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METHOD FOR THE PRODUCTION OF CAST IRON AND ALLOY ADDITION AGENT USED IN METHOD

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1

The present invention relates to a new article of manufacture comprising a new magnesium-containing addition agent for the treatment of iron-base melts and to a process for treating iron-base melts with said addition agent to produce ferrous products with improved properties and characteristics and to produce cast iron with graphite in a compacted form, particularly a spheroidal form.

Heretofore, the art has considered that the introduction of magnesium into molten cast iron on a practical scale was not possible. The art has taught that magnesium does not alloy with iron and, as a matter of fact, when it has been attempted to introduce metallic magnesium in elemental form into a molten bath of iron when the latter was at the ordinary elevated temperature required for satisfactory casting, a reaction of such explosive violence took place that the molten iron was blown from the receptacle in which it was held. In addition, it is known that the temperatures of molten iron baths usually exceed the boiling temperature of magnesium. The fact that the introduction of elemental magnesium into molten iron baths produces a reaction of explosive violence has been well recognized in the art, even up to a very recent date (see American Foundryman, March 1949, page 38, and Iron Age, April 7, 1949, page 149).

In the development of the new type cast iron containing spheroidal graphite, described in co-pending U. S. application, Serial No. 787,420, now Patent No. 2,485,760, entitled "Cast Ferrous Alloy," filed November 21, 1947, new addition materials adapted to introduce magnesium into cast iron were essential.

The present invention provides a new magnesium-containing addition agent which solves the problems which have long confronted the art and which is adapted to introduce magnesium into cast iron.

It is an object of the present invention to provide a new magnesium-containing agent which enables quiet introduction of magnesium into molten iron-base compositions.

Another object of the invention is to provide an addition agent particularly adapted to introduce useful amounts of magnesium into cast iron even when only small amounts of the addition are employed.

The invention also contemplates providing a magnesium-containing agent which enables a high recovery of contained magnesium in a cast iron melt when said agent is added thereto.

Broadly stated, the agent of the invention is a

2

nickel-base alloy containing about 4% to 30% magnesium and more than 1% up to about 4% carbon.

In its preferred embodiments, the agent contains more than 10% up to about 15% or 20% magnesium. Preferably the alloy contains more than 10% to about 20% magnesium, more preferably about 12% to 15% magnesium, in combination with about 1.25% or 1.3% up to about 2.5% carbon, with the balance of the alloy being essentially nickel. Thus, the alloy of the invention which enables the production of unexpected results in the treatment of iron-base melts is essentially a ternary alloy.

The present invention also contemplates the treatment of molten iron-base baths, e. g., molten cast iron baths, with the alloy of the invention for the purpose of introducing magnesium into said molten baths. As pointed out hereinbefore, the introduction of metallic magnesium into a molten iron bath, particularly a molten cast iron bath, has always been attended heretofore by burning of the magnesium and an explosive reaction and has been considered heretofore to be practically impossible on a commercial scale. It has been found that nickel-magnesium alloys containing, for example, 4% to 20% magnesium, may be employed for the purpose of introducing magnesium into molten cast iron. However, these alloys have been attended by the disadvantage that, in order to achieve quiet introduction and high magnesium recovery therefrom, the magnesium content was required to be kept rather low. It has been found that the introduction of carbon into nickel-magnesium alloys in accordance with the present invention provides unexpected higher magnesium recovery and more quiet magnesium introduction than carbon-free nickel-magnesium alloys having the same magnesium content. This discovery has provided the practical advantage that carbon-containing nickel-magnesium alloys having higher magnesium contents can be employed successfully for the purpose of introducing magnesium into a cast iron melt than was the case when carbon-free nickel-magnesium alloys were employed. As a further advantage of the invention, smaller total amounts of the addition are required to introduce a given amount of magnesium into a particular molten cast iron composition.

The alloys defined hereinbefore represent the practical compositions useful for the purpose of introducing magnesium into molten cast iron. Thus, when the magnesium content is increased above about 30%, the alloy is sufficiently reactive

3

to cause spattering and consequent excessive loss of magnesium when added to the surface of a molten cast iron bath. At magnesium contents below about 20% and within the invention quiet addition of magnesium is promoted. On the other hand, when the magnesium content is reduced below 10%, an excessive amount of carrier metal may be introduced into the melt being treated and martensitic structures undesirable in non-alloyed or unalloyed cast iron compositions may be produced therein, particularly when the bath being treated is high in sulfur. Magnesium contents between about 12% and 15% in the agent of the invention are very satisfactory and promote quiet addition and high recovery of magnesium in the treated melt. When the carbon content is reduced below 1%, the improved addition characteristics contributed by the carbon content are materially reduced and, on the other hand, it is not practical to attempt producing alloys containing more than about 4% carbon. Within the preferred carbon range of 1.25% to 2.5% the beneficial effects due to the presence of carbon are particularly marked and alloys containing carbon within this range are easily prepared. Particularly satisfactory results are obtained with nickel alloys containing 12% to 15% magnesium and 1.5% to 2.5% carbon.

