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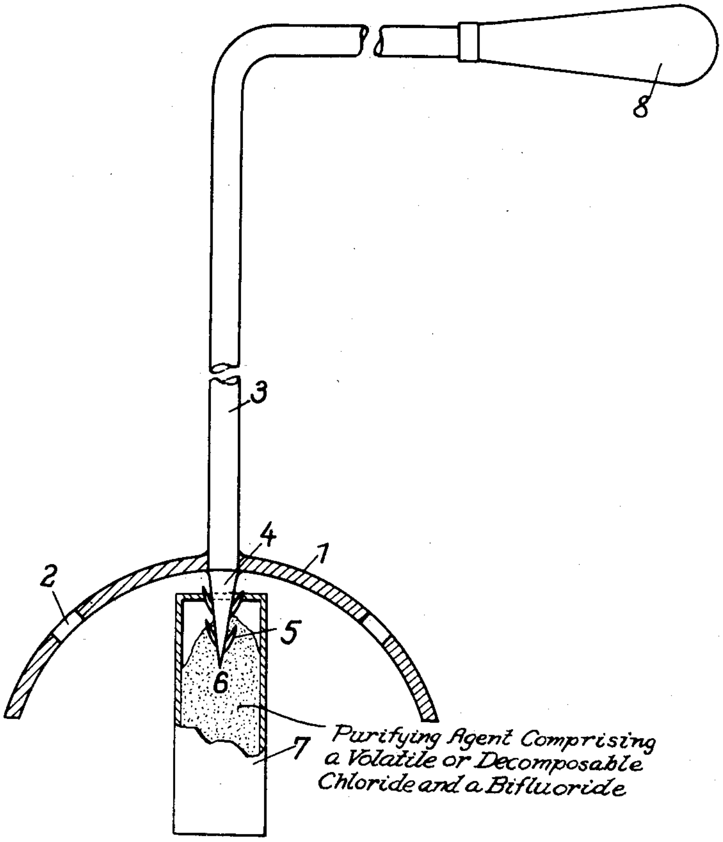

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PROCESS OF SEPARATING OXIDES AND GASES FROM MOLTEN ALUMINIUM AND ALUMINIUM ALLOYS

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Various reports have been published on attempts aiming at separating gases and oxides from aluminium alloys by passing a current of chlorine gas through the metal while in the molten state. It has also been proposed to perform the purifying process by means of chlorides, such as boron trichloride, vanadium chloride, titanium tetrachloride. While the treatment with chlorine in many cases was not successful, the chlorides named are so expensive that they cannot be used per se in practice. Chloride of zinc which has been used for purifying molten aluminium for a long time past has remained the most suitable chloride and the only one in practical use up to the present time. Yet the purification by means of zinc chloride is not entirely perfect. Moreover it cannot be used for alloys which are to remain free from zinc, for instance silumin (Si 13%, Al remainder), piston alloys, or aluminium alloys resisting corrosion, not only because by the treatment with zinc chloride these metals will be contaminated with zinc, but especially because the alloy recovered from the residues contains so much zinc that it cannot be used for the same purpose.

The object of the present invention is a process for separating gases as well as oxides from aluminium and aluminium alloys while in the molten state. For carrying on this process, those chlorides are added to the metal bath that vaporize at or shortly above the melting point of aluminium or the aluminium alloys, for instance, at temperatures from 600–800°. A portion of these chlorides suffer a thermal decomposition at these temperatures, the compound CCl_4 for instance decomposing into gaseous chlorine on the one hand and carbon on the other hand. The selection of the chloride is therefore to be made with the idea that gaseous products will result, since the aim of the process requires that bubbles be formed in the melt by the gases produced, so that in this way the impurities contained in the melt and in particular the unmelted impurities are removed. It has been found, however, that the treatment with chlorides alone, which has already been proposed, is not sufficient to produce a complete removal of the impurities contained in the melt and particularly of any gases which may be dissolved in the melt. For this purpose, the invention provides for the combination of the addition of chlorides with the addition of volatile fluorides. Suitable volatile fluorides are bifluoride of alkali metals and ammonium bifluoride. If a mixture of these substances, i. e., volatile or decomposable chlorides and volatile fluorides of the group consisting of alkali metal and ammonium bifluorides are brought together in the melt, the result is a purified and gas-free metal which when cast yields dense castings. In this manner a purification of the molten metal can easily be attained to such an extent, that perfect castings can be made at only small expenditures. Of the chlorides which answer these requirements, first of all those mentioned above are to be considered, i. e. boron trichloride, vanadium chloride, titanium tetrachloride, and zinc chloride.

