METHOD FOR ADDING SPECIAL ELEMENTS TO MOLTEN PIG IRON

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A method of adding a magnesium containing additive selected from the group consisting of metallic magnesium and alloys or mixtures of magnesium with at least one other metal selected from the group consisting of rare earth metals, calcium, aluminum, vanadium, zirconium, niobium, titanium, copper, nickel, chromium, molybdenum, cobalt and mixtures thereof, which comprises introducing said magnesium containing additive to at least one enclosure at the bottom of a molten pig iron ladle, covering said additive with a granular or powdered covering layer containing at least one material selected from the group consisting of carbon, silicon carbide and silicon, whereby the melting point of said covering layer is adjusted to between 1,100°C and 1,600°C and thereafter pouring the molten pig iron into said layer over said enclosure so that contact between said molten pig iron and said additive is delayed until at least a portion of the covering layer is melted.

7 Claims, 8 Drawing Figures
METHOD FOR ADDING SPECIAL ELEMENTS TO MOLTEN PIG IRON

BACKGROUND OF THE INVENTION

1. Field of the Invention
The present invention relates generally to a method for adding special elements to molten pig iron, and more particularly to a method for adding metals or alloys of elements such as magnesium or other additives to molten pig iron in a ladle.

2. Description of the Prior Art
In order to improve the quality of castings from cast iron, it is conventional to add to the cast iron either magnesium (Mg) or a combination of magnesium and one or more other elements such as the rare earth metals (RE), calcium (Ca), aluminum (Al), vanadium (V), zirconium (Zr), niobium (Nb), titanium (Ti), copper (Cu), nickel (Ni), chromium (Cr), molybdenum (Mo) and/or cobalt (Co). However, it is difficult to add these elements directly to the molten pig iron in their free metal state and accordingly it has become the practice to alloy the additive element with iron or with a ferro-silicon (Fe – Si), which is compatible with molten pig iron, and to introduce the element into the molten pig iron in the alloy form. Usually, for purposes of practicality and to increase the yield of elements remaining in the molten pig iron, this is accomplished by preparing the alloys such that their inherent specific gravities and melting points are compatible with those of the molten pig iron and their temperatures are approximately the same as the molten pig iron.

Nevertheless, such special elements as Mg have very low boiling and melting points as compared with cast iron, so that even in the alloy form their addition to the cast iron is difficult. In order to overcome this difficulty, it has become customary to alloy the Mg with Ni, Cu, or Fe – Si, and to introduce the alloy by a pressure ladle or plunger into the molten cast iron.

Another conventional technique is to place the alloys on the bottom of the ladle and to pour the molten pig iron onto the alloys. An improvement of this method known as the “sandwich method,” has also been reported, according to which the alloys placed on the bottom of the ladle are first covered with steel scraps or the like before the introduction of the molten pig iron.

Even with these devices, however, the above methods are not exempt from such disadvantages or problems as low yield of additives remaining in the molten pig iron; violent reaction; and sharp drops in temperature of the molten pig iron.

As mentioned above, the addition of special elements to molten pig iron is conventionally almost always carried out in the form of alloys, and various devices are usually provided for facilitating the addition. These techniques, however, have caused a serious rise in production costs of the castings.

A need exists, therefore, for a technique for carrying out the addition of the additives in the ladle, so as to meet the special characteristics of the casting operation, in which a variety of castings can be produced in small quantities. From an economical standpoint it would be desirable to provide a technique which can be easily used without the necessity for any special added elements or any special equipment.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a method for adding Mg or Mg in combination with other elements, to molten pig iron or other high temperature molten metal without the necessity of such special devices or processes as pressure ladles or plungers.

Another object of this invention is to provide a technique whereby additive alloys can be introduced without difficulty and without the use of special equipment.

Still another object of this invention is to provide a technique whereby the additives can be used in the form of free metals thereby dispensing with the necessity of pre-forming of alloys.

A further object of this invention is to provide a technique for additive addition which can be carried out safely and easily without sharp drops in the temperature of the molten pig iron, therefore improving the yield of additives remaining in the molten pig iron and reducing production costs.

