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METHOD OF MANUFACTURING NODULAR GRAPHITE-CAST STEEL
AND -CAST IRON HAVING EXCELLENT CASTABILITY

Filed Jan. 15, 1962

2 Sheets-Sheet 1

Fig-1-

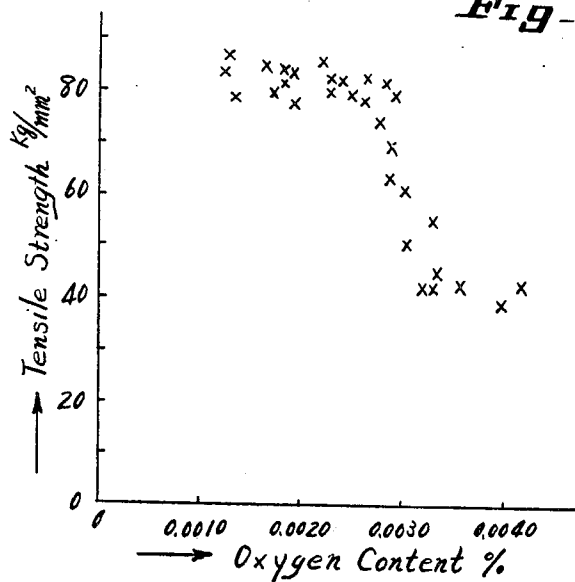
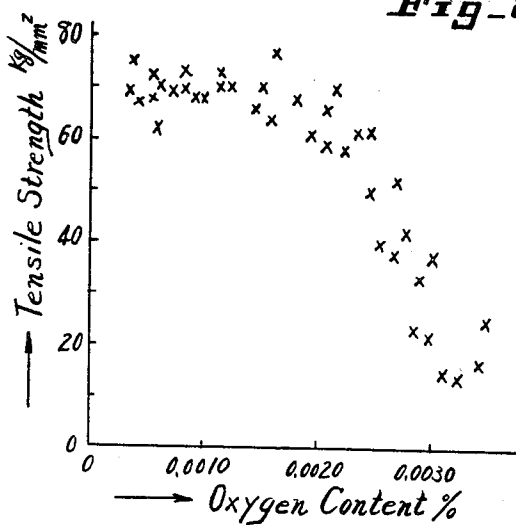


Fig-2-



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2 Sheets-Sheet 2

Fig-3-

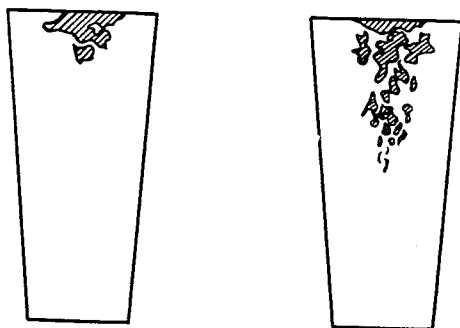
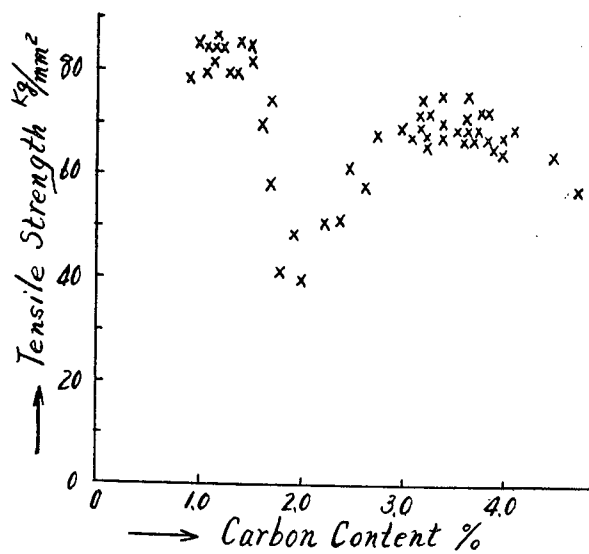


Fig-4-



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3,210,183

METHOD OF MANUFACTURING NODULAR GRAPHITE-CAST STEEL AND -CAST IRON HAVING EXCELLENT CASTABILITY

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The present invention relates to a method of manufacturing the nodular graphite-cast steel or -cast iron having excellent castability and higher tensile strength.

