

(19)



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des brevets



(11)

EP 1 816 223 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

08.08.2007 Bulletin 2007/32

(51) Int Cl.:

C22C 23/02 ^(2006.01)(21) Application number: **07101254.6**(22) Date of filing: **26.01.2007**

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI
SK TR**

Designated Extension States:

AL BA HR MK RS(30) Priority: **27.01.2006 JP 2006019632**

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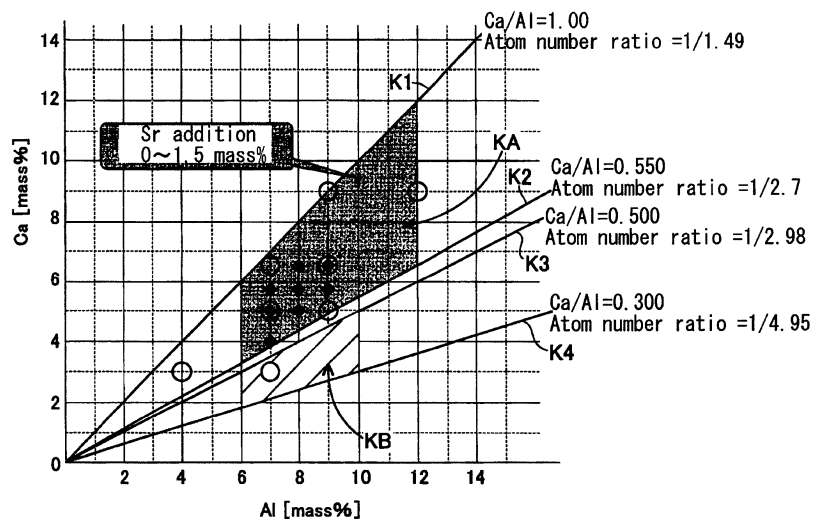
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(57) A magnesium alloy containing aluminum, manganese and calcium, characterized in that the magnesium alloy includes 6~12% by weight of aluminum,

0.1~1.5% by weight of manganese, a calcium/aluminum mass ratio being 0.55~1.0, and balance being magnesium and inevitable impurities.

FIG. 1

- ◆ Alloys whose bolt-load retention rates are equal to or greater than 90, provided that the bolt-load retention rate of ADC12 is 100 at 175 degrees C
- Alloys whose bolt-load retention rates are equal to or greater than 80, provided that the bolt-load retention rate of ADC12 is 100 at 175 degrees C

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Description

FIELD OF THE INVENTION

[0001] This invention relates to a magnesium alloy and a casting, each of which excels in heat resistance and castability.

BACKGROUND

[0002] In the industrial world such as automobile industry, magnesium alloys have been applied for the purpose of weight reduction and a scope of the application is expected to expand in the future. Particularly, the application to peripheral components of engines and the likes, which have effects in weight reduction, is considered.

However, high heat resistance is required for the peripheral components of engines and the likes, and thus there is a need for developments for magnesium alloys which excel in heat resistance. Magnesium-aluminum-silicon based alloys, magnesium-aluminum-RE based alloys, and the likes have been developed for enhancement of the heat resistance of conventional magnesium-aluminum based alloys. However, these alloys are not sufficient in terms of corrosion resistance, castability and cost. Magnesium-aluminum-calcium based alloys, which are excellent in heat resistance, corrosion resistance, and castability compared to the aforementioned alloys, have been developed. For example, an aspect that a magnesium-aluminum-calcium based alloy has high strength and is excellent in the castability is disclosed in JP8-269609A. Enhancement of strength of a magnesium-aluminum-calcium based alloy by addition of strontium is disclosed in JP 2001-316752A. Enhancements of strength by increasing the amounts of aluminum and calcium compared to known inventions are disclosed in JP2004-23867A and JP2005-113260A.

[0003] More specifically, a magnesium-aluminum-calcium alloy, which contains 1.0~5.0 % aluminum, 0.3~3.0 % calcium, is disclosed in JP8-269609A. In JP2001-316752A, a magnesium alloy for die-casting is disclosed and the magnesium alloy contains 2.0~6.0 % aluminum and 0.3~2.0 % calcium, and 0.01~1.0 % strontium. In JP2004-23867A, a magnesium alloy, which contains 4.7~7.3 % aluminum, 1.8~3.2 % calcium, 0.0~0.8 % zinc, 0.3~2.2 % tin, is disclosed. In JP2005-113260A, a magnesium alloy is disclosed. The magnesium alloy contains more than 6 %~10 % aluminum, 1.8~5 % calcium, 0.05~1.0 % strontium, and 0.1~0.6 % manganese and the calcium/magnesium mass ratio is set to 0.3~0.5%.