These and other objects have now herein been achieved by the method of adding Mg or Mg in combination with one or more such special elements as Re, Ca, Al, V, Zr, Nb, Ti, Ni, Cr, Mo, Co and Cu, to cast iron by preparing metals and/or alloys of these metals or a mixture of metals and/or alloys with one or more items selected from a group consisting of carbon (C), iron (Fe), Fe – Si, Si and SiC_, by charging the metals or alloys to at least one pocket provided in the molten pig iron ladle. The metals or alloys are then covered with a powder or granular form of C, SiC and/or Si, wherein the melting point of said covering materials is adjusted to between 1,100° and 1,600° C. by changing the mixing ratios of these materials with the addition of C, ferro-silicon (Fe – Si) or the like. The molten pig iron is then poured into the ladle, which melts the covering materials and thereby causing the charged metals or alloys to contact and react with the molten pig iron and to become intimately associated with the molten pig iron. The additive metals can be used in this process in the form of the free metal, metal mixture and/or alloys with one or more materials including carbon (C), iron (Fe), Fe – Si, Si and/or SiC.

BRIEF DESCRIPTION OF THE DRAWINGS

Various other objects, features and attendant advantages of this invention will be more fully appreciated as the same becomes better understood from the following detailed description when considered in connection with the accompanying Drawings, wherein:

FIGS. 1A and B show, respectively, a cross-sectional view and a plane view of the apparatus embodying the method of the present invention.

FIGS. 2A and B, FIGS. 3A and B, and FIGS. 4A and B show, respectively, cross-sectional views and plane views of respective embodiments of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following is an explanation of the present invention with respect to the preferred embodiments:

As shown in FIGS. 1A and B, the method of the present invention relates to use of an enclosure such as a pocket 3 provided on the bottom 2 of a molten pig iron ladle 1. Said pocket 3 is formed in a semi-circular con-
figuration by enclosing a portion of the bottom 2 of the ladle 1 with an appropriate refractory material. Into the pocket 3 is charged a metal of Mg or an alloy of Mg in combination with such special elements as rare earth metals, calcium, aluminum and vanadium or a mixture thereof (hereinafter referred to as the additive alloy 5). The additive alloy 5 is preferably in a granular form, but may be in the form of appropriate size chips. The additive alloy 5 is covered with covering materials 6 in powder or granular form which consist of one or more items selected from the group consisting of C, SiC and metallic Si. If necessary, adjusting materials such as C and Fe–Si may be added to the covering materials 6, so as to adjust their melting temperatures within a range of between 1,100° and 1,600°C. The thickness of the layer of covering materials 6, and the type and mixing ratios of the covering materials will determine the period of time elapsing between the time the molten pig iron is introduced into the ladle and the time the additive alloy starts to react with the molten pig iron. It is preferred that the covering materials 6 be composed of either SiC or metallic Si alone or SiC or Si in combination with C or Fe–Si. The melting point of the covering material mixture should be adjusted within a range of between 1,100° and 1,600°C. When SiC is used, it is preferred that it contain 61 to 62 percent by weight SiC and 26 to 28 percent by weight C, the remaining 8 to 10 percent by weight may be composed of such impurities as Fe, Al and/or free C. It is preferred that the melting point of the SiC be between 1,350° and 1,450°C. It should be noted that much of the conventional SiC is composed of 60 to 65 percent by weight Si and 25 to 30 percent by weight C, with melting points of about 2,500°C and, therefore, is not suitable alone for the methods of the present invention. It can be made suitable, however, by the addition of about 10 percent by weight Fe so that its melting point will be reduced to about 1,400°C. When metallic Si is used, it is preferred that it have a purity of at least 97 percent by weight and preferably at least 98 percent by weight. Its melting point should be between 1,400° and 1,450°C. It should be noted, however, that the melting points of the SiC and Si can be reduced by adding such low melting point materials as Fe–Si.

