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MAGNESIUM BASE ALLOYS

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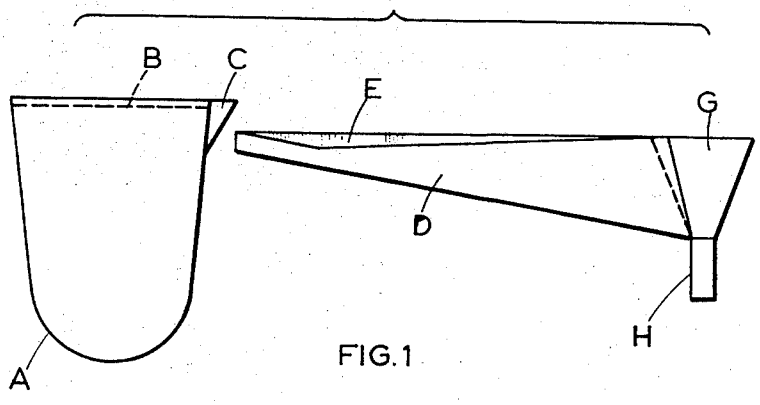


FIG.1

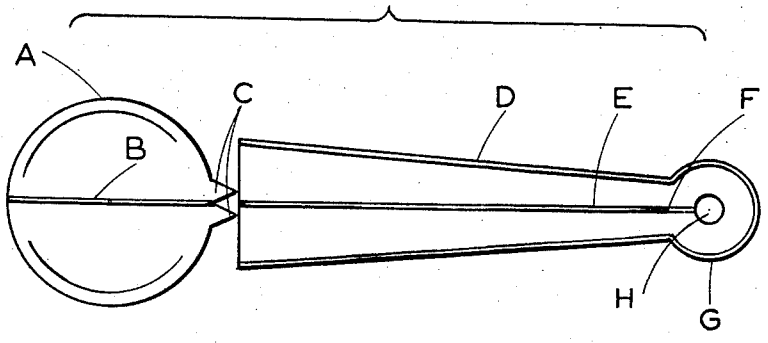


FIG.2

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MAGNESIUM BASE ALLOYS

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This invention relates principally to the production of magnesium base alloys of the kinds which incorporate from 0.25% up to 10% aluminium by weight of the alloy and more particularly from 0.25% to 2% aluminium. One object of the invention is to obtain a finer grain in the cast state than has hitherto been possible by any process with such alloys when containing up to 2% aluminium. A further object of the invention is to obtain magnesium aluminium alloys in the worked state which are particularly resistant to grain growth upon annealing. Still another object of the invention is to produce alloys containing both zirconium and one or more of the incompatible elements such as aluminium, silicon, tin, manganese, cobalt, nickel, antimony, beryllium and iron which in molten magnesium will form a compound with zirconium which tends to precipitate out of the melt. This phenomenon is described in the specification of British Patent No. 511,137. Hereinafter we term these elements zirconium-precipitating elements.

It is well known that magnesium alloys containing at least 2% aluminium can be treated with carbonaceous materials as described in British patent specification No. 608,942, in order to produce a finer grain size in the cast state. By this carbon grain refinement process it has hitherto been possible to obtain an average grain size of about 0.009 mm. in a three inch thickness cast billet of an alloy containing 8% aluminium and the grain size of a similar billet in an alloy containing 1% aluminium is about 0.6 mm.

Another method of refining the grain of such alloys is by the "super-heating method" which consists in heating the molten metal to a temperature above about 850° C. for a period of about 10–60 minutes before casting. This will produce approximately the same order of grain size as the carbon inoculation treatment.

The addition of beryllium to such alloys has the advantageous effect of reducing oxidation of metal in the molten state, but has the serious disadvantage that it prevents grain refinement by either carbon inoculation or superheating. Moreover, beryllium itself coarsens the grain size so that Mg-Al alloys containing beryllium are more coarse grained than the same alloys when made without beryllium and given no grain refining treatment. The average grain size of a three inch thick cast billet of an alloy containing 0.8% aluminium and 0.005% beryllium is about 2 mm.

With a view to restoring the fine grain after adding beryllium it was proposed in British patent specification No. 511,291 to add zirconium. However, the real effect of this was to precipitate both zirconium and beryllium from the melt so that the final cast alloy contained little or no beryllium with consequent restoration of the grain size. The melt likewise contained no zirconium. As correctly stated in British patent specification No. 511,137, zirconium is precipitated from molten magnesium in the presence of aluminium and certain other elements but is not so precipitated by other "permissible" elements such as zinc, cadmium, rare earth metals, silver, thallium, thorium, copper, bismuth, lead an calcium.

