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METHOD OF MAKING NODULAR CAST IRON

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This invention relates to the production of cast iron with graphite in the nodular form and is based on the discovery that fluorides of rare earth metals, fluorides of alkali metals and fluorides of alkaline earth metals may be used to promote effective solution of alkaline earth, alkali metals, and carbides and silicides of these metals.

This invention has for its object the controlled production of cast iron with nodular graphite by a selection of carbide metastabilizing agents and fluoride carriers in relation to the characteristics of the base metal, the section of the casting to be made and the physical properties desired.

Another object of this invention is the production of nodular cast iron having pre-selected "as cast" elongations of a higher order than was hitherto possible on a commercial scale.

Another object of this invention is an improved nodular cast iron produced by a positive control procedure using carbide measuring tests to determine the progress of conversion of the graphite to the nodular form.

It has been disclosed in U. S. Patent No. 2,527,037 that certain carbide metastabilizing agents when added to a gray cast iron melt so as to produce a mottled to white iron, will result in nodular graphite when this iron is subsequently graphitized. This patent further disclosed that wedge tests could be used to follow the process of carbide metastabilization followed by graphitization and that the carbide wedge values should be related to the section of the casting to be cast.

The present invention describes for the first time simultaneous carbide metastabilizing and graphitization, which can be followed by means of carbide measuring tests. This simultaneous action is made possible by the use of a fluoride carrier which maintains a condition of metastability in the melt that will give the desired graphite structure as well as the desired matrix structure in the final casting.

The full significance of this invention can be appreciated by a consideration of the known principles involved. When a carbide metastabilizing agent such as sodium, potassium, magnesium, lithium, cerium, calcium, barium or strontium is added to a cast iron melt so that it is absorbed by the melt, the agent will produce undercooling on solidification which will result in an increased carbide value directly related to the carbide metastabilizer dissolved in the metal and the inherent graphitizing power of the metal itself. This undercooling can only occur when all nuclei which may precipitate graphite from the melt have been taken into solution or eliminated.

Examples of such nuclei are the common metalloids of manganese, silicon, oxygen and sulphur and undissolved particles of graphite. Carbide metastabilizing elements in general tend to combine with said nuclei themselves, but vary considerably in their efficacy.

Thus, some metastabilizing elements have a strong tendency to form metalloids but are relatively weak carbide stabilizers such as magnesium and calcium. Others may be strong metalloid formers and stronger carbide stabilizers, such as cerium and lithium, whereas still others may be weak in this direction and weaker carbide stabilizers such as barium and strontium.

The fact is that various carbide metastabilizers will behave differently under different circumstances, depending on their particular effectiveness to purify the melt and/or on the relative stability of the metastable carbides that they produce. This difference in behavior is a function of this invention and this is made possible by the principle of fluoride incorporation.

In order to utilize the particular ability of certain carbide metastabilizing agents, this invention in its preferred form uses a plurality of carbide metastabilizers combined with fluoride carriers. It uses mixtures of fluorides and compounds of carbon and silicon in combination with carbide metastabilizing agents of the nodular impelling type according to the conditions of operating and the results desired. In this specification the term "carbonsilicon" compound is taken to mean a compound containing either carbon or silicon or both. Unlike other disclosures relating to the use of metastabilizers, this invention contemplates the treatment of a melt by combining carbide metastabilization and graphitization in a concurrent mechanism. Specifically, the invention consists of adding successively a plurality of mixtures to a molten bath, these mixtures consisting of fluorides and a carbon-silicon compound with said fluorides and said carbon-silicon compounds both being selected from the group consisting of calcium, magnesium, barium, lithium, zirconium, strontium, sodium, potassium and rare earths. These elements fall within the groups known as alkaline earth, alkalies and rare earths.

The first step of the invention in its preferred form, uses a carbide metastabilizer and fluoride carrier particularly adapted to the condition of the molten metal and renders it in a receptive state to a second addition combination selected to give the exact structure desired in the final casting.

A combination consisting of from 10–30% rare earth fluoride and from 70–90% calcium silicide is particularly suited to purifying the molten bath to the point where calcium as a carbide metastabilizing agent will produce metastable carbides of calcium in the melt. Where it is desired to strongly emphasize carbide formation as in a soft gray iron or where a heavy casting is to be poured, it is preferred to add from 10–30% of calcium carbide to this mixture. A typical mixture would consist of 10–30% calcium carbide, 10–30% rare earth fluoride and 40–80% calcium silicide.

