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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 therewith 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 the usual proportions of 4 to 10 per cent of aluminium, 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 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 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 K_3).

The tendency of these known magnesium base 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 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 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 relatively high content of alloying components, 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 alloyed 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 cooling the areas where the structure is endangered. 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 micro-shrinkage 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 solidification 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. mm., 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 improved 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 dissolved in the molten magnesium to form high melting compounds which separate out or otherwise physically combine therewith to form components which settle out. In this respect, for example, the metals cerium, thorium, and calcium are suitable alloying components. 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 alloy may contain in addition to magnesium and its 0.05 to 2.0 per cent zirconium component between about 0.05 and about 15 per cent of cerium, or between about 0.05 and about 15 per cent of thorium, or between about 0.05 and about 5 per cent, and preferably not more than about 1.0 per cent of calcium, or up to about 25 per cent of two or all of the aforesaid metals jointly, each within the aforesaid limits.

In addition to magnesium and the aforesaid alloying components, viz. zirconium, cerium, and/or thorium, and/or calcium, the alloys according to the invention may also contain at least one metal of the group consisting of zinc 0.1 to 14 per cent, and cadmium 0.1 to 24 per cent, the total amount of cerium, thorium, calcium, zinc, and cadmium jointly not exceeding about 25 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 best of the hitherto known magnesium base alloys, so that the addition of manganese, which has hithereto 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 with.

The fine grain which is formed in the solidification 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 whether the zirconium be introduced into pure 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 following are typical examples of suitable ternary or complex casting alloys in accordance with the invention.

Alloy	Tensile strength	Elongation	Yield point
	Kgs./sq. mm.	*Per cent*	*Kgs./sq. mm.*
Mg with— 1.0% Zr, 1.0% Ce	15.9	8.0	8.0
Mg with— 1.0% Zr, 4.0% Ce	15.5	3.0	11.0
Mg with— 1.0% Zr, 2.0% Th	17.7	14.2	9.0
Mg with— 1.0% Zr, 1.0% Ca	15.8	6.2	9.0
Mg with— 1.0% Zr, 3.3% Ce, 3.5% Th	13.4	1.0	10.8
Mg with— 1.0% Zr, 2.2% Th, 0.5% Ca	17.0	11.0	8.0
Mg with— 1.0% Zr, 1.0% Ce, 6.0% Zn	20.0	4.0	14.0

Alloy	Tensile strength	Elongation	Yield point
	Kgs./sq. mm.	*Per cent*	*Kgs./sq. mm.*
Mg with— 1.0% Zr, 0.2% Ca, 1.0% Zn	21.9	10.5	10.6
Mg with— 1.0% Zr, 0.7% Ca, 4.0% Zn	22.2	7.8	12.8
Mg with— 1.0% Zr, 0.2% Ca, 6.0% Zn	20.7	4.3	14.1
Mg with— 1.0% Zr, 0.7% Ca, 2.0% Cd	15.8	5.6	9.4
Mg with— 1.0% Zr, 0.2% Ca, 0.2% Ce, 1.0% Zn	21.0	10.8	9.8
Mg with— 1.0% Zr, 0.4% Ca, 0.2% Ce, 1.0% Zn	20.9	18.2	7.4

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 cerium and/or thorium and/or 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 known wrought magnesium alloys are approximately as follows:

Tensile strength	kgs. per sq. mm	28 to 37
Yield point	do	20 to 28
Elongation	per cent	7 to 16

(See "Werkstoffhandbuch Nichteisenmetalle," 1936, Sheet K_4, alloys AZM, AZ 855, VI). By comparison, typical wrought alloys of the present invention give the following values:

Alloy	Tensile strength	Elongation	Yield point
	Kgs./sq. mm.	*Per cent*	*Kgs./sq. mm.*
Mg with— 1.0% Zr, 0.2% Co	45.5	3.3	41.6
Mg with— 1.0% Zr, 2.0% Th	42.5	3.0	40.0
Mg with— 1.0% Zr, 0.5% Ca	23.1	23.3	17.4
Mg with— 1.0% Zr, 0.2% Ca, 1.0% Zn	29.8	18.2	27.6
Mg with— 1.0% Zr, 0.2% Ca, 0.2% Ce, 1.0% Zn	35.5	7.4	33.8
Mg with— 1.0 Zr, 0.7% Th, 3.0% Zn, 2.0% Cd	43.5	3.0	40.0

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