TREATMENT OF LIQUID METAL

Inventors: Edward Frederick Emley, Chalfont St. Giles; Malcolm Victor Brant, Stoke Poges, both of England

Assignee: The British Aluminium Company Limited, Gerrards Cross, England

Filed: Sept. 10, 1970

Appl. No.: 71,112

Related U.S. Application Data
Continuation-in-part of Ser. No. 835,872, June 2, 1969, abandoned.

Foreign Application Priority Data
Sept. 12, 1969 Great Britain 45,163/69

U.S. Cl. .................... 75/68 R, 75/93, 75/94, 266/34

Int. Cl. .................... C22b 21/06, C22b 9/10

Field of Search .................. 75/67, 68, 93, 94; 148/23, 26; 210/10, 69

References Cited
UNITED STATES PATENTS

3,025,153 3/1962 Lee................................. 75/68
3,281,238 10/1966 Bachowski.......................... 75/93
2,865,558 12/1958 Brondyke........................... 210/69
2,715,068 8/1955 Weiss............................. 75/68
3,189,491 6/1965 Robbins............................. 148/26
3,198,625 8/1965 Stroup............................. 75/68
3,272,667 9/1966 Siegel............................ 148/23

Primary Examiner—L. Dewayne Rutledge
Assistant Examiner—Peter D. Rosenberg
Attorney—Karl W. Flocks

ABSTRACT
A process for removing non-metallic constituents in molten metal, particularly aluminium and its alloys. In one treatment the metal is flowed through a multiplicity of flux-lined channels which are conveniently provided by a bed of flux-coated granules of a size such that the channels are large enough not to become clogged during use. In another treatment the metal is degassed by continuously passing it through a containing vessel while passing a substantially inert gas such as nitrogen therethrough under a flux cover; this can be followed by passing the metal through the flux-lined channels.

14 Claims, 17 Drawing Figures
TREATMENT OF LIQUID METAL

This application is a continuation-in-part of our application Ser. No. 835,872 filed on 2nd June, 1969, and now abandoned.

FIELD OF THE INVENTION

This invention relates to improvements in the treatment of liquid metal, particularly but not exclusively molten aluminium and especially molten aluminium intended for the production of ingots for working.

BACKGROUND OF THE INVENTION

It is well known that liquid aluminium contains varying amounts of non-metallic constituents, i.e. gas and non-metallic inclusions, and that their presence may give rise to defects in finished products. Many procedures have been proposed for the removal of the gas and inclusions. Thus the gas content may be reduced to an acceptable level by bubbling chlorine, nitrogen or argon through the melt or by treatment of the metal with hexachloroethane. The use of chlorine and hexachlorehthane give rise to a fume disposal problem necessitating expensive equipment, whereas with the nitrogen treatment as heretofore proposed, the metal becomes contaminated through formation of non-metallic inclusions.

For removal of inclusions various filtration procedures have been suggested, for example, those of British Patent Specifications Nos. 701,273 and 831,637 in which the metal is caused to flow from one chamber to another through a bed of refractory granules, the two chambers being separated by a baffle. The preferred filter material of British Patent Specification No. 831,637 is a tabular alumina of 3-14 A.S.T.M. mesh size (0.085-0.250 ins. aperture) supported on a bed of coarse granules ¾ in. - ¾ in. size. In U.S. Pat. No. 3,039,864 it is proposed to pass the metal down through a filter bed and at the same time to pass an inert gas, e.g. argon, through the bed in an upward direction, thereby effecting a degree of degassing at the same time as the filtration. It is, however, usual to carry out a degassing operation, e.g. with chlorine, in a holding furnace prior to passage of the metal through the filter unit. U.S. Pat. No. 3,039,864 states that nitrogen can be used in place of argon if the formation of nitrides can be tolerated, but that chlorine is undesirable since it gives rise to chlorides which cause rapid blocking of the filter. Examination of the filter bed of such a filter after use shows that oxide and other non-metallic inclusions are trapped in the metal in the interstices between flakes of tabular alumina, but that the metal does not wet the flakes. In consequence, the filtered impurities are loosely contained in the filter bed and are readily released if the filter is accidentally jolted or is prodded in order to promote a faster metal flow. The action of the filter bed is not one of filtration but of settlement of impurities from the liquid during quiescent flow through the many channels between the flakes. Special procedures are needed at the outset to persuade the liquid metal to pass through this type of filter bed, the minimum thickness of which is 6 in., and that partial blockage of flow may occur during use so that a considerable hydrostatic head is needed to maintain the desired rate of flow which, for multi-strand casting of large blocks, may exceed 600 lb/min.

SUMMARY OF THE INVENTION

We have discovered that non-metallic inclusions can be removed from molten aluminium by causing the aluminium to flow through a cleaning device comprising a bed providing a multiplicity of flux-lined tortuous channels, e.g. very coarse granules the surface of which have been coated with a thin layer of liquid flux. Alumina balls of ¾ in. diameter are suitable. With such a cleaning device removal of inclusions is at least as effective as with the flake filter of U.S. Pat. No. 3,039,864 but the present invention presents additional advantages. Because of the flux layer on the alumina balls, they are wetted by the metal and inclusions therein coming in contact with the flux film readily adhere thereto. In consequence, the inclusions are retained in the bed and are not readily released on jolting the bed. Furthermore, because of the coarse nature of the granular bed which can be used, no special steps are needed to start the metal flow, there is no fear of blockage of the system, and metal flows through the bed without the need for a hydrostatic head of metal.

According to one aspect of the present invention there is provided a process for removing non-metallic constituents in molten metal especially aluminium which comprises flowing the metal through a multiplicity of flux-lined channels.

The channels are desirably provided by a bed or layer of coarse refractory granules coated with a flux.

