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(54) Method of casting aluminium and aluminium alloy

(57) A method of casting aluminium or aluminium alloy wherein a fluoride agent is added to aluminium or alloy and admixed therein prior to casting.

A flux composition useful for refining aluminium or aluminium alloy, which contains fluoride agent.

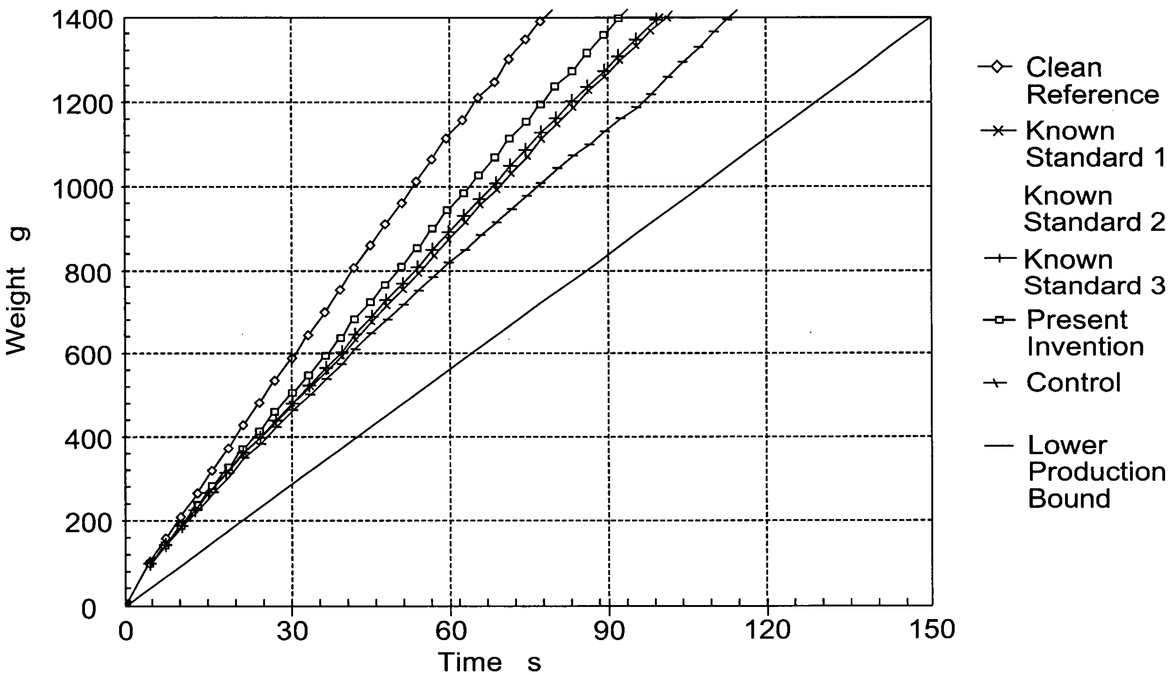

FIG 1 Extrapolated Prefil Results

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Description

[0001] This invention is concerned with flux compositions useful in aluminium and aluminium alloy casting, and with casting methods using such fluxes.

[0002] In the production of semi finished aluminium ingots, problems have been encountered with certain alloys (designated 5000 series and 7000 series) of high magnesium content, due to their tendency to form surface oxide skins during casting. The presence of such oxide formations has led to serious defects such as vertical folds, pits, oxide patches and cracks which have necessitated supplementary processing stages of the solidified alloy such as heavy surface scarfing of the ingot or when cracks are formed, even scrapping of the ingot.

[0003] To mitigate these deleterious effects, it was known to add beryllium metal to the ingot composition. However, use of this additive has been banned due to health, safety and environmental concerns.

[0004] Alternative additives have also been proposed in place of beryllium, for example, US-A-6334978 and 6412164 disclose use of calcium and strontium respectively to alleviate the oxide patch problem. These patents however, do not describe the specific calcium additive.

[0005] In addition to the aforementioned oxide skin formation problems, there have also been problems associated with the presence of excessive levels of alkali metals in the liquid aluminium or aluminium alloy melt. Consequently it is desirable to achieve reductions in alkali metal content and especially sodium content.

