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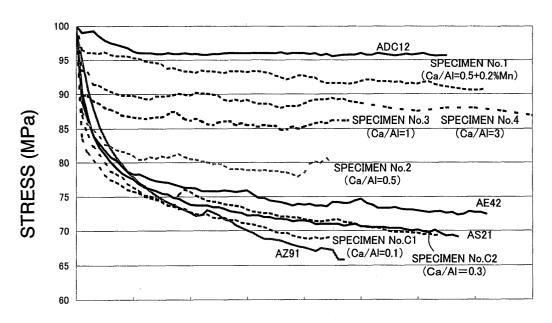
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### (54) Heat resistant magnesiun alloy

(57) A heat resistant magnesium alloy contains 1 to 6 percentage by mass of aluminum, 0.5 to 3 by mass ratio of calcium to aluminum, and the remainder made from magnesium and unavoidable impurities.

# FIG. 1



TIME (HOUR)

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### Description

### BACKGROUND OF THE INVENTION

[0001] The present invention relates to a low-cost heat resistant magnesium (Mg) alloy.

**[0002]** Because it is a lightweight material, Mg alloy, which is more lightweight than aluminum (Al) alloy, has recently attracted attention. Mg alloy is the most lightweight among suitable materials used to construct airplanes and automobiles. Mg alloy is used, for example, for wheels and head covers of engines of the automobiles.

**[0003]** In recent years, making automobiles more lightweight has been environmentally important. Therefore, use of Mg alloy is considered even in equipment and apparatus for use in high-temperature environments. In this case, it is the heat resistance of Mg alloy that matters. Prior art Mg alloy is characterized by a lack of high-temperature strength and is unsuitable for use in high-temperature environments. Additionally, when prior art Mg alloy is used for a structural material to which relatively large stress is applied, it is susceptible to creep deformation.

[0004] An additional element, when added to Mg alloy, improves the heat resistance of Mg alloy. The following publications disclose such a heat resistant Mg alloy.

[0005] Japanese Unexamined Patent Publication No. 9-272945 discloses Mg-Al-Ca-Si series alloy where Ca and Si respectively denote calcium and silicon. Also, Japanese Unexamined Patent Publication No. 9-291332, which corresponds to United States Patent No. 3,229,954, discloses Mg-Al-Ca-RE-Mn series alloy where RE and Mn respectively denote a rare-earth element and manganese. In addition, Japanese Unexamined Patent Publication No. 2002-157979 discloses Mg-Al-Zn series alloy where Zn denotes zinc. Further, other publications or references disclose heat resistant Mg alloy such as Mg-Al-Zn-Mn series alloy, Mg-Al-Si-Mn series alloy, Mg-Zn-Ca series alloy, and Mg-RE-Zn series alloy in such a manner that the heat resistant Mg alloy contains various elements and amounts of the elements.

**[0006]** However, most prior art Mg alloys contain a plurality of elements in large amounts. Some prior art Mg alloys contain costly RE. Consequently, these prior art Mg alloys are expensive.

### SUMMARY OF THE INVENTION

**[0007]** The present invention is directed to a heat resistant magnesium alloy excellent in heat resistance, which is produced using a low-cost element and by appropriately adjusting an amount of the element.

**[0008]** The present invention has a following feature. A heat resistant magnesium alloy contains about 1 to about 6 percentage by mass of aluminum, about 0.5 to about 3 by mass ratio of calcium to aluminum, and the remainder made from magnesium and unavoidable impurities.

### BRIEF DESCRIPTION OF THE DRAWINGS

**[0009]** The invention together with objects and advantages thereof, may best be understood by reference to the following description of the presently preferred embodiments together with the accompanying drawings in which:

FIG. 1 is a graph illustrating results from a relaxation test applied to specimens made of various magnesium alloys;

FIG. 2A is a picture of metallic formation of a specimen No. 3 observed by a metallographical microscope; and

FIG. 2B is a picture of metallic formation of a specimen No. C2 observed by a metallographical microscope.

### 45 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0010]** A heat resistant magnesium (Mg) alloy according to a first preferred embodiment of the present invention will now be described. In the first embodiment, the Mg alloy contains 1 to 6 percentage (%) by mass of aluminum (Al), 0.5 to 3 by mass ratio of calcium (Ca) to Al, and remainder being Mg and unavoidable impurities.

**[0011]** In the first preferred embodiment, the heat resistant Mg alloy essentially contains only Al and Ca together with Mg so as to improve heat resistance of the Mg alloy. Since only a few kinds of elements that are low cost and commonplace are used, not only the material cost of the heat resistant Mg alloy but also the total manufacturing cost is reduced. Therefore, a competitive heat resistant Mg alloy is obtained.