The coarse refractory granules are preferably of alumina and may be in the form of alumina balls of approximately ¾ in. diameter and preferably not less than ¾ in. diameter. Suitable flux compositions are given in Table 1 below.

Although tests have shown little tendency for the flux coating to be removed from the coated alumina balls by passage of the metal over them, the treated metal can, if desired, be stripped of any entrained chloride by passing it through a bed of uncoated granules, for example, alumina balls, which are readily wetted by chloride-base fluxes.

Whilst the cleaning step of the present invention is very effective in removing non-metallic constituents, it is less so in removing clusters of intermetallic particles, e.g. titanium-rich particles, which may be suspended in the liquid metal. To remove these, the metal may be flowed through a second bed composed of uncoated refractory granules, whereby the intermetallic particles settle out in the interstices of the second bed.

Advantageously, the metal is flowed upwardly through the second bed.

The dirtying effect of nitrogen in the degassing of aluminium is well known, and because of this effect nitrogen has found little practical favour as a degassing agent for aluminium. The inclusions produced on nitrogen treatment give rise to bubbling when a sample of the liquid is solidified under low pressure, as in the Straube-Pfeiffer test, even when the hydrogen content of the metal is very low. In consequence, the progress of gas removal by nitrogen cannot readily be assessed by using this test. Instead use has been made of more expensive degassing agents such as chlorine and hexachlorehthane which do not give rise to inclusions and in fact exert a cleaning effect by virtue of their fluxing action.

We have now discovered that the dirtying effect produced by nitrogen treatment of the molten metal can
be materially reduced, if not entirely obviated, by introducing the nitrogen into the molten metal whilst maintaining a continuous liquid flux cover over the molten metal. This treatment is not limited to the use of nitrogen as other gases inert to the molten metal being treated, such as argon, carbon monoxide and carbon dioxide may be used at least with some alloys.

Thus, in another aspect the invention provides a process for removing non-metallic constituents from molten metal, especially aluminium, by passing a substantially inert gas therethrough whilst maintaining a liquid flux cover over the molten metal and subsequently flowing the metal through a device comprising a plurality of flux-lined channels.

It is preferred to introduce the gas, e.g. nitrogen, into the molten metal through a tube or brick of porous non-carbonaceous refractory material.

The worst conditions for dirtying the metal are provided by introducing the gas through porous graphite or carbon tubes in the absence of a flux cover. However, such carbonaceous tubes can be employed if the liquid flux cover is maintained over the molten metal and especially where the latter is subsequently flowed through a bed or layer of coarse refractory granules coated with flux. Even a perforated iron tube can be used, but this is not preferred since, even though the metal does not become dirtied, any protective dressing applied to the tube is liable to become wetted by the flux cover with consequent attack of the tube by the molten aluminium. The iron tube may be coated with a vitreous enamel to reduce attack by molten aluminium.

If a porous non-carbonaceous refractory tube or brick is used for introducing the nitrogen and a liquid flux cover is applied to the metal surface, then dirtying of the metal does not occur. In fact, metal which has been made dirty for experimental purposes, e.g. by addition of a proportion of oily swarf and/or by nitrogen treatment through a graphite tube in the absence of a flux cover, can actually be cleaned by providing a liquid flux cover and passing the metal with nitrogen. The more rapid the stream of nitrogen the greater the cleaning action because of the increased contact between metal and flux cover. By contrast, in the conventional treatment of aluminium through carbonaceous tubes in the absence of a continuous liquid flux cover, the more rapid the nitrogen flow the dirtier the metal becomes. When nitrogen degassing is carried out with porous refractory tubes, no difficulty is encountered in applying the Straube-Pfeiffer test to assess the progress of gas removal.

If the turbulence produced in the liquid aluminium which gives rise to intimate contact between metal and flux is sufficiently prolonged, it is possible not only to remove oxide and other non-metallic inclusions originally present in the metal to be treated but also to wet and absorb inclusions arising from the introduction of nitrogen through carbonaceous refractories as rapidly as these inclusions can form. Under such circumstances it is not essential to flow the degassed metal through a bed of flux-coated coarse refractory granules in order to produce clean degassed metal, and we have found that when dirty gassy metal is degassed with nitrogen under a flux layer metal of very low gas content is readily obtained in a high state of cleanliness and showing complete freedom from bubbles when subjected to the Straube-Pfeiffer vacuum solidification test, even though the nitrogen is introduced through porous carbonaceous refractories.

Such a process of degassing under a liquid flux is not readily applicable to the treatment of metal in a holding furnace such as the large reverberatory furnaces used in conventional practice, because of the quantity of flux required to maintain a liquid flux film over such a large area; it may however be carried out in a forewell to, or alcove, or cubicle within, such a reverberatory furnace or in a vessel of small cross-sectional area placed between the holding furnace and the casting machine and through which the metal is caused to flow.

The achieve best results it is necessary to provide a minimum quantity of nitrogen in relation to the quantity of metal to be treated, a sufficiently long time of contact between the metal and flux, a minimum quantity of flux per unit area of metal surface, and adequate turbulence.

According to a further aspect of the present invention liquid aluminium is cleaned and degassed in continuous manner by causing a stream of liquid metal to flow through a containing vessel of such capacity in relation to the metal flow that the residence time of the metal in the containing vessel is at least 1 min., passing a substantially inert gas into the metal in the containing vessel at a rate sufficient to provide at least 10 cubic feet per ton of liquid metal, and maintaining a cover of liquid flux upon the surface of the metal in the containing vessel.

Preferably the residence time of the metal in the degassing chamber is at least 3 min.

The inert gas is preferably nitrogen.

The nitrogen flow rate may conveniently be such as to provide 30 cubic feet per ton liquid metal in order to give a wide margin of safety, but good results have been obtained with flow rates as low as 10 cubic feet per ton.

