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PROCESS FOR PRODUCING A MAGNESIUM-CONTAINING SPHERICAL GRAPHITE CAST IRON HAVING LITTLE DROSS PRESENT

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ABSTRACT OF THE DISCLOSURE

A two step process for producing a magnesium-containing spherical graphite cast iron having only a small amount of dross present. In the first step, a magnesium alloy is added to molten cast iron, and in the second step, an additive consisting of a mixture of a calcium-silicon alloy and alkali metal fluorides, alkaline earth metal fluorides, or rare earth metal fluorides is added to the molten cast iron.

SPECIFICATION

This application is a continuation of application Ser. No. 399,270, filed Sept. 25, 1964, now abandoned.

This invention relates generally to processes for producing a magnesium-containing spherical graphite cast iron and more particularly to processes for producing a magnesium-containing spherical graphite cast iron having little dross present.

The object of the present invention is to obtain a spherical or nodular graphite cast iron containing preferably 0.01 to 0.08% magnesium as a residual cast iron constituent and a slight amount of calcium and having little dross present. The process comprises chemically treating a preparatorily desulphurized molten cast iron with magnesium or a magnesium alloy to desulphurize the molten cast iron and make it spherical, then adding to said molten cast iron a small amount, preferably 0.4 to 1.5%, of an additive consisting mostly of a fluoride of magnesium or rare earth and a mixture of calcium and silicon, preventing the reduction of the temperature of the molten cast iron and removing a magnesium dross.

It is well known to those skilled in the art that, in the known process for producing a magnesium-containing spherical graphite cast iron, it is difficult for a magnesium dross produced in the sphericalizing treatment to separate from the molten cast iron and that the magnesium dross will remain as it is in the molten cast iron. It will stay on the surface or in the center part of the casting and will be likely to greatly reduce the value of the cast product. Further, it is difficult to remove such dross by any subsequent treatment. The presence of such dross in a magnesium-containing spherical graphite cast iron is considered unavoidable.

The present invention provides a method for removing such dross as is described above. The process for producing a magnesium-containing spherical graphite cast iron having little dross present comprises chemically treating a molten cast iron with magnesium or a magnesium alloy, adding to said molten cast iron small amount, preferably 0.4 to 1.5%, of an additive prepared by mixing a calcium-silicon series alloy powder with at least one member selected from a group consisting of single salts and double salts of fluorides of alkali metals, alkaline earth metals in order and rare earth metals to remove the dross from the molten cast iron and then casting the molten cast iron as

it is or after it is treated with ferrosilicon or calcium silicon.

An object of the present invention is to provide a high quality spherical graphite cast iron having much less magnesium dross than that produced by any already known process for producing a magnesium-containing spherical graphite cast iron.

The salts of fluorides employed in the additive which is used to remove the dross in accordance with the present invention are single or double salts of such alkali metals, alkaline earth metals and rare earth elements as, for example, NaF, CaF_2, CeF_3, LaF_3, YF_3, $NaBF_4$, $NaRF_4$, Na_3AlF_6, $MgNaF_3$ and $MgSiF_6$.

The calcium-silicon series alloys which are used together with the fluoride are alloys containing calcium and silicon as, for example, not only Ca-Si alloys per se but also Ca-Ce-Si, Ca-La-Si, Ca-Y-Si, Ca-Fe-Si, Ca-Mn-Si, and Ca-Zr-Si alloys.

The rare earth metals, cerium, yttrium and lanthanum are symbolized by the letter "R" herinafter in this specification.

The reasons why a spherical graphite cast iron having little dross will be produced when the process of the present invention is applied shall be pointed out in detail later. First of all, this known process of production shall be described.

As a known process for producing a spherical graphite cast iron to which magnesium or a magnesium alloy is added, there is a patent published as Japanese patent publication No. 104/1952 (U.S. Patent No. 2,485,761 of 1948). The process of said patent is prevalent in the world.

