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METHOD FOR PRODUCING CAST IRON

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This invention relates to cast iron, and more particularly to a new cast iron, and the production thereof, which in the as-cast state produces finished castings which are markedly different in characteristics and composition from the cast irons as heretofore known.

One of the principal objects of this invention is to provide a molten iron mix which in the molten state is such that the addition of small quantities of selected materials including calcium, as in the ladle before pouring into the mold, will produce this new iron of characteristics widely differing from the long and widely known gray irons, from the long known white iron castings, and also from malleableized iron castings which result from the annealing or heat treatment of while iron castings.

Another object of this invention is to produce thus such a new iron which in the as-cast condition and without subsequent annealing has substantially all of the graphitic carbon formed during the cooling thereof in spherical or nodular form substantially uniformly distributed throughout the castings.

Still another object of this invention is to provide a method for the production of such improved nodular iron of increased commercial practicability and ease of operation.

It is a further object of this invention to provide an agent for addition to a molten iron mix to produce this new nodular iron having the desired characteristics, which addition agent has not heretofore been known nor heretofore used in such production of such new nodular iron.

A still further object of this invention is to provide a method for the production of such so-called nodular iron castings utilizing instead of expensive metallic alloys as nodular graphite forming agents an inexpensive and readily obtainable material containing calcium for economic addition to the molten iron mix without excessive loss by oxidation or volatilization.

Other objects and advantages will be apparent from the following description and the appended claims.

Cast iron produced from a so-called gray iron mix has long been recognized to include graphitic or uncombined carbon which precipitates upon cooling to become dispersed in flake-like form throughout the solid cast iron. Such a gray iron casting including such flake-like graphitic carbon is well recognized in the foundry industry.

If it is desired, however, to produce a cast iron in which uncombined or graphitic carbon is present in spherical or so-called nodular form rather

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than in the flake form characteristic of gray iron castings, additional steps must be taken. For example, the composition of the molten mix may be altered so that the as-cast product will be a so-called white iron containing substantially no uncombined or graphitic carbon and then this white iron casting may be annealed or heat treated for substantial periods in order to cause the carbides contained therein to break down so that they will be changed to graphitic carbon in spherical form to give a so-called malleableized iron. On the other hand, an as-cast iron with the graphitic carbon present in spherical or nodular form and having characteristics widely varying from malleableized iron may be produced from a gray iron mix by adding thereto before pouring a material which will so influence the precipitation or formation of uncombined or graphitic carbon during the casting and cooling of the mix that such graphitic carbon will be produced in spherical or nodular form substantially uniformly distributed throughout the casting.

According to this invention such a cast iron with nodular graphite microstructure is produced from a molten gray iron mix by adding to the mix before the pouring and casting thereof a small modifying amount of a calcium containing substance such as will provide a controlled proportion of effective calcium alloyed with or dissolved in the molten iron mix to produce formation of such graphitic nodules. The composition of the molten iron mix and of the iron casting without such nodular producing agent present is substantially that of a so-called gray iron casting normally containing uncombined or graphitic carbon in flake-like form, but by the addition of small quantities of nodular producing agents according to this invention, an iron casting is produced with such nodular graphite microstructure and with substantially no flake-like graphitic carbon typical of gray iron. The uncombined or graphitic carbon nodules are comparable in size and distribution and regularity of shape with the graphitic nodules or so-called temper carbon in malleableized white iron, but the physical characteristics of the nodular iron product of this invention are widely different from the physical characteristics of so-called malleableized white iron.

This invention, therefore, has produced a new nodular cast iron, which in its as-cast form and without subsequent annealing or other heat treatment, has free or uncombined graphitic carbon present in nodular form and of such size and arrangement to give increased strength to the iron

matrix so that the castings as produced have much greater strength under the standard impact or shock test and also under the standard transverse test as these testing procedures are well understood in the foundry industry. The tensile strength of this new nodular iron is much above that of ordinary gray iron castings and good grades of malleableized iron castings. As a fair comparison the tensile strength of this new nodular iron containing calcium is upwards of 70,000 pounds per square inch and said castings have been made with still higher tensile strengths, whereas the higher grade malleableized castings have tensile strengths up to only about 53,000 pounds to 55,000 pounds per square inch and ordinary gray iron castings have tensile strengths varying widely from under 20,000 pounds up to about 45,000 pounds per square inch.