The preferred mixture as described utilizing a rare earth fluoride and calcium silicide or calcium carbide, is a good purifier and will, when given the opportunity, reduce sulphur from as much as about 0.10% to as low as about .005%. Where opportunity for sulphur reduction is not always present as where time of contact with the slag produced by the addition is limited, the mixture is still able to effectively neutralize the effects of sulphur without necessarily removing it from the melt. This means that sulphur reduction per se, is no guide as to effective neutralization of the melt prior to carbide metastabilization. Good nodular irons have been produced by this invention with sulphur contents as high as about .08%.

Carbide metastabilization, however, does not occur until impurities in the melt have been rendered inoperative. The point of neutralization is always followed by an increase in the carbide value of the melt when a slight further addition of the preferred mixture is made. This can conveniently be followed by carbide measuring tests.

The preferred mixture of rare earth fluorides and calcium silicide will graphitize a melt while it is combining with subversive elements. This is because it contains a

high proportion of silicon, which element is not fundamental to the process of purification. Calcium which is rendered operative by the fluoride carrier and possibly some of the rare earth fluoride carrier itself, is involved in purification. When once this purification is complete, further calcium rendered operative by the rare earth fluoride carrier becomes available to act as a carbide metastabilizer.

The first step of this invention involves the addition of the preferred rare earth fluoride, calcium silicide mixture until the carbide value of the molten metal starts to increase, that is until carbides are obtained in the melt. These carbides, which are undoubtedly carbides of calcium and rare earth elements may be detected by means of noting the difference between a carbide measuring test taken on the original bath and another taken after treatment in amount sufficient to neutralize unwanted impurities and meta-stabilize the melt.

If then this mixture is added until the carbide value of the melt is very slightly higher than it was before the addition, it may be considered that neutralization of impurities is complete. This applies regardless of the carbide content of the original bath. All that is necessary in the first step of this invention is to add the mixture until the carbide value of the original melt has been increased by a detectable amount.

The carbide value referred to is preferably detected by fracture or wedge tests. While this is the preferred method of measuring carbide values, the invention is equally operative when using other methods. The important feature is to make the addition of step one until a detectable or measurable increase in carbide value is obtained. When using wedge tests as disclosed in U. S. Patent No. 2,527,037, a value of about $\frac{2}{32}$ represents a just measurable increase, whereas a value of about $\frac{4}{32}$ is a well defined increase.

When a cast iron melt has been purified and neutralized by the preferred mixture to the point where the carbide value as shown by the carbide measuring test has increased by at least $\frac{2}{32}$, the microstructure will show a portion of the free graphite in nodular form. All types of iron regardless of the initial carbide content will, when correctly treated, show a higher carbide value.

Thus the product of the first step of this invention is a cast iron melt which has been undercooled and which is in a condition where it is immediately responsive to further additions for further undercooling. The first step may be modified in degree by varying the base metal in such a way that larger or smaller additions are required for purification, but in any event the final product of the first step will show a higher carbide value than the original melt.

The second step of this invention in its preferred form contemplates the additions of a carbide metastabilizer and fluoride combination which is different from that used in the first step in that it is less powerful as a carbide metastabilizer than the mixture used in the first step.

It has been found that an alkaline earth or alkali silicide and an alkaline earth or alkali fluoride combination is particularly effective as an addition in the second step of this invention.

A preferred mixture contains 20–40% of calcium fluoride and 10–15% magnesium silicide with the balance as calcium silicide. Another mixture is 20–40% calcium fluoride, 10–30% barium silicide and the balance calcium silicide. A third mixture is 15–35% calcium fluoride, 5–15% magnesium fluoride and the balance as calcium silicide.

The tendency of the mixture used in the second step to give metastable carbides may also be increased by using a proportion of rare earth fluoride and/or a proportion of alkaline earth carbide. This is particularly useful when the metal is being processed for heavy casting sections or for increased quantities of pearlite in the microstructure. Particularly effective mixtures are 20–40% calcium fluoride, 5–10% rare earth fluoride and the balance as calcium silicide or 20–40% calcium fluoride, 10–30% calcium carbide with the balance as calcium silicide.

