

Dec. 6, 1960

J. M. CROCKETT ET AL
MANUFACTURE OF CAST IRON

2,963,364

Filed Aug. 20, 1952

6 Sheets-Sheet 1

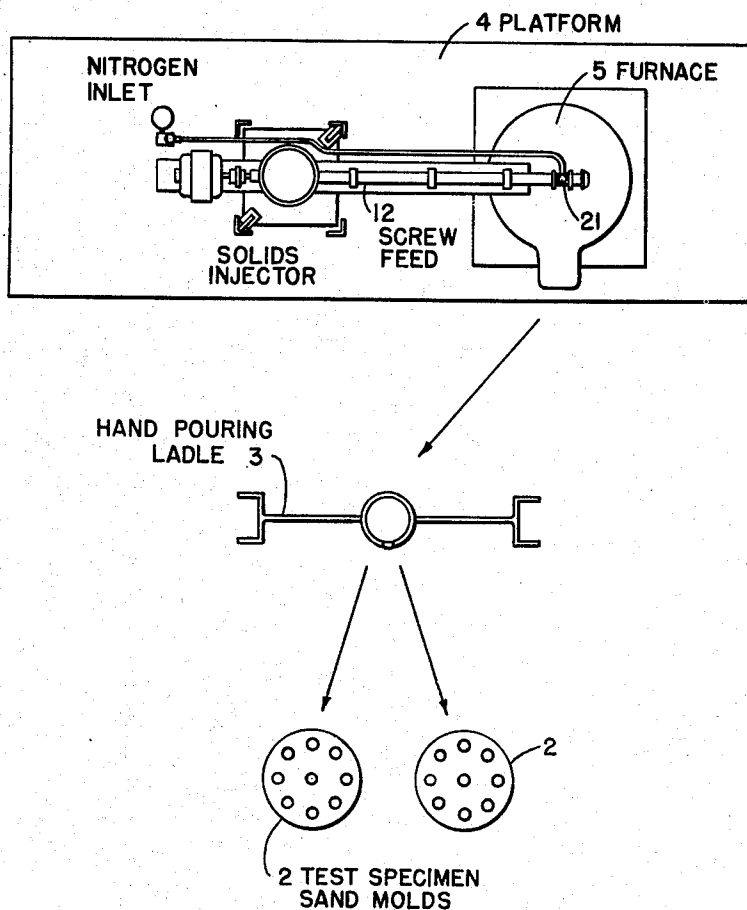


FIG. 1
FOUNDRY LAYOUT

INVENTORS
JOHN M. CROCKETT
PHILIP M. HULME
BY *A. Anne Mathews*
ATTORNEY

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6 Sheets-Sheet 2

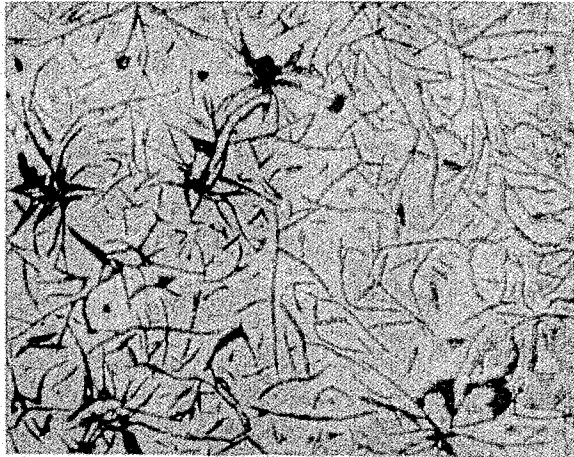


FIG. 2
MICROSTRUCTURE OF AN AS-CAST GRAY IRON
HAVING THE UNCOMBINED CARBON IN FLAKE
FORM. 4 PER CENT PICRAL ETCH. 100X

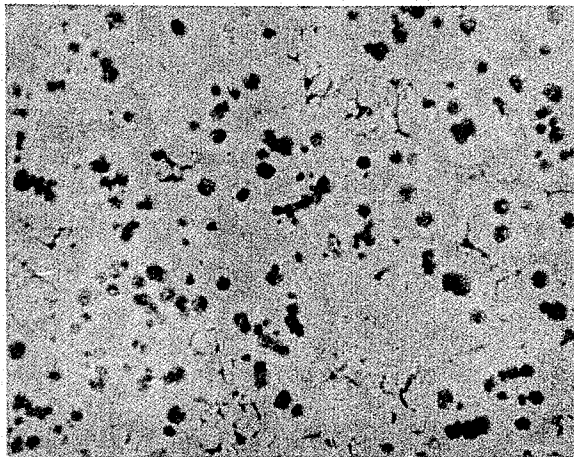


FIG. 3
MICROSTRUCTURE OF A GRAY IRON PRODUCT,
CAST SEVEN MINUTES AFTER TREATMENT
ACCORDING TO THE INVENTION, SHOWING PRE-
DOMINANTLY NODULAR OR COMPACTED FORM
OF UNCOMBINED CARBON. 4 PER CENT
PICRAL ETCH. 100X

INVENTORS
JOHN M. CROCKETT
PHILIP M. HULME
BY *H. Hume Matheson*
ATTORNEY

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6 Sheets-Sheet 3

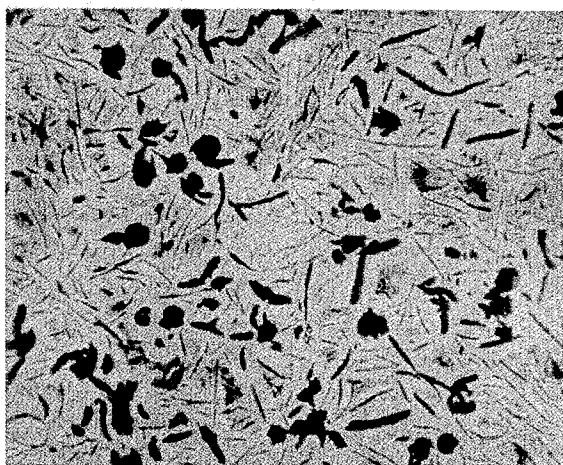


FIG. 4

MICROSTRUCTURE OF A GRAY IRON PRODUCT,
CAST FOURTEEN MINUTES AFTER TREATMENT
SHOWING THE UNCOMBINED CARBON IN PRE -
DOMINANTLY FLAKE FORM. 4 PER CENT
PICRAL ETCH. 100X

INVENTORS
JOHN M. CROCKETT
PHILIP M. HULME

BY *W. Hume Matthews*
ATTORNEY

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6 Sheets-Sheet 4



FIG. 5
MICROSTRUCTURE OF AN AS-CAST GRAY IRON
HAVING THE UNCOMBINED CARBON IN FLAKE
FORM. 5 PER CENT NITAL ETCH. 250X

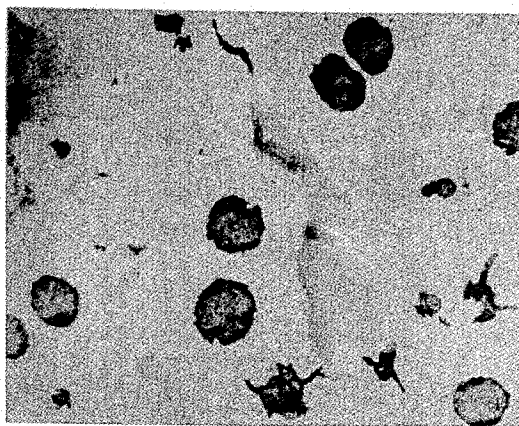


FIG. 6
MICROSTRUCTURE OF A GRAY IRON PRODUCT,
CAST AFTER TREATMENT WITH CALCIUM
CARBIDE AND MAGNESIUM, SHOWING SUB-
STANTIALLY ALL UNCOMBINED CARBON IN
NODULAR FORM. 5 PER CENT NITAL
ETCH. 250X

INVENTORS
JOHN M. CROCKETT
PHILIP M. HULME
BY *H. Hume Matthews*
ATTORNEY

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6 Sheets-Sheet 6

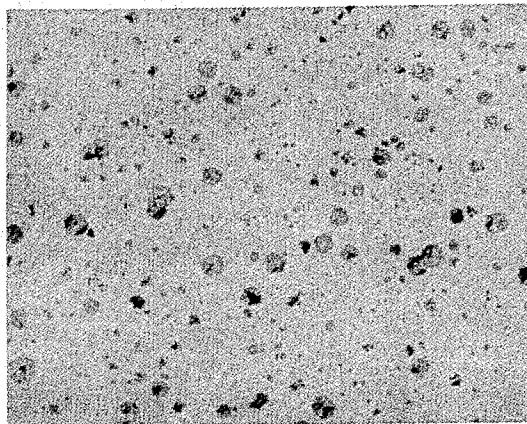


FIG. 9

MICROSTRUCTURE OF A GRAY IRON PRODUCT,
OBTAINED BY ANNEALING A CASTING MADE
IN A CHILL MOLD FOLLOWING TREATMENT
WITH CALCIUM CARBIDE, MAGNESIUM, AND
MAGNESIUM OXIDE, SHOWING SUBSTANTIAL
ALL UNCOMBINED CARBON IN NODULAR FORM
100X

INVENTORS
JOHN M. CROCKETT
PHILIP M. HULME
BY *A. Anne Matheson*
ATTORNEY

1

2,963,364

MANUFACTURE OF CAST IRON

John M. Crockett, Metuchen, and Philip M. Hulme, Morristown, N.J., assignors to Air Reduction Company, Incorporated, New York, N.Y., a corporation of New York

Filed Aug. 20, 1952, Ser. No. 305,315

3 Claims. (Cl. 75—130)

This invention relates to a new method for producing upgraded cast iron or cast iron having its graphitic carbon wholly or partially in the form of nodules, and to novel cast iron products which may be produced thereby. The present application is a continuation-in-part of application Serial No. 246,314, filed September 12, 1951, now abandoned, entitled Production of Upgraded and Nodular Gray Cast Iron.