In addition to nickel, magnesium and carbon, the alloys also may contain small amounts of incidental impurities, including phosphorus, etc., introduced from the raw materials employed in producing the alloy, etc. These impurities do not materially affect the properties of the alloy and should not exceed a total of about 0.5%. In addition to impurities, the alloy may also contain up to 40% cobalt, e. g., 0.1% to 40% cobalt, up to 15% copper, e. g., 0.1% to 15% copper, up to 20% iron, e. g., 0.1% to 20% iron, up to 40% manganese, e. g., 0.1% to 40% manganese, and up to 5% of silicon, molybdenum and/or aluminum, e. g., 0.1% to 5% of each. The alloy may also contain a small amount of chromium up to 0.5%, e. g., 0.1% to 0.5% chromium, but it is preferred that the alloy be devoid of chromium. The nickel content of the alloy, however, should always be at least 40% and preferably higher. The alloy should be practically devoid of the elements arsenic, antimony, tin, lead, bismuth, selenium and tellurium as these elements have been found to be subversive to the desired effects of magnesium in treating iron-base melts.

For the purpose of giving those skilled in the art a better understanding of the invention, the compositions of some magnesium-containing alloys produced according to the invention are set forth in the following table:

Table

No.	Per Cent C	Per Cent Mg	Per Cent Ni	Per Cent Others
1	3.7	14	Balance	
2	2.8	12	Balance	
3	2.24	13.56	Balance	
4	2-2.5	14	Balance	
5	2	13.5	84.5	
6	1.94	15.83	Balance	
7	1.8	16.46	Balance	
8	1.55	14.37	Balance	0.65 Si
9	1.33	14.05	Balance	

The agent of the invention is adapted to the treatment of molten iron-base alloys for the general improvement thereof, e. g., for deoxidation, desulfurization, etc. leading to improved properties in the treated iron-base alloys. Improved

4

results are obtained when iron-base melts, including cast iron, steel and other melts containing 50% or more of iron, are treated with about 0.25% to about 2% of the magnesium-containing agent of the invention. Particularly satisfactory results have been obtained in the treatment of molten cast iron compositions with the alloy of the invention, especially when about 0.03% up to 0.4% or 0.5% magnesium is retained therein. When an amount of magnesium within the aforesaid range is retained in a white cast iron composition, the resulting castings are characterized by markedly improved hardness and strength and when such an amount is retained in a gray cast iron composition, the resulting castings are characterized by a compacted graphite structure and by greatly improved strength and ductility. It has been found that magnesium is a powerful whitener of itself and, in cases where the production of graphitic cast iron castings is desired, it is generally necessary to introduce a graphitizing inoculant into the bath after the magnesium introduction in order that graphite will be present in castings made from the bath. When an inoculant, e. g., about 0.2% to 1% silicon, is employed after the magnesium introduction, the bath should be cast shortly after the inoculation as it has been found the inoculation effect wears off if the bath is held too long, e. g., more than about 10 minutes after inoculation.

As those skilled in the art know, cast iron is a eutectiferous iron-carbon alloy usually containing about 1.7% to 5% carbon and about 1% to 6% silicon with the balance essentially iron, said balance usually being 87% or more iron, whereas steel is an iron-carbon alloy containing less than the eutectic amount of carbon. Preferably, cast iron contains about 2% to 4.5% carbon and about 1.3% to 5% silicon or about 2.5% to 4% carbon and about 1.5% to 4.5% silicon. For purposes of the invention, the molten cast iron composition to be treated to produce graphitic castings may contain the common alloying elements in the amounts usually found in cast iron, e. g., the cast iron may contain up to 36% nickel, up to about 0.6% molybdenum, up to about 1% chromium, up to about 2.5% manganese, etc. Of course, when it is desired to produce a white cast iron, larger amounts of carbide stabilizing elements may be present. In order to realize the preferred effects obtainable through the introduction of magnesium into cast iron, the copper content should be kept below about 2%. The cast iron bath to be treated should be practically devoid of tin, lead, antimony, bismuth, arsenic, selenium and tellurium as these elements have been found to be subversive to the desired effects of magnesium when present in amounts greater than about 0.1%, respectively. The impurities phosphorus and sulfur may be present in the cast iron bath to be treated in the usual amounts found in cast iron. Thus, the bath to be treated may contain up to 0.5% or up to 0.25% phosphorus although it is preferred that the phosphorus content be below about 0.15%, e. g., about 0.02% to 0.06%. Similarly, the sulfur content may be as high as 0.3% or more, e. g., 0.005% to 0.3%, although it is preferred that the sulfur content be below 0.15%, e. g., 0.03% to 0.1%.