The preferred mixture used in the second step of this invention is designed to be neutral in its effect on carbide value or to be slightly carbide forming. The carbide forming properties decrease with increasing additions. By adding a carbide metastabilizer it is possible to convert the carbon into nodular form. When the first step of the invention has not been carried to the desired degree, complete conversion of the carbon into the nodular form by the addition in the second step, cannot be accomplished unless abnormally large additions of the second step are used. Such large additions have an adverse effect on the physical properties and the structure because they raise the silicon content of the metal to a very high level. It is a feature of this invention that complete nodularity can be obtained with relatively small additions, practiced in both steps No. 1 and No. 2, because of the sensitive structural changes that occur.

The second step of this invention contemplates the addition of the alkaline earth silicide and alkaline earth fluoride mixture in an amount in excess of ½% by weight so that the carbide value of the metal of the first step remains neutral or is increased by a detectable amount. Thus the second step mixture is added in such amount that graphitization does not occur. If graphitization occurs the end product may not have sufficient graphite in the nodular form. If, on the other hand, carbide metastabilization is carried too far, the end product may contain excessive carbides which when annealed may give conventional malleable iron graphite, because the carbides are unduly stable.

In the process of this invention, the second step is intimately linked with the first step and failure to carry both steps to the desired conclusion will not give the product of the invention. When using wedge tests as a measure of carbide value, the combined steps 1 and 2 in the process of this invention will give a carbide value increase of not less than about $\frac{2}{32}$, being a detectable amount, and preferably not more than about $\frac{9}{32}$. When using other method of carbide value measurement in the process of this invention, the combined steps 1 and 2 will give a carbide value increase of about 1 to 6% over that of the first carbide value and preferably not more than about 24 to 36% over that of the first carbide value, giving a total carbide range of about 1% to about 36% over that of the first carbide value. The addition of the first step will give a carbide value detectably greater than the initial carbide value but still lying in the total carbide range of from about 1 to 36%. This carbide increase insures that undercooling has taken place. On the other hand, the limiting maximum carbide increase insures that sufficient silicon has been added for graphitization so that the carbide metastability produced by the alkaline earth metal is opposed in sufficient degree to give nodular graphite in the section of casting to be poured. It is an important feature of this invention that the carbide value of the original melt be adjusted in accordance with the section of the casting to be poured.

The function of the fluoride in this invention is primarily as a wetting agent to assure solution of the volatile alkaline earth or alkali metal in the molten cast iron, thus permitting the formation of alkaline earth carbides by reaction between the carbon and the additive. The degree of carbide forming effect is quickly measured in the treated molten iron by carbide measuring tests.

The exact same mechanism occurs in the second step, but in this case the rate of absorption of alkaline earth metal by the bath is decreased by changing the composition of the additive in order to assure recovery from the surfusion or undercooling of the carbide effect.

Another feature of this invention is the production of a suitable "as cast" structure with respect to combined carbon to insure any desired degree of "as cast" ductility

in the final product. It is well known that carbide metastabilizing agents promote combined carbon by stabilizing the carbide that occurs in pearlite that results in the microstructure of the "as cast" product. By very careful control of the degree of undercooling to insure completely nodular graphite and by balancing the undercooling with silicon in such a way that all the combined carbon is precipitated as nodular graphite, it is possible to secure a fully ferritic matrix with a very high "as cast" ductility.

I find that the use of a rare earth fluoride as a carrier favors the production of relatively strong metastable carbides, whereas an alkaline earth fluoride favors the production of weaker metastable carbides. By varying the composition of the mixture added as a second step to make it more weakly carbide forming, so that relatively large amounts have to be added for the desired carbide increase, a condition of higher "as cast" ductility is favored. The use of barium silicide in the mixture used for the second step, is particularly good in this direction.

Conversely, by making the composition of the mixture of the second step so that it is more strongly carbide forming, it is possible to obtain a more pearlitic structure with lower ductility, but with improved yield strength. The use of calcium carbide in the mixture used for the second step is particularly good in this direction.

If there were no first step to this invention, or if the first step was not carried far enough, some of the carbide metastabilizers added in the second step would be used up unnecessarily. This would result in an uncontrolled or unbalanced condition where the silicon added in the second step mixture would be predominant and where incomplete nodularity of the graphite would result. Conversely, if the first step were carried too far, carbide metastabilization would be favored and silicon added in the second step mixture would be ineffective, resulting in free carbides in the structure. An essential feature of this invention, therefore, lies in complete neutralization of harmful impurities by the procedure outlined in the first step. This conditions the melt and even starts the graphite on the way to being nodular. Subsequent additions in the second step, therefore, can be regulated to be fully effective in promoting nodular graphite with a controlled matrix structure in the finished casting.

