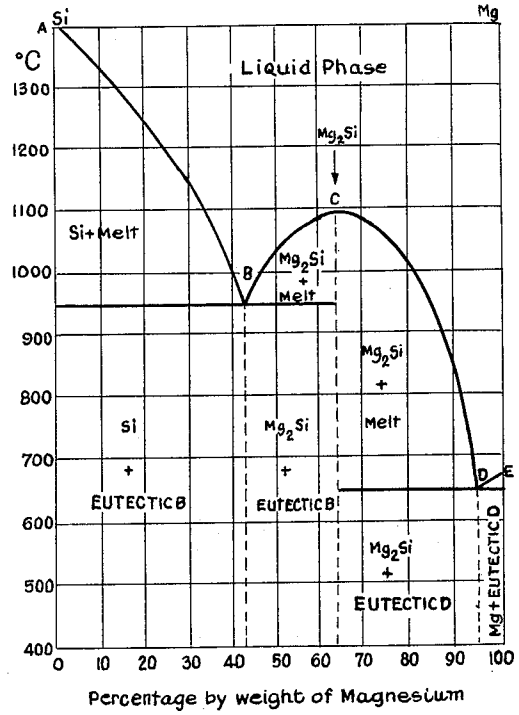
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PROCESS FOR THE MANUFACTURE OF IRON-SILICON MAGNESIUM PREALLOYS

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Phase diagram of the Magnesium-Silicon Alloys
(Cf. R. Vogel, Zeitschrift für Anorganische Chemie, Vol. 61, 1909, Page 50)

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PROCESS FOR THE MANUFACTURE OF IRON-SILICON MAGNESIUM PREALLOYS

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The present invention is concerned with a process for the manufacture of iron-silicon-magnesium prealloys.

It is known that in ordinary cast iron containing 2.5 to 3.5% carbon and 1.5 to 2.5% silicon the graphite portion of the carbon content separates in lamellar form between the basic structure, whereby the solidity of the cast structure is impaired. If the graphite can be caused to separate in globular or spherical form, the pattern of the stress lines within the basic structure is no longer affected by the graphite separated. Cast iron in which the graphite is caused to so separate therefore possesses improved strength properties. Theoretically, the agglomeration of the graphite in globular or spherical form is the result of:

(1) A substantial desulfurization of the cast iron, down to a sulfur content of 0.02%;
(2) A structural change due to the incorporation of elements having small atomic radiuses into the cast iron;
(3) The separation of graphite in globular or spherical form which is favored by (1) and (2) while supplying germs, preferably ferrosilicon germs.

The ferrosilicon used for inoculation should contain as high a proportion of silicon as possible in order to produce a sufficient number of germs.

The cast iron can be desulfurized while using all customary desulfurizing agents such, for example, as soda, carbide, lime, calcium, magnesium or cerium mixed metals.

By incorporating other elements into γ-iron the solidification curve with a break at 1160° C. for ordinary cast iron is so modified that it shows a solidification interval without break.

Magnesium and Ce-mixed metals, i.e., elements whose atomic radiuses are similar to the carbon radius, have proved to be especially useful for incorporation.

The above-mentioned different course of the solidification curve can be considered to equal some sub-cooling and this is confirmed by the influence exerted by the casting temperature and the cooling conditions which were observed in the manufacture of sphero-graphite. Higher casting temperatures involve greater sub-cooling and partially enable sphero-graphite to be obtained without adding magnesium and Ce-mixed metals, but they do not reliably ensure the separation of graphite in globular or spherical form.

Besides Ce-mixed metal which in spite of its excellent efficiency in the preparation of sphero-graphite is only reluctantly used due to its high price, it has been proposed to use the commercialized nickel-magnesium alloys and copper-magnesium alloys. The statements made under (1) and (3) above suggest the conclusion that a ferrosilicon-containing multiple component prealloy consisting of a strongly desulfurizing element for example calcium, and magnesium is most favorable, the corresponding element reducing the consumption of Mg.