Since C has a melting point of between 3,600° and 3,700°F, it is better to use C together with SiC and/or metallic Si, as an additive for adjusting their melting points. C can be used alone, however, if desired, in which instance the C will function both as an agent for adding C to the molten pig iron and as a covering material. The carbon will also act as an effective deoxidizing and engraining agent for the molten pig iron.

Commercial carborundum powder can be used as the SiC for the objects of the present invention. Such carborundum powder as is commercially available for metallurgical purposes usually contains 80 percent by weight SiC with the remainder being mostly Fe. The melting point of such SiC is usually about 1,500°C, which is slightly higher than required for the present invention.

The covering materials 6, such as the carborundum powder, when supplied in amounts of from 0.2 to 0.3 percent by weight based on the weight of molten pig iron and in a thickness of 1 to 2 mm., will not melt as soon as the molten pig iron is introduced, but will turn into a half molten state forming a kind of film for 30 seconds to 2 minutes according to the volume of the ladle and the temperature of molten pig iron. This film prevents contact of the molten pig iron with the additive alloy 5 until the ladle is filled with the molten pig iron. The additive alloy 5 will then gradually melt with the molten pig iron and react with same. This phenomenon is due to the fact that the covering materials 6 have a melting point of between 1,350° and 1,450°C, which is similar to the temperature of the molten pig iron ranging from 1,350° to 1,550°C, thereby preventing quick melting and requiring a period of time before the additive alloy 5 is contacted with the molten pig iron. In other words, the delay time before the reaction between the additive alloy 5 and the molten pig iron begins can be easily adjusted by varying the thickness of the SiC powder or granular cover. Such adjustment is easily provided by pre-selecting the appropriate covering materials.

Instead of the pocket 3, a concave part 4 formed in the bottom of the ladle 1, as shown in FIGS. 2A and B, can be provided for receiving the additive alloy 5. The additive alloy 5 in said concave part 4 is then covered, on its upper surface, with the covering materials 6. In this instance, the contact delay time can similarly be adjusted as above.

The concave portion 4 or pocket 3 can be in any variety of shapes such as circular, semi-circular or square. The size will depend upon the capacity of ladle, the quantity of molten pig iron to be treated, the particular additive alloy used, or other conditions. For example, a ladle having a capacity of 100 kg. of molten pig iron may be provided with a concave portion 4 or a pocket 3 of 100 mm. in diameter and about 50 mm. in depth, shaped circular or semi-circular, on the circumferential portion of the bottom 2 of the ladle 1. If desired, more than one such concave portion 4 or pocket 3 may be provided. In the case of plural pockets or concave portions, it is possible to vary the types of additive alloy 5 and covering materials 6, in each pocket or portion so that more than one type of additive alloy 5 is introduced or the various additive alloys will be added in multiple stages. That is to say, the method of the present invention can be used, as modified as shown in FIGS. 3A and B. In these Figures, two recessed concave parts 7 and 8 are formed in the bottom 2 of the ladle 1. In one concave portion 7, one type of additive can be added, for example, an expensive Mg alloy (5A) covered with the covering materials 6 according to the present invention. Into the other concave portion 8 can be added an inexpensive Mg alloy (5B) covered with steel scraps 9 according to the sandwich method.

According to the method shown in FIG. 3, the additive alloy 5B charged in the concave portion 8 will react first with the molten pig iron, and then the additive alloy 5A charged in the concave part 7 will enter the reaction during a subsequent time period so that the addition occurs in two stages, making the addition effective and economical. FIG. 4 shows a modification of the method of FIG. 3, in which the expensive Mg alloy 5A is charged into the recessed concave portion 10. This alloy 5A is then covered with the SiC covering powder or granular 6, and over this covering layer an additional inexpensive Mg alloy 5B is charged.

The process and effect of such addition are almost the same as those mentioned in relation to the method of FIG. 3.
The additive alloy 5 used in the present invention may be in the form of a free metal or may be in the form of an alloy of Mg and/or another metal or alloy of Mg, in admixture with another metal or a mixture of alloys. Other metals which can be either admixed with or alloyed with the Mg or Mg alloy include such special elements as RE, Ca, V, Zr, Al, Nb, Ni, Cr, Mo, Co and Cu, or mixtures thereof or alloys thereof with one or more items selected from the group consisting of C, Fe, Fe – Si, metallic Si and SiC.