[0004] The industrial world requires to use magnesium alloys in severe conditions such as in higher heat and under larger loading stress. Heat resistance of the magnesium-aluminum-calcium based alloys which have been proposed so far is not necessarily adequate under the severe circumstances. Therefore, further improvements in the heat resistance are required.

[0005] The present invention has been made in view of the above circumstances, and provides a magnesium alloy which excels in heat resistance and castability for further improvement of the heat resistance.

SUMMARY OF THE INVENTION

[0006] According to an aspect of the present invention, a magnesium alloy containing aluminum, manganese and calcium, characterized in that the magnesium alloy comprises 6~12% by weight of aluminum, 0.1~1.5% by weight of manganese, a calcium/aluminum mass ratio being 0.55~1.0, and balance being magnesium and inevitable impurities.

[0007] The inventors of the invention work hard on developments of magnesium-aluminum-calcium based alloys. Observing a composition of a magnesium-aluminum-calcium based alloy, generally, the alloy is likely to contain two or three phases among a Mg phase (including Mg-Al solid solution and Mg-Ca solid solution), a β phase ($\text{Mg}_{17}\text{Al}_{12}$), a Al_2Ca (Mg) phase, and a Mg_2Ca (Al) phase as main structures.

[0008] In a relatively low temperature range, in other words, in a temperature range that is equal to or less than 120 degrees C, when the β phase, the Al_2Ca (Mg) phase, and the Mg_2Ca (Al) exist in a grain boundary of the Mg phase, boundary sliding is restricted to improve creep resistance more easily.

[0009] However, according to research findings of the inventors of this invention, it has been observed that the β phase is likely to prevent the improvements of creep resistance properties in a high temperature range (a temperature range which is over 120 degrees C). Also, it has been observed that the Al_2Ca (Mg) phase is effective for the improvement of the creep resistance properties.

[0010] The inventors have developed the study based on the above concept. As a result, it has been observed that if a calcium/magnesium mass ratio is set in a range 0.55~1.0 in the magnesium alloy, which contains aluminum, calcium, and manganese, more specifically, contains aluminum of 6~12 % and manganese of 0.1~1.5 % by weight, a structure where the formation of the β phase is restrained with the Mg phase and the Al_2Ca (Mg) phase being fundamental structures (a small amount of the Mg_2Ca (Al) phase is contained in some cases) is formed to obtain a magnesium alloy which excels in the further heat resistance (for example, the creep resistance) and the castability. The observation is confirmed by tests and then the magnesium alloy according to the invention is completed.

[0011] Namely, the magnesium alloy, according to the invention, contains aluminum, calcium, and manganese and is characterized in that aluminum of 6~12 % and manganese of 0.1~1.5 % by weight is contained, the calcium/magnesium mass ratio is in a range of 0.55~1.0 and the balance is magnesium and inevitable impurities.

[0012] According to the invention, it is possible to provide a magnesium alloy and which excels in the heat resistance and the castability.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The foregoing and additional features and characteristics of the present invention will become more apparent from the following detailed description considered with reference to the accompanying drawings, wherein:

[0014] Fig.1 is a graph illustrating a relationship between an amount of aluminum and an amount of calcium and a Ca/Al mass ratio;

[0015] Fig.2 is a conceptual scheme diagrammatically illustrating a cutting form of a ring test piece for measuring a bolt-loading of a bolt;

[0016] Fig.3 is a conceptual structure view schematically illustrating a measurement of the bolt-loading of the tightened bolt;

[0017] Fig.4 is a perspective view illustrating a test piece for evaluating casting cracks;

[0018] Fig.5 is a graph illustrating results of minimum strain rates;

[0019] Fig.6 is a photomap of a metal structure;

[0020] Fig.7 is a photomap of a metal structure;

[0021] Fig.8 is a photomap of a metal structure;

[0022] Fig.9 is a photomap of a metal structure;

[0023] Fig. 10 is a photomap of a metal structure;

[0024] Fig.11 is a photomap of a metal structure;

[0025] Fig. 12 is a photomap of a metal structure; and

[0026] Fig. 13 is a photomap of a metal structure.

