

April 10, 1973

KAZUKI KUSAKA

3,726,670

NODULAR GRAPHITE CAST IRON CONTAINING CALCIUM, RARE EARTH

METALS AND MAGNESIUM AND A METHOD FOR ITS PRODUCTION

Filed Nov. 25, 1970

2 Sheets-Sheet 1

FIG. 1

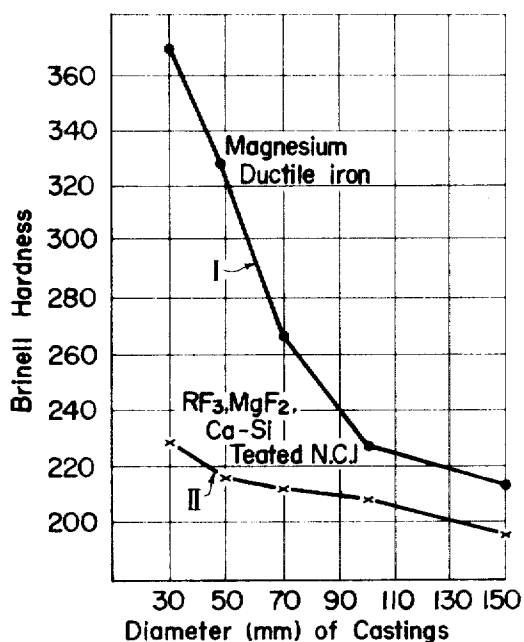
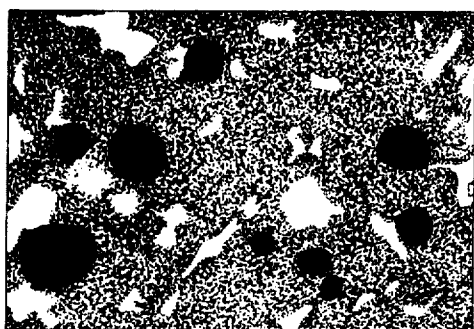


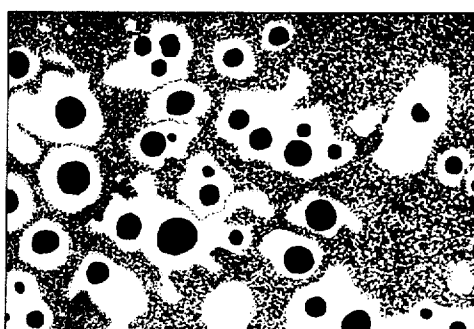
FIG. 2

(a)



x200. Etched 3% nitro
Hard nodular cast iron
331 Brinell

(b)



x200. Etched 3% nitro
RF₃.MgF₂, Ca-Si mixture
treated Nodular iron 217 Brinell

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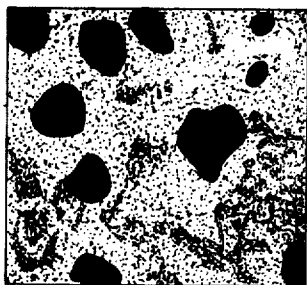
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2 Sheets-Sheet 2

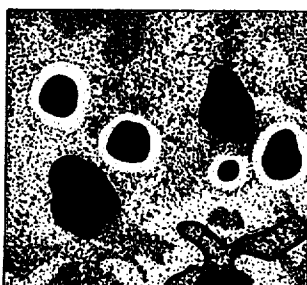
FIG. 3

Micro structures of nital etched D-iron
(Effect of section size)



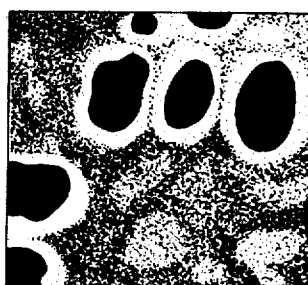
A₁

Regular Mg-Ductile iron
φ of Test piece...70m/m
269 Brinell



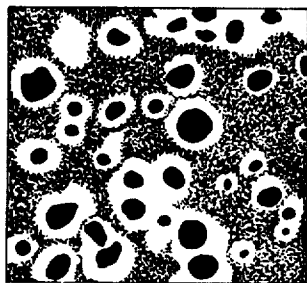
A₂

Regular Mg-Ductile iron
φ of Test piece...100m/m
229 Brinell



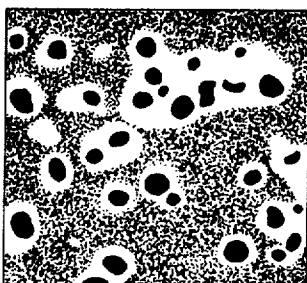
A₃

Regular Mg-Ductile iron
φ of Test piece...150m/m
217 Brinell



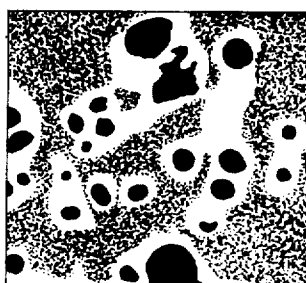
B₁

RF₃, Mg F₂, Ca-Si mixture
Treated Ductile iron
φ of Test piece...70m/m
212 Brinell



B₂

RF₃, MgF₂, Ca-Si mixture
Treated Ductile Iron
φ of Test piece...100m/m
207 Brinell



B₃

RF₃, MgF₂, Ca-Si mixture
Treated Ductile iron
φ of Test piece...150m/m
197 Brinell

1

3,726,670

NODULAR GRAPHITE CAST IRON CONTAINING CALCIUM, RARE EARTH METALS AND MAGNESIUM AND A METHOD FOR ITS PRODUCTION

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Continuation-in-part of application Ser. No. 622,854, Jan. 30, 1967, which is a continuation-in-part of application Ser. No. 186,704, Apr. 11, 1962, both now abandoned. This application Nov. 25, 1970, Ser. No. 92,805 Claims priority, application Japan, July 3, 1961, 36/23,178