The minimum quantity of flux required is 1 lb for each 100 square inches of surface area of liquid metal in the degassing chamber and 2-3 lb per 100 square inches is preferred.

The degree of turbulence required is vigorous but should not be so great as to give rise to splashing of metal from the containing vessel. Introduction of the required flow rate of gas into a chamber of the required size will normally result in an adequate degree of turbulence when the gas is diffused in through porous refractory bricks, tubes or diffuser plates. If a greater degree of turbulence is needed it is possible to introduce a proportion of the nitrogen into the degassing chamber through one or more narrow tubes whereby the jets of gas so produced give rise to a tumbling action of the metal which enhances the cleaning and degassing effect. It is possible in this way to reduce the total flow rate of gas required. Satisfactory results have also been obtained where the whole of the nitrogen is introduced via jets.

The temperature of the molten aluminium during treatment should normally be in the range of 675°-800°C. 700°-750°C being preferred.

We have now applied our discoveries of the cleaning effect of coarse flux-coated refractory granules and of how to degas aluminium with nitrogen under non-fouling conditions to the problems of devising a single metal treatment unit capable of receiving on the ingoing side, liquid metal which has been given no degassing or settling treatment whatever, and delivering, on the outgoing side, cleaned, degassed metal suitable for immediate casting into billet or rolling block intended
for the most exacting applications. We have shown that such a result can be achieved by combination of the following features:

1. The metal enters the first chamber of the unit by falling through a liquid flux cover on the metal in the chamber, or is introduced into the first chamber under a flux cover, e.g. by the use of a baffle.
2. Nitrogen is passed through the liquid metal in the first chamber under the flux cover, preferably using non-carbonaceous porous refractory tubes or bricks to introduce the gas.
3. The metal is passed through the bed or column of flux-coated coarse refractory granules into a second chamber.
4. The metal is passed through a layer or column of uncoated coarse refractory granules in the second chamber and is then ready to be cast.

BRIEF DESCRIPTION OF THE DRAWING

Some embodiments of the invention will now be described by way of example, reference being made to the accompanying drawings in which:

FIG. 1 is a somewhat schematic sectional view of an apparatus for degassing and cleaning molten aluminium in accordance with the invention;
FIG. 2 is a view similar to FIG. 1 illustrating a modification;
FIGS. 3, 4 and 5 illustrate modifications of a part of the apparatus shown in FIG. 1;
FIG. 6 is a view similar to FIG. 1 but illustrating a further modification;
FIGS. 7 and 8 illustrate still further modifications;
FIG. 9 is a sectional view of an apparatus suitable for cleaning and degassing molten metal;
FIG. 10 is a fragmentary view illustrating a modification of the apparatus of FIG. 9;
FIG. 11 is a sectional view of another cleaning and degassing apparatus;
FIG. 12 is a sectional view of a further cleaning and degassing apparatus;
FIG. 13 is a sectional view of another cleaning and degassing apparatus;
FIGS. 14A and 14B are plan and sectional views respectively, of part of a reverberatory furnace modified for use in the method according to the invention; and
FIGS. 15A and 15B are plan and sectional views respectively, of part of a reverberatory furnace modified in an alternative manner for use in the method according to the invention.

DETAILED DESCRIPTION OF EMBODIMENTS

In the arrangement shown in FIG. 1, a crucible 1 having a long pouring lip 1a is fitted with a baffle 2 which extends into the crucible and effectively divides it into two chambers A and B which are in communication by way of a space left below the baffle 2. A tube 3 extends into the chamber A towards the floor thereof and terminates in a porous plug 3a of non-carbonaceous refractory material. A gas jet 4 is provided externally of the crucible 1 to heat the contents thereof. A bed of flux-coated aluminia balls 5 of about 3/16 in. diameter is provided in the chamber A and a bed of uncoated aluminia balls of about 3/16 in. diameter is provided in the chamber B. The bed of uncoated balls 6 can extend below the baffle 2 and below the bed 5. A launder 7 is provided to flow molten aluminium from a holding furnace (not shown) to the chamber A. The pouring lip 1a extends from the chamber B to a casting launder 8.

In the operation of the apparatus described, a body of molten aluminium is maintained in the chamber A and a flux cover 9 is maintained thereover. Molten aluminium enters the chamber A from the launder 7 by falling through the flux cover 9. The metal is degassed by a gas such as nitrogen which is supplied through the tube 3 and escapes from the plug 3a to bubble up through the molten aluminium in chamber A. As the pouring lip 1a is below the level at which molten aluminium is maintained in the chamber A, there is a continuous flow of molten aluminium from chamber A to chamber B and out over the pouring lip 1a to the casting launder 8. The molten aluminium therefore leaves the launder 7, falls through the flux cover 9 into chamber A where it is degassed by the nitrogen, flows downwards through the bed of flux-coated balls 5 in which non-metallic inclusions are removed, passes under the baffle 2 and upwards through the bed of uncoated balls 6 in which intermetallic particles and residual flux are removed and then flows out over the pouring lip 1a to the casing launder 8 in a condition ready for casting.

Accordingly, the arrangement shown in FIG. 2 is similar in many respects to that described with reference to FIG. 1 and like references are used to denote like parts. In this case, the crucible 1 of the previous example is replaced by a box 1b lined with refractory brick and the plug 3a is replaced by a porous refractory tube 3b of non-carbonaceous material. In this case, the launder 7 opens to the chamber A below the level of the flux cover 9 which is confined between the baffle 2 and a further baffle 2a and the walls of the box 1b. The baffle 2a also serves to skim the molten aluminium flowing to the chamber A from the furnace tap hole which is shown at 10.