The ductility or susceptibility to elongation under tension of this new nodular iron is somewhat less than malleableized iron and consequently the resistance to bending or distortion upon impact is greater, although these characteristics may vary according to alterations in the molten composition and may be affected by the amount of such constituents as phosphorus or manganese and, to some extent, zirconium if the latter be used in the nodular forming material as hereinafter described.

Thus an entirely new nodular iron is made available in as-cast form with such characteristics as will give the great superiority over ordinary gray iron castings as well as over malleableized white iron as to increased tensile strength, machinability and capability of withstanding shocks which might cause bending or distortion of the casting.

In the practice of the invention it has been found that small proportions of calcium, when introduced into a molten gray iron mix having a composition as illustrated by the range of proportions set out below, will result in the production of castings which, when completed and taken from the mold without subsequent annealing, will have the nodular form of graphitic carbon substantially uniformly distributed through the casting and with the various characteristics referred to above. The characteristics of calcium are such, however, that practical difficulty may be experienced in attempting to add calcium to the molten iron mix in metallic or elemental form. For example, difficulty has been experienced in causing the solution of metallic calcium in the molten gray iron mix under conditions usually encountered in commercial foundry operations, which difficulty may be attributable to the chemical activity of metallic calcium and its tendency to combine readily with carbon present in the molten mix to form insoluble calcium carbide.

Calcium compounds such as calcium oxide, for example, being considerably lighter than the molten gray iron mix, have a tendency to float on top of the mix when added thereto while the calcium therein combines to form insoluble carbide. Such calcium carbide may be caused to break down at substantially elevated temperatures (of the order of as high as 3000° F.), but such temperatures are considerably in excess of the usual operating temperature ranges encountered in cast iron foundry practice. Accordingly, if it is desired to operate with usual commercial foundry equipment and temperature ranges, etc., the introduction of calcium into the molten iron mix should be accomplished by means of a calcium introducing agent effective to introduce calcium into the molten mix without the intermediate formation of calcium carbide and of satisfactory practicability within the limits of such usual foundry practices.

Satisfactory results have been achieved according to this invention using as such a calcium introducing agent a substance containing calcium silicide. In this form it has been observed that calcium may practicably be introduced into or dissolved in or alloyed with a molten gray iron mix under conditions of usual commercial operation to provide cast iron with the desired nodular graphite microstructure. Apparently such introduction of calcium in the form of its silicide may be explained by the fact that the high solubility of silicon in molten iron may tend to promote the solution of at least a substantial proportion of the calcium silicide in the molten iron mix notwithstanding the fact that calcium itself apparently is more inclined to combine with carbon present in the mix to form calcium carbide rather than to become dissolved in the molten iron. For example, with additions of approximately 10% calcium silicide on the molten mix, sufficient of the calcium has been introduced into the mix to produce a nodular microstructure instead of forming carbide. Such additions, however, apparently tend to include excessive amounts of silicon in the molten iron thus producing certain undesirable properties in the finished casting notwithstanding the nodular graphite formation.

Since calcium silicide is both substantially less dense than molten iron and also has a relatively higher melting point, large additions of such material also have a tendency to float on top of the molten iron mix. Apparently because of such characteristics and the fact that calcium is an extremely active element and calcium silicide is a vigorous deoxidizer, such large additions of calcium silicide tend to float on the molten iron and become burned or oxidized to calcium oxide, with part of the calcium contained in the silicide or the oxide forming calcium carbide but with comparatively little of the added calcium going directly into solution to act as an effective nodular graphite forming agent at normal commercial temperature and operational ranges encountered in foundry practices, while the proportion of the calcium which forms the oxide or carbide does not appear to contribute to the desired nodular formation.

Very satisfactory results have been produced, however, and very much smaller additions of calcium silicide effective to produce the desired nodular microstructure have been accomplished when a fluxing material or calcium carbide formation inhibitor such as calcium fluoride is added to the molten mix along with calcium silicide. Thus a mixture of calcium silicide and calcium fluoride in approximately the proportions of 2 parts silicide to 1.5 parts fluoride can be added to a molten gray iron mix in the ladle and caused to dissolve therein either by stirring or by placing the calcium material in the empty ladle and thereafter tapping the molten iron into the ladle on top of the calcium material. In this way it has been discovered that a substantially smaller amount of calcium silicide need be added for effective introduction into the molten mix satisfactorily to produce the desired nodular iron structure.