[0006] We have now surprisingly found beneficial results with additions of a fluoride agent, either directly by addition to the liquid metal melt or alternatively by way of inclusion of such an agent in the refining fluxes used to reduce sodium levels and oxide inclusions from the aluminium charge in the furnace prior to casting. These fluxes are typically fused granular refining compositions comprising fused potassium and magnesium chlorides.

[0007] We have further unexpectedly found that fluoride agent additions are effective in increasing the fluxes refining efficiency - in particular, we found that a fluoride agent such as an alkaline earth fluoride like magnesium fluoride was very effective - increasing efficiency by up to 50%.

[0008] According to a first aspect of this invention, there is provided a method of casting aluminium or aluminium alloy wherein a fluoride agent is added to the said alloy and admixed therein prior to casting.

[0009] According to a second aspect of this invention, there is provided cast aluminium or aluminium alloy which contains at least one fluoride agent or which contains reaction byproducts(s) derived from said fluoride having reacted with the said aluminium or aluminium alloy and/or with other component(s) present therein.

[0010] According to a third aspect of this invention, there is provided a flux composition useful for refining aluminium and/or aluminium alloy, which contains fluoride agent.

[0011] The fluoride agent is preferably an agent capable of generating fluoride ions in the molten metal and/or in the molten flux composition. The fluoride agent can be at least one inorganic fluoride salt, such as a fluoride of an alkaline earth metal. Preferred fluoride agents include magnesium, calcium, strontium and barium fluorides. Of these, calcium and/or magnesium fluorides are more preferred.

[0012] The addition of fluoride agent is conveniently made through its incorporation within an intermediary flux composition, where a flux is added to the aluminium or aluminium alloy charge prior to and/or during melting within a furnace. Preferably the proportion of $MgCl_2$ in the flux is of the order 15 to 45% by weight, KCL 53 to 83% by weight and the balance being the fluoride agent

[0013] Surprisingly, we have found that a flux composition with a very small addition of fluoride agent such as magnesium fluoride, strontium fluoride or calcium fluoride but preferably calcium fluoride, in the range of 0.1% to 10%, preferably 0.2% to 7%, more preferably 0.5% up to 5% by weight, based on the total weight of the flux composition has proved to be highly effective at reducing or eliminating formation of oxide skins as well as improving the rate of removal of oxides and alkali metals such as sodium from the liquid aluminium or alloy melt.

[0014] The aluminium alloys to be modified by means of the present fluoride additive(s) are preferably those of relatively high magnesium content, more preferably aluminium alloys of the type designated 5000 and 7000 series in the Aluminium Association Registered Alloys which do have relatively high magnesium levels. The amount of, e.g. CaF_2 to be added (to the flux or directly to the melt) can be up to 10% by weight, but is preferably significantly lower such as up to 5% or up to 2%.

[0015] However, magnesium fluoride whilst preferred in terms of performance, is less preferable economically than calcium fluoride which is a cost effective alternative. Barium and/or strontium fluoride may also be less preferred economically.

[0016] We have considered the disadvantageous propensity for calcium compounds if present in the flux to lead to calcium pick-up in the aluminium or alloy melt because calcium has been generally thought to be undesirable along with sodium. However, the specifications for most alloys allow up to 9 to 10 ppm of calcium and therefore, calcium fluoride can be well tolerated as a preferred fluoride agent without adversely affecting the aluminium or aluminium alloy.

[0017] In relation to the 5000 series oxide skins problem we have surprisingly found that the addition of between 1% to 10%, preferably 2% up to 10% such as 0.5% to 5.0% (by weight), e.g. up to 2% by weight of calcium fluoride to the fused flux enables controlled pickup of calcium in the melt sufficient to overcome the surface defect problem and providing therefore, a convenient, practical and cost effective means of addition to the aluminium or alloy

[0018] The flux can be added to the furnace by a variety of normally used techniques, such as adding 5 kg entrained bags to the heel of liquid metal left in the furnace and then making subsequent additions of liquid metal from potline crucibles and/or making ingot or scrap additions to complete the furnace charge. This ensures that the flux is properly entrained in the melt and this is further aided by stirring with a rake mounted on a forklift. Alternatively, the flux very conveniently can be added through a hollow rotating graphite shaft immersed in the melt, a technique known as Rotary Flux Addition.

[0019] In order that the invention may be illustrated reference will now be made to the following non-limiting embodiments by way of example and to the attached Figure, wherein

Figure 1 is a representative flowchart comprising the cleaning efficienty of comparative fluxes and a flux composition according to the invention.

