

## UNITED STATES PATENT OFFICE

2,497,551

## COMPOSITION FOR INTRODUCING ZIRCONIUM AND BERYLLIUM SOLUBLY INTO MAGNESIUM

Alfred Claude Jessup, Clifton Junction Works, Manchester, and Joseph Beattie Wilson, Swinton, Manchester, England, assignors to Magnesium Elektron Limited, London, England, a British company

No Drawing. Application August 11, 1948, Serial No. 43,766. In Great Britain May 17, 1946

4 Claims. (Cl. 75-168)

1

This invention relates to magnesium base alloys.

It has heretofore been proposed to incorporate a very small proportion of beryllium in magnesium alloys for the purpose mainly of rendering the alloys less liable when molten to reaction with the atmosphere. It has generally been found that such an addition of beryllium has a pronounced tendency to produce grain coarsening of the alloy.

It has also previously been proposed in the specification of British Patent No. 511,137 to produce magnesium alloys of particularly fine grain structure by incorporating therewith a proportion of zirconium in the absence of any elements such as aluminium, manganese and silicon which form high melting point compounds with the zirconium (and which we term zirconium alloying inhibitor elements), other elements such as zinc, silver, thallium, thorium, copper, bismuth, lead, cadmium, and rare earth metals (which we term permissible elements) being incorporated in the alloy if desired.

In the course of our experiments we have endeavoured to produce magnesium alloys having the combined advantages which would appear to be offered by the incorporation of both beryllium and zirconium.

According to the specification of British Patent No. 511,291 it has already been proposed to add both beryllium and zirconium to a magnesium base alloy, the specific example quoted being a magnesium base alloy containing aluminium. We have endeavoured to obtain this combined advantage in magnesium base alloys with and without aluminium, initially without any success. We have confirmed that beryllium will in fact coarsen the grain of a magnesium base alloy containing aluminium, but we have found that the addition of Zr to the Mg-Al-Be alloy so produced results in total precipitation of the zirconium without producing the fine grain which is obtainable in accordance with the invention described in the specification of British Patent No. 511,137. We have further endeavoured to add beryllium both in the form of a metal alloy hardener and as a reducible salt followed by the addition of zirconium in various forms; but we found that the grain coarsening effect of the beryllium cannot be wholly overcome in any of these ways. Similarly the addition of beryllium to a magnesium alloy not containing aluminium

2

and already containing an adequate proportion of zirconium has the effect of producing a grain size which whilst finer than that commonly obtained with magnesium-aluminium alloys, is nevertheless considerably coarser than can be obtained with a magnesium-zirconium alloy free from beryllium. This grain coarsening is accompanied by considerable deterioration in mechanical properties.

It would appear to be particularly desirable to make the beryllium addition at an early stage of the melting and alloying process and accordingly to add the beryllium before effecting the more difficult zirconium alloying particularly since magnesium produced by oxidation of the melt militates against effective introduction of zirconium. Moreover there would seem to be no advantage to be gained by intimately mixing the beryllium material with the composition for introducing the zirconium.

We have however made the surprising discovery that if we incorporate a reducible halide of beryllium into a composition which is suitable for introducing zirconium solubly into magnesium, introduction of beryllium can be effected while retaining the full grain refinement associated with a maximum addition. The beryllium may be provided in the form of beryllium fluoride or sodium or potassium fluoberyllate, and the proportion of zirconium to beryllium in the composition (reckoned as metals) may be between 50 and 500 to 1. By thus adding to the molten magnesium a mixture which contains both beryllium and zirconium, we have found that not only is the grain coarsening (and consequent loss of mechanical properties) avoided but actually a considerable improvement in mechanical properties is achieved, as compared with the properties of alloys free from beryllium but otherwise of the same composition. This unexpected result could not have been foreseen from prior publications or experiments; but further experimental work has suggested a possible explanation along the following lines. We have found that if the beryllium is first added to the magnesium followed by the zirconium, imperfect grain refinement with erratic mechanical properties results; whereas if the zirconium is first added and the beryllium then added subsequently, consistently poor grain size and mechanical properties result. From this it is evident that beryllium acts as a partial alloying inhibitor element, so

3

that if the elements and zirconium are added in separate stages to magnesium, some precipitation of zirconium will occur accompanied by grain coarsening and loss of mechanical properties. If, however, the zirconium and beryllium are added simultaneously by co-reduction of their reducible compounds, it appears that precipitation of neither metal will occur and that a super-saturated solution results. This supersaturated solution can in fact be so rich in zirconium that increased mechanical properties can be obtained.

