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Meng et al.(10) **Pub. No.: US 2009/0116993 A1**(43) **Pub. Date: May 7, 2009**(54) **AE SERIES HEAT RESISTANT
COMPRESSION CASTING MAGNESIUM
ALLOY CONTAINING CERIUM AND
LANTHANUM**(30) **Foreign Application Priority Data**

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C22C 23/02 (2006.01)(52) **U.S. Cl.** **420/405**(57) **ABSTRACT**

This invention relates to an AE series heat resistant compression casting magnesium alloy containing cerium and lanthanum and the composition ingredients and the weight percentage thereof are as follows: Al: 3%~5%, Ce: 0.4%~2.6%, La: 0.4%~2.6%, Mn: 0.2%~0.6%, and the remainder is magnesium. The raw material of cerium lanthanum mixture of rare earth used is the residual, cheap and overstocked cerium lanthanum mixture of rare earth obtained from common cerium rich mixture of rare earth after the Nd, Rr with high value and good market have been separated. The mechanical performance of this invention at room temperature and high temperature excels that of AE 44 and AZ 91 alloys, and the minimum creep rate of 1.82×10^{-9} S-1 and the creep percentage elongation in 100 h of 0.17% at the condition of 200° C. and 70 MPa excel these of AE 44 alloy.

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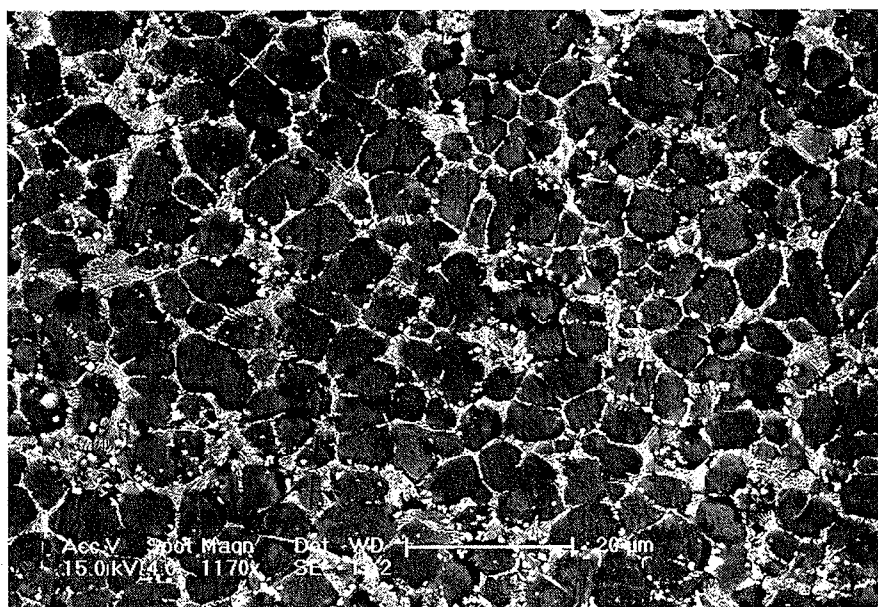


