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2,663,635

ADDITION AGENT AND METHOD FOR INTRODUCING MAGNESIUM INTO CAST IRON

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The present invention relates to a new article of manufacture comprising a novel magnesium-containing addition agent having reduced reactivity when added to molten cast iron and adapted to provide an increased proportion of the uncombined carbon in "as-cast" cast iron as compacted graphite including spheroidal graphite, and to an improved process utilizing said agent to produce cast iron products having improved properties and characteristics in the "as-cast" condition.

It is now well known that retained magnesium will cause uncombined carbon in cast iron to occur in the form of compacted graphite, preferably spheroidal graphite, and that such cast iron will possess a combination of properties entirely different from and higher than that obtained in gray cast iron in which the uncombined carbon is present as normal flake graphite. To produce a magnesium-containing cast iron in which the amount of magnesium retained therein is sufficient to obtain in the "as-cast" iron the desired amount of uncombined carbon as compacted graphite, preferably spheroidal graphite, a molten cast iron bath of such composition that if cast after inoculation it would be a gray cast iron is first established. This includes a molten bath having such high graphitizing power that it would be gray cast iron when solidified regardless of whether or not it was inoculated. A bath of this type is treated with a sufficient amount of a magnesium-containing agent, e. g., elemental magnesium, a nickel-magnesium alloy, a nickel-magnesium-carbon alloy, a nickel-magnesium-silicon alloy, a silicon-magnesium-iron alloy, etc., to obtain in the cast iron when subsequently cast the desired amount of retained magnesium. In practice, the magnesium is at present often added as an alloy containing from about 14% to about 16% magnesium. If required, the bath is inoculated at least once, either simultaneously with or shortly after the magnesium introduction, with a graphitizing agent, e. g., ferrosilicon, and then cast in an inoculated condition. The development of this new type cast iron containing graphite in a compacted form, including the spheroidal form and the compacted-flake form, is described in U. S. Patents Nos. 2,485,760 and 2,485,761, and some magnesium-containing addition agents adapted to introduce magnesium into cast iron are disclosed in U. S. Patents Nos. 2,485,760, 2,485,761, 2,529,346, and 2,563,859.

The introduction into a molten cast iron bath of the essential amounts of magnesium required to produce the desired compacted graphite struc-

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ture is accomplished in a number of ways and the amount of magnesium to be added to the bath will depend upon (1) the final retained magnesium content desired in the iron after solidification, (2) the additional amount of magnesium required to overcome the presence of undesirable elements, such as sulfur, etc., in the molten iron, (3) the amount of magnesium lost from the molten iron by delaying the casting of the bath after the magnesium introduction and (4) the proportion of magnesium recovered in the bath from the magnesium addition agent. This last factor (4) presents considerable difficulties since varying losses of magnesium are incurred when introducing magnesium, either as elemental magnesium or in the form of a magnesium-containing addition agent, into the molten bath. It is well known that the addition of elemental magnesium to molten iron leads to a very violent reaction with the result that all or very nearly all the magnesium is lost. If the magnesium is added as an alloy with, for example, nickel, there is still a reaction, the reactivity of which decreases as the magnesium content of the alloy is decreased.

For the reasons set forth hereinbefore, the production of cast iron containing small critical amounts of retained magnesium is highly advantageous and, in present practice, the magnesium is usually incorporated in molten cast iron as a magnesium-containing alloy addition containing from about 2% to about 30% or 40% magnesium, for instance, a nickel-base alloy containing about 4% to 20% magnesium, such as an alloy containing about 13% to 17% magnesium. This type of addition agent is not excessively reactive when added to molten cast iron, but, nevertheless, an appreciable reaction does occur. Moreover, the fact that the magnesium content of the addition alloy is low means that the total amount of alloy which must be added is high, so that the molten iron is chilled to some extent and an undesirable amount of the metal or metals with which the magnesium is alloyed may be introduced into the molten iron.

Although many attempts were made to overcome the foregoing difficulties and other difficulties, none, as far as I am aware, was entirely successful when carried into practice commercially on an industrial scale.

A new magnesium-containing addition agent has been discovered which has substantially decreased reactivity when added to molten cast iron as compared to the reactivity resulting when prior art magnesium-containing agents were added to

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molten cast iron and which also produces improved conversion of uncombined carbon to compacted graphite, i. e., as spheroidal graphite such as found in the ferrous castings described in the aforesaid U. S. Patent No. 2,485,760 and/or as compacted-flake graphite such as found in the ferrous castings described in the aforesaid U. S. Patent No. 2,485,761.

It is an object of the present invention to provide an improved addition agent for incorporating magnesium in molten iron which has substantially lessened reactivity when added to cast iron and which augments the occurrence of uncombined carbon as compacted graphite in the "as-cast" magnesium-containing cast iron.