As the gas jet 4 of the previous example is not essential, it is omitted from FIG. 2. In this case, the box 1b would be pre-heated with a gas flame before being charged with molten aluminium and the balls 5 and 6. Also, immersion heaters may be placed in the chamber A to provide a greater control over the metal temperature.

FIGS. 3, 4 and 5 illustrate alternative ways in which the molten aluminium can be introduced into the chamber A from the launder 7. In FIG. 3, the launder 7 terminates in a spout 7a which extends through the flux cover 9. In FIGS. 4 and 5 the launder 7 terminates in a slight bowl the floor of which is in the form of a perforated refractory screen 7b which breaks up the molten metal as it enters the chamber A. In the embodiment shown in FIG. 4, the porous screen 7b is disposed within the flux cover 9 and in the embodiment shown in FIG. 5 it is disposed above the flux cover 9. In addition to use of a perforated refractory screen 7b or as an alternative thereto, a splash plate (not shown) immersed in the flux cover 9 may be used in order to break up the molten aluminium as it enters the chamber A and so assist in the cleaning and degassing of the molten metal.

In the arrangement shown in FIG. 6, the chambers A and B of the previous examples are followed by further chambers C and D defined by additional baffles 2b and 2c, the baffle 2b extending upwardly from the floor of the crucible 1 or box 1a (as the case may be) to below the level of the molten aluminium and the baffle 2c extending downwardly into the molten aluminium and...
into a further bed of uncoated coarse refractory balls 6a, e.g. of alumina, of about ¾ in. diameter. Thus, the molten aluminium leaving the chamber B flows over the baffle 2b into the chamber C, downwardly through the bed of uncoated balls 6a, under the baffle 2c, upwardly through the bed of uncoated balls 6a and out over the casting launder 8. This passage of the metal through the bed of balls 6a renders the treatment more effective particularly in respect of stripping the metal of any residual flux entrained therein due to the downward flow of the metal through the uncoated balls 6a in the chamber C. The flux, being lighter than the molten aluminium tends to rise in the chamber.

It will be appreciated that the two stages of the process described above, namely, the first stage of degassing the molten aluminium and flowing it through the bed of flux-coated balls 5 and the second stage of flowing it through a bed of uncoated balls 6, can be carried out in separate vessels. In such event, the chamber B could be omitted and replaced by chambers C and D, also where space between the holding furnace is not sufficient to accommodate apparatus such as shown in FIG. 2, at least one of the beds of balls 5 and 6 could be disposed along the casting launder 8 and retained by suitable baffles. The degassing step could be carried out under a flux cover in the holding furnace, for example, in an alcove or forewell thereof.

Another way of separating the process into two convenient stages is shown in FIG. 7. This is very similar to that shown in FIG. 6 except in this case the chambers A and B are contained in one crucible 1 and the chambers C and D are contained in a separate crucible 12, the two crucibles communicating by way of a launder 12. Also, in this example, the molten metal is introduced into the chamber A below the flux layer 9 by way of baffle 2a as in the example illustrated in FIG. 2 and the nitrogen is introduced through a side wall to escape from the porous refractory tube 3b.

In the arrangement illustrated in FIG. 8, the degassing under the flux is carried out in a separate first vessel 13 which may be a brick-lined box, the metal being introduced below the flux-layer 9 by means of baffle 2a and flowing under baffle 2 upwards to spill over into the launder 12 from which it pours into the baffled crucible 14 containing a bed of alumina balls of which at least the upper layers are flux-coated balls 5 followed on the other side of the baffle 2 by a bed of uncoated balls 6. As mentioned previously, for practical purposes, the bed of balls 5 need not be initially be coated with flux as it takes but a few minutes of operation of the process for at least enough of them to become sufficiently coated with flux for the process to operate efficiently. As can be seen from FIG. 8, the nitrogen is supplied to the molten metal under the flux cover 9 through two porous refractory tubes 3b.

The porous refractory non-carbonaceous material used to introduce the gas, e.g. nitrogen, into the molten aluminium may be of any suitable known type. Examples are refractories with a high alumina content, silicon carbide, silicon carbide bonded with silicon nitride and zircon. These are generally satisfactory if of sufficient porosity, but a high silica content should be avoided. Lumps of the refractory material may be shaped into plugs or bricks and drilled to receive a refractory tube through which the gas is fed to the plug, or the refractories may be in tube form. The porous plugs or tubes may be cemented into the walls of the vessel or may even form part of the floor.

The coarse refractory granules used in the beds 5, 6 and 6a may be of chromite, corundum, forsterite, magnesia spinel, magnesium fluoride, periclase, taynite, silicon carbide or zircon, all of which may be regarded as chemically inert to molten aluminium. They may be, in the case of beds 6 an 6a of porous or non-porous graphite, but balls of tubular alumina are, in general preferred to provide the loose packing and freedom from blockage which is desirable and which the concept of a bed of flux-coated coarse balls 5 makes possible.

The granules should be of such a size as to be retained by a ½ in. screen and ¾ in. diameter balls are preferred.

The temperature of the molten aluminium during treatment should be in the range of 675°-800°C, 700°-750°C being preferred.

Suitable compositions for the flux cover 9 and the flux coating of the bed of balls 5 are given in Table 1. The flux should be substantially free from oxides, oxysalts and fluosilicates and from volatile halides. It should consist essentially of the chlorides and fluorides of the alkali and alkaline earth metals including magnesium and should be thinly fluid at the melting point of the metal; when melted it should have a lower density than liquid aluminium.

