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MASTER ALLOY FOR INTRODUCING ZIRCONIUM INTO MAGNESIUM

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1

This invention relates to magnesium base alloys which contain zirconium.

The addition of zirconium to magnesium on 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, thorium, copper, bismuth, beryllium, calcium, 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 compound 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.

It was also proposed in British Patent application No. 26,438/39 to form a suspension of metallic

2

zirconium in the magnesium and to diffuse the zirconium into magnesium by heat treatment but this again is inconvenient and costly for a commercial purpose.

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.

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 satisfactorily used zirconium fluoride and oxyfluoride 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 found that a satisfactory quantity of zirconium can be introduced into magnesium at temperatures below 900° C. and as low as 800° C. by means of a suitable master alloy.

According to the present invention a master alloy for introducing zirconium into magnesium comprises at least the following three phases (1) a metallic matrix phase consisting mainly of magnesium and/or one or more permissible elements, (2) a metallic phase consisting mainly or wholly of zirconium, the master alloy being substantially free from zirconium alloying inhibitor elements, and containing at least 1 per cent of zirconium and preferably at least three per cent zirconium, and (3) a salt phase comprising not more than 30 per cent (preferably less than 10 per cent) of the whole and consisting mainly or wholly of one or more halides. The salt phase is preferably sufficiently fluid at temperatures below 900° C. (preferably below 850° C.) to permit alloying at such temperatures. If the salt phase only becomes molten at higher temperatures it is necessary to provide a fluid layer of suitable halides at the bottom of the crucible during alloying.

The salt phase may be a magnesium halide or halides together with one or more other suitable halides.

Preferably, however, the salt phase comprises

a mixture of fluorides especially two or more of the fluorides of lithium, calcium, barium, strontium, and magnesium. One or more fluorides of the permissible alloying elements may also be included.

Such traces of zirconium alloying inhibitor elements that may be present will prevent a certain quantity of zirconium from alloying but provided that there is a sufficient excess of zirconium over any such traces the master alloy will be satisfactory in this respect so long as sufficient of the master alloy is used.

Some impurities are however permissible and especially zirconium oxide which may be present in large quantities and if in highly reactive form can be reduced by the magnesium to produce alloyable zirconium.

The master alloy is particularly useful for supply to persons having limited experience and facilities and wishing to introduce zirconium into magnesium, as it is much easier for such persons to effect alloying with the master alloy than by using various other methods such as the direct alloying methods described in the specification of our British Patent application No. 7,227 of 1945.

According to the present invention also the master alloy is produced by reacting molten magnesium with a molten or prefused substance consisting of a zirconium halide with or without other suitable halides under conditions permitting reduction of the zirconium halide to produce metallic zirconium. Preferably the magnesium in considerable excess is poured on to the said substance and the reaction is effected with the minimum of stirring so as to prevent any substantial incorporation of the zirconium in the excess magnesium and the excess magnesium is then removed; thereby leaving a master alloy having the characteristics above defined. If desired, the magnesium and the said substance containing a zirconium halide may be mixed in vacuo or in an inert atmosphere such as argon.

The zirconium halides preferably comprise the fluoride or oxyfluorides (which latter are hereafter included in the term zirconium fluoride) but may alternatively comprise the chloride, bromide, oxide, chlorozirconates, or (if special precautions are taken) fluozirconates. The chloride or bromide may sometimes be used alone but the fluoride must be mixed with one or more suitable salts or the salt phase may consist of magnesium chloride or magnesium bromide alone or of these halides, or magnesium fluoride, together with one or more suitable halides.

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 this may 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.

The master alloy may be made by pouring molten magnesium on to the following substances in the form of fused lumps or in the molten state:

(1) Potassium or sodium chlorozirconate or any mixture of chlorides inert to magnesium containing $ZrCl_4$ or $ZrBr_4$ or $ZrCl_4$ or $ZrBr_4$ alone.

(2) A mixture of potassium fluozirconates with inert halides, comprising a chloride.

(3) Potassium fluozirconates alone, if special precautions against violent reaction are taken.

(4) A mixture of zirconium fluoride with inert halides.

If the master alloy is made with fluorides, some chlorides may be stirred into the master alloy to reduce the melting point of the salt phase.

Reducible halides of permissible elements may also be used, suitable precautions being taken where violent reactions are likely to be encountered.

According to one method of making a master alloy, described by way of example, we proceed as follows: A mixture is made of lithium, calcium, and barium fluorides in the proportions respectively of 28, 24 and 48 per cent. We melt the mixture in a crucible and add thereto an equal weight of zirconium oxyfluorides containing about 33% of fluorine and free from hydroxides and inhibitor elements. We then pour into the crucible a quantity of magnesium at a temperature of 680° C. under an atmosphere of sulphur dioxide or other protective gas. A considerable excess of magnesium over that required to react with the fluoride is used. The quantity of magnesium poured is increased until it provides a thick layer of magnesium to blanket the zirconium against burning. The melt is stirred for about 10 or 15 seconds. The heat of reaction will considerably increase the temperature of the melt and this is then cooled to about 700° C. whereupon excess magnesium and fluoride residue are poured off, leaving the master alloy in the form of a paste which is scraped out using flux or known inhibitors such as sulphur containing boric acid to prevent burning and which cools to a solid. Alternatively the master alloy can be allowed to solidify in the crucible.

Other fluoride mixtures containing less proportion of lithium fluoride may be employed.

Master alloys containing chlorides or bromides should be kept in an airtight container or coated with Canada balsam or some other suitable substance.

When high temperatures are involved there is a tendency to introduce iron from the crucible into the alloy and we may 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.

Traces of lithium, strontium, calcium, and/or barium, in the finished alloy can if desired for some special reason be removed by a flux containing magnesium chloride with simultaneous or subsequent inspissation. The inclusion of these elements however has certain advantages as described in our co-pending British patent application No. 7,225 of 1945.

The invention also comprises a method of al-

loying zirconium with magnesium by stirring such a master alloy into molten magnesium.

The master alloy is introduced into the magnesium at about 800° C. and the melt is agitated until alloying is completed. The magnesium may contain permissible alloying elements if desired or these may be introduced later.

We claim:

1. A master alloy for introducing zirconium into magnesium consisting of (1) a salt phase in quantity not exceeding 30% of the composition and consisting of at least two salts selected from the group of halides consisting of the halides of magnesium, lithium, calcium, barium and strontium, said salt phase containing at least some magnesium fluoride; (2) a matrix phase consisting essentially of at least one of the metals selected from the group consisting of magnesium, zinc, cadmium, cerium, silver, thallium, thorium, copper, bismuth, beryllium, calcium, and lead; and (3) metallic zirconium produced by reduction of zirconium fluoride by magnesium in the presence of the salt phase; the master alloy containing at least 3% of metallic zirconium and being substantially free from aluminum, manganese, tin, silicon, cobalt, nickel, and antimony.

2. A master alloy as claimed in claim 1 wherein

the salt phase includes at least one chloride of the group consisting of potassium chloride and sodium chloride.

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