As mentioned above, the additive alloy 5 of the present invention will not come into contact with the molten pig iron until after the covering materials 6 are melted, thereby avoiding the previously dangerous situation which occurred when Mg or the high Mg content alloy was directly contacted with the molten pig iron. Moreover, when using the present technique, additive alloys having a higher melting point than molten pig iron can be added without difficulty to molten pig iron in a ladle, by combining said high melting point alloys with lower melting point Mg or its alloys. Another unique aspect of the present invention is that the additives can be used in the form of free metals and several different metals can be used in any desired mixing ratios.

The additive alloys 5 can also be used in admixture with one or more other additives selected from the group consisting of C, Fe, Fe – Si, metallic Si and SiC. This makes it easier to use a wider variety of special elements in the form of metals, and makes it possible, as well, to have the additive alloys 5 react with molten pig iron slowly even after the covering materials have melted.

Moreover, it permits the addition of the additives in stages merely by proper selection of the ratios of the various additives and additive alloys.

In the present invention, the additive alloy 5 is subjected to heat from the molten pig iron even before the covering material is melted, thereby forming a kind of powder-metallurgically produced alloy. As time passes, and as the covering materials 6 melt, the additive alloy 5 is gradually melted from the top to the bottom into the molten pig iron. There is therefore a gradual reaction of the additive alloy 5 with the molten pig iron and there is no sudden burst of reaction as has occurred in some prior art processes.

According to the method of the present invention, therefore, it is possible to prescribe useful elements in a more exact quantitative manner than when adding such elements in the form of alloys, thereby saving costs for the production of such alloys.

The following are some samples of combinations of elements which can be added either in the form of mixtures or in the form of alloys.

Mg: Ca-Si-Mg; Fe-Si-Mg; Fe-Si-Mg-RE; RE (Mischmetal); Fe-Si-RE; Fe-Ca-Si; Fe-B; Fe-Ni; Si-Ni; Ni; of powder or granular form; Fe-Cr; Si-Cr; Cr-Si-Mn-Zr; NCR; Ca-Si-Cr; Fe-Mn; Si-Me; Si-Mn-Zr; Ca-Si-Mn; Fe-Si; metallic Si; Fe-V; Fe-Nb; Fe-Zr; Si-Zr; Ca-Si-Ti; Ca-Si-RE; Ca-Mg; Mg-RE; Fe-Ti; Si-Ti; Fe-Co; Mo-Si; Fe-Mo; other carbon powder (non-metallic) nodulizing agents.

The following is a summary of advantages of the method of the present invention:

1. The delay time between introduction of the molten pig iron and the contact with the Mg metal or alloy and also the velocity of the reaction between the pig iron and Mg metal or alloy can be readily varied by varying the kinds of covering materials and the thickness of the cover layer. This eliminates the sharpness of the reaction so greatly that alloys of high Mg content and even Mg metal can be used without difficulty.

2. In addition to the use of the particular covering materials, the reaction between the molten pig iron and the additive metal or alloy can be delayed even further by admixture of the additive with such additional materials as C, Fe, Fe-Si, metallic Si and SiC or with materials similar thereto. Use of these secondary additives also enables the possibility of having the additive metal or alloy come into contact with the molten pig iron in stages or by small degrees.

It can be easily seen, therefore, that Mg metal is made more usable; and special elements can be added in the form of free metals without the prior necessity of forming alloys with Fe, Si or the like.

3. The yield of Mg remaining in molten pig iron is improved by about 20 percent over that according to the conventional method of pouring molten pig iron directly onto the additive alloys, so that nodulization can be effected with a small amount of a nodulizing agent.

4. Because a smaller amount of the additive alloy is used when the covering materials are used, there is no need to cover the additive alloy with a great amount of steel scraps as in conventional methods. This results in the advantage that a smaller temperature drop in the molten pig iron will occur, as compared with the latter method. This constitutes a great advantage in the production of nodular graphite cast iron.