It has heretofore been well known that remarkably tough cast iron called nodular graphite cast iron can be produced from molten iron by adding thereto much amount of metal or its alloys containing so-called graphite spheroidizing elements such as Mg, Ce, Ca, Sr, Li, Na, K, Te and Zn, etc., and that, industrially, said tough cast iron can be produced from the molten metal by adding thereto metallic magnesium or its alloys.

However, since the boiling point of the graphite spheroidizing elements is low in comparison with the temperature of the molten metal, it is not only difficult to effect the above mentioned addition but also unavoidable to cause pin hole, dross and large shrinkage cavities to occur by the addition of the graphite spheroidizing elements, thereby decreasing the yield of the cast products. These casting defects prevent the above mentioned nodular graphite cast iron from being further improved.

The object of the invention is to obviate the above drawback.

The invention is characterized, in a method of manufacturing nodular graphite-cast steel or -cast iron containing 1.0 to 4.5% carbon and occluding substantially rare shrinkage cavity, pin hole and dross, comprising a first step of effecting an intense deoxidation and desulfurization of molten metal such that the content of oxygen and of sulfur of said molten metal becomes less than 0.0030% and 0.020%, respectively, and a second step of adding 0.2 to 7.0% of silicon in either of metallic state or as silicon alloys to the refined molten metal.

As can be seen from the above, in accordance with the invention the nodular graphite-cast iron and -cast steel can be manufactured by adding silicon or its alloys to the molten metal deoxidized and desulfurized without adding any graphite spheroidizing elements.

The invention is based on the recognition that whatever the process may be, it is quite possible to produce the nodular graphite-cast steel and -cast iron from molten iron if the molten iron does satisfy the following three conditions necessary for the graphite spheroidization.

(1) The oxygen content of the molten metal should be less than 0.0030%.

(2) The sulfur content of the molten metal should be less than 0.020%.

(3) The activity of the carbon in the molten metal should be increased to cause direct and instantaneous forced crystallization or deposition of the graphite out of the molten metal.

If the above conditions 1 and 2 are fulfilled the graphite in the molten metal becomes of substantially spheroidizing nature. But, if the condition 3 is not yet satisfied, the residual oxygen or sulfur in the molten metal is locally segregated around the crystallized or the deposited graphite or adsorbed thereto, so that the conditions 1 and 2 are not locally fulfilled. The graphite thus surrounded by the residual oxygen or sulfur is converted into a flaky state and it is quite impossible to obtain a complete nodular graphite structure. Accordingly, in order to obtain the complete nodular graphite structure, it is necessary

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to perform processes defined by the conditions 1 and 2 together with the process defined by the condition 3, that is, it is necessary to perform the process of accelerating the crystallization or deposition of the graphite and of preventing the residual oxygen or sulfur from segregating around the deposited graphite, thereby effecting forced crystallization or deposition of the graphite directly from the molten metal.

If metallic silicon or its alloys are added to the molten metal in such a large amount so as to diffuse unsatisfactory thereto the activity of the carbon in the molten metal is locally increased in the place added and makes it possible to crystallize or deposit the nodular graphite instantaneously and directly from the molten metal. Therefore, if the intense reduction refining is effected to produce the molten metal satisfying the above conditions 1 and 2, the nodular graphite-cast steel or -cast iron can be obtained by mere addition of metallic silicon or silicon alloys without adding any special graphite spheroidizing element.

The inventors have found out that the above mentioned spheroidizing elements serve to deoxidize, desulfurize and to increase the activity of the carbon in the molten metal.

