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(57) Abstract: This invention relates to gadolinium-containing magnesium alloys, particularly those which possess high strength combined with corrosion resistance, and an optimised balance of strength and ductility. The described alloys consist of 2.0 to 5.0, preferably 2.3 to 4.6, at% in total of gadolinium and at least one of soluble heavy lanthanides and yttrium, wherein the ratio of the aggregate amount of soluble heavy lanthanides and yttrium to the amount of gadolinium is between 1.25:1 and 1.75:1, and preferably approximately 1.5:1, from 0 up to 0.3 at% of zirconium, preferably at least 0.03 at%, optionally with zinc, wherein when zinc is present the amount of zinc is such that the ratio of the weight of zinc to the weight of zirconium is preferably less than 2:1, and more preferably less than 0.75:1, all other lanthanides, viz. lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium and ytterbium in an aggregate amount of less than at 0.2 at%, and preferably less than 0.1 at%, the balance being magnesium, with any other element being present in an amount of no more than 0.2 at%, and preferably no more than 0.1 at%, and more preferably being present only as an incidental impurity.



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MAGNESIUM GADOLINIUM ALLOYS

This invention relates to gadolinium-containing magnesium alloys, particularly those which possess high strength
5 combined with corrosion resistance, and an optimised balance of strength and ductility. The described alloys also have exceptional high temperature performance for magnesium alloys. The alloys of the present invention have been developed as extrusion alloys, but can be
10 rolled to produce sheets and are also suitable for forging and machining. Although they can be cast successfully to form billets, these alloys are not as suitable to use as shape casting alloys in processes such as die casting or sand casting as other magnesium alloys
15 due to a tendency to form cracks.

There is considerable prior art concerning the Mg-Y-Gd system.

20 The United States patent US3391034 teaches that binary alloys of magnesium and 8 to 11wt% yttrium can be produced that are age-hardenable.

It states that the ductility of these alloys is inversely
25 proportional to their yield strength, and that an acceptable ductility is greater than 3-5%. It teaches that for the magnesium yttrium system levels of yttrium less than 8wt% do not produce sufficient mechanical properties compared with other magnesium alloys.

30

The mechanical properties claimed in US3391034 are shown in Table 1.

Table 1

Yttrium Content (wt%)	Yield Stress (Mpa)	UTS (Mpa)	Elongation %
8.2	303	344	3
9.0	323	374	6
10.6	335	374	5

The Russian patent SU1010880 teaches about magnesium alloys containing yttrium and gadolinium, optionally with zirconium. The two specific alloys discussed in the patent specification have the mechanical properties summarised in Table 2.

Table 2

Alloy Composition (wt%)	Yield Stress (MPa)	UTS (MPa)	Elongation (%)
4-6% Y, 8-10% Gd, 0.3-1.0% Mn	378-390	393-442	4.4-9.8
5-6.5% Y, 3.5-5.5% Gd, 0.15-0.7% Zr	353-387	397-436	4.0-6.0

This prior art teaches that these types of manganese-containing alloy form cracks while casting, but that this effect is reduced by the replacement of the manganese with zirconium. This teaching is silent regarding the corrosion behaviour or isotropy of these alloys.

The Japanese patent JP10147830 teaches that an alloy containing 1-<6 wt% Gd and 6-12 wt% Y produces good strength at high temperature. Zirconium in an amount of up to 2 wt% can also be present.

Also the Japanese patent JP9263871 teaches that an alloy containing 0.8-5 wt% Y and 4-15 wt% Gd or Dy produces a product that can be forged to produce an alloy of good strength. There is however no recognition in this document of the importance of not only the amount of each alloying element but their respective ratios.

Using peak hardness as a measure some tests were carried out on alloys with constant values of atomic percent rare earths (Total Rare Earths), while varying the ratio of yttrium plus other soluble lanthanides to gadolinium.

5 The results are as follows:

Melt Number	At%Gd	At% Y+ other soluble lanthanides	At% TRE	Ratio of Y + other soluble lanthanides to Gd	Wt% Gd	Wt%Y+ Other soluble lanthanides	Peak Hardness (Hv)
DF9122	1.33	2.00	3.33	1.5	7.6	6.5	127
DF9123	0.83	2.50	3.33	3.0	4.8	8.2	110
DF9124	2.50	0.83	3.33	0.3	13.1	2.6	118

JP9263871 also discusses the addition of Ca and other
 10 lanthanides, but we have found that the addition of Ca and certain lanthanides is very deleterious to these types of alloys.

The Chinese patent CN1676646 purports to teach that a
 15 broad range of alloys containing 1-6 wt% Y, 6-15wt% Gd, 0.35-0.8 wt% Zr and 0-1.5 wt% Ca can be extruded to produce extrudates of good strength, but there is little specific description of the alloys of the Examples and no clear demonstration of the utility of the described
 20 alloys near the limits of the claimed range.

