

# (11) **EP 2 251 443 A1**

(12)

# **EUROPEAN PATENT APPLICATION**

(43) Date of publication:

17.11.2010 Bulletin 2010/46

(21) Application number: 09251258.1

(22) Date of filing: 06.05.2009

(51) Int Cl.:

C21C 1/06 (2006.01) C22C 33/10 (2006.01) C21C 1/10 (2006.01) F27D 3/00 (2006.01)

(84) Designated Contracting States:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK TR

**Designated Extension States:** 

**AL BA RS** 

(71) Applicant: FOSECO INTERNATIONAL LIMITED Central Park Barlborough Links Derbyshire S43 4XA (GB) (72) Inventor: Berthelet, Emmanuel 60800 Crèpy - en - Valois (FR)

(74) Representative: Ward, David Ian

Marks & Clerk LLP Alpha Tower Suffolk Street Queensway Birmingham B1 1TT (GB)

## (54) Treatment ladle

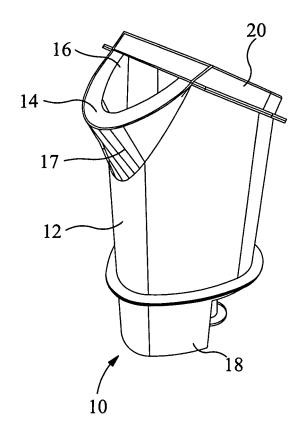
(57) A treatment ladle comprising a ladle shell containing a generally tubular refractory ladle liner, said ladle being pivotable between a horizontal position and a vertical position, said ladle liner having a first end and a second end with a continuous sidewall therebetween, an interior space being defined between said first and second ends and the continuous sidewall,

said ladle liner additionally comprising a pocket for holding a treatment agent, said pocket being located adjacent the first end and in fluid communication with the interior space and located closer to the top than the bottom of the interior space when the ladle is in its horizontal position and closer to the bottom than the top of the interior space when the ladle is in its vertical position, and a spout for receiving and pouring molten metal located closer to the top than the bottom of the interior space when the ladle is in its horizontal and vertical positions,

wherein in the horizontal position, a lower volume of the interior space defined below a plane midway between the top and bottom of the interior space and between the first end and a vertical plane intermediate the first and second ends is greater than an upper volume of the interior space defined above the midway plane and between the first end and said vertical plane.

The treatment ladle is designed for the treatment of molten metal with vaporisable additives, in particular in the preparation of ductile iron. The invention also relates to a method of treating molten metal employing the ladle.

# FIG 1A



EP 2 251 443 A1

#### Description

15

20

25

30

35

40

45

50

55

[0001] The present invention relates to a ladle for treating molten metal with vaporisable additives, in particular, to a ladle for treating iron with magnesium (Mg) to form ductile iron.

**[0002]** Ductile iron, also known as spheroidal graphite (s.g.) iron or nodular iron, is made by treating liquid iron with a so-called nodulariser (or noduliser) before casting. The nodulariser promotes the precipitation of graphite in the form of discrete nodules. In practice, the nodulariser will usually contain magnesium, as pure magnesium, or as an alloy, such as magnesium-ferrosilicon (MgFeSi alloy) or nickel-magnesium (NiMg alloy), which may contain rare earth metals. In a typical process, magnesium is added to the liquid iron to give a residual magnesium content of about 0.04%, the iron is inoculated and cast. It is difficult to add magnesium to iron because magnesium boils at a relatively low temperature (1090°C) so there is violent agitation of the liquid iron and considerable loss of magnesium in vapour form.

[0003] Various methods have been developed to prepare ductile iron, including:

The sandwich ladle - a treatment alloy is contained in a recess in the bottom of a ladle and covered with steel scrap. The ladle may be covered, for example with a tundish cover. The iron is then poured into the ladle and reaction with the treatment alloy is slowed by the steel scrap barrier. This method is simple and widely used but Mg recovery rates are inconsistent. Moreover it is necessary to use more nodulariser to successfully achieve the required level of treatment.

Plunger - the treatment alloy is plunged into the ladle using a refractory plunger bell. This method is only practical for large quantities of metal.

Converter - nodulariser is placed in a pocket in the base of a cylindrical ladle. The ladle is filled with liquid iron whilst it is in a horizontal orientation, sealed and rotated to a vertical position so that the magnesium is submerged under the iron.

Cored wire treatment - wire containing nodulariser (e.g. MgFeSi alloy) is fed mechanically into the iron using a purpose built station.

Inmould treatment - nodulariser (e.g FeMgSi alloy) is placed in a chamber moulded into the running system such that the iron is continuously treated as it flows over the alloy.

[0004] One object of the present invention is the provision of a ladle for the treatment of metal with vaporisable additives.

[0005] Another object of the present invention is to provide a method for the treatment of molten metal with vaporisable additives.

**[0006]** According to a first aspect of the present invention there is provided a treatment ladle comprising a ladle shell containing a generally tubular refractory ladle liner, said ladle being pivotable between a horizontal position and a vertical position.

said ladle liner having a first end and a second end with a continuous sidewall therebetween, an interior space being defined between said first and second ends and the continuous sidewall,

said ladle liner additionally comprising a pocket for holding a treatment agent, said pocket being located adjacent the first end and in fluid communication with the interior space and located closer to the top than the bottom of the interior space when the ladle is in its horizontal position and closer to the bottom than the top of the interior space when the ladle is in its vertical position, and a spout for receiving and pouring molten metal located closer to the top than the bottom of the interior space when the ladle is in its horizontal and vertical positions,

wherein in the horizontal position, a lower volume of the interior space defined below a plane midway between the top and bottom of the interior space and between the first end and a vertical plane intermediate the first and second ends is greater than an upper volume of the interior space defined above the midway plane and between the first end and said vertical plane.