5. The method of adding the additives according to this invention is not difficult and does not require any special apparatus or device and, therefore, production costs are reduced.

6. The materials used in the covering layer such as SiC, have high deoxidizing capacities, and also are effective as subsidiary agents for nodulization. They also have the quality of being able to form nodular graphite grains in cast iron which are smaller and more uniform, thereby improving the quality of nodular graphite castings made from the cast iron.

7. An inexpensive additive alloy can be combined with an inexpensive additive alloy and used in the same ladle. In this manner, it is possible to nodulize molten pig iron by stages, and thus produce nodular graphite cast iron of very good quality.

The following are examples of the present invention:

Having generally described the invention, the following specific Examples are provided for purposes of illustration only and are not intended to be limiting unless otherwise specified.

**Example 1**

Cast iron having the following chemical composition was melted in an electric arc furnace.

TC: 3.72%, Si: 1.80%, Mn: 0.20%, P:0.068%, S: 0.024%, the rest being Fe and impurities (all being weight percent).

Table 1 shows the results of the tests made on the method of the present invention, using the above molten pig iron, in comparison with the conventional
method of pouring molten pig iron directly onto the additive alloy (hereinafter referred to as the conventional method).

For comparison, the same additive alloy was used in the method of the present invention and for the conventional method. The additive alloy 5 is an alloy consisting of Mg, RE, Ca, and Si (balance essentially Fe) at respective mixing ratios by weight of 8 percent, 4 percent, 2 percent and 45 percent. The drop in temperature of the molten pig iron after pouring was compared and the degree of nodulization and contact reaction between the molten pig iron and additive alloy were measured.

The ladle used had a capacity of 200 kg., and the ratio between the diameter of bottom and height was 1 : 1.5, with a pocket 3 (shown in FIGS. 1A and B) being sized 100 mm. in diameter and 50 mm. in depth and shaped semi-circular, provided on the circumferential part of the bottom.

The amount of molten pig iron poured was 200 kg. The additive alloy 5 was an alloy of Fe-Mg-Ca-RE-Si or 3 to 10 mm. in granular size.

It has also been found that if 1.0 percent metallic Si is used for covering the Mg alloy and also for being mixed with it, the contact between the molten pig iron and the Mg alloy becomes intermittent, preventing more and more of the boiling of the molten pig iron.

**EXAMPLE 2**

3 kg. of the additive alloys 5 of the following chemical composition were charged in the pocket 3 of the same specifications as that used in Example 1.

| Metallic Si | 60% by volume (of a granular size of 3 to 5 mm.) |
| Mg metal | 10% do. (shaped like a bar, 10 mm. in diameter) |
| Reductive iron powder | 30% do. |

100%

After the above additive alloy 5 was covered with covering materials 6 consisting of Fe-containing carburendum (SiC) powder 0.5 percent by weight of molten pig iron, 200 kg. of molten pig iron taken from the same lot as in Example 1 were poured from opposite to the pocket 3 into the ladle 1 (the temperature of the molten pig iron was than 1,500°C); after the ladle was partially filled, a sample was withdrawn for microscopic examination, which observation proved that nodular graphite cast iron of 85 percent in nodulizing degree was produced.