In the copending application of P.M. Hulme, Serial No. 125,607, filed November 4, 1949, now Patent No. 2,577,764, issued December 11, 1951, assigned to the assignee of the present application, there is disclosed and claimed a process for treating molten ferrous metal containing sulphur with calcium carbide to produce a reaction between the sulphur and the carbide. According to the present invention, certain features of the calcium carbide injection process disclosed in the Hulme application may be utilized in the provision of a novel method for producing upgraded and nodular gray cast iron castings which have improved physical properties and a novel composition.

Cast irons are alloys of iron, carbon, and silicon, the carbon content always being in excess of the amount which can be retained in solid solution in austenite at the eutectic temperature. Of the various cast irons, gray iron is the most widely used engineering material, its production exceeding that of all other cast metals combined. The uncombined carbon present as graphite in the gray iron imparts the typical dark "gray" fracture to such iron, and produces its characteristic properties, such as ready machinability, good damping properties, and resistance to wear. The wide range of tensile strengths in gray irons and their manufacturing economy account for their extensive use. However, many gray cast irons do have limitations of use because of their relatively low tensile strength and poor shock resistance. It is believed that these undesirable properties are caused by the fact that the graphitic carbon is distributed throughout the metallic matrix of gray irons in the form of many flakes. These flakes are the sources of relative weakness and softness, being similar in crystalline structure to that of natural graphite; and graphite whether amorphous or crystalline has very low tensile and impact strength. At first glance, it would appear that the volume occupied by the graphite flakes determines the relative strength of the iron. But such is not the case actually, because gray irons of exactly the same composition have been found to have widely different physical properties. The difference resides rather in the physical shape that the free or graphitic carbon assumes in the matrix of the cast material. The flake form of the graphite in gray cast iron unduly interrupts continuity of the iron matrix, and thus imparts certain undesirable properties, such as brittleness, lack of ductility, and low tensile strength.

It has been common knowledge for some years that if the uncombined carbon in gray cast irons (which usually

2

appears as graphite flakes) could be made to occur in a more compacted form or in nodules or particles of more or less spheroidal form, the strength and toughness of the iron would be greatly increased. Such properties result from a minimum interruption of the matrix continuity by the graphite.

Numerous attempts have been made to develop chemical treating processes for modifying the physical shape of the uncombined or free carbon as it occurs in conventional gray cast iron, and many metals and alloys (including relatively large quantities of the expensive metal magnesium or metallic calcium in a wide variety of forms) have been suggested as addition agents for use in such treating processes. However, none of these chemical inoculant processes have proved entirely satisfactory for large scale commercial production.

An object of the present invention is to provide an improved method, adapted for large scale commercial use, for chemically treating a molten gray cast iron composition (containing more than 90% iron, with carbon from 1.7% to 4.5% and silicon from 1% to 3.5%) with inexpensive upgrading or nodulizing additions comprising commercially available calcium carbide, to produce a resulting gray cast iron product having upgraded or improved physical and mechanical properties.

Another object is to provide an improved chemical treatment method for modifying and controlling the physical shape of the uncombined carbon or graphite in gray cast iron.

A further object of the present invention is to provide a novel upgraded gray cast iron containing free carbon or graphite having a nodular, spheroidal or compacted flake form.

A still further object of the present invention is to provide an improved method for treating a molten gray cast iron composition with calcium carbide together with an addition agent or agents and/or a heat treatment step to insure the occurrence of most or all of the graphitic carbon in nodular or spheroidal form in the upgraded cast iron product.

Still another object of the invention is to provide an improved method for treating a molten gray cast iron composition to neutralize the deleterious effects of relatively small amounts of elements in the cast iron which inhibit the formation of nodular graphite.

These and other objects and advantages of the present invention will become more apparent from the following detailed description and drawings of a specific embodiment of the invention, in which:

Fig. 1 is a schematic view of a foundry layout and apparatus shown to illustrate one manner in which the treatment method of the present invention may be practiced on a small scale.

Fig. 2 is a reproduction of a photomicrograph taken at a magnification of 100 diameters showing the flake form of uncombined carbon in a polished and etched section of a conventional gray cast iron as normally obtained in the as-cast condition.

Fig. 3 is a reproduction of a photomicrograph taken at a magnification of 100 diameters and showing the etched section of a gray cast iron, in the as-cast condition, which has been treated with calcium carbide and magnesium oxide prior to casting. The molten iron was originally (i.e. prior to treatment) of the same composition as the alloy in Fig. 2. The structure was produced in a casting poured in a sand mold seven minutes after injection of the treating agent into the molten gray iron bath in accordance with the present invention; the casting contains the spheroidal or nodular form of carbon in a ferrite matrix.

Fig. 4 is a reproduction of a photomicrograph taken at a magnification of 100 diameters and showing the etched section of a gray cast iron in the as-cast condition and having the same composition and treatment as the alloy in Fig. 3. The casting was poured in a sand mold fourteen minutes after injection of the treating agent. The cast material contains predominantly relatively large graphite flakes and approximately 5% of spheroidal or nodular graphite in a ferrite matrix.

Fig. 5 is a reproduction of a photomicrograph taken at a magnification of 250 diameters showing the flake form of uncombined carbon in a polished and etched section of a gray cast iron, like that of Figure 2 but of slightly different composition, as normally obtained in the as-cast condition.

Fig. 6 is a reproduction of a photomicrograph taken at a magnification of 250 diameters and showing the etched section of a gray cast iron, in the as-cast condition, which has been treated with calcium carbide and magnesium prior to casting. The molten iron was originally (i.e. prior to treatment) of substantially the same composition as the alloy in Fig. 5.

Fig. 7 is a reproduction of a photomicrograph taken at a magnification of 100 diameters and showing the unetched section of a gray cast iron, in the as-cast condition, which has been treated with calcium carbide, magnesium, and magnesium oxide prior to casting. The molten iron was originally (i.e. prior to treatment) of substantially the same composition as the alloy in Fig. 5.

Fig. 8 is a reproduction of a photomicrograph taken at a magnification of 100 diameters and showing the unetched section of a gray cast iron, in the as-cast condition, which has been treated with calcium carbide and rare earth oxides prior to casting. The molten iron was originally (i.e. prior to treatment) of substantially the same composition as the alloy in Fig. 5.

Fig. 9 is a reproduction of a photomicrograph taken at a magnification of 100 diameters and showing the unetched section of a cast iron of the same composition and treated in the same manner as the cast iron of Fig. 7, but which has been cast in a chill mold and annealed.

The preferred method of the invention involves the injection of a predetermined amount of finely divided calcium carbide particles into a molten gray iron bath of selected composition which is then promptly poured to form upgraded or nodular gray iron castings. Other addition agents may also be introduced preferably simultaneously with the carbide or subsequent to the carbide injection. In some instances, the casting is heat treated or annealed. The process may be carried out, for example, with the apparatus schematically shown in Fig. 1, and which is more specifically shown and described in the said Hulme application Serial No. 125,607.

Commercial calcium carbide, composed chiefly of CaC_2 but also containing calcium oxide and traces of other elements present in the coke and limestone from which the carbide is made, is fed into the molten metal bath in furnace 5 on platform 4 by a screw conveyor 12 which feeds finely divided carbide from a hopper (not shown) into the top of the refractory injection tube 21 at a selected rate of feed. A gas which is inert with respect to the metal being treated (such as nitrogen, carbon dioxide, carbon monoxide or mixtures thereof) is introduced at a controlled rate of flow into the carbide stream as it enters the top of the refractory tube and the carbide and gas then pass down through the refractory tube into the molten metal in which the lower end of the tube is submerged. The gas pressure is maintained at a value sufficient to keep the molten metal from rising up into the lower end of the tube submerged therein. Both the rate of carbide flow and the rate of gas flow are controlled, preferably relative to each other. With an injection apparatus such as shown in Fig. 1, the gas flow, for example, is preferably within the range from about $\frac{1}{4}$ cubic foot

to about 2 cubic feet (STP) per pound of carbide injection.