We have now found it possible to incorporate both zirconium and aluminium in the same alloy in such a manner as to obtain a fine grain size even with less than 2% aluminium present, and moreover to produce wrought articles which are resistant to grain growth at elevated

temperatures, so maintaining well their tensile properties after hot forming, annealing, etc. We have also found it possible to include other zirconium precipitating elements instead of or in addition to aluminium.

According to the present invention the alloy contains from 0.1 to 0.7 percent by weight zirconium and at least one of the following zirconium-precipitating elements, viz:

Aluminium	Over 0.1 and up to 10%.
Tin	Over 0.1 and up to 10%.
Silicon	Over 0.1 and up to 5%.
Nickel	Over 0.1 and up to 2%.
Cobalt	Over 0.1 and up to 2%.
Antimony	Over 0.1 and up to 2%.
Iron	Over 0.01 and up to 0.1%.
Beryllium	Over 0.005 and up to 0.03%.
Manganese	Over 0.5 and up to 2%.

with or without other elements as follows:

Zinc	Up to 6.0
Thorium	Up to 4.0
Cadmium	Up to 6.0
Silver	Up to 3.0
Rare earth metals	Up to 8.0

One particularly useful range of alloys includes at least 0.25 percent aluminium and at least 0.2 percent zirconium.

The inclusion of aluminium has the advantage that a substantial proportion of it may remain out of combination with zirconium and therefore be available for strengthening the alloy. The lower solubility of iron in liquid magnesium will result in a smaller proportion of zirconium compound being formed (although this may not be a disadvantage) while manganese and silicon both fall in a position intermediate between aluminium and iron.

The alloys of the present invention are of course distinct from mixtures of similar composition formed by powder metallurgy and the alloys of the present invention are free from the "stringers" of oxide inclusions characteristic of articles made by powder metallurgy. The term alloys as used herein and in the appended claims is intended to exclude materials made by powder metallurgy.

The invention further comprises a method for obtaining such an alloy which consists in flowing together two streams of molten magnesium base alloys one of which includes the zirconium-precipitating element or elements and the other of which includes the zirconium, casting the combined stream and chilling it quickly whereby at least some of the solid crystal nuclei derived from the molten zirconium alloy remain undissolved and so initiate crystallisation and at least some of the precipitated zirconium-compound particles are retained in suspension in the alloy. Preferably the quantity of suspended zirconium (i.e. the total zirconium content) is at least 0.2%. The soluble zirconium content of the alloy if any is of course very small (e.g. <0.05%) because of the presence of the zirconium precipitating element.

A particular method of carrying out the invention consists in flowing the streams down separate ducts into a common launder whence it flows to the tundish of a continuous or semi-continuous casting machine having a bottomless mold. The two streams mix thoroughly in the launder and tundish and flow through into the mould which is open at the top and closed at the bottom only by the solidified billet. Streams of cold water are sprayed on to the billet as it is drawn continuously out of the bottom of the mould. Alternatively, a crucible divided into two parts by a baffle plate may be used and the two metal streams flowed together at the crucible lip.

When this casting is subsequently extruded, forged or

rolled, a wrought product is produced which by virtue of the suspended zirconium-compound particles is very resistant to grain growth when the product is subjected to annealing or hot forming at elevated temperatures.

The invention has the further advantage of making it possible to include for the first time substantial amounts of beryllium in a magnesium alloy with a fine grained cast structure. Thus it is possible to include from 0.001% to 0.05% beryllium still retaining the required fine grain size. The beryllium will be incorporated in the stream which does not contain the zirconium, since beryllium has a very low solubility in the presence of zirconium and is moreover a partial zirconium precipitator and is therefore included as a zirconium-precipitator for the purpose of the present invention.

The proportions of the two streams may be about equal or can be varied according to the required final composition.

The zirconium-bearing stream is preferably at a lower temperature than that at which zirconium was alloyed so as to ensure the presence of crystal nuclei in suspension.

For example, alloying may be carried out at 800° C. and pouring carried out at 760° C.

By means of the present invention it is possible to obtain an average grain size of 0.1 mm. in a three inch thickness cast billet of an alloy containing ¾% aluminium and 0.005% beryllium.

A specific application of the invention is to make Mg—3% Al—1% Zn alloy rolling slab with fine grain size.

The quantities of elements other than aluminium and zirconium will normally be within the following ranges:

Zinc	0 to 6
Cerium	0 to 4
Thorium	0 to 4
Beryllium	0 to 0.05
Cadmium	0. to 6
Silver	0 to 3
Silicon	0 to 5
Manganese	0 to 2
Rare earth metals	0 to 8

The following are examples of compositions of the two streams and the final alloy produced.

