DEVICE FOR SUPPLYING TREATING AGENTS SEQUENTIALLY TO MOLTEN METAL

Jeromo Strauss, New York, N.Y., assignor to Vanadium Corporation of America, New York, N.Y., a corporation of Delaware

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This invention relates to a device for supplying treating agents sequentially to molten metal and to a method for automatically supplying, a plurality of treating agents to molten metal sequentially in the desired order.

In the treatment of a metal, it is highly desirable to add two, three, or more treating agents, one after the other, so as to produce a succession of desired effects. It may be of considerable importance to have these treatments follow one another in a predetermined sequence and with a controllable and accurate time interval elapsing between each successive step. To accomplish this effect, I have designed a suitable apparatus or device which is illustrated in the form of one preferred embodiment in the accompanying drawing.

The figure is a longitudinal section of one form of the device. It comprises a cylindrical container 1 having an internal diameter 2 divided by partitions 3, 4 and 5 into compartments A, B and C containing treating agents A', B' and C' with the base 6 thicker than the side wall 1. The entire container can be made of a metal that is most suitably related in character to the metal to be treated, e.g., steel or cast iron in order to treat a ferrous metal, aluminum for treating aluminum alloys and magnesium for treating magnesium alloys. It may, however, also consist wholly or partially of an alloying element, e.g., ferrochromium, ferromanganese, alloys of molybdenum, nickel and others, the metals themselves or a treating agent such as aluminum or silicon. Suitable treating agents are placed into their respective compartments in such a manner that, as partitions 3, 4 and 5 successively melt, treating agents A', B' and C' are released to the metal bath into which the container has been immersed. In some cases, the side wall 1 may be given a taper and the bottom 6 may be made substantially thicker than any portion of the side wall, or the inner diameter may be constant with the wall thickness increasing from compartment to compartment, being least for the compartment at the mouth of the container and greatest for the compartment at the base. The thickness of partitions 3, 4 and 5 can also be varied or more or less difficulty fusible alloys may be used for the different partitions or for different portions of the side wall to respond to certain desired time intervals between additions.

In use, the device is placed in the bottom of a ladle and the molten metal is poured on top, or the device is introduced into the molten metal after the latter has been partially or wholly added to the ladle. In any event, the device sinks below the surface of the molten metal, preferably to the bottom of the ladle. The cover separating agent A' from the melt may be omitted or, if it is retained, it is so much thinner so or much more fusible than the side wall 1 that it will melt before any substantial amount of the side wall has melted, thereby releasing agent A'. After the treating agent A' has passed into the molten bath, partition 4 separating chambers A and B will be heated and may then melt. The side wall 1 has still not had time to melt down. This permits treating agent B' to pass into the metal bath before agent C'.

It now becomes a question of the relation of the temperature of the metal bath and of the relative wall thicknesses and materials of walls 1 and 6 and of the separating partition or membrane 5 dividing compartments B and C from each other, and thus how soon, and through which wall treating agent C' will be released.

It is possible that some of the treating agents used may be of such nature that they will tend to vaporize and thereby develop pressure at a time in advance of the desired moment of release, either by rupturing the separating partition or the container. Where this condition may exist, as, for example, when using magnesium metal or magnesium-rich alloys for the treatment of high carbon iron, prevention of such undesirable effect may be insured by packing the agent in a thermal insulator such as asbestos, magnesia, lime, alumina, or a combination thereof, or any other suitable substance. The insulating agent may be, for example, a calcium aluminate, or a preformed lime-alumina compound which in addition has insulating qualities has the advantage of controllable low melting temperature. In this or other ways, the insulating material may be caused to flow readily to the top of the metal bath. This insulating material thus may be chosen either for its chemical or physical characteristics, particle size, etc., in order to yield the desired metallurgical results, which may include removal of solid non-metallic impurities from the metal bath.

In some instances, it may be desirable to subject the metal bath to vigorous stirring, either following the complete metallurgical treatment, or at some stage during the metallurgical treatment herein described. For this purpose, one of the compartments of the device, possibly the last compartment to release its contents, may contain a salt or other compound which will dissociate or volatilize when suitably heated. Or it may be desirable to use such compound to fluidify the products of the metallurgical reaction or other solid non-metallic material in the molten metal bath. Such a substance may be, for example, calcium carbonate, or anhydrous ferric chloride, or a mixture of sodium fluoride and silicon tetrachloride in a suitable quantity, or any other agent suited to the desired reaction in the molten bath being treated; for example, calcium fluoride and sodium fluoride may be advantageously employed for this purpose. The release of a substance of the character described will aid the removal of impurities by rendering them fluid or by providing a fluid which will take them into solution, or assist in their liberation by the mere gassing of the melt.