In commercial practice the molten metal can be treated continuously rather than in batches as shown in Fig. 1. With such an arrangement, the rate of carbide flow into the molten metal is preselected in terms of the weight of carbide injected per ton of metal. For example, if the molten metal is flowing at the rate of ten tons per hour, the carbide flow might be selected at some rate within the range from 0.25 lb. per minute to 25 lbs. per minute, i.e. 1.5 to 150 lbs. of carbide per ton of metal treated. The gas flow is then adjusted so as to carry this amount of carbide into the bath. Preferably a minimum rate of gas flow is used. Thus, if the rate of carbide injection were set at 1.3 lbs. per minute for a 10 tons per hour flow of the iron, the nitrogen gas pressure at the injection end of the refractory injection tube would be maintained, for instance, at about 6 p.s.i. and the gas flow rate would be between 60 and 100 cubic feet per hour, for a refractory tube of approximately one inch internal diameter submerged in the molten metal from 5 inches to 30 inches.

While Fig. 1 shows the molten metal bath as being treated in an induction furnace 5, the molten metal could also be treated in other containers such as a trough, ladle, forehearth, etc. The arrangement should be such that the castings may be poured promptly following termination of the carbide treatment. Though some benefit from the treatment may be retained indefinitely, the maximum effect is transitory and therefore the upgrading or nodulizing treatment should not be made until just before the metal is ready to be cast.

The composition of the metal in the molten bath is that which is conventionally used to make gray cast iron, and in which the iron constitutes more than 90%, the carbon from 1.7% to 4.5% and the silicon from 1% to 3.5%. Other elements conventionally found in such cast irons are present, such as sulphur, manganese and phosphorus in usual amounts and impurities or traces of other elements such as titanium, zirconium, etc. The composition, if cast in sand molds in the conventional way without the inoculation or treatment of the present invention, is such as would produce gray cast iron castings in which uncombined carbon would be present in typical flake graphite form.

Carbide injected in accordance with this invention will react with and remove certain undesirable impurities in the molten iron, such as sulphur and oxygen. The higher the content of such impurities in the untreated molten metal, the greater should be the amount of carbide injected. Thus the total quantity of carbide injected can be regarded as equal to the sum of two amounts—the amount necessary to remove or counteract any unduly large quantities of undesirable impurities (for example, the sulphur present in excess of .04%) plus a further amount (for example an amount, such as 15 lbs. per ton, within the range from 1.5 to 150 lbs. per ton) for upgrading and nodulizing the iron as herein explained.

As shown in Fig. 1, the treated metal is cast in sand molds 2 by means of a ladle 3, promptly following the termination of injection of the carbide into the molten bath in furnace 5. Other types of molds may be used, but the relatively slow cooling provided by the sand molds tends to promote the formation of nodular or spheroidal graphite. It has been noted that the carbide treatment of a cast iron as herein disclosed suppresses the tendency for the formation of white iron; the carbide may be said to suppress the chill. This is the opposite effect to that obtained with previously known magnesium treated irons. In this connection it should be noted that the conventional graphitizing inoculation with ferro-silicon may not be necessary subsequent to the carbide treatment to produce an upgraded readily machinable cast iron. The type of chill tests ordinarily used to measure the chilling tendencies, or the "chill," of cast irons are thoroughly discussed in the Handbook of Cupola

5

Operations, American Foundrymen's Society, 1946, pp. 65-68, and in volume 59, American Foundrymen's Society, 1951, pp. 78-91, Chill Tests and Metallurgy of Gray Iron. The term "chill tests" is generally applied to include two types of tests. In one test, a small rectangular casting or test piece is poured with one edge against a chill plate, while in the other a wedge-shaped test piece is cast in a sand core. The amount of chill is the depth or thickness of the white portion of the fractured test piece. The white portion shows the carbide stability of the iron or the tendency for the iron to solidify as a hard white iron instead of a soft gray iron.

We have found that both hypo- and hypereutectic gray cast irons possess improved characteristics when treated with calcium carbide according to the method described above; however, these improved characteristics are obtained more readily and to a greater degree, particularly in the production of nodular irons, with hypereutectic cast iron compositions. The microstructure of the cast product or article of manufacture made by the present invention (particularly castings of a hypereutectic composition) is characterized by the appearance of free carbon or graphite in the form of compacted flakes, approaching a spheroidal or nodular form, and in some cases much or substantially all of the graphite appears in a nodular, spherical, or spherulitic form. In other words, the graphite flakes in the product of the present invention are generally smaller and more compact than the flakes which normally occur in conventional gray cast irons. The magnitude of the graphite flake modification, i.e., from the normal flake to compacted flakes or spheroidal or nodular particles, was found to be a function of various factors, such as composition of the iron before treatment (i.e. hyper as distinct from hypo compositions), and more importantly the amount of calcium carbide reacted with a unit weight of molten iron. Calcium carbide does not melt at the temperatures of molten iron conventionally used in foundry, so that any reaction must be effected between a solid reagent and the liquid molten metal. Hence, the reaction will depend upon surface contact between the solid calcium carbide and the molten iron; and to insure an intimate contact, the calcium carbide is introduced substantially below the surface of the metal and in finely divided form, so that the calcium carbide will be sufficiently wetted by the molten metal and will react while still below the surface of the metal. It is disseminated through the molten iron as it rises therethrough and reacts therewith. The smaller the particle size, the greater the surface area is in proportion to the weight of the carbide; and greater surface area results in better wetting of the particles by the molten metal to produce a high reaction efficiency. Further, since the specific gravity of calcium carbide is much less than that of molten iron, the importance of introducing calcium carbide properly is even more apparent. Experiments have shown that only the carbide which is wetted and reacts is effective; the present invention includes a means for efficiently reacting solid finely divided carbide with molten gray cast iron compositions without the necessity of altering the foundry procedures or apparatus used by the cast iron industry in large scale commercial manufacture.

The product of the present invention can be obtained in the as-cast condition, without the necessity of resorting to any heat treatment or any other additional step. However, additional treatment, such as annealing or other heat treatment of the castings may be used in some instances to improve the properties of gray cast iron compositions treated in accordance with the present invention. For example, the molten composition after treatment thereof may be cast in a chill mold which causes the carbon to be retained predominantly or wholly in combined form. The resultant chilled casting may be annealed to provide a cast product containing uncombined carbon in spheroidal or nodular form.

6

The carbide injection operation can be carried out readily in any suitable receptacle containing a charge of molten iron for treatment in a batch operation; or molten metal having been previously melted in a conventional furnace is allowed to flow in a suitable treating vessel, such as a forehearth or ladle, the metal flow being either continuous or intermittent. Finely divided calcium carbide is introduced below the surface of the molten metal, preferably at least 5 or 6 inches. After the metal is separated from the resulting slag, the metal is then cast into suitable molds. The time interval in minutes between the final injection of calcium carbide and the casting (holding time) is found to be important. When said holding time is too large, the effect of the treatment is decreased. The temperature of the molten metal at the time of injection is not critical, though it does have some effect on the holding time permitted; the temperatures conventionally used in foundry are satisfactory.

The following examples are cited for the purpose of showing that the addition of calcium carbide in accordance with the invention to molten gray cast iron produces improved properties in the resulting cast product when compared to a cast product of untreated iron from the same molten gray cast iron bath.

EXAMPLE I

A hypereutectic cast iron bath was established, containing about 3.79% carbon, 3.01% silicon, 0.60% manganese, 0.019% phosphorus, and 0.043% sulphur. Finely divided calcium carbide entrained in nitrogen was introduced below the surface of the metal bath held in an acid lined furnace. The amount of calcium carbide was in the proportion of 100 pounds per ton of molten iron; the treated metal was cast three (3) minutes after the injection of calcium carbide. The metal was inoculated with ferrosilicon in an amount sufficient to add from 0.2% to 0.4% silicon to the metal after carbide treatment and prior to casting. The resulting gray cast iron had a tensile strength of 36,500 pounds per square inch. The untreated cast iron from the same metal bath (with the ferrosilicon inoculation but omitting the carbide treatment) had a tensile strength of 15,500 p.s.i. The structure of the untreated cast iron included relatively large flakes of graphite in a matrix of coarse pearlite; while the structure of the treated iron had areas of small and large graphite flakes, some nodules, ferrite matrix, and an open eutectic network of coarse pearlite and graphite.

EXAMPLE II

A hypoeutectic cast iron bath was established, containing about 3.5% carbon, 1.9% silicon, 0.9% manganese, 0.075% phosphorus, and 0.1% sulphur. Finely divided calcium carbide entrained in nitrogen was introduced below the surface of the metal bath. The amount of calcium carbide injected was in the proportion of about 8 pounds per ton of molten iron; the treated metal was cast about five (5) minutes after the injection of the carbide. The molten metal was treated as it flowed continuously through an acid lined forehearth, at a rate of 10 tons per hour. The resulting gray cast iron had a tensile strength of 45,000 p.s.i., as compared to 34,000 p.s.i. for the same iron as cast without treatment. No graphitizing inoculant was used; the only treatment was the carbide addition.

The preceding example of treatment with calcium carbide alone (the conventional inoculation with ferrosilicon and similar known graphitizers being omitted) shows a definite improvement or upgrading of gray cast iron. The example of treatment with both carbide and ferrosilicon shows that a considerable improvement can also be obtained with a combined treatment of carbide and a conventional inoculant.