All this prior art seems to be focussed on maximising the strength of the alloy at the expense of its ductility, but this latter is an equally important material
 25 property. Furthermore there is no recognition in the prior art of the effect of the levels of the different alloying element on the corrosion behaviour of the described alloys. What the present invention teaches is a way to obtain improved ductility while also achieving

high strength levels, without sacrificing corrosion resistance. None of this prior art recognises that when two or more of lanthanides and yttrium are in the same alloy, it is the specific ratio of their atomic concentrations that is the key factor in the effectiveness of the additions.

By selecting alloying additions within the range claimed in this invention and controlling the isotropy of the alloy, in addition to these improved mechanical properties, the alloys of the present invention will generally have corrosion rates of less than 100 mils per year (mpy) in the industry standard ASTM B117 salt-fog test, and preferably less than 50 mpy. Since the above prior art does not mention the corrosion performance of the described alloys and so it can be assumed that this feature of the described alloys was in line with conventional alloys, i.e. inferior to that of the alloys of the present invention and greater than a corrosion rate of 50 mpy.

In particular, in the academic published work by Rokhlin, namely the book entitled "Magnesium Alloys Containing Rare Earth Metals" Rokhlin, L L, published 2003, the inventor of SU1010880 states that increasing the yttrium content of magnesium alloys is detrimental to the corrosion rate of the alloy as shown in Table 3. The text states that this is due to the presence of $Mg_{24}Y_5$ compounds which are cathodic to the solid solution.

Table 3

Yttrium Content	Corrosion Rate	
	mg/cm ² /hour	Mills/years
Wt%		
0.5	0.025	48
3.8	0.14	268
10.5	0.36	690

In accordance with the present invention there is provided a magnesium alloy consisting of:

2.0 to 5.0, preferably 2.3 to 4.6, at% in total of gadolinium and at least one element selected from the group consisting of soluble heavy lanthanides and yttrium, wherein the ratio of the aggregate amount of soluble heavy lanthanides and yttrium to the amount of gadolinium is between 1.25:1 and 1.75:1, and preferably approximately 1.5:1,

from 0 up to 0.3 at% of zirconium, preferably at least 0.03 at %, optionally with zinc, wherein when zinc is present the amount of zinc is such that the ratio of the weight of zinc to the weight of zirconium is preferably less than 2:1, and more preferably less than 0.75:1,

all other lanthanides, viz. lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium and ytterbium, in an aggregate amount of less than at 0.2 at%, and preferably less than 0.1 at%,

the balance being magnesium, with any other element being present in an amount of no more than 0.2 at%, preferably no more than 0.1 at%, and more preferably being present only as an incidental impurity.

In this specification soluble heavy lanthanides are defined as elements with atomic numbers 65 to 69 inclusive and 71. Soluble heavy lanthanides (SHL) are those which display substantial solid solubility in magnesium. They are terbium, dysprosium, holmium,

erbium, thulium and lutetium. These elements are characterised by all of them having the same hexagonal close packed metallic structure as possessed by yttrium and magnesium, and by having a metallic radius of between 5 0.178nm and 0.173nm. They also exist only in a trivalent state when oxidised, which thus distinguishes them from elements such as europium and ytterbium which show both tri- and bivalency and do not show any appreciable solid solubility in magnesium. When present the aggregate 10 level of soluble heavy lanthanides should be greater than 0.1 at% in order to contribute significantly to the mechanical properties of the alloy. A particularly preferred soluble heavy lanthanide is erbium.

15 It is well known that the strengthening of alloys by precipitation hardening is a function of the amount and type of particles that are formed. This effect is related to both the amount of alloying elements that can be dissolved in the matrix expressed as atomic percent 20 and not as weight percent, and to the potential to precipitate intermetallic particles by heat treatment. The binary phase diagrams for the soluble heavy lanthanides and magnesium, for yttrium and magnesium, and for gadolinium and magnesium all show this potential.

25 From these phase diagrams it has been assumed to date that the soluble heavy lanthanides, gadolinium and yttrium will all strengthen magnesium in similar ways. It has, however, surprisingly been found that when gadolinium is present in a specific amount the addition 30 of a soluble heavy lanthanide or yttrium within a defined range causes the formation of at least one indeterminate ternary phase which affects the alloy's mechanical properties. This at least one ternary phase requires a ratio between the soluble heavy lanthanide or yttrium and

gadolinium of 3:2. Alloys having this ratio demonstrate a better combination of mechanical properties, namely strength, ductility and transverse properties, than can be achieved using other combinations of amounts of the lanthanides, yttrium and gadolinium. Significantly improved properties can be found where the ratio is between 1.25:1 and 1.75:1 for alloys which contain from 2.3 to 4.6 at% in total of gadolinium and at least one of soluble heavy lanthanide or yttrium. Outside this range either the strength and/or the ductility of the alloys declines. This decline becomes noticeable when the total amount of gadolinium, soluble heavy lanthanide and yttrium is below 2.0 at% and above 5.0 at%.