**[0007]** It will be understood from the foregoing that in the vertical position, the first end of the ladle liner constitutes the lower extent of the interior space.

[0008] In use, a treatment agent will be placed in the pocket and the ladle will be filled with molten metal whilst it is in the horizontal position. In general, the ladle will be half filled such that the molten metal is filled to a height corresponding to the midway plane. The ladle is then pivoted 90° to the vertical position such that the metal flows into the pocket containing the treatment agent. The treatment agent vaporises on contact with the molten metal and bubbles through the head of metal above the pocket. The ladle is then pivoted again in order to dispense the treated molten metal through the spout. In a particular embodiment, the ladle is pivoted greater than 90° from the horizontal position, via the vertical position, to a third position in which the treated molten metal is dispensed (the dispensing position).

[0009] The ladle of the present invention is useful because it minimises the surface area of the metal that is exposed to the air when the ladle is in the horizontal position. The reduction in surface area is associated with a reduction in heat

loss from the metal. If the heat loss is reduced, metal may be poured into the ladle at a lower temperature thereby reducing the wear on the refractory lining and other foundry apparatus. A lower temperature for pouring into the ladle will also favour lower magnesium vapour expansion, which reduces the violence of the reaction (between the magnesium and the hot metal). This is thought to improve magnesium recovery since more magnesium vapour is efficiently kept within the liquid iron, and reduces the temperature loss after treatment since lower reaction violence means that there is less contact of metal with the colder atmosphere.

**[0010]** Another advantage of the ladle of the present invention is that it maximises the head of metal above the treatment agent when the ladle is in the vertical position. An increased head of metal is associated with a reduction in the violence of the reaction between the metal and the treatment agent and in the case of a magnesium-containing treatment agent, improved and more consistent magnesium recovery.

[0011] It will be understood that the advantages of the invention are obtained due to the shape of the ladle liner, in particular the shape of the parts of the ladle liner which are in contact with the molten metal when the ladle is being filled (the horizontal position) and when the molten metal is being treated (the vertical position). A vertical plane (intermediate the first and second ends of the liner when the ladle is in its horizontal position) is chosen in order to evaluate the shape of the ladle liner. The vertical plane should be chosen such that it represents a typical cross-section of the ladle liner. Where the ladle liner is of a regular shape such that the cross-section of the continuous sidewall is consistent along its length, the vertical plane may be chosen at any point between the first and second ends. Conveniently, the vertical plane may be equidistant the first and second ends of the liner when the ladle is in its horizontal position.

[0012] In a particular embodiment, the pocket extends from the first end of the ladle liner away from the interior space (i.e. extends below the first end when the ladle is in its vertical position). This provides an additional increase in the head of metal over the treatment agent when the ladle is in the vertical position because molten metal can fill the pocket. As discussed above, an increased head of metal is associated with a reduction in the violence of the reaction between the metal and the treatment agent and in the case of a magnesium-containing treatment agent, improved and more consistent magnesium recovery. In an embodiment where the pocket extends from the first end, the length of the pocket may be from 50 to 1200mm, from 200 to 1000mm or from 400 to 600mm.

20

30

35

40

45

50

55

[0013] In an alternative embodiment, the pocket is located within the interior space. In any case, the pocket must either be in fluid communication with the interior space or be capable of being in fluid communication therewith upon contact with the metal. For example, the pocket may be defined by a mesh or grille having sufficiently small openings to retain the treatment agent whilst still permitting molten metal therethrough or it may be made of material that melts (such as metal) thereby providing access to the contents of the pocket. It will be understood that the volume of the pocket will generally be small relative to the volume of the interior space. The shape of the pocket is not particularly limited but conveniently the pocket will be elongate to ensure retention of the treatment agent. It may have a circular or a triangular cross-section.

[0014] The ratio of the lower volume to the upper volume may be at least 1.5:1, at least 2:1 or at least 3:1.

**[0015]** The height of the interior space (the distance between the top and bottom of the interior space, as defined by the interior of the continuous sidewall) when the ladle is in its horizontal position may be from 200mm to 1500mm, from 400mm to 1000mm, or from 600mm to 800mm.

**[0016]** The height of the interior space (the distance between the top and bottom of the interior space) when the ladle is its vertical position may be from 400mm to 3000mm, from 800mm to 2000mm or from 1000mm to 1500mm.

**[0017]** The ratio of the height of the interior space when the ladle is in its vertical position to the height of the interior space when the ladle is in its horizontal position may be at least 1:1, at least 2:1, at least 3:1 or at least 5:1. The ratio of the height of the interior space when the ladle is in its vertical position to the height of the interior space when the ladle is in its horizontal position may be no more than 6:1, no more than 4:1, or no more than 3:1.

**[0018]** In an embodiment where the pocket extends from the first end away from the interior space, the ratio of the height of the interior space when the ladle is in its vertical position to the length of the pocket may be at least 1.5:1, at least 2:1, at least 2:5:1 or at least 3:1.