We have also discovered that gray cast irons, both hypo- and hypereutectic, can be upgraded or nodularized

by a treatment with finely divided calcium carbide and magnesium oxide in the form of finely divided particles of MgO mixed with the carbide. The process, except for the addition of the MgO, is the same as that described hereinbefore for calcium carbide alone. As before, the holding time is important, i.e., the time in minutes between the final injection of mixture and the casting of molten metal into suitable molds should not be unduly long. The mixture of calcium carbide and magnesium oxide usually produces greater improvements in the cast iron than the calcium carbide alone. The presence of magnesium oxide insures a nodular form of graphite to some degree, resulting in greater tensile strength; and reduces the amount of calcium carbide necessary to obtain a predetermined tensile strength. The magnesium oxide can also be supplied, either wholly or partially, by using it in the form of a basic or magnesia lining for the vessel in which the molten bath is maintained during the carbide injection.

The following is a table of examples of hypereutectic cast irons, their compositions, and physical and mechanical properties both before and after treatment with the mixture of calcium carbide and magnesium oxide.

Table I

BASIC LINED FURNACE

Untreated Alloy No.	Treated Alloy No.	Holding Time	C Percent	Si Percent	S Percent	Mn Percent	P Percent	C Equiv.	Ultimate Tensile Strength (p.s.i.)	Brinell Hardness No.
270	270 ¹	4	3.04	2.27	0.029	0.59	0.017	3.80 (Hypo)	24,800	132
271	271 ¹	6	3.70	2.66	0.011	0.57	0.023	4.59	70,250	159
272	272 ¹	7	3.85	2.49	0.031	0.77	0.019	4.68	14,300	100
273	273 ¹	6	3.86	2.91	0.032	0.74	0.026	4.83	52,130	180
			3.86	2.80	0.025	0.59	0.018	4.79	13,350	78
			3.89	2.91	0.013	0.62	0.017	4.86	63,700	195
			3.74	2.72	0.023	0.57	0.022	4.65	13,630	82
			3.93	2.51	0.016	0.62	0.022	4.77	42,000	144

ACID LINED FURNACE

282	a 282 ¹	6	3.88	3.33	0.044	0.54	0.013	4.99	14,550	88
283	b 283 ¹	12	3.82	3.18	0.013	0.55	0.017	4.88	52,000	197
286	c 286 ¹	20	3.84	2.95	0.045	0.54	0.018	4.82	14,630	79
287	d 287 ¹	28	3.83	3.23	0.013	0.55	0.011	4.91	46,500	179
288	e 288 ¹	28	3.73	2.74	0.019	0.42	0.017	4.64	10,500	88
			3.82	2.94	0.013	0.46	0.021	4.80	29,350	126
			3.78	3.19	0.013	0.47	0.010	4.84	13,380	82
			3.83	3.19	0.012	0.49	0.010	4.89	37,750	131
			3.76	3.07	0.020	0.47	0.019	4.78	14,300	85
			3.78	2.81	0.010	0.43	0.023	4.72	34,000	149

¹ Plus MgO in an amount equal to 3.6% of the CaC₂-MgO mixture.

^a Same but with 4.8% MgO.

^b Same but with 5.0% MgO.

^c Same but with 10% MgO.

^d Same but with 20% MgO.

The results in the above table illustrate the upgrading of as-cast hypereutectic ferrous alloys by the application of our invention, using calcium carbide and magnesium oxide, and a conventional inoculant (ferrosilicon). The alloys include a variety of matrix structures, chiefly ferritic or pearlitic, or a mixture of both. The proportional amount of calcium carbide injected varied from thirty (30) to one hundred and five (105) pounds to each ton of molten metal; said carbide was fed at a rate of 3 to 5 pounds per minute; and 0.2 to 0.4 cubic foot of a gaseous carrier (nitrogen) was used for each pound of calcium carbide. The holding time ranged from four (4) to twenty-eight (28) minutes, the maximum improvements (for the 60 lb. test quantities of iron cast) occurring in holding times up to fifteen minutes. The tensile strength of the treated irons showed an increase of 130% to 377% over the untreated irons of the same compositions; or an increase of 19,700 to 50,350 pounds

per square inch. The ferrosilicon inoculating agent addition (added to both the treated and untreated irons) amounted to 0.25% to 0.50% of the molten metal, sufficient to add 0.2 to 0.4% silicon to the metal. A microscopic examination of the treated irons revealed considerable modification when compared to the respective untreated irons. The latter had relatively large graphite flakes, and usually a closed eutectic network of pearlite and graphite. In the treated irons were found graphite flakes of small length, more compacted; nodules ranging from 10 to 90% of the total graphite structure; and an open eutectic network of pearlite and graphite. The treatment definitely produced nodules and smaller graphite flakes, thus resulting in improved mechanical and physical properties.

The influence of a mixture of calcium carbide and magnesium oxide on the structure of a specific gray iron, designated in the preceding table as Alloy No. 272, is illustrated in Figs. 2, 3, and 4. Fig. 2 shows the structure of a normally as-cast gray iron of a definite composition; Fig. 3 shows the structure of an as-cast gray iron produced seven minutes after final injection of the mixture; while Fig. 4 shows the structure obtained four-

teen minutes after injection. Fig. 2 shows the relatively large graphite flakes obtained in normally cast irons; and Fig. 3 shows a large percentage of nodular or spheroidal form of graphite. Fig. 4 clearly shows how the effect of carbide treatment is decreased if the holding time is long, in this instance (for the 60 lb. test batches cast) only fourteen minutes. Large quantities or batches of iron as used in commercial production may be held for longer times after treatment and prior to casting without appreciable decrease of the treatment effect.

The following table includes examples of hypoeutectic cast irons, their compositions, and properties both before and after treatment. The cast irons were treated with finely divided calcium carbide and magnesium oxide (either in the form of a basic vessel lining or as a combination of finely divided MgO particles and a magnesia vessel lining); but no ferrosilicon inoculating material was added.

Table II
BASIC LINED FURNACE

Untreated Alloy No.	Treated Alloy No.	Holding Time	C Percent	Si Percent	S Percent	Mn Percent	P Percent	C Equiv.	Ultimate Tensile Strength (p.s.i.)	Brinell Hardness No.
303	303 ^a	4	3.21	2.21	0.011	1.11	0.520	3.95	32,125	217
304	304 ^a	6	3.28	2.26	0.009	1.10	0.510	4.03	41,500	217
305	305 ^a	7	3.49	1.74	0.016	0.86	0.106	4.07	27,000	187
308	308 ^a	4	3.73	1.77	0.011	0.91	0.108	4.32	40,000	179
309	309 ^a	4	3.47	1.99	0.014	0.85	0.108	4.13	26,750	163
			3.67	1.74	0.012	0.89	0.108	4.25	41,230	172
			3.49	1.79	0.126	0.79	0.089	4.09	30,830	156
			3.59	1.65	0.018	0.81	0.090	4.14	51,750	217
			3.50	1.68	0.101	0.82	0.094	4.06	31,100	179
			3.62	1.73	0.033	0.88	0.098	4.20	57,750	229

^a Plus MgO in an amount equal to 10% of CaC₂-MgO mixture injected.

^b Same but with 5% MgO.

The results in the above table indicate the upgrading of as-cast hypoeutectic cast irons by the application of our invention, using a mixture of calcium carbide and magnesium oxide. The irons included a variety of matrix structures, including ferritic, pearlitic, or a combination of both.

A ratio of approximately 105 to 115 pounds of finely divided calcium carbide per ton of molten metal was used; the carbide was fed at a rate of 4 to 7 pounds per minute, with approximately one-quarter cubic foot of nitrogen per pound of carbide. The holding time, after the treatment of a 400 lb. induction melted heat poured with 60 lb. test ladles, ranged from 2 to 6 minutes for the maximum improvements. The treated irons have tensile strengths which are 33% to 85% greater than those of the untreated iron having the same compositions, or an increase of 10,375 to 20,650 pounds per square inch. A microscopic examination revealed that the treated iron had graphite structures modified considerably when compared to those of the respective untreated irons.

Upgrading is definitely obtained by introducing into the molten metal, finely divided calcium carbide alone, followed by casting into a suitable mold. The casting should be poured promptly after the carbide injection, preferably within about 20 minutes. Treatment with finely divided calcium carbide and magnesium oxide followed by casting promptly after the treatment, not only changes the relatively large graphite flakes to smaller, more compacted flakes, but produces some

the tensile strength of the treated iron was increased from 33% to 377%, but the increase in Brinell hardness number was surprisingly low for such increase in tensile strength. The new cast composition, therefore, has not only greater tensile strength but superior machining qualities because of the low hardness.

The use of conventional inoculants, such as ferrosilicon, impels or tends to aid the formation of carbon nodules or compacted graphite flakes in the treated irons. In some cases, nodules are obtained without the aid of an inoculant, especially in connection with hypereutectic cast irons treated with a mixture of finely divided calcium carbide and magnesium oxide; but in other cases an inoculant such as ferrosilicon may be necessary to aid in precipitating carbon nodules out of the metal solution.

To determine the effect of adding various percentages of a late inoculant in combination with the calcium carbide treatment of hypereutectic cast irons, several tests were conducted. The following table includes examples of such irons, their compositions and properties after treatment either with a late ferrosilicon inoculant alone or with the combination of calcium carbide and a late ferrosilicon inoculant. The calcium carbide was injected into the molten metal in the induction furnace, while the ferrosilicon was added to iron in the ladle just prior to casting. Of course, the silicon may be introduced in other forms, such as, calcium silicide, nickel-silicon alloys, silicon metal, and the like.