It has already been proposed to prepare Mg-containing alloys with silicon, calcium, cerium and other elements by first melting magnesium or a prealloy containing a great proportion of magnesium with pure silicon to obtain

an intermediate alloy and then to introduce such intermediate alloy in solid or liquid form into hot silicon alloys. Attempts have also been made (cf. German Patent 209,914 and its Patent of Addition 349,746) to introduce magnesium into thickly liquid iron or ferrosilicon melts.

As taught in DAS 1,022,014 (German patent application as laid open to public inspection), magnesium can be reacted with silicon melts at temperatures up to 1500° C. with the proviso that the Si-contents are at least so high that all the other accompanying elements, including the magnesium to be added, form silicides. Still further, it has been proposed to prepare prealloys by melting magnesium (12%) with the same proportion of copper and nickel while adding ferrosilicon in lump form. In this latter process, the alloy components are used cold and melted together.

The manufacture of appropriate magnesium-containing prealloys was hitherto rather difficult to carry out and dangerous for the reason that magnesium has a relatively low boiling point of 1106° C. and at that temperature combines very readily with oxygen with the formation of flames. Losses of magnesium by vaporization of burning off were inevitable, and the risk of superheated magnesium being expelled from the melt had always to be feared. As taught in DAS 1,022,014, the losses of magnesium apparently can be kept very low and the feared vaporization reaction avoided, but the great amounts of heat required to produce temperatures as high as 1300 to 1500° C. make this process very expensive and uneconomic.

Proposals have also been made (DAS 1,022,014) to cover solid or liquid magnesium or its alloys by pouring silicon or silicon alloy melts thereover. It has been found that this is an especially disadvantageous proposal because a liquid silicon alloy, for example ferrosilicon or calcium silicon, has a temperature at least 600° C. higher than magnesium at its melting point. Such sudden strong superheating of magnesium is more than dangerous.

The present invention is based on the unexpected observation that all the aforesaid disadvantages can be avoided by first preparing a magnesium melt in a suitable crucible, advantageously a carbon crucible. Melting can be effected in an indirectly heated furnace. It is, however, advantageous to use a graphite rod furnace or a mains-frequency induction crucible furnace. The magnesium liquefied in the crucible (melt bath), which has a temperature of more than 650° C., is covered with flowers of sulfur or another protecting slag customarily used for the manufacture of magnesium, for example a salt melt layer. The melt bath is slowly admixed with solid ferrosilicon containing at least 70% by weight Si, and the temperature in the crucible is gradually increased. Care must be taken that the silicon (in the form of solid ferrosilicon) is added and the temperature increased in harmony with the Si-Mg diagram. As shown in the accompanying diagram, the temperature, starting from the magnesium melting point (about 650° C.) must always be situated shortly above (up to about 50° C.) the liquidus line with an increasing Si-addition along the curve line EDC (cf. R. Vogel, Zeitschrift für anorganische Chemie, vol. 61, 1909, page 50). (As taught by L. Wöhler and O. Schliephake (loc. cit., vol. 151, 1926, page 16) the liquidus curve is about 30° C. lower, i.e., point C at 1070° C. rather than at 1102° C.; it has not yet been settled how such deviation is caused, but this is substantially of no consequence to the present case; cf. M. Hansen, Constitution of Binary Alloys, McGraw-Hill Book Company, New York 1958, page 917.)

In this manner, a liquid Mg-Si-Fe alloy is obtained, in which the Mg:Si ratio at point C=1102° C. corresponds

according to R. Vogel to the compound Mg_2Si, and in which the iron (emanating from the ferrosilicon) is bound as FeSi. The alloy so prepared can be heated to 1200° C. without noteworthy losses by vaporization of magnesium being observed, and further alloy components in the form of solid ferrosilicon having a low Si-content, or copper or nickel can be alloyed therewith.

The liquid alloy of 1150° C. could also be alloyed with liquid ferrosilicon since there is substantially not temperature difference but solid ferrosilicon is preferred.