The invention will now be described with reference to the accompanying drawings, in which

FIG. 1 is a plotted diagram showing relation between the oxygen content in percent of the molten nodular graphite cast steel containing 1.0 to 1.5% of carbon less than 0.020% of sulfur and the tensile strength in kg./mm.² of the cast product thereof under the as-cast condition;

FIG. 2 is a plotted diagram showing relation between the oxygen content in percent of the molten nodular graphite cast iron containing 2.8 to 4.5% of carbon less than 0.020% of sulfur and the tensile strength in kg./mm.² of the cast product thereof under the as-cast condition;

FIG. 3 shows sectional views of the cast products of the nodular graphite cast iron produced by the method according to the invention and of that produced by the conventional method in which magnesium is added, the shrinkage cavities formed in the cast products being shown; and

FIG. 4 is a plotted diagram showing relation between the carbon content in percent of the nodular graphite-cast steel and -cast iron and the tensile strength in kg./mm.² of the cast products thereof under the as-cast condition.

As can be seen from FIGS. 1 and 2, if the molten metal contains less than 0.0030% of oxygen and less than 0.020% of sulfur, the graphite becomes spheroidized.

The maximum allowable limit range of the oxygen content necessary for graphite spheroidization of the cast steel or cast iron containing 1.6 to 2.7% of carbon is 0.0025 to 0.0030%.

As above mentioned, it will be understood that the graphite in the cast steel or cast iron containing 1.0 to 4.5% of carbon may be spheroidized if the sulfur and oxygen contents of the cast steel or iron are less than 0.020% and 0.0030%, respectively.

In case of solidify the nodular graphite-cast iron and -cast steel by the conventional methods, there occurs considerable shrinkage cavity. On the contrary, the method according to the invention has the following advantages:

(a) If the molten metal containing less than 0.0030% of oxygen and less than 0.020% of sulfur is spheroidized by the addition of Fe-Si alloy, the lower the amount of the oxygen and sulfur is added, the smaller the total volume of the shrinkage cavity.

(b) If Mg, Ce, Li, K and Zn selected from the graphite spheroidizing elements are added to the molten metal by the conventional manner its cavity shows a remarkable

dendrite form as shown in the right side of FIG. 3. Accordingly, in order to decrease the shrinkage cavity it is necessary to effect an intense deoxidation and desulfurization and in order to avoid the formation of the dendrite cavity which decreases the yield of the castings, the graphite spheroidizing elements should not be added, or even if added, the amount added should be very small. The left side of FIG. 3 shows the shrinkage cavity formed in the nodular graphite cast iron produced by the method according to the invention.

The dross occurs mainly due to the existence of the oxides and sulfides of the above mentioned special elements, so that the amount of the dross to be produced by the method according to the invention is small because by the method the amount of the oxygen and sulfur in the molten metal can extremely be reduced.

Moreover, in the method according to the invention, substantially no deoxidation in which much amount of the graphite spheroidizing element is added in a ladle is effected, so that occurrence of the pin hole is extremely small.

As above mentioned, the invention provides the best method of manufacturing the nodular graphite-cast steel and -cast iron based on the novel idea obtained as the result of the extensive fundamental studies and a number of industrial experiments.

In the embodiment of the method according to the invention, the raw material iron is melted in a Heroult arc furnace, high frequency furnace and low frequency furnace. Then the composition of the molten metal is adjusted and at the same time use is made of lime stone and fluorspar as a slag forming agent and refining is effected with a slag having basicity of more than 1 to reduce the oxygen and sulfur in the molten metal to less than 0.0030% and 0.020%, respectively. The molten iron is then tapped out and transferred to a ladle in which Fe-Si alloy is added in an amount of more than 0.2% of Si. In the present embodiment, use may be made of the acid lining, neutral lining and basic lining as a furnace lining, but the basic lining is most preferable. The reason why the basic lining is preferable is that use of the basic lining makes it easy to accelerate the deoxidation and desulfurization and to effect the refining necessary for the production of the graphite spheroidization if compared with the acid lining and further makes it the shrinkage cavity small.

Since the deoxidation and desulfurization are accelerated in accordance with the basicity of the slag, a higher basicity of the slag is desirable.

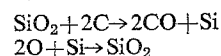
As the raw material, use may be made of an ordinary material such as blast furnace pig iron, steel scrap and electric pig iron, which contains less than 0.3% of Ti, less than 0.05% of As and less than 0.05% of Sn.