According to the said process, molten cast iron is received in a ladle, magnesium alloy such as a Cu-Mg, ni-Mg, or Ni-Mg-Si alloy is added thereto, then a graphitizing inoculating agent such as Fe-Si, Ca-Si, or Ni-Si is added and the molten cast iron is cast.

Further, as a recent trend, there is carried out a process wherein molten cast iron is treated with magnesium alloy such as a Mg-Ce, Mg-La, Mg-Fe-Si or Mg-Ca-Si alloy or with a magnesium alloy and Mischmetal and is then inoculated with ferrosilicon. However, when the above mentioned magnesium alloy is added to the molten cast iron, due to affinity, the magnesium will first combine with sulphur and oxygen contained in the molten cast iron so as to be fine grains in the form of MgS and MgO and such fine grains will be widely distributed and suspended in the molten cast iron and will not easily float up.

When a long time elapses, such distributed and suspended fine grains will gradually combine with carbon and silicic acid SiO_2 contained in the molten cast iron and will become a new dross easy to separate from the molten cast iron.

It is widely recognized that, in order that a spherical graphite cast iron may be obtained, the metallic magnesium in the molten cast iron must remain above a certain value. Further, whereas the temperature of the molten cast iron is above 1300° C., the boiling point of magnesium is as low as 1107° C. Therefore, unless the molten cast iron treated with a magnesium alloy is cast within at least 15 minutes, the effective magnesium will be likely to boil and escape. Therefore, the molten cast iron treated with the above mentioned magnesium alloy can not be left as it is for a long time.

In other words, it may be said that, in the known process for producing a magnesium-containing spherical graphite cast iron, the cast iron must be cast as containing both magnesium required and MgS and MgO not required to make graphite spherical.

While the cast molten cast iron gradually coagulates in the mold, MgS, MgO, C and SiO_2 will combine together and will segregate within the casting or will appear as

black points on the surface of the casting to thus reduce the value of the casting as of the so-called dross.

It has already been described that, in the process according to the present invention, a spherical graphite cast iron in which such dross as is described above is present only in small amounts can be obtained. The reasons for this can be explained as follows.

In the process for producing a spherical graphite cast iron according to the present invention, a molten cast iron is treated with magnesium or a magnesium alloy and then, in the next and second step, a small amount of an additive consisting of a combination of at least one member selected from a group consisting of salts of fluorides of alkali metals, alkaline earth metals and rare earth elements with a powder of a calcium-silicon alloy or calcium-silicon series alloy is added to said molten cast iron to remove the dross. There can be many combinations for the additive composition to be added to remove the dross. It will be necessary to describe what variation such combination will make within the molten cast iron.

Now, in the instances where the combinations are NaF with Ca-Si, MgF_2 with Ca-Si and RF_3 with Ca-Si (Ca-Si is represented by Ca-Si_2), the mixed powder will chemically react at the high temperature of the molten cast iron and the additive will become a new substance.

The reactions can be represented by the following chemical equations or formulas similar to them:

$$2NaF+CaSi_2=2Na+2Si+CaF_2$$

$$MgF_2+CaSi_2=Mg+2Si+CaF_2$$

$$\tfrac{2}{3}RF_3+CaSi_2=\tfrac{2}{3}R+2Si+CaF_2$$

As a result of experiments, it is found that such change is not accompanied with severe reaction phenomenon but is an exothermic reaction which proceeds in the molten cast iron within a short time and that therefore the reaction product is likely to be diffused within the molten cast iron. Further, if the molten cast iron is mechanically stirred for 1 to 2 minutes, the reaction product will be more likely to come into contact with the molten cast iron.

That is to say, a part of the new product represented by the right side of each of the foregoing formulas will melt into the molten cast iron and will effectively operate and the other part will combine with the already existing MgS or MgO to be a new dross and will float up.