For positive control the addition of the second step may be varied in composition and in amount. Its composition can be varied according to the potency of its carbide metastabilizer content.

This invention contemplates the use of calcium as its preferred carbide metastabilizer, balanced by silicon as the preferred graphitizer. It is possible, therefore, to express the composition of the second step additive in terms of its equivalent calcium content as a ratio to its silicon content. This ratio we have called its C. M. F. factor or carbide metastability factor.

The working calcium equivalent of carbide metastabilizing elements that are operative in this invention, in terms of their ability to form metastable carbides, is tabulated below. In this table calcium has been given a value of unity.

Carbide Metastabilizer	Working Calcium Equivalent
Lithium	4.0
Rare earths	3.0
Magnesium	2.0
Calcium	1.0
Strontium	0.5
Zirconium	0.4
Barium	0.3
Sodium	0.2
Potassium	0.1

The rare earths referred to in this table are those of the lanthanide series having atomic numbers of 57 through 71 and the actinide series having atomic numbers of 89 through 98. With the aid of the calcium equivalent it is possible to calculate the carbide metastability factor of any addition agent used in the process of this invention.

As an example, consider an addition agent consisting of:

	Percent
Calcium silicide (30% Ca 60% Si)	45
Magnesium silicon (10% Mg 40% Si)	20
Calcium fluoride (50% Ca)	25
Calcium carbide (60% Ca)	10

The equivalent calcium and silicon content of this mixture would be:

	Calcium Equivalent	Silicon Content
Calcium Silicide	30% of 45%×1=13.5	60% of 45%=27.0
Magnesium Silicon	10% of 20%×2= 4.0	40% of 20%= 8.0
Calcium Fluoride	50% of 25%×1=12.5	
Calcium Carbide	60% of 10%×1= 6.0	
	Total Calcium 36.0	Total Silicon 35.0

The calcium to silicon ratio of this mixture would be 36.0/35.0 or 1.03 or the C. M. F. (carbide metastability factor)=1.03.

As a further example, consider an addition agent consisting of:

	Percent
Calcium silicide (30% calcium 60% silicon)	35
Magnesium silicon (10% magnesium 40% silicon)	20
Calcium carbide (60% calcium)	20
Rare earth fluoride (60% cerium)	10
Calcium fluoride (50% calcium)	15
	100

The equivalent calcium and silicon content of this mixture would be:

	Calcium Equivalent	Silicon
Calcium Silicide	30% of 35%×1=10.5	60% of 35%=21.0
Magnesium Silicon	10% of 20%×2= 4.0	40% of 20%= 8.0
Calcium Carbide	60% of 20%×1=12.0	
Rare Earth Fluoride	60% of 10%×3=18.0	
Calcium fluoride	50% of 15%×1= 7.5	
	Total Calcium 52.0	Total Silicon 29.0

The calcium to silicon ratio of this mixture would be:

$$\frac{52.0}{29.0} \text{ or } 1.79$$

or the C. M. F. (carbide metastability factor)=1.79.

The addition in the first step is selected more for its ability to neutralize harmful impurities than for its C. M. F. value. It should, however, have a C. M. F. in excess of 1.0 in order that it may rapidly raise the carbide value as soon as neutralization of impurities is complete. This rapid increase in carbide value with small additions, prevents large excess of carbide metastabilizing agents from being incorporated into the melt at this stage. This is an important feature of this invention where the first step contemplates the incipient formation of nodular form of graphite and relies on the second step for controlled and complete matrix and graphite control.

In the process of this invention the nature of the original metal bath is important in that the carbide value of this bath must be adjusted in relation to the section of the casting to be poured and also in relation to the degree of "as cast" ductility required in the casting. For maximum "as cast" elongation it is preferred that the working carbide value of the original bath is not more than about 10% of the casting section and is normally at about 7½% of the casting section. For moderate "as cast" elongation it is preferred that the working carbide value of the original bath is not more than about 15% of the casting section and is normally about 12½% of the casting section. For maximum "as cast" modulus values it is preferred that the working carbide value of

the original bath is not more than about 25% of the casting section and is normally at about 20% of the casting section. Where free carbides are desired in the final casting it is preferred that the working carbide value of the original bath is at least about 50–80% of the casting section.