DETAILED DESCRIPTION

[0027] A magnesium alloy, according to examples of the embodiments 1 and 2 of the invention, contains aluminum, calcium, and manganese. The magnesium alloy contains 6~12% by weight of aluminum and 0.1~1.5 % by weight of manganese, and calcium/magnesium mass ratio is in a range of 0.55~1.0. The balance is composed of magnesium and inevitable impurities. Therefore, the magnesium alloy, according to the examples of the embodiments 1 and 2 of the invention, is a magnesium-aluminum-calcium-manganese based alloy. Reasons for definition of composition will be explained below. In the specification, unless otherwise indicated, % regarding contents or amounts is % by weight.

(6~12% Aluminum)

[0028] Aluminum contributes to improvement of castability, especially improves fluidity of the alloy. Aluminum also contributes to enhancement of alloy strength to improve mechanical properties. However, an excessive amount of aluminum tends to lower the ductility and the strength. In the case of an insufficient amount of aluminum, it is difficult to obtain the adequate heat resistance due to shortage in an absolute amount of an Al_2Ca (Mg) phase. Further, temperature of a liquid phase of the alloy becomes high and a liquidus-solidus temperature range is broadened, resulting in casting cracks. When the amount of aluminum exceeds 12 %, the rough and large Al_2Ca (Mg) phase as a primary crystal is easily crystallized and the castability is considerably lowered. Considering these circumstances, 6-12 % of aluminum is contained in the alloy.

[0029] In this case, the amount of aluminum may be set to equal to or greater than 6 % and may exceed 6 %. Thus, the amount of aluminum may be set to 6~10%, 6.1~9%, 6.2~8.5%, and so on. A lower limit of aluminum may be set to 6.05%, 6.1%, 6.2%, 6.4%, and 6.6% as an example. An upper limit of aluminum, which may be paired with the lower limit described above, may be set to 11.5%, 10.5%, and 9.5% as an example. However, the lower and upper limits are not limited to these figures. In this specification, the word "equal to or less than" is meant to describe the value including the stated value and the words "exceed" and "less than" are meant to describe the value not including the stated value.

(Calcium/aluminum mass ratio is 0.55~1.0)

[0030] Calcium/aluminum mass ratio affects formation of a β phase ($Mg_{17}Al_{12}$). A melting point of the β phase ($Mg_{17}Al_{12}$) is relatively low and is likely to be formed in a grain boundary. If the formation of the β phase is large, boundary sliding is likely to occur in a high temperature range and it is difficult to attain the satisfactory heat resistance. When the above-

mentioned is less than 0.55, the β phase is likely to appear. Consequently, the heat resistance is lowered. On the other hand, when the calcium/aluminum mass ratio exceeds 1.0, an Mg_2Ca (Al) phase shows a relative increase to considerably lower the castability. If the calcium/aluminum mass ratio is in a range of 0.55~1.0, it is possible to restrain the formation of the β phase in the structure. Thus, the β phase is not or unlikely to be formed. It is preferable to restrain the β phase in terms of the area ratio in a microscope field. Thus, the area ratio of the β phase should be equal to or less than 0.5%, and it is further preferable that the area ratio is equal to or less than 0.2% or 0.1 %. Alternatively, it is preferable that the β phase does not exist virtually. Therefore, it is more preferable that the area ratio is 0.0%. In regard to the area ratio, % is not weight %.

[0031] Considering the above circumstances, it is preferable to set the calcium/aluminum mass ratio to 0.58~0.90 or 0.6~0.88. A lower limit of the calcium/aluminum mass ratio may be set to 0.58, 0.60, 0.62, 0.65 or the likes as an example and an upper limit may be set to 0.98, 0.95, 0.90, 0.88 or the likes as an example to be paired with each lower limit described above. However, the upper and lower limits are not limited to these figures.

[0032] When the calcium/aluminum mass ratio is 0.55~1.0, a minimum value of calcium is 3.3 % ($6 \% \times 0.55=3.3\%$), and a maximum value of calcium is 12% ($12\% \times 1.0=12\%$). Thus, the amount of calcium is set to 3.3~12 %, and the amount of calcium may be set to 4~11%, 5~10%, or 6~9% as an example. However, the amount of calcium is not limited to these figures.

[0033] Fig.1 illustrates a relationship between the amount of aluminum and the amount of calcium in the magnesium alloy. As illustrated in Fig. 1, a characteristic line K1 represents a case that the Ca/Al mass ratio = 1.00 (atomicity ratio: 1/1.49). A characteristic line K2 represents a case that the Ca/Al mass ratio = 0.550 (atomicity ratio: 1/2.7). A characteristic line K3 represents a case that the Ca/Al mass ratio = 0.500 (atomicity ratio: 1/2.98). A characteristic line K4 represents a case that the Ca/Al mass ratio = 0.300 (atomicity ratio: 1/4.95).