Apparently the presence of calcium fluoride has a fluxing effect and also protects the calcium silicide to some extent from oxidation. That is to say, both calcium fluoride and cal-

cium silicide are relatively insoluble in molten iron and both have relatively higher melting temperatures than are normally encountered in a ladle of molten iron. When both such substances are added together to a ladle of molten iron, however, a melting of both such materials occurs so that the solid calcium silicide becomes softened or fluent and an effective melting and/or solution is obtained whereby the calcium material is effectively introduced into the molten iron mix for the successful production of castings having the desired nodular graphite microstructure.

The satisfactory introduction of calcium silicide may be further enhanced if both the calcium silicide and the calcium fluoride fluxing material are reduced to relatively finely divided state and intimately admixed with each other before being added to the molten metal. Satisfactory results have been obtained when the calcium silicide and calcium fluoride are crushed or pulverized sufficiently to pass through a 100 mesh screen and the two materials in such crushed state are intimately admixed with each other before the addition is made. It will be understood, of course, that a nodular structure can be obtained from a molten mix into which such materials are added in substantially larger particles. The use of the small particle size, however, has been found to enhance the effectiveness of the introduction of the material so that a satisfactory casting can be made using less of the additive calcium material when such material is added in finely divided form.

While calcium silicide thus introduced into the molten iron mix enables the production of cast iron with desired characteristics, it has been found that the duration of the nodular producing effect of the calcium material may be relatively limited as is noted hereafter. It has been discovered that this duration of nodular forming effect can be extended if additional materials are incorporated into the nodular graphite producing agents. Satisfactory results have been obtained using as such supplementary addition agents materials containing zirconium or titanium or alminum.

One convenient and satisfactory material for this purpose is zirconium-ferro-silicon composed of approximately ⅓ each zirconium, iron and silicon. Zirconium-ferro-silicon may preferably be added in an amount to give approximately 0.25% to 1% zirconium on the molten iron mix (i. e., as by the addition of approximately 0.75% to 3% zirconium-ferro-silicon) in combination with approximately 1.5% to 3% calcium silicide and approximately 1% to 3% calcium fluoride. Satisfactory results have been obtained by adding to provide in the molten mix approximately 2% calcium silicide, 1.5% calcium fluoride and 0.5% zirconium. Such zirconium additions, it has been found, should preferably be kept less than a maximum figure of approximately 1% zirconium for the reason that the presence of zirconium in substantial excess of 1% may cause a certain observable embrittlement of the final as-cast product.

In addition to zirconium, titanium provides another such supplementary addition material when added in amounts of from approximately 0.5% to 1% along with calcium silicide and calcium fluoride in the above proportions. Ferrotitanium is one satisfactory material from which titanium may be added. Additionally satisfactory results have been obtained by the addition of approximately 6% of a material containing approximately 6% calcium, 50% silicon and 10% titanium alloyed together. If 0.5% zirconium be added along with such calcium-silicon-titanium alloy, satisfactory results have been obtained by the addition of but approximately 4% of such alloy and similar results obtained when 3% calcium fluoride was added along with 4% of such alloy. A practicable range for the alloy alone is approximately 5% to 10% although additions of approximately 6% are preferred.

As it has been noted above, the crushing or pulverizing of the above mentioned materials to a relatively small particle size, e. g., sufficiently small to pass through a 100 mesh screen, enhances the ease of introduction of the materials into the molten iron mix and the effectiveness of the amount of such materials added to the mix in the production of the desired nodular graphite microstructure.

One of the reasons for the observed enhanced effectiveness of finely divided material, in addition to the more intimate admixture of zirconium and calcium, may be that such pulverizing prior to addition presents a greatly increased surface area of added material when introduced into the molten mix in such finely divided form. Furthermore, as follows from the above noted observation that intimate admixture of the silicide and the fluoride enhances the effect of both, it has been observed that the supplementing effect of zirconium on the nodular-producing effect of calcium is decreased and may not even occur when the zirconium is added to the mix either before or after the calcium addition. Consequently it has been discovered that the preferred procedure is to add the zirconium, not only simultaneously with, but also intimately admixed with the calcium material.

Such addition may be quite adequately accomplished by forming an alloy containing both calcium material and zirconium material. The formation of such an alloy, however, may be both expensive and complicated because of the excessive activity and scarcity of the pure metals on the one hand, and the high melting points and low solubilities of their compounds on the other hand. In any case such an alloy has not been found necessary to achieve satisfactory results.