**[0019]** The continuous sidewall has an interior surface and an exterior surface which may have the same or different shapes. Conveniently the continuous sidewall will have a uniform thickness such that the interior and exterior surfaces have the same shape. It will be understood that it is the interior surface of the continuous sidewall which defines the shape of the interior space and therefore references to the cross-section of the continuous sidewall refer to the cross-section of the interior surface of the continuous sidewall.

**[0020]** The continuous sidewall may be defined by three or more wall portions such that the cross-section of the continuous sidewall is substantially polygonal. In an embodiment where the continuous sidewall is defined by three wall portions, the cross-section of the continuous sidewall is substantially triangular. In an embodiment where the continuous sidewall is defined by three wall portions of equal length, the cross-section of the continuous sidewall has the shape of an equilateral triangle. In any of the embodiments where the cross-section is based on a polygon, the corners may be radiussed/rounded and/or the sides may be bowed outward. Conveniently, the cross-section of the sidewall may be measured in the vertical plane intermediate the first and second ends.

**[0021]** In an embodiment where the continuous sidewall is defined by three sidewall portions, such that the cross-section of the continuous sidewall is substantially triangular, the ratio of the height of the interior space when the ladle is in its vertical position to the length of a sidewall portion may be at least 1:1, at least 1.5:1 or at least 2:1.

**[0022]** In an embodiment where the continuous sidewall is defined by three sidewall portions, such that the cross-section of the continuous sidewall is substantially triangular, the triangular cross-section will define an inscribed circle, i.e. the largest circle that can be contained within the triangle. In such a case, the ratio of the height of the interior space when the ladle is in its vertical position to the radius of the circle inscribed by the triangular cross-section may be at least 1.5:1, at least 2:1, at least 2:5:1 or at least 3:1.

**[0023]** The ladle comprises a spout for initially receiving and then dispensing the molten metal after treatment. This is particularly beneficial since it allows metal to be poured directly from the ladle into the casting moulds, without the need for re-ladling operations. This has a dual benefit of reducing temperature loss, and improving casting productivity by eliminating a step in the casting process.

**[0024]** Suitable refractory materials include those described in EP0675862B1 and in particular KALTEK (RTM) which is a refractory lining made from silica, alumina and magnesite which is bonded by an organic material such as phenolic resin. In a particular embodiment, the continuous sidewall is of unitary construction.

[0025] The ladle may be mounted onto a crane or a forklift or other machinery in order to pivot the ladle.

**[0026]** The ladle shell may be a conventional cylindrical shell or a modified shell adapted to the shape of the ladle liner. If a conventional cylindrical shell is employed, it will be necessary for the interior and exterior surfaces of the continuous sidewall to have different shapes, i.e. the refractory liner will not have a uniform thickness. If a non-cylindrical shell is employed, the interior and exterior surfaces of the continuous sidewall may have the same shape. For example, where the ladle liner comprises a sidewall having a triangular cross-section, the shell may also have a triangular cross-section i.e. it may be a triangular prism.

**[0027]** In a particular embodiment, the ladle shell and the ladle liner have substantially the same shape. This has the advantage that a minimum amount of refractory material may be employed. Alternatively, the ladle may comprise a conventional cylindrical ladle shell. This may be convenient when re-using a conventional cylindrical shell. The efficiencies of the ladle liner would at least partially offset the expense of the additional refractory material needed to fit the ladle liner within the shell.

**[0028]** According to a second aspect of the present invention there is provided a method for the treatment of molten metal comprising loading the ladle of the first aspect by placing a treatment agent in the pocket,

filling the ladle whilst it is in its horizontal position to a level below the pocket with molten metal, and pivoting the ladle to its vertical position such that molten metal flows onto the treatment agent in the pocket.

**[0029]** In a particular embodiment, the method comprises pivoting the ladle greater than 90° from the horizontal position, via the vertical position to a dispensing position in which the molten metal is dispensed through the spout after treatment. In a further embodiment, the method comprises pivoting the ladle approximately 180° from the horizontal position, via the vertical position to the dispensing position in which the treated metal is dispensed.

**[0030]** In a particular embodiment, the ladle is filled to a level corresponding to the plane midway between the top and bottom of the interior space when the ladle is in its horizontal position.

**[0031]** The method of the present invention is particularly suitable for the preparation of ductile iron, in which case the treatment agent is a nodulariser and the molten metal is iron.

**[0032]** In one embodiment, the treatment agent is a magnesium-containing nodulariser. Suitable nodularisers include pure magnesium, magnesium ferrosilicon alloy (MgFeSi alloy), nickel-magnesium alloy and magnesium-iron briquettes.

**[0033]** The ladle and method of the present invention may be used for the production of both ductile (spheroidal graphite) iron and vermicular (compacted graphite) iron.

**[0034]** The method may comprise inoculation of the molten metal after reaction with the treatment agent (e.g. the nodulariser). Inoculants are alloys added in small amounts to induce eutectic graphite nucleation. Suitable inoculants include those based on ferrosilicon and calcium silicide.

**[0035]** The method may comprise initialisation of the molten metal prior to reaction with the treatment agent. An initialiser is thought to inactivate the oxygen activity of the molten metal so that subsequent treatment is more successful. Suitable initialisers include those described WO2008/012492.

[0036] Embodiments of the invention will now be described by way of example only with reference to the accompanying drawings in which:-

Fig 1A is perspective view of a ladle in accordance with an embodiment of the invention.