The above process can also be used for making alloys containing relatively great proportions of calcium. In this case the Mg-melt is first admixed with solid ferrosilicon containing 75% by weight Si; alternatively, due to the favorable Ca-Mg linkage in Ca_3Mg_4, the 75% FeSi is replaced and the Mg-melt first admixed with a solid Ca-Si alloy which, owing to the aforesaid Ca-Mg linkage, the Si-Mg linkage and the Si-Ca linkage, sufficiently reduces the Mg-vapor pressure, so that further components can then be alloyed with the melt after temperature increase to 1100 to 1200° C.

In this manner, any desired alloy composition can be prepared consisting of

10 to 40% by weight Mg
30 to 60% by weight Si
10 to 25% by weight Ca
10 to 30% by weight Fe

and optional additions of Cu, Ni or Mn.

As compared with the process disclosed in DAS 1,022,014, the process of this invention offers the advantage that it can be carried out at substantially lower temperatures, i.e., at a maximum temperature of 1200° C.

In accordance with the present invention, solid rather than molten ferrosilicon is added to a magnesium melt while the temperature thereof is increased concurrently with such addition. Such procedure, which above all is harmless and actually involves but small losses of magnesium, is quite different from the addition of magnesium to a ferrosilicon melt having a temperature of 1300° C. or covering solid or liquid magnesium by pouring a silicon alloy thereover, which has a temperature at least 600° C. higher than the temperature of magnesium at its melting point.

The prealloys prepared by the process of this invention can be alloyed in the usual manner with cast iron to ensure the separation of graphite in globular or spherical form.

The present invention relates more particularly to a process for making iron-silicon-magnesium prealloys which may also contain further constituents, such as Ca, Cu, Ni, Mn, and lanthanides, wherein a liquid magnesium melt having a temperature of about 650° C. is first produced, the melt being covered in known manner, for example, with flowers of sulfur and thereby protected against air oxidation, solid ferrosilicon containing at least 70% by weight Si is then slowly added to the melt while the temperature thereof is gradually increased to about 1070° to 1100° C. with the resultant formation of an alloy composed of Mg_2Si and FeSi, and further alloy constituents are incorporated while the alloy is superheated to 1150 to about 1200° C.

Prealloys containing a relatively great proportion of calcium can be obtained by adding solid calcium-silicon in addition to solid ferrosilicon to the magnesium melt while the temperature thereof is gradually increased.

On superheating to 1150° C. to about 1200° C. the alloy may be further alloyed with further ferrosilicon containing less than 70% by weight silicon, preferably 40 to 48% by weight silicon.

The silicon, which is used in the form of ferrosilicon or calcium silicon is added to the magnesium melt having a temperature of about 650° C. and the temperature of the melt is gradually increased to about 1070° to 1100° C. in harmony with the known liquidus curves of the Si-Mg diagram, the ferrosilicon being added at a temperature up to about 50° C. above the liquidus curve of the Si-Mg diagram.

The following examples serve to illustrate the invention but they are not intended to limit it thereto, the percent figures being by weight.

EXAMPLE 1

Preparation of an iron-calcium-silicon-magnesium alloy containing about 10% magnesium

120 kg. Mg were melted in a carbon crucible under chloride and fluoride slag. 60 kg. FeSi (75% Si) were added to the melt while the temperature was gradually increased to 850° C. Care was taken that the bath remained liquid. The temperature was then increased to a final temperature of 1150° C. while adding 920 kg. calcium-silicon containing 30.5% Ca and 61% Si. The liquid alloy was then poured into molds painted with clay milk. 1000 kg. of an alloy containing 10.7% Mg were obtained. 1200 kw./hr. were consumed.

EXAMPLE 2

Preparation of an iron-silicon-magnesium alloy containing about 10% magnesium

130 kg. magnesium were melted in a carbon crucible covered with flowers of sulfur. The temperature was slowly raised to 1100° C. while adding 250 kg. FeSi (75% Si). During the ferrosilicon addition care was taken that the bath remained liquid. The ferrosilicon addition and the temperature increase were so balanced against one another that the alloy could not solidify and that undesired vaporization of magnesium could not appear. The melt bath, which preferably consisted of Mg_2Si and FeSi with an excess of free Si, was admixed with 720 kg. FeSi (45% Si). Good castability was produced by increasing the temperature of the melt bath towards the end of the FeSi-addition to 1150° C. and casting the finished alloy into molds prepared with luting sand. 1000 kg. of an alloy containing 11.2% magnesium were obtained. 1200 kw./hr. were consumed.