Satisfactory results have also been obtained by the use of a 50–50 alloy of aluminum and calcium silicide by adding to the molten iron mix approximately 6% of such alloy. Similar results have been obtained with but 4% of such alloy when 1% calcium fluoride was added with the alloy and 5% of such alloy has produced satisfactory results when 0.5% zirconium was mixed with alloy. It should be noted that both the step of pulverizing the alloy as well as the addition of calcium fluoride aid in the effective introduction of the alloy into the mix, but the use of the calcium fluoride material with this alloy has been found not to be necessary since the alloyed aluminum appears effective to inhibit calcium carbide formation. A satisfactory range for the alloy alone is approximately 5% to 10% although 6% is preferred. This is also true of the titanium-calcium-silicon alloy mentioned above.

It should be noted, furthermore, that the addition of a mixture or alloy of which the components effective to produce nodular graphite structures make up but a very minor portion should be considered with care, since the addition of such a mixture containing a large preponderance of

materials which are ineffective for nodular graphite formation may require the introduction of substantial bulk of material which must be melted by the residual heat in the molten iron mix. That is to say, it is desired that as great a proportion as practicable of the solid ladle addition be effective nodular producing material so that the total bulk of material added to the ladle and which must be melted by residual heat therein be as low as possible while still adding sufficient nodular producing material to obtain satisfactory results.

It is to be noted that calcium silicide, aluminum, zirconium, and titanium have been used previously in the foundry industry as so-called graphitizers or deoxidizers in fractional percentage additions to certain metallurgical products. The use of calcium silicide alone or in combination with the calcium carbide formation inhibitors and other materials mentioned according to this invention, however, is not such a graphitizing or deoxidizing step or method. That is to say, in the first place, the percentage ranges of, for example, calcium silicide herein disclosed vary substantially from such usual graphitizing additions. Furthermore, it has been observed that other so-called graphitizing and deoxidizing substances do not produce nodular graphitic microstructures when added to molten gray iron mixtures according to this invention. Furthermore, calcium silicide may be a so-called carbide stabilizer when added in percentages substantially above 5% and it is to be noted that when calcium silicide, for example, is added in small amounts as a graphitizer or in larger amounts as a carbide stabilizer, it is added alone and without benefit of the calcium fluoride fluxing material herein disclosed or the pulverizing operation above noted. It is accordingly apparent that such graphitizing or carbide stabilizing properties do not form a complete basis for explaining the phenomenal advantages of the materials disclosed herein as nodular microstructure producing agents and, conversely, that materials possessing graphitizing or deoxidizing properties do not function equivalently to the materials herein according to this invention merely because of such graphitizing properties.

An iron mix containing constituents within the following percentage ranges before adding calcium material as a nodular graphite forming agent has been found satisfactory for the production of cast iron with a nodular graphite microstructure when calcium containing materials are added to the molten mix in the ladle before pouring according to this invention:

Carbon	3.0 to 4.3%
Silicon	Up to 4.0%
Manganese	Up to 2.0%
Phosphorus	0.01 to 0.4%
Sulfur	Less than 0.02%

and the balance substantially all iron.

It has also been found that when a calcium containing material is added to the molten metal, there is a comparatively short time interval during which sufficient of the calcium material will remain available in the molten material to have the effect of producing a nodular microstructure in the iron. That is to say, the nodules of graphite are apparently produced as graphitic carbon precipitates during pouring and cooling of the iron. Consequently a nodular graphite producing agent must be effectively available to control this precipitation of graphitic carbon so that the carbon will be caused to form the desired nodular microstructure rather than such flake-like graphite as is typical of gray iron castings produced without the calcium nodular forming agent. Accordingly, whatever may be the theory of the mechanism whereby these calcium containing materials control the carbon precipitation, such materials must be available for nodular formation in the cooling metal throughout the critical period during which nodular formation may occur.

It has been observed that when insufficient amounts of nodular forming agent are added to the metal, the carbon precipitated in castings poured from the ladle of molten mix first may indeed form nodules but the nodule forming effect of the calcium material becomes exhausted so that carbon precipitated in subsequent castings poured from the same ladle will not occur in the nodular form. Accordingly, sufficient of the nodular forming agent must be added to the molten mix so that the duration of its nodular forming effect will be sufficiently prolonged as to control the precipitation of substantially all the graphitic carbon in the ladle of molten iron to form a nodular microstructure. On the other hand, too great an addition of such nodular forming agents may have pronounced undesirable effects on the finished product such as, for example, a carbide stabilizing effect tending to inhibit graphite formation in the first place.