Example 1

[0020] The following flux compositions were prepared

TABLE 1	Flux Composition B	(Invention)	
Description:	Fused granular refining agent		
Chemical data:	**Min %**	**Max %**	
$MgCl_2$	20.0	25.0	%
KCl	60.0	75.0	%
NaCl	0.0	1.2	%
F	0.5	10	%
H_2O		1.2	%
Physical data:			
Grain Size	0.6	3.0	mm
<0.60 mm		3.0	%
<0.85 mm		7.0	%
> 3.0 mm		3.0	%
>5.0 mm		0.0	%
Density	calculated	2.17	g/cm^3
Bulk weight	calculated	1.0	kg/l
Re-solidifying temperature	400	450	°C
Note: the Flux composition B contains an addition of 2% calcium fluoride during manufacture and this results in 1% F in the final mix.			

TABLE 2	Flux Composition A	(comparative)	
Description:	Fused granular refining	agent	
Chemical data:	**Min %**	**Max** %	
$MgCl_2$	20.0	30.0	%
KCl	60.0	75.0	%

(continued)

TABLE 2	Flux Composition A	(comparative)	
Description:	Fused granular refining	agent	
Chemical data:	**Min %**	**Max** %	
NaCl	0.0	1.2	%
Ca^{++}	0.0	0.1	%
H_2O		1.2	%
Physical data:			
Grain Size	0.6	3.0	mm
< 0.60 mm		3.0	%
< 0.85 mm		7.0	%
>3.0 mm		3.0	%
>5.0 mm		0.0	%
Density	calculated	2.17	g/cm^3
Bulk weight	calculated	1.0	kg/l
Re-solidifying temperature	400	450	°C

Example 2

[0021] A furnace with an 80 tonne charge of 8000 series alloy was treated by introducing a flux composition B (invention) containing 2% of fluoride additive through a RFI rotary flux injector and the kinetic index performance compared with that of a standard flux with a composition A (comparative).
[0022] In each case the addition conditions were the same:
[0023] Amount of flux added: 35 kg
Speed of addition: 1kg/minute
Rotation speed: 300rpm
Set Up: High Shear
Treatment time: 35 minutes
[0024] Test number 1 in Table 3 below 1 shows the average of results with standard flux A and the slope of the curve (not shown), y, referred to as the Kinetic Index was 0.0335.
[0025] Tests 2-7 gave the following y values in Table 3 below.

TABLE 3

Test Number	y value (Kinetic Index)
1	0.0335
2	0.0458
3	0.0221
4	0.0432
5	0.0616
6	0.1022
7	0.0595
8	0.0423
Mean 2-8	0.0538

[0026] It was noted that in test 3 the metal bath was not skimmed prior to flux addition and this was considered to have reduced the effectiveness of the flux addition, nonetheless this result was included in the total test results.

[0027] The mean value for the tests with Flux B was 0.0538 representing a surprising 60% increase in Kinetic Index compared to flux A.

Example 3

[0028] In another series of tests, this time in a laboratory, the effectiveness of flux B in removing oxide inclusions from liquid aluminium was measured using a known technique referred to as Pre Fill.

[0029] 2 kg samples of aluminium thin gauge scrap were compacted together with additions of various test fluxes melted in a small HF induction furnace and poured into a special crucible in the Pre Fill device. The liquid aluminium is then pressurized and the metal caused to flow through a small Podfa frit filter placed at the bottom of the crucible and the metal flowing through the filter collected continuously in a pan placed underneath on a load cell. Thus the flow rate of the metal through the filter can be plotted on a chart (not shown) and the cleanliness of the metal exiting assessed according the slope of the curve shown in Figure 1.

[0030] The assessment of the flow curves can be expressed as a numerical value arrived at by the formula:

$$\frac{\text{Flux Curve} - \text{control}}{\text{Clean reference} - \text{control}} \times 100 = \text{Efficiency (\%)}$$

and provided data compiled in Table 4 below:

TABLE 4

Flux	Efficiency (%)		
	Oxide Removal	Fines Removal	Overall Cleanliness Improvement
Clean Reference	100	100	100
Standard Flux C	10.6	20.0	29.0
Standard Flux D	21.9	27.1	35.5
Standard Flux A	15.5	24.9	32.3
Test Flux B	32.4	41.8	51.4

[0031] The results generally and Table 4 in particular shows that the ability of the fluoride agent-containing test flux B to improve overall cleanliness is 60% better than the standard flux A. The improvement over other standard fluxes which do not contain the active fluoride additive is also of a similar degree.

[0032] Thus the improvement in performance in the field trials observed of 60% matches almost exactly with the improvement seen in the laboratory tests and is quite remarkable in view of the very low addition level of additive.

Claims

1. A method of casting aluminium or aluminium alloy wherein a fluoride agent is added to aluminium or alloy and admixed therein prior to casting.

2. A method as claimed in Claim 1, in which the fluoride agent is at least one alkaline earth metal fluoride.

3. A method as claimed in Claim 1 or 2, wherein the fluoride agent comprises magnesium fluoride and/or calcium fluoride.

4. A method as claimed in any preceding Claim, wherein the amount of fluoride agent added is less than 2% by weight, based on the weight of the aluminium or alloy.

5. A method as claimed in any preceding Claim, wherein a flux composition is added to the aluminium or alloy, and the fluoride agent comprises a component of the flux composition.

6. A method as claimed in Claim 5, wherein the flux composition is a fused blend of magnesium and potassium chlorides.

7. A method as claimed in Claim 6 or 7, wherein the fluoride agent comprises 0.1% to 10% by weight, preferably 0.2 to 7.0% by weight, even more preferably 0.5 to 5% such as up to 2% by weight based on the weight of the flux composition.

8. A cast aluminium or aluminium alloy which contains at least one fluoride agent or which contains reaction by-product (s) derived from said fluoride having reacted with the said aluminium or aluminium alloy and/or with other component (s) present therein.

9. A flux composition useful for refining aluminium or aluminium alloy, which contains fluoride agent.

10. A flux composition as claimed in Claim 9, in which the fluoride agent is capable of generating fluoride ions in the molten metal and/or in the flux composition.

11. A flux composition as claimed in Claim 9 or 10, wherein the fluoride agent is at least one alkaline earth metal fluoride.

12. A flux composition as claimed in Claim 11, wherein the fluoride agent comprises magnesium and/or calcium fluoride.

13. A flux composition as claimed in any one of Claims 9 to 12. which is a fused granular refining composition.

14. A flux composition as claimed in Claim 13, in which the refining composition is a fused blend of magnesium and potassium chlorides.

15. A flux composition as claimed in Claim 14, in which the proportion of magnesium chloride is 15 to 45% by weight, the proportion of potassium chloride is 53 to 83% by weight and the balance consisting of or consisting essentially of the said fluoride agent.

16. A method of casting aluminium or alloy thereof as claimed in any one of Claims 1 to 8, using a flux composition as claimed in any one of Claims 10 to 15.

17. A method of casting as claimed in Claim 16, using an aluminium alloy selected from the type designated 5000 series or 7000 or 8000 series in the Aluminium Association Registered Alloys or other alloys which do not comprise significant levels of magnesium.

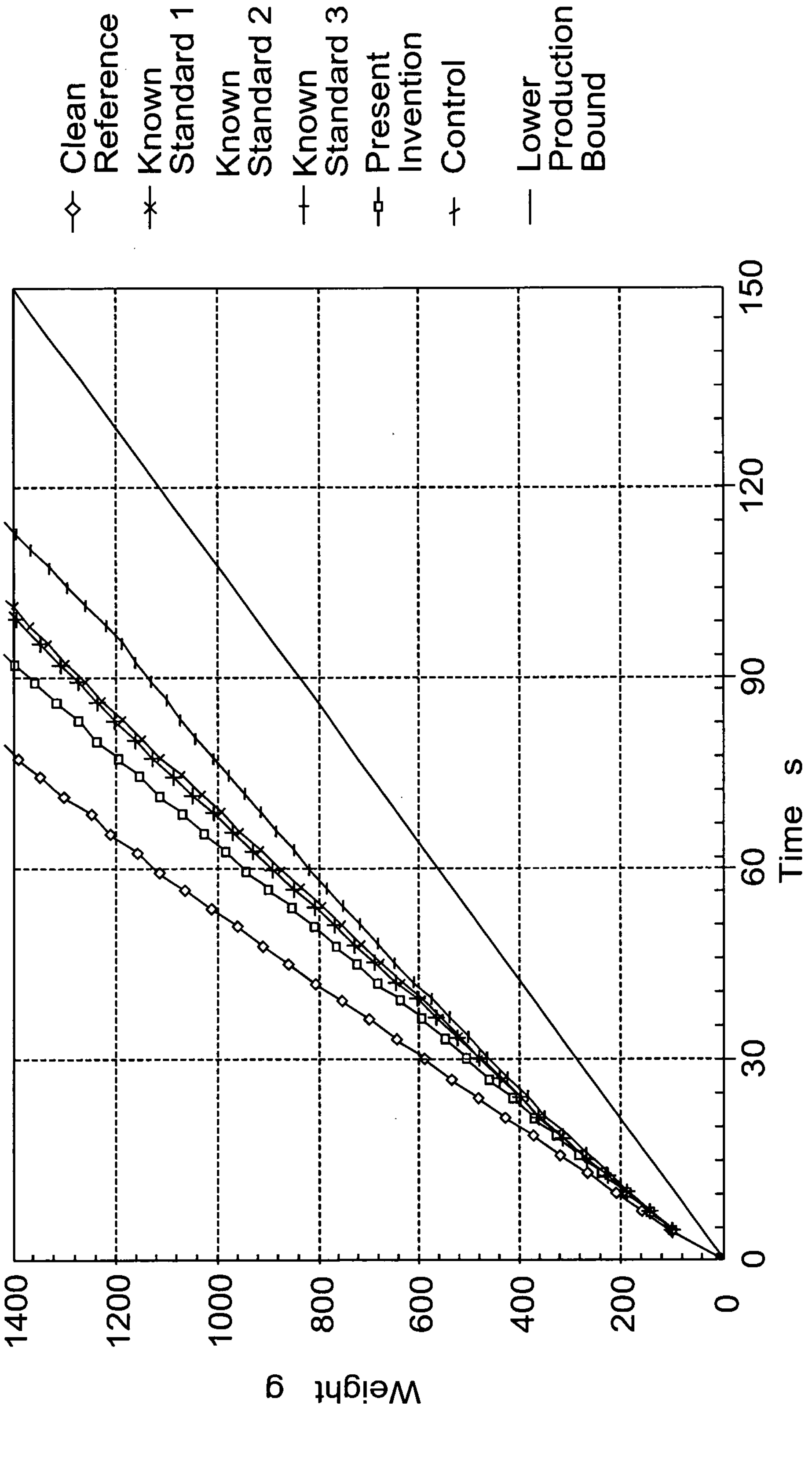

FIG 1 Extrapolated Prefil Results

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EUROPEAN SEARCH REPORT

Application Number
EP 07 01 3585

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	FRIESEN K J ET AL: "Coalescence behaviour of aluminum droplets under a molten salt flux cover" LIGHT METALS, TMS - THE MINERALS, METALS AND MATERIALS SOCIETY, WARRENDALE, US, no. 126th, 1997, pages 857-864, XP009088088 ISSN: 0147-0809 * the whole document * -----	1-17	INV. C22B9/10
X	US 3 194 695 A (RIKIZO YANAGAWA) 13 July 1965 (1965-07-13) * the whole document * -----	1-17	
X	JP 59 047337 A (KOBE STEEL LTD; FOSECO JAPAN LTD) 17 March 1984 (1984-03-17) * abstract; tables 1-21 * -----	1-17	
X	US 4 695 320 A (CHRISTINI ROY A [US] ET AL) 22 September 1987 (1987-09-22) * the whole document * -----	9-15	TECHNICAL FIELDS SEARCHED (IPC)
X	RU 2 203 337 C1 (OOO PROMTREJDINTELL) 27 April 2003 (2003-04-27) * abstract * -----	1-17	C22B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	16 August 2007	Swiatek, Ryszard

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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16-08-2007

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 3194695	A	13-07-1965	DE 1188292	B	04-03-1965
			GB 981795	A	27-01-1965
JP 59047337	A	17-03-1984	NONE		
US 4695320	A	22-09-1987	NONE		
RU 2203337	C1	27-04-2003	NONE		

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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Patent documents cited in the description

- US 6334978 A **[0004]**
- US 6412164 A **[0004]**