutes from start of impeller operation
d—continuous feed for 1.0 minutes from start of impeller operation
e—continuous feed for 0.5 minutes from start of impeller operation
f—33% added at start, 33% after 15 seconds, 33% after 30 seconds of impeller operation
g—33% added at start, 33% after 10 seconds, 33% after 20 seconds.

These data illustrate the adverse effect of increased metal temperature on efficiency of lithium removal, attributable to a thermodynamically controlled lithium equilibrium between the fluoride material and the metal which prevents 100% efficient lithium removal from the hot metal; a similar effect could not be observed for sodium because of the higher vapour pressure of sodium, which assists in its removal.

The average lithium removal efficiency, after 10 minutes' treatment time, was 93% for the twenty tests included in the foregoing table. This corresponds to a lithium level (for the treated metal) which is satisfactory, i.e. below the maximum acceptable limit, for most purposes.

Example 3

Several series of treatments were performed in transfer crucibles on aluminium which had been siphoned into the crucibles from electrolytic reduction cells. The aluminium fluoride powder used (92% AlF_3, about 8% Al_2O_3 by weight) had a bulk density of 1.5—1.7 g/cm^3 and a particle size distribution as follows: 25% larger than 100 µm, 50% larger than 80 µm, 75% larger than 65 µm. In these treatments, the crucibles contained approximately 3,500 kg of molten aluminium each. A three-bladed impeller having a blade pitch (angle θ) of 35°, diameter (d) of 46 cm, and blade height (h) of 25 cm was employed, and rotated to establish and maintain a stable vortex; the ratios d/D and h/H were each 0.25, and the maximum treatment time was six minutes. The rotor eccentricity, x, was d/2. Several crucibles were treated in each series. For purposes of comparison, one series (Series 1) was run without use of aluminium fluoride. The remaining six series of treatments embodied the process of the invention. In series 2-5, all the aluminium fluoride was added at or before the start of stirring; in series 6 and 7, one third of the aluminium fluoride was added at the start, one third after one half minute, and one third after one minute of stirring. The metal in the crucibles of series 7 initially contained 101 p.p.m. of magnesium; the metal in the other six series contained less than 10 p.p.m. magnesium.

Results were as follows:

Test Series No.	Number of treated crucibles	Quantity of added AlF_3 kgAlF_3/metric tonne Al	Stirring speed (r.p.m.)	Metal temperature (°C)	Analytical results: Lithium start ppm	Lithium 3 min. ppm	Lithium 3 min. % Removal	Lithium 6 min. ppm	Lithium 6 min. % Removal	Sodium start ppm	Sodium 3 min. ppm	Sodium 3 min. % Removal	Sodium 6 min. ppm	Sodium 6 min. % Removal	Calcium start ppm	Calcium 3 min. ppm	Calcium 6 min. ppm
1	7	0	175	811	21	17.9	15%	17	19%	54	21	61%	15	72%	2	1	<1
2	10	0.7	100	771	17.9	10.2	43%	8.0	55%	36	8.7	76%	4.9	86%	3	1	<1
3	11	2.0	100	744	18.1	7.6	58%	4.7	74%	30	6.8	77%	3.2	89%	3	2	<1
4	4	3.3	100	759	15.0	5.3	65%	3.3	78%	34	6.5	81%	3.3	90%	2	1	<1
5	4	2.0	150	752	18.5	6.6	64%	2.7	85%	42	7.1	83%	3.2	92%	3	1	<1
6	7	2.0	175	765	17.0	5.5	68%	2.2	87%	37	6.6	82%	1.5	96%	2	1	<1
7	7	2.0	175	780	14.1	5.1	64%	2.4	83%	37	7.2	81%	2.5	93%	2	1	<1

Series 1 illustrates the removal of alkali metals due to the aluminium stirring effect only. The greater sodium removal after 3 and 6 minutes (61% and 72%) compared to the lower lithium removal efficiency (15% and 19%) is attributable to the much lower vapour pressure of lithium than sodium. In effect, sodium has a boiling point at atmospheric pressure of 882°C compared with 1,329°C for lithium.