Fig 1B is a perspective view and Fig 1C is a cross-section of the ladle shown in Fig 1A during assembly.

Fig 1D and 1E are cross-sections of formers used in the assembly of the ladle shown in Fig 1A.

Fig 1F is a cross-section of the ladle shown in Fig 1A.

20

30

35

40

45

50

55

Fig 2A and 2B are schematic drawings of the ladle shown in Fig 1A.

Fig 3A to 3C show a ladle in accordance with an embodiment of the invention.

Fig 4A and 4B show a conventional ladle for comparision.

Fig 5A to 5D show simulations using MAGMASOFT (RTM) software.

5

20

30

35

40

45

50

55

[0037] Fig 1A shows a ladle 10 in accordance with an embodiment of the invention. The ladle 10 comprises a generally tubular steel shell 12 and a generally tubular refractory liner 14 (partially visible) within the shell 12. The ladle 10 has an opening 16 at its upper end and a projection 18 at its lower end. The shape of the shell 12 is complementary to the exterior shape of the refractory liner 14 such that the projection 18 corresponds to the shape of a pocket (not visible) for holding a treatment agent. The ladle also comprises a closable lid 20, the inner surface of which defines the second end of the refractory liner 14. The shell 12 and the refractory liner 14 flare out toward the upper end, adjacent the opening 16 to form a spout 17. The ladle 10 is shown in its vertical position such that the spout is at the top of the ladle and the pocket in at the bottom of the ladle. In this configuration a treatment agent can be easily loaded into the pocket via the opening 16.

[0038] The ladle 10 is made in two parts as shown in figures 1B and 1C. The main body of the ladle 10a is made by placing a former 22a within the shell 12 and filling the gap between the shell 12 and the former 22a with a refractory material (KALTEK (RTM)). Once the refractory material solidifies the former 22a is removed. Similarly the projection part of the ladle 10b is made by placing another former 22b in the shell corresponding to the projection 18 and filling the gap between the former 22b and the projection 18 with refractory material. It will be understood that the external surfaces of the formers 22a, 22b correspond to the shape of the interior of the refractory ladle liner 14. The two parts 10a,b are then attached to one another.

[0039] Fig 1C shows a cross-section of the ladle 10 before the formers 22a, 22b have been removed and without the lid 20. The refractory liner 14 comprises a continuous sidewall 24, a lower end 26 (a first end) and since the lid 20 is not fitted, the ladle is entirely open at its upper end. The uppermost part of the continuous sidewall defines the position where the lid 20 will be fitted (the second end 28). The ladle liner 14 comprises a pocket 30 for holding a treatment agent. The pocket 30 extends away from the first end 26. This provides an advantage in that there will be a greater head of metal above the treatment agent. It will be noted that the walls of the pocket 30 are thicker that the continuous sidewall 24. The thicker wall provides additional insulation for the vaporisation of the treatment agent.

**[0040]** The height of the interior space when the ladle is in its vertical position is labelled x. The height of the interior space when the ladle is pivoted to be in its horizontal position is labelled y. The depth of the pocket is labelled z. In this embodiment the approximate values of x, y and z are 1380mm, 640mm and 480mm respectively. Hence the ratio of x: y is approximately 2.2:1 and the ratio of x:z is approximately 2.9:1.

[0041] Fig 1D shows a cross-section of the former 22a. The external surface of the former 22a defines the interior surface of the continuous sidewall 24 and hence the cross-section of the interior space. The cross-section of the former 22a is based upon an equilateral triangle in which the corners have been rounded and the sides have been bowed outward. [0042] Fig 1E shows a cross-section of the former 22b. The external surface of the former 22b defines the walls of the pocket 30. In this embodiment, the cross-section of the former 22b is related to the cross-section of the former 22a (shown in dashed lines). The cross-section of the former 22b is again approximately triangular. It will be understood that the pocket 30 could have a different cross-section, for example a circular cross-section. However a triangular cross-section is believed to be advantageous because it assists in retaining a treatment agent within the pocket 30 when the ladle is pivoted from a vertical to a horizontal position.

**[0043]** Fig 1F shows a cross-section of the main part of the ladle 10a comprising the shell 12 and the continuous refractory sidewall 24. The sidewall 24 is based on an equilateral triangle (shown in dotted lines) where each corner makes contact with the sidewall 24. In this embodiment, the length of each side of the triangle is approximately 740mm such that the ratio of the height of the interior space when the ladle is in its vertical position (labelled x in figure 1 C) to the length of a length of the sidewall portion is approximately 1.8:1. The triangle comprises an inscribed circle (also shown as a dotted line). In this embodiment, the inscribed circle has a diameter of approximately 427mm such that the ratio of the height of the interior space when the ladle is in its vertical position (labelled x in figure 1 C) to the length of a diameter of the circle is approximately 3.2:1

**[0044]** The proportions of the ladle shown in figures 1A to 1F are considered to be particularly beneficial for the treatment of metal with a treatment agent, combining good heat retention with efficient treatment.