The process of this invention is particularly useful for the treatment of remelted zirconium-containing alloy whereby revivification of the zirconium content is obtained at the same time as introduction of the beryllium.

This wholly unexpected result has been achieved consistently with a number of different types of compositions. Thus for example, readily appreciable increase of mechanical properties may be obtained by incorporating a reducible beryllium halide into the following types of composition:

1. A composition which consists of an intimate fused anhydrous mixture comprising at least one of the chlorides of barium and/or strontium, and zirconium chloride, the mixture containing at least 15 per cent of barium chloride or at least 20 per cent of strontium chloride or a mixture of barium and strontium chlorides in amounts equivalent to at least 15 per cent of barium chloride reckoning one per cent of strontium chloride as equivalent to 0.7 per cent of barium chloride, the mixture containing at least four per cent of zirconium.

2. A composition which consists of zirconium fluoride mixed or combined with one or more of the fluorides of the lithium, barium, strontium, calcium, and magnesium, selected so as to be fluid at the alloying temperature.

3. A "master alloy" composition which consists of 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 and (3) a salt phase in quantity not exceeding 30% of the whole (preferably less than 10%) and consisting mainly or wholly of one or more halides; 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.

4. A composition which consists of one or more chlorides of alkali and alkaline earth metals including magnesium together with mixtures or compounds of zirconium fluoride with potassium and/or sodium fluoride.

5. Sodium or potassium chlorozirconate.

Whereas the introduction of beryllium into the magnesium melt before or after adding zirconium produces either no improvement of mechanical properties or a reduction of such properties, the method according to the invention shows improvements as illustrated by the following examples.

A. A composition suitable for introducing zirconium solubly into magnesium was made up in accordance with Example No. 1 above consisting of:

	Per cent
ZrCl <sub>4</sub> .....	40
KCl .....	18
BaCl <sub>2</sub> .....	42

Part of this mixture was used for making up two

4

alloys having the following compositions and the following cast test bar mechanical properties:

	Zn	Zr	Cd	Mg
(i) .....	Percent 1.5	Percent 0.7	Percent nil	Remainder.
(ii) .....	1.5	0.7	2	Do.

	0.1% Proof Stress, tons/sq. inch	Ultimate Tensile Stress, tons/sq. inch	Elongation percent on 2"
Alloy (i) .....	3.4	12.6	25.3
Alloy (ii) .....	3.7	12.9	28

Part of the same composition to which was added potassium fluoberyllate (0.2 per cent of the total mixture and equal to 1 gram per pound of alloy) was used to make up similar alloys containing a trace of beryllium which had the following cast test bar properties:

	0.1% Proof Stress, tons/sq. inch	Ultimate Tensile Stress, tons/sq. inch	Elongation percent on 2"
Alloy (i) .....	4.3	13.1	30.2
Alloy (ii) .....	4.0	13.2	28.4

B. Similarly the following alloys were made by using sodium chlorozirconate (Na<sub>2</sub>ZrCl<sub>6</sub>).

	Zn	Zr	Cd	Mg
Alloy (iii) .....	3	0.7	nil	Remainder.
Alloy (iv) .....	4	0.7	4	Do.
Alloy (v) .....	4.5	0.7	nil	Do.

These alloys gave the following cast test bar figures, the figures in brackets being those obtained with additions of potassium fluoberyllate, in amounts varying from 0.5 to 5 grams per pound of alloy.

