## ALIEN PROPERTY CUSTODIAN

## MAGNESIUM BASE ALLOYS

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This invention relates to magnesium base alloys and is a continuation-in-part of our application Serial No. 236,552, filed October 22, 1938, for Magnesium Base Alloys.

The development of high percentage magnesium base alloys for castings, was primarily determined by the circumstance that the only possible method of obtaining a cast crystalline structure of technically useful strength properties, from magnesium, was by the incorporation there 10 with of alloying components having hardening properties. Up to the present, aluminium and zinc have been almost exclusively employed for this purpose. These metals, when employed in tne usual proportions of 4 to 10 percent of alumin- 15 ium, on occasion together with up to 3 per cent of zinc, exert a hardening and grain-size reducing action on the magnesium, which in itself is soft and solidifies with a coarse radial crystalline structure. According to their special composition, 20 and the method of casting (sand, permanent mould, or injection) employed, these known magnesium base casting alloys have, in the as-cast condition, a tensile strength of from 16 to 22 kgs. per sq. mm., with an elongation of 3 to 12 per 25 cent, a yield point of 8 to 16 kgs. per sq. mm. and a notched-bar impact strength of 0.5 mkgs. per sq. cm. ("Werkstoffhandbuch Nichteisenmetalle," 1936, Sheet K3.)

The tendency of these known magnesium base 30 alloys to form so-called "micro-shrinkage" cracks during solidification must, however, be regarded as a defect. These micro-shrinkage cracks not only render the castings permeable, to some extent, to liquids or gases, but also, in 35 certain circumstances, considerably impair, by the "notch" effect which said cracks produce, the good mechanical properties attainable by castings of sound crystalline structure. This tendency is especially marked in highly stressed 40 portions of the castings which have thus to be correspondingly thickened. The tendency of the known casting alloys to form such micro-shrinkage cracks appears to be connected with their the addition of which in appreciable amounts causes a widening of the solidification interval, i. e. the temperature range between the points of incipient and completed solidification, respectively, as compared with pure or only slightly al- 50 loyed magnesium. Attempts to counteract the formation of these micro-shrinkage cracks have hitherto been confined to the extensive use of chill plates and other measures for rapidly cool-

Such measures are, however, expensive and also frequently difficult to control in practice.

Bearing in mind the conditions, viz. fineness of grain and narrow solidification interval, which are the main causes for the formation of cast structures of high strength and free from microshrinkage cracks, systematic experiments were conducted for the purpose of finding an alloying component or components which would produce a powerful grain-size reducing effect on magnesium, even when employed in such small proportions as are insufficient to cause any appreciable widening of the solidification interval.

As a result of these experiments it was found that zirconium is a metal which fulfills the foregoing requirements, in that even when alloyed with magnesium in proportions of about 0.05 to 2.0 per cent it reduces the grain-size to a far greater extent than the hitherto customary far greater proportions of aluminium and zinc. Moreover, when adding zirconium to the magnesium in the foregoing proportions, the temperature of incipient solldification of the resulting alloys still practically coincides with the temperature at which the resulting alloys become totally solidified so that such alloys solidify without any appreciable formation of micro-shrinkage cracks. The grain-size reducing action of zirconium on pure magnesium (tensile strength in the as-cast condition 9 to 13 kgs. per sq. mm., elongation 5 to 6 per cent) is so powerful that an addition of 0.5 per cent of zirconium imparts to the resulting alloy a tensile strength of 18.5 kgs, per sq. mm. and a yield point of 7 kgs. per sq. mni., which values are nearly equal to those of the casting alloys hitherto in use. Moreover, the elongation is increased to 21.0 per cent and the notched-bar impact strength to 1.5 mkgs. per sq. cm., these values being thus considerably higher than the corresponding values exhibited by the usual casting alloys.

These values exhibited by the binary magnesium-zirconium alloys can be still further imrelatively high content of alloying components, 45 proved by the addition of other alloying components. It has, however, transpired that by no means all the components adapted to alloy with magnesium are suitable for this purpose but that, on the contrary, the presence of various of such alloying components more or less prevents the zirconium from exercising its favourable grain refining effect. Thus it has been found that only such alloying components are permissible as are incapable of combining with the zirconium dis-... ing the areas where the structure is endangered 655 solved in the molten magnesium to form high

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melting compounds which separate out or otherwise physically combine therewith to form components which settle out. In this respect, for example, the metals silver, copper, cerium, thorium, and calcium are suitable alloying components, and we have found that very useful alloys may be obtained by adding to magnesium and its 0.05 to 2.0 per cent zirconium component at least one metal of the group consisting of silver and copper, and at least one metal of the group consisting of cerium, thorium, and calcium. Other metals, however, for example, aluminium, silicon, tin, cobalt, nickel, antimony, and manganese, which appear to form with zirconium segregating intermetallic high melting compounds, when present in molten magnesium jointly with zirconium, are unsuitable. Moreover, bearing in mind the main objective of the invention, the amount of alloying components should preferably be insufficient to cause any appreciable widening of the solidification interval of the binary magnesium-zirconium alloys, since otherwise the advantage of freedom from micro-shrinkage cracks will progressively disappear. Thus the alloys may contain in addition to its 0.05 to 2.0 per cent zirconium component, at least one metal of the group consisting of copper 0.05 to 6 per cent, preferably not more than about 0.3 per cent, and silver 0.1 to 15 per cent, preferably not more than about 3.0 per cent, and at least one metal of the group consisting of cerium 0.05 to 15 per cent, thorium 0.05 to 15 per cent, and calcium 0.05 to 5 per cent, preferably not more than about 1.0 per cent, or up to about 30 per cent of two or more a of the five last-named metals jointly, each within the aforesaid limits.