Accordingly, the duration of the nodular forming effect of added calcium materials becomes quite significant in commercial operation since the length of time required to complete pouring of the castings and the cooling thereof may be determined by many practical causes not readily susceptible to change—e. g., size and complexity of the castings, quantity of molten mix desired to be poured from one ladle, proximity of the molds to the furnace from which the molten iron is drawn, etc.

When using a calcium addition agent such as calcium silicide in connection with a fluxing material such as calcium fluoride, the duration of the nodular forming effect may be sufficiently short that sufficient material may not be effectively added to produce nodular microstructure throughout the period of pouring and cooling without exceeding the maximum limit of calcium silicide additions beyond which other undesirable properties may be imparted to the finished casting.

As noted above, the duration of nodular forming effect of calcium silicide additions according to this invention may be extended by combining an addition of other materials. Also as noted above, however, excessive amounts of zirconium may cause undesirable embrittlement of the finished casting. Consequently, it has been found that a point may be reached under commercial operating conditions where the time necessary for the pouring and cooling of the cast iron may exceed the duration of nodular producing effect of added calcium silicide even when combined with zirconium or titanium in amounts below the limit above which undesirable properties may be imparted to the castings. It has been observed that additions of calcium agents according to this invention within the ranges disclosed will provide nodular forming material in sufficient quantity to produce desired results for a period from about 7 to 10 minutes, after which time the carbon is found no longer to form in the desired nodular microstructure.

If a longer period than the 7 to 10 minutes referred to is required before the molten iron is all poured into a mold and is in such condition of cooling that nodular formation has been completed, additional amounts of the nodular forming agents may be introduced into the molten mix to restore the effectiveness of nodular graphite formation after the 7 to 10 minute period stated. Accordingly, should the original period of duration of the nodular graphite forming effect of the addition agents of this invention expire, additional quantities of the agents may be introduced into the mix to extend the nodular forming period as required by the foundry procedure.

Approximately the same proportionate additions of the nodular producing agents may be added as before to extend the nodular forming period for another 7 to 10 minutes, but a preferred practice is to make subsequent additions of nodular producing agents in substantially less amounts than the first addition to extend the nodular forming period by short intervals of but several minutes each as required by the foundry procedure instead of making a second addition of sufficient quantity of nodular forming agent to extend the nodular forming period beyond several minutes. Consequently, additional small amounts of nodular forming agents less than the first addition may be added to the molten mix from time to time so that approximately the disclosed percentages of unexhausted nodular producing calcium material will be present for nodular formation throughout the period of pouring and cooling during which nodular graphite microstructures may be formed.

Furthermore, the length of time necessary to pour a casting as well as the size and shape of the casting being poured will have an effect on the temperature and cooling rate of the molten iron mix and such temperature variations, it has been observed, have some effect on the nodular forming duration of a given amount of the calcium addition agents. Thus a given amount of addition agent may provide nodular forming effect of sufficient duration for the pouring of a number of small simple castings which cool almost immediately upon being formed whereas the same amount of addition agent may not be found sufficient to control the nodular precipitation of the same amount of molten iron when poured more slowly into a large complex casting of such character and in such manner as to prolong the cooling period. Thus the amount of nodular graphite producing agent will be somewhat controlled by the pouring technique employed as well as by the number, size and complexity of the castings being produced, and it will be understood that such effect of casting size and shape and number upon the pouring and cooling is considered in adjusting the amount, frequency and number of subsequent nodular-producing agent additions in commercial foundry practices.

While the processes and products herein described constitute preferred embodiments of the invention, it is to be undertsood that the invention is not limited to these precise processes and products and changes may be made therein without departing from the scope of the invention which is defined in the appended claims.

What is claimed is:

1. A process for producing iron castings of the character described in which graphitic carbon formed during the casting and cooling thereof is substantially entirely present in spherical or nodular form without subsequent annealing and which are substantially free of flake-like graphitic carbon, which process comprises the steps of preparing a molten gray iron mix, adding to said mix before pouring a limited modifying amount of calcium silicide as a nodular graphite forming agent with calcium fluoride as a calcium carbide formation inhibitor and fluxing agent for introducing said calcium silicide into said mix, and pouring said molten mix into a mold for producing said iron casting.