In order to assist this precipitation hardening effect a grain refining element can be added in an amount up to its solid solubility limit in the alloy. A preferred such element is zirconium. This can be added with increasing amounts generally improving the alloy's yield stress and elongation-to-failure properties. For such an effect at least 0.03 atomic per cent of zirconium should be present, and the maximum amount is the solid solubility limit of Zr in the alloy which is generally at about 0.3 atomic percent. However with both high and low levels of zirconium corrosion resistance may decline. The most preferred composition for a zirconium containing alloy of the present invention is 5.5 to 6.5 wt% Y, 6.5 to 7.5 wt% Gd and 0.2 to 0.4 wt% Zr, with the remainder being magnesium and incidental impurities. For some alloy compositions the level of zirconium should be from 0.3 to below 0.35% by weight in order to pass the 50 mpy salt-fog test.

It has been found that the presence of small amounts of zinc are beneficial to the corrosion performance of the alloys of the present invention, but that as the level of zinc is increased the alloy's corrosion performance
5 deteriorates. Preferably the level of zinc should be from 0.07 to below 0.5at%. There also appears to be a linkage regarding the formation of different types of precipitates when both zirconium and zinc are present in the alloy, and it has been found that the ratio of zinc
10 to zirconium should not exceed 2:1, and should be preferably less than 0.75:1.

Any lanthanide other than the required soluble heavy lanthanide or yttrium should be present in a total amount
15 of less than 0.2 atomic per cent, and preferably below 0.1 at%, otherwise there is interference with the formation of the desired at least one indeterminate ternary phase as described above. Similarly any other element should be present in an amount of no more than
20 0.2 at%, preferably no more than 0.1 at%, and more preferably be present only at an incidental impurity level.

The alloys of the present invention may be used for
25 extrusions, sheet, plate and forgings. Additionally they may be used for parts machined and/or manufactured from extrusions, sheet, plate or forgings.

Examples

30

A magnesium alloy DF8791 was produced containing 3.04 at % in total of yttrium and gadolinium, where the yttrium to gadolinium ratio was 1.52:1. Additionally it

contained 0.15 at% zirconium, with other elements being at impurity levels.

Another magnesium alloy, DF8961, was produced containing
5 2.65 at% in total of yttrium and gadolinium, with an yttrium to gadolinium ratio of 1.46:1. Additionally, it contained 0.12 at% Zr and 0.08 at% Zn, with other elements being at impurity levels.

10 Another magnesium alloy DF9380 was produced containing a 3.03 at% of a mixture of erbium, gadolinium and yttrium with a soluble rare earth plus yttrium to gadolinium ratio of 1.38:1. Additionally it contained 0.125 at% zirconium.

15

All these alloys possessed yield stresses greater than 300MPa and elongations-to-failure greater than or equal to 10%.

20 Three further magnesium alloys were tested, namely alloys DF8915, DF9386 and DF8758, which had similar total levels of yttrium and gadolinium to those of DF8961 but in different ratios. DF8915 had a significantly higher ratio of 3.9:1 and this produced a reduced yield stress
25 of only 250MPa. DF9386 and DF8758 both had a significantly lower ratio of 0.72:1 and 0.93:1 respectively. These low ratios had the effect of reducing the ductility of these alloys to below 5% to levels that are commercially unacceptable for this type of product.

30

A further alloy magnesium alloy DF9381 was produced containing 2.99 at% of a mixture of ytterbium, gadolinium and yttrium with a soluble rare earth plus yttrium to gadolinium ratio of 1.39:1. Additionally it contained

0.121 at% zirconium. The ytterbium in this alloy is not a soluble heavy lanthanide, and as a result of its addition to the alloy the strength of the alloy was reduced to unacceptably low levels.

5

A further set of test alloys were produced to examine the effect of zirconium on corrosion for the alloys of the present invention. Melts DF9382a to DF9382e all had the same composition except for varying levels of zirconium.

10 Alloy DF9382a shows that if the material is zirconium free (i.e. below detectable limits with standard industrial spark emission spectroscopy) the corrosion rate is above the acceptable level of 50 mils per year corrosion in the standard salt fog test. Further, at
15 higher levels of zirconium for this alloy, DF9382b and DF9382c also show this poor behaviour. However at levels of zirconium between 0.03 at % (0.1 wt %) and 0.12 at % (0.4 wt%) good corrosion performance is achieved. This is demonstrated by DF9382d and DF9382e.

20

A summary of these test results is shown in Table 4, in which some of the data has been rounded.

Table 4

Melt No	Analysis										Tensile Properties			Corrosion
	Y		Others		Gd		Zr		Total HL+Y+Gd	HL+Y: Gd	0.2% MPa	UTS MPa	%El	MPY
	Wt %	At %	Wt %	At %	Wt %	At %	Wt %	At %						
DF8791	6	1.83			7	1.21	0.5	0.15	3.04	1.52	317	444	10	
DF8961	5.2	1.57	Zn 0.2	Zn 0.08	6.3	1.08	0.4	0.12	2.65	1.46	308	424	17	
DF9380	5.09	1.55	Er 0.94	Er 0.15	7.72	1.33	0.42	0.125	3.03	1.38	306	409	13	
DF8915	8.1	2.44			3.7	0.63	0.5	0.15	3.07	3.9	250	356	13	
DF9386	5.13	1.64			12.64	2.29	0.24	0.075	3.93	0.72	359	450	3.5	
DF8758	4.7	1.45			8.9	1.55	0.4	0.12	3.0	0.93	319	433	3.9	
DF9381	5.18	1.58	Yb 1.0	Yb 0.16	7.28	1.25	0.41	0.121	2.99	1.39	264	367	15	
DF9382a	6	1.83			7	1.21	0	0	3.04	1.52				58
DF9382b	6	1.83			7	1.21	0.41	0.13	3.04	1.52				58
DF9382c	6	1.83			7	1.21	0.5	0.147	3.04	1.52				285
DF9382d	6	1.83			7	1.21	0.33	0.098	3.04	1.52				17
DF9382e	6	1.83			7	1.21	0.24	0.071	3.04	1.52				9

CLAIMS:

1. A magnesium alloy consisting of:
 - 5 2.0 to 5.0 at% in total of gadolinium and at least one element selected from the group consisting of soluble heavy lanthanides and yttrium, wherein the ratio of the aggregate amount of soluble heavy lanthanides and yttrium to the amount of
10 gadolinium is between 1.25:1 and 1.75:1, all other lanthanides in an aggregate amount of less than 0.2 at %, and the balance being magnesium, with any other element being present in an amount of less than 0.2 at%.
- 15 2. An alloy as claimed in claim 1 wherein the total amount of gadolinium, at least one soluble heavy lanthanide and yttrium is 2.3 to 4.6 at%.
- 20 3. An alloy as claimed in claim 1 or claim 2 wherein the said ratio is approximately 1.5:1.
4. An alloy as claimed in any one of claims 1 to 3 wherein at least one soluble heavy lanthanide is
25 present in an amount of at least 0.1 at%.
5. An alloy as claimed in claim 4 wherein the at least one soluble heavy lanthanide is erbium.
- 30 6. An alloy as claimed in any one of the preceding claims wherein all other lanthanides are present in an aggregate amount of less than 0.1 at%.

7. An alloy as claimed in any one of the preceding claims wherein any other element is present in the amount of less than 0.1 at%.
- 5 8. An alloy as claimed in claim 7 wherein any other element is present only as an incidental impurity.
9. An alloy as claimed in any one of the preceding claims additionally containing zinc in an amount of
10 from 0.06 to 0.6 at%.
10. An alloy as claimed in claim 9 wherein zinc is present in an amount of from 0.07 to less than 0.5at%.
- 15 11. An alloy as claimed in any one of the preceding claims additionally containing a grain refining element in an amount up to its solid solubility limit in the alloy.
- 20 12. An alloy as claimed in claim 11 wherein the grain refining element is zirconium in an amount of from 0.03 to 0.3 at%.
- 25 13. An alloy as claimed in claim 12 wherein zirconium is present in an amount of from 0.06 to 0.1 at%.
14. An alloy as claimed in claim 12 or claim 13 additionally containing zinc wherein the amount of
30 zinc is such that the ratio of the weight of zinc to the weight of zirconium is less than 2:1.
15. An alloy as claimed in claim 14 wherein the zinc/zirconium ratio is less than 0.75:1.

16. An alloy as claimed in any one of the preceding claims having a corrosion rate less than 50 mils per year in a standard salt-fog test.
- 5
17. A magnesium alloy consisting of 5.5-6.5 wt% Y, 6.5-7.5 wt% Gd and 0.2-0.4 wt% Zr with the remainder being magnesium and incidental impurities.
- 10 18. An alloy as claimed in claim 17 containing 0.3 to 0.35 wt% Zr.
- 15 19. An alloy as claimed in any one of the preceding claims when wrought and in the form of an extrusion, sheet, plate forging or mechanical part.