Series 2, 3 and 4 compare the effect of the AlF_3 quantity on sodium and lithium removal. It can be seen that increasing the ratio kg AlF_3/metric tonne Al from 0.7 to 3.3 had a marked effect on lithium removal. The effect is not so apparent for sodium due to the faster sodium removal by oxidation only.

Series 5 is identical to series 3 except for an increased r.p.m. from 100 to 150. This increased the sodium and lithium removal efficiency from 89% to 92% and from 74% to 85%, respectively. Series 6 illustrates, for 7 transfer crucibles, the influence of a sequential addition of AlF_3 powder on the removal rate of alkali metals. It can be seen that this also helps in increasing the removal rate, probably by increasing the interfacial area between the powder and the aluminium (the addition of a large quantity of AlF_3 in one "shot" can cause powder agglomeration and decrease the effective contact with the aluminium).

Series 7 illustrates the influence of Mg metal present in addition to Li, Na and Ca. The Mg content after 3 minutes stirring was 46 p.p.m. (54% removal) and after 6 minutes as 30 p.p.m. (70% removal). It can be concluded that the presence of Mg, even in a concentration larger than other alkali metals, does not significantly affect process efficiency. The presence of Mg in these tests was due to the use of a mixed LiF-MgF_2 electrolyte in the reduction cells. The presence of magnesium in the metal due to other causes (e.g. contamination from Al-Mg alloys) could also be tolerated. However, if Mg concentration increases, the addition of AlF_3 would have to be adjusted accordingly, to ensure a constant lithium and sodium removal efficiency.

Example 4

In two further series of tests using the same equipment as in Example 3, groups of transfer crucibles each containing about 3,400 kg of molten aluminium were treated in accordance with the present method. AlF_3 powder was added at the rate of 2.0 kg. AlF_3/metric tonne Al to each crucible in three equal increments, viz. at the start; after 30 seconds of stirring; after one minute stirring. The stirring was performed for six minutes at 175 r.p.m., producing and maintaining a stable vortex as in Test 6 of Example 3. The treated metal from one series was used to prepare a first alloy (having the Aluminum Association designation AA-1350) and the treated metal of the second series was used to prepare a second alloy (Aluminum Association designation AA-5154). Alkali metal and alkaline earth metal content was measured again after alloying. Results were as follows:

			Average analysis		
Alloy prepared	Total metal weight treated (metric tonnes)	Before treatment ppm	After treatment ppm	% Removal	Before casting (after alloying) ppm
AA-1350	7.1 (21 crucibles)	Na—29	1.7	94%	<1
		Li—17	2.6	85%	0.2
		Ca—2	<1		<1
AA-5154	85 (25 crucibles)	Na—37	2.1	94%	<1
		Li—17	2.7	84%	0.6
		Ca—3	<1		<1

It can be seen that the efficiency is of the same order as in Test 6 of Example 3. It can also be concluded that the sodium and lithium concentration continues to decrease after the treatment. This can be attributed to various metal operations and treatment (transfer, alloying, stirring, heating, holding, etc.) which accelerate the oxidation of alkali metals in the furnace.

Example 5

Again using the same equipment and the same AlF_3 powder as in Examples 3 and 4, molten aluminium in transfer crucibles each containing 3,500 kg of aluminium was stirred for 10 minutes at 100 r.p.m., a stable vortex being created and maintained. After treatment, the metal stood for 10 minutes and the alkali metal content was remeasured. Results were as follows:

			Analysis (p.p.m.)				
				During treatment (min.)			10 min. after treatment
Test No.	AlF$_3$ kgs/tonne	Temp. (°C)		Start	6	10	
A	2.0	760	Li	18.3	6.0	3.6	3.1
			Na	43	9.0	4.0	3
B	2.6	825	Li	15	4.3	2.7	2.5
			Na	40	5	2	1

The observed further decrease in alkali metal content after stirring was ended may be explained by the high level of activity of the AlF$_3$-rich reaction products in contact with molten aluminium. Even if this alkali metal decrease on standing after treatment is not significantly important as compared to the reduction during the treatment itself, it nevertheless indicates that there is no risk of back-reaction (alkali metal pick-up) during holding in the transfer crucible between the treatment and the transfer to the casting furnace. This would not be the case if the alkali metal were removed using a treatment with chlorine gas reaction only.