Int. Cl. C22c 37/04

U.S. Cl. 75-130 B

4 Claims

ABSTRACT OF THE DISCLOSURE

Nodular graphite cast iron containing carbon in the range of from 3.2 to 4.2% by weight, silicon in the amount of from 1 to 4.5% by weight and in which the percent carbon plus one-third the percent silicon is equal to or greater than 4.0% is provided. The nodular graphite cast iron is characterized by contents of rare earth metal (R) 0.010-0.12% by weight, magnesium (Mg) 0.006-0.040% by weight and calcium (Ca) 0.002-0.025% by weight, and having the content ratio of rare earth metal and magnesium within the range $R/Mg=1.0-4.0$. The nodular graphite cast iron is produced by adding to a molten iron having a sulphur content of less than 0.03% by weight, a nodular graphite cast iron additive consisting essentially of 10 to 30% by weight of magnesium fluoride, from 10 to 30% by weight rare earth metal fluoride, and from 40 to 80% by weight calcium-silicon.

This application is a continuation-in-part of application Ser. No. 622,854, filed Jan. 30, 1967, now abandoned, which in turn is a continuation-in-part of application Ser. No. 186,704, filed Apr. 11, 1962, and now abandoned.

The present invention relates to nodular graphite cast iron containing calcium, rare earth metals, and magnesium as well as to the method for producing the nodular graphite cast iron. The invention further relates to an additive composition useful in the production of such nodular graphite cast iron.

In the first aspect of the present invention there is provided a nodular graphite cast iron characterized in that it contains rare earth metals in the range of from 0.010 to 0.120%, magnesium in the amount of from 0.006 to 0.040% calcium from 0.002 to 0.025% and in having the weight ratio of magnesium and rare earth metal within the range $Mg:R=1.0:1.0$ to 4.0. R represents rare earth metals.

In this aspect of the invention, there is provided a method of making nodular graphite cast iron containing calcium, rare earth metal and magnesium characterized in adding to the cast iron in molten state the addition agent consisting of the mixture of the fluorides of rare earth metal and magnesium and calcium-silicon grains, the finished casting having residual contents in the ranges rare earth metal 0.010-0.120%, magnesium 0.006-0.040%, and calcium 0.002-0.025%, and having the residual content ratio of rare earth metal and magnesium maintained within the range, $Mg:R=1.0:1.0-4.0$ (weight ratio).

It is an object of this aspect of the invention to simplify the method of making nodular graphite cast iron and to obtain nodular graphite castings of excellent quality with minimized shrinkage cavity, drossy scum, mass effect and good castability.

Another object of this aspect of the invention is to provide a method of producing nodular graphite cast iron involving the minimum risk during the operation and

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to obtain an inexpensive nodular graphite cast iron of excellent quality containing rare earth metal magnesium and calcium, by dispensing with the use as additives of the expensive mischmetal of rare earth metals, magnesium alloys, etc., and using as additives the mixture of their respective fluorides (which are less expensive and easier to use), and calcium silicon powder instead.

Still another object of this aspect of the invention is to obtain a nodular graphite cast iron which is excellent in various respects (minimum drossy scum, etc.) to be stated hereinafter, by virtue of the characteristics of the nodular graphite cast iron of the invention which always contains calcium in a slight quantity, rare earth metal elements in an appreciably higher quantity, and magnesium on the contrary in a small quantity.

As reported by Prof. A. Wittmoser et al. (Metal Progress, January 1957, p. 84), it has been known that the residual Mg content of the nodular graphite cast iron made by addition of Mg metal ranged from 0.05% to 0.090%.

Where the pig iron contains elements detrimental to spheroidization of graphite such as titanium (Ti), bismuth (Bi), antimony (Sb), or lead (Pb), it has been well known that to control the harmful effect of these elements a small quantity of cerium (Ce) may be added in addition to making nodular graphite castings and that in such case the residual contents of the casting is 0.04% Mg, or above.

Further, reference may be made to an earlier proposal for a method of making nodular graphite cast iron in which the residual content of Mg is 0.040% and above, and to yet another proposal which defines the main contents of nodular graphite cast iron in the ranges of 0.040-0.50% Mg and 0.004-0.020% La.

As seen from the above, in any of these known processes for making nodular graphite cast iron with only Mg, both Mg and Ce or Mg and La, the residual Mg content is more than 0.040%.

However, castings having a residual Mg content as high as that stated above are found to involve many faults as enumerated below even though spheroidization of the graphite is effected. In consequence unless these problems are solved further development of nodular graphite casts cannot be hoped for.

The common faults inherent in nodular graphite cast iron high in residual Mg content are:

(1) When adding Mg metal and Mg alloy to the molten iron, it is always necessary to take precautions to prevent an explosion and thereby the production process is made more complicated.

(2) A nodular graphite casting having a residual Mg content ranging from 0.04% to 0.09% is subject to a greater change in the structure and hardness depending upon the difference in mass effect.

(3) Because of the higher percentage of the shrinkage cavity formed in the casting, and also because of the extra quantity of molten iron therein required for the dead head, yield of the casting tends to deteriorate adversely affecting the cost of production.

(4) To make a casting having a residual Mg content ranging from 0.04% to 0.09%, it is necessary to add a larger quantity of Mg alloy, but the presence of an excessive Mg content is liable to cause a defective casting because of the drossy slay or scum thereby formed.