As pointed out hereinbefore, the carbon-containing nickel-magnesium alloy of the invention provides a higher recovery of retained magnesium and a more quiet introduction of magnesium into

an iron-base melt than is the case when a carbon-free nickel-magnesium alloy having the same magnesium content is employed. As an example of the foregoing, a cast iron melt containing about 3.5% carbon, about 1.5% silicon, about 0.024% sulfur, with the balance essentially iron, was established and to separate portions of the melt 0.25% additions of magnesium as a nickel-magnesium alloy containing 13.28% magnesium with the balance essentially nickel and of a nickel - magnesium - carbon alloy containing 13.25% magnesium, 2.3% carbon, balance essentially nickel, were made to the surface of each portion as it was held in a ladle. Each portion was then inoculated with about 0.75% silicon as a ferro-silicon alloy containing about 85% silicon and quickly cast. It was found that the casting from the first portion of the melt contained 0.055% magnesium and the casting from the second portion of the melt contained 0.08% magnesium. This test demonstrates that a higher recovery of magnesium was obtained when the carbon-containing alloy of the invention was employed and, in addition, it was observed that the carbon-containing alloy had improved addition characteristics manifested by quiet introduction, little evolution of heat and light, and generally non-violent behavior completely different from the behavior found in the case where magnesium alone is added to an iron-base bath.

The proportion of the magnesium content of a given addition alloy which will be introduced into a particular iron-base bath depends upon a number of factors. The high reactivity of magnesium is still felt even in the alloy of the invention having improved addition characteristics and, in general, it can be said that the higher the magnesium content of the alloy, the lower will be the recovery of magnesium in an iron-base bath, e. g., a cast iron bath. As magnesium has been found to be a powerful desulfurizer even under acid conditions and in the absence of a slag, the sulfur content of the bath is also a factor. When magnesium is introduced into a sulfur-containing cast iron melt, the sulfur content will be reduced and magnesium will be consumed in the resulting reaction. For example, when sufficient magnesium is introduced into a cast iron bath containing more than about 0.02% sulfur (e. g., 0.03% to 0.1% or more) to produce a retained magnesium content of 0.03% or more, the sulfur content will be reduced below about 0.02%. Practically speaking, about one part by weight of magnesium must be introduced in the bath for each part by weight of sulfur removed. Other factors influencing the magnesium recovery from the addition alloy include the temperature of the bath, the actual method of carrying out the introduction, etc. It has been found that the higher the bath temperature, the greater is the loss of magnesium due to the addition reactions. Magnesium recovery is usually comparatively low when the alloy is simply thrown on the surface of the molten bath and the recovery is improved when the addition is made to the molten stream of metal flowing into a ladle or other container. It has been found that the recovery is usually greater when additions of the alloy are made on a large scale as in a commercial foundry than when additions are made on a laboratory scale. As there is a tendency for magnesium to be lost from the bath after it is introduced, the bath should be cast rather quickly after the magnesium introduction, e. g., within about 15 minutes thereafter. As an example, it can be said that when

the preferred alloy of the invention is employed to treat a molten cast iron containing about 0.15% sulfur, an addition of about 2% of the alloy to the molten cast iron stream running into a ladle or other container will be required to desulfurize the melt to a value of about 0.15% and to provide a retained magnesium content of about 0.08% therein.

The carbon-containing magnesium addition alloy of the invention can be prepared by a method which comprises melting nickel and carbon, e. g., about 4% or more of carbon, to establish a nickel-carbon melt. After the melt has been established it is then superheated to about 2800° to 2900° F. to insure solution of a large amount of carbon. The melt is then cooled to about 2450° to 2500° F. and the desired amount of magnesium is stirred in. The melt is then cast. It is preferred that the alloy be prepared in an induction furnace although other types of furnaces may be employed.