Example 6

To illustrate the effect of impeller blade angle, a series of tests were performed on 125 kg samples of molten aluminium of 99.7% purity at a temperature of 825°C, using −35 mesh (−0.5 mm) aluminium fluoride powder in a proportion of 0.8 kg/metric tonne Al. Impellers with blades of various pitches were employed; in each case, d=12.5 cm, h=11 cm, d/D=0.25, and h/H=0.25 and x=d/2. Stirring was performed for six minutes at 250 r.p.m. Results were as follows:

		Lithium concentration p.p.m. (% removal)		
		Stirring time—Min.		
Number of blades	Angle to vertical θ	Start	3	6
4	0°	27	13(52%)	11(60%)
4	30°	40	12(70%)	8(80%)
4	35°	26	5(81%)	3.5(86%)
4	45°	26	4(85%)	3(88%)
3	35°	26	4(85%)	1(96%)

Increase in pitch angle increased the percentage removal of Li after three and six minutes, and the number of blades appeared also to affect the removal efficiency.

Example 7

A synthetic mixture containing 50% each (by weight) of cryolite (Na_3AlF_6) and AlF$_3$ (weight ratio of NaF/AlF$_3$=0.43) was prepared by fusion of the two compounds, ground to −35 mesh (−0.5 mm) particle size, and employed for treatment of molten aluminium in accordance with the present invention. Two 150 kg samples of aluminium, both at 825°C, were treated, using a stirrer having four blades, with a pitch angle θ of 30°, diameter (d) of 12.5 cm, blade height h of 11 cm, in a crucible so dimensioned that the ratios d/D and h/H were each equal to 0.25; one of the two tests employed a fluoride-containing material constituted of 85% AlF$_3$, 15% Al_2O_3 by weight, and the other employed the aforementioned cryolite-AlF$_3$ mixture, both in a proportion of 2.0 kg per metric tonne of aluminium. Results were as follows:

	Lithium concentration (ppm) vs. stirring time (min.)					
AlF_3-containing material	Start	1	2	3	4	5
85% AlF_3 15% Al_2O_3	21	6.3	3.8	2.5 (88%)	1.5	1.0 (95%)
50% AlF_3/ 50% Na_3AlF_6	30	7.5	3.6	2.4 (92%)	1.5	<1 (>97%)

The high efficiency of the AlF_3/Na_3AlF_6 mixture is possibly attributable to the formation of low melting point (about 700°C) phases. It therefore melts after contact with the liquid aluminium providing a liquid-liquid reaction rather than the solid-liquid reaction with the AlF_3 powder which compensates for the aluminium fluoride dilution.

In addition, aluminium fluoride powder in mixtures of a wide range of particle size distribution have been used, with the average particle size dimension varying between 1 and 0.05 mm.

Claims

1. A method of removing contaminant alkali metals and alkaline earth metals from molten aluminium by reaction with aluminium fluoride to form fluoaluminates of such contaminants which comprises

(1) placing a charge of the contaminated aluminium metal within an upright cylindrical vessel which also contains a multi-bladed impeller positioned eccentrically in relation to the axis of the container and having blades which are pitched downwardly in relation to the axis of rotation

(2) stirring molten aluminium in said vessel by means of the impeller under conditions to establish a vortex therein and flow currents in said molten aluminium having both downward and lateral components at the bottom of said vortex and upwardly spiralling currents in the region of the periphery of said vessel

(3) supplying particulate aluminium fluoride-containing material into said vortex for dispersion and recirculation in said molten aluminium by means of said spiralling currents

(4) continuing the stirring of the molten aluminium until the alkali metal and alkaline earth metal content is reduced to a desired low level

(5) separating the molten aluminium from the alkali and alkaline earth metal fluoaluminate reaction products.