For example when using a wedge test as an index of the carbide value, the relationship between the carbide value and the final structure desired for a one inch section, is tabulated below. For sections outside of this tabulation the percentage relationships already discussed are used. In this table the desired working wedge values at all steps of the process are indicated:

Preferred working carbide values for 1" casting section

	Carbide Value of Bath	Carbide Value After Step 1 Addition	Carbide Value After Step 2 Addition
	In 32nds	In 32nds	In 32nds
For maximum "as cast" elongation	1–3	3–7	3–9
For moderate "as cast" elongation	3–5	5–9	5–11
For maximum "as cast" modulus values	5–8	7–12	7–14
For free carbides	16–19	18–23	18–25

An improved feature of this invention is that the desired carbide value must be obtained at each step of the invention. Having the desired carbide value at one step of the invention alone, will not result in the improved product of the invention.

As already indicated the C. M. F. (carbide metastablizing factor) of the alkaline earth metal silicide and alkaline earth, alkali or rare earth fluoride carrier mixture, must be adjusted according to the degree of carbide metastability aimed at in the final treated melt. This control, coupled with the control of the carbide value of the original bath allows a positive control of both the nodularity of the graphite and the nature of the metallic matrix structure, particularly with respect to its combined carbon content.

Alloying elements not normally included in the addition agents may modify the structures according to their influence on the carbide values of the metal. Under the process of this invention, obtaining the correct carbide value at each step of the invention automatically compensates for the effect of such alloying elements, whether they be present in the melt by chance or whether they be added deliberately for special property characteristics.

When using the preferred carbide values already outlined for varying casting sections or degrees of ductility, the C. M. F. of the second alloy addition may be varied to give specific "as cast" elongation values according to the following table. This table is based on the fact that the first step addition mixture has a C. M. F. of at least 1.05 and is carried to the specified carbide increase value required:

"As Cast" elongation range desired	Preferred carbide metastabilizing factor C. M. F. of second addition
Above 20%	0. 85–0. 90
15–20%	0. 90–0. 95
10–15%	0. 95–1. 00
5–10%	1. 00–1. 05
1–5%	1. 05–1. 25

The full process of this invention in its preferred form may be illustrated by a number of examples.

It was desired to make a casting having a moderate "as cast" elongation in the 5–10% range and having a controlling section of 2". A cast iron melt was prepared having a carbide value in the "as melted" condition of 8/32. This melt was treated with a 1½% by weight addition of a mixture consisting of:

	Percent
Calcium silicide	80
Rare earth fluoride	20

and having C. M. F. (carbide metastability factor) of 1.25. This addition was sufficient to raise the carbide value of the melt from the original 8/32 to a value of 12/32.

As a second step, the melt was treated with 1½% by weight addition of a mixture consisting of:

	Percent
Calcium silicide	50
Magnesium silicon	15
Calcium fluoride	25
Calcium carbide	10

and having a C. M. F. (carbide metastability factor) of 1.05.

This second step addition resulted in a carbide value of 14/32 which is an increase of 2/32 over the carbide value of the bath after the addition of step one.

The metal was cast and a test bar was machined from a 2" section extension bar cast on the casting. Examination of this test piece under the microscope showed 85% of the graphite in the nodular form and a matrix consisting of 40% ferrite and 60% pearlite. The physical properties of this test bar were:

Tensile strength	p. s. i.	82,000
Yield strength	p. s. i.	61,000
Elongation on 2"	%	8.5
Modulus of elasticity	p. s. i.	24,000,000

The chemical analysis of this test bar was as follows:

	Percent
Total carbon	3.30
Silicon	2.70
Manganese	0.45
Phosphorous	0.05
Sulphur	0.025

In a second example of the process of this invention it was desired to make a casting of ¾" section with a maximum "as cast" elongation in the 15–20% range.

A cast iron melt was prepared having a carbide value of 2/32 and to this melt 1% by weight of a mixture consisting of:

	Percent
Calcium silicide	75
Calcium fluoride	5
Rare earth fluoride	20

and having a C. M. F. of 1.35. This addition raised the carbide value of the metal bath from 2/32 to 4/32.

As a second step addition of 2% by weight, a mixture was added. This mixture consisted of:

	Percent
Calcium silicide	35
Barium silicide	40
Calcium fluoride	25

and had a C. M. F. of 0.94.

The second step addition raised the carbide value of 4/32, resulting from the first step addition, to 5/32.