Another object of the invention is to provide as a new addition agent a unique mixture of a reaction-inhibiting ingredient and a magnesium-containing ingredient for treating molten cast iron.

It is a further object of the invention to provide a unique magnesium-containing agent which, when used to incorporate magnesium into molten cast iron for the production of compacted graphite in the resulting castings, enables improved recovery in said castings of uncombined carbon in the form of compacted graphite, particularly spheroidal graphite.

It is still another object of the present invention to provide an improved method for incorporating magnesium into cast iron to produce magnesium-containing cast iron.

The invention also contemplates as a further object an improved method for producing cast iron containing compacted graphite, especially spheroidal graphite.

Other objects and advantages will become apparent from the following description.

Generally speaking, the present invention comprises a new magnesium-containing addition agent for addition to molten cast iron to provide reduced reactivity when used to incorporate magnesium in molten cast iron. The new addition agent comprises a special mixture containing special proportions of calcium cyanamide as a reaction-inhibiting ingredient and a magnesium-containing ingredient. It is an important feature of the present invention that the calcium cyanamide reaction-inhibiting ingredient be added in conjunction with the magnesium-containing ingredient in order to achieve the cooperative effect which the reaction-inhibiting ingredient exerts in decreasing the reactivity of the magnesium-containing ingredient. In other words, the magnesium-containing ingredient must be incorporated into the molten cast iron in the presence of the reaction-inhibiting ingredient.

This invention is based on the striking discovery that calcium cyanamide reduces the violence of the reaction if it is added with the magnesium. It is preferred to mix calcium cyanamide powder with the magnesium, which itself is preferably added as an alloy crushed to small pieces ranging in size from, for example, about one-eighth to about three-eighths of an inch. It has been found, for instance, that if an alloy containing from about 14% to about 16% magnesium and the rest nickel is mixed with an equal quantity of calcium cyanamide powder, the calcium cyanamide in the mixture burns quietly while the magnesium desulfurizes and dissolves in the molten metal with hardly any visible sign of reaction. The calcium cyanamide does not chill the molten iron appreciably and leaves a residue which is easily skimmed off when the reaction is

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complete. As a specific example, molten iron may be treated with about 1.1% of a nickel-magnesium alloy containing about 15% magnesium and with an equal amount of calcium cyanamide powder, then be inoculated with an amount of silicon (for example, as ferrosilicon containing 80% silicon) equal to about 0.5% of the weight of the molten metal, and then be cast. With alloys richer in magnesium or with smaller quantities of calcium cyanamide, the reactivity is likewise reduced.

The reactive magnesium-containing materials which can be employed in conjunction with calcium cyanamide, preferably as a mixture therewith, include those known to the prior art and can be elemental magnesium or an alloy of magnesium or a mixture of magnesium with one or more carrier materials, e. g., as a compacted mass or briquette. Some examples of reactive magnesium-containing ingredients include elemental magnesium, nickel-magnesium alloys, silicon-magnesium alloys, and copper-magnesium alloys. It is to be understood that the aforementioned alloys may be in the form of binary alloys or more complex alloys such as ternary alloys, etc. Illustrative examples of nickel-magnesium alloys are binary nickel-magnesium alloys, nickel-magnesium-carbon alloys, such as described in the aforesaid U. S. Patent No. 2,529,346, and nickel-magnesium-silicon alloys, such as described in the aforesaid U. S. Patent No. 2,563,859. Illustrative examples of silicon-magnesium alloys include binary silicon-magnesium alloys and silicon-magnesium-iron alloys. In general, the reactive magnesium-containing ingredient will contain up to a total of about 90% of one or more of the elements nickel, silicon, copper, iron and/or manganese with the balance consisting essentially of magnesium. In addition, the magnesium-containing ingredient may contain small amounts of carbon, calcium, etc. In usual practice, the magnesium-containing ingredient will contain about 60% to about 90% of the aforesaid elements, the balance being essentially magnesium and being within the range of about 10% to about 40%. In utilizing calcium cyanamide in conjunction with the magnesium-containing ingredient, preferably as a mixture, the weight ratio of the calcium cyanamide ingredient to the magnesium-containing ingredient should be at least about 0.5 of calcium cyanamide to 1 of magnesium-containing ingredient. Usually a ratio within the range between about 0.5:1 and about 6:1 gives satisfactory results. In most cases, it is preferred to maintain the ratio between about 0.5:1 and about 2:1.

The addition agent comprising a mixture of the foregoing ingredients can be added to the molten cast iron either as a loose mixture or as a compacted mixture, e. g., as a briquette. The calcium cyanamide preferably is employed as a powder and the magnesium-containing ingredient preferably is employed as lumps of about one-eighth inch to about three-eighths inch in size although improved results are still obtained when either or both ingredients have other particle sizes.