2. A method according to claim 1 for removing contaminant lithium, sodium and calcium from the molten aluminium.

3. A method according to any preceding claim, further characterised in that the molten metal is treated with powdered AlF_3 or $NaF . AlF_3$ having a NaF/AlF_3 ratio below 1.5 by weight.

4. A method according to any preceding claim, further characterised in that the vessel has an internal diameter D, and is filled with the molten aluminium to a height H, and the impeller has a diameter d and a blade height h, such that the ratio d/D is between 0.1 and 0.6 and the ratio h/H is between 0.1 and 0.7.

5. A method according to claim 4, further characterised in that the axis of impeller rotation is eccentric in relation to the vessel axis by a distance, x, having a value 0.1—0.25D.

6. A method according to claim 5, further characterised in that the midpoint of said blades is spaced above the bottom of said vessel by a distance, y, between 0.25H and 0.75H.

7. A method according to claim 4, further characterised in that d/D is between 0.15 and 0.40 and the impeller is rotated at a rate between 100 and 300 r.p.m.

8. A method according to any preceding claim, further characterised in that the treatment material is fed to the molten metal in separate quantities or continuously during a short period after establishment of the vortex.

9. A method according to claim 4 further characterised in that the axis of impeller rotation is eccentric in relation to the vessel axis by a distance, x, having a value of 0.25—0.7 d.

10. Apparatus for mixing particulate aluminium fluoride-containing material with molten aluminium to remove dissolved contaminant alkali metals and alkaline earth metals from the molten aluminium, said apparatus comprising

(a) a cylindrical vessel, having a vertical geometric axis and an internal diameter D, for containing a body of molten aluminium to a height H above the floor of the vessel; said vessel being free from internal baffles;

(b) a cover of said vessel supporting a multi-bladed impeller and means for driving said impeller about a vertical axis and means for rotating the impeller, said impeller having a diameter, d, and its blades having a height, h, the midpoint of said blades being spaced above the floor of the vessel by a distance, y, the axis of impeller rotation being spaced from said geometric axis by a distance, x, and said blades having major surfaces pitched downwardly at an angle θ to the vertical;

(c) the values of d, D, h, H, x and θ being such that d/D is between 0.1 and 0.6, h/H is between 0.1 and 0.7, x is between 0.1—0.25 D, y is between 0.25H and 0.75H, and θ is above 0° and not more than 45°;

(d) said cover also supporting means for feeding said particulate material and for discharging fumes.

11. Apparatus according to claim 10, further characterized in that d/D is between 0.15 and 0.40, h/H is between 0.2 and 0.40, x is 0.25—0.7 d, y is between 0.4H and 0.6H, and θ is between 30° and 40°.

Patentansprüche

1. Verfahren zum Entfernen von verunreinigenden Alkalimetallen und Erdalkalimetallen aus geschmolzenem Aluminium durch Umsetzen mit Aluminiumfluorid unter Ausbildung von Fluoaluminaten der Verunreinigungen, dadurch gekennzeichnet, dass man

(1) einen Ansatz des verunreinigten Aluminiummetalls in ein aufrechtes zylindrisches Gefäss einbringt, welches auch einen exzentrisch in bezug auf die Achse des Behälters eingestellten mehrblättrigen Rührer enthält, wobei die Schaufeln in bezug auf die Drehachse nach unten geneigt sind,

(2) geschmolzenes Aluminium in dem Gefäss mittels des Rührers unter Bedingungen rührt, dass dort ein Wirbel und Fliessströme in dem geschmolzenen Aluminium ausgebildet werden, die sowohl nach unten als auch seitlich ausgerichtete Komponenten am Boden des Wirbels aufweisen und nach oben spiralenförmige Ströme in Richtung des Gefässumfanges ausgebildet sind,

(3) teilchenförmiges, aluminiumfluoridhaltiges Material in den Wirbel einführt, um es in dem geschmolzenen Aluminium mittels des spiralenförmigen Stroms zu dispergieren und im Kreislauf zu führen,

(4) das geschmolzene Aluminium weiterrührt bis der Alkalimetall- und Erdalkalimetall-Gehalt auf ein gewünschtes Niveau verringert ist, und

(5) das geschmolzene Aluminium von den Alkali- und Erdalkalimetallfluoaluminat-Reaktionsprodukten abtrennt.