2. A process for producing iron castings of the character described in which graphitic carbon formed during the casting and cooling thereof is substantially entirely present in spherical or nodular form without subsequent annealing and which are substantially free of flake-like graphitic carbon, which process comprises the steps of preparing a molten gray iron mix, adding to said mix before pouring a limited modifying amount of calcium silicide as a nodular graphite forming agent and calcium fluoride as a calcium carbide formation inhibitor and fluxing agent in combination with zirconium for prolonging the duration of the nodular forming effect of said calcium silicide, and pouring said molten mix into a mold for producing said iron casting.

3. A process for producing iron castings of the character described in which graphitic carbon formed during the casting and cooling thereof is substantially entirely present in spherical or nodular form without subsequent annealing and which are substantially free of flake-like graphitic carbon, which process comprises the steps of preparing a molten gray iron mix, adding to said mix before pouring a limited modifying amount of calcium silicide as a nodular graphite forming agent and calcium fluoride as a calcium carbide formation inhibitor and fluxing agent in combination with titanium for extending the duration of the nodular forming effect of said calcium silicide, and pouring said molten mix into a mold for producing said iron casting.

4. A process for producing iron castings of the character described in which graphitic carbon formed during the casting and cooling thereof is substantially entirely present in spherical or nodular form without subsequent annealing and which are substantially free of flake-like graphitic carbon, which process comprises the steps of preparing a molten gray iron mix, adding to said mix before pouring a limited modifying amount of finely divided calcium silicide as a nodular graphite forming agent intimately admixed with calcium fluoride as a fluxing agent for introducing said calcium silicide into said mix, and pouring said molten mix into a mold for producing said iron casting.

5. A process for producing iron castings of the character described in which graphitic carbon formed during the casting and cooling thereof is substantially entirely present in spherical or nodular form without subsequent annealing and which are substantially free of flake-like graphitic carbon, which process comprises the steps of preparing a molten gray iron mix, adding to said mix before pouring a limited modifying amount of a nodular graphite forming reaction mixture comprising a finely divided intimate admixture of calcium silicide and zirconium combined with calcium fluoride as a fluxing material for aiding the solution of said mixture into said molten mix, and pouring said molten mix into a mold for producing said iron casting.

6. A process for producing iron castings of the

character described in which graphitic carbon formed during the casting and cooling thereof is substantially entirely present in spherical or nodular form without subsequent annealing and which are substantially free of flake-like graphitic carbon, which process comprises the steps of preparing a molten gray iron mix, adding to said mix before pouring a limited modifying amount of a nodular graphite forming reaction mixture comprising a finely divided intimate admixture of calcium silicide and titanium combined with calcium fluoride as a fluxing material for aiding the solution of said mixture into said molten mix, and pouring said molten mix into a mold for producing said iron casting.

7. A process for producing iron castings of the character described in which graphitic carbon formed during the casting and cooling thereof is substantially entirely present in spherical or nodular form without subsequent annealing and which are substantially free of flake-like graphitic carbon, which process comprises the steps of preparing a molten gray iron mix, adding to said mix before pouring a limited modifying amount of a nodular graphite producing agent comprising calcium silicide alloyed with aluminum as a calcium carbide formation inhibitor and material for effecting direct incorporation of said calcium silicide into said mix for nodular graphite formation therein, and pouring said mix into a mold for producing said casting.

8. A process for producing iron castings of the character described in which graphitic carbon formed during the casting and cooling thereof is substantially entirely present in spherical or nodular form without subsequent annealing and which are substantially free of flake-like graphitic carbon, which process comprises the steps of preparing a molten gray iron mix, adding to said mix before pouring a limited modifying amount of approximately 2% calcium silicide and 1.5% calcium fluoride both finely divided and intimately admixed together, and pouring said molten mix into a mold for producing said iron casting.

9. A process for producing iron castings of the character described in which graphitic carbon formed during the casting and cooling thereof is substantially entirely present in spherical or nodular form without subsequent annealing and which are substantially free of flake-like graphitic carbon, which process comprises the steps of preparing a molten gray iron mix, adding to said mix before pouring a limited modifying amount about 1.5% to 3% calcium silicide as a nodular graphite forming agent, 1% to 3% calcium fluoride as a fluxing agent, in combination with approximately 0.25% to 1% zirconium for extending the duration of the nodular forming effect of said calcium silicide, and pouring said molten mix into a mold for producing said iron casting.