To obtain cast iron which, in the as-cast condition, contains uncombined carbon in the form of compacted graphite, usually at least about 0.02% magnesium should be retained in the cast iron. If it is desired that the cast iron contain compacted graphite in the form of spheroids, usually at least about 0.03% or 0.04% or more magnesium should be retained in the "as-cast" iron.

It is known that the presence of certain interfering elements in cast iron counteracts the formation of compacted graphite, either as compacted-flake graphite or as spheroidal graphite. Thus, in producing magnesium-containing cast iron by the processes disclosed in the aforesaid U. S. Patents Nos. 2,485,760 and 2,485,761, the uncombined carbon sometimes can wholly occur as flake graphite even though an amount of retained magnesium is present which, were interfering elements not present, would produce uncombined carbon in the compacted form. This condition is traceable to the presence of interfering elements such as lead, etc. One of the unexpected advantages obtained by employing the novel addition agent provided by the present invention is believed due to the neutralizing or offsetting effect of calcium cyanamide on the harmful effects of these detrimental interfering elements which may be present in the molten cast iron. This offsetting or counteracting effect of the calcium cyanamide ingredient when employing the present addition agent in treating cast iron containing interfering elements results in a greater proportion of the uncombined carbon becoming compacted, i. e., as compacted-flake graphite and/or as spheroidal graphite, and hence results in better mechanical properties in the cast iron than are obtained when employing the same magnesium-containing ingredient without calcium cyanamide.

In employing the present invention to produce cast iron containing compacted graphite, a molten bath of cast iron is established which, if then cast in an inoculated condition, would result in gray cast iron containing normal flake graphite; adding to said bath the calcium cyanamide in conjunction with the magnesium-containing ingredient in an amount sufficient to incorporate in the molten bath and to retain in castings made therefrom at least a small but effective amount, e. g., at least about 0.02%, of magnesium; and thereafter casting metal from the thus-treated bath with sufficient graphitizing power, usually contributed by the addition of a graphitizing agent or inoculant, such as a silicon-containing agent, to produce castings containing uncombined carbon in the gray cast iron range. When the amount of retained magnesium is at least about 0.03% or about 0.04%, a substantial proportion of the compacted graphite will be in the form of spheroids. As indicated hereinbefore, the molten bath may be treated after the addition of the calcium cyanamide and the magnesium-containing ingredient, preferably as a mixture, with a graphitizing agent or inoculant to impart the required final graphitizing power if the composition is such that it does not have sufficient graphitizing power to oppose the whitening tendency of the magnesium. In some instances, the graphitizing agent or inoculant may be added simultaneously with the magnesium-containing ingredient although in most cases the addition of the graphitizer or inoculant subsequent to the addition of the magnesium-containing ingredient is more satisfactory. The graphitizer or inoculant is usually a silicon-containing agent, such as ferro-silicon, nickel silicide or nickel-silicon alloys, calcium silicide or calcium-silicon alloys, silicon metal, etc., although other graphitizing agents may be employed.

In carrying out the present invention to produce cast iron containing compacted graphite, the combined weight of calcium cyanamide and magnesium-containing ingredient added to the

molten cast iron will usually be within the range of about 1% to about 8%, more usually within the range of about 1% to about 5%, by weight of the molten iron.

Illustrative examples of addition agents within the scope of the present invention which have been successfully employed to obtain improved recovery of uncombined carbon as compacted graphite in cast iron together with a substantially reduced addition reactivity are as follows:

Addition agent	Composition of agent	
	Percent CaCN ₂	Percent Ni-Mg alloy ¹
A	50	50
B	42	58

¹ 15% Mg, 2% C, balance Ni.

To illustrate the application of the process provided by the present invention, an embodiment thereof comprises adding to the molten cast iron bath about 2% to about 4% by weight of a mixture in about equal proportions of calcium cyanamide powder and crushed nickel-magnesium alloy. A nickel-magnesium alloy containing about 15% magnesium, about 2% carbon and the balance essentially nickel, and having a lump size of about $\frac{3}{8}$ inch, provides satisfactory results when employed in conjunction with calcium cyanamide.

The present invention may be applied to the manufacture of a wide variety of ferrous products and articles which will be apparent to those skilled in the art. These products and articles include those set forth in the aforementioned U. S. Patents Nos. 2,485,760 and 2,485,761. The present invention particularly contemplates a novel article of manufacture, namely, a new addition agent, to be employed in the production of magnesium-containing cast iron to provide substantially reduced reactivity during the addition of magnesium to molten cast iron.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

I claim:

1. As a new article of manufacture, an addition agent particularly adapted for incorporating magnesium into molten cast iron which comprises calcium cyanamide and such a proportion of a reactive ingredient containing at least 10% magnesium and up to a total of 90% of metal from the group consisting of nickel, copper and silicon that the weight ratio of calcium cyanamide to said reactive ingredient in said addition agent is between about 0.5 to 1 and about 2 to 1, said agent being characterized by decreased reactivity when added to molten cast iron.