FIG. 1A

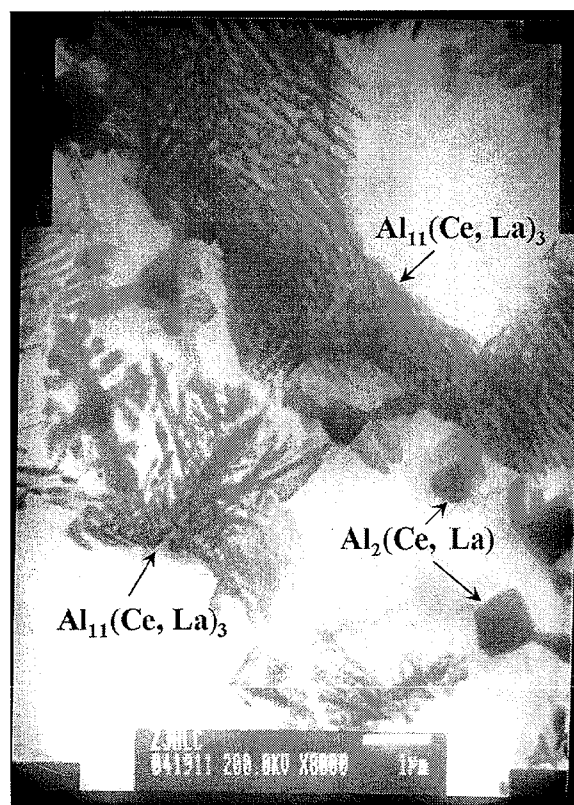
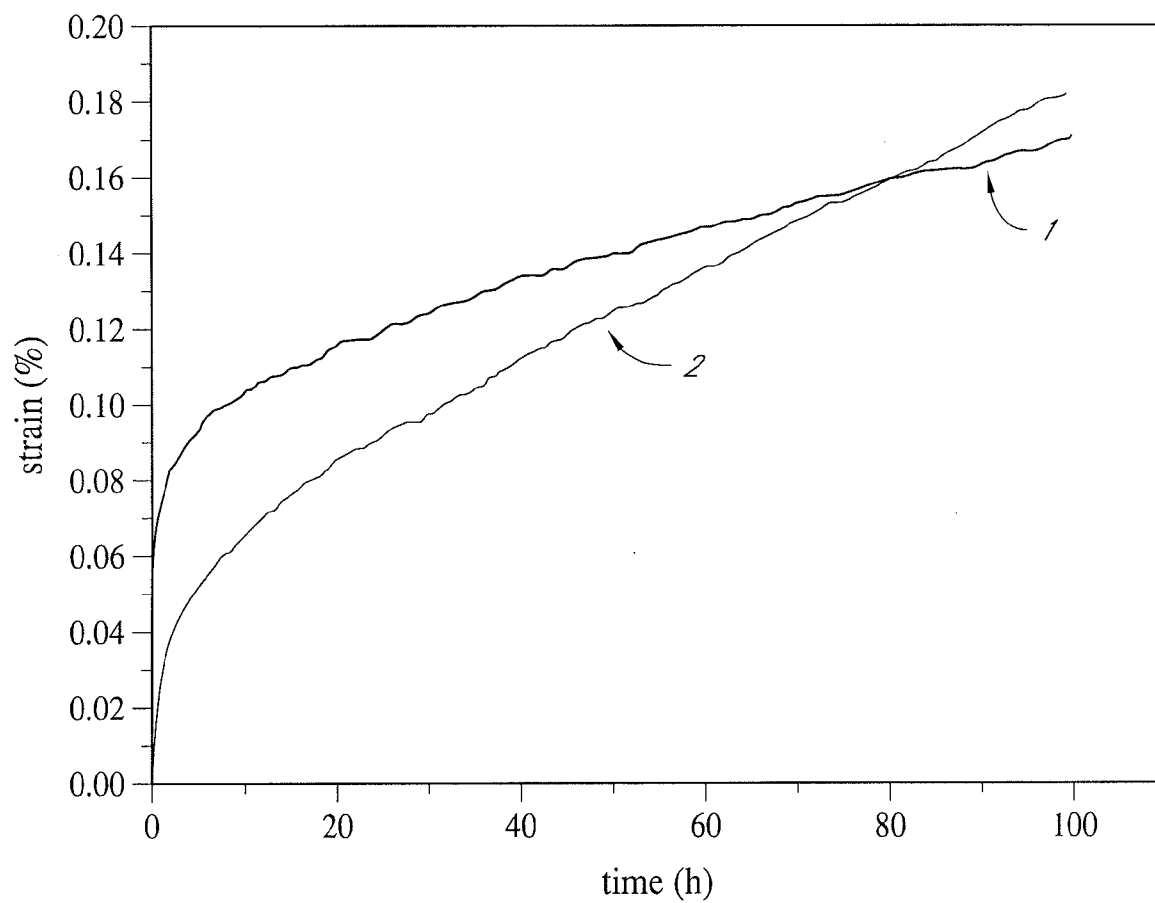


FIG. 1B

*FIG. 2*

AE SERIES HEAT RESISTANT COMPRESSION CASTING MAGNESIUM ALLOY CONTAINING CERIUM AND LANTHANUM

TECHNICAL FIELD

[0001] The present invention relates to a magnesium alloy material, and more particularly, to an AE series heat resistant compression casting magnesium alloy containing cerium and lanthanum.