Table III

Untreated Alloy No.	Treated Alloy No.	Calcium Carbide Injected Lbs./Ton	Magnesium Oxide Injected Lbs./Ton	Ferrosilicon (75% Silicon) Added, Lbs./Ton	Chemical Analysis					Carbon Equivalent	Ultimate Tensile Strength (p.s.i.)	Brinell Hardness No.
					C percent	Si percent	Mn percent	S percent	P percent			
435 ¹	-----	-----	-----	10	4.10	1.73	.227	.014	.027	4.67	12,780	89.7
435 ²	-----	-----	-----	20	4.00	2.18	.225	.014	.027	4.73	11,620	87.2
435 ³	-----	-----	-----	40	3.87	3.07	.223	.015	.026	4.89	12,930	84.9
-----	435 ⁴	15	5	10	4.11	1.73	.224	<.005	.028	4.68	28,900	125.0
-----	435 ⁵	15	5	20	4.01	2.34	.218	<.005	.028	4.79	45,000	143.0
-----	435 ⁶	15	5	40	3.58	3.02	.219	<.005	.030	4.59	56,900	169.0
436 ¹	-----	-----	-----	10	3.83	2.45	.199	.015	.027	4.65	15,750	97.7
436 ²	-----	-----	-----	20	3.71	2.93	.199	.014	.028	4.69	15,300	94.9
436 ³	-----	-----	-----	40	3.61	3.69	.200	.014	.032	4.83	12,250	97.7
-----	436 ⁴	15	5	10	3.83	2.48	.198	<.005	.041	4.66	24,900	111.0
-----	436 ⁵	15	5	20	3.77	2.90	.196	<.005	.040	4.73	43,300	156.0
-----	436 ⁶	15	5	40	3.51	3.77	.195	<.005	.039	4.77	65,000	179.0

nodules, the degree of nodular structure varying from 10 to 90 percent of the total uncombined carbon. In general, treatment with our process produces greater improvements and more nodules in hypereutectic than hypoeutectic cast irons, or stated in another way, the amount of calcium carbide alone or the amount of the mixture of calcium carbide and magnesium oxide required to produce a given structure in hypereutectic iron is generally less than that required to produce the same structure in hypoeutectic iron. As shown in the examples,

The results in the above table show that increasing the quantity of the ferrosilicon inoculant alone had practically no effect on the tensile strength or hardness of the metal in the case of alloy Nos. 435¹, 435², 435³, 436¹, 436² and 436³. But when increasing amounts of ferrosilicon are added as late inoculants to substantially the same molten iron composition but which has been previously treated with calcium carbide and magnesium oxide, the ultimate tensile strength is progressively increased. Referring specifically to No. 436⁶, the ultimate

tensile strength showed an increase of about 50,000 p.s.i. over that of the untreated iron No. 436³ of substantially the same composition; and the No. 436⁶ iron had a predominately nodular graphite structure whereas the No. 436³ iron had no nodules. The calcium carbide and the ferrosilicon late addition have a mutually cooperative effect producing unexpected and advantageous results.

Treatment of gray cast iron compositions in accordance with the methods described above results in upgrading (i.e. effecting a net benefit or increase in desirable properties of the molten or cast metal) and, depending

kept lower than in the case where the iron is treated with magnesium alone.

The following is a table of a series of heats of hypereutectic iron showing compositions and physical and mechanical properties in the as-cast state, both before and after treatment with (1) magnesium, (2) calcium carbide and (3) calcium carbide-magnesium. The magnesium was added in the form of the alloy described above. Results of treatment with magnesium alone are shown to indicate the economic advantages of the carbide-magnesium combination treatment.

Table IV

Un-treated Alloy No.	Treated Alloy No.	Calcium Carbide Injected, Added, Lbs./Ton	Magnesium Alloy Added, Lbs./Ton	Chemical Analysis						Brinell Hardness No.	Ultimate Tensile Strength (p.s.i.)	Elongation in 2", Percent	FeSi (75% Silicon) Added, Lbs./Ton
				C Percent	Si Percent	Mn Percent	S Percent	P Percent	C Equiv.				
381 ¹	-----	-----	-----	3.89	3.44	.220	.014	.038	5.04	87.2	12,500	1.0	30
-----	381 ²	-----	28	3.57	3.28	.178	.009	.011	4.66	170.0	67,000	11.0	18
-----	381 ³	30	-----	3.92	3.49	.202	<.005	.040	5.08	167.0	41,900	1.5	30
-----	381 ⁴	30	20	3.54	3.57	.207	<.005	.040	4.73	187.0	73,200	8.0	20
390 ¹	-----	-----	-----	3.91	3.32	.196	.018	.046	5.01	89.7	14,300	0.5	30
-----	390 ²	-----	28	3.58	3.09	.192	.009	.045	4.61	174.0	68,900	10.0	18
-----	390 ³	30	-----	3.45	3.34	.191	<.005	.045	4.56	137.0	37,600	1.0	30
-----	390 ⁴	30	20	3.44	3.02	.191	<.005	.044	4.45	163.0	68,900	12.5	20
391 ¹	-----	-----	-----	3.90	3.18	.198	.011	.044	4.96	94.9	15,070	1.0	30
-----	391 ²	-----	28	3.32	3.16	.199	.006	.043	4.37	174.0	72,100	11.0	18
-----	391 ³	30	-----	3.57	3.19	.197	<.005	.045	4.63	134.0	40,630	1.0	30
-----	391 ⁴	30	20	3.49	3.21	.197	<.005	.040	4.17	179.0	70,150	7.0	20

upon the degree and nature of the treatment, may also result in modifying the uncombined or graphitic carbon so that it exists in the nodular form.

Another form of treatment, which is found particularly useful in the large scale production of a substantially wholly or totally nodular cast iron product, involves the addition of a small amount of a nodulization-impelling agent to the molten metal, in addition to the calcium carbide or calcium carbide and magnesium oxide. The amount of such agent contemplated by the present invention may be by itself insufficient to control the occurrence of a substantial amount of nodular graphite; and the amount of calcium carbide used may be by itself insufficient to produce a substantially nodular product. But the combination of calcium carbide and the nodulization-impelling agent has been found effective consistently to produce a gray cast iron which is predominantly or wholly nodular. The term nodulization-impelling agent is used herein to means those agents which may directly or indirectly cause the occurrence of nodular graphite in gray cast irons. The uncombined or free carbon of the cast irons treated in this manner ordinarily exists entirely in nodular or spheroidal form without resorting to any heat treatment. Experiments have shown that the nodulization-impelling agent may be added or injected into the molten metal simultaneously with, or added or injected subsequent to, the calcium carbide injection. One example of such an agent is magnesium; but its introduction as the pure metal into molten iron is impractical, a fact well known in the art. Because of its comparatively low boiling point and high degree of reactivity, substantial losses occur when pure magnesium is introduced in the usual way into a molten cast iron bath. It is therefore preferred to inject the magnesium with the calcium carbide or to add the magnesium as an alloy, such as one containing approximately 15% magnesium, 35% nickel, 10% copper, 25% silicon, and 15% iron. The prior art discloses the treatment of molten iron with sufficient magnesium to given a residual magnesium content in excess of about 0.04 percent, in order to obtain a nodular product. But the use of magnesium alone is much more costly than the combination carbide-magnesium treatment of the present invention. Further, improved results can be obtained with the combination carbide-magnesium treatment, and the retained magnesium content of the final nodular product may be

The results in the above table illustrate the upgrading of as-cast hypereutectic cast irons by the application of the invention to produce a substantially totally nodular cast iron product without resorting to any heat treatment, using calcium carbide and magnesium in the form of the alloy previously described, and a conventional inoculant (ferrosilicon). The matrix structures of the alloys as-cast without treatment are chiefly ferritic and pearlitic, and the pearlitic structure predominates as shown in Fig. 5; the matrix structure of the alloys as-cast after treatment is predominantly ferritic. The proportional amount of calcium carbide was thirty pounds per ton of molten metal; said carbide was fed at a rate of 4 pounds per minute; approximately 0.2 cubic foot of a gaseous carrier (nitrogen) was used for each pound of calcium carbide; and the holding time ranged from two to six minutes. The ferrosilicon inoculating agent addition, added to both the treated and untreated irons amounted to 0.9 to 1.5% of the molten metal, sufficient to add 0.8 to 1.20% silicon to the metal. A microscopic examination of the structures of the treated irons reveal considerable modification when compared to the respective untreated cast irons, especially with regard to uncombined carbon. As shown in Fig. 5, a typically untreated cast iron employed in the above examples had relatively large graphite flakes. Referring to Fig. 6, alloy No. 381⁴ treated with the combination of calcium carbide and magnesium was practically devoid of any flake graphite and had a substantially 100% nodular graphite formation. The tensile strength of irons treated with such a combination of materials showed an increase of 372% to 486% over the untreated irons of the same compositions, or an increase of 54,600 to 60,700 pounds per square inch. The amount of magnesium used in the combination carbide-magnesium treatment may be at least 30% less than the amount of magnesium required for treatment with magnesium alone, for products of approximately the same tensile strength. While this amount may not seem large percentagewise, economically it represents a large saving when considering a large scale commercial operation. The cost of the magnesium alloy is so much greater than that of carbide, and the total quantities of treatment agents for commercial production are so large that a considerable difference results in cost of treatment material per ton of metal cast.