<table>
<thead>
<tr>
<th>TABLE 1.—SUITABLE FLUX COMPOSITIONS (PERCENT BY WEIGHT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>B</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>D</td>
</tr>
<tr>
<td>E</td>
</tr>
<tr>
<td>F</td>
</tr>
<tr>
<td>G</td>
</tr>
<tr>
<td>H</td>
</tr>
</tbody>
</table>

As a flux for coating the balls and for providing a liquid flux cover on the top of the metal in the degassing chamber, mixtures of KCl and NaCl with small additions of CaF₂ are normally preferred (Flux A). Additions of NaF or cryolite may be included to reduce the melting point (Flux B), but a small amount of sodium will then be introduced into the metal and this may be detrimental to aluminium-magnesium alloys, e.g. of the A A 5356 type. For such alloys it is preferable to use a flux which, far from introducing sodium into the alloy, will reduce the very small content initially present as an impurity in primary metal. Suitable fluxes contain MgCl₂ (Fluxes C, F.G.H.).

Thus by using a suitable flux cover such as one of Fluxes C.F.G. or H the method of the present invention may be applied to the continuous removal of sodium from liquid metal without the generation of objectionable fumes such as occur when liquid aluminium is treated with chlorine or hexachlorethane.

If desired a heavy fluid flux may be used to coat the alumina balls and thereby obviate the risk of flux being washed off the balls by the flow of aluminium (Fluxes
Such fluxes contain BaCl₂ and are in consequence more expensive. There is some advantage in using a flux of type A in that as the cleaning process proceeds any flux which becomes entrained in the metal is absorbed on the uncoated balls which thereby become flux coated and so extend the available area to which inclusions can adhere. Once the chloride layer on the balls has become completely coated with non-metallic inclusions this does not exhaust the useful life of the filter, since more inclusions (e.g. oxide particles and films) can adhere to those already adhering to the flux layer.

It is also possible to incorporate KF or potassium cryolite into the flux in place of NaF or cryolite. When MgCl₂ is also present, the KF will be converted to KCl however, and the MgCl₂ to MgF₂.

By way of example the following experiment is cited. An apparatus essentially as shown in FIG. 2 was constructed preheated by removable gas jets, and a 6 in. deep layer of preheated 4% in. diameter alumina balls added to each chamber. Metal was run into the equipment until the chambers were approximately half full. Preheated 4% in. diameter alumina balls were then dipped in a bath of liquid flux and removed by means of a preheated hand ladle for transfer to the ingoing side (Chamber A) of the baffle 2. A 4 in. layer of flux-coated balls 5 was built up in the way in Chamber A. A 6 in. layer of preheated 4% in. diameter alumina balls was then built up in chamber B. When this was complete, approximately 20 lb. of flux was placed on the metal in chamber A, and as soon as this had melted the nitrogen supply was turned on and a flow rate of 2 cu.ft/min established. 5 tons of liquid A A 6063 type alloy which had been subjected to neither a degassing nor a settling treatment was passed through the equipment at a temperature of approximately 725°C and a flow rate of 150 lb/min and cast by the semi-continuous direct chill process into two rolling blocks of sections 30 in. x 10 in. Samples were taken from the metal entering and leaving the equipment to determine gas and inclusion content. The results obtained are shown in Table II.

<table>
<thead>
<tr>
<th>Cleanliness assessment (by fracture examination)</th>
<th>Bubbling during cooling and solidification</th>
<th>Appearance of solidified surface</th>
<th>Hydrogen content, cm/300 g.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dirty to fairly clean</td>
<td>Continuous</td>
<td>Arched porous crusts</td>
<td>0.48 0.32 0.31</td>
</tr>
<tr>
<td>Clean</td>
<td>Nil</td>
<td>Smooth surfaces free from blisters and with central depression</td>
<td>0.04 0.06 0.08</td>
</tr>
</tbody>
</table>

The metal charge used consisted entirely of scrap metal and included approximately 1 ton of scalings. In this particular experiment the porous refractory tube shown in FIG. 2 was replaced by porous carbon, so that the experiment represented a severe test of the efficiency of the equipment in removing inclusions as well as gas. We have carried out comparative experiments with the process described by U.S. Patent No. 3,039,864 on the same scale as the experiment described and subjecting the metal to a prior chlorine degassing treatment, but even so the hydrogen contents which result have been in the range 0.12-0.17 cm³/100g which, though very satisfactory for normal purposes, is not as low as the figures obtained with the process of the present invention (0.04-0.12 cm³/100g).

In considering why the latter process should be the more effective, even though starting from completely degassed metal, it is probably significant that a solid froth of chilled metal and argon, together with oxide formed from adventitious air, tends to accumulate on the surface of the metal in the degassing chamber during operation of the process of U.S. Patent No. 3,039,864, whereas in the process of the present invention the metal surface is maintained free from oxide. It is well established that oxide scum on liquid aluminium hinders both pick-up by and escape of gas from the metal, whereas a very thin fluid flux layer on the metal surface allows gas to pass in or out readily. The fluid flux layer used in the present invention prevents all gas formation, despite the turbulence, and a clean metal surface through which gas can readily escape is continually maintained. Maintenance of a continuous layer of liquid flux is unnecessary so long as the metal surface remains well fluxed.

If desired, argon may be used in place of nitrogen but there is no obvious technical advantage in doing so, since metal of high cleanliness and low gas content can be prepared with the cheaper gas nitrogen. For best results the "white spot" grade of nitrogen may be used but the ordinary commercial grade is nevertheless satisfactory.

It is to be appreciated that although the bed of flux-coated alumina balls 5 is the preferred way of obtaining the flux-lined channels through which the molten metal is flowed, such channels can be obtained in other ways. Thus, for example, the metal could be flowed between overlapping spaced flux-lined baffles which together form a tortuous path for the metal and provide the same or similar effect as the flux-coated balls, or flowed through one or more pads of coarse steel wool or turnings which have been first dipped in liquid flux and then placed in a trough launder or crucible, the pads being kept in position by means of suitably placed baffles.

