Patented Feb. 14, 1950 2,497,529

UNITED STATES PATENT OFFICE

2,497,529

PROCESS FOR PRODUCTION OF MAGNESIUM BASE ALLOYS CONTAINING ZIRCONIUM

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No Drawing. Application March 8, 1946, Serial No. 653,147. In Great Britain March 22, 1945

2 Claims. (Cl. 75—168)

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This invention relates to magnesium base alloys which contain zirconium.

The addition of zirconium to magnesium or magnesium base alloys facilitates the production of castings and wrought goods having a fine grained crystalline texture and desirable mechanical properties.

However, considerable difficulties have been experienced in alloying zirconium with magnesium, particularly in order to produce an alloy containing at least 0.4 per cent zirconium which is necessary if alloys having the most desirable mechanical properties are to be produced. Research on this problem resulted in the invention described in British Patent No. 511,137 according to which, elements such as aluminium, silicon, tin, manganese, cobalt, nickel, and antimony, which form high melting point compounds with zirconium and which we term "zirconium alloying inhibitor elements," are omitted from the alloy, whilst other elements (which we term "permissible alloying elements") such as zinc, cerium, silver, thallium, copper, bismuth, lead and cadmium may be included.

In order to introduce the zirconium into the alloy it has been suggested to add metallic zirconium or alternatively zirconium salts capable of reduction by the magnesium to metallic zirconium in the melt. However, the use of metallic zirconium has not given satisfactory results and the use of zirconium salts has presented considerable difficulty. The salt specifically suggested was zirconium chloride, but as this is a highly volatilisable componnd it is easily lost by evaporation when introduced into molten magnesium. Accordingly it was suggested in the specification of British Patent No. 511,482 to introduce the volatilisable compound together with a reducing agent in a container of metallic magnesium forming a capsule which can be introduced into the molten magnesium. An alternative proposal described in the specification of British Patent No. 533,264 was to compress the zirconium chloride with calcium fluoride or the chloride by itself to form moulded pieces of high specific gravity which will readily sink in the molten magnesium. The production of such capsules or moulding of pieces of high density is however somewhat inconvenient for commercial purposes.

Attempts have also been made to bubble zirconium chloride vapour through a melt of magnesium but this also has not given satisfactory results.

We have achieved some success by the use of zirconium chloride mixed with sodium or potassium chloride (e. g. in the proportions producing the chlorozirconates) but this gives rise to a large quantity of very fluid chlorides at the bottom of the crucible which tend to flow over with the molten magnesium on pouring thereby producing flux inclusions in the metal and to minimise this a large quantity of the magnesium must be left in the crucible after pouring with consequent loss of output.

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A further substance which we have tried is potassium fluozirconate (K_2ZrF_6) but the use of this is attended by much too violent a reaction to be suitable for general commercial use.

Moreover, we have used zirconium fluoride and oxyfluorides using temperatures of 900° C. and over, but such high temperatures are undesirable because of difficulties of avoiding oxidation of the magnesium when alloying, loss of time and fuel, and possibility of dissolving iron if an iron or steel crucible is used.

We have now discovered that a satisfactory quantity of zirconium can be introduced into the magnesium at temperatures below 900° C. and even lower than 800° C. by the use of mixtures of zirconium fluoride or oxyfluoride with other suitable salts in the absence of certain impurities.

According to one feature of the present invention a zirconium containing substance is reacted with molten magnesium in the absence of any appreciable quantity of zirconium alloying inhibitor elements, said substance comprising zirconium fluoride as hereinafter defined, mixed or combined with one or more of the fluorides of lithium, barium, strontium, calcium, and magnesium, which are so selected that the fluoride or fluorides both with and without the magnesium fluoride produced during alloying will be sufficiently fluid to alloy at the alloying temperature, the mixture containing at least five per cent zirconium. The aforesaid substance preferably consists solely of these fluorides. The said substance may however also contain one or more chlorides or bromides of potassium, sodium, lithium, barium, strontium, calcium, and magnesium, and of reducible halides of permissible elements. Fluorides or such other halide mixtures as are viscous at pouring temperatures of the metal are preferred.