While the data for alloys Nos. 381³, 390³, and 391³ treated with calcium carbide alone indicate a definite upgrading and some nodular structure, the ultimate tensile strength and the amount of nodular graphite are less than those for the alloys treated with the combination of calcium carbide and magnesium.

Using cast iron of substantially the same composition as those indicated in the preceding table, several tests were conducted in which the carrier gas was either argon or carbon dioxide. The resulting products and their properties were similar to those obtained with nitrogen as the gaseous carrier, provided other conditions were the same. The gas used in the injection process of the present invention is preferably substantially inert with respect to the metal being treated; the gas should not appreciably or detrimentally react in a manner which might unfavorably change or modify the ideal conditions for upgrading and nodulizing.

Experiments conducted with magnesium added as an alloy containing approximately 15% magnesium, 65% silicon and 20% iron under substantially the same conditions gave results which were about the same as those obtained involving the use of the alloy containing approximately 15% magnesium, 35% nickel, 10% copper, 25% silicon, and 15% iron.

As indicated hereinbefore, treatment of the cast irons with calcium carbide and magnesium oxide and a late ferrosilicon inoculating addition produced up to a 90% nodular structure of graphite and 10% of compacted flake graphite. We have found that an additionally relatively small amount of magnesium incorporated into the molten iron insures reproducibility of results and a substantially complete nodular graphite structure. The extent of the nodular formation may be controlled by the amount of magnesium introduced. The following table includes examples of hypereutectic cast irons, their compositions and physical and mechanical properties in the as-cast state, both before and after treatment with (1) magnesium, (2) calcium carbide and magnesium oxide and (3) calcium carbide, magnesium oxide and magnesium. The magnesium was added in the same alloy form as in Table IV.

Table V

Alloy No. (Untreated)	Alloy No. (Treated)	CaC ₂ Injected, Lbs./Ton	Mg Alloy Added, Lbs./Ton	MgO Injected, Lbs./Ton	Chemical Analysis					CE	BHN	Ultimate Tensile Strength (p.s.i.)	Elongation in 2 inches, Per-cent	FeSi (75% Si) Added, Lbs./Ton	Magnesium Retained, Per-cent
					C Per-cent	Si Per-cent	Mn Per-cent	S Per-cent	P Per-cent						
383 ¹	388 ²	-----	28	-----	4.08	3.62	.224	.012	.043	5.29	92.3	16,200	1.5	30	<.001
-----	388 ²	-----	28	-----	3.53	3.32	.225	<.005	.043	4.64	167.0	71,150	11.0	18	.055
-----	388 ²	30	-----	5	3.65	3.48	.222	<.005	.046	4.81	170.0	56,000	1.5	30	.008
-----	388 ²	30	10	5	3.87	3.58	.222	<.005	.044	4.92	174.0	65,000	6.5	26	.029
386 ¹	386 ²	-----	-----	-----	3.96	3.54	.195	.017	.054	5.14	87.2	14,600	1.5	30	<.001
-----	386 ²	-----	28	-----	3.67	3.09	.199	.008	.042	4.70	163.0	64,750	8.5	18	.037
-----	386 ²	15	-----	5	3.72	3.36	.189	<.005	.053	4.84	149.0	54,400	2.0	30	.006
-----	386 ²	15	10	5	4.03	3.36	.195	<.005	.046	5.15	167.0	62,700	6.0	26	.026

The above table illustrates the upgrading and nodulization of as-cast hypereutectic ferrous alloys by the application of our invention and without resorting to any heat treatment, using calcium carbide, two nodulization-impelling agents (magnesium oxide and magnesium) and a conventional late inoculant (ferrosilicon). The proportional amount of calcium carbide injected was 30 and 15 pounds per ton of molten metal; the carbide was fed at a rate of 4 pounds per minute; about 0.2 cubic foot of the nitrogen carrier gas was used for each pound of calcium carbide; and the holding time varied from three to six minutes, the carbide and magnesium

oxide being injected into 400 lb. heats and the magnesium and ferrosilicon additions being made to 60 lb. ladles poured therefrom. The ferrosilicon inoculant, added to both the treated and untreated irons, amounted to 0.9 to 1.5% of the molten metal sufficient to add about 0.75 to 1.20% silicon to the metal. As shown in Fig. 5, the matrix structures of the alloys listed in the above table are chiefly ferritic and pearlitic before treatment, and predominantly pearlitic after treatment. The tensile strength of irons treated with calcium carbide, magnesium oxide, and magnesium in the proportional amounts listed in the preceding table showed an increase of 301% to 329% over the untreated irons of the same compositions—or an increase of 48,100 to 48,800 pounds per square inch. The Brinell hardness number was increased from about an average of 90 to an average of 170. The sulphur content was reduced from .012 to .005%. Fig. 7 is a microstructure of alloy No. 383⁴. It shows a predominantly nodular cast iron product, with a pearlitic-ferritic matrix. Alloy Nos. 383³ and 386³ show definite upgrading and the major part of the graphite in nodular formation. The small addition of magnesium as shown in alloy Nos. 383⁴ and 386⁴ produced more nodules and increased the tensile strength. The combination, including magnesium, gives consistently good results.

For the purpose of showing comparatively the effects of (1) magnesium oxide alone and (2) the combination of calcium carbide and magnesium oxide, a molten metal bath was established of substantially the same composition indicated in the preceding table. Before treatment and in the as-cast state, the iron had an ultimate tensile strength of 14,250 p.s.i. After treatment of the original metal with 30 pounds of magnesium oxide per ton of metal, the ultimate tensile strength of the iron was only 14,450 p.s.i. Yet, as the preceding tables show, the combination of calcium carbide and magnesium oxide increases the tensile strength of the cast iron as much as several hundred percent. It is believed that the calcium carbide reacts with magnesium oxide to reduce it and free elemental magnesium, which then participates in the calcium carbide injection treatment to

cause the subsequent formation of nodular iron.

Other nodulization-impelling agents may be used instead of, or in addition to, the magnesium addition of Table IV. For example, rare earth metals, alloys, or compounds or mixtures thereof, such as alloys of lanthanum and the lanthanum series rare earth metals or mixtures of their oxides, may be used. The following is a table of heats of hypereutectic iron showing compositions and physical and mechanical properties in the as-cast state, both with and without a combination treatment using calcium carbide, magnesium oxide and rare earth metal compounds.

Table VI

Alloy No. (Untreated)	Alloy No. (Treated)	CaC ₂ Injected, Lbs./Ton	MgO Injected, Lbs./Ton	Rare Earth Oxides Injected, Lbs./Ton	Chemical Analysis					CE	BHN	Ultimate Tensile Strength (p.s.i.)	Elongation in 2 inches, Percent	FeSi (75% Si) Added, Lbs./ton, Percent
					C Percent	Si Percent	Mn Percent	S Percent	P Percent					
443 ¹	-----	-----	-----	-----	3.84	3.35	.211	.020	.045	4.96	84.9	12,000	0	1.5
-----	443 ³	15	5	a 1	3.66	3.25	.212	<.005	.042	4.74	163.0	64,000	6.1	1.5
437 ¹	-----	-----	-----	-----	3.78	3.32	.198	.013	.048	4.89	87.2	12,920	0	1.5
-----	437 ³	15	5	b 2	3.59	3.27	.197	<.005	.053	4.68	167.0	64,750	5.5	1.5

^a Rare earth oxide mixtures.

^b 12% calcium boride, 8% sodium nitrate, 80% rare earth oxide mixtures.

The data tabulated above illustrate the upgrading and nodulization of hypereutectic ferrous alloys by treatment with calcium carbide, magnesium oxide, and rare earth metal or metals in the form of reducible rare earth compounds or mixtures thereof to produce a substantially totally nodular cast iron product without resorting to any heat treating operation. The proportional amounts of each are indicated in the preceding table, as pounds per ton of metal. The usual late ferrosilicon addition was included. As the table shows, surprisingly improved results are obtained with an exceptionally small amount of the rare earth oxides. In the case of alloy No. 443³, the use of one pound of rare earth oxides per ton of metal produced a cast iron having an ultimate tensile strength of 64,000 p.s.i., an increase of 52,000 p.s.i. over the untreated iron of the same composition. The rare earth oxides, injected in admixture with the calcium carbide, comprised a mixture sold commercially as "Rare Earth Oxide Mixture" containing approximately 48% cerium oxide, 24% lanthanum oxide, 19% neodymium oxide, and the balance other rare earth oxides.

In the case of alloy No. 437³, similar results were obtained from the use of two pounds of a mixture of rare earth oxides with calcium boride and sodium nitrate per ton of metal. The mixture, sold commercially as "T-compound," comprised approximately 80% of the above rare earth oxide mixture plus 12% calcium boride and 8% sodium nitrate. Though calcium boride and sodium nitrate were present (because they are included in the commercial "T-compound" for reduction purposes) they apparently were not required for nodulization in view of the fact that similar results were produced in the alloy No. 443³ with "Rare Earth Oxide Mixture." The ultimate tensile strength of the treated iron (alloy No. 437³) was increased 400% over that of the untreated iron of the same composition.