	Percent
(1) Stream A:	
Al	1.8
Be	0.03
Stream B:	
Zr	0.6
Final alloy (50% A and 50% B):	
Al	0.9
Zr	0.3
Be	0.015
(2) Stream A:	
Al	12
Zn	0.8
Mn	0.5
Stream B:	
Zr	0.6
Final alloy (70% A and 30% B):	
Al	8.4
Zn	0.56
Mn	0.35
Zr	0.18
(3) Stream A:	
Th	6.0
Mn	1.0
Stream B:	
Zr	0.6
Final alloy (50% A and 50% B):	
Th	3.0
Mn	0.5
Zr	0.3
(4) Stream A:	
Zn	12
RE	1
Mn	1
Fe	0.04
Stream B:	
Zr	0.6
Final alloy (50% A and 50% B):	
Zn	6
RE	0.5
Mn	0.5
Fe	0.02
Zr	0.3

An apparatus suitable for the production of the alloys of the present invention is as shown in the accompanying diagrammatic drawings wherein:

FIGURE 1 is a side elevation of the apparatus; and

FIGURE 2 is a plan view thereof.

This apparatus comprises a crucible A divided into two compartments by a partition B which extends from top to bottom of the crucible. The compartments have pouring lips C respectively adjacent one end of the top of the partition. The partition is placed centrally to divide the crucible into two equal halves each of which contains one of the two alloys to be used. Providing that equal volumes of the two alloys are placed in the crucible, when tilted this will deliver equal quantities of the two alloys simultaneously.

The partition may, however, be placed in a non-central position and so arranged that, on tilting, the desired proportions of the two alloys to be mixed will be automatically delivered.

The alloys may be poured into an inclined trough D divided into two compartments or channels by the partition E which extends to the position F. The alloys are poured in separate streams until they meet in a tundish G where they mix and emerge through a funnel H. The mould into which they are to be cast will normally be placed immediately beneath this funnel.

The apparatus may be of metallic construction, e.g. of steel, or of any other material suitable for holding molten magnesium alloy.

The alloys may, however, also be prepared in, and poured from, completely separate crucibles providing that these are so arranged as to deliver the required proportions of each alloy simultaneously.

The launder D may also be dispensed with, the alloys being poured directly into a mixing compartment such as the tundish G.

The alloys may also be prepared in completely separate crucibles and separately pumped to the mixing chamber, delivery of the required proportions of each alloy being arranged by suitable control of the pumping device.

We claim:

1. A magnesium base alloy containing from 0.1 to 0.7 percent by weight zirconium and at least one of the following zirconium-precipitating elements, viz:

Aluminium	Over 0.1 and up to 10%.
Tin	Over 0.1 and up to 10%.
Silicon	Over 0.1 and up to 5%.
Nickel	Over 0.1 and up to 2%.
Cobalt	Over 0.1 and up to 2%.
Antimony	Over 0.1 and up to 2%.
Iron	Over 0.01 and up to 0.1%.
Beryllium	Over 0.005 and up to 0.03%.
Manganese	Over 0.5 and up to 2%.

characterized by a matrix of magnesium alloy containing a dispersion of insoluble intermetallic compounds consisting of zirconium with one or more zirconium precipitating elements, the matrix being substantially free from oxide, the quantity of suspended zirconium being at least 0.2 percent while the dissolved zirconium is less than 0.05 percent.

2. An alloy as claimed in claim 1 containing at least 0.25 percent aluminium.

3. A wrought article made from the alloy claimed in claim 1.

4. An alloy as claimed in claim 1, containing at least one of the following non-precipitating, optional elements in the proportions stated:

Zinc	Up to 6.0
Thorium	Up to 4.0
Cadmium	Up to 6.0
Silver	Up to 3.0
Rare earth metals	Up to 8.0

5. A process for the production of magnesium alloys containing both zirconium and at least one element capable of precipitating zirconium from a magnesium alloy which comprises the separate production of a molten magnesium zirconium alloy and a molten magnesium alloy containing at least one such element and flowing said alloys in separate streams into admixture with each other and thereupon rapidly solidifying the mixture in a mold to retain the precipitate in solution.

6. A process for the production of magnesium alloys containing both zirconium and at least one element capable of precipitating zirconium from a magnesium alloy which comprises the separate production of a molten magnesium zirconium alloy and a molten magnesium alloy containing at least one such element and flowing the two alloys down separate ducts into a common launder

whence the mixed alloy flows to the mold of a bottomless mold casting machine and then rapidly solidifying the mixture in said mold to retain the precipitate in solution.

7. A process for the production of magnesium alloys containing both zirconium and at least one element capable of precipitating zirconium from molten magnesium alloy which comprises the separate production of a molten magnesium zirconium alloy and a molten magnesium alloy containing at least one such element and flowing said alloys in separate streams into admixture with each other and thereupon rapidly solidifying the mixture in a mold to retain the precipitate in solution, the casting temperature of the molten magnesium zirconium alloy being below that at which the zirconium was alloyed to the magnesium.

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