BACKGROUND ART

[0002] In recent years, due to the pressure of environment protection and the enhancement of energy saving consciousness, the light compression casting magnesium alloys mainly in Mg—Al based alloys have found extended application in automobiles. However, as compared with aluminum alloys, the application of magnesium alloys still drops behind greatly and one of the reasons thereof is being short of sufficient high temperature property. At present, the long-term service temperatures of the AZ, AM series compression casting magnesium alloys used widely can not exceed 120° C., which makes them can not be used in manufacturing automobile driving assemblies that requires high creep resistant performance at high temperature, therefore the further application of magnesium alloys is blocked greatly. On the basis of that, the rare earth and alkali earth elements have been introduced into Mg—Al based alloys to develop a magnesium alloy with a creep resistant performance at high temperature, however, there are still some problems existing in this kind of heat resistant magnesium alloys developed recently. The main disadvantages existing in Mg—Al—Ca (AX) and Mg—Al—Sr (AJ) alloys are that thermal cracking occurs easily and the inferior plastic property of the alloys, and the like. The rare earths used in Mg—Al—Re alloys (herein, referred to as “AE series alloys”) developed are cerium rich mixture of rare earths (including La, Ce, Pr and Nd), however, the prices of Pr, Nd keep rising at present which makes the costs of this kind of AE series alloys increased. Additionally, the mechanical performances of the heat resistance magnesium alloys developed presently still need to be improved.

[0003] As the alloying (microalloying) elements for improving the heat resistant performance of the traditional magnesium alloys and developing new heat resistant magnesium alloys, rare earths have been recognized by the scientific research departments and manufacturers in China and abroad, and the rare earths used include single pure rare earth (such as Nd, Y, Gd) and mixture of rare earths. At present, the mixture of rare earths used mostly are: cerium rich mixture of rare earths with La, Ce, Pr, Nd as the main ingredients thereof, yttrium rich mixture of rare earths with Y, Ho, Er, Gd as the main ingredients thereof, praseodymium neodymium mixture with Pr and Nd as the main ingredients thereof. However, at present what overstocked abundantly is another cerium lanthanum mixture which is cheaper than the rare earths described above. Therefore, developing an application market of the cerium lanthanum mixture is pressing and significant for the complex utilization and equilibrium development of the rare earths.

[0004] Due to the specific chemical activity of cerium and lanthanum, after being added into magnesium alloys, both of them can produce the following four effects: purification, activation, fining and alloying/microalloying effects. As com-

pared with other rare earth elements, lanthanum has better impurity removing (remove the hydrogen and oxides inclusions) and purification effects on alloys. Comparing with lanthanum, cerium has a higher solid dissolving degree and a better effect of fining the alloy texture in magnesium alloys. It has been recognized widely by researchers that lanthanum and cerium can elevate the allround performance of magnesium alloys. By utilizing cerium lanthanum rare earths in combination, exerting their respective advantages and developing new rare earths magnesium alloys with high performance, it can help to solve the problem of overstocking abundantly rare earth resource of cerium lanthanum mixture, to alleviate the contradiction of the resource between production and demand and to solve the problem of imbalance between production and distribution.

DISCLOSURE OF THE INVENTION

[0005] For overcoming the shortcomings of the present compression casting magnesium alloys, this invention provides an AE series heat resistant compression casting magnesium alloy containing cerium and lanthanum. This alloy has a low cost, a good heat resistant performance and a long-term service temperature up to 200° C.

[0006] The ingredients and their mass percentage proportions of the AE series heat resistant compression casting magnesium alloy containing cerium and lanthanum are as follows: Al: 3%~5%, Ce: 0.4%~2.6%, La: 0.4%~2.6%, Mn: 0.2%~0.6%, the total amount of impurity elements of Fe, Cu and Ni is less than 0.03%, and the remainder is magnesium.