**[0012]** A Mg alloy excellent in heat resistance is obtained by restricting Ca content and Al content respectively in the above ranges. Al is an element that is dissolved in the crystal grain of Mg so as to improve the strength of the Mg alloy at room temperature. Also, Al lowers the melting point of the Mg alloy and improves the casting performance thereof. At the same time, Al narrows the temperature range of coagulation of the Mg alloy and reduces stress caused by solidification shrinkage of the Mg alloy, and thereby prevents casting crack. Therefore, when the Mg alloy can be formed

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not only by metal mold casting but also by die casting whose cooling speed is relatively high, Al is an useful element for improving the casting performance of the Mg alloy.

**[0013]** If the amount of Al is less than 1% by mass, the above effect is not sufficiently achieved. Even if the amount of Al is more than 6% by mass, the above effect is not improved and is not economical. Mg alloy preferably contains 2 to 4% by mass of Al.

**[0014]** Meanwhile, if the amount of AI that is contained in the Mg alloy becomes more than a predetermined amount of AI, AI is dissolved in Mg matrix including dendritic cell and alpha crystal grain to excessive saturation to form AI-rich phase. Since AI-rich phase is thermally unstable, if temperature of Mg alloy is raised to a predetermined value, AI-rich phase and Mg alloy change to Mg-AI compound such as Mg<sub>17</sub>AI<sub>12</sub> and separates from Mg matrix and Mg crystal grain boundary. If Mg alloy is left to stand in a range of high temperature for an extended period, intermetallic compound coheres and becomes coarse. Thereby, creep deformation of Mg alloy is increased. That is, heat resistance of Mg alloy is reduced.

**[0015]** However, in the first preferred embodiment, a proper amount of Ca is contained in the Mg alloy in accordance with Al content. Ca inhibits deterioration of the heat resistance of the Mg alloy accompanied by increase of Al content. The reason is considered as follows. Ca reacts with the Mg-Al compound and the Mg alloy matrix and thereby reduces the amount of Mg<sub>17</sub>Al<sub>12</sub>, which causes an increase of creep deformation to Mg alloy, while forming Ca-Al compound and Mg-Ca compound, which are stable in a range of high temperature, together with Al and Mg.

**[0016]** These intermetallic components are crystallized or separated mainly from grain boundary so as to form a network. Thereby, it is considered that the intermetallic components serve as a wedge for preventing transposition of Mg alloy. For these reasons, when proper amounts of Al and Ca are contained in the Mg alloy according to the first preferred embodiment of the present invention, it is considered that the Mg alloy excellent in heat resistance with very little creep deformation even in a range of high temperature is produced.

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[0017] If the mass ratio of Ca to Al is lower than 0.5, separation of  $Mg_{17}Al_{12}$ , which causes an increase of creep deformation of the Mg alloy, is not sufficiently inhibited. Therefore, heat resistance of Mg alloy becomes insufficient. On the other hand, even if the mass ratio of Ca to Al is more than 3, improvement of heat resistance of Mg alloy is not achieved. In this case, it is not economical either. Also, since an excessive increase of the amount of Ca causes deterioration of castability, casting crack, burning to die, and deterioration of extensibility, it is not preferable. The mass ratio of Ca to Al is preferably 1 to 2.

**[0018]** A heat resistant Mg alloy according to a second preferred embodiment of the present invention will now be described. The Mg alloy contains the same elements of the first preferred embodiment and the same amounts thereof. In the second embodiment, the Mg alloy further contains 0.2 to 1% by mass of Manganese (Mn). More preferably, the Mg alloy contains 0.5 to 0.7% by mass of Mn.

[0019] Mn is an element that is also dissolved in the crystal grain of Mg so as to improve the strength of the Mg alloy. Mn also reacts with Al so as to prevent separation of Mg<sub>17</sub>Al<sub>12</sub>, which causes an increase of creep deformation of the Mg alloy while forming a thermally stable intermetallic compound together with Al. Thus, Mn is an element that improves not only the strength of the Mg alloy at room temperature but also the strength thereof in high temperature. Further, Mn settles out impurities such as iron (Fe), which causes corrosion, in order to remove the impurities. If the amount of Mn is less than 0.2% by mass, the above effect is not sufficiently achieved. Even if the amount of Mn is more than 1% by mass, the above effect is not improved. In this case, it is not economical either.