Permissible alloying elements may be added to the magnesium before or after or during alloying with zirconium.

Alloying temperatures as low as 750° C. or even lower, may be obtained by suitably increasing the proportion of said one or more fluorides in pro-

portion to the zirconium fluoride, or varying the composition of the mixture to make it more fluid at the temperature concerned. If desired a bath of lithium fluoride, calcium fluoride, and barium fluoride, may be used in such proportions that these fluorides together with the magnesium fluoride produced by reaction between magnesium and zirconium fluoride will form the quaternary eutectic.

The presence of sodium fluoride in the alloying substance appears to increase the tendency of the alloy to oxidise and we therefore preferably treat any of the required fluorides that may be contaminated with sodium fluoride with water to leach out any sodium fluoride that may be present.

Some potassum fluoride may also be included in the mixture of fluorides but too much tends to produce violent reaction particularly in the absence of chlorides.

Although the fluorides of lithium, calcium, strontium, and barium, are substantially inert with respect to molten magnesium, nevertheless a certain, if small, reduction of these fluorides takes place with consequent formation of magnesium fluoride and the resulting alloy contains traces of one at least of the four elements mentioned which produces improvements in mechanical properties. The inclusion of the elements lithium, barium, and strontium, may increase the tendency of the alloy to oxidise thereby rendering the usual inhibitors such as sulphur and sulphur dioxide inadequate when the metal is poured at temperatures above 740°. In the same way these alloys show a slightly increased tendency to attack green sand when the usual inhibitors are used in the usual proportions but if the simple technique outlined in Examples I and II (hereinafter described) is followed no difficulties whatever are experienced.

The term "zirconium fluoride" as used herein is intended to include a group of chemicals the precise composition of which is not easy to determine. In particular we have made a material having the composition approximately ZrF_4 in a condition in which it alloys quietly in accordance with the present invention and in a condition in which it reacts violently. Tests should therefore be made on new batches of such material so as to reject those which react violently. Other substances which are suitable for the present invention contain oxygen in addition to zirconium and fluorine and may thus possibly be present as combined water (e. g. ZrF_4 H_2O) or may possibly form an oxyfluoride such as $ZrOF_2.2HF$. Hydroxyl groups should however not be present as these introduce considerable difficulties in alloying. A suitable grade of zirconium fluoride can be made by mixing zirconium chloride and an aqueous solution of hydrofluoric acid (at least 40% concentration) evaporating down and drying at about 550° C.

It is also to be understood that reference herein to fluorides is intended to include fluozirconates e. g. some or all of the zirconium fluoride and say barium fluoride, may be provided in the form of barium fluozirconate.

For the purpose of definition the zirconium fluoride used for the present invention will comprise materials which contain at least twenty per cent of fluorine, and the fluorine, oxygen, and zirconium together total at least ninety per cent, and which materials are substantially free from hydroxyl groups.

The zirconium fluoride appears in general to show little or no volatility apart from decomposition at temperatures below 700–800° C.

If temperatures for alloying of above 850° C. are involved there is a tendency to introduce iron from the crucible into the alloy and we may in such cases use a crucible the inner surface of which is free from iron which can dissolve in the magnesium at the temperatures involved and a graphite crucible is satisfactory.

We have found it to be desirable to use the alloying substance either by pouring the molten metal on to the substance in molten state or in the form of solid prefused lumps, or by adding solid fused lumps of the substance (preferably preheated) to the molten metal. The metal, if poured on to the alloying substance, may be at a low temperature, and the melt will then be heated to a temperature suitable for alloying. If solid lumps are added to the molten metal, the latter may already be at the temperature necessary for alloying.