[0034] In Fig. 1, $\blacklozenge$ mark represents alloys whose bolt-load retention rates are equal to or greater than 90, provided that the bolt-load retention rate of ADC 12 is 100 at 175 degrees C. $\bullet$ represents alloys whose bolt-load retention rates are equal to or greater than 80, provided that the bolt-load retention rate of ADC12 is 100 at 175 degrees C. In Fig. 1, an area KA represents a range of the calcium and aluminum amounts specified in the embodiments 1 and 2 of the invention. An area KB represents a range specified in JP2005-113260A. The formation of the β phase is restrained in the area KA. Considering the Ca/Al ratio, the β phase is more likely to be formed in the area KB.

(0.1~1.5 % Manganese)

[0035] Manganese contributes to improvement of corrosion resistance and an insufficient amount of manganese lowers the corrosion resistance. Also, an excessive amount of manganese is not completely melted in a molten metal, and thus it is not possible to attain adequate effects for the corrosion resistance and the heat resistance. Considering these circumstances, the amount of manganese is set to 0.1~1.5%. For the reasons stated above, for example, the amount of manganese may be set to 0.12~1.3%, 0.2~1.0%, and 0.3~0.8%. A lower limit of manganese may be set to 0.15%, 0.20%, or 0.30% as an example and an upper limit of manganese may be set to 1.3%, 1.2%, 1.0%, or 0.8% as an example to be paired with the lower limit described above. However, the upper and lower limits are not limited to these figures.

[0036] In the magnesium alloy, according to the examples of the embodiments of the invention, preferably, it is possible to contain at least one of equal to or less than 1.5% of strontium, equal to or less than 2.5% of rare earth elements, equal to or less than 1% of silicon, and equal to or less than 2% of tin. A phase, which is formed when at least one of strontium, rare earth elements, silicon, and tin are added, is different from the Al_2Ca (Mg) phase, however, has a similar effect with the Al_2Ca (Mg) phase for the heat resistance, and contributes to further improvement of the heat resistance. Moreover, additions of strontium and rare earth elements improve the corrosion resistance of castings. Silicon and tin are effective for improvement of the castability. However, according to the magnesium alloy of the embodiments of the invention, strontium, rare earth elements, silicon and tin do not have to be contained unless there are particular needs.

(equal to or less than 1.5 % Strontium)

[0037] Strontium has an advantage in the improvement of the heat resistance. However, if strontium is contained more than the amount stated above, Mg-Al-Sr based chemical compounds or formation of Al_4Sr are/is increased and the ductility is lowered. Considering the circumstances, when strontium is contained, the amount of strontium should be equal to or less than 1.5%. In this case, the amount of strontium may be less than 1.3% or less than 1.1%. A lower limit of strontium may be set to 0.1%, 0.2% or 0.3% as an example and an upper limit of strontium may be set to 1.4% or 1.3% as an example to be paired with the lower limit. However, the lower and upper limits are not limited to these figures.

(equal to or less than 2.5% rare earth elements)

[0038] Rare earth elements contribute to the improvement of the heat resistance by solid solution strengthening by being solved in a primary crystal of α -magnesium matrix. The rare earth elements form compound phases in the grain boundary of the primary crystal of the α -magnesium matrix to restrain boundary sliding to contribute to the improvement of the heat resistance. However, an excessive amount of rare earth elements tends to lower the ductility, the strength, the fluidity and the corrosion resistance. Considering the circumstances, if rare earth elements are contained, the amount of rare earth elements should be equal to or less than 2.5%. In this case, the amount of rare earth elements may be equal to or less than 2.3% or equal to or less than 2.0%. A lower limit of the rare earth elements may be set to 0.1%, 0.2%, 0.4% or 0.6% as an example and an upper limit of the rare earth elements may be set to 2.4% or 2.3% to be paired with the lower limit described above. However, the upper and lower limits are not limited to these figures.

[0039] It is costly to separate the rare earth elements as elementary substance, thus misch metal is employed as the rare earth elements. Generally, misch metal is a rare earth elements alloy mainly including at least one of cerium, lanthanum, praseodymium and neodymium. Any one of cerium series misch metal, neodymium series misch metal, and lanthanum series misch metal can be used. Elementary substance of cerium, lanthanum, praseodymium, neodymium, or the likes may be used depending on conditions. Further, other rare earth elements may be used. When the amount of calcium is relatively large, the castability may be lowered. Thus, the amount of the rare earth elements may be reduced to 0~2%. However, the amount of the rare earth elements is not limited to those values.

(equal to or less than 1% silicon)

[0040] Silicon is effective for the improvement of the heat resistance and the castability. However, if an amount of silicon is excessive, the amount of crystallization of Mg_2Si compounds is increased to lower the ductility and the strength. Therefore, if silicon is contained, the amount of the silicon should be equal to or less than 1%. Particularly, it is preferable that the amount of silicon is equal to or less than 0.8% or equal to or less than 0.6%. However, the amount of silicon is not limited to these figures.

(equal to or less than 2% Tin)

[0041] Tin contributes to the improvement of the heat resistance by being solved in the primary crystal of the α -magnesium matrix. Furthermore, tin contributes to the improvement of the castability by crystallizing in the grain boundary and spaces between dendrite cells at nearly an end of complete solidification. However, an excessive amount of tin has a disadvantage for weight saving as tin has large specific gravity approximately 7.3. For the reason, when tin is contained, the amount of tin should be equal to or less than 2%. In this case, the amount of tin may be set to 0.1~1.8%, 0.1~1.0%, and 0.2~0.8%, and so on. As considering above circumstances, a lower limit of tin may be set to 0.15%, 0.2% or 0.3% as an example and an upper limit of tin may be set to 1.8% or 1.5% as an example to be paired with the lower limit described above. However, the upper and the lower limits are not limited to these figures.

(Castings)

[0042] Magnesium alloys, according to the examples of the embodiments of the invention, have the good castability and are suitable for die casting, gravity die casting, sand casting and the likes. Cold chamber system or hot chamber system can be used for die casting. The magnesium alloys according to the example of the embodiments of the invention is applicable to components which require both the weight saving and the heat resistance. For example, the magnesium alloy is applicable for a cylinder head cover, a cylinder block, a piston, and a transmission case of vehicles. However, the application is not limited to these components.

[0043] Hereinafter, the embodiments of the invention are specifically described.

[0044] As a series of the examples of the embodiment 1, ingredients are formulated so that manganese is fixed at 0.3% and the amount of aluminum, the amount of calcium, the Ca/Al ratio is able to be changed. Similarly, as a series of the examples of the embodiment 2, ingredients are formulated so that the amounts of aluminum, calcium, and manganese are changed based on the compositions shown in Table 2, and the Ca/Al ratio is also changed. In the series of the examples and comparative examples of the embodiment 2, the amount of strontium, the amount of misch metal, the amount of silicon, and the amount of tin may be contained.

[0045] Ingredients are melted at a gas melting furnace by a flux free method. Then, temperature of the molten metal is held at 690 degrees C and the molten metal is charged into a molding cavity of a die casting mold of 7.8MN die casting machine to cast test pieces (die castings). Meanwhile, the compositions shown in Tables 1 and 2 are desired values.

[0046]

Table 1 (Embodiment 1)

	Composition				Strength Properties			Castability	Overall evaluation
	Al [mass%]	Ca [mass%]	Mn [mass%]	Ca/Al [-]	β phase ratio [%]	Bolt-load retention rate (ratio of the test piece to ADC12) [%]	Evaluation		
Example 1-1	6.00	3.30	0.30	0.55	0	81	○	Not observed	○
Example 1-2	6.00	3.60	0.30	0.60	0	82	○	Not observed	○
Example 1-3	6.00	4.50	0.30	0.75	0	83	○	Not observed	○
Example 1-4	6.00	5.28	0.30	0.88	0	84	○	Not observed	○
Example 1-5	6.00	6.00	0.30	1.00	0	84	○	Not observed	○
Example 1-6	7.00	3.85	0.30	0.55	0	83	○	Not observed	○
Example 1-7	7.00	4.20	0.30	0.60	0	86	○	Not observed	○
Example 1-8	7.00	5.00	0.30	0.71	0	85	○	Not observed	○
Example 1-9	7.00	6.16	0.30	0.88	0	87	○	Not observed	○
Example 1-10	7.00	7.00	0.30	1.00	0	87	○	Not observed	○
Example 1-11	9.00	4.95	0.30	0.55	0	81	○	Not observed	○
Example 1-12	9.00	5.40	0.30	0.60	0	84	○	Not observed	○
Example 1-13	9.00	6.50	0.30	0.72	0	85	○	Not observed	○
Example 1-14	9.00	7.92	0.30	0.88	0	85	○	Not observed	○
Example 1-15	9.00	9.00	0.30	1.00	0	85	○	Not observed	○
Example 1-16	12.00	6.60	0.30	0.55	0	82	○	Not observed	○
Example 1-17	12.00	7.20	0.30	0.60	0	83	○	Not observed	○
Example 1-18	12.00	9.00	0.30	0.75	0	89	○	Not observed	○
Example 1-19	12.00	10.58	0.30	0.88	0	88	○	Not observed	○
Example 1-20	12.00	12.00	0.30	1.00	0	85	○	Not observed	○

(continued)

	Composition				Strength Properties			Castability	Overall evaluation
	Al [mass%]	Ca [mass%]	Mn [mass%]	Ca/Al [-]	β phase ratio [%]	Bolt-load retention rate (ratio of the test piece to ADC12) [%]	Evaluation		
Comparative example 1-1	4.00	3.00	0.30	0.75	0	77	×	Not observed	×
Comparative example 1-2	7.00	1.00	0.30	0.14	4	47	×	Not observed	×
Comparative example 1-3	7.00	3.00	0.30	0.43	0.7	68	×	Not observed	×
Comparative example 1-4	9.00	3.00	0.30	0.33	3	55	×	Not observed	×
Comparative example 1-5	9.00	4.00	0.30	0.44	0.9	69	×	Not observed	×
Comparative example 1-6	12.00	5.00	0.30	0.42	1.5	61	×	Not observed	×
Comparative example 1-7	13.00	10.00	0.30	0.77	0	82	○	Observed	×
Comparative example 1-8	7.00	9.00	0.30	1.29	0	88	○	Observed	×

[0047]

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Table 2 (Embodiment 2)

	Composition								Strength	Overall evaluation
	A1 [mass%]	Ca [mass%]	Ca/A1 [-]	Sr [mass%]	Mm [mass%]	Si [mass%]	Sn [mass%]	Mn [mass%]		
									Bolt-load retention rate (ratio of test piece to ADC 12) [%]	
Example 2-1	6.00	3.30	0.55	0.50	0.00	0.00	0.00	0.30	83	○
Example 2-2	6.00	6.00	1.00	0.50	0.00	0.00	0.00	0.30	86	○
Example 2-3	7.00	4.20	0.60	0.50	0.00	0.00	0.00	0.30	88	○
Example 2-4	9.00	6.50	0.72	0.50	0.00	0.00	0.00	0.30	87	○
Example 2-5	12.00	6.60	0.55	0.50	0.00	0.00	0.00	0.30	83	○
Example 2-6	12.00	12.00	1.00	0.50	0.00	0.00	0.00	0.30	87	○
Example 2-7	6.0	3.30	0.55	1.50	0.00	0.00	0.00	0.30	87	○
Example 2-8	6.0	6.00	1.00	1.50	0.00	0.00	0.00	0.30	90	○
Example 2-9	7.00	4.20	0.60	1.50	0.00	0.00	0.00	0.30	92	○
Example 2-10	9.00	6.50	0.72	1.50	0.00	0.00	0.00	0.30	91	○
Example 2-11	12.00	6.60	0.55	1.50	0.00	0.00	0.00	0.30	82	○
Example 2-12	12.00	12.00	1.00	1.50	0.00	0.00	0.00	0.30	91	○
Example 2-13	6.00	3.30	0.55	0.00	2.50	0.00	0.00	0.30	83	○
Example 2-14	6.00	6.00	1.00	0.00	2.50	0.00	0.00	0.30	86	○
Example 2-15	7.00	4.20	0.60	0.00	2.50	0.00	0.00	0.30	88	○

(continued)

	Composition								Strength	Overall evaluation
	A1 [mass%]	Ca [mass%]	Ca/A1 [-]	Sr [mass%]	Mm [mass%]	Si [mass%]	Sn [mass%]	Mn [mass%]	Bolt-load retention rate (ratio of test piece to ADC 12) [%]	
Example 2-16	9.00	6.50	0.72	0.00	2.50	0.00	0.00	0.30	87	○
Example 2-17	12.00	6.60	0.55	0.00	2.50	0.00	0.00	0.30	83	○
Example 2-18	12.00	12.00	1.00	0.00	2.50	0.00	0.00	0.30	87	○
Example 2-19	6.00	3.30	0.55	0.00	0.00	1.00	0.00	0.30	82	○
Example 2-20	6.00	6.00	1.00	0.00	0.00	1.00	0.00	0.30	84	○
Example 2-21	7.00	4.20	0.60	0.00	0.00	1.00	0.00	0.30	86	○
Example 2-22	9.00	6.50	0.72	0.00	0.00	1.00	0.00	0.30	85	○
Example 2-23	12.00	6.60	0.55	0.00	0.00	1.00	0.00	0.30	83	○
Example 2-24	12.00	12.00	1.00	0.00	0.00	1.00	0.00	0.30	85	○
Example 2-25	6.00	3.30	0.55	0.00	0.00	0.00	2.00	0.30	82	○
Example 2-26	6.00	6.00	1.00	0.00	0.00	0.00	2.00	0.30	85	○
Example 2-27	7.00	4.20	0.60	0.00	0.00	0.00	2.00	0.30	87	○

(continued)

	Composition								Strength	Overall evaluation
	A1 [mass%]	Ca [mass%]	Ca/A1 [-]	Sr [mass%]	Mm [mass%]	Si [mass%]	Sn [mass%]	Mn [mass%]	Bolt-load retention rate (ratio of test piece to ADC 12) [%]	
Example 2-28	9.00	6.50	0.72	0.00	0.00	0.00	2.00	0.30	86	○
Example 2-29	12.00	6.60	0.55	0.00	0.00	0.00	2.00	0.30	81	○
Example 2-30	12.00	12.00	1.00	0.00	0.00	0.00	2.00	0.30	86	○
Example 2-31	6.00	3.30	0.55	0.00	0.00	0.00	0.00	0.20	81	○
Example 2-32	6.00	6.00	1.00	0.00	0.00	0.00	0.00	0.20	84	○
Example 2-33	7.00	4.20	0.60	0.00	0.00	0.00	0.00	0.20	86	○
Example 2-34	9.00	6.50	0.72	0.00	0.00	0.00	0.00	0.20	85	○
Example 2-35	12.00	6.60	0.55	0.00	0.00	0.00	0.00	0.20	82	○
Example 2-36	12.00	12.00	1.00	0.00	0.00	0.00	0.00	0.20	85	○
Example 2-37	6.00	3.30	0.55	0.00	0.00	0.00	0.00	1.00	81	○
Example 2-38	6.00	6.00	1.00	0.00	0.00	0.00	0.00	1.00	85	○
Example 2-39	7.00	4.20	0.60	0.00	0.00	0.00	0.00	1.00	86	○

(continued)

	Composition								Strength	Overall evaluation
	A1 [mass%]	Ca [mass%]	Ca/A1 [-]	Sr [mass%]	Mm [mass%]	Si [mass%]	Sn [mass%]	Mn [mass%]	Bolt-load retention rate (ratio of test piece to ADC 12) [%]	
Example 2-40	9.00	6.50	0.72	0.00	0.00	0.00	0.00	1.00	85	○
Example 2-41	12.00	6.60	0.55	0.00	0.00	0.00	0.00	1.00	83	○
Example 2-42	12.00	12.00	1.00	0.00	0.00	0.00	0.00	1.00	85	○
Example 2-43	6.00	3.30	0.55	0.50	1.00	0.00	1.00	0.50	84	○
Example 2-44	6.00	6.00	1.00	0.50	0.00	0.50	1.00	0.50	87	○
Example 2-45	7.00	4.20	0.60	1.00	1.00	0.00	1.00	0.50	92	○
Example 2-46	9.00	6.50	0.72	1.00	0.00	0.50	1.00	0.50	90	○
Example 2-47	12.00	6.60	0.55	1.50	1.00	0.00	1.00	0.50	81	○
Example 2-48	12.00	12.00	1.00	1.50	0.00	0.50	1.00	0.50	92	
Comparative Example 2-1	7.00	3.00	0.43	0.50	0.00	0.00	0.00	0.30	79	×
Comparative Example 2-2	7.00	3.00	0.43	1.50	0.00	0.00	0.00	0.30	78	×
Comparative Example 2-3	7.00	3.00	0.43	0.00	2.50	0.00	0.00	0.30	72	×

[0048] According to the examples and the comparative example of the embodiment 2, a misch metal is used as a rare earth element. The misch metal contains 50 % of cerium, 27 % of lanthanum, 11 % of neodymium, 5 % of praseodymium and other rare earth elements for balance, adding up to the 100% of misch metal. The major constituents such as cerium, lanthanum, neodymium, and praseodymium occupy 93% from the 100% of misch metal used in the examples and the comparative example of the embodiment 2.