2. Verfahren gemäss Anspruch 1 für die Entfernung von Lithium, Natrium und Calcium als Verunreinigung aus dem geschmolzenen Aluminium.

3. Verfahren gemäss einem der vorhergehenden Ansprüche, welches weiterhin dadurch gekennzeichnet ist, dass man das geschmolzene Metall mit pulverisitertem AlF_3 oder $NaF \cdot AlF_3$, mit einem NaF/AlF_3-Verhältnis unterhalb 1,5 Gew.%, behandelt.

4. Verfahren gemäss einem der vorhergehenden Ansprüche, weiterhin gekennzeichnet dadurch, dass das Gefäss einen Innendurchmesser D aufweist und mit dem geschmolzenen Aluminium bis zu einer Höhe H gefüllt ist, und dass der Rührer einen Durchmesser d und eine Schaufelhöhe h aufweist, so dass das Verhältnis d/D zwischen 0,1 und 0,6 und das Verhältnis h/H zwischen 0,1 und 0,7 liegt.

5. Verfahren gemäss Anspruch 4, weiterhin dadurch gekennzeichnet, dass die Achse der Rührerdrehung exzentrisch in bezug auf die Gefässachse durch eine Entfernung x mit einer Grösse von 0,1 bis 0,25D ist.

6. Verfahren gemäss Anspruch 5, weiterhin dadurch gekennzeichnet, dass der Mittelpunkt der Schaufeln vom Boden des Gefässes sich in einem Abstand y, der zwischen 0,25H und 0,75H beträgt, befindet.

7. Verfahren gemäss Anspruch 4, weiterhin dadurch gekennzeichnet, dass d/D zwischen 0,15 und 0,40 liegt und dass sich der Rührer mit einer Geschwindigkeit zwischen 100 und 300 Upm dreht.

8. Verfahren gemäss einem der vorhergehenden Ansprüche, weiterhin dadurch gekennzeichnet, dass das Behandlungsmaterial in das geschmolzene Metall in einzelnen Mengen oder kontinuierlich eine kurze Zeit nachdem der Wirbel ausgebildet wurde, eingeführt wird.

9. Verfahren gemäss Anspruch 4, weiterhin dadurch gekennzeichnet, dass die Achse der Rührerdrehung exzentrisch in bezug auf die Gefässachse durch eine Entfernung x mit einem Wert von 0,25 bis 0,7 d ist.

10. Vorrichtung zum Mischen von teilchenförmigem, Aluminiumfluorid enthaltenden Material mit geschmolzenem Aluminium, um die verunreinigenden, gelösten Alkalimetalle und Alkalierdmetalle aus dem geschmolzenen Aluminium zu entfernen, wobei die Vorrichtung umfasst

(a) ein zylindrisches Gefäss mit einer vertikalen geometrischen Achse und einem Innendurchmesser D zur Aufnahme eines Körpers aus geschmolzenem Aluminium bis zu einer Höhe H oberhalb des Bodens des Gefässes, wobei das Gefäss keine inneren Prallflächen aufweist,

(b) eine Abdeckung für das Gefäss zum Halten eines mehrblättrigen Rührers und einer Vorrichtung zum Antrieb des Rührers über einer vertikalen Achse und Mittel zum Drehen des Rührers, wobei der Rührer einen Durchmesser d hat und die Schaufeln eine Höhe h haben und der Mittelpunkt der Schaufeln sich in einem Abstand y über dem Boden des Gefässes befindet und die Achse der Rührerdrehung von der geometrischen Achse durch eine Entfernung x entfernt ist und wobei die Schaufeln grössere Oberflächen habeb, die nach unten in einem Winkel θ zur Vertikalen geneigt sind,

(c) wobei die Werte d, D, h, H, x und θ so sind, dass d/D zwischen 0,1 und 0,6, h/H zwischen 0,1 und 0,7, x zwischen 0,1 und 0,25D, y zwischen 0,25H und 0,75H und θ oberhalb 0° und nicht mehr als 45° betragen,

(d) und die Abdeckung auch Mittel trägt zum Einführen des teilchenförmigen Materials und zum Abführen von Dämpfen.