[0045] Figures 2A and 2B are schematic drawings of the ladle 10 shown in Fig 1A in its horizontal position. The ladle 10 comprises a first end 26, a second end 28 and a continuous sidewall 24 as described previously. In this horizontal configuration, the upper part of the sidewall defines the top 40 of the interior space and the lower part of the sidewall defines the bottom 42 of the interior space. A vertical plane 44 intermediate the first and second ends is shown. The vertical plane is chosen to be closer to the first end 26 than the second end 28 because this corresponds to a position where the continuous sidewall 24 has a regular shape. A horizontal plane 46 midway between the top 40 and the bottom 42 of the interior space is shown. The volume of the interior space defined between the bottom of the interior space 42,

the first end 26, the midway plane 46 and the vertical plane 44 is labelled I (the lower volume). The volume of the interior space defined between the top of the interior space 40, the first end 26, the midway plane 46 and the vertical plane 44 is labelled II (the upper volume). Referring to Fig 2A volumes I and II appear to be equal but it is clear from Fig 2B that volume I is greater than volume 2 due to the shape of the cross-section of the continuous sidewall 24.

**[0046]** The triangular prism shape of the ladle in accordance with an embodiment of the present invention is advantageous as compared to a cylindrical ladle in terms of heat loss from the metal when it is horizontal position and an increased head of metal over the treatment agent when it is in a vertical position (the second position). As is clear from the schematic drawing Fig 2B, if the ladle is filled half-way the surface of the metal exposed to the air will be smaller than a comparable cylindrical ladle. Similarly, when the ladle is pivoted from a horizontal position to a vertical position the metal height will be greater than a comparable cylindrical ladle.

#### **Example 1 and Comparative Example 1: Simulations**

[0047] In order to fairly evaluate the rate of heat loss for a ladle in accordance with an embodiment of the present invention (Example 1) the inventors designed two ladles, Example 1 (in accordance with an embodiment of the invention) and a further ladle for comparison (Comparative Example 1) and ran simulations using the MAGMASOFT simulation tool. MAGMASOFT is a leading simulation tool supplied by MAGMA Gießereitechnologie GmbH that models the mould filling and solidification of castings. It is typically used by foundries to avoid expensive and time consuming foundry trials.

[0048] The Example 1 ladle is shown in fig 3A (vertical position) and fig 3B and 3C (horizontal position). The interior space has a substantially triangular cross-section. Comparative Example 1 is shown in fig 4A (vertical position) and fig 4B and 4C (horizontal position). The interior space has a circular cross-section. A dotted line is shown in each figure to demonstrate the level of the molten metal when the ladles are filled to their working capacities. A comparison of the properties of the two ladles is shown in the table below.

	Example 1	Comparative Example 1
Working Capacity (kg)	3000	3000
Metal volume total surface area (mm²)	3719746	3892335
Top surface area (mm²)	1028446	1354917
Height of metal - horizontal (mm)	417.7	427
Height of metal - vertical (mm)	897	747
Geometric Modulus (volume/surface area) (cm)	11.5	11

**[0049]** As can be seen, even though both ladles hold the same quantity of metal, they are filled to different levels because of their differing shapes. In the horizontal position, the metal is filled to a similar height in both cases but when the ladles are rotated to a vertical position, the metal height is much greater for Example 1 than for Comparative Example 1. The greater height of metal above the vaporisable treatment agent means that the vaporised treatment agent must travel through more metal and so is more likely to remain within the molten metal, leading to better recovery rates.

**[0050]** Further, the total surface area of the metal (in contact with the air or the walls of the ladle) and the top surface area of the metal (in contact with the air) is smaller for Example 1 than for Comparative Example 1. This corresponds to a greater geometric modulus for Example 1 than Comparative Example 1. Therefore the molten metal in the ladle of Example 1 would cool more slowly than the molten metal in the ladle of Comparative Example 1.

**[0051]** In the simulations, the ladle was modelled as containing molten steel and having a refractory lining with insulating properties as that of KALTEK (RTM) material. The model considers the boundary material above the metal to be air. The simulation was run with two different starting temperatures (1400°C and 1580°C) for the refractory lining. The results after 240 seconds are shown in figures 5A to 5D. The simulation output is a shaded contour diagram of the metal, with the darkness of the shading being inversely proportional to the temperature of the liquid metal, i.e. the darker the shading the colder the metal - the actual values are indicated by the temperature key in the simulation.

**[0052]** Figures 5A and 5B show the surface temperature of the metal when the refractory lining has a starting temperature of 1400°C for Example 1 and Comparative Example 1 respectively. The surface temperature of the metal is higher for the ladle of the invention than for the comparative example even though both ladles contain the same amount of metal and have identical starting temperatures. This is shown by the higher proportion of darker contours (shading) on the metal surface in figure 5B compared to 5A because the darker the shading, the colder the metal is.

**[0053]** Figures 5C and 5D show the surface temperature of the metal when the refractory lining has a starting temperature of 1580°C for Example 1 and Comparative Example 1 respectively. Again, the surface temperature of the metal

6

25

10

15

20

30

35

45

40

50

is higher for the ladle of the invention than for the comparative example as shown by the lighter shading in figure 5C compared to figure 5D. This demonstrates that the ladle of the invention allows the metal to remain hotter for longer.