| TABLE 1 |

<table>
<thead>
<tr>
<th>Samples</th>
<th>Composition and Amount of Covering Materials</th>
<th>Temp. of Molten Pig Iron When Poured (°C.)</th>
<th>Temp. After Reaction (°C.)</th>
<th>When Reaction Started</th>
<th>Reaction</th>
<th>Amount of Added Alloys (% by wt.)</th>
<th>Nodulizing Degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional (A) None</td>
<td></td>
<td>1520</td>
<td>1460</td>
<td>Upon pouring</td>
<td>Sharp</td>
<td>1.0</td>
<td>80%</td>
</tr>
<tr>
<td>(B) Steel scraps 1.5% by weight of molten pig iron</td>
<td>1540</td>
<td>1400</td>
<td>After poured</td>
<td>Rather slow</td>
<td>0.8</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>Reference (C) Fe-Si of less than 5 mm. in granular size 1.0% by weight of molten pig iron</td>
<td>1530</td>
<td>1440</td>
<td>During pouring</td>
<td>Rather sharp</td>
<td>1.0</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>The (D) Carborundum powder covering in 2 mm. thick 0.2% by weight of molten pig iron</td>
<td>1530</td>
<td>1460</td>
<td>Slowly after poured</td>
<td>Slow</td>
<td>0.8</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Present (E) Carborundum powder and carbon powder (at 8:2) 0.2% by weight of molten pig iron</td>
<td>1520</td>
<td>1440</td>
<td>up do.</td>
<td>do.</td>
<td>0.8</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Invention (F) Carborundum powder 0.2% by weight of molten pig iron (Fe-Cr (60%) mixed 0.3% by weight into added alloy)</td>
<td>1540</td>
<td>1460</td>
<td>After poured up</td>
<td>do.</td>
<td>0.8</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>(G) Metallic Si of 3 to 5 mm. in granular size 0.2% by weight of molten pig iron</td>
<td>1540</td>
<td>1450</td>
<td>do.</td>
<td>do.</td>
<td>0.8</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>(H) Metallic Si of 3 to 5 mm. in granular size 1.0% by weight of molten pig iron (also mixed into added alloy)</td>
<td>1520</td>
<td>1420</td>
<td>do.</td>
<td>Very slow</td>
<td>0.8</td>
<td>90</td>
<td></td>
</tr>
</tbody>
</table>

NOTE: (H) marked with * is a case in which the necessity of using a great quantity of covering material (1.0 percent by weight) was anticipated for adding a great quantity of elements to cast iron, so that a portion of the metallic Si was mixed with Mg alloy, and the remainder majority amount was used in the covering layer.

It can be seen from Table 1 that the method of the present invention is superior to the conventional method, and that, according to this experiment, the later the time between contact of the Mg alloy and molten pig iron, the less the boiling of the molten pig iron, which is due to the pressure weight of the poured molten pig iron on the additive alloy. This provides a better yield of Mg alloy remaining in the molten pig iron.
In the above process, the contact between the additive alloy 5 and the molten pig iron was delayed temporarily due to the SiC charged into the pocket 3. Boiling of the molten pig iron caused by the contact between Mg and the additive alloy and molten pig iron did not occur for 2 minutes after the completion of the pouring. Even then, boiling was not as severe as when a Mg-Si alloy of the same mixing ratios as in the above additive alloy 5 (mixture) was used, thereby confirming that Mg metal covered with a covering layer can be used safely.

EXAMPLE 3

Using the same conditions as in Example 1, 2 kg. of the additive alloy 5 of the following chemical composition was charged into pocket 3:

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg metal (shaped like a bar, 10 mm. in diameter)</td>
<td>10% by volume</td>
</tr>
<tr>
<td>Fe-Ni (Ni 20% by weight)</td>
<td>5% by weight</td>
</tr>
<tr>
<td>Fe-Si (Si 75% by weight)</td>
<td>5% by weight</td>
</tr>
</tbody>
</table>

After the above additive alloy 5 was covered with the covering materials 6 consisting of Fe-containing carborundum (SiC) powder, 0.2 percent by weight of molten pig iron, 200 kg. of molten pig iron taken from the same lot as in Example 1 were poured from opposite to the pocket 3 into the ladle 1 (the temperature of the molten pig iron was then 1,500°C). After pouring, a sample was withdrawn for microscopic examination, which showed that nodular graphite cast iron of 90 percent in nodulizing degree was produced. The reaction between the contact between additive alloy 5 and the molten pig iron was nearly the same as in Example 2.