11. Vorrichtung gemäss Anspruch 10, weiterhin dadurch gekennzeichnet, dass d/D zwischen 0,15 und

0,40, h/H zwischen 0,2 und 0,40, x 0,25 und 0,7 d, y zwischen 0,4H und 0,6H und θ zwischen 30° und 40° betragen.

Revendications

1. Procédé pour éliminer les métaux alcalins et alcalino-terreux contenus en impuretés dans l'aluminium fondu par réaction avec du fluorure d'aluminium conduisant à la formation de fluoaluminates de ces métaux, caractérisé en ce que:

(a) on place un chargement de l'aluminium métallique impur dans un récipient vertical contenant également un rotor à lames multiples placé avec excentration par rapport à l'axe du récipient et comportant des lames inclinées vers le bas par rapport à l'axe de rotation;

(b) on agite, au moyen du rotor, l'aluminium fondu contenu dans ce récipient dans des conditions propres à l'établissement dans l'aluminium fondu d'un tourbillon et de courants d'écoulement ayant à la fois des composantes dirigées vers le bas et des composantes latérales au fond dudit tourbillon et de courants hélicoïdaux ascensionnels dans la région de la périphérie dudit récipient;

(c) on envoie une matière en particules contenant du fluorure d'aluminium dans ledit tourbillon pour dispersion et recirculation dans l'aluminium fondu au moyen desdits courants hélicoïdaux;

(d) on poursuit l'agitation de l'aluminium fondu jusqu'à ce que la teneur en métaux alcalins et alcalino-terreux soit abaissée au bas niveau voulu;

(e) on sépare l'aluminium fondu des fluoaluminates de métaux alcalins et alcalino-terreux formés en produits de réaction.

2. Procédé selon la revendication 1, caractérisé en ce qu'il est utilisé pour éliminer de l'aluminium fondu, le lithium, le sodium et le calcium.

3. Procédé selon l'une quelconque des revendications précédentes, caractérisé en outre en ce que le métal fondu est traité par AlF_3 en poudre ou NaF . AlF_3 à un rapport pondéral NaF/AlF_3 compris entre 1,3 et 1,5.

4. Procédé selon l'une des revendications précédentes, caractérisé en outre en ce que le récipient a un diamètre intérieur D et est rempli de la masse fondu jusqu'à une hauteur H, le rotor a un diamètre d et une hauteur de lame H, et le rapport d/D se situe entre 0,1 et 0,6 et le rapport h/H entre 0,1 et 0,7.

5. Procédé selon la revendication 4, caractérisé en outre en ce que l'axe de rotation du rotor est excentrique par rapport à l'axe du récipient, d'une distance x dont la valeur va de 0,1 à 0,25 D.

6. Procédé selon la revendication 5, caractérisé en outre en ce que le point médian des lames est placé au-dessus du fond du récipient et espacé de ce fond d'une distance y dont la valeur va de 0,25 H à 0,75 H.

7. Procédé selon la revendication 4, caractérisé en outre en ce que le rapport d/D va de 0,15 à 0,40 et en ce que le rotor tourne à une vitesse de 100 à 300 tours/mn.

8. Procédé selon l'une quelconque des revendications précédentes, caractérisé en outre en ce que la matière de traitement est introduite dans le métal fondu en quantités séparées ou en continu au cours d'une courte période après établissement du tourbillon.

9. Procédé selon la revendication 4, caractérisé en outre en ce que l'axe de rotation du rotor est excentrique par rapport à l'axe du récipient, d'une distance x ayant une valeur de 0,25 à 0,7 d.