It has been already described that there can be made many combinations of additives of salts of fluorides and calcium-silicon series alloy powders to be used in the second step. However, though all of them can not be considered to operate effectively to the same degree, at least all of those additives have the same tendency. Specifically for the additive, the combinations of $CaSi+RF_3$,

$$\text{Ca-R-Si}+MgF_2$$

and $CaSi+MgF_2+RF_3$ are preferred.

In this invention the method of first making the molten cast iron spherical, i.e. the first step of the process, by addition of magnesium or a magnesium alloy is the same as in the known method. The amount of addition of magnesium need not be as high as the conventional range which must be sufficient to make the molten cast iron perfectly spherical, rather the amount may be smaller than in the conventional range. Even in the case where such amount is used as will make the molten cast iron imperfectly spherical, by the sufficient addition of the present additive, i.e. in the second step, the insufficient spherication can be compensated for and the magnesium dross can be removed.

When the molten cast iron is sufficiently preparatorily desulphurized and is then treated with magnesium or a magnesium alloy, the amount of magnesium or magnesium alloy used in this first step is reduced and the amount of the above described additive of the present invention used in the next step can thus be reduced.

From the above mentioned viewpoint, in the present invention, it is considered to be most proper that the final spherical casting contains preferably about 0.01 to 0.08% magnesium and a slight amount of calcium.

The present invention shall be described with reference to the following examples that merely illustrate the additives that may be used in the second step of the present invention.

EXAMPLE 1

All percentages expressed in this specification, including those in the tables and drawings are in weight percent as is in accordance with custom and usage in the metallurgy arts, unless otherwise specified.

First of all, the chemical compositions of calcium-silicon series iron alloys mixed in were as follows:

Ca-Si.—32.3% Ca and 2.6% Fe, the balance being Si,
Ca-R-Si.—24.0% Ca, 15.2% R and 8.7% Fe, the balance being Si,
Ca-Mn-Si.—18.2% Ca and 15.8% Mn, the balance being Si,
Ca-Fe-Si.—2.7% Ca and 18.0% Fe, the balance being Si.

Examples of mixtures of those calcium-silicon series alloy powders with salts of fluorides of RF_3, MgF_2, CaF_2 and $NaRF_4$ were as follows:

No. I.—Mixture of 80% Ca-Si alloy powder and 20% RF_3,
No. II.—Mixture of 80% Ca-R-Si alloy powder and 20% MgF_2,
No. III.—Mixture of 70% Ca-Mn-Si alloy powder, 15% CaF_2 and 15% MgF_2,
No. IV.—Mixture of 60% total of Ca-Fe-Si and Ca-Si, and 40% $NaCeF_4$.

The products obtained by using the additives of Nos. I, II, III and IV above were compared with a spherical graphite cast iron obtained by a known process.

That is to say, the results of Y-type test pieces (B_1, B_2, B_3 and B_4) of the spherical graphite cast iron obtained by the process of the present invention were compared with the results of Y-type test pieces (A_1, A_2, A_3 and A_4) of the spherical graphite cast iron obtained by the known process. First of all, when high quality cast iron and steel scraps were mixed together in a small electric-arc furnace having a melting capacity of 50 kg., the temperature of the obtained molten cast iron was 1550 to 1600° C. and its chemical composition was of 3.58% C, 1.61% Si, 0.42% Mn, 0.63% P, and 0.026% S.

5 kg. of this molten cast iron were put into a ladle. 2, 1.7, 1.4 and 1.1% of a silicon-magnesium alloy (containing 15% mg.) were respectively added to the molten cast iron. Further, a small amount of an ordinary ferrosilicon alloy (of 8.5% Fe, 89.2% Si and 0.30 Ca) was inoculated into the molten cast iron. Within 10 minutes after the molten cast iron was treated with the magnesium alloy, it was cast into respective Y-type test pieces.

These were designated test pieces A_1, A_2, A_3 and A_4 of the spherical graphite cast iron obtained by the known producing process and their analysis values are as shown in Table 1.