In addition to magnesium and the aforesaid alloying components, viz. zirconium and copper and/or silver, and cerium and/or thorium and/or 4 calcium, the alloys according to the invention may also contain at least one metal of the group consisting of zinc 0.01 to 14 per cent and cadmium 0.01 to 24 per cent, the total amount of copper, silver, cerium, thorium, calcium, zinc, and cadmium jointly not exceeding 30 per cent.

Since the corrosion resistance of casting alloys is enhanced by a fine grained and compact crystalline structure, the alloys of the present invention are equal with respect to corrosion resistance and especially with respect to resistance to stress corrosion, to the hitherto known corresponding magnesium base alloys free from zirconium, so that the addition of manganese, which has hitherto been considered essential for improving the corrosion resistance but which, in this case, would prevent the zirconium from exercising its beneficial effects, can be dispensed

The fine grain which is formed in the solidi-  $^{60}$ fication of the magnesium-zirconium alloys of the present invention, also persists after repeated remeltings and pourings of the alloys. The formation of the fine grained structure is practically independent of the cooling velocity of the poured alloys, and therefore occurs both in casting in permanent moulds and in sand moulds. It is equally immaterial to the fineness of grain magnesium or into a magnesium alloy, provided that the alloying components already present in the magnesium do not form any segregating intermetallic compounds with zirconium. The folnary or complex casting alloys in accordance with the invention.

5	Alloy	Tensile strength	Elonga- tion	Yleld point	
	Mg with— 1.0% Zr	Kgs./sq. mm.	Per cent	Kgs./sq. mm.	
10	2.4% Ag 1.5% Th	14.9	6.8	7. 1	
10	Mg with— 1.0% Zr 3.0% Ag 0.2% Ca	21.0	12.0	8, 9	
15	Mg with— 1.0% Zr	} 17.8	9.6	6.8	
	Mg with— 1.0% Zr 0.2% Cu 0.3% Ca	18.3	12, 9	8.3	
20	Mg with— 1.0% Zr 0.3% Cu 3.0% Ag 0.7% Ca Mg with— Mg with—	17.1	4.1	11.8	
	0.3% Cu 0.5% Ce 0.2% Ca	انمدا	12. 4	8.6	
25	Mg with— 1.0% Zr	14.1	4. 9	7.4	
30	Mg with— 1.0% Zr		ð. O	11.3	
	Mg with— 1.0% Zr	19.8	10.0	10, 1	
35	Mg with—  1.0% Zr  0.3% Cu  0.3% Ca  3.0% Zn	17.3	4, 1	10.7	
40	Mg with—  1.0% Zr	17.9	7.1	8. 6	
45	Mg with— 1.0% Zr. 2.4% Ag 0.5% Ce 1.5% Th 2.0% Cd	17.3	7.8	7.8	

The desirable properties of the above described alloys, and especially their excellent ductility and notched-bar impact tenacity, render them also suitable for wrought goods. Even a binary alloy containing up to about 2.0 per cent of zirconium exhibits, after extrusion, strength values equal to those of the usual wrought magnesium alloys containing considerable amounts of aluminium and on occasion also zinc, whilst being substantially superior thereto in respect of tenacity. The introduction of further permissible alloying components, such as at least one metal of the group consisting of copper and silver and at least one metal of the group consisting of cerium, thorium, calcium, increases the strength of the wrought alloys as well, or improves the ratio between tensile strength and elongation. Another important point is that the wrought alloys in particular are often enough distinguished from the known wrought alloys by their suitability for welding.

The mechanical properties obtainable with the whether the zirconium be introduced into pure 70 known wrought magnesium alloys are approximately as follows:

Tensile strength 28 to 37 kgs. per sq.mm.: Yield point 20 to 28 kgs. per sq.mm.; eiongation 7 to 16 per cent (See "Werkstoffhandbuch Nichteisenlowing are typical examples of suitable quater- 75 metalle", 1936 Sheet K4, alloys AZM, AZ 855, VI).

By comparison, typical wrought alloys of the present invention give the following values:

ent invention give the following values:					Alloy	Tensile strength	Elonga- tion	Yield point
Alloy	Tensile strength	Elonga- tion	Yield point	5	Mg with—	Kgs./sq. mm.	Per cent	Kgs./sq. mm.
Mg with— 1.0% Zr	Kgs./sq. mm.	Per cent	Kgs./sq. mm. 28.6		1.0% Zr	39. 2	7.0	35.8
0.2% Ca Mg with— 1.0% Zr	1			10	2.0% Cd Mg with— 1.0% Zr	1		
0.3% Cu 1.0% Th Mg with— 1.0% Zr	29.6	12.0	28. 5		0.3% Cu	34.9	6, 5	32.9
0.3% Cu 0.7% Ca Mg with—	27.9	12.8	26. 1	15	1.0% Zr 0.3% Cu	41.1	5. 9	38.8
1.0% Zr 0.3% Cu 3.0% Ag 0.7% Ca Mg with—	30.8	12. 9	27.3	,	Mg with— 1.0% Zr 0.3% Cu	33.6	11.1	32.7
1.0% Zr 0.3% Cu 0.5% Ce	41.6	3.8	38.8	20	C.7% Ca	<b>J</b>		
0.2% Ca Mg with— 1.0% Zr 0.3% Cu	, 1				0.3% Cu 3.0% Ag 0.7% Ca 3.0% Zu	35.8	8.9	31.7
1.0% Th	30.9	9. 5	30. 9			<u> </u>	<u> </u>	<u> </u>
1.0% Zr 2.4% Ag. 0.5% Ce. 1.5% Th. 2.0% Zu	41.4	5. 0	36.8	25		HAN	NZ SAUE S EISEN: WIG HO	