#### Example 2 and Comparative Example 2 - preparation of ductile iron

**[0054]** Ductile iron was prepared using a ladle in accordance with an embodiment of the invention (Example 2) and a standard tundish ladle (Comparative Example 2). In each case molten iron was treated with magnesium ferrosilicon alloy (FeSiMg). Magnesium recovery after 4 and 9/10 minutes was measured. Magnesium recovery was calculated using the following formula:

Mg recovery % =  $(0.76 \times (S\% \text{ in base metal} - S\% \text{ residual}) + \text{residual Mg\%}) \times 100 / Mg\%$  added

#### Example 2

5

10

15

20

25

30

35

40

45

50

55

[0055] The ladle 10 shown in Fig 1A was placed in a vertical position with the pocket 18 at the lowest point. 20.8kg magnesium ferrosilicon alloy (5.38% Mg) was then loaded into the pocket using a long necked funnel placed in the opening. After the treatment agent was loaded the ladle was rotated 90° to a horizontal position. The ladle was then filled with 1600kg molten iron at a temperature of 1480°C. The ladle was then rotated back to the vertical position such that the molten iron flowed into the pocket. A white flare was seen as the molten iron reacted with the magnesium alloy. The metal was poured out of ladle by tilting it and pouring out of the spout 17. The results are below.

#### **Comparative Example 2**

**[0056]** 14.4kg magnesium ferrosilicon alloy (5.38% Mg) was placed in a recess in a standard tundish ladle and 800kg molten iron at a temperature of 1500°C (standard practice) was poured into the ladle. The results are below.

	Exar	Example 2 Comparative Example 2		
	4 minutes	10 minutes	4 minutes	9 minutes
Mg residual (%)	0.0550	0.0474	0.0450	0.0350
S before treatment (%)	0.0140	0.0140	0.0070	0.0070
S after treatment (%)	0.0110	0.0104	0.0046	0.0040
Mg added (%)	0.06994	0.06994	0.09684	0.09684
Mg Recovery (%)	82	72	48	38

The magnesium recovery is considerably higher for Example 2 than Comparative Example 2. Therefore the ladle in accordance with an embodiment of the present appears to provide better recovery rates than the standard tundish ladle.

#### **Claims**

1. A treatment ladle comprising a ladle shell containing a generally tubular refractory ladle liner, said ladle being pivotable between a horizontal position and a vertical position, said ladle liner having a first end and a second end with a continuous sidewall therebetween, an interior space being defined between said first and second ends and the continuous sidewall, said ladle liner additionally comprising a pocket for holding a treatment agent, said pocket being located adjacent the first end and in fluid communication with the interior space and located closer to the top than the bottom of the interior space when the ladle is in its horizontal position and closer to the bottom than the top of the interior space when the ladle is in its vertical position, and a spout for receiving and pouring molten metal located closer to the top than the bottom of the interior space when the ladle is in its horizontal and vertical positions, wherein in the horizontal position, a lower volume of the interior space defined below a plane midway between the

top and bottom of the interior space and between the first end and a vertical plane intermediate the first and second ends is greater than an upper volume of the interior space defined above the midway plane and between the first end and said vertical plane.

- 5 2. The ladle in accordance with claim 1, wherein the pocket extends from the first end of the ladle liner away from the interior space.
  - 3. The ladle in accordance with claim 1 or claim 2, wherein the ratio of the lower volume to the upper volume is at least 1.5:1.
  - **4.** The ladle in accordance with any one if the preceding claims, wherein the ratio of the height of the interior space when the ladle is in its vertical position to the height of the interior space when the ladle is in its horizontal position is at least 2:1
- 5. The ladle in accordance with any one of the preceding claims, wherein the ratio of the height of the interior space when the ladle is in its vertical position to the height of the interior space when the ladle is in its horizontal position is no more than 6:1.
- 6. The ladle in accordance with any one of the preceding claims, wherein the pocket extends from the first end of the ladle liner away from the interior space and the ratio of the height of the interior space when the ladle is in its vertical position to the length of the pocket is at least 2:1.
  - 7. The ladle in accordance with any one of the preceding claims, wherein the continuous sidewall is defined by three or more wall portions such that the cross-section of the continuous sidewall is substantially polygonal.
  - **8.** The ladle in accordance with claim 7, wherein the continuous sidewall is defined by three wall portions, such that the cross-section of the continuous sidewall is substantially triangular.
- **9.** The ladle in accordance with claim 7 or 8, wherein the corners of the polygon are rounded and/or the sides of the polygon are bowed outward.
  - 10. The ladle in accordance with any one of the preceding claims, wherein the continuous sidewall is defined by three sidewall portions, such that the cross-section of the continuous sidewall is substantially triangular and the ratio of the height of the interior space when the ladle is in its vertical position to the length of at least one of the sidewall portions is at least 1.5:1.
  - 11. The ladle in accordance with any one of the preceding claims, wherein the continuous sidewall is of unitary construction.
- **12.** The ladle in accordance with any one of the preceding claims, wherein the ladle shell and the ladle liner have substantially the same shape
- 13. A method for the treatment of molten metal comprising loading the ladle of any one of claims 1 to 12 by placing a treatment agent in the pocket,
   filling the ladle with molten metal whilst it is in its horizontal position to a level below the pocket, and pivoting the ladle to its vertical position such that molten metal flows onto the treatment agent in the pocket.
  - **14.** The method of claim 13, wherein the ladle is pivoted greater than 90° from the horizontal position, via the vertical position to a dispensing position in which the treated molten metal is dispensed through the spout.
  - **15.** The method of claim 13 or 14, wherein the treatment agent is a nodulariser.