[0007] According to some embodiments, the preparation method of the AE series heat resistant compression casting magnesium alloy containing cerium and lanthanum of this invention is as follows:

[0008] Firstly, weighting according to the proportions, pure magnesium, aluminum, aluminum manganese intermediate alloy and manganese-cerium lanthanum intermediate alloy are pre-heated to 200° C., then pure magnesium, aluminum, aluminum manganese intermediate alloy are put into a crucible preheated to 300° C. and a protective gas with a SF₆/CO₂ volume ratio of 1:100 is introduced. After the materials added have been molten completely and when the temperature of the melt reaches 720° C.~740° C., manganese-cerium lanthanum intermediate alloy is added and the introduction of the protective gas is continued. After the manganese-cerium lanthanum intermediate alloy added has been molten completely and when the temperature rises back to 720~740° C., stirring for 5~10 min, then refining for 5~10 min with blowing argon. After the refining, settling for 28~32 min and the melt is cooled to 680° C.~700° C. A compression casting is performed on a cold chamber compression casting machine under a mould clamping force of 500 KN and an AE series heat resistant compression casting magnesium alloy containing cerium and lanthanum is obtained. Said cerium and lanthanum as raw material used in the manganese-cerium lanthanum intermediate alloy can take the form of residual and cheap cerium lanthanum mixture obtained by separating Nd and Rr with high value from the common cerium rich mixture of rare earths.

[0009] The features and beneficial effects of this invention are as follows:

[0010] 1) Aluminum is a main alloy element in an alloy, and an adequate amount of aluminum can provide an alloy with balanced strength, plastic property and casting processing performance, and makes this invention

be fit for mass production. 2) Cerium lanthanum rare earth mixture is an element of this invention for increasing the strength and the heat resistant property of an alloy in a strengthen mechanism as follows: on the one hand, as $Al_{11}RE_3$ and Al_2RE are formed by the combination of rare earth and aluminum in the alloy, $Mg_{17}Al_{12}$ phase with poor thermal stability is reduced or restrained which helps to increase the high temperature performance of the alloy; on the other hand, the Al-RE compounds of $Al_{11}RE_3$ and the like produced have very high melting point (e.g., the melting point of $Al_{11}RE_3$ can be up to $1200^\circ C$). These compounds disperse in grain boundary and show very high thermal stability which can nail the grain boundary effectively to block the slippage of the grain boundary and restrain the climb of dislocation in crystal. Additionally, during smelting, cerium lanthanum rare earth mixture can remove the impurities in manganese alloy melt to achieve the effects of degas refining and purifying the melt. Cerium lanthanum rare earth mixture is a surface-active element of manganese alloy. During the smelting of an alloy, the rare earths gather on the surface of the alloy liquid and a multiple composite dense oxide layer of MgO , RE_2O_3 and Al_2O_3 is formed, which alleviates the oxidation phenomenon, elevates the initial burning temperature and favors the melt casting of the alloy. During the freezing of the alloy liquid, the rare earths gather at the advancing front of the solid and liquid to increase the supercooling degree of the ingredients and help to fine the alloy texture. Therefore, cerium lanthanum mixture of rare earth benefits the improvement of the allround performance of an alloy. 3) The main effect of manganese is to increase the corrosion resistant performance of an alloy, and manganese can form a compound with iron or other heavy metal elements in magnesium alloy so as to remove them as a slag. As a result, the harmful effect of iron or other heavy metal elements on the corrosion resistance of the magnesium alloy can be eliminated. 4) The cerium lanthanum rare earth mixture is the residual and cheap cerium lanthanum rare earth mixture obtained by separating Nd, Rr with high value from common cerium rich mixture of rare earth. From 1990s up till now, the experts on rare earth in China and abroad have paid great attention to the problem of imbalance on the application of rare earths. At present, a difficult problem affecting the complex utilization and equilibrium development of the rare earths is the abundant overstock of cerium lanthanum rare earth mixture. Only in China, almost 12,0000 tons of cerium lanthanum rare earth with a value of one hundred million dollars is produced each year, however, this cerium lanthanum rare earth mixture is always kept overstocked and has not been widely utilized, which becomes a bottleneck for the complex utilization and equilibrium development of the rare earths. The reasons that this invention develops an AE series heat resistant compression casting magnesium alloy containing cerium and lanthanum by utilizing cheap cerium lanthanum mixture of rare earth lie in: 1. utilizing the cerium lanthanum rare earth overstocked in magnesium alloy which has been referred to as "a green light engineering material of the 21st century", which can alleviate the problem of imbalance between production and distribution for rare earth source and can benefit the harmonious development of the utilization of many