To control the above drawbacks, the use of Ce metal instead of Mg has been known in making nodular graphite castings, but Ce is more expensive and moreover the nodular graphite cast iron obtained by using Ce shows a far greater mass effect than that of the Mg nodular graphite cast iron and such casting tend to give various difficulties in service. This is well known in the art.

As a result of studies made for eliminating the aforesaid well-known drawbacks inherent in the Mg or Ce-

addition nodular graphite castings, these problems are solved according to this aspect of the invention by providing, as stated above, the residual contents of these elements in the castings by adding to the molten iron a powdered mixture of the fluorides of rare earth elements and Mg and calcium-silicon.

In the accompanying drawings:

FIG. 1 is a diagram showing the comparative features of the casting made according to the first aspect of this invention and those made in the conventional method. Curve I plots the relative change of the mass and Brinell hardness of a conventional nodular graphite cast iron containing Mg, and curve II shows the relative change in the nodular graphite cast iron according to this first aspect of the invention containing calcium, rare earth metals and Mg, with the diameter (mm.) of the casting shown in the abscissa and Brinell hardness in the ordinate.

FIG. 2(a) shows the microstructure $\times 200$ of an etching of an example of a conventional Mg-nodular graphite cast iron and FIG. 2(b) shows the microstructure $\times 200$ of an etching of a typical example of a nodular graphite cast iron according to this first aspect of the invention.

FIG. 3 is a photo-micrograph comparing the mass effect of a conventional Mg-nodular graphite cast iron and that of the similar cast iron made by this invention, with A₁, A₂ and A₃ showing the conventional products and B₁, B₂ and B₃ the ones made by the first aspect of this invention.

The process according to the first aspect of the invention comprises adding to molten iron in a ladle an addition agent made of a certain mixture in which there are mixed in various proportions the powder of magnesium fluoride (hereinafter expressed MgF₂), rare earth metal fluoride (hereinafter expressed RF₃) and calcium-silicon alloy. As a result of the comparative study made on the behavior of the casting produced by the above method, the following findings have been made.

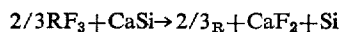
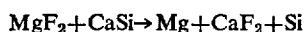
By using this addition agent consisting of MgF₂, RF₃ and Ca—Si, the chemical reaction can proceed even in the molten iron at a temperature from 1,400° C. to 1,500° C. without any explosive hazard but generating only slight smoke and light and the castings thereby obtained are found to contain certain residual contents of Ca, R and Mg.

When magnesium, calcium and rare earth metal are added directly to the molten iron, these metals will burn immediately and in case of magnesium, although it is an easy metal to add, will emit a blue-white blaze during burning which is liable to do harm to the eyes of the operator.

In accordance with this invention, the addition agent is made from a mixture of fluorides of the metals and calcium-silicon powder instead of magnesium and rare earth metal and said addition agent is added to the molten iron before this is charged into the ladle, thus making operation more simple.

Adding to this addition agent can be made by any process, such as injection, dumping or pouring and this process needs no extra care as in the case of the conventional method of making nodular graphite cast iron using an Mg alloy.

These addition agents produce metallic R and Mg by reduction accompanying a weak chemical reaction under the influence of Ca—Si in the molten iron in the temperature from 1,400°–1,500° C. The reactions may be represented as follows:



R and Mg being in very fine particulate form, will disperse extensively in the molten iron and combine with S and O in the molten iron and seem to promote spheroidization of graphite.

The excellent quality nodular graphite casting made by this aspect of the invention which gives the minimum shrinkage cavity, drossy scum, mass effect and good castability, has residual contents of three elements of the casting as follows:

	Percent
Ca -----	0.002–0.025
Mg -----	0.006–0.04
R -----	0.010–0.120

Also the weight ratio between Mg and R is maintained by controlled addition of additive as under:

$$\text{Mg:R} = 1.0.1.0-4.0$$

A method has been proposed of producing nodular graphite cast iron by adding to the molten iron the mixture of only three elements, i.e. RF₃, Ca—Si and CaC₂. But, in the casting produced by this method, the spheroidized structure can be obtained only in very thin castings. In thick castings it is always difficult to obtain spheroidized structure.

It is well known that even when R and Ca contents of the castings are as high as 0.035% and 0.012% respectively, the structure shows appreciable variation depending upon thickness (mass) as seen below:

Structure of casting piece 20-mm. dia.: Pearlite matrix and nodular graphite.

Structure of casting piece 40-mm. dia.: Pearlite matrix and flake and nodular graphite.

In the method of producing nodular graphite cast iron in which only a mixture of the three ingredients RF₃, Ca—Si and CaC₂ is added, the casting obtained will show a high mass effect and therefore will be found to be of less practical value.

In the method of this aspect of the invention in which the addition agent made of a mixture of RF₃, MgF₂ and Ca—Si, all in powder form, is added to the molten iron, the casting obtained will show very little mass effect and it will make an excellent quality nodular graphite casting which is also excellent in other properties as explained later on.

As mentioned above, the number of elements of the nodular graphite cast iron according to the present invention is limited to three, that is, Ca, Mg and R; so are their content ranges and also the content ratio of R/Mg to a range between 1.0 and 0.4.

The reason for and the effect of such limitation are:

(1) The addition of Ca is to improve fluidity of molten iron and also facilitate its nodulization, which constitutes another gist of the present invention than the so prescribed ratio of R/Mg. Generally speaking, nodular graphite cast iron containing Mg and the like, is very low in fluidity when being molten, as compared with the normal type of cast iron, and is nearly the same as cast steel; therefore, the casting of such cast iron is made with great difficulty particularly for making thin parts. In order to avoid this complication, a great quantity of Ca—Si is mixed with the nodulizing agent according to the present invention, which is for the reduction of MgF₂ and RF₃ in the agent, and which is also to have its element Ca remain in the cast iron as much as possible in a range between 0.002 and 0.025%, thus improving the low fluidity of the nodular graphite cast iron as the above-mentioned effect of Ca addition. The reason for prescribing said residual range is that whatever greater addition of Ca would increase with difficulty the residual content beyond the upper limit of 0.025%, and the residual content below the lower limit of 0.002% would hardly facilitate fluidity and nodulization.