On the other hand, in the process of the present invention, the magnesium alloy added in the first step was somewhat decreased and small amounts of the additives Nos. I–IV were added in the second step. The thus obtained Y-type test pieces B_1, B_2, B_3 and B_4 were treated in the second step and were then cast within 10 minutes in the same manner as in the above mentioned A_1, A_2, A_3 and A_4.

Those Y-type test pieces A_1, A_2, A_3 and A_4 by the known process and B_1, B_2, B_3 and B_4 by the present invention were cut in the middle. Sulphur prints of the respective cross-sections were taken.

It has been already described that, in the molten cast iron as treated with magnesium in the known process, MgS is suspended and will not float up to become a dross

within a short time. Now it can be acutally understood from this comparison.

The sulphur print was made by dipping a photographic sensitized paper in a solution of 5% H_2SO_4 and statically placing the ground Y-type test piece thereon for 1 minute. Therefore, as represented by the reaction formulas

$$MgS+H_2SO_4=H_2S+MgSO_4$$

and

$$H_2S+2AgBr=Ag_2S+2HBr$$

the part in which MgS was present appeared as a brown stain of AgS in the photograph.

The presence of MgS is distributed in the whole of each of the test pieces A_1, A_2, A_3 and A_4 by the known process by the above description.

On the other hand, the test pieces B_1, B_2, B_3 and B_4 are by the process of the present invention and it is well seen that the presence of MgS is concentrated only in the upper layer part of the Y-type cast piece.

In other words, when the process of the present invention was applied, MgS floated up to become a dross within a very short time and therefore the amount of dross remaining in the casting was very small.

The kinds and amounts of the additives, the compositions of chemical analysis samples taken in the positions of the middle heights of the Y-type test pieces and the results of sulphur prints of the cross-sections of the Y-type test pieces respectively in the known process and the process of the present invention are shown in Table 1.

TABLE 1

Number	Si-Mg, percent	Secondary treatment in percent	Inoculated Fe-Si in percent	Percent C	Percent S	Percent Mg	Distribution of MgS in the Y-type piece
Known process:							
A_1	2.0	----------	0.4	3.5	0.014	0.056	MgS was present in the whole and specifically much in the upper half.
A_2	1.7	----------	0.6	3.5	0.015	0.044	
A_3	1.4	----------	0.8	3.4	0.016	0.039	
A_4	1.1	----------	1.0	3.5	0.016	0.024	
Process of the present invention:							
B_1	1.5	No. I,* 0.5	----------	3.3	0.010	0.045	MgS was present only in the uppermost part.
B_2	1.0	No. II,* 0.8	0.3	3.4	0.011	0.042	
B_3	0.8	No. III,* 1.0	----------	3.2	0.013	0.033	
B_4	0.8	No. IV,* 1.2	0.5	3.3	0.015	0.019	

*Nos. I, II, III, and IV are the above-mentioned treating agents.

The results of tension tests of Japanese Industrial Standard No. 4 test pieces (50 mm. long and 14 mm. in diameter) cut and made of the lowest parts of the Y-type test pieces, the Brinell hardnesses in the bundle parts and the shapes of graphite in the structural tests were as shown in Table 2. It is seen in the table that the rate of elongation was much higher in the test pieces B by the process of the present invention than in the test pieces A by the known process.

TABLE 2

Number	Tensile strength, kg./mm.²	Rate of elongation in percent	Brinell hardness	Shape of graphite
Known process:				
A_1	58.2	3.5	241	Spherical.
A_2	56.5	3.8	235	Do.
A_3	54.2	3.0	229	Do.
A_4	42.0	1.5	170	Spherical and fragmental.
Process of the present invention:				
B_1	55.0	8.3	212	Spherical.
B_2	55.3	7.6	192	Do.
B_3	51.5	8.5	187	Do.
B_4	50.8	4.2	187	Do.

EXAMPLE 2

This example is to compare a roll made of a spherical graphite cast iron obtained by the process of the present invention with a roll made of a spherical graphite cast iron obtained by the known process in the treatment of a molten cast iron obtained in an acid cupola of a capacity of 3 tons.

The mixture used in the cupola was of 40% ductile cast iron, 30% scrap steel and 30% return cast iron. The chemical composition of the molten cast iron obtained by melting it by using 15% coke and 4% limestone was of 3.4% C, 1.0% Si, 0.45% Mn, 0.058% P and 0.06% S.

This molten cast iron was put into a ladle of a capacity of 1 ton and, according to a known process, 2% of a silicon-magnesium alloy (contaning 20% Mg) was added to it with a help of a phosphorizer, the dross was removed, further 0.5% of a ferrosilicon alloy (containing 75% Si) was added and the molten cast iron was cast to be a roll (300 mm. in diameter and 600 mm. long) by vertical casting. In such case, it took 12 minutes from the treatment with magnesium to the casting.

Then, 1% of a silicon-magnesium alloy (containing 20% Mg) was added in the same manner as in the above, the dross was removed, 1% of the above mentioned treating agent No. II was added in the next second step, the mixture was stirred, further 0.20% of a ferrosilicon alloy was inoculated and the molten cast iron was cast during a period of 14 minutes.

The difference between the additives and the analyses of the castings in both producing processes were as in the following Table 3.

TABLE 3

Producing process	Si-Mg, percent	Second step	Inoculation in percent	C	Si	Mn	P	S	Mg
Known process	2	----------	Fe-Si, 0.5	3.3	2.1	0.44	0.056	0.018	0.060
Process of the present invention.	1	No. II,* 1%	Fe-Si, 0.2	3.1	2.2	0.45	0.054	0.013	0.038

*Mixture of 80% Ca-R-Si alloy powder and 20% MgF_2.

Both castings in the above Table 3 were rolls of spherical graphite structures and a sufficient pressure of the molten cast iron was applied to the upper mold in the vertical casting of the roll. However, in the known process, a large amount of dross was present in the neck part of the roll and the product was not good, whereas, in the producing process of the present invention, the dross concentrated in the pressure part of the roll and the product was good.

I claim:

1. A process for producing nodular graphite cast iron which comprises adding a member selected from the group consisting of magnesium and magnesium alloys to molten cast iron containing graphite to produce nodular graphite, and subsequently treating said molten cast iron with an additive comprised of a mixture of at least one member selected from the group consisting of alkali metal fluorides, alkaline earth metal fluorides and rare earth metal fluorides with a reducing agent for said fluorides comprising a Ca-Si alloy, and recovering an excellent nodular graphite cast iron.

2. The method of claim 1 wherein the magnesium alloy in the first stage is selected from the group consisting of Cu-Mg, Ni-Mg, Ni-Mg-Si and Si-Mg.

3. The method of claim 1 in which the said additive is added in an amount of from 0.4–1.5% by weight of the molten iron.

4. The method of claim 1 in which the magnesium alloy is added in a total amount of from 1.5–0.8% by weight of the molten iron, and the said additive is added in an amount of from 0.5–1.2% by weight of molten iron.

5. The method of claim 1 wherein the metal fluoride added in the second step is comprised of a member selected from the group consisting of NaF, CaF_2, MgF_2, CeF_3, LaF_3, YF_3, $NaBF_4$, Na_3AlF_6, $NaRF_4$, $MgNaF_3$, and $MgSiF_6$ wherein R represents rare earth metal.

6. The method of claim 1 wherein the reducing agent is selected from the group consisting of Ca-Si, Ca-La-Si, Ca-Y-Si, Ca-Ce-Si, Ca-Fe-Si, Ca-Mn-Si and Ca-Zr-Si.

7. The method of claim 1 wherein the produced nodular graphite cast iron contains from 0.01 to 0.08 weight percent magnesium and more than a trace amount of calcium.

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