**[0020]** In the present specification, a compositional range of each element is indicated in a form of x to y% by mass of the element. In this case, unless it is specifically noted, the compositional range of the element includes a minimum value or x% by mass itself. In a similar manner, the compositional range of the element also includes a maximum value or y% by mass itself.

**[0021]** In the present invention, the heat resistance is estimated by a mechanical property of Mg alloy in a high-temperature environment. The heat resistance is estimated, for example, by creep characteristics or high-temperature strength resulting from a test such as a relaxation test or an axial force retaining test.

**[0022]** In the Mg alloy according to the present invention, the manufacturing process of the Mg alloy is not restricted. Therefore, the Mg alloy may be obtained by any method of sand-cast, metal mould cast and die-cast. The materials used are also not restricted. That is, pure metallic materials such as Mg, Al, Ca and Mn may be used. On the other hand, a relatively low-cost alloy such as Mg-Al alloy may be used.

**[0023]** Mg alloy according to the present invention is used in various fields, such as space, military affairs, aviation, automobile and household electrical apparatus. It is further preferable if Mg alloy according to the present invention is applied to a product used in a high-temperature environment in order to utilize its heat resistance. The product is, for example, an engine, a transmission, a compressor for an air conditioner and an associated product that is placed in an engine compartment.

**[0024]** Examples of the Mg alloy according to the first and second embodiments of the present invention will now be described. In the examples, specimens of the Mg alloy are produced in such a manner that amounts of Al, Ca and Mn contained in or added to the Mg alloy are varied, and properties of the specimen are measured by various tests.

**[0025]** First, specimens of the Mg alloy are produced as follows. A halide flux is applied to an inner surface of crucible made of iron that is preheated in an electric furnace. Pure Mg metal, pure Al and Mg-Mn alloy are selectively introduced into the applied crucible by a predetermined amount and dissolved therein. The molten metal is maintained at a temperature of  $750^{\circ}$ C and a predetermined amount of Ca is added thereinto. TABLE 1 illustrates the amount of each element in each specimen. After those elements are completely dissolved in the molten metal by stirring the elements into the molten metal, the molten metal including the elements is cooled down and is maintained at a predetermined temperature. While Ca is dissolved in the molten metal, the surface of the molten metal is sprayed with mixed gas of carbon dioxide and sulfur hexafluoride (SF<sub>6</sub>) gas and is sprayed with flux in order to prevent combustion of Mg.

TABLE 1

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SPECIMEN No.	COMPOSOTION (% BY MASS: REMAINDER Mg)				TENSILE STRENGTH (MPa)	EXTENSION (%)	
	Ca	Al	Mn	MASS RATIO Ca/Al			
1	2	4	0.2	0.5	-	-	
2	3	6	-	0.5	128.5	1.75	
3	1	1	-	1	104.8	2.08	
4	3	1	-	3	136.3	2.46	
C1	1	9	-	0.1	158.0	2.53	
C2	1	3	-	0.3	131.9	2.38	

**[0026]** Thus, an alloyed molten metal is obtained. The alloyed molten metal is poured into a die and is solidified in the atmosphere. A test piece is cut from the obtained ingot and cylindrical specimens of  $\Phi$  10  $\times$  10 mm are machined from the test piece.

[0027] Then, the specimens are measured as follows. Referring to the above specimens Nos. 1, 2, 3 and 4, which are shown in TABLE 1, the relaxation test is performed in order to examine heat resistance of the specimens Nos. 1, 2, 3 and 4, or creep characteristics thereof. In the relaxation test, stress applied to the specimens is relaxed in accordance with passage of time in such a manner that displacement of each specimen is retained at a predetermined value in the atmosphere of 150°C. Specifically, when compressive stress of 100 MPa is first applied to each specimen and displacement of each specimen is a predetermined value, the compressive stress is reduced in accordance with passage of time in such a manner that displacement of each specimen is retained at the predetermined value. At this time, the relationship between stress, which is applied to each specimen, and time is shown in FIG. 1.

**[0028]** For a comparative test, a similar relaxation test is applied to specimens Nos. C1 and C2, which are made of various alloys in a market. The result from the test is shown in FIG. 1. Note that the alloys used are an Al alloy ADC12 (Al-11Si-2.5Cu), Mg alloys AE42 (Mg-4Al-2.7R.E.), AS21 (Mg-2Al-1Si), and AZ91 (Mg-9Al-0.9Zn).

**[0029]** Subsequently, normal tensile test is applied to each specimen. Also, mechanical property of each specimen is measured at room temperature. The results from the test and the measurement are also shown in TABLE 1.

