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MAGNESIUM BASE ALLOYS

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1 Claim. (Cl. 75-168)

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This invention relates to the magnesium base alloys of the kind described in the specification of British Patent No. 511,137 which contain zirconium but contain no additions of elements, such as aluminium, silicon, tin, manganese, cobalt, nickel, and antimony, which in a molten magnesium-zirconium alloy combine with the zirconium present to form high melting compounds and which may contain "permissible" elements which are incapable of combining with the zirconium dissolved in the molten magnesium, to form high melting compounds which settle out.

We have now ascertained that special advantages are obtained by the inclusion in alloys of the foregoing kind of barium or strontium or both barium and strontium.

The total amount of these two elements barium and/or strontium may be up to 1% but as a matter of fact, traces of these elements are usually sufficient. The amount of these elements comprising said traces may be merely such as are sufficient to produce a visible line when the alloy is spectroscopically examined by an uncontrolled condensed spark. The quantitative lower limit for the beneficial action of these two elements should therefore be set at the order of 0.001%, but for practical purposes it is advantageous to have said element or elements present in somewhat larger amounts of the order of 0.01% to 0.1%.

It has been discovered that the above mentioned metals, barium and strontium, exercise an entirely unexpected beneficial effect when alloyed together with magnesium and zirconium in that they aid the introduction of zirconium into magnesium and magnesium base alloys, thereby refining the grain and notably increasing the proof stress, both of cast and wrought alloys.

As is well known, it is difficult to introduce zirconium into magnesium in such a state that it will effectively act as a grain refiner and improve the mechanical properties of the alloy. A great many methods for alloying zirconium with magnesium have been proposed, and many of these alloy a greater or less proportion of the zirconium in a form in which it is effective as a grain refiner. Whereas zirconium which is not effective in refining the grain and improving the mechanical properties is found to be suspended in an insoluble state in the magnesium or magnesium base alloy, the zirconium which is effective as a grain refiner appears to be in solution and may be easily distinguished from the aforementioned insoluble zirconium because it is, contrary to any other known form of zirconium

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metal, easily soluble in an aqueous solution of hydrochloric acid consisting of 15 ccs. HCl of sp. gr. 1.16 to 85 ccs. of water, sufficient acid being added during dissolution to maintain the initial acid concentration.

Thus the term "insoluble zirconium" used herein is intended to denote zirconium which is ineffective as a grain refiner, whilst the term "soluble zirconium" used herein is intended to denote zirconium which is effective as a grain refiner.

In the absence of barium or strontium the greatest grain refinement which can be obtained by the addition of zirconium to magnesium to form an alloy containing zirconium in the soluble state, which is die cast into a one inch diameter bar, results in an average grain size between 0.045 and 0.060 mm.; but in the presence of about 0.05% of barium an average grain size between 0.025 and 0.040 mm. is normally produced when the resulting alloy is similarly die cast into a one inch diameter bar. However on occasion, grain sizes of the order of 0.015 mm. have been obtained, in the presence of barium. As is well known, mechanical properties are largely dependent on grain size, and this very fine grain size is therefore highly desirable.

The alloys in accordance with the present invention should contain at least 0.3% of soluble zirconium and they may in addition contain one or more "permissible" elements such as zinc, cadmium, silver, cerium or other rare earth metal, lithium or calcium.

Similarly, the proof stress of an alloy such as a magnesium base zinc-zirconium alloy is markedly influenced by barium and strontium both in the as cast and the wrought state, as the following examples will show:

Example I

Three alloys "A," "B" and "C" were made up containing the following percentages by weight of zinc, soluble zirconium, barium and strontium:

Alloy	Zinc	Soluble zirconium	Barium	Strontium	
A-----	2.9	0.38	0.015	-----	Remainder commercial magnesium.
B-----	3.0	0.47	0.055	-----	
C-----	2.9	0.43	0.015	0.050	

These alloys were cast by the direct chill process and extruded at a temperature of 320° C.

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at a speed of 12 ins. per minute with the following resultant proof stresses:

Alloy	0.1 Proof stress tons/sq. in.
A-----	17.6-18.7
B-----	17.8-19.2
C-----	19.3-20.0

Example II

Two alloys, "D" and "E," were again made up to contain the four above mentioned elements in the following percentage proportions:

Alloy	Zinc	Soluble zirconium	Barium	Strontium	
D-----	3.0	0.64			Remainder commercial magnesium.
E-----	2.9	0.68	0.07		

These alloys were again cast by the direct chill process and the proof stress of the resulting cast metal determined.

Alloy	0.1 Proof stress tons/sq. in.
D-----	4.2-4.4
E-----	4.9-5.1

Example III

The above two alloys "D" and "E" were extruded at a temperature of 370° C. at a speed of 15 ins. per minute with the following resultant proof stresses:

Alloy	0.1 Proof stress tons/sq. in.
D-----	17.5-18.0
E-----	20.3-21.0

Example IV

The above two alloys "D" and "E" were again extruded at a temperature of 370° C., alloy "D" at a speed of 4½ ft. per minute and alloy "E" at a speed of 6½ ft. per minute.

Alloy	0.1 Proof stress tons/sq. in.
D-----	16.6-16.8
E-----	20.1-20.5

Example V

It will be seen from Example IV that although the extrusion speed of alloy "D" was slower than that of alloy "E," the proof stress of alloy "E" was still greatly superior to that of alloy "D." Even when alloy "E" was extruded at a temperature of 370° C. at a speed of 13 ft. per minute, the proof stress remained greatly superior to that of alloy "D" when extruded at a speed of 4½ ft. per minute.

Alloy	0.1 Proof stress tons/sq. in.
E-----	19.2-19.8

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In general, this increase of proof stress is accompanied by a corresponding decrease in elongation, and the elongation materially decreases when the quantity of barium or strontium exceeds about 0.1%. Nevertheless, the elongation of alloys containing about 0.1% of barium or strontium still remains appreciable and sufficient for many purposes, while the elongation of alloys in which the barium and/or strontium content does not exceed 0.07-0.8% still remains very substantial. Thus the elongations of the various alloys in the above examples were as follows:

Example	Alloy	Elongation, Per Cent
I-----	A	12.5-19.0
	B	11.0-14.0
	C	8.0-9.0
II-----	D	20.0-21.5
	E	6.5-9.0
III-----	D	12.0-21.0
	E	6.0-6.0
IV-----	D	22.0-22.5
	E	6.0-9.5
V-----	E	6.0-9.0

The elements barium and strontium may be added to the molten magnesium in the form of the individual metals, or in the form of master alloys, or in the form of their fluorides or oxides. If used in the metallic form, the alloying is preferably effected with the use of fluxes not containing magnesium halides, or under an inert atmosphere such for instance as argon, or in vacuo.

A suitable method for introducing the zirconium, strontium and barium into the magnesium is described in the specification of our co-pending British application No. 7227/1945, according to which molten magnesium is reacted with a fluid bath comprising a mixture of zirconium fluoride, and fluorides of barium or strontium, and if desired of calcium, lithium, and magnesium.

The inclusion of the elements barium and strontium and also lithium, if this element is present, appears to increase the tendency of the resultant alloys to oxidise, thereby rendering the usual inhibitors, such as sulphur and sulphur dioxide, inadequate when the metal is poured at temperatures above 740° C. 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. However, if simple precautions are taken, no difficulties in casting are experienced. For example, if a mixture of 1 part by weight of sulphur and 1 part by weight of boric acid, dried at 150° C., is shaken on to the pouring jet, and if a somewhat larger quantity than usual of sulphur and boric acid is incorporated in the moulding sand, no undue oxidation results. It has been found that 6 per cent of sulphur and 4 per cent of boric acid incorporated in the moulding sand is satisfactory.

It is generally known by those skilled in the art that magnesium base alloys containing zirconium are unusually difficult to prepare in a condition in which they are free from contamination with flux and from chloride inclusions, and so far all attempts to prepare uncontaminated alloys have failed.

We have however made the surprising discovery that even minute proportions of the two above mentioned elements, barium and strontium, have a remarkable and unforeseen effect on the elimination of flux, in that they considerably assist in the separation of the flux and of chloride inclusions from the molten metal, not only during

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the initial preparation, but also on remelting; and as the preparation of ingot for subsequent remelting is a most important outlet for magnesium base alloys, the property of remelting without flux contamination is of equal importance to that of the initial preparation of the metal in a flux free state.

We claim:

A magnesium base alloy consisting essentially of magnesium and at least 0.3 per cent of zirconium effective as a grain refiner, together with at least one metal from the group consisting of barium and strontium in total within the limits of 0.001 and 0.1 per cent.

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

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