10. A process for producing iron castings of the character described in which graphitic carbon formed during the casting and cooling thereof is substantially entirely present in spherical or nodular form without subsequent annealing and which are substantially free of flake-like graphitic carbon, which process comprises the steps of preparing a molten gray iron mix, adding to said mix before pouring a limited modifying amount of approximately 1.5% calcium silicide as a nodular graphite forming agent, 2% calcium fluoride as a fluxing agent, in combination with approximately 0.5% zirconium for extending the duration of the nodular forming effect of said calcium silicide, and pouring said molten mix into a mold for producing said iron casting.

11. A process for producing iron castings of the character described in which graphitic carbon formed during the casting and cooling thereof is substantially entirely present in spherical or nodular form without subsequent annealing and which are substantially free of flake-like graphitic carbon, which process comprises the steps of preparing a molten gray iron mix, adding to said mix before pouring a limited modifying amount of approximately 1.5% to 3% calcium silicide and a nodular graphite forming agent, 1% to 3% calcium fluoride as a fluxing agent, in combination with approximately 0.5% to 1% titanium for extending the duration of the nodular forming effect of said calcium silicide, and pouring said molten mix into a mold for producing said iron casting.

12. A process for producing iron castings of the character described in which graphitic carbon formed during the casting and cooling thereof is substantially entirely present in spherical or nodular form without subsequent annealing and which are substantially free of flake-like graphitic carbon, which process comprises the steps of preparing a molten gray iron mix, adding to said mix before pouring a limited modifying amount of approximately 6% of a nodular graphite forming agent comprising approximately 6% calcium, along with approximately 50% silicon and 10% titanium as calcium carbide formation inhibitors for effecting direct incorporation of said calcium into said mix for nodular graphite formation therein, and pouring said molten mix into a mold for producing said iron casting.

13. A process for producing iron castings of the character described in which graphitic carbon formed during the casting and cooling thereof is substantially entirely present in spherical or nodular form without subsequent annealing and which are substantially free of flake-like graphitic carbon, which process comprises the steps of preparing a molten gray iron mix, adding to said mix before pouring a limited modifying amount of approximately 4% of a nodular graphite forming agent comprising approximately 6% calcium, 50% silicon, and 10% titanium in combination with approximately 0.5% zirconium, and pouring said molten mix into a mold for producing said iron casting.

14. A process for producing iron castings of the character described in which graphitic carbon formed during the casting and cooling thereof is substantially entirely present in spherical or nodular form without subsequent annealing and which are substantially free of flake-like graphitic carbon, which process comprises the steps of preparing a molten gray iron mix, adding to said mix before pouring a limited modifying amount of approximately 3% calcium silicide and 3% aluminum from a nodular graphite forming alloy of calcium silicide and aluminum, and pouring said molten mix into a mold for producing said iron casting.

15. A process for producing iron castings of the character described in which graphitic carbon formed during the casting and cooling thereof is substantially entirely present in spherical or nodular form without subsequent annealing and which are substantially free of flake-like graphitic carbon, which process comprises the steps of preparing a molten gray iron mix, adding to said mix before pouring a limited modify-

ing amount of a nodular graphite forming agent consisting of calcium silicide, effecting direct incorporation into said mix of an effective nodular graphite producing proportion of calcium from said calcium silicide substantially free of intermediate formation of calcium carbide, beginning to pour said molten mix into a mold immediately after said addition, thereafter, upon the exhaustion of the nodular graphite forming effect of said agent and before the pouring of said mix is completed, making a second addition of said agent less than said first addition to extend said nodular graphite forming effect and continuing to pour said molten mix to form said iron casting.

16. A process for producing iron castings of the character described in which graphitic carbon formed during the casting and cooling thereof is substantially entirely present in spherical or nodular form without subsequent annealing and which are substantially free of flake-like graphitic carbon, which process comprises the steps of preparing a molten gray iron mix, adding to said mix before pouring a limited modifying amount of calcium silicide as a nodular

graphite forming agent with calcium fluoride as a calcium carbide inhibitor and fluxing agent for introducing said calcium silicide into said mix to maintain the graphite formation controlling effect of said added materials in the iron cast into a mold throughout the graphite forming temperature range in the cooling of said casting, and pouring said molten mix into a mold for producing said iron casting.

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