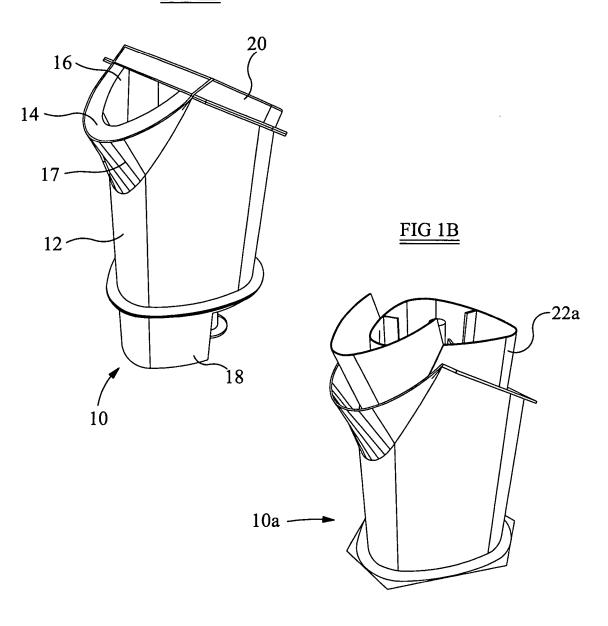
55

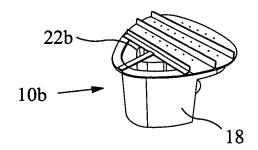
50

10

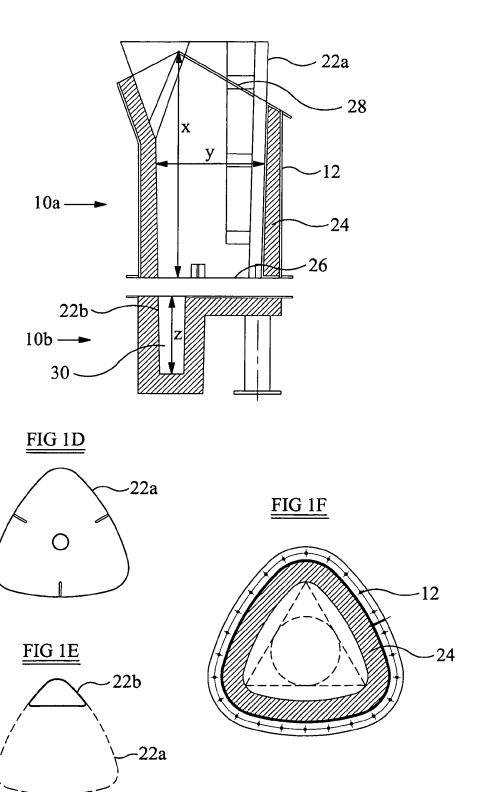
25

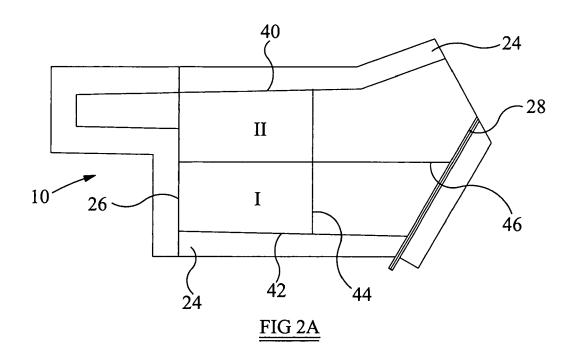
# FIG 1A

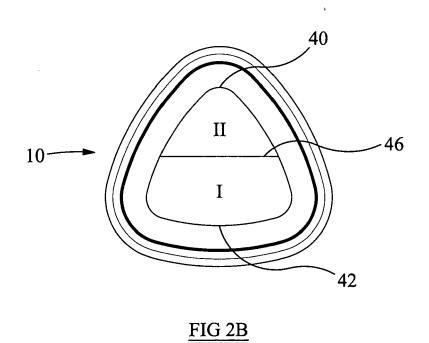


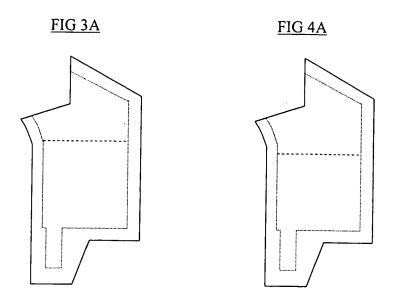


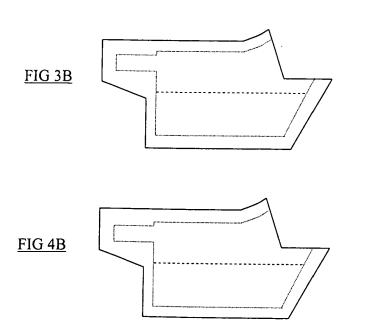
# FIG 1C













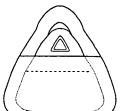
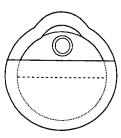
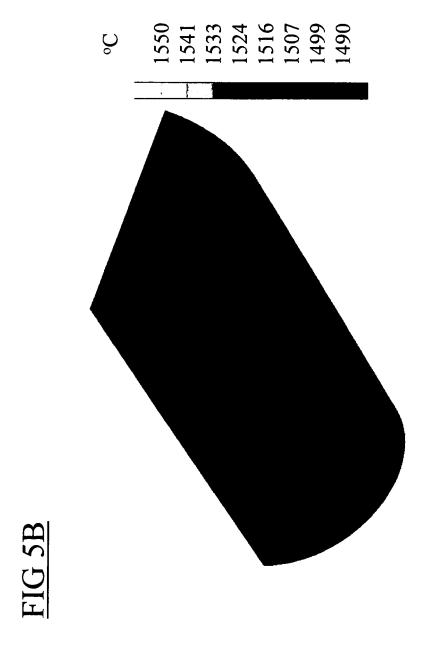
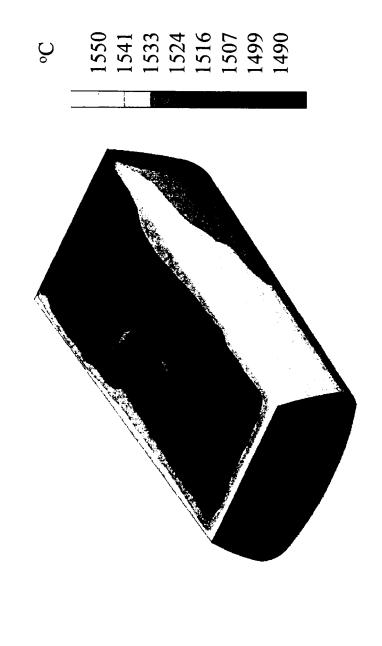


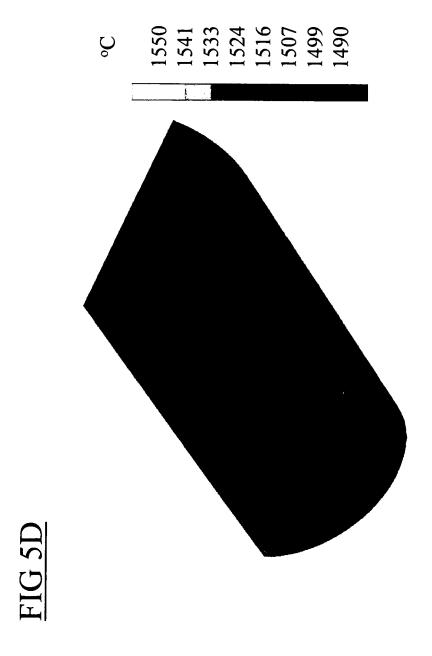
FIG 4C













# **EUROPEAN SEARCH REPORT**

Application Number EP 09 25 1258

Category	Citation of document with ir of relevant passa	ndication, where appropriate, ages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)	
A,D		NBERG GERRY E [US] ET 4 (1984-12-18)	1-15	INV. C21C1/06 C21C1/10 C22C33/10	
A	EP 1 887 090 A1 (F0 13 February 2008 (2 * paragraphs [0029] * figure 1 *		1-15	F27D3/00	
A	US 3 833 361 A (KUS 3 September 1974 (1 * claims 1-7; figur	974-09-03)	1-15		
A	US 3 724 829 A (ALT 3 April 1973 (1973- * claims 1-15; figu	04-03)	1-15		
A	EP 0 703 297 A1 (ME MIT B [DE]) 27 Marc * claims 1-18; figu		1-15	TECHNICAL FIELDS	
A	EP 0 512 255 A1 (GH 11 November 1992 (1 * claims 1-12; figu	992-11-11)	1-15	SEARCHED (IPC) C21C C22C	
A	US 4 391 636 A (WIN 5 July 1983 (1983-0 * claims 1-10; figu	7-05)	1-15	F27D	
A	EP 0 178 593 A2 (AS 23 April 1986 (1986 * claims 1-5; figur	-04-23)	1-15		
	The present search report has I	peen drawn up for all claims  Date of completion of the search	-	Examiner	
	Munich	17 March 2010	l on	nbois, Thierry	