EXAMPLE 3

Preparation of an iron-silicon-magnesium alloy containing about 30% magnesium

300 kg. magnesium were melted in a carbon crucible under pulverulent sulfur as agent avoiding oxidation. The temperature was slowly raised to about 1100° C. while adding 360 kg. FeSi (75% Si). The ferrosilicon addition and temperature increase were so balanced against one another that the melt bath just remained liquid. The resulting liquid alloy had a composition which approximately corresponded to that of the compounds FeSi and Mg_2Si.

Copper, nickel and iron, respectively, or another silicide-forming element desired in the alloy, may be added while taking care that the silicon content of the liquid alloy remains constant at 46% Si, so that all metals present are bound as silicides.

380 kg. FeSi containing 42% Si were added while the temperature was increased to 1200° C. After the addition of ferrosilicon was complete, 60 kg. iron were incorporated with the alloy. At about 1220° C., 1000 kg. of an alloy containing 27.1% Mg and 35.5% Si were cast into molds coated with clay milk. 1280 kw./hr. were consumed.

We claim:

1. A process for the manufacture of iron-silicon-magnesium prealloys, which comprises preparing a liquid magnesium melt having a temperature of about 650° C., protecting the melt against air oxidation, and slowly adding solid ferrosilicon containing at least 70% by weight silicon to the melt while gradually increasing the temperature thereof to about 1070° to 110° C. with the resultant formation of an alloy composed of Mg_2Si and FeSi.

2. A process as claimed in claim 1, which comprises preparing a prealloy containing calcium by adding solid calcium-silicon in addition to solid ferrosilicon to the magnesium melt while gradually increasing the temperature thereof.

3. A process as claimed in claim 1, which comprises protecting the liquid magnesium melt against air oxidation by covering the melt with flowers of sulfur.

4. A process as claimed in claim 1, which comprises adding the ferrosilicon to the magnesium melt having a temperature of 650° and gradually increasing the temperature of the melt to 1070 to 1100° C. in harmony with the liquidus curves of the Si-Mg diagram.

5. A process as claimed in claim 2, which comprises adding the calcium-silicon to the magnesium melt having a temperature of 650° C. and gradually increasing the temperature of the melt to 1070 to 1100° C. in harmony with the liquidus curves of the Si-Mg diagram.

6. A process as claimed in claim 4, which comprises increasing during the ferrosilicon addition the temperature of the melt to a degree up to about 50° C. above the liquidus curve of the Si-Mg diagram.

7. A process as claimed in claim 5, which comprises increasing during the calcium-silicon addition the temperature of the melt to a degree up to about 50° C. above the liquidus curve of the Si-Mg diagram.

8. A process as claimed in claim 1, which comprises superheating the alloy to a temperature within the range of 1150 to about 1200° C. while incorporating at least one further element selected from the group consisting of calcium, copper, nickel, manganese and lanthanides into the alloy as a further alloy constituent.

9. A process as claimed in claim 1, which comprises superheating the alloy to a temperature within the range of 1150 to 1200° C. while adding and thereby incoroporating therewith ferrosilicon containing less than 70% by weight silicon.

10. A process as claimed in claim 9, wherein the ferrosilicon contains 40 to 48% by weight silicon.

References Cited by the Examiner

UNITED STATES PATENTS

2,762,705 9/56 Spear et al. ---------- 75—123

DAVID L. RECK, *Primary Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,177,071 April 6, 1965

Hans Ebert et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 73, for "110° C." read -- 1100° C. --; column 6, lines 13 and 14, for "incoroporating" read -- incorporating --.

Signed and sealed this 21st day of December 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents