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3,138,450

PRODUCTION OF SILICON ALLOYS CONTAINING ONE OR MORE RELATIVELY VOLATILE METALS

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No Drawing. Filed Mar. 24, 1960, Ser. No. 17,267
Claims priority, application Germany Mar. 26, 1959
4 Claims. (Cl. 75-10)

The present invention relates to an improved process for the production of alloys, used in iron and non-ferrous metallurgy, containing at least 15% of silicon which also contain one or more relatively more volatile metals, such as magnesium, calcium and the like, and may also contain other metals, such as iron, nickel, copper, manganese, aluminum, rare earths and the like. The production of such alloys presents certain difficulties in view of the low boiling point of constituents thereof, such as calcium or magnesium, and their high affinity for oxygen as they have a tendency to undergo uncontrollable burning off which renders it difficult to produce alloys of definite reproducible compositions.

According to the invention it was found that such difficulties can be avoided in the production of such high silicon containing alloys which also contain relatively more volatile metals and that such alloys can be produced with good yields upon the metal components introduced and with definite reproducible compositions, by producing such alloys in an induction furnace using a crucible which primarily is constructed of carbon or graphite. The crucible preferably is composed of a carbon tamping mass, graphite or shaped bodies of hard burned carbon or electro graphite. However, crucibles constructed of graphite-clay can also be used. The use of crucibles constructed primarily of carbon has the advantage that such materials are not attacked by the melt as was the case with the materials previously employed for the usual smelting furnaces, as the oxides of the alloying metals in general belong to the group of materials from which the lining walls of the usual smelting furnaces are constructed. As a consequence the formation of slags often occurred in view of reactions between the melt and the furnace lining which not only made it difficult to produce alloys having the desired composition but also caused premature destruction of the furnace lining. When a crucible according to the invention which is primarily composed of carbon is used, the upper portion of the crucible which does not come into contact with the melt after a period of time becomes coated with a layer of oxides which prevent burning off of the upper portion of the crucible upon contact with oxygen of the air. On the other hand, such oxide coating does not disturb the composition of the alloy produced.

In the production of alloys containing over 15% of silicon and iron and, in addition, metals having a low melting and boiling point, such as calcium or magnesium, it is preferable to fuse the magnesium together with the remaining alloying components by supplying the magnesium to the crucible in solid form and cover it with the remaining alloying components to prevent burning off of the magnesium during the fusion and prevent inaccuracies in the composition of the desired alloy.

It also can be expedient first to melt the magnesium in the crucible of the induction furnace and then to add calcium silicon, for example, at the rate at which it is dissolved in the molten magnesium, and then to add ferro-silicon or silicon metal in portions in such a manner that

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the surface of the melt remains covered with the solid material as long as possible. It was found, for example, that molten magnesium can completely dissolve silicon alloys, such as 70-90% ferrosilicon or calcium silicon, as well as granular silicon, in a relatively short period of time at 750° C. It can be expedient to preheat the solid alloy components before they are added, for example, with waste heat to reduce the current consumed by the induction furnace.

One of the advantages of the process according to the invention is that temperatures can be employed for the production of alloys of predetermined composition which are 200-300° C. below those required in the customarily employed processes. The temperatures employed according to the invention do not exceed 1250° C. The dissolution process proceeds very quietly and the movement of the molten bath engendered by the induction furnace is of great significance for the liquefaction as the portions which have not yet been dissolved are rinsed by the melt and a complete homogenization is attained thereby. When the melt has been homogenized by the induction it should be cast in such a way that it cools and solidifies with sufficient rapidity that no separation or segregation of the components can occur. This expediently is effected by casting the melt in flat chill molds.

Considerably lower losses by burning off of the lower boiling components of the alloys produced occur in the process according to the invention than when other procedures are employed. Furthermore, the use of crucible material containing substantial proportions of carbon insures a sufficient heat transfer whereby local overheating is avoided and considerably less wear occurs. The carbon containing crucibles are more or less conductive and therefore take up up to 80% of the induced capacity in the case of highly conductive electro graphite and 10 to 40% in the case of amorphous graphite, electrode tamping masses or a carbon base containing oxidic or siliceous additions and consequently the furnace charge is not only heated directly by induction but also by radiation from the walls of the crucible. However, there is no tendency for the crucible walls to overheat and therefore prevention of losses through burning off is facilitated. In view of the homogenization of the melts by the induction current it is not necessary to provide exterior stirring of the melt. This materially reduces smoking and the danger of accidents. Previously alloys such as are produced according to the present invention were produced in at least two furnaces and in several working steps. The possibility of producing such alloys in one furnace and in one working step by the process according to the invention makes considerable savings in current possible and therefore a simplification and a reduction in the costs of the process.

Instead of proceeding in the previously described manners, it is also possible to produce magnesium containing melts by pouring the alloying components, such as ferrosilicon, calcium silicon and/or silicon metal or mixtures thereof in molten form over the magnesium in the induction furnace in solid or liquid form and subsequently homogenizing the mixture.

In some instances it may be expedient to melt some or all of the alloying components in the carboniferous crucible of the induction furnace by resistance heating and then to homogenize the melt by induction heating.

It also was found advantageous in some instances when the induction coil for the induction furnace is not one continuous winding but rather is subdivided and each portion connected individually to the transformer. In this way it is possible to supply strong inductive forces to those portions of the crucible which must take up the greatest quantities of energy.

The process according to the invention fundamentally

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can be carried out in induction furnaces at frequencies between about 50 and 10,000 Hertz (c.p.s.). The intensity of the movement of the molten bath in the crucible can be considerably influenced by the selection of the frequency of the heating current. The preferred intensity can be different for different types of alloys. The stronger the bath movement the greater the danger of oxidation by the oxygen of the atmosphere, the weaker the bath movement the slower the progress of the dissolution and homogenization. Preferably a powerline frequency induction furnace operating at, for example, a frequency of 50 Hertz of a rated capacity 450 kw. and a rated voltage of 400 volts is employed for the process according to the invention.

The process according to the invention is especially adapted for the production of the alloys of U.S. Patent 2,837,422, namely, pre-alloys essentially composed of 15–50% of magnesium, 2–10% of calcium, 35–60% of silicon and the remainder iron, which in addition can contain up to 2% of rare earths.

The following examples will serve to illustrate several embodiments of the invention.

Example 1

91 kg. of magnesium bars were introduced into an empty preheated crucible produced from a carbon tamping mass and covered with 40 kg. of CaSi and 170 kg. of coarse pieced 75% FeSi and 3.2 kg. of cerium misch metal. The induction furnace employed for the heating was one operating at a frequency of 50 Hertz and having a rated capacity of 450 kw. and a rated voltage of 400 volts. The electric current was turned on and the contents of the crucible melted down in 40–45 minutes, care being taken that the temperature did not exceed 1250° C. After the contents had been liquefied they were homogenized for 5 minutes at a lower current load. After the current was turned off the crucible was tipped and emptied in about 1 minute into a pan having a surface area of 2000 x 1400 mm. which was clad with cast iron plates 50 mm. thick. The height of the alloy in the pan was only about 30–40 mm. and it solidified in a maximum of 1–2 minutes in view of the rapid heat transfer to the base so that a segregation of the alloy components was avoided. The alloy plate formed, after completely cooling down, was broken up to the desired sized pieces.

Example 2

91 kg. of manganese bars were placed in an empty crucible as in Example 1 and melted down in 10–15 minutes at a frequency of 50 Hertz. The temperature of the resulting molten magnesium was about 750° C. Then 100 kg. of pieces of 75% FeSi were added. As soon as the crucible contents started to liquefy a further 70 kg. of 75% FeSi were poured in. Then a layer of 40 kg. of CaSi (about 30% Ca) was added over the top. After complete dissolution, which was attained in about 35–40 minutes while taking care that a temperature maximum of 1250° C. was not exceeded by regulating the current load on the crucible, the crucible contents were homogenized for 5–10 minutes. After the current was turned off the contents were completely emptied in about 1 minute by tipping the crucible and rapidly solidified.

Example 3

93 kg. of magnesium bars were introduced into an empty crucible as used in Example 1 and a liquid mixture of 40 kg. of CaSi and 170 kg. of 75% FeSi poured thereover. The current was turned on and the mixture homogenized by induction for about 10 minutes, care being taken that the temperature did not exceed 1250° C. After the current was turned off the crucible was tipped and emptied in about 1 minute. Analogous results were obtained when the magnesium bars were first melted in the crucible before adding the remaining alloying components.

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Example 4

An induction furnace with an operating frequency of 50 Hertz and a rated capacity of 450 kw. and a rated voltage of 400 volts similar to that used in the previous examples was employed except that its induction coil was provided with two separate current connections.

First a manganese silicide alloy containing 50% manganese and 50% of silicon was prepared by fusing a mixture of such metals in the preheated carbon crucible of such furnace. The melting point of such mixture was about 1130° C. The resulting alloy was poured out of the crucible, solidified rapidly in a chilled mold and broken into small pieces (max. size 10 mm.).

Then 34 kg. of Mg₂Si were produced in the same crucible by melting magnesium bars and adding the required quantity of silicon. Only the lower portion of the coil was activated while such alloy was prepared to prevent overheating of the portion of the crucible not covered by the melt. When the crucible charge had melted completely 66 kg. of the previously prepared fine piece manganese silicide were added in portions and the temperature of the charge slowly raised until such additions were completely dissolved. After the last addition had melted the upper portion of the coil was activated and the charge homogenized for 5 minutes, care being taken that its temperature did not exceed 1250° C. The crucible was tipped and emptied in about 1–2 minutes into a chilled mold where the alloy was rapidly solidified. The composition of the resulting alloy was 20% Mg, 33% Mn and the remainder Si.

Example 5

10 kg. of Mg bars and 56 kg. Al bars were placed in a preheated carbon tamping mass crucible in a furnace as in Example 1 and melted down. Then 39 kg. of CaSi (31% Ca, 61% Si and 8% Fe) were added and the crucible contents liquefied by slowly raising the temperature. After the charge had liquefied it was homogenized for a further 5–10 minutes and was then tipped out in 1 minute and rapidly solidified in a chilled mold.

The composition of the resulting alloy was about 10% Ca, 10% Mg, 20% Si, 56% Al and the remainder Fe.

Example 6

91 kg. of Mg bars were placed in a crucible as used in Example 1 and melted down in about 10 minutes at a frequency of 50 Hertz. The temperature of the liquid Mg was about 750° C. Then 40 kg. of CaSi (about 31% Ca, 61% Si and 8% Fe) were added and dissolved by slowly increasing the temperature. Then the melt was covered with 100 kg. of pieces of 75% FeSi and, in the measure in which such FeSi was dissolved, a further 70 kg. of 75% FeSi was spread on so that the liquid crucible contents were covered as long as possible by the FeSi which had not yet dissolved. The last residues of the FeSi dissolved in about 30–35 minutes, care being taken that the temperature did not exceed 1250° C. during such dissolution. Thereafter the crucible contents were homogenized for a further 5 minutes and after the current was cut off they were poured out in 1 minute into a chilled mold.

Example 7

50 kg. of Al pigs were introduced into a preheated carbon tamping mass crucible and covered with 150 kg. of small pieced CaSi (max. 50 mm., Ca=32%, Si=60% and Fe=8%) and this in turn covered with 100 kg. of silicomanganese (70.6% Mn, 19% Si and remainder Fe). The crucible was contained in an induction furnace as in Example 1 which, however, was also provided with graphite rod resistance heating. The contents of the crucible were first melted down by turning on the resistance heating. When the major portion of the crucible contents were liquid, the resistance heating was turned off and the induction heating turned on to effect the complete liquefaction and homogenization of the crucible contents. The

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contents were then rapidly poured into a flat open pan lined with carbon blocks. The composition of the resulting alloy was about 16% Ca, 17% Al, 36% Si, 23% Mn and the remainder Fe.

We claim:

1. A process for the production of homogeneous silicon containing alloys containing at least 15% of silicon and at least one metal selected from the group consisting of magnesium and calcium which comprises melting the components of the alloy in a crucible produced from carbon containing material in an induction furnace, homogenizing the resulting melt by induction and casting and cooling the alloy to solidify it before segregation of the components can take place therein.

2. A process for the production of an alloy containing magnesium, calcium, iron and at least 15% of silicon which comprises introducing magnesium in solid form into a crucible produced primarily from carbon, covering such solid magnesium with the remaining alloying components, induction heating such alloying components to melt them down at a temperature up to 1250° C., homogenizing the resulting melt by induction and casting and cooling the alloy to solidify it before segregation of the components can take place.

3. A process for the production of an alloy containing magnesium, calcium, iron and at least 15% of silicon which comprises introducing magnesium in solid form into a crucible produced primarily from carbon, induction heating said magnesium to melt it down, gradually adding calcium silicon to said molten magnesium at the rate at which it is dissolved, then covering the surface of the melt with solid ferrosilicon, heating the crucible charge by induction to effect fusion of the ferrosilicon and adding further quantities of solid ferrosilicon to maintain cover-

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age of the surface of the melt with solid ferrosilicon as long as possible, after the last ferrosilicon has fused homogenizing the melt by induction, the temperature of the crucible contents during fusion and homogenization being up to 1250° C., and casting and cooling the alloy to solidify it before segregation of the components can take place therein.

4. A process for the production of an alloy containing magnesium, calcium, iron and at least 15% of silicon which comprises introducing magnesium in solid form into a crucible produced primarily from carbon, induction heating said magnesium to melt it down, gradually adding calcium silicon to said molten magnesium at the rate at which it is dissolved, then covering the surface of the melt with solid silicon, heating the crucible charge by induction to effect fusion of the silicon and adding further quantities of solid silicon to maintain coverage of the surface of the melt with solid silicon as long as possible, after the last silicon has fused homogenizing the melt by induction, the temperature of the crucible contents during fusion and homogenization being up to 1250° C., and casting and cooling the alloy to solidify it before segregation of the components can take place therein.

References Cited in the file of this patent

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