Also carbon tetrachloride, antimony pentachloride, silicon chloride, manganous chloride and chlorides of tin and iron may be applied for carrying out the process according to the invention. Most of these chlorides are known to have been used separately for the purpose of purifying metals, particularly for separating gases from molten aluminium; however the present invention does not relate to using such chlorides separately, but to using them in combination with alkali bifluorides.

Carbon tetrachloride was found to be a suitable agent for separating oxides from the molten metals; it was however found, that, in using this agent a significant separation of gases only took place, if there was taken a large amount, i. e. 4–15 cm.^{3}/kg. of metal treated or if the metal was treated a longer time, for instance 20 mintues with this material. If however carbon tetrachloride is used jointly with alkali bifluoride, especially with ammonium-bifluoride, it will be found that both gases and oxides can be completely separated even from a highly contaminated and oxidized melt of aluminium in a short time with a small amount of the flux. In place of carbon tetrachloride, antimony pentachloride or manganous chloride or an analogous compound of chlorine may be used with almost equally good success. These agents too, if used separately, effectuate up to a certain degree a separation of oxides, but only if they are used jointly with alkali bifluoride will a good separation of both oxides and gases be attained.

The action of the aforesaid mixtures upon the metallic melts will however be considerably increased, if silicon chloride is added to these mixtures. Though silicon chloride alone has a very strong purifying and degasifying effect, it evolves by its action hydrochloric acid fumes in such a quantity, that, when used by itself, it will raise practical difficulties. If however it is added to the aforesaid agents the action of the latter can be increased by the silicon chloride, without hydrochloric acid vapours being evolved to such an extent as to be noxious.

The small amount of purifying agents required in carrying out the process according to the invention deserves particular notice. To prove this, a few examples may be disclosed which were ascertained by experiments. In carrying out these tests a comparative sample of about 100 g. was first taken from the metal bath and cooled down in vacuo. Then the agent employed in each particular case was pressed into the molten metal at the same temperature by means of an immersing-bell, until the reaction had ceased. About 200–300 g. of metal were treated in each case. Of the total of this treated metal a sample of 100 g. was at once allowed to cool down in vacuo in a pre-heated crucible, while another sample was taken 10 minutes later, during which waiting-time the melt in the furnace was constantly kept up at its temperature. This second sample was then also allowed to cool down in vacuo. Hereafter the reguli were sawn through and the size of the pores planimetrically measured.

The percentages stated in column 2 under the heading "agent used" refer to the quantity of the purifying agent employed in relation to the quantity of the treated metal.

The following results were obtained:

Comparative tests carried out with K. S. Seawater—alloy of the composition Mg 2–8%, Mn 1.3%, Sb 0.2%, Al remainder at 850° C. temperature of treatment

No.	Agent used	Time	Result, appearance of the reguli
1	Without treatment	At once	Great number of pores, abt. 20% of the volume
1a	Without treatment	After 10 min.	The same
2	0.1% carbon tetrachloride	At once	10 larger pores, abt. 10% of the volume
2a	0.1% carbon tetrachloride	After 10 min.	3 smaller pores, abt. 3% of the volume
3	1% antimony pentachloride	At once	10 larger pores, abt. 20% of the volume
3a	1% antimony pentachloride	After 10 min.	6 larger pores, abt. 20% of the volume
4	1% sodium bifluoride	At once	5 larger pores, abt. 15% of the volume
4a	1% sodium bifluoride	After 10 min.	The same
5	0.5% carbon tetrachloride 2 parts plus sodium bifluoride 1 part	At once	Totally free from pores
5a	0.5% carbon tetrachloride 2 parts plus sodium bifluoride 1 part	After 10 min.	The same

The results of these tests unmistakably show, that in employing the proposed agents individually, the effect is far inferior to that attained by using a mixture of carbon tetrachloride and sodium bifluoride. Naturally the molten metals are, in practice, not treated in vacuo. Yet these tests show, that even under such severe conditions it is possible to attain the positive absence of pores, and therefore the positive absence of gas in the molten metal by treatment in accordance with the invention.

The small amount of the agent required allows now, also to employ in practice those chlorides hitherto considered to be too expensive, such as vanadium chloride, boron trichloride and titanium tetrachloride. In doing this the particular advantage is attained, that a minute quantity of the titanium, or the vanadium contained in the salt forms an alloy with the aluminium, causing a finer grain in the casting. Simultaneously the risk of an absolute purification of the treated metal causing coarse crystals in the castings is hereby avoided.