**[0030]** Further, metallic formation of the specimens Nos. 3 and C2, which are shown in TABLE 1, is observed using a metallographical microscope with a magnifying power of 500. Pictures of the metallic formation are shown in FIGs. 2A and 2B.

**[0031]** The result from the relaxation test, which is shown in FIG. 1, is now analyzed. In view of the result of FIG. 1, since the Mg alloy whose mass ratio of Ca to AI is equal to or more than 0.5 has a relatively small rate of diminution of stress, it is understood that the Mg alloy has sufficient heat resistance. In addition, as the mass ratio of Ca to AI increases, the rate of diminution of stress becomes small. The Mg alloy whose mass ratio is equal to or more than 1.0 is equivalent to AI alloy (ADC12) in heat resistance.

**[0032]** Further, even if the mass ratio of Ca to Al is equal to 0.5, it is understood that the Mg alloy, which includes a proper amount of Mn, is substantially equivalent to the above Al alloy in heat resistance. Further, Mg alloys according to the present invention are superior to prior art heat resistant Mg alloys in terms of creep characteristics.

**[0033]** This reason is also understood from the pictures of metallic formation, which is shown in FIGs. 2A and 2B. Specifically, as shown in FIG. 2B, a relatively large amount of  $Mg_{17}AL_{12}$ , which reduces the creep characteristics of Mg alloy, separates from metallic formation of Mg alloy of the specimen No. C2 whose mass ratio of Ca to Al is equal to 0.3. In contrast, as shown in FIG. 2A, every  $Mg_{17}AL_{12}$  of Mg alloy of the specimen No. 3 whose mass ratio of Ca to Al is equal to 1.0 is replaced by Al-Ca compound, which is thermally stable, or by Mg-Ca compound, which is also thermally stable.

[0034] The present examples and preferred embodiments are to be considered as illustrative and not restrictive, and the invention is not to be limited to the details given herein but may be modified within the scope of the appended claims.

[0035] A heat resistant magnesium alloy contains 1 to 6 percentage by mass of aluminum, 0.5 to 3 by mass ratio of

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calcium to aluminum, and the remainder made from magnesium and unavoidable impurities.

### **Claims**

1. A heat resistant magnesium alloy comprising:

aluminum in an amount by weight of about 1 to about 6 percent; calcium in an amount such that the weight ratio of calcium to aluminum is from about 0.5 to about 3; and the remainder magnesium and unavoidable impurities.

- 2. The heat resistant magnesium alloy of claim 1, wherein aluminum is present in an amount by weight of about 2 to about 4 percent.
- 15 3. The heat resistant magnesium alloy of claim 1, wherein calcium is present in an amount such that the weight ratio of calcium to aluminum is from about 1 to about 2.
  - 4. The heat resisting magnesium alloy of claim 1 further comprising manganese in an amount by weight of about 0.2 to about 1 percent.
  - 5. The heat resistant magnesium alloy of claim 4, wherein the manganese is present in an amount by weight of about 0.5 to about 0.7 percent.

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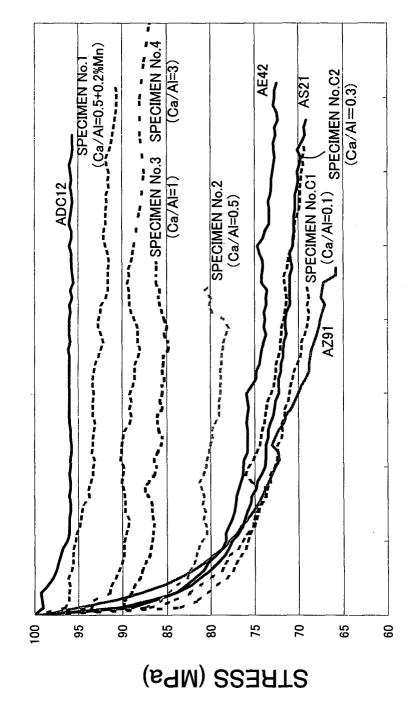
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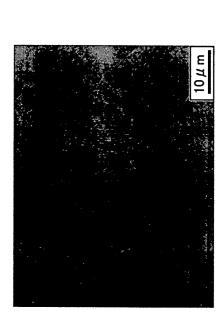
TIME (HOUR)

# FIG. 2A

FIG. 2B



SPECIMEN No.C2 (Ca/AI=0.3)



SPECIMEN No.3(Ca/Al=1)



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Application Number EP 03 02 5817

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