10. Appareillage pour mélanger une matière contenant du fluorure d'aluminium en particules avec de l'aluminium fondu et en éliminer les métaux alcalins et alcalino-terreux dissous à l'état d'impuretés, cet appareillage se caractérisant en ce qu'il comprend:

a) un récipient cylindrique à axe géométrique vertical et diamètre intérieur D servant à contenir une masse d'aluminium fondu jusqu'à une hauteur H au-dessus du fond du récipient, ledit récipient étant essentiellement dépourvu de déflecteurs internes;

b) un couvercle pour ledit récipient, supportant un rotor à lames multiples et un dispositif pour entraîner ce rotor autour d'un axe vertical et un dispositif pour faire tourner le rotor, ledit rotor ayant un diamètre d et ses lames une hauteur h, le point médian de ces lames étant placé au-dessus du fond du récipient à une distance y de ce fond, l'axe de rotation de l'agitateur étant espacé de l'axe géométrique du récipient cylindrique d'une distance x, et les lames ayant des surfaces principales inclinées vers le bas à un angle θ par rapport à la verticale;

c) les valeurs de d, D, h, H, x et θ étant telles que le rapport d/D va de 0,1 à 0,6, le rapport h/H va de 0,1 à 0,7, la valeur de x va de 0,1 à 0,25 D, la valeur de y va de 0,25 H à 0,75 H, et l'angle θ a une valeur de 0 à 45°; et

d) le couvercle supportant également des dispositifs permettant d'introduire la matière en particules et d'évacuer les fumées.

11. Appareillage selon la revendication 10, caractérisé en outre en ce que le rapport d/D va de 0,15 à 0,40, le rapport h/H va de 0,2 à 0,40, le rapport x va de 0,25 à 0,7 d, la valeur de y va de 0,4 H à 0,6 H et l'angle θ a une valeur de 30 à 40°.

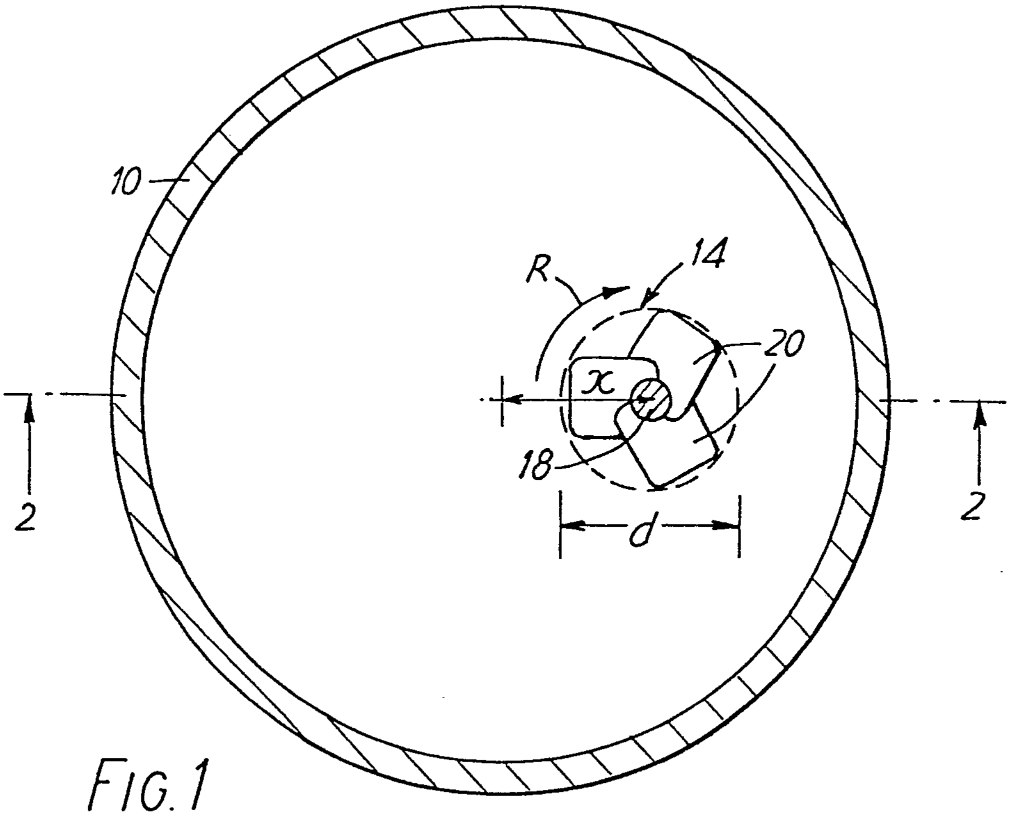
10
R
14
20
x
18
d
2
2

FIG.1

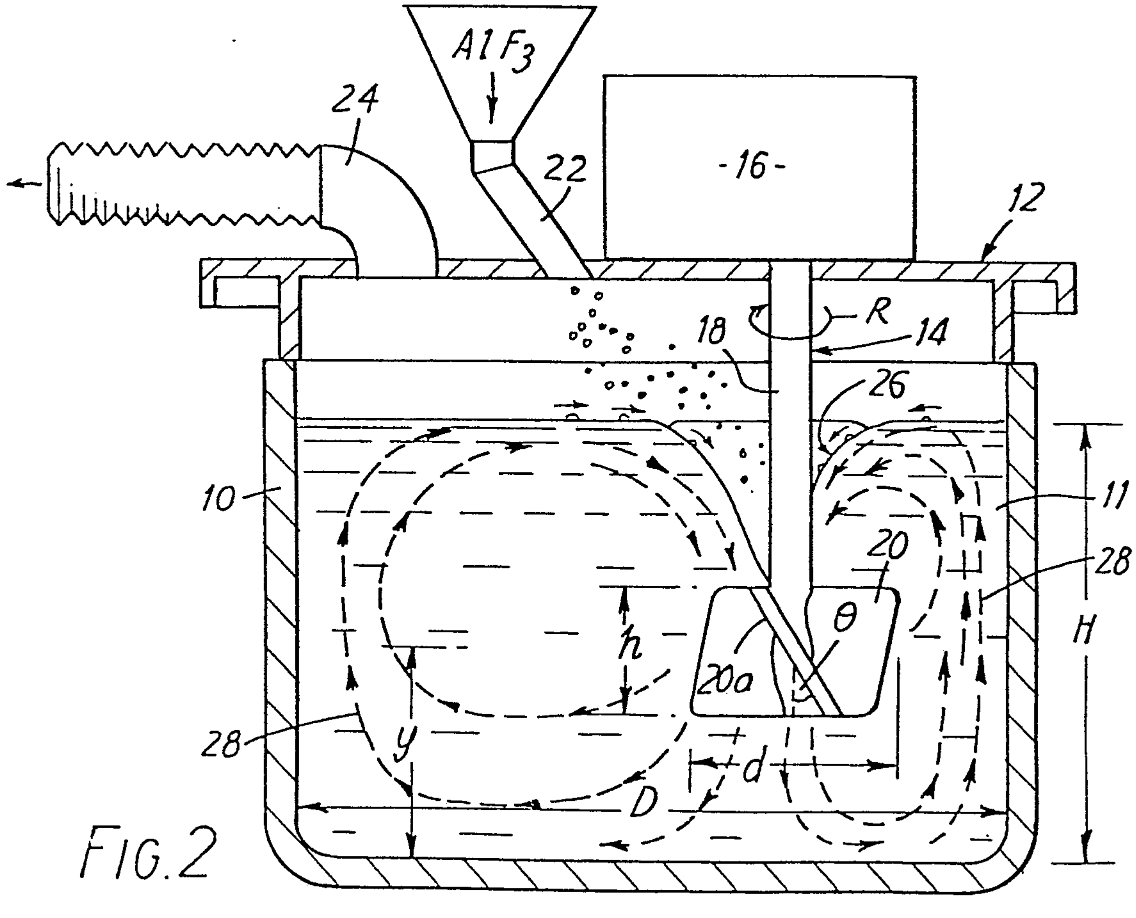
AlF3
24
22
-16-
12
R
14
18
26
10
11
20
28
θ
20a
h
H
28
y
d
D

FIG.2