It is preferable to carry out the deoxidation and desulfurization by utilizing a method of adding carbon while melting of metal, that is, effecting an intense reduction by using molten metal the total carbon content of which is less than 0.5% that of the cast products to be obtained and adding more than 0.5% of carbon while melting of iron by means of neutral or basic slag.

In order to attain the object of the invention it is essential to make the total carbon content of raw iron material less than 4% and the amount of carbon, while melting added be 0.5 to 4%. Because, if the raw iron material contains more than 4% of carbon, the amount of carbon to be added becomes less than 0.5%, which is too small to remove oxygen included in the raw iron mainly in the form of non-metallic inclusions such as SiO₂, FeO, MnO, Al₂O₃ etc., to less than 0.0030% of oxygen. If the amount of carbon added be more than 4%, the carbon content included in the molten metal becomes excessive and carbon locally segregates in the molten metal to cause casting defects.

The main object of adding carbon to the raw iron material is to remove SiO₂. If the molten iron contains SiO₂ flaky graphite nucleus is formed, so that removal of SiO₂

results in a state adapted for producing nodular graphite, since the nucleus is not formed by the presence of the other impurities such as FeO, MgO, MnO, CaO, etc. Removal of SiO₂ by adding carbon reacts as follows:



CO forms a reducing atmosphere and Si becomes melted in the molten iron to effect deoxidation.

The method of the invention for adding carbon to the melt accelerates the above mentioned reaction.

The inventors found out that under the above circumstances if metallic silicon or alloys thereof is added to the molten iron nodular graphite cast steel and cast iron having an excellent castability and a high tensile strength can easily be manufactured.

A higher melting temperature is desirable since it is thermodynamically proved that the higher the melting temperature is the more it can easily be proceeded to deoxidize the molten metal by adding carbon while melting thereof.

It is preferable in principle to use a melting temperature of more than 1,540° C. In practice, however, it is convenient to use a melting temperature range from 1,400° C. to 1,700° C.

The reason why the amount of Fe-Si alloy to be added is limited to 0.2% to 7.0% of Si is that it is always necessary to add 0.2 to 2.0%, preferably 0.3 to 1.5%, of Si to obtain the nodular graphite cast steel containing less than 1.5% of carbon and to add 0.7 to 5.0% of Si to obtain the nodular graphite cast iron containing more than 2.8% of carbon, and also to add from 5.0 to 7.0% of Si to obtain the refractory nodular graphite cast steel. One of the characteristic features of the method according to the invention is that Fe-Si alloy is added in an amount which is more than that if compared with the conventional methods.

The upper limit of the amount of Si to be added is 7%. Because, if the cast products include in the structure thereof more than 7% of Si the cast products become brittle and could not be used for their practical purposes. Accordingly the limiting range of silicon to be added to the molten metal is 0.2 to 7%, preferably 0.3 to 5%.

As to the Fe-Si alloy added in the ladle, it is desirable to limit the amount of the non-metallic inclusions as SiO₂ to less than 0.15% by analysis chlorinate method for the purpose of obtaining the above result.

The inventors have found out that since the silicon alloys occasionally include much amount of the non-metallic inclusions mainly in the form of SiO₂, the graphite spheroidization is interfered by the existence of more than 0.15% of the non-metallic inclusions.

Accordingly, it is not suitable to use the silicon alloys containing silica sand or much amount of air oxidizing compounds.

In the method according to the invention, it is desirable to use metallic silicon or its alloys containing more than 0.5% of Al. Because, if use is made of metallic silicon or its alloys having a higher content of Al, a part of the oxide in the form of SiO₂ is replaced by that in the form of Al₂O₃, thereby effecting a preferable graphite spheroidization.

As above mentioned if silicon alloys are added to the refined molten metal, crystallization or deposition of the nodular graphite is accelerated to produce complete nodular graphite-cast steel and -cast iron.