A casting was poured and a test bar of equivalent section was examined. The graphite was found to be 75% in the nodular form and the matrix consisted of 85% ferrite and 15% pearlite. The "as cast" physical properties of the test bar were found to be:

Tensile strength	p. s. i.	68,000
Yield strength	p. s. i.	48,000
Elongation on 2"	percent	16.5
Modulus of elasticity	p. s. i.	23,000,000

A chemical analysis conducted on this test bar gave the following results:

	Percent
Total carbon	3.50
Silicon	2.95
Manganese	0.35
Sulphur	0.009
Phosphorous	0.04

In still another example of the process of this invention it was desired to cast a 3" section having a predominately pearlitic structure which would give a maximum modulus value.

A melt was prepared having a carbide value of 19/32 and to this was added a 1¼% by weight addition of a mixture consisting of:

	Percent
Calcium silicide	60
Rare earth fluoride	20
Calcium carbide	10
Magnesium silicon	10

and having a C. M. F. of 1.55. This addition was sufficient to raise the original bath carbide value of 19/32 to a new carbide value of 22/32.

A second step addition of 1¼% by weight of a mixture was then conducted. The mixture consisted of:

	Percent
Calcium silicide	35
Lithium silicon	10
Calcium carbide	20
Magnesium silicon	10
Calcium fluoride	25

and had a C. M. F. of 1.07.

The addition was sufficient to result in a final carbide value of 22/32. An equivalent section test bar cast from this melt was examined and found to have 90% of its graphite in the nodular form and the matrix was found to consist of 85% pearlite and 15% ferrite.

The "as cast" physical properties of this test bar were found to be:

Tensile strength	p. s. i.	93,000
Yield strength	p. s. i.	71,000
Elongation on 2"	percent	1
Modulus of elasticity	p. s. i.	25,000,000

A chemical analysis on this bar gave the following results:

	Percent
Total carbon	3.20
Silicon	2.40
Manganese	0.50
Molybdenum	0.30
Sulphur	0.020
Phosphorous	0.06

In still another example of the process of this invention, it was desired to cast a 1" section with free carbides present for wear resisting qualities. A melt was prepared having a carbide value of 18/32 and to this was added a mixture consisting of calcium silicide and rare earth fluoride and having a C. M. F. of 1.231.

This first step addition increased the carbide value to 22/32. A second step addition consisting of calcium silicide, calcium carbide, rare earth fluoride and calcium fluoride and having a C. M. F. of 1.12 was made to give a final carbide value of 23/32. The metal was cast and a portion cut from the casting was examined under the microscope. The free graphite was in nodular form and in addition the matrix contained 30% carbides and 70% pearlite.

In the process of this invention the additives may be incorporated by any of the means normally used by those skilled in the art. It is found that for convenience the addition of the first step may be made as the metal leaves the furnace. For the addition of the second step the preferred method is to add the material directly to the stream while the metal is being transferred to another ladle. This may be done by means of a spout through which the metal is passed. The preferred method of addition obtains good agitation between the metal and the additive.

Another good method of making the addition of the first step or the second step or both, is by using inert gas to blow the additive into the metal through a refractory tube immersed under the surface of the molten bath. This method had the advantage of giving intimate contact between the slag of the additive and the molten metal bath.

It may be regarded in carrying out this invention that the iron melt has an initial first carbide value to produce a cast iron containing some free graphite if cast. The first material which is added to the melt increases the first carbide value to a second carbide value to produce a cast iron containing less free graphite if cast. The second material which is added to the melt causes the third carbide value to be of a value which is less than that which is required to produce a cast iron containing substantially no free graphite if cast.

This invention has been described in its preferred form, it being understood that many variations may be resorted to in practice that will still come within the scope of this invention.

What is claimed is:

1. The method of producing cast iron with nodular graphite comprising preparing a cast iron melt having an initial first carbide value, adding a first material to the melt which includes calcium as a carbide metastabilizer to increase the first carbide value to a second carbide value, adding a second material to the melt which includes magnesium as a carbide metastabilizer to produce a third carbide value higher than said second carbide value, and thereafter casting the melt.

2. The method of producing cast iron with nodular graphite comprising preparing a cast iron melt having an initial first carbide value, adding a first material to the melt which includes calcium as a carbide metastabilizer to increase the first carbide value to a second carbide value, adding a second material to the melt which includes a substance which has a higher calcium equivalent than calcium as the carbide metastabilizer to produce a third carbide value higher than said second value, and thereafter casting the melt.

3. The method of producing an improved cast iron comprising preparing a cast iron melt having an initial first carbide value, adding a first material to the melt having a first carbide metastability factor value to increase the first carbide value to a second carbide value, adding a second material to the melt having a second carbide metastability factor value lower than said first carbide metastability factor value to produce a third carbide value higher than said second carbide value, and thereafter casting the melt.