rare earth elements; 2. reducing the costs of this kind of alloys and ensuring the continuable development of these alloys by the abundant cerium lanthanum rare earth resource, which can increase the competition of magnesium alloys and accelerate the development of rare earth magnesium alloys nicely and quickly.

DESCRIPTION OF THE DRAWING

[0011] FIG. 1 shows the scanning electron microscope and transmission electron microscopy microtexture scheme for AlCeLa 4, 2.4, 1.6 alloy in Example 4. It can be seen that the main reason that the alloy has good mechanical performance lies in a fine grain strengthen of the alloy produced by fined alloy grains and a dispersion strengthen (mainly grain boundary strengthen) of the alloy produced by the abundant fine high melting Al-RE at the grain boundary.

[0012] FIG. 2 shows curve 1 and curve 2 as the creep curves of AlCeLa 4, 2.4, 1.6 alloy in Example 4 of this invention and AE 44 alloy under the condition of $200^\circ C$. and 70 MPa, respectively.

BEST MODE OF CARRYING OUT THE INVENTION

EXAMPLE 1

AlCeLa 3, 0.6, 0.4 Alloy

[0013] The mass percentage proportions of the AE series heat resistant compression casting magnesium alloy containing cerium and lanthanum are as follows: Al: 3%, Ce: 0.6%, La: 0.4%, Mn: 0.2%, the total amount of impurity elements of Fe, Cu and Ni is less than 0.03%, and the remainder is magnesium. The performance of the alloy is shown in FIG. 1 and FIG. 2.

EXAMPLE 2

AlCeLa 5, 1.2, 0.8 Alloy

[0014] The mass percentage proportions of the AE series heat resistant compression casting magnesium alloy containing cerium and lanthanum are as follows: Al: 5%, Ce: 1.2%, La: 0.8%, Mn: 0.4%, the total amount of impurity elements of Fe, Cu and Ni is less than 0.03%, and the remainder is magnesium. The performance of the alloy is shown in FIG. 1 and FIG. 2.

EXAMPLE 3

AlCeLa 4, 1.8, 1.2 Alloy

[0015] The mass percentage proportions of the AE series heat resistant compression casting magnesium alloy containing cerium and lanthanum are as follows: Al: 4%, Ce: 1.8%, La: 1.2%, Mn: 0.4%, the total amount of impurity elements of Fe, Cu and Ni is less than 0.03%, and the remainder is magnesium. The performance of the alloy is shown in FIG. 1 and FIG. 2.

EXAMPLE 4

AlCeLa 4, 2.4, 1.6 Alloy

[0016] The mass percentage proportions of the AE series heat resistant compression casting magnesium alloy containing cerium and lanthanum are as follows: Al: 4%, Ce: 2.4%, La: 1.6%, Mn: 0.6%, the total amount of impurity elements of

Fe, Cu and Ni is less than 0.03%, and the remainder is magnesium. The performance of the alloy is shown in FIG. 1, FIG. 2 and FIG. 3.

TABLE 1

The mechanical performances of Example 1, 2, 3 and 4 of this invention at room temperature			
Alloy No.	Tensile strength (MPa)	Yield strength (MPa)	Percentage elongation (%)
Example 1	228	130	15
Example 2	245	135	10
Example 3	257	148	13
Example 4	271	160	14
AE44	248	140	11
AZ91	222	145	3

TABLE 2

The mechanical performances at high temperature of Example 1, 2, 3 and 4 in this invention						
Alloy No.	150° C.			200° C.		
	Tensile strength (MPa)	Yield strength (MPa)	Percentage elongation (%)	Tensile strength (MPa)	Yield strength (MPa)	Percentage elongation (%)
Example 1	134	94	26	105	80	23
Example 2	140	103	21	108	87	20
Example 3	145	111	24	112	96	21
Example 4	147	120	31	120	107	26
AE44	140	109	27	115	100	19
AZ91	150	105	13	99	84	15

TABLE 3

the creep resistant performance at high temperature of AlCeLa 4, 2.4, 1.6 alloy in Example 4 of this invention			
Alloy No.	200° C., 70 MPa		
	Persistent life (hours)	Percentage elongation over 100 hrs (%)	Minimum creep rate ($\times 10^{-9} \text{ s}^{-1}$)
Example 4	>100	0.17	1.82
AE44	>100	0.18	3.42

[0017] Table 1 shows the mechanical performances of the alloys in Example 1, 2, 3 and 4 of this invention and AE 44, AZ 91 at room temperature.

[0018] Table 2 shows the mechanical performances at high temperature of Example 1, 2, 3 and 4 in this invention and AE 44, AZ 91.

[0019] Table 3 shows the creep resistant performance at high temperature of AlCeLa 4, 2.4, 1.6 alloy in Example 4 of this invention and AE 44.

[0020] AE 44 is a new high temperature creep resistant compression casting magnesium alloy developed by Hydro Magnesium Industry Company in Norway in 2005 and has been applied to produce automobile parts, such as the cradle for engine in automobile. AZ 91 is a magnesium alloy with a standard trademark and is also one of the magnesium alloys with the most use level in industry at present, however the service temperature thereof can not exceed 120° C. The data of AE 44 and AZ 91 in FIG. 1, FIG. 2 and FIG. 3 are the data obtained by preparing the samples at the same condition and testing them at the same condition

What is claimed is:

1. An AE series heat resistant compression casting magnesium alloy containing cerium and lanthanum, characterized in that the composition ingredients and the weight percentage thereof are as follows: Al: 3%~5%, Ce: 0.4%~2.6%, La: 0.4%~2.6%, Mn: 0.2%~0.6%, the total amount of impurity elements of Fe, Cu and Ni is less than 0.03%, and the remainder is magnesium.

2. The AE series heat resistant compression casting magnesium alloy containing cerium and lanthanum according to claim 1, characterized in that the composition ingredients and the weight percentage thereof are as follows: Al: 3%~4%, Ce: 0.4%~0.6%, La: 0.4%~0.6%, Mn: 0.2%~0.6%, the total amount of impurity elements of Fe, Cu and Ni is less than 0.03%, and the remainder is magnesium.

3. The AE series heat resistant compression casting magnesium alloy containing cerium and lanthanum according to claim 1, characterized in that the composition ingredients and the weight percentage thereof are as follows: Al: 4%~5%, Ce: 1.0%~1.2%, La: 0.8%~1.0%, Mn: 0.2%~0.6%, the total amount of impurity elements of Fe, Cu and Ni is less than 0.03%, and the remainder is magnesium.

4. The AE series heat resistant compression casting magnesium alloy containing cerium and lanthanum according to claim 1, characterized in that the composition ingredients and the weight percentage thereof are as follows: Al: 4%~5%, Ce: 1.8%~2.0%, La: 1.0%~1.2%, Mn: 0.2%~0.6%, the total amount of impurity elements of Fe, Cu and Ni is less than 0.03%, and the remainder is magnesium.

5. The AE series heat resistant compression casting magnesium alloy containing cerium and lanthanum according to claim 1, characterized in that the composition ingredients and the weight percentage thereof are as follows: Al: 4%~5%, Ce: 2.4%~2.6%, La: 1.4%~1.6%, Mn: 0.2%~0.6%, the total amount of impurity elements of Fe, Cu and Ni is less than 0.03%, and the remainder is magnesium.

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