Regarding the nodulizing effect of Ca, it is experimentally confirmed that Ca is so effective that nodulization of cast iron of low sulphur content, say, 0.005% can be attained safely with the residual content of 0.020% Ca.

Moreover, the residual content of Ca in the cast iron in a residual range between 0.002 and 0.025% according to the present invention, as mentioned above, improves the

low fluidity of nodular graphite cast iron, from the level of cast steel to that of ordinary cast iron or better.

(2) The reason for prescribing the residual content of Mg in a range between 0.006 and 0.040% is to reduce the drossy scum in the cast iron and the shrinkage cavity to a minimum; and to attain nodulization of cast iron in cooperation with the co-additives of R and Ca, while it is not attainable with the exclusive use of Mg. This range is justified, because a residual content beyond the upper limit of 0.04% would produce drossy scum and a shrinkage cavity on a greater scale in the cast iron, and cause chilling of the cast iron; and because a residual content below the lower limit of 0.006% would hardly facilitate nodulization even with the co-existence of R and Ca.

(3) The reason for prescribing the residual content of R in a range between 0.010 and 0.120% is to attain nodulization of cast iron in cooperation of Mg and Ca. As mentioned above, in spite of its great effectiveness in the nodulization of cast iron, Mg tends to produce drossy scum and shrinkage cavity on a greater scale in the cast iron, and cause chilling of the cast iron. According to the present invention, therefore, the addition of Mg is to be reduced to a minimum, and the lowering of the nodulizing effect due to such reduction is made up with the addition of R and Ca. R is inferior to Mg in nodulizing effect, but it does not produce so much drossy scum and shrinkage cavity as Mg. Ca improves fluidity of cast iron, as mentioned above.

The reason for the residual range of R is prescribed as above is because a residual content beyond the upper limit of 0.120% would cause chilling of the cast iron at great occurrence rate irrespectively of the any content ratio of R/Mg; and because a residual content below the lower limit of 0.010% would not facilitate nodulization of cast iron even at the co-existence of Mg and Ca.

The reason for prescribing the content ratio of R/Mg between 1.0 and 4.0 is to make the residual content of R equal to or much greater than that of Mg, thereby facilitating nodulization, reducing drossy scum and shrinkage cavity, and also preventing chilling of the cast iron. This constitutes another gist of the present invention than the abovementioned additive of Ca for facilitating the fluidity of cast iron. The effect obtainable from the content ratio of R/Mg being set between 1.0 and 4.0 is to prevent the chilling of the cast iron when being cast into products of, say, 3 mm., 10 mm. and 20 mm. in thickness by making the ratio of R/Mg respectively about 1.0, to 1.20 and 3.0.

(4) According to the present invention, the three elements of Mg, R and Ca are added with the residual content of R/Mg being set as mentioned above. This is to obtain nodular graphite cast iron with its graphite fully nodulized, of low tendency to chill, of good fluidity, and with a presence of little drossy scum and shrinkage cavity, thus solving the problems occurring in conventional nodular graphite cast iron containing more than 0.04% Mg, as such the presence of large quantity of dead head metal due to a large amount of drossy scum and shrinkage cavity and the resulting low yields and high production costs of castings.

On the other hand, the use of the nodulizing agent of the present invention consisting of fluorides of Mg and R and great quantities of such Ca—Si alloys are as formulated as $MgF_2 + RF_3 + Ca-Si$, makes it possible to easily retain the above mentioned three elements of Mg, R and Ca in the prescribed content ranges in cast iron by chemical reaction, whereas the conventional additives produce causing strong flash light or big bounces of molten iron, making the method of the present invention easier.

The flux method using the additive of the present invention is to obtain nodular graphite castings with a minimum amount of drossy scum present and shrinkage cavity.

If the addition of Mg, R and Ca, the three elements of the additive according to the present invention, is made

by means of the addition of such alloys as Mg—Si, Mg—R—Si, R—Ca—Si, and misch metal, the following difficulties and disadvantages will occur: Because strong flash light and bounces of molten iron are produced when such alloy additives are injected, a special adding method for the prevention of them is needed; as R is greater than Mg in affinity with oxygen, sulphur, etc., R in the alloy additive is lost through such reactions as deoxidization and desulphurization, prior to the effect of Mg, making it sometimes difficult to attain the prescribed residual content of R, therefore, a stage-by-stage-adding means or apparatus, that is, for adding R alloys into cast iron after the addition of Mg alloys is needed. Further, the addition of the three elements of Mg, R and Ca into cast iron by means of the prior art additives mentioned above, leaves a low residual yield of the respective elements in the cast iron, as compared with the addition by the flux method of the present invention, resulting in the presence of drossy scum in cast iron with no floatation of such scum and the production of a shrinkage cavity on a large scale.

As mentioned above, the addition according to the present invention is carried out by using the additive containing such flux as MgF_2 and RF_3 that is prepared specially for this purpose, and also Ca—Si alloy for the reduction of the flux. This method is very effective in solving problems to occur with the use of the abovementioned alloy additives.

(5) The gist of the present invention lies in that the three elements of Mg, R and Ca are retained easily and efficiently respectively in the above prescribed residual contents in cast iron, which is shown by the effect obtained in actual operations conducted as preferred embodiments, as follows:

(a) Molten iron: C: 3.2–4.2%; S: 0.03% max.; P: 0.01–0.10%; Si: 0.5–2.5%; Mn: 0.03–0.60%.

(b) Additive: MgF_2 : 20%; RF_3 : 10%; Ca—Si: 70%.

Additive (b) was added in a range between 0.5 and 2.5% according to the sulphur content of the molten iron (a), as follows:

S content of molten iron, percent:	Addition of additive, percent
0.005	0.5
0.010	0.8
0.015	1.2
0.020	1.6
0.025	2.0
0.030	2.5

As a result of the above addition, the residual contents of Mg, R and Ca were respectively about 0.024%, 0.035% and 0.01%. The nodulization rate of cast iron was 90%. Drossy scum and shrinkage cavity were present very little. As the R/Mg ratio of the molten iron obtained by means of the above treated was about 1.15, a casting having as this as about 3 mm. of thickness of its thinnest part, could be produced without chilling. Also, because of a Ca content of 0.010% of said molten iron, such thinnest part of as thin as about 3 mm. of said casting was produced very precisely as prescribed.

The constituents of the cast iron to which the present invention is applicable, are carbon in the range of from 3.2% to 4.2% by weight, silicon in the amount of from 1.0% to 4.5% by weight, and in which the percent carbon plus one-third the percent silicon is equal to or greater than 4.0% ($C\% - \frac{1}{3} Si\% \geq 4.0\%$). This means that the thus-produced nodular graphite cast iron is an eutectic or hypereutectic cast iron.

The difference in mass effect between the nodular graphite cast iron produced by the method of this aspect of the invention and the nodular graphite cast iron made by the conventional Mg metal addition method will be seen in Table I, II and also in the attached FIG. 1.

The pig iron to which graphite spheroidizing treatment was applied in this comparative test was made by melting

70% ductile pig iron, 30% steel scraps with fine quality coke and limestone.

Upon pouring the molten iron at the tapping temperature of about 1,520° C. into the ladle, 300 kg. in capacity, Na₂CO₃ is added and agitation is given to lower the S content in the molten iron down to 0.04–0.06%. Immediately after removal of the scum formed by reaction of the molten iron with the soda ash, the graphite spheroidizing treatments, by the conventional Mg-addition method and the method of this invention, were made.

The two types of the molten iron which had undergone the spheroidizing treatment by the conventional method and the method of this aspect of the invention were moulded, using CO₂ process sand moulds, into five different sized column typed castings, of diameters, 30 mm., 50 mm., 70 mm., 100 mm., and 150 mm., and later analytical tests were made on each of them.

Then, the column-typed castings were cut into halves at the middle of their height and their chemical compositions were analyzed and their peripheral brinell hardness as well as their microstructure were examined. The results are shown in the Tables I and II as follows:

TABLE I.—CHEMICAL COMPOSITION OF NODULAR GRAPHITE CASTINGS

Type of specimen	Component (percent)							
	C	Si	Mn	P	S	Mg	R	Ca
Conventional Mg addition casting.....	3.6	1.8	0.56	0.058	0.008	0.062	0.038	0.007
Casting made by method of this invention.....	3.6	2.2	0.54	0.062	0.012	0.022	0.038	0.007

TABLE II.—BRINELL HARDNESS AND MASS-EFFECT OF NODULAR GRAPHITE CASTINGS

Diameter in mm.	Type of specimen			
	Conventional type Mg alloy addition casting		Casting made by method of this invention	
	Brinell Hardness	Constitution	Brinell Hardness	Constitution
30.....	370	NG+P+Cm	229	NG+F+P
50.....	331	NG+P+Cm	217	NG+F+P
70.....	269	NG+P+Cm	212	NG+F+P
100.....	229	NG+F+P	207	NG+F+P
150.....	617	NG+F+P	197	NG+F+P+MG

NOTE.—NG=Nodular graphite; P=Pearlite; F=Ferrite; Cm=Cementite; MG=Massive graphite.

As seen in the above table, the nodular graphite casting made by the conventional Mg alloy addition of diameter ranging from 30 mm. to 70 mm. will contain free cementite and be much higher in Brinell hardness while more massive casting of diameter ranging from 100 mm. to 150 mm. will have a soft structure with ferrite deposited instead of free cementite. In other words, nodular graphite castings produced by the convention Mg alloy addition method vary greatly in hardness and structure depending upon the difference in the mass effect as is well known by the foundry engineers; (see C. K. Dono, p. 97, Iron Age, Feb. 24, 1949).

The nodular graphite castings of this first aspect of the present invention, though low in residual Mg contents, will make castings of softer structure rich in well spheroidized graphite and ferrite areas, and will be subject to considerably less change by the mass effect, as seen in Table II.

The difference between the two types of nodular graphite castings will be more clearly understood by referring to FIG. 1 in which curve I shows the conventional nodular graphite casting and its hardness-diameter relation and curve II shows the new nodular graphite casting made by this invention and said relation.

The structure of the two types of castings, each 50 mm. in diameter, as given in Table II are illustrated in FIG. 2 in which the photograph *a* shows the microstructure of the conventional casting and the photograph *b* shows that

of the casting of this invention. From these photographs it will be clearly understood that the conventional casting by Mg addition method is in its structure NG+P+Cm and the casting made by the method of this invention is NG+F+P in structure.

Table III shows the results of tests on specimen bars, as cast and after annealing, which were prepared by casting the said two types of molten iron in Y-shaped specimen moulds. These results clearly indicate the difference in the mechanical properties of the two types of casting.

TABLE III.—MECHANICAL PROPERTIES OF NODULAR GRAPHITE CASTINGS

Test	Tensile strength, kg./mm. ²	Elongation	Hardness (Brinell)
Type of specimen:			
Conventional Mg alloy addition casting:			
As cast.....	64.9	1.0	262
Annealed.....	53.6	16.5	179
Casting made by this invention:			
As cast.....	67.7	6.0	212
Annealed.....	48.6	23.8	156

As seen in the above table, the results of both tests,

made as cast and after annealing, show that the casting made by this invention is much lower in hardness and higher in elongation.

The foregoing facts clearly indicate that the nodular graphite cast iron according to the present invention has excellent strength, hardness and elongation and low mass effect. This is considered to be due to the presence of Ca, Mg and R in the proper percentage as seen in the residual contents of the cast iron made by the method of this invention.

Tables IV and V show the results of tests made on the second groups of examples of this invention.

These show some examples of compositions of addition agents as well as the relation between shrinkage cavity of the castings and their residual contents of Ca, Mg and R.

Although, as stated before, the addition agent used in making nodular graphite casting of this invention is the mixture, in certain proportion, of the three ingredients, RF₃, MgF₂ and Ca—Si powder, this example also discloses some subsidiary agents which may be used in addition to the main components, RF₃, MgF₂ and Ca—Si within the scope of the first aspect of this invention.

Six column-shaped specimen castings were prepared by moulding in a sand mould, using molten iron to which addition agents of five different compositions were added. Those six specimen castings show residual contents and shrinkage cavity as in Tables IV and V.

TABLE IV.—COMPOSITION OF ADDITION AGENTS

		Component					
		RF ₃	MgF ₂	CaF ₂ *	Ca-Si	Mg-Si*	Fe-Si*
Control addition.....	I	5	28	-----	67	-----	-----
	II	13	17	-----	65	5	-----
	III	16	14	-----	70	-----	-----
Addition agents according to this invention....	IV	20	10	-----	60	-----	10
	V	10	10	5	60	-----	5

NOTES:

1. Marks (*) indicate optional addition agents.
2. Analysis of the compounds and alloy iron contained in the addition agents used: Ca-Si=(Ca 31.5%, Fe 7.5, Si balance); Mg-Si=(Mg 20.5%, Si, Fe balance); Fe-Si=(Si 77%, balance mostly Fe); CaF₂=(CaF₂ 98%, balance mostly SiO₂); CaC₂=(CaC₂ 80%, balance mostly CaO).
3. The addition agent No. I is a control specimen of a composition in range other than that of this invention.

The pig iron used in the second example was melted in an acid lined cupola combining ductile pig iron 80% and steel scraps 20% and adding for fuel coke 16% and CaC₂ lump 2%, and the molten iron was poured into a ladle 100 kg. in capacity. The tapping temperature was between 1,500° C. and 1,530° C. and the percentage of S in the molten iron ranged from 0.045% to 0.058%.

Each of the addition agents as enumerated in Table IV was added to the molten iron contained in the ladle by injection using N₂ gas and the quantity of the agent added was 2% for the molten iron. After the temperature of the molten iron went down to about 1,400° C., the molten metal was cast in a sand mould and thus a column-shaped specimen casting was made. In this way, all specimen castings, in column shape, 50 mm. in diameter and 250 mm. in height, were prepared by casting with addition of each of the addition agents as given in Table IV.

These specimen castings were cut lengthwise in the center and shrinkage cavities were measured.

In the above test, the castings made by addition of addition agents of different compositions, No. I-V in the Table IV, were all found to contain graphite in nodular form but to show considerable variation in the depth of the shrinkage cavity.

As clearly seen in Table V, the castings lower in R/Mg

those containing, in addition to the above three, small quantities of one or more than two of supplementary components such as CaF₂, Mg-Si, Fe-Si and CaC₂ are used. Within the scope of this invention small amounts of CaF₂, NaF and KF may be used as partial substitutes for RF₃ and MgF₂, the main components of the addition agents of this invention; an alloy similar to Ca-Si alloy (such as Mg-Si, Fe-Si, R-Mg-Si [rare-earth bearing Mg-Si alloy]) may partially replace Ca-Si. A small amount of CaC₂ may also be used as partial substitute for Ca-Si.

The above principal components of the addition agents according to this invention are employed in the following weight percentage ranges:

MgF₂ 10-30%; RF₃ 10-30%; CaSi 40-80%

With regard to the rare earth metals hereinbefore expressed as R or RF₃, further details must be given below.

The rare earth metal oxides separated from monazite sand, etc., consist of about 50% Ce₂O₃, 25% La₂O₃, and 25% other rare earth expressed by Dy₂O₃.

In consequence, it is well known that RCl₃ made of these rare earth metal oxides, and the mischmetal made of RF₃ or their salts are of composition generally in the proportions 50% Ce, 25% La, and 25% Dy.

TABLE V.—CHEMICAL COMPOSITION AND DEPTH OF SHRINKAGE CAVITY OF NODULAR GRAPHITE CASTINGS

Type of addition agents used		Components					Depth of shrinkage cavity in mm.
		C	Si	Ca	R	Mg	
Control specimen casting.....	I*	3.4	2.6	0.006	0.011	0.052	0.21
	II	3.5	2.6	0.013	0.041	0.028	1.46
Castings according to this invention.....	III	3.3	2.9	0.015	0.042	0.025	1.69
	IV	3.4	2.6	0.010	0.051	0.013	3.93
	V	3.2	3.2	0.016	0.022	0.009	2.44

*Optional addition agents.

ratio give deeper shrinkage cavity, and conversely those higher in R/Mg ratio give less shrinkage cavity.

Referring to Table V, the casting in which addition agent No. I was used is excluded from this invention because the residual contents are not as specified, even the residual Mg being slightly in excess of the residual Mg content of the castings of this invention. The castings in which addition agents, Nos. II-V, are used, are included within the range of the nodular graphite casting according to this aspect of the invention because they contain a small quantity of Ca, their Mg/R ratios are within the range of 1.0/1.0-4.0, and moreover the Mg contents are below 0.04%.

The nodular graphite castings of this aspect of the invention are specified to contain a small quantity of Ca, up to 0.04% of Mg and also R in the ratio in the range of Mg/R=1.0/1.0-4.0, because by so adjusting these components nodular graphite castings of excellent quality which give minimized mass effect and drossy scum, the least shrinkage cavity and the good castability are obtained.

In the second example of this invention, the results of experiments are shown in which the addition agents containing as main components RF₃, MgF₂ and Ca-Si and

Because these Ce, La, Dy (Praseodymium+Neodymium+Promethium+Samarium), etc., are elements difficult to separate from one another, it has been the usual practice to employ them as they are without separating.

In the addition agents used in this invention, RF₃ composed of 50% Ce, 25% La and 25% Dy, the fluorides obtained by treating rare earth metal oxides, is used. Further, in treating rare metal oxides with acid and alkali, a precipitate may be made by carefully controlling the pH value of the solution in which two groups of fluorides can be separated with relative ease as follows:

(1) Ce-rich group (Ce 60-84%, other rare earth metals balance).

(2) La-rich group (La and Dy 6-084%, Ce balance). Now, in this aspect of the invention these two groups of RF₃ are prepared and MgF₂ and Ca-Si are both mixed with each of them so that two types of addition agent are prepared. By adding these addition agents to the molten iron, excellent quality nodular graphite castings are obtained, all of them showing alike good results in shrinkage cavity and mass effect.

However, when examined with a microscope, the casting in which the Ce-enriched addition agent was used has less ferrite area and the casting in which La-enriched RF₃

addition agent was used showed larger ferrite area and this causes the difference in the chemical composition and the results of mechanical test as shown in Table VI.

TABLE VI.—CHEMICAL COMPOSITION AND RESULT OF MECHANICAL TESTS ON NODULAR GRAPHITE CAST IRON

Type of casting	Components, percent					Tensile str., kg./mm.	Elongation, percent	BNH
	C	Si	R	Mg	Ca			
(1) Ce-enriched addition agent used.....	3.4	2.8	0.038	0.038	0.009	5.86	5.4	235
(2) La-enriched addition agent used.....	3.3	2.9	0.029	0.028	0.010	53.0	14.5	192

No difference is seen in spheroidizing of graphite between the casting in which a Ce-enriched RF_3 addition agent was used and that in which an La-enriched RF_3 addition agent was used, but they show a considerable difference in ferrite deposition area. When an La-enriched RF_3 addition agent was used, a nodular graphite casting, high in elongation as cast can be obtained, because La promotes ferrite deposition.

However, as long as the residual contents remain within the range as defined by this invention, namely

$$Mg:R=1:1.0-4.0$$

an excellent quality nodular graphite castings giving least shrinkage cavity and mass effect can be obtained.

Further, a third group of examples is as follows. The various examples hereinbefore given refer to unalloyed nodular graphite cast irons. Now, reference will be made to the case where, in addition to ordinary components of cast iron, one or more of such components as Cu, Ni, Cr, and Mo are added to the cast iron and further to cases where the assumption that carbon

$$\text{equivalent} = C\% + \frac{1}{3}Si\%$$

is taken into account in the percentages of C and Si in the nodular graphite casting.

The results of chemical analysis and mechanical tests in these examples are shown in Table VII. The mechanical properties, it is seen, are subject to some variation according to the element added.

TABLE VII.—CHEMICAL COMPOSITION AND MECHANICAL TEST RESULTS OF SPECIAL NODULAR GRAPHITE CASTINGS [Ca, R and Mg content is the same in case]

Percent							Carbon equiv. kg./mm. ²	Tensile str., kg./mm. ²	Elongation	BHN
C	Si	Mn	Ou	Ni	Cr	Mo				
3.5	3.3	0.28	0.02	-----	-----	-----	4.60	56.2	10.2	197
3.6	1.4	0.45	0.01	-----	-----	-----	4.10	59.5	6.0	217
3.4	2.5	0.62	0.73	-----	-----	-----	4.23	62.4	4.3	235
3.6	2.6	0.58	-----	1.5	-----	-----	4.47	70.0	3.5	217
3.7	2.2	1.20	-----	-----	0.30	0.25	4.40	62.5	1.0	255

All these examples of this aspect of the invention are cases where addition agents made of the mixture of RF_3 , MgF_2 and Ca—Si are added to the molten iron. Even if carbon equivalent differs somewhat or even when a small quantity of addition elements such as Ni, Cr, Mo, or Cu is added to the casting, the method of this invention can make nodular graphite castings which all give low shrinkage cavity and mass effect.

As shown in Table VIII, it is further confirmed that the castings of this aspect of the invention can make excellent castings having good nodular graphite not only with grey cast iron but also with chilled castings.

TABLE VIII.—CHEMICAL COMPOSITION AND RESULTS OF MECHANICAL TESTS OF NODULAR GRAPHITE CHILLED CASTINGS

Type	C	Si	Mn	R	Mg	Ca	R/Mg ratio	Shore Hardness	Chill depth, mm.
(1).....	3.4	2.25	0.56	0.018	0.066	0.007	0.27	49-53	28
(2).....	3.3	2.23	0.56	0.094	0.027	0.008	3.5	56-58	35

Casting Type (1) in the above table in which the addition agent made of MgF_2 -enriched mixture is added to a molten iron and casting Type (2) in which the addition

agent consisting of RF_3 -enriched mixture was added to another batch of the same molten iron, were made by casting in a mould with cooling metal placed at the

bottom to give plate-shaped chilled castings and the properties of the two were compared.