X : parti Y : parti docu A : tech O : non	ATEGORY OF CITED DOCUMENTS icularly relevant if taken alone icularly relevant if combined with anothent of the same category nological background written disclosure mediate document	T : theory or principle E : earlier patent doc after the filing dat ner D : document cited fi L : document cited fo	e underlying the is sument, but publi e n the application or other reasons	nvention shed on, or	

## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 09 25 1258

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

17-03-2010

cite	Patent document ed in search report		Publication date		Patent family member(s)		Publication date
US	4488711	Α	18-12-1984	NON	E		<u>'</u>
EP	1887090	A1	13-02-2008	AU CA CN EA WO JP KR	2007279060 2653172 101473047 200870500 2008012492 2009544848 20090033419	A1 A A1 A1 T	31-01-2 31-01-2 01-07-2 28-04-2 31-01-2 17-12-2 03-04-2
US	3833361	Α	03-09-1974	DE	2135026		20-01-1
US	3724829	A	03-04-1973	BE DE FR GB JP JP SE US	727380 1815214 2000779 1231372 49011971 49006968 49006969 391947 3666449	A A1 A5 A B B B	01-07-1 11-12-1 12-09-1 12-05-1 20-03-1 18-02-1 18-02-1 07-03-1 30-05-1
EP	0703297	A1	27-03-1996	DK ES	703297 2127445		16-08-1 16-04-1
EP	0512255	A1	11-11-1992	AU IT JP US	1408392 1248457 5125434 5215709	B A	08-10-1 19-01-1 21-05-1 01-06-1
US	4391636	Α	05-07-1983	NON	 Е		
EP	0178593	A2	23-04-1986	JP SE SE US	61095767 453302 8405156 4684109	B A	14-05-1 25-01-1 17-04-1 04-08-1

#### REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

## Patent documents cited in the description

• EP 0675862 B1 [0024]

• WO 2008012492 A [0035]