EXAMPLE 4

Using the same conditions as in Example 1, 2 kg. of the added alloy 5 of the following chemical composition was charged into the pocket 3:

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg metal (shaped like a bar, 10 mm. in diameter)</td>
<td>10% by volume</td>
</tr>
<tr>
<td>Ca (30% by weight)</td>
<td>5% by weight</td>
</tr>
<tr>
<td>RE (30% by weight)</td>
<td>5% by weight</td>
</tr>
<tr>
<td>Metallic Si (3 to 5 mm. in granular size)</td>
<td>10% by weight</td>
</tr>
<tr>
<td>Reductive iron powder</td>
<td>15% by weight</td>
</tr>
</tbody>
</table>

After the above additive alloy 5 was covered with covering materials consisting of SiC 0.2 percent by weight of molten pig iron, 200 kg. of molten pig iron were poured as in Example 1. When pouring was completed, a sample was withdrawn for microscopic examination which proved that nodular graphite cast iron of 85 percent in nodulizing degree was produced. The reaction between the added alloy 5 and the molten pig iron, started 1.5 minutes after being poured, and was very mild.

EXAMPLE 5

In this experiment, a cast iron having the following chemical composition was produced by melting in an electric arc furnace:

- C: 3.58%; Si: 1.80%; Mn: 0.24%; P: 0.0588%;
- S: 0.086 percent; the rest being Fe and impurities (all being weight percent).

This molten pig iron was given a particularly higher S content than that of Example 1, so that it was of the same quality as molten pig iron in an acidic cupola. After an expensive Mg-Si-RE-Ca alloy, as the added alloy 5A, 0.8 percent by weight of molten pig iron and an inexpensive Mg-Si alloy, as the additive alloy 5B, 1.4 percent by weight, were charged, by the method of FIG. 2, the former being covered with carborundum of powder or granular form in a layer of 2 mm. thick, and the latter being without any cover, 200 kg. of molten pig iron were poured.

The purpose of this experiment was to develop a method for treating molten pig iron of high S content, in which one of the two additive alloys of inexpensive composition was consumed for desulphurization; saving the other of expensive composition from being so much consumed, and this was used for graphite nodulization.

During the experiment, the additive alloy 5B first contacted molten pig iron for desulfurization, and then, as SiC melted gradually, the additive alloy 5A was drawn into the reaction, thus nodular graphite cast iron of as good quality and as great ductility as in Example 1 was produced.

Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit and scope of the claims.

Accordingly, what is claimed as new and intended to be secured by Letters Patent of the United States is:

1. A method of adding a magnesium containing additive selected from the group consisting of metallic magnesium and alloys or mixtures of magnesium with at least one other metal selected from the group consisting of rare earth metals, calcium, aluminum, vanadium, zirconium, niobium, titanium, copper, nickel, chromium, molybdenum, cobalt and mixtures thereof, which comprises introducing said magnesium containing additive into at least one enclosure at the bottom of a molten pig iron ladle, covering said additive with a granular or powdered covering layer of silicon carbide, whereby the melting point of said SiC is adjusted compositionally with impurities of Fe, Al and/or free carbon or Fe-Si, so as to have a melting point of 1,100°C - 1,600°C, and thereafter pouring the molten pig iron onto said layer over said enclosure so that contact between said molten pig iron and said additive is delayed until at least a portion of the covering layer is melted.

2. The method of claim 1, wherein said magnesium containing additive is admixed with a powdered or granular secondary additive containing at least one material selected from the group consisting of carbon, iron, iron-silicon, silicon carbide and silicon.

3. The method of claim 1, wherein said enclosures are in the form of one or more pockets formed on the bottom of said ladle.

4. The method of claim 1, wherein said enclosures are in the form of one or more recesses formed in the bottom of said ladle.

5. The method of claim 3, wherein said pockets are semicircular, circular or square in shape and wherein the walls of said pockets are composed of a refractory material.
6. The method of claim 1, wherein 0.2 to 1.0 percent by weight of said covering materials are used, based on the weight of the molten iron.

7. The method of claim 1, wherein said magnesium containing alloy consists essentially of 8 percent magnesium, 4 percent rare earth, 2 percent calcium, 45 percent silicon and the remainder iron, wherein said covering material is in the form of granules having sizes of from 3 mm. to 10 mm. and wherein the total quantity of said Mg containing additive is from 0.8 to 1.0 percent by weight based on the weight of the molten pig iron.

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