Casting Type (1) is excluded from the casting according to this aspect of the invention because this type of casting is high in Mg residual content and low in R content and R/Mg ratio is 0.27 while casting type (2) is included in the scope of the invention.

When these two types of casting are compared, the one of greater R/Mg ratio is found to show a greater depth of chill and also greater hardness. These results were unexpected but repeated experiments showed the same results and the characteristics of the casting of this aspect of the invention can thus be seen also in chilled castings.

In brief, it was found that according to the method of this invention using the addition agent consisting of RF_3 , MgF_2 and Ca—Si powder in a proper proportion an excellent nodular graphite casting having minimized shrinkage cavity was obtainable even with grey cast iron, alloy cast iron or with white pig iron casting and even when the carbon equivalent reaches around 4.3. Owing to the aforesaid reason, when the addition agent according to this aspect of the invention is employed, it becomes unnecessary to select a ductile pig iron for the pig iron and grey pig iron, alloy pig iron and also white pig iron can be used with good results.

With reference to the ductile pig iron to be used for making nodular graphite cast iron, the chemical components of the commercially available grade are generally guaranteed C min. 3.8%, Si max. 2.20%, Mn max. 0.50%, P max. 0.100%, S max. 0.035%, and Cr max.

0.03%, Ti max. 0.07%. Ductile pig iron of this grade as well as those containing components other than those stated above can be proceed with the same good effect by the method of this invention.

Lastly, with regard to the economic aspect of the manufacture of the castings of this invention, this method will appear more uneconomic because the castings according to this invention contain a higher percentage of the more expensive R and a lower percentage of Mg compared with conventional nodular graphite castings in which Mg alloy is used and their Mg residual contents range from 0.04 to 0.09%.

However, it should be pointed out that in the manufacturing method according to this aspect of the invention R is added by using, instead of expensive alloys

such as misch metal and Lance-lamp, the much less expensive fluoride RF, which reacts with Ca—Si and gives R and therefore the presence in the casting of R in relating high percentage does not adversely affect the production cost of the casting.

Compared with the conventional nodular graphite castings in which more Mg alloy is used, the castings of this invention give much improved yield as shown in Table IX and consequently the production cost of nodular graphite casting is reduced because they give no deep shrinkage cavity and thereby minimize the wastage in dead head metal and the like.

TABLE IX

Yield of nodular graphite castings

Type:	Yield, percent
Conventional casting containing Mg	53-60
New casting made by the method of this invention	64-70

The process of adding to the molten iron the addition agent consisting of the mixture of the powder of RF₃ and Ca—Si in a certain proportion is easy and involves no danger of explosion.

All of the castings obtained according to this aspect, whether they are grey cast iron, alloy cast iron, white pig iron or cast iron of common composition, have a good nodular graphite and they are excellent quality castings with minimized shrinkage cavity, drossy scum, mass effect and good castability.

What is claimed is:

1. A method for producing nodular graphite cast iron consisting essentially of carbon in the range of 3.2 to 4.3% by weight, silicon in the range of 1.0 to 4.5% by weight, calcium, a rare earth metal, magnesium, and the balance being iron, wherein the percentage of carbon plus one-third the percentage of silicon is equal to or greater than 4.0% by weight of the cast iron, comprising using an additive in powdered form consisting essentially of a mixture of 10-30% by weight of the fluorides of a rare earth metal, 10-30% by weight of magnesium fluoride, and 40-80% by weight of calcium-silicon by adding said mixture together in a single stage to the cast iron in the molten state, in such amounts that the finished nodular graphite cast iron has a residual content of the calcium, rare earth metal, and magnesium in the ranges of:

calcium—0.002 to 0.025%;
rare earth metal—0.010 to 0.12%, and
magnesium—0.006 to 0.04%

and has a residual content of rare earth metal to magnesium within the weight ratio range of Mg:R or 1.0:1.0 to 4.0, whereby the ratio of the Mg:R within the aforesaid range increases in proportion to the thickness of the castings produced from said cast iron.

2. The method according to claim 1 wherein the ratio of Mg to R varies in such a manner that when the thickness of the casting (T) is 3 mm., the ratio of R/Mg is 1.0; when T=20 mm., R/Mg is 3.0 and when T is greater than 20, R/Mg is between 3 and 4.

3. A nodular graphite cast iron consisting essentially of carbon in the range of from 3.2 to 4.3% by weight, silicon in the range of from 1.0 to 4.5% by weight, wherein silicon is equal to or greater than 4.0% by weight of the cast iron, calcium in the range of 0.002 to 0.025%, magnesium in the range of 0.006 to 0.040%, and a rare earth metal in the range of 0.010 to 0.12%, and the weight ratio of Mg:R being within the range of 1.0:1.0 to 4.0, whereby the ratio of the Mg:R within the aforesaid range increases in proportion to the thickness of the castings produced from said cast iron, said nodular graphite cast iron possessing a soft structure, high elongation characteristics, low mass effect and high tensile strength as a result of the magnesium, rare earth metal and calcium being present in the proportions claimed.

4. A nodular graphite cast iron according to claim 3 wherein the ratio of Mg to R varies in such a manner that when the thickness of the casting (T) is 3 mm., the ratio of R/Mg is 1.0; when T=20 mm., R/Mg is 3.0 and when T is greater than 20, R/Mg is between 3 and 4.

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75-123 CB