The microstructure of this alloy is shown in Fig. 8. The as-cast structure is substantially completely nodular.

Magnesium oxide need not be used in the combination calcium carbide-rare earth oxide treatment. This is shown by the following summary of representative tests involving the treatment of cast irons having substantially the same compositions as those in the preceding table, but using only calcium carbide and rare earth oxides as the treating agents, the magnesium oxide being omitted. The operating conditions were virtually identical. In one example (Heat No. 467³), the finely divided calcium carbide was injected in a ratio of 15 pounds of carbide per ton of metal, and the rare earth oxides in the form of the commercial "Rare Earth Oxide Mixture" were injected in admixture with the carbide in a ratio of 1 pound of rare earth oxides per ton of metal. The untreated iron had an ultimate tensile strength of 13,900 p.s.i. and a Brinell hardness number of 85; whereas, the treated iron had a tensile strength of 69,600 and a hardness number of 170. The latter iron had a tensile strength which was 400% greater than that of the untreated iron, or an increase of 55,700 p.s.i. In another example (Heat No. 462³), the ratio of carbide to metal was 15 pounds per ton, and the rare earth oxides were

15 injected in a ratio of 2 pounds of "Rare Earth Oxide Mixture" per ton of metal. The ultimate tensile strength of the treated iron was 62,800 p.s.i. as compared to the 14,800 p.s.i. of the untreated iron.

The invention not only enables extremely small amounts of the rare earth nodulization-impelling agents to be used but also enables the rare earths to be used in their inexpensive, readily available, oxide form. Tests show that rare earth oxides when injected alone (the calcium carbide and other agents being omitted) are ineffective. For example (Heat No. 461¹), two pounds of "Rare Earth Oxide Mixture" injected into a representative molten gray cast iron composition, followed by the usual late ferrosilicon addition, gave no noticeable improvement in the as-cast product. Similarly (Heat No. 462¹) the addition of two and one-half pounds of "T-compound" produced no noticeable improvement in the properties of the as-cast product. But the combination treatment, using calcium carbide and about one or two pounds of rare earth oxides, produced high quality upgraded and nodular iron having the properties given above for the Heat No. 467³ and Heat No. 462².

It is believed that when the combination calcium carbide-rare earth oxide treatment is used, the carbide reduces the oxide and frees the rare earth metal element, which then participates in the combination treatment to form the upgraded or nodular iron. Thus, the rare earth metal itself could be used, if desired, in combination with the calcium carbide to effect the combination treatment. As shown above only very small amounts of the rare earth metal oxides are required in the combination treatment and similarly only extremely small amounts of the rare earth metals need be added when used in combination with calcium carbide, and which amounts are insufficient by themselves to control the occurrence of any appreciable upgrading or significant amount of nodular graphite.

The nodulization-impelling agents, if in reducible compound or oxide form, are preferably injected simultaneously with the calcium carbide, in finely divided form, and they may be in admixture with the finely divided calcium carbide. The nodulization-impelling agents, if in elemental or metallic form, are preferably added to the molten metal either simultaneously with the calcium carbide injection or just subsequent thereto, and they may be injected in finely divided form and may be in admixture with the finely divided calcium carbide.

The rare earth oxides as used with the present invention are believed to be reduced by the injected calcium carbide at the normal founding temperatures (2400° F. to 2900° F.) of the metal baths to liberate cerium, lanthanum, and other rare earth elements. In contrast, magnesium oxide is a refractory oxide and is therefore not as readily reduced by the injected calcium carbide at the temperatures of the bath, and this may be one of the reasons why it is not as effective in the combination treatment as the rare earth oxides for purposes of nodulization.

The data listed in the preceding tables was taken from test samples, such as arbitration bars and keel blocks, as-cast in dry sand molds. The iron was melted and

injection treated in approximately 400 lb. heats in an induction furnace. Additions were made in some instances directly into the molten metal while in the furnace and in other cases to the metal while in the ladle from which it was poured into the molds.

The cast iron products obtained from molten irons treated in accordance with the methods described above have markedly improved properties (for example, the improved tensile strengths indicated in the various tables) in the as-cast condition. The calcium carbide treatments of the present invention, as described above, may each also be used in combination with a heat treatment step, wherein the carbide treated product is heat treated or annealed subsequent to casting. Such combination treatment, involving a heat treatment operation, is particularly useful in the production of products such as cast iron pipe produced by the de Lavaud process, wherein the iron

both as-cast in dry sand molds (without heat treatment) and as heat treated or annealed following casting in a chill or graphite mold. In all cases, a late ferrosilicon inoculant was added to each alloy. The compositions

- 5 of the cast irons in the as-cast condition included carbon in the range from 3.40% to 3.90%, silicon from 2.40% to 3.20%, manganese from 0.18% to 0.26%, phosphorous from .010% to .050%, less than .005% sulphur, and the balance substantially all iron. These irons in the
- 10 untreated sand cast state (the carbide treatment and the heat treatment both being omitted) had tensile strengths ranging from 10,000 to 16,000 p.s.i. and Brinell hardness numbers of 75 to 95. The same untreated iron composition, when cast in a chill mold according to the de Lavaud
- 15 practice (including a heat treatment but omitting the carbide treatment) has tensile strengths of about 20,000 to 25,000 p.s.i.

Table VII

Alloy No. (No Heat Treat- ment)	Alloy No. (Heat Treated)	CaC ₂ Injected, Lbs./Ton	FeSi (75% Si) Added, Lbs./Ton	MgO In- jected, Lbs./Ton	Ni-Mg Alloy Added, Lbs./Ton	Rare Earth Oxides Injected, Lbs./Ton	Elonga- tion in 2 inches, Percent	Reduction in Area, Percent	BHN	Ultimate Tensile Strength (p.s.i.)
376 ²	---	30	10	---	---	---	1.0	---	128	30,100
---	376 ²	30	10	---	---	---	7.1	---	149	56,800
379 ²	---	30	10	---	---	---	2.0	---	143	38,350
---	379 ²	30	10	---	---	---	5.0	---	159	55,400
380 ²	---	60	10	---	---	---	2.0	---	129	39,350
---	380 ²	60	10	---	---	---	10.1	---	149	62,200
381 ³	---	30	30	---	---	---	1.5	2.0	167	41,900
---	381 ³	30	30	---	---	---	21.4	---	---	73,400
391 ³	---	30	30	---	---	---	1.0	---	134	40,630
---	391 ³	30	30	---	---	---	16.0	17.6	159	72,500
393 ³	---	30	30	---	---	---	9.5	7.3	137	40,000
---	393 ³	30	30	---	---	---	18.0	18.0	154	72,100
436 ⁴	---	15	10	5	---	---	0	0	111	24,900
---	436 ⁴	15	10	5	---	---	6.4	6.0	129	55,900
436 ⁵	---	15	40	5	---	---	2.0	3.5	179	65,000
---	436 ⁵	15	40	5	---	---	9.3	11.0	165	79,500
394 ³	---	15	30	10	---	---	---	---	146	47,250
---	394 ³	15	30	10	---	---	17.0	16.0	159	74,000
440 ³	---	15	30	5	---	---	0	0	142	37,400
---	440 ³	15	30	5	---	---	18.8	20.0	148	67,000
383 ⁴	---	30	26	5	10	---	6.5	---	174	65,000
---	383 ⁴	30	26	5	10	---	10.0	18.0	171	78,800
394 ⁴	---	30	26	10	10	---	4.5	3.0	167	60,600
---	394 ⁴	30	26	10	10	---	17.0	24.0	165	75,000
381 ⁴	---	30	20	---	20	---	8.0	6.1	187	73,200
---	381 ⁴	30	20	---	20	---	24.3	---	---	72,400
391 ⁴	---	30	20	---	20	---	7.0	4.8	179	70,150
---	391 ⁴	30	20	---	20	---	20.0	17.6	165	76,300
393 ⁴	---	30	20	---	20	---	6.0	3.0	170	65,000
---	393 ⁴	30	20	---	20	---	19.0	19.0	159	74,850
443 ²	---	30	30	5	---	1	6.1	7.5	163	64,000
---	443 ²	30	30	5	---	1	11.1	13.0	159	73,000

is cast partially or wholly "white" in a chill mold. Greatly improved properties in the final product are provided by a chemical treatment with calcium carbide (and preferably a nodulization-impelling agent) as described above, casting in a chill mold (for example by the de Lavaud process) and then heat treating or annealing the resulting as-cast product to produce a wholly or predominantly nodular product of relatively high ductility and high strength.