The finally mentioned chlorides of iron, tin, or zinc, naturally may only be employed in such cases, in which the entrance of zinc, tin, or iron into the alloy are of no detrimental influence. When for example it is intended to purify an aluminium-sandcasting alloy containing zinc one may use zinc chloride in admixture with carbon tetrachloride or antimony pentachloride and alkalibifluoride, because the individual action of zinc chloride is not so intensive as that of its mixtures mentioned. Herewith however an appreciable saving in the working expenses is attained, zinc chloride being obtainable at a low price.

A suitable preparation for purifying a bath of molten aluminium only is composed as follows:

	Per cent
Carbon tetrachloride	60
Ammonium bifluoride	5
Ammonium chloride	20
Titanium tetrachloride	5
Infusorial earth	10

This preparation is filled into an aluminium tube of about 20–25 g. capacity. The metal which may have been considerably overheated is cooled down to 750° C. The immersing device is chosen to suit the shape of the bath containing the molten metal which is to be treated, and is charged with one tube per every 20 kg. of metal. It is then immersed into the metal bath and removed when the reaction has ceased. During the subsequent waiting time of 10 minutes the temperature should drop to 730° C. Then the dross is skimmed off and the metal is taken out of the furnace and cast.

For an alloy of the composition Si 13% Al remainder the following mixture has been found suitable:

	Per cent
Carbon tetrachloride	50
Ammonium bifluoride	10
Boron trichloride	5
Antimony pentachloride	10
Manganous chloride	15
Infusorial earth	10

German alloy is suitably purified with the following mixture:

	Per cent
Carbon tetrachloride	50
Ammonium bifluoride	10
Zinc chloride	30
Infusorial earth	10

For American alloy containing Cu 8% Al remainder, Y-alloy containing Cu 4%, Ni 2%, Ng 1.5%, Al remainder, and similar alloys, for example, the following mixture may be used:

	Per cent
Carbon tetrachloride	50
Copper chloride	20
Manganous chloride	15
Vanadium chloride	5
Infusorial earth	10

If the separation of gases and oxides is intended for example from an alloy of aluminium containing about 0.5% antimony, 1.4% manganese, 2% magnesium, so as to attain a good castibility, it is sufficient to use 1 to 2 per thousand of the weight of the alloy of the above named salts.

The chlorides which occur in the liquid state are preferably allowed to be soaked up by inert material before they are applied. Besides charcoal powder, infusorial earth is particularly suitable for this purpose, because the latter can be ground to an exceedingly fine powder and possesses a good absorptivity. If the chlorides are not in the liquid state, infusorial earth is also a suitable admixture, because it has a saving effect upon the consumption of material, causing the more volatile chlorides not to be released before a certain time of their action has elapsed. Therefore the action upon the molten metal is more intensive and longer lasting, if the chlorides are mixed with infusorial earth or soaked into it. Similar to the action of infusorial earth, though not quite as favourable, is that of asbestos wool.

Since a satisfactory effect of the purifying material can only be attained if the chlorine gas liberated or formed from the chlorides is caused to penetrate into the whole mass of the molten metal, it has been found desirable to use a special device for introducing the material into the molten metal. This device is shown in the accompanying drawing. In the figure (1) denotes a semicircular bell provided with holes (2) at the side to allow the escape of gases, and in the centre of it a pointed plunging rod (3). The point (4) of the plunging rod is provided with beards (5) to allow a firm fastening of the shell (7) which is preferably an aluminium tube, filled with the purifying material (6). The other end of the plunging rod is bent at a right angle and provided with the handle (8), so as to allow the workmen calmly and steadily to insert the purifying material without being spattered or molested by the rising fumes. The bell which is firmly connected with the plunging rod serves the purpose of preventing the chemicals from rising up, and of allowing the evolved gases to be distributed in the molten metal and to escape.

In case of metal baths being shallow, it is advisable to unite a plurality of these bells with each other, forming an aggregate which is simultaneously charged and introduced into the metal.

After the reaction has taken place and after a short waiting-time the slags are taken off and the metal may be cast.

I claim:

1. A process for removing oxides and gases from molten aluminium and aluminium alloys which comprises treating the molten metal with a purifying agent consisting of a chloride which produces a gaseous product at the temperature of treatment and a volatile fluoride of the group consisting of alkali metal and ammonium bifluorides.

2. A process for removing oxides and gases from molten aluminium and aluminium alloys which comprises treating the molten metal with a purifying agent of the group consisting of carbon tetrachloride, antimony pentachloride, manganous chloride, zinc chloride and silicon tetrachloride and a volatile fluoride of the group consisting of alkali metal and ammonium bifluorides.

3. A process for removing oxides and gases from molten aluminium and aluminium alloys which comprises treating the molten metal with a purifying agent of the group consisting of carbon tetrachloride, antimony pentachloride, manganous chloride, zinc chloride and silicon tetrachloride and ammonium bifluoride.

4. A process for removing oxides and gases from molten aluminium and aluminium alloys which comprises treating the molten metal with a purifying agent consisting of carbon tetrachloride and ammonium bifluoride.

5. A process for removing oxides and gases from molten aluminium and aluminium alloys which comprises treating the molten metal with a purifying agent consisting of a chloride which produces a gaseous product at the temperature of treatment and a volatile fluoride of the group consisting of alkali metal and ammonium bifluorides together with a chloride of a metal which alloys with the molten metal causing a finer grain in the cast metal.

6. A process for removing oxides and gases from molten aluminium and aluminium alloys which comprises treating the molten metal with a purifying agent consisting of a chloride which produces a gaseous product at the temperature of treatment and a volatile fluoride of the group consisting of alkali metal and ammonium bifluorides together with a chloride of a metal selected from the group consisting of vanadium and titanium.

7. A process for removing oxides and gases from molten aluminium and aluminium alloys which comprises treating the molten metal with a purifying agent consisting of carbon tetrachloride, a chloride of the group consisting of antimony pentachloride, manganous chloride, zinc chloride and silicon tetrachloride and a volatile fluoride of the group consisting of alkali metal and ammonium bifluorides.

8. A process for removing oxides and gases from molten aluminum and aluminum alloys which comprises treating the molten metal with a purifying agent consisting of a chloride which produces a gaseous product at the temperature of treatment and a volatile fluoride of the group consisting of alkali metal and ammonium bifluorides, said purifying agent being associated with an inert absorptive material.

9. A process for removing oxides and gases from molten aluminium and aluminium alloys which comprises treating the molten metal with a purifying agent consisting of a chloride which produces a gaseous product at the temperature of treatment and a volatile fluoride of the group consisting of alkali metal and ammonium bifluorides, said purifying agent being associated with infusorial earth.

10. A composition for removing oxides and gases from molten aluminium and aluminium alloys comprising a chloride which produces a gaseous product at the temperature of the molten metal and a volatile fluoride of the group consisting of alkali metal and ammonium bifluorides.

11. A composition for removing oxides and gases from molten aluminium and aluminium alloys comprising a chloride selected from the group consisting of carbon tetrachloride, antimony pentachloride, manganous chloride, zinc chloride, silicon tetrachloride, and a volatile fluoride of the group consisting of alkali metal and ammonium bifluorides.

12. A composition for removing oxides and gases from molten aluminium and aluminium alloys comprising a chloride selected from the group consisting of carbon tetrachloride, antimony pentachloride, manganous chloride, zinc chloride, silicon tetrachloride, and ammonium bifluoride.

13. A composition for removing oxides and gases from molten aluminium and aluminium alloys comprising carbon tetrachloride and ammonium bifluoride.

14. A composition for removing oxides and gases from molten aluminium and aluminium alloys comprising a chloride which produces a gaseous product at the temperature of the molten metal and a volatile fluoride of the group consisting of alkali metal and ammonium bifluorides, together with a chloride of a metal which alloys with the molten metal causing a finer grain in the cast metal.

15. A composition for removing oxides and gases from molten aluminium and aluminium alloys comprising a chloride which produces a gaseous product at the temperature of the molten metal and a volatile fluoride of the group consisting of alkali metal and ammonium bifluorides, together with a chloride of a metal selected from the group consisting of vanadium and titanium.

16. A composition for removing oxides and gases from molten aluminium and aluminium alloys comprising carbon tetrachloride, a chloride of the group consisting of antimony pentachloride, manganous chloride, zinc chloride and silicon tetrachloride, and a volatile fluoride of the group consisting of alkali metal and ammonium bifluorides.

17. A composition for removing oxides and gases from molten aluminium and aluminium alloys comprising a chloride which produces a gaseous product at the temperature of the molten metal, and a volatile fluoride of the group consisting of alkali metal and ammonium bifluorides, said purifying agent being associated with an inert absorptive material.

18. A composition for removing oxides

and gases from molten aluminium and aluminium alloys comprising a chloride which produces a gaseous product at the temperature of the molten metal, and a volatile fluoride of the group consisting of alkali metal and ammonium bifluorides, said purifying agent being associated with infusorial earth.

In testimony whereof, I affix my signature.

ROLAND STERNER-RAINER.