	0.1% Proof Stress, tons/sq. inch	Ultimate Tensile Stress, tons/sq. inch	Elongation percent on 2"
Alloy (iii) .....	5.8 (6.8)	14.7 (15.5)	21.5 (29.7)
Alloy (iv) .....	6.2 (8.0)	14.7 (16.8)	10.1 (18.0)
Alloy (v) .....	7.7 (9.2)	15.9 (17.7)	11.5 (19.3)

C. Again, alloy (v) which was made up using a potassium fluozirconate-chloride mixture in accordance with Example No. 4, gave the following average cast test bar results:

0.1% Proof Stress, tons/sq. inch	Ultimate Tensile Stress, tons/sq. inch	Elongation percent on 2"
7.6 (8.1)	15.4 (16.4)	9.4 (11.6)

Test bars from the same batch after heat treatment for 24 hours at 180° C. gave the following figures:

0.1% Proof Stress, tons/sq. inch	Ultimate Tensile Stress, tons/sq. inch	Elongation percent on 2"
9.5 (9.8)	16.7 (17.1)	7.0 (8.4)

In both the above cases, the figures in brackets

5

are those obtained for the same alloys after an addition of 1 gram of sodium fluoberyllate per pound of alloy. The above mechanical test results cited under A and B were obtained on horizontally cast die bars, while those cited under C were obtained on vertical sand cast bars of DTD type.

The composition should be capable of introducing at least 0.5% of soluble zirconium into the magnesium. The soluble zirconium may be easily distinguished from the remainder of the zirconium content because it is, contrary to any other known form of the metal, easily soluble in an aqueous solution of hydrochloric acid consisting of 15 ccs. HCl of specific gravity 1.16 to 85 ccs. of water, sufficient acid being added during dissolution to maintain the initial acid concentration. We have found that by proceeding in accordance with the present invention, this desirable quantity of at least 0.5% of soluble zirconium can be retained in the final alloy, together with the required quantity of beryllium.

The quantity of beryllium which is desired in the final alloy is such as to ensure an appreciable protection of the molten alloy against attack by the atmosphere, and for this purpose we have found that the quantity of beryllium which should be present in the final alloy should be at least 0.0005% and preferably about 0.004%.

It is well known that commercially produced beryllium metal and beryllium compounds may contain certain proportions of elements such as aluminium and silicon which are present in beryl ore and which are undesirable in the production of magnesium alloys containing zirconium. It is evident that a process in accordance with the present invention would enable use to be made of beryllium compounds containing a reasonable quantity of such impurities.

The composition containing zirconium and beryllium will be stirred into the molten magnesium or magnesium base alloy in sufficient quantity to introduce the requisite quantity of zirconium solubly whereinafter the metal is cast into appropriately shaped moulds.

Instead of using beryllium fluoride, e. g. fluoberyllate, we can use any other reducible halide of beryllium. The quantity of mixed salts introduced into the molten magnesium is preferably such that the weight ratio of molten magnesium to beryllium is between 2,000 and 40,000 to 1.

We claim:

6

1. A composition capable of introducing zirconium and beryllium solubly into magnesium, consisting of at least one zirconium halide, at least one beryllium halide, at least one salt selected from the group consisting of the chlorides and fluorides of metals of the group consisting of the alkali and alkaline earth metals including magnesium, the total zirconium calculated as metal being at least three per cent, and the ratio of zirconium to beryllium being between 50 and 500 to 1.

2. A composition capable of introducing zirconium and beryllium solubly into magnesium, consisting of an intimate mixture of at least one beryllium halide with at least one chloride selected from the group consisting of the chlorides of the metals calcium, barium, strontium, magnesium, and alkali metals, a product which is a chemical association of zirconium fluoride and at least one of the fluorides of potassium and sodium, together with any reaction products of the aforementioned salts, the ratio of zirconium to beryllium in the composition calculated as metals being between 50 and 500 to 1, and the total zirconium calculated as metal being at least 3 per cent.

3. A composition as claimed in claim 1 which also contains at least one salt selected from the chlorides and fluorides of zinc, cadmium, silver, thallium, thorium, copper, bismuth, lead, and rare earth metals.

4. A composition as claimed in claim 2 which also contains at least one salt selected from the chlorides and fluorides of zinc, cadmium, silver, thallium, thorium, copper, bismuth, lead and rare earth metals.

ALFRED CLAUDE JESSUP.  
JOSEPH BEATTIE WILSON.

#### REFERENCES CITED

The following references are of record in the file of this patent:

#### UNITED STATES PATENTS

Number	Name	Date
1,515,082	Veazey	Nov. 11, 1924
2,224,151	Gauthier	Dec. 10, 1940

#### FOREIGN PATENTS

Number	Country	Date
511,291	Great Britain	Aug. 16, 1939