4. The method of producing an improved cast iron comprising preparing a cast iron melt having an initial first carbide value, adding to the melt a first material consisting of silicides and carbides of alkaline earth materials and fluorides of rare earth materials to increase the first carbide value to a second carbide value, adding to the melt a second material consisting of silicides and carbides of alkali and alkaline earth materials and fluorides of alkali and alkaline earth materials to produce a third carbide value higher than said second carbide value, and thereafter casting the melt.

5. The method of producing an improved cast iron comprising preparing a cast iron melt having an initial first carbide value, adding a first material to the melt having a first carbide metastability factor value to increase the first carbide value to a second value ranging from 2/32 to 4/32 over that of the first carbide value,

adding a second material to the melt having a second carbide metastability factor value lower than said first carbide metastability factor value to produce a third carbide value which lies in a range having a minimum value not less than the second carbide value and having an upper limit not greater than 2/32 more than the second carbide value, and thereafter casting the melt.

6. The method of producing cast iron with nodular graphite comprising preparing a cast iron melt having an initial first carbide value, adding to this melt a first mixture having a first carbide metastability factor value and consisting of silicides and carbides of alkaline earth materials and fluorides or rare earth materials to increase the first carbide value to a second carbide value, adding to this melt a second mixture having a second carbide metastability factor value which is less than said first carbide metastability factor value, and consisting of silicides and carbides of alkali and alkaline earth materials and fluorides of alkali and alkaline earth materials to produce a third carbide value greater than said second carbide value, and thereafter casting the melt.

7. The method of producing a cast iron having preselected elongation ranges comprising preparing a cast iron melt having a first carbide wedge value, adding to this melt a first mixture having a carbide metastability factor value of at least 1.05 and consisting of silicides and carbides of alkaline earth materials and fluorides of rare earth materials to increase the carbide wedge value to a second value ranging from 2/32 to 4/32 over that of the first carbide wedge value, adding a second mixture consisting of silicides and carbides of alkali and alkaline earth materials and fluorides of alkali and alkaline earth materials to produce a third carbide wedge value which lies in a range having a minimum value not less than the second carbide wedge value and having an upper limit not greater than 2/32 more than the second carbide wedge value, said second mixture having a carbide metastability factor value in the range of 0.85 to 0.90 to give an elongation above 30%, 0.90 to 0.95 to give an elongation range from 15 to 20%, 0.95 to 1.00 to give an elongation range from 10 to 15%, 1.00 to 1.05 to give an elongation range from 5 to 10%, and 1.05 to 1.25 to give an elongation range from 1 to 5%, and thereafter casting the melt.

8. The method of producing a cast iron having preselected physical properties comprising preparing a cast iron melt having a first carbide wedge value in the range of from 1/32 to 3/32 for maximum "as cast" elongation, from 3/32 to 5/32 for moderate "as cast" elongation, from 5/32 to 8/32 for maximum "as cast" modulus values, and from 16/32 to 19/32 for free carbides, adding to this melt a first mixture consisting of silicides and carbides of alkaline earth materials and fluorides or rare earth materials to increase the carbide wedge value to a second value in the range of from 3/32 to 7/32 for maximum "as cast" elongation, 5/32 to 9/32 for moderate "as cast" elongation, 7/32 to 12/32 for maximum "as cast" modulus values, 18/32 to 23/32 for free carbides, adding a second mixture consisting of silicides and carbides of alkali and alkaline earth materials and fluorides of alkali and alkaline earth materials to produce a third carbide wedge value in the range of from 3/32 to 9/32 for maximum "as cast" elongation, from 5/32 to 11/32 for moderate "as cast" elongation, from 7/32 to 14/32 for maximum "as cast" modulus values, and from 18/32 to 25/32 for free carbides, and thereafter casting the melt.

9. The method of producing cast iron with nodular graphite comprising adding successively a first and a second addition to a molten bath of pre-selected first carbide value, each of said additions comprising fluorides and a carbon-silicon compound, said fluorides and said compound both being selected from the group consisting of calcium, magnesium, barium, lithium, zirconium, strontium, sodium, potassium and rare earths and said additions being added in amount sufficient to produce a third final carbide value lying in the range of from one to thirty-six percent over that of said first carbide value, and said first addition being added in amount to give a second carbide value which is greater than the first carbide value and less than the third final carbide value.