Example I

A steel crucible capable of holding 60 lbs. of magnesium base alloy was heated to bright red heat and 6.4 lbs. of a mixture of fluorides of calcium, barium, and magnesium, in the respective proportions of 15, 70 and 15 were added and melted therein. 4.8 lbs. of zirconium fluoride were added to the inert fluoride bath at 800° C. in several portions with stirring between additions thereby producing a molten alloying substance. Sixty pounds of a magnesium-zinc alloy containing 2¼ lbs. zinc were then poured at 680° C. on to the fluoride alloying mixture using sulphur dioxide to protect the metal from oxidation during transfer. The melt was immediately stirred for 15 seconds to ensure complete reaction and flux specified in British Patent Specification No. 539,024 applied to the metal surface after which the sulphur dioxide supply was cut off. The temperature of the melt was raised to 875° C. and the alloy stirred for 2 minutes using fluxes specified in British Patent Specifications Nos. 539,023 and 539,024 as required to prevent burning. The stirrer used consisted of a rod to which a perforated disc was attached at right angles. This stirrer was inserted in the fluoride alloying substance before the magnesium was added. After removing the stirrer sufficient calcium fluoride was sprinkled on to the flux cover to render it of a suitable consistency for pouring the metal. The crucible was then removed from the furnace and approximately 45 lbs. of alloy cast at 760° C. into green sand moulds containing various known substances to inhibit burning. A mixture of one part by weight of sulphur to 1 part by weight of boric acid dried at 150° C. was shaken from a muslin bag on to the metal stream to prevent oxidation of the alloy during pouring. The resulting alloy was found by analysis to contain 0.7 per cent zirconium, and 3.8 per cent zinc. Metal poured into sand moulds containing six per cent sulphur and 4 per cent boric acid showed no signs of burning.

Example II

A steel crucible capable of holding 60 lbs. of magnesium base alloy was heated to bright red heat and 6.4 lbs. of a mixture of fluorides of lithium, calcium, barium and strontium, in the respective proportions of 28, 24, 40 and 8 were added and melted therein. 48 lbs. of a mixture of zirconium oxyfluorides having a general com-

position of 54.5 per cent zirconium, 30.7 per cent fluorine were added to the fluoride bath at 700° C. in several portions with stirring between additions thereby producing a molten alloying substance. 60 lbs. of molten magnesium were then poured at 680° C. on to the fluoride alloying substance using sulphur dioxide to protect the molten metal from oxidation during transfer. The melt was immediately stirred for 15 seconds to ensure complete reaction, and flux according to the specification of British Patent No. 539,024 was applied to the metal surface after which the sulphur dioxide supply was cut off. The temperature of the melt was raised to 800° C. and the metal stirred for 2 minutes using fluxes specified in British Patent Specifications Nos. 539,023 and 539,024 as required to prevent burning. The stirrer used consisted of a rod to which a perforated disc was attached at right angles. This stirrer was inserted in the fluoride alloying mixture before the magnesium was added. After removing the stirrer from the melt 2¼ lbs. zinc were added and the melt stirred with a straight rod. Sufficient calcium fluoride was sprinkled on the flux cover to render it of a suitable consistency for pouring the metal. The crucible was then removed from the furnace and approximately 45 lbs. of alloy were poured at 760° C. into sand and die moulds. A mixture of one part by weight of sulphur to 1 part by weight of boric acid dried at 150° C. was shaken from a muslin bag on to the metal stream to prevent oxidation of the alloy during pouring. The resulting alloy was found by analysis to contain 0.7 per cent zirconium and 3.8 per cent zinc.

We claim:

1. A process for the production of magnesium base alloys containing zirconium comprising reacting molten magnesium, in the absence of any appreciable quantity of aluminum, silicon, manganese, cobalt, nickel, tin and antimony, with a substance consisting of at least 5% of zirconium

in the form of zirconium fluoride together with at least two of the fluorides of lithium, barium, strontium, calcium, and magnesium, said fluorides being present in quantities relative to each other to cause the fluorides both with and without the magnesium fluoride produced during alloying to be fluid at the alloying temperature between 750° C. and 900° C.

2. A process as claimed in claim 1 wherein said substance also contains at least one substance selected from the group consisting of the halides of zinc, cadmium, cerium, silver, thallium, thorium, copper, bismuth, and lead.

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