The reason why the nodular graphite-cast steel and -cast iron can be produced by mere addition of the Fe-Si alloy without occluding dross, pin hole and shrinkage cavity is that, as above mentioned, the deoxidation and desulfurization are considerably accelerated and that the Fe-Si alloy has a boiling point which is higher than that of the graphite spheroidizing elements such as Mg, Ce, etc., and can react with the molten iron without occurring the above mentioned casting defects.

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In another embodiment of the method according to the invention, the cast iron is melted in a basic cupola furnace and the molten metal is transferred to the high frequency furnace or the low frequency furnace. Subsequently, the nodular graphite cast iron is manufactured in the manner similar to the above embodiment.

The carbon and silicon contents of the cast product obtained by the above mentioned embodiments and the mechanical properties thereof are as follows:

As to the nodular graphite cast steel, the common composition range is 1.0 to 1.5% of carbon and 1.0 to 1.6% of silicon and 0.4 to 0.7% of the graphite carbon is deposited in the cast condition. The tensile strength is 75 to 90 kg./mm.² and the elongation is 1.0 to 4.0%. As to the nodular graphite cast iron, the common composition range is 2.8 to 4.0% of carbon and 2.0 to 3.0% of silicon, which is free from the equivalent amount of carbon.

The mechanical properties of the nodular graphite cast iron is the as-cast condition obtained by the method according to the invention are as follows:

The tensile strength is 60 to 75 kg./mm.² and the elongation is 1.0 to 8.0%.

In carrying out the method of the invention if necessary, in order to improve the deoxidation and desulfurization it is possible to add to the molten metal one or more of alkali metals such as Na, alkaline earth metals such as Ca, Mg, rare earth metals such as Ce and aluminum or alloys of said metals and fluorides, chlorides and carbonate compounds of said metals, which are not required to remain in the melt.

The method according to the invention will now be illustrated by the following examples.

Example 1

The raw material iron having a composition consisting of 40% of blast furnace pig iron, 25% of return scrap and 35% of steel scrap and having 2.3% of total carbon content is melted in a 1 ton basic Heroult arc furnace provided with the dolomite lining and the carbon content of the molten cast iron is adjusted to 3.8% and subsequently use is made of lime stone and fluorspar as a slag forming agent. An intense deoxidation and desulfurization refining is effected to reduce the content of the oxygen and sulfur in the molten cast iron to 0.0014% and 0.006%, respectively. Then, Fe-Mn alloy and Fe-Si alloy necessary for adjusting the composition are added. The molten cast iron thus obtained is tapped out of the furnace at 1,440° C., and transferred to a ladle in which Fe-Si alloy containing 0.035% of non-metallic inclusion as SiO₂ and 74% of Si is added in an amount of 1.7% of Si. The nodular graphite cast iron thus obtained has the following chemical composition and mechanical properties:

C	-----percent---	3.62
Si	-----do-----	2.70
Mn	-----do-----	0.48
P	-----do-----	0.092
S	-----do-----	0.005
Tensile strength	-----kg./mm. ² ---	71.6
Elongation	-----percent---	3.0
Brinell Hardness	-----	252

Example 2

The raw material iron having a composition consisting of 40% of blast furnace pig iron for use in producing common cast products, 30% of return scrap and 30% of steel scrap is melted in a 2 ton acid Heroult arc furnace provided with the SiO₂ lining and the carbon content of the molten cast iron is adjusted to 3.8% and subsequently use is made of lime stone as a slag forming agent. An intense deoxidation and desulfurization refining is effected to reduce the content of oxygen and sulfur of the molten cast iron to 0.0017% and 0.013%, respectively. Then, Fe-Mn alloy and Fe-Si alloy necessary for adjusting composition are added. The molten cast iron thus obtained

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is tapped out of the furnace at 1,450° C. and transformed to a ladle in which Fe-Si alloy containing 0.031% of non-metallic inclusions as SiO₂ and 77% of Si in an amount of 1.9% of Si. The nodular graphite cast iron thus obtained has the following chemical composition and mechanical properties:

C	-----percent---	3.74
Si	-----do-----	2.88
Mn	-----do-----	0.49
P	-----do-----	0.032
S	-----do-----	0.010
Tensile strength	-----kg./mm. ² ---	67.6
Elongation	-----percent---	3.2
Brinell Hardness	-----	246

Example 3

The raw material iron having a composition consisting of 50% of steel scrap, 20% of blast furnace pig iron for use in producing the common cast products, and 30% of return scrap is melted in a 1.5 ton basic cupola and then the molten cast iron is transferred to a 500 kg. low frequency furnace provided with the neutral lining and subsequently use is made of lime stone and fluorspar as a slag forming agent and an intense deoxidation and desulfurization refining is effected to reduce the content of oxygen and sulfur in the molten cast iron to 0.0021% and 0.012%, respectively, and subsequently Fe-Mn alloy and Fe-Si alloy necessary for adjusting the composition are added thereto. The molten cast iron thus obtained is tapped out of the furnace at 1,450° C. and transferred to a ladle in which Fe-Si alloy containing 0.039% of the non-metallic inclusions as SiO₂ and 75% of Si are added in an amount of 2.1% of Si. The nodular graphite cast iron thus obtained has the following chemical composition and mechanical properties:

C	-----percent---	3.69
Si	-----do-----	2.65
Mn	-----do-----	0.55
P	-----do-----	0.042
S	-----do-----	0.012
Tensile strength	-----kg./mm. ² ---	66.6
Elongation	-----percent---	1.8
Brinell Hardness	-----	252

Example 4

The raw material iron having a composition consisting of 30% of blast furnace pig iron, 35% of steel scrap and 35% of return scrap is melted in a 1 ton basic Heroult arc furnace provided with the dolomite lining and the carbon content of the molten cast steel is adjusted to 1.4% and subsequently use is made of lime stone and fluorspar as a slag forming agent. An intense deoxidation and desulfurization refining is effected to reduce the content of oxygen and sulfur in the molten cast steel to 0.0024% and 0.010%, respectively. Then, Fe-Mn alloy and Fe-Si alloy necessary for adjusting the composition are added. The molten cast steel thus obtained is tapped out of the furnace at 1,540° C. and transferred to a ladle in which Fe-Si alloy containing 0.035% of non-metallic inclusions as SiO₂ and 76% of Si are added in an amount of 0.6% of Si. The nodular graphite cast steel thus obtained has the following chemical composition and mechanical properties:

T.C.	-----percent---	1.34
Si	-----do-----	1.26
Mn	-----do-----	0.43
P	-----do-----	0.030
S	-----do-----	0.009
G.C.	-----do-----	0.61
Tensile strength	-----kg./mm. ² ---	82.4
Elongation	-----percent---	2.7
Brinell Hardness	-----	276

As above mentioned, by the method according to the invention nodular graphite-cast steel and -cast iron having

excellent chemical and mechanical properties may be obtained by adding Fe-Si alloy based on the above described definite conditions necessary for graphite spheroidization, the method being entirely novel and basically different from the methods heretofore proposed.

Moreover, the method according to the invention requires no special expensive raw materials and makes it possible to obtain about 30% higher yield of the cast products if compared with the methods heretofore proposed, so that the cast products are remarkably cheap.

As above mentioned, the method according to the invention provides nodular graphite-cast steel and -cast iron having excellent properties at lower cost.

What we claim is:

1. A method of manufacturing nodular graphite-cast steel and -cast iron consisting essentially of 1.0 to 4.5% of carbon and the balance essentially iron and having an excellent castability, which comprises a first step of adding 0.5 to 4% of carbon to the raw iron material containing less than 4% of the total amount of carbon, while

melting to effect strong deoxidation and desulfurization of molten metal such that the oxygen and sulfur contents of said molten metal become less than 0.0030% and 0.020%, respectively, and a second step of adding 0.2 to 7% of a material selected from the group consisting of silicon and silicon alloys containing less than 0.15% of non-metallic inclusions.

2. A method according to claim 1, which comprises adding in said second step 0.2% to 7% of silicon as a silicon alloy consisting essentially of at least 0.5% of aluminum to the molten metal.

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DAVID L. RECK, *Primary Examiner.*