10. The method of producing cast iron with nodular graphite comprising adding successively a plurality of additions to a molten bath of preselected first carbide value, each of said additions including fluorides, carbon and silicon compounds, said compounds being selected from the group consisting of alkali metals, alkaline earths and rare earths, said additions being added in amount sufficient to produce a third carbide value lying in the range of from one to thirty-six percent over that of said first carbide value, and said first addition being added in amount to give a second carbide value which is greater than the first carbide value and less than the third carbide value.

11. The method of producing cast iron with nodular graphite comprising adding successively a plurality of additions to a molten bath of preselected first carbide value, each of said additions including a graphite affecting agent to change the physical shape of the graphite in the finished casting, each said additions being added in amount sufficient to produce a third carbide value lying in the range of from one to thirty-six percent over that of said first carbide value, and said first addition being added in amount to give a second carbide value which is greater than the first carbide value and less than the third carbide value.

12. The method of producing cast iron with nodular graphite comprising adding successively a plurality of additions to a molten bath of preselected first carbide value, each of said additions including a combined carbide metastabilizing and graphitizing agent, each said additions being added in amount sufficient to produce a third carbide value lying in the range of from one to thirty-six percent over that of said first carbide value, and said first addition being added in amount to give a second carbide value which is greater than the first carbide value and less than the third carbide value.

13. The method of securing pre-selected "as cast" ductility in cast irons of nodular graphite comprising the steps of melting a bath of a preselected first carbide value, adding to this bath a first addition of calcium silicide and rare earth fluoride so as to increase the carbide value of the bath by 2/32 to 4/32 as measured by a wedge test to a second carbide value, then adding to the bath a second addition selected from the group consisting of alkaline earth silicides, alkaline earth fluorides and alkali metal fluorides to produce a third carbide value which is greater than said second carbide value, said second addition being compounded to have a lower carbide metastabilizing power than said first addition, and thereafter casting the bath.

14. The method of securing pre-selected "as cast" ductility in cast irons of nodular graphite comprising the steps of melting a bath of pre-selected first carbide value, adding successively to this bath first and second additions, said additions comprising fluoride, carbon, and silicon compounds selected from the group consisting of alkali metals, alkaline earths and rare earths, said first addition increasing the carbide value of the bath by 2/32 to 4/32 as measured by a wedge test to a second carbide value, addition of said second addition producing a third carbide value which is greater than said second carbide value, said second addition being compounded to have a lower carbide metastabilizing power than said first addition, and thereafter casting the bath.

15. The method of securing pre-selected "as cast" ductility in cast irons of nodular graphite comprising the steps of melting a bath of pre-selected first carbide value, adding successively to this bath first and second additions, said additions comprising fluoride, carbon, and silicon compounds selected from the group consisting of alkali

metals, alkaline earths and rare earths, said first addition increasing the carbide value of the bath by 2/32 to 4/32 over the first carbide value as measured by a wedge test to a second carbide value, addition of said second addition producing a third carbide value which is greater than said second carbide value.

16. The method of securing pre-selected "as cast" ductility in cast irons of nodular graphite comprising the steps of melting a bath of pre-selected first carbide value, adding successively to this bath first and second additions, said additions comprising fluoride, carbon, and silicon compounds selected from the group consisting of calcium, magnesium, barium, lithium, zirconium, strontium, sodium, potassium and rare earths, said first addition increasing the carbide value of the bath by 2/32 to 4/32 over the first carbide value as measured by a wedge test to a second carbide value, addition of said second addition producing a third carbide value which is greater than said second carbide value.

17. The method of securing pre-selected "as cast" ductility in cast irons of nodular graphite comprising the steps of melting a bath of pre-selected first carbide value, adding successively to this bath first and second additions, each of said additions including a graphite affecting agent to change the physical shape of the graphite in the finished

casting, said first addition increasing the carbide value of the bath by 2/32 to 4/32 over the first carbide value as measured by a wedge test to a second carbide value, addition of said second addition producing a third carbide value which is greater than said second carbide value.

18. The method of securing pre-selected "as cast" ductility in cast irons of nodular graphite comprising the steps of melting a bath of pre-selected first carbide value, adding successively to this bath first and second additions, each of said additions including a combined carbide metastabilizing and graphitizing agent, said first addition increasing the carbide value of the bath by 2/32 to 4/32 over the first carbide value as measured by a wedge test to a second carbide value, addition of said second addition producing a third carbide value which is greater than said second carbide value.

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