Patented Nov. 2, 1948 2,452,894

UNITED STATES PATENT OFFICE

2,452,894

PROCESS FOR PRODUCING MAGNESIUM-ZIRCONIUM ALLOYS

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No Drawing. Application July 17, 1946, Serial No. 684,263. In Great Britain July 24, 1945

3 Claims. (Cl. 75—168)

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This invention relates to a process for producing magnesium-zirconium alloys.

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 in amounts of at least 0.4 per cent zirconium which are 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 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 the 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 to form a suspension of metallic zirconium in the magnesium and to diffuse the zirconium into magnesium by heat

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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 quanitity 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.

Morever, we have satisfactorily used zirconium fluoride and oxyfluoride, using temperatures of 900° C. and over for alloying, 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.

According to the present invention, alloying is effected by means of a compound or mixture containing fluorides of the elements potassium and zirconium, characterized by the fact that the ratio of zirconium fluoride to potassium fluoride exceeds that in K_2ZrF_6. A particularly favourable ratio is that covered by the approximate empirical formula $KZrF_5$. The compound or mixtures may also contain one or more of the chlorides of zirconium and alkali and alkaline earth metals (including magnesium). We originally found it to be undesirable to include chlorides of magnesium, calcium and strontium, because the inclusion of these chlorides was accompanied by a reaction giving rise to volatilisation and consequent loss of zirconium chloride. This difficulty may be overcome however, by taking the precautions of having the composition including chlorides selected to be substantially fluid at 700° C. or less, and melting the fluozirconate separately from the chloride melt and mixing the two at comparatively low temperatures (e. g. below 750° C.). And of course the molten mixture is either cast rapidly into molds for subsequent use or the magnesium is poured on without delay, or if it is necessary to hold the mixture molten for any appreciable period, a close-fitting lid should be applied. The mixture may, among other permitted constituents, con-

tain potassium and/or barium chloride, calcium fluoride and/or fluozirconate and small proportions of zirconium oxyfluorides, but a limitation of the quantity of sodium salts is generally desirable if the resulting alloy is to possess optimum mechanical properties. Chlorides and/or fluorides of the constituent metals forming the alloy may also be added in certain cases. If potassium chloride is added, a suitable mixture consists of equal parts by weight of $KZrF_5$ and KCl. Another satisfactory mixture consists of 40% K_2ZrF_6, 10% $CaZrF_6$ and 50% KCl.

We have found that certain compounds or mixtures having a ratio of zirconium fluoride to potassium fluoride greater than that in K_2ZrF_6 can be produced with a remarkably low melting point. The melting point of K_2ZrF_6 is about 840° C. whereas $KZrF_5$ melts at the surprisingly low temperature of about 470° C., whilst a mixture of 80% K_2ZrF_6 and 20% $CaZrF_6$ melts at about 550° C. The use of mixtures or compounds having these comparatively low temperatures enables the alloying process to be carried out without violent reaction. Nevertheless chlorides of alkali or alkaline earth metals (including magnesium), particularly potassium chloride, may be added to the alloying substance, i. e. the composition of the chloride mixture is added, to ensure absence of violent reaction in the event of overheating of the crucible. The use of the compound or mixture according to the present invention, enables magnesium alloys to be produced containing a satisfactory proportion of zirconium, e. g. 0.7%.

In carrying out the invention the mixture or compound may be melted in a crucible and molten magnesium or magnesium alloy poured on it whilst dusting with sulphur to minimise oxidation. In the absence of chloride additions the temperature of the alloying mixture should be less than 600° C. and that of the metal should not be above 680° C.; this method of alloying should however be restricted to small scale melts. The magnesium or magnesium alloy may be at a

temperature of say 700° C. when using a mixture of $KZrF_5$ and KCl.

Again, with particular convenience on a larger scale, $KZrF_5$ may be alloyed directly with magnesium without the addition of chloride thereto provided suitable precautions are taken. In particular the $KZrF_5$ should be used in the form of small lumps, preheated to about 300° C. and introduced into magnesium which is at a temperature of about 850–900° C., and after holding for a period of say ten minutes, working the residues into the alloy with an alloying tool for some minutes, an inspissated flux such as is described in British Patent No. 539,024 being applied to prevent oxidation.

We claim:

1. A process for producing magnesium base alloys containing zirconium wherein alloying is effected by reacting the magnesium with at least one substance selected from the group consisting of double compounds and mixtures of fluorides of the elements potassium and zirconium, the ratio of zirconium fluoride to potassium fluoride exceeding that in K_2ZrF_6, and subsequently agitating the melt.

2. A process as claimed in claim 1 wherein the ratio of zirconium fluoride to potassium fluoride is approximately equimolecular.

3. A process as claimed in claim 1 wherein the mixture also contains calcium fluoride.

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