Whilst however the step of flowing the degassed molten metal through the bed or column of flux-coated granules followed by the bed or column of uncoated granules will ensure a high degree of freedom from oxide inclusions etc., it is possible by controlling the conditions, as already indicated, to remove non-metallic inclusions so effectively at the prior stage of nitrogen treatment under a liquid flux cover that subsequent passage through one or more columns of granules may not be required even for critical applications, provided some alternative means is available for stripping from the outflowing metal any entrained flux which may be present. In operating the present inven-
tion in the absence of a column of granules we find that some liquid flux passes into the exit chamber and coats the walls with a thin layer any excess of which is displaced upwards to the metal surface. By placing one or more baffles in the exit launder from the degassing chamber it is possible to prevent seepage of liquid flux into the casting, but this can be more effectively ensured by applying to the metal surface on the inflowing side of an exit launder baffle a thin layer of powdered CaF₂ or MgF₂. This layer may be confined by two baffles to a short length of the launder, e.g. 6–9 in. The CaF₂ may if desired, be applied also to the surface of the metal in the exit chamber. Alternatively, CaF₂ may be replaced by an inspissated flux of the kind well known in the magnesium industry so as to form a pasty viscous flux cover with a high absorptive power for fluid fluxes of the type shown in Table 1.

The operation of the present invention whereby the columns of balls is reduced in depth or eliminated is further illustrated by the examples of FIGS. 9–15.

In the arrangement illustrated in FIG. 9 there is provided a crucible 101 provided with a baffle wall 102 extending towards the floor of the crucible to form the chambers A and B. A launder 103 supplies molten metal to the chamber A allowing it to pass through a flux cover 104 floating on the metal in the chamber A. As will be appreciated, the launder 103 can be disposed to admit molten metal to the chamber A under the flux cover 104 or into the flux cover 104. The molten metal flows through the chamber A under the baffle 102 to the chamber B and overflows along an exit or casting launder 106.

The apparatus, so far described, is broadly sufficient for the purpose of the present invention. However, various modifications may optionally be made to improve it. Thus a shallow bed 7 of ¾ in. diameter alumina balls may be disposed in the chamber A to provide a layer of porous plugs 105 to reduce buoyancy effects and to assist in in situ delivery. Furthermore, as shown, the bed 107 of balls may extend to a point above the level of the base of the baffle 102 to reduce possible channeling effects of the molten metal in its flow from chamber A to chamber B. Additionally, as also shown, the bed 107 of balls may extend to the chamber B.

The bed 107 of balls tend to remove any flux entrained in the metal passing therethrough. Instead of the bed 107 of balls, or in addition thereto, a launder baffle 108 may be disposed in the exit or casting launder 106 to prevent seepage of liquid flux to the casting location. This can even more effectively be prevented by applying to the metal surface on the inflowing side of the exit launder baffle 108 a thin layer 109 of powdered CaF₂ or MgF₂. This can extend over the surface of the metal in the chamber or can be confined between two baffles 108a and 108b in the exit or casting launder a shown in FIG. 10.

The apparatus of FIG. 11 is generally similar to that of FIG. 9 and comprises a crucible 101 divided by a baffle 102 into chambers A and B. Chamber A is supplied with molten metal through a launder 103, the molten metal passing under a flux cover 104 being prevented from running back along the launder by a baffle 110. An open ended graphite tube 111 extends into the chamber A for admitting nitrogen into the molten metal. The molten metal flows through the chamber A under the baffle 102 to the chamber B and overflows into an exit launder 112. The launder 112 may lead directly to a casting launder (not shown) or to an intermediate baffle crucible (not shown) filled with coarse alumina balls or other coarse refractory granules.

The apparatus of FIG. 12 comprises a box 120 of refractory brick divided by a baffle 102 into two chambers A and B. Immersion heaters each consisting of a refractory sheath 121 of silicon carbide or nitride containing a gas burner 122 extends into the chamber A. Molten metal enters the chamber A from a launder 103 and falls in a short unsupported stream 123 through a flux cover 104. Rows of porous brick 124 communicate with steel tube inserts 125 through which nitrogen is directed into the chamber A. As in the previously described apparatus, the molten metal flows through the chamber A, under the baffle 102 to the chamber B and overflows into an exit launder 126 where entrapped salts are removed by means of a baffle 127 and a layer 128 of fluospar.

In the apparatus of FIG. 13 a refractory brick box 120 is divided into three chambers A, B and C by baffles 102 and 132. A low deflecting wall 133 extends upwardly from the base of the box 101 between the baffles 102 and 132. Molten metal enters the chamber A from a launder 103 and falls in a stream 123 through a flux cover 104 as described with reference to FIG. 12. Nitrogen is introduced into the chamber A through a graphite tube 111 as described with reference to FIG. 3. The molten metal flows through the chamber A under the baffle 102 and is deflected upwardly into chamber C by the wall 133. The metal flows from the chamber C under the baffle 132 into the chamber B and overflows into an exit launder 134. As the metal flows from chamber C to chamber B entrained flux is deposited on the surface 135 of the baffle 132 leaving little, if any, to be removed in the exit launder 134.

EXAMPLE I

Dirty, undegassed Al-21/2%Mg alloy at 710°C was flowed at a speed of 600 lb per min into a brick box divided by a baffle wall to form two chambers, the ingoing chamber having a capacity of 2,400 lb of metal corresponding to a residence time of the metal in this chamber of 4 min. Commercial purity nitrogen was introduced via porous graphite diffuser tubes into the ingoing chamber at a flow rate of 400 cu.ft/hr corresponding to approximately 27 cu.ft nitrogen per ton of metal. Flux (c) was applied to the metal surface in the ingoing chamber in amount corresponding to 3 lb per 100 sq.in. of surface area. Coarse alumina balls (¾ in. diameter) were used to cover the diffuser tubes to a depth of two balls in the degassing chamber and to a few inches above the base of the baffle in the exit chamber. Frequent Straube-Pfeiffer test samples were taken from the exit launder during the progress of the cast and the metal (12 ton) found to be of excellent quality, all the test samples being bubble-free on solidification at a pressure of approx. 2 Torr.

EXAMPLE II

Dirty, undegassed primary metal at 730°C was flowed at a speed of 250 lb per min into a brick box divided by a baffle wall to form two chambers, the ingoing chamber having a capacity of 1,000 lb of metal corresponding to a residence time of 4 min. White spot nitrogen was introduced via porous graphite diffuser tubes into the ingoing chamber at a flow rate of 150. cu.ft/hr
corresponding to approx. 20 cu.ft/ton. Coarse alumina balls (3/8 in. dia) were placed in the bottom of the brick box to a depth sufficient to cover the bottom of the baffle. Flux F was applied in amount corresponding to approx. 3 lb per 100 sq. in. of surface area. Straube-Pfeiffer test samples were taken from the exit launder at frequent intervals during the course of the cast (12 tons) and no bubble was developed in any of the tests during solidification at a pressure of 2 Torr. The sodium content of the ingoing metal was 0.0020–0.0025 percent and all outgoing samples analysed less than 0.0005 percent. Two refractory baffles were placed in the outgoing launder approximately 8 in. apart and between them a layer of CaF₂ approximately one-eighth in. deep was sprinkled on the metal surface. Chloride tests carried out on skimmings taken from the metal surface in the launder at a position 6 inches beyond the surface baffle gave negative results.

EXAMPLE III

In a test similar to that of Example II, dirty underdegassed alloy of the A A 6063 type flowing at a rate of 200 lb/min, was successfully cleaned and degassed to show nil bubbles in the Straube-Pfeiffer test using a nitrogen flow rate corresponding approximately to 30 cu.ft. per ton of metal introduced via porous graphite diffusers. During the course of the cast the two 3/8 in. steel tubes were inserted into the degassed chamber and nitrogen passed through at a flow rate corresponding approximately to 5 cu.ft. per ton. The nitrogen passing through the diffusers was then reduced to approximately 15 cu.ft/ton making a total consumption of 20 cu.ft/ton of nitrogen. Straube-Pfeiffer samples were obtained bubble-free. Under the original conditions of operation i.e. with all the nitrogen entering via the diffuser tubes it was not possible to obtain nil bubbles consistently in the Straube-Pfeiffer test with only 20 cu.ft/ton of nitrogen passing, although the degassing achieved was satisfactory.

Actual hydrogen analyses on samples of metal degassed and cleaned in accordance with the present invention have shown the gas contents achieved to be extremely low, i.e. 0.04–0.15 cc/100 g in comparison with 0.15–0.20 cc/100g for conventional furnaces degassing with chlorine.

Metal processed by the present invention has been shown to be suitable for production of high quality semi-fabricated products for critical applications. In particular the incidence of blister defects in soft annealed sheet for deep drawing purposes is extremely low and frequently nil. The corrosion resistance of the metal is somewhat better than that of conventionally furnace degassed metal, as judged by the Cass test.

Operation of the process of the present invention brings with it a number of important practical advantages. Its use eliminates the capital and operating costs of fume treatment equipment. Substitution of nitrogen and flux for chlorine brings savings in degassing costs. The time of treatment of metal with chlorine or hexachloroethane in a holding furnace is saved so that the output can be increased. Most valuable of all economically, metal losses are greatly reduced since dross formation in the holding furnace is far less than with conventional furnace degassing where chlorine or a chlorine-nitrogen mixture is being passed into a reverberatory furnace for periods up to 60 min.

In addition to carrying out the process of the present invention in a containing vessel such as a brick box or crucible placed between holding furnace and casting point, it is also practicable to use as a containing vessel a foreweld to, or an alcove within, the holding furnace itself, particularly where this is of a reverberatory type. Best results will then be obtained if the metal in the foreweld or alcove is protected from direct contact with the products of combustion of the furnace. In the case of the alcove or cubicle within the furnace, brick walls may be built inwards from the wall of the furnace which includes the tapping hole, or from this wall and an adjacent wall, so as to partition off a cubicle of suitable size from the main part of the furnace, metal entering the cubicle by a passage underneath the partitioning walls or through holes left therein for the purpose. A dressing door is needed through which to apply flux to the metal within the cubical walls. Nitrogen or other inert gas may be introduced via porous bricks built into the floor of the cubicle or more conveniently by porous or non-porous graphite tubes, or steel or cast iron tubes protected by vitreous enamelling. These tubes may be introduced through the furnace walls into the cubicle.

Operation of the process in a reverberatory furnace within a reverberatory furnace has advantages under some conditions and particularly where it is desired to make frequent alloy changes or to operate the process intermittently.

When operating with a foreweld it is convenient to divide the foreweld by means of a baffle into two chambers so that molten metal enters one chamber, flows underneath the baffle or through one or more holes therein to the other chamber, and then through a tap hole into a casting launder.

The molten metal in the foreweld being in direct communication with that in the main body of the reverberatory furnace will be maintained hot thereby, but if desired additional heating may be provided.

FIGS. 14a and 14b show a reverberatory furnace R with a cubicle C defined by walls 140 of refractory brick extending inwardly from walls 141 of the furnace R. The walls 140 may, if desired, extend up to the ceiling (not shown) of the furnace. A tapping hole 142 and a door 143 for core removal are provided in respective walls 141 of the furnace to communicate with the cubicle C. A drain hole 144 may also be provided in one of the walls 141 at a location outside the cubicle C, the floor 145 of the cubicle preferably sloping downward towards the drain hole 144. Apertures 146 are provided at or near the bases of the walls 140 so that the cubicle C is in communication with the furnace R. A flux cover 147 extends over the surface of the molten metal in the cubicle C and a graphite tube 148 extends into the cubicle for admitting an inert gas into the molten metal.

FIGS. 15a and 15b show a reverberatory furnace R with a foreweld F. Walls 150 extend outwardly from a wall 151 of the reverberatory furnace R to define the foreweld F which is divided by a baffle 152 into two chambers F₁ and F₂. Openings 153 at or near the base of the wall 151 permit the flow of molten metal to the chamber F₁ into which nitrogen is introduced through graphite or enamelled steel tubes 154. A flux cover 155 is maintained over the liquid metal in the chamber F₁. The molten metal flows under the baffle 152 into the chamber F₂ from which it flows to a casting launder (not shown) through a tapping hole 156. Heat is conserved in the molten metal by use of refractory lined
3,753,690

lids 157. Additional heating is provided, where required, by means of gas burners 158.

It will be seen that the present invention provides a process for cleaning and degassing molten aluminium in a continuous manner which comprises flowing molten aluminium through a chamber in which a substantially inert gas such as, for example, nitrogen is passed into the metal whilst a liquid flux layer is maintained on the aluminium in the chamber, followed, if desired, by flowing the molten aluminium through a bed or column of coarse refractory flux-coated granules and then flowing the molten aluminium through a bed or column of uncoated coarse refractory granules. Metal treated by this process has given excellent results when used for the production of bright anodised and other critical products.

The invention has application to the treatment of molten metals other than aluminium.

We claim:

1. A process for removing solid, non-metallic constituents from molten metal which comprises flowing the molten metal at a temperature up to 800°C through a bed of coarse refractory granules substantially of such a size as to be retained on a 35 μm aperture screen, while maintaining in a molten state on at least some of said granules in said bed a molten salt flux coating, said bed being submerged beneath the surface of the molten metal, maintaining said temperature whereby the salt flux on said granules is in molten condition, said salt flux being selected from the group consisting of mixtures, which are molten at said temperature, of salts selected from the group consisting of chlorides and fluorides of alkali metals, alkaline earth metals and magnesium.

2. A process in accordance with claim 1, wherein said coarse refractory granules are Al₂O₃ balls of 96 in. minimum size.

3. A process in accordance with claim 1, wherein said coarse refractory granules are Al₂O₃ balls of 96 in. minimum size.

4. A process in accordance with claim 1, further comprising flowing said molten metal through a second bed of substantially uncoated coarse refractory granules.

5. A process for removing non-metallic constituents including hydrogen and solid particles from liquid aluminium and its alloys in a continuous manner which comprises flowing such liquid metal at a temperature up to 800°C through a containing vessel, maintaining a molten salt flux layer on the surface of metal in the containing vessel, simultaneously passing a substantially inert gas into the liquid metal, and thereafter flowing the liquid metal through a bed of coarse refractory granules substantially of a size to be retained on a 35 μm aperture screen, said bed being submerged beneath the surface of the molten metal, the inert gas being passed into the container and into the liquid metal in such a manner as to create vigorous turbulence whereby a coating of said molten salt flux is produced and maintained on at least 65% of said granules, said salt flux being selected from mixtures of salts which are molten at said temperature and which salts are selected from the group consisting of chlorides and fluorides of alkali and alkaline earth metals and magnesium.

6. A process in accordance with claim 5, wherein said containing vessel is divided by a baffle wall to provide a substantially U-shaped vessel in which the direction of liquid metal flow is down a first leg of the U and up a second leg of the U, wherein said process comprises passing said inert gas upwardly through the liquid metal in said first leg with said molten salt layer being maintained on the surface of the liquid metal in said first leg.

7. A process in accordance with claim 5, wherein said substantially inert gas is nitrogen.

8. A process in accordance with claim 5, wherein said bed of coarse refractory granules is located in a second vessel downstream from said containing vessel.

9. A process in accordance with claim 5 for additionally removing sodium metal from the liquid aluminium, wherein said flux contains at least 5 percent by weight of MgCl₂ and is substantially free of the fluoride and complex fluorides of sodium.

10. A process for removing solid non-metallic constituents from molten aluminium and its alloys in a continuous manner which comprises continuously flowing the molten metal at a temperature up to 800°C through a containing vessel, maintaining a molten salt flux layer on the surface of molten metal in the containing vessel, continuously creating vigorous turbulence in the molten metal in contact with the molten flux within the containing vessel; and thereafter continuously flowing the molten metal having some molten flux entrained therein through a flux trap comprising a bed of coarse refractory granules substantially of a size to be retained on a 35 μm aperture screen, said bed being submerged beneath the surface of the molten metal, whereby at least some of said granules become coated with said molten salt flux, said salt flux being selected from mixtures of salts which are molten at said temperature and which salts are selected from the group consisting of chlorides and fluorides of alkali and alkaline earth metals and magnesium.

11. A process in accordance with claim 10 for removing hydrogen and solid particles wherein the residence time of said molten metal in said containing vessel is at least 1 1/2 min., said vigorous turbulence is created by passing a substantially inert gas into said molten metal at a rate sufficient to provide at least 10 cu. ft. of inert gas per ton of molten metal.

12. A process in accordance with claim 11, wherein said molten flux layer is provided in an amount of at least 1 lb. of flux for each 100 sq. in. of surface area of said molten metal and wherein said flux is substantially free of oxides, oxysalts, fluorosilicates and volatile halides.

13. A process in accordance with claim 12, wherein said gas is nitrogen.

14. A process in accordance with claim 11, wherein said flux trap further comprises a layer of fluoride.