The above discussion sets forth in general terms the manner in which the device can be used to act upon the metals. The invention can be used for adding treating agents sequentially to molten metals in general. A specific application in which this device may be employed is in the treatment of cast iron to yield a product in which the graphite is in the form of nodules. To accomplish this purpose, it is customary to add to molten iron of suitable composition limits, more particularly in respect to carbon and silicon, a metal such as magnesium or cerium alone or associated with other assisting metals or a reaction mixture that will yield one or more of these metals or combinations of them.

It has been observed that if the iron to be treated contains more than a small amount of sulphur, the sulphur tends to prevent the formation of nodular graphite. It is, therefore, desirable to use initially, iron of relatively low sulphur content or when irons of higher sulphur content only are available, to remove the sulphur prior to the nodulizing treatment.

It has also been observed that in order to produce complete or nearly complete nodulizing of the graphite, it is necessary, subsequent to the addition of the nodulizing alloy or reaction mixture containing magnesium.
or cerium or both, to add an agent of the type generally referred to in iron foundry practice as an inoculant. This material, usually ferrosilicon, serves to germinate the precipitation of graphite providing a large number of small graphite particles (in this instance, nodules). I have discovered that this purpose may be served by means of a device which will sequentially:

1. Lower the sulphur content to a suitable non-interfering level.
2. Add a suitable amount of nodulizing element or elements, and
3. Add a proper amount of an inoculating agent to effect the formation of a large number of small graphite particles.

Referring again to the figure which shows a cylindrical container having three chambers separated by partitions of suitable thicknesses and three materials, an inoculant C' is placed in compartment C and partition 5 is secured in place. Then a desulphurizing agent B' is placed in compartment B and partition 4 is secured in place. Finally, a desulphurizing agent A' is placed in compartment A and a cover 3 is secured in place. Instead of employing a cover, the desulphurizing agent may be, for example, sodium hydrate, poured in place in the compartment A.

Various desulphurizing and nodulizing agents and inoculants may be employed. As desulphurizing agents, I may employ sodium hydroxide, soda ash, sodium sulphide or other suitable sulphide, any one or more of the alkali metals such as sodium, or any one or more of the alkaline earth metals such as calcium, or alloys containing substantial amounts of these metals as, for example, an aluminum-calcium alloy.

As the nodulizing agent, I may employ a magnesium-copper-silicon-iron alloy with low magnesium content, say 8.0%, such as is currently in use for nodulizing, or a magnesium-copper-silicon alloy of higher magnesium content, say 40%, such as is now used as an intermediate alloy in producing the presently, directly added, low magnesium alloys. I may also use magnesium metal or cerium metal or misch metal. I may also employ reaction mixtures such as calcium-silicon, plus rare earth oxide concentrates, or mixtures of magnesium oxide and ferrosilicon of high silicon content, such as 75.0% or 85.0%.

As the inoculant, I may use ferrosilicon of any suitable silicon content such as 50% or 75% or 85% or any other metallic alloy rich in silicon.

Utilization of the nodulizing agent and particularly of a nodulizing agent containing or generating magnesium is much more effective with this device than when alloys alone or reaction mixtures alone are added to a bath of molten iron. The reason lies, of course, in the inability of the magnesium to be lost by issuing as vapor without passing through an appreciable depth of the molten iron, whereby most of the magnesium is retained in the iron. By improving agent recovery of the nodulizing element such as magnesium, and by using a more concentrated magnesium alloy (including magnesium itself), it becomes more readily possible to reduce the amounts of other elements that are added to the iron, as for example the silicon. In this way, a low-silicon nodular iron can be produced, which for some ultimate uses is desirable.

The process and device herein described are particularly advantageous when only a part of the production of a given foundry or, more specifically, of a given melting unit is to be converted to nodular iron in that they provide simple, readily usable means for application to a portion of the iron being melted.

The invention may also be advantageously applied in making boron treated steels in the manufacture of which it is important to protect the highly reactive boron from loss by combination with oxygen and with nitrogen.

To illustrate this, it may be pointed out that when treating molten steel with the most effective type of alloy for the purpose, the full boron effect is secured by the addition of only 0.0004 percent of boron if the added alloy is a complex of aluminum, titanium, vanadium and boron; when the vanadium is not present, the addition of boron to secure the full effect is greater, but necessary only to the extent of 0.001%. If the same steel practice is employed but the final additions are of aluminum followed by or admixed with ferrotitanium, and these are in turn followed by separately added ferroboron, 0.003% of boron is required to obtain the same effect in hardenability, but with other properties not quite equal to those resulting from use of a complex alloy addition, due perhaps to the residue (in excess) of boron reaction products. The frequency of reproduction from heat to heat also is less.

By the use of the herein described process and device, results may be obtained with a boron addition comparable with or less than the above best practice of 0.0004 to 0.001%, even though using ferroboron rather than the complex alloys.

The container may be made of cast steel or cast iron. Aluminum and/or other deoxidizing agent is placed in compartment A, ferrotitanium or ferrozirconium or ferro-silicon-zirconium or other nitrogen combining agent is placed in compartment B and a boron-containing alloy is placed in compartment C. The proportions of these agents should be such as to be adequate to treat a specified quantity of a given steel made in a given manner; the proportions and amounts will vary with the steel making practice and steel composition. The boron-containing agent may be ferroboron containing 15% or over 17% boron or it may be manganese-boron containing 17% boron and 75% manganese. There are other suitable boron alloys such as iron-silicon-boron alloys containing 40% silicon and 3.5% boron.

In use, the container may be placed in the bottom of the ladle before pouring the steel or it may be added to the steel in the ladle. The action is similar to that described in the treatment of cast iron to produce nodular graphite. The aluminum is liberated first, reacting with the residual oxygen of the steel as well as some of the nitrogen and refining the grain of the steel. Thereafter, as the partition 4 melts down, the ferrotitanium or zirconium alloy is set free to act upon the nitrogen in the steel. Finally, the boron alloy is released from the container to exert its beneficial action upon the steel. It is, of course, understood that the grain refining action of the aluminum is generally desired in the preparation of the steel for the beneficial effect of boron.

Although the invention has been described for purposes of illustration as applied to processes in which three different treating agents are employed in treating the metal, it will be understood, of course, that two, or more than three, different treating agents can be added to the metal by varying the number of the compartments in the container. The container enclosing the treating agents may be in different sizes, depending upon the volume of metal to be treated as a unit and the convenience of handling the weights of treating agents required, so that for small melts a single container may be employed and for larger masses several containers may be necessary for a single treatment; where several are used they, of course, be placed in the bottom of a ladle simultaneously or added simultaneously to a ladle of molten steel during pouring of metal from a melting or refining furnace.

The invention provides an improved procedure for the sequential treatment of a molten metal without loss or ineffective use of any of the reagents. The reagents are caused to reach a point considerably below the molten metal surface before being released for reaction with the molten metal. They are not heated quickly while in contact with air or with supernatant slag and each is released after a previous one has combined with some ele-
ment present which would cause ineffective combination with a reagent. Each reagent reacts with the molten metal with maximum efficiency, which is of great importance. Thus, in adding magnesium to molten iron, instead of obtaining 15 or even 25% recovery of the magnesium, values about 50% may be secured, approaching under some conditions as much as 70%.

Other effective means of applying the process and device of this invention will be obvious to those skilled in various fields of metallurgical practice.

The invention is not limited to the preferred embodiment but may be otherwise embodied or practiced within the scope of the following claims.

I claim:

1. A device for supplying treating agents sequentially to molten metal, which comprises an open ended container having a base and a side wall, the base being thicker than the side wall, the container being divided into a plurality of compartments by at least one transverse partition, the partition melting before the base, a different treating agent in each compartment, the treating agent in the compartment adjacent to the base, a different treating agent in each compartment, the treating agent in the compartment adjacent to the base, a second partition dividing said container into a plurality of compartments, a different treatment agent in each compartment, the treating agent in the compartment farthest from said base being the one desired to be first liberated from the container when the device is immersed in molten metal and the treating agent in the compartment nearest to said base being the one desired to be liberated last, the partition dividing the compartment farthest from said base from its adjacent compartment having a melting point not higher than the temperature of the molten metal and being of such thickness and composition that it remains solid substantially all of the treating agent in the compartment farthest from said base is liberated from said container, said base and all portions of said side walls between said base and the partition dividing the compartment farthest from said base from its adjacent compartment being of such thickness and composition that they remain solid until substantially all of the treating agent in the compartment farthest from said base is liberated from said container.

2. A device for supplying treating agents sequentially to molten metal, said device comprising a container having a base, an axial bore opening toward the end of the container opposite the base and divided transversely by partitions to form at least three compartments lying one above the other, an inoculating agent in a compartment adjacent to the base, a nodulizing agent in a compartment more remote from the base than the inoculating agent and a desulphurizing agent in a compartment more remote from the base than the nodulizing agent, the partitions melting successively, the partition nearest the base being the last to melt.

3. A device for supplying treating agents sequentially to molten metal, which comprises a container having a base, an axial bore opening toward the end of the container opposite the base and divided transversely by partitions to form at least three compartments lying one above the other, a boron-containing agent in a compartment adjacent to the base, a nitrogen removing agent in a compartment more remote from the base than the boron-containing agent and a deoxidizing agent in a compartment more remote from the base than the nitrogen removing agent, the partitions melting successively, the partition nearest the base being the last to melt.

4. A device for supplying treating agents sequentially to molten metal, which comprises a container having an axial bore divided transversely by partitions to form a plurality of compartments which lie one above the other, the partitions melting successively, a different treating agent in each compartment, the different treating agents being arranged in the compartments in such order and the partitions being arranged in such order that when the device is immersed in molten metal the different treating agents are liberated from the device sequentially in the desired order.

5. A device for supplying treating agents sequentially to molten metal, which comprises a cylindrical container having an axial bore divided transversely by partitions to form a plurality of compartments which lie one above the other, the partitions melting successively, a different

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