2. As a new article of manufacture, an addition agent particularly adapted for incorporating magnesium into molten cast iron which comprises calcium cyanamide and such a proportion of a reactive ingredient containing at least 10% magnesium and up to a total of 90% of metal from the group consisting of nickel, copper and silicon that the weight ratio of calcium cyanamide to said reactive ingredient in said addition agent is be-

tween about 0.5 to 1 and about 6 to 1, said agent being characterized by decreased reactivity when added to molten cast iron.

3. As a new article of manufacture, an addition agent particularly adapted for incorporating magnesium into molten cast iron which comprises calcium cyanamide and such a proportion of a reactive 10 to 40% magnesium-containing alloy that the weight ratio of calcium cyanamide to said alloy in said addition agent is between about 0.5 to 1 and about 2 to 1, said agent being characterized by decreased reactivity when added to molten cast iron.

4. As a new article of manufacture, an addition agent particularly adapted for incorporating magnesium into molten cast iron which comprises calcium cyanamide and such a proportion of a reactive 10 to 40% magnesium-containing alloy that the weight ratio of calcium cyanamide to said alloy in said addition agent is between about 0.5 to 1 and about 6 to 1, said agent being characterized by decreased reactivity when added to molten cast iron.

5. An improved process for producing magnesium-containing cast iron containing compacted graphite which comprises establishing a bath of molten cast iron of such a composition that if cast at least after inoculation it would be a gray cast iron; incorporating at least a small but effective amount of magnesium in said bath by treating said molten bath with about 1% to 8% of an addition agent comprised of calcium cyanamide and such a proportion of a reactive ingredient containing at least 10% magnesium and up to a total of 90% of metal from the group consisting of nickel, copper and silicon that the weight ratio of calcium cyanamide to said reactive ingredient in said addition agent is between about 0.5 to 1 and about 6 to 1; and casting a magnesium-containing casting from metal of said bath in an inoculated condition to obtain therein uncombined carbon as compacted graphite.

6. An improved process for producing magnesium-containing cast iron containing compacted graphite which comprises establishing a bath of molten cast iron of such a composition that if cast at least after inoculation it would be a gray cast iron; incorporating at least a small but effective amount of magnesium in said bath by treating said molten bath with an addition agent comprised of calcium cyanamide and such a proportion of a reactive ingredient containing at least 10% magnesium and up to a total of 90% of metal from the group consisting of nickel, copper and silicon that the weight ratio of calcium cyanamide to said reactive ingredient in said addition agent is between about 0.5 to 1 and about 6 to 1; and casting a magnesium-containing casting from metal of said bath in an inoculated con-

dition to obtain therein uncombined carbon as compacted graphite.

7. An improved process for producing magnesium-containing cast iron containing spherical graphite which comprises establishing a bath of molten cast iron of such a composition that if cast it would be a gray cast iron; incorporating at least a small but effective amount of magnesium in said bath by treating said molten bath with an addition agent comprised of calcium cyanamide and such proportions of a reactive 10 to 40% magnesium-containing alloy that the weight ratio of calcium cyanamide to said alloy in said addition agent is between about 0.5 to 1 and about 6 to 1; and casting metal from said bath to obtain a casting containing uncombined carbon and at least about 0.03% retained magnesium.

8. An improved process for producing magnesium-containing cast iron containing compacted graphite which comprises establishing a bath of molten cast iron of such a composition that if cast it would be a gray cast iron; incorporating at least a small but effective amount of magnesium in said bath by treating said molten bath with an addition agent comprised of calcium cyanamide and such proportions of a reactive 10 to 40% magnesium-containing alloy that the weight ratio of calcium cyanamide to said alloy in said addition agent is between about 0.5 to 1 and about 2 to 1; and casting a magnesium-containing casting from metal of said bath with sufficient graphitizing power to obtain therein uncombined carbon as compacted graphite.

9. An improved process for producing magnesium-containing cast iron containing compacted graphite which comprises establishing a bath of molten cast iron of such a composition that if cast it would be a gray cast iron; incorporating at least a small but effective amount of magnesium in said bath by treating said molten bath with an addition agent comprised of calcium cyanamide and such proportions of a reactive 10 to 40% magnesium-containing alloy that the weight ratio of calcium cyanamide to said alloy in said addition agent is between about 0.5 to 1 and about 6 to 1; and casting a magnesium-containing casting from metal of said bath with sufficient graphitizing power to obtain therein uncombined carbon as compacted graphite.

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References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,335,370	Ellis	Mar. 30, 1920
2,543,853	Jordan	Mar. 6, 1951