Although the theoretical explanation is not fully understood, it has been established through many tests that carbon has a very beneficial effect in improving the addition characteristics of and in improving the magnesium recovery from the agent of the invention. In this connection, it appears that melting point is not an important factor; for example, a 90% aluminum-10% magnesium alloy having a low melting point was found to have very poor addition characteristics and to produce very low recoveries of magnesium when added to a cast iron melt, e. g., only about 3% of the amount of magnesium added. The improvement in addition characteristics found in the agent of the invention appears to be associated with the rate at which magnesium is released therefrom when the agent is added to a molten ferrous bath.

This application is a continuation-in-part of our co-pending U. S. application Serial No. 787,420, filed November 21, 1947, now Patent No. 2,485,760.

Although the present invention has been described in conjunction with certain preferred embodiments thereof, those skilled in the art will understand that variations and modifications thereof can be made. Such variations and modifications are to be considered within the purview and scope of the specification and the appended claims.

We claim:

1. The method for producing improved iron-base castings which comprises establishing an iron-base melt containing about 0.03% up to about 0.3% sulfur, incorporating in said melt about 0.25% to about 2% of an agent containing at least about 1.25% but not more than about 4% carbon, more than about 10% to about 20% magnesium, with the balance essentially nickel, to introduce in said melt at least one part of magnesium for each part of sulfur contained in said melt and to provide a small retained magnesium content in said melt, and shortly thereafter casting said melt to produce iron-base castings having improved properties and containing a small amount of magnesium, said small amount being at least about 0.03% of the total composition.

2. The method for producing improved cast iron castings which comprises establishing a bath of molten cast iron containing about 0.03% to about 0.3% sulfur, incorporating in said bath an agent containing about 1.3% to about 2.5% carbon, about 12% to about 15% magnesium, and

7

the balance essentially nickel, to reduce the sulfur content of said bath below about 0.02% and to provide a retained magnesium content of at least about 0.03% in said bath, and thereafter casting said bath to produce cast iron castings having improved properties and containing a small amount of magnesium, said small amount being at least about 0.03% of the total composition.

3. The method for producing improved gray cast iron castings which comprises establishing a bath of molten cast iron containing about 0.03% to about 0.3% sulfur, incorporating in said bath at least about 0.25% of an agent containing about 1.3% to about 2.5% carbon, about 12% to not more than about 20% magnesium, with the balance essentially nickel, to reduce the sulfur content of said bath below about 0.02%, inoculating said bath with an effective amount of a silicon inoculant, and thereafter casting said bath in an inoculated condition to produce cast iron castings containing less than about 0.02% sulfur, containing graphite in a compacted form, and containing a small but effective amount of magnesium.

4. The method for producing improved gray cast iron castings which comprises establishing a bath of molten cast iron containing about 0.03% to about 0.3% sulfur, incorporating in said bath about 0.25% to about 2% of an agent containing about 1.3% to not more than about 4% carbon, about 12% to about 15% magnesium, with the balance essentially nickel, to reduce the sulfur content of said bath below about 0.02% and to provide a small magnesium content in said bath of at least about 0.03%, inoculating said bath with a silicon inoculant at a time not prior to the incorporation of said agent in said bath, and casting the inoculated bath to produce cast iron castings containing less than about 0.02% sulfur, containing graphite in a compacted form, and containing a small but effective amount of magnesium.

5. As a new article of manufacture, an agent particularly adapted for the incorporation of

8

magnesium into iron-base melts with attendant high recovery of magnesium and low evolution of heat and light, said agent containing about 1.25% to not more than 4% carbon, about 12% to not more than about 20% magnesium, with the balance essentially nickel.

6. As a new article of manufacture, an addition agent particularly adapted for the incorporation of magnesium into molten cast iron with high recovery of contained magnesium, said agent containing about 1.25% to not more than 4% carbon, about 12% to about 15% magnesium, with the balance essentially nickel.

7. As a new article of manufacture, an addition agent particularly adapted for the incorporation of magnesium into molten cast iron with high recovery of contained magnesium, said agent containing about 1.3% to about 2.5% carbon, about 12% to not more than 20% magnesium, with the balance essentially nickel.

8. As a new article of manufacture, an addition agent particularly adapted for the incorporation of magnesium into molten cast iron with high recovery of contained magnesium, said agent containing about 12% to about 15% magnesium, about 1.3% to about 2.5% carbon, with the balance essentially nickel.

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The following references are of record in the file of this patent:

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Number	Country	Date
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