The following is a table which compares the properties of products cast from the same molten hypereutectic gray cast iron bath following carbide treatment in one of the ways disclosed above, and which products were (a) cast in a sand mold without subsequent heat treatment and (b) heat treated or annealed following casting in a chill mold. The compositions of the different baths (i.e. 376², 379², etc.) were slightly different, within the range of compositions for the as-cast product as stated below. The various forms of carbide treatments included all of the following, as indicated in the table: (1) calcium carbide alone, (2) calcium carbide and magnesium oxide, (3) calcium carbide, magnesium, and magnesium oxide, (4) calcium carbide and magnesium, and (5) calcium carbide, magnesium oxide, and the "Rare Earth Oxide Mixture" mentioned above. The tensile strengths and hardness of such carbide treated irons are given

The various heat treated products of the above table were poured into graphite molds to produce $\frac{3}{8}$ x $\frac{1}{2}$ inch cross-section test bars. The resulting "white" or chilled castings were then annealed as follows. They were heated in a furnace to a temperature of 1700° F. to 1750° F. and maintained at such temperature for a period of about 1 and $\frac{1}{2}$ hours; the casting was cooled to about 1500° F. and held there for about one hour and fifteen minutes, and then cooled to 1300° F. at a rate not exceeding about 100° per hour. The casting was held at 1300° F. for about 1 and $\frac{1}{2}$ hours, and then cooled to 1000° F. and kept there for about one hour, followed by air cooling to room temperature.

The non-heat treated products of the above table were cast in the conventional keel blocks.

The above data clearly shows the advantages of the combination carbide treatment-heat treatment of the present invention. Not only were the tensile strengths increased by as much as 32,000 p.s.i., but also the ductility increased greatly, as evidenced by the percentage increase of elongation in a 2" length, and the relative low Brinell hardness number. Referring, for example to alloy Nos. 381³, 394⁴, and 393⁴, heat treated products were produced with a tensile strength of about 75,000 p.s.i., about 20% elongation in 2", about 22% reduction in area, and a Brinell hardness number of about 165. The

combination carbide-annealing treatment produced a very desirable combination of properties—high tensile strength coupled with high ductility. Fig. 9 shows the microstructure of alloy No. 383⁴, a gray iron product annealed in the manner indicated above. Prior to casting, the molten iron composition had been treated with calcium carbide, magnesium oxide, and magnesium. Fig. 9 shows substantially all of the uncombined carbon in nodular form; the alloy has a tensile strength of 78,800, a Brinell hardness number of 171, 10% elongation in 2", and 18% reduction in area. The matrix of the microstructure is predominantly ferritic.

The heat treatment contemplated by the invention produces a product having its uncombined carbon predominantly or substantially wholly in the form of nodules which generally are well distributed, uniform, regular, and fairly dense. Comparing Fig. 9 to Fig. 7, it will be noted that the sand cast product is partially nodular whereas the chill cast and annealed product is completely nodular.

It has been found that a relatively small amount of chromium when added to a calcium carbide treated iron produces an inexpensive product with desirable characteristics. Chromium is a powerful carbide former which intensifies the chilling tendencies of gray cast iron, which in many cases (particularly for thin section castings) is a disadvantage. But when chromium is used in combination with the carbide treatment the resulting product is an inexpensive high quality iron with a surprisingly low hardness and small depth of chill. In one application of this invention, a hypoeutectic cast iron was established, containing about 3.5% carbon, 1.9% silicon, .07% sulphur, and the balance substantially all iron. The untreated iron had a tensile strength of about 34,000 p.s.i., a Brinell hardness number of 187, and a chill depth of about 3/8". Treating this metal with about 8 pounds of calcium carbide per ton of metal and adding about 12 pounds of chromium per ton of metal produced an iron containing about .02% sulphur and having a tensile strength of about 45,000 p.s.i. with the same Brinell hardness number of 187, and the same depth of chill. Chromium is relatively inexpensive compared to other alloying elements; and the combined treatment of calcium carbide and chromium results in a cast iron product having properties even superior to those obtained heretofore by the use of very expensive alloying elements.

It has been found that treatment of irons with calcium carbide or with carbide and a nodulization-impelling agent to produce improved properties does not depend upon any critical temperature of the molten metal; as stated above, normal founding temperatures may be used. The calcium carbide does not adversely affect the metal temperature, so that good results are obtained as long as such temperature before treatment is satisfactory (in accordance with conventional procedures) for a given casting operation. While it has not been established conclusively that the carbide treatment adds heat to the molten metal, at least no lowering of temperature is experienced, which is the case when adding a similar quantity of previously known addition alloys to the iron bath. It is well known in the art that if the casting temperature is maintained constant, the fluidity of gray cast iron increases with the carbon content until a carbon equivalent of 4.3% is reached, and thereafter the fluidity decreases at higher carbon contents. In the application of our invention to the treatment of gray cast irons with calcium carbide, we have found that the fluidity of the carbide treated iron is not only superior to that of the untreated iron, but that it appears to increase past the eutectic concentration. The treated metal is relatively clear, flows freely, and before any freezing occurs it fills the mold completely, resulting in a superior casting. In general, the founding properties of the calcium carbide-treated cast iron are substantially improved when com-

pared to untreated irons of the same composition at the same temperature.

In the preceding examples involving treatment with calcium carbide alone or with carbide and nodulization-impelling agents, followed with ferrosilicon, the cast iron product contained a residual trace or retained an amount of calcium not exceeding 0.01%. Several spectrographic analyses of the as-cast articles of manufacture disclosed a retained calcium content of not more than 0.005%. In the examples involving treatment with calcium carbide and magnesium oxide alone, either with or without ferrosilicon inoculation, the cast iron product contained an amount of retained calcium not exceeding 0.01% and an amount of retained magnesium not exceeding 0.01%. Spectrographic analyses of some of these products revealed not more than 0.005% retained calcium nor more than 0.01% retained magnesium. With the combined carbide-magnesium treatment, a substantially wholly nodular as-cast product can be produced having a retained magnesium content of less than .04%; a predominantly nodular product may be produced having a retained magnesium content of less than .02%; and a high quality upgraded partially nodular product may be produced having a retained magnesium content of less than .01%. With the combined carbide-rare earth treatment predominantly or substantially wholly nodular as-cast products can be produced with no magnesium added, and the amount of rare earth retained is so small as not to be detectable by conventional analytical methods in the as-cast product.

For optimum results, it has been found that the calcium carbide particles should preferably be finer than 10 mesh and that at least 50% of the total carbide should preferably be finer than 48 mesh. The quantity of carbide injected should be within the range from 1.5 lbs. to 150 lbs. of carbide per ton of molten metal treated, and preferably for baths of the typical commercial cast iron compositions the amount of carbide injected should be within the range from 5 lbs. to 75 lbs. of carbide per ton of metal treated.

The most important element usually present in cast iron baths which affects the calcium carbide treatment is sulphur. Fortunately, calcium carbide is an efficient desulphurizing agent, as disclosed in the aforementioned pending application Serial No. 125,607. The same method of introduction can be used both for removing sulphur from the cast iron bath and for modifying the structure of the cast iron product to improve its properties. Thus, if the sulphur content is high, the amount of carbide used to upgrade the cast iron may be made larger than that used when the sulphur content is low. Examples Nos. 309 and 309¹ above show how the sulphur content is decreased and upgrading is effected by the injection of carbide.

Where magnesium oxide is introduced into the bath along with the calcium carbide, the MgO should constitute from 1% to 40% of the CaC₂-MgO mixture.

The invention is particularly applicable to gray iron compositions which as normally cast in sand molds provide a structure in which the graphite appears in the typical flake form, and which is composed of more than 90% iron, 1.7% to 4.5% carbon, 1.0% to 3.5% silicon, manganese 0.1% to 1%, not more than about 1% phosphorus, and sulphur. Beneficial results may also be obtained by the application of the invention to other cast irons, for example to cast irons containing more than 85% iron and having carbon from 1.7% to 4.5%, silicon from .20 to 4.0%, phosphorous up to 1%, and sulphur, with or without one or more alloying additions, such as the following in the ranges indicated: chromium .20 to 2.00%, nickel .50 to 2.0%, molybdenum .25 to 1.0%, copper .30 to 1.0%, vanadium .05 to .20%, magnesium up to .10%, and manganese .15 to 2.00%.

It is to be understood that the invention is not limited to the specific embodiment above described but may be practiced in other ways without departing from the spirit

and scope of the invention as defined in the following claims.

We claim:

1. In the art of manufacturing gray cast iron in which the uncombined carbon appears predominantly in flake graphite form, the improvement which comprises injecting finely divided calcium carbide into a molten hypoeutectic cast iron composition, continuing said injection until the chill of the resulting treated iron, as measured by the depth or thickness of the white iron in a chill test piece, is substantially reduced or suppressed, and casting the resulting treated iron to provide a cast product containing uncombined carbon predominantly in flake graphite form and which is substantially free of nodular graphite and elemental calcium, said product being characterized by improved machineability without reduction in tensile strength.

2. A process according to claim 1 in which chromium is introduced into the molten metal prior to casting thereof.

3. A method for treating gray cast iron prior to casting thereof, comprising establishing a bath at normal founding temperature of a gray cast iron composition containing iron more than 90%, carbon from 1.7% to 4.5%, silicon from 1.0% to 3.5%, and manganese from 0.1% to 1.0%, injecting into said bath a mixture com-

prising essentially a major proportion of finely-divided calcium carbide and a minor proportion of finely-divided rare earth oxide, said mixture being injected with a carrier gas stream in an amount such that the total amount of carbide injected is in the range from 5 to 75 pounds of carbide per ton of molten metal, and casting the resulting treated molten metal promptly following said carbide-oxide treatment to provide an as-cast product which is substantially free of retained elemental rare earth and elemental calcium and which is characterized by the presence of uncombined carbon in nodular form.

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