[0049] According to the embodiment 2, the analytical values of the amounts of cerium, lanthanum, neodymium, and praseodymium are obtained from each magnesium alloy and the total amount (%) of cerium, lanthanum, neodymium, and praseodymium is obtained by adding the analytical values. The amount of the misch metal (Mm) is obtained by multiplying the total amount (%) of cerium, lanthanum, neodymium, and praseodymium by 100/93. Then, the amount of the misch metal is shown in column Mm in Table 2. Accordingly, the amount of the misch metal (Mm) shown in Table 2 corresponds the amount of the misch metal containing not only cerium, lanthanum, neodymium, and praseodymium but also other rare earth elements.

[0050] As a characteristic evaluation of the series of the embodiment 1, a β phase ratio (area ratio), a bolt-load retention rate (the ratio of the test piece to ADC12), and the castability (cast cracks) are measured. As a characteristic evaluation of the series of the embodiment 2, the bolt-load retention rate (the ratio of the test piece to ADC 12) is measured. The measurement results are shown with the compositions in Tables 1 and 2.

[0051] In order to measure the β phase ratio, a test piece cutting from a casting is polished and etched with 10 weight% aqueous solution of acetate for observation. The test piece is observed by a scanning electron microscopy (SEM) to classify compounds. Additionally, the analysis is conducted by EDAX to check the presence of the β phase. In this case, SEM photographs are taken and the area ratio of the β phase is obtained by means of an image analysis software (ImagePro and the likes) to determine the β phase ratio. An average value is taken from 5 visual fields to be used as the area ratio.

[0052] In the axial force test, a u-shaped die-casting 150 is formed. As illustrated in Fig. 2, the die casting 150 has arms 151 and 152 which are formed by a magnesium alloy. The die casting 150 is cast in the following condition. The injection rate (plunger moving speed) is 0.3~0.35 meter/second, the injection pressure is 28Mpa, injection molten metal temperature is liquidus temperature +30 degrees C, pressing time is 5 seconds, and mold temperature is room temperature of up to 40 degrees C. A ring test piece 100 is cut from one of the arms 151 of the die casting 150 and the test piece 100 is used as a fastening portion (outer diameter 20mm, inner diameter (bolt through hole) 9 mm, thickness approximately 10 mm). As schematically illustrated in Fig.3, a bolt 200 having an external thread is inserted through a bolt through hole of the test piece 100 via a washer 105 (outer diameter 18 mm, thickness 3 mm, A6061-T6) and is tightened to a screw hole 301 of a counter member 300. The bolt 200 is made of steel, M8 $\times$ 25, strength grade 10.9. The counter member 300 is an aluminum die casting alloy, ADC12 in JIS standard (Japanese Industrial Standards). The bolt 200 is tightened with 8kN of an initial axial force. The axial force is measured by using a strain gauge 400 attached to the bolt 200. Subsequently, a test piece consisting of the test piece 100 and the counter member 300 tightened to the test piece 100 by the bolt 200 is inserted into an air atmosphere furnace to be held at a high temperature (175degrees C) for 300 hours and then be cooled down to room temperature. After the process, the axial force is re-measured and the bolt-load retention rate against the initial axial force is obtained. In this case, the average value of plural test pieces is used as the bolt-load retention rate. 76 % of the bolt-load retention rate means that the axial force of the test piece held at a high temperature in the above condition is reduced to the axial force 8kN (the initial axial force) $\times$ 0.76. The axial force of the bolt 200 is also measured by an ultrasonic axial force measurement method and the similar results to that of the strain gauge measurement are obtained. As the bolt-load retention rate, the ratio of the bolt-load retention rate of each alloy to the bolt-load retention rate of an ADC12 alloy is obtained, provided that the bolt-load retention rate of the ADC12 alloy is 100. O is filled in evaluation column if the alloy has the bolt-load retention rate exceeding 80 and $\times$ is filled in the evaluation column if the bolt-load retention rate does not exceed 80.

[0053] Further, a die casting 302 is produced in a shaped illustrated in Fig.4 as a sample, and examined the die casting 302 for the occurrence of crack by the naked eye. The casting condition is as follows. The injection rate (plunger moving speed) is 1 meter/second, the injection pressure is 64 MPa, temperature of the mold is 200 degrees C, and molten metal temperature is liquidus temperature +30 degrees C.

[0054] In comparative examples shown in Table 1, one of the amount of aluminum and the Ca/Al ratio is not in the specified range of the examples of the embodiment 1. As shown in Table 1, the β phase ratio is high and the bolt-load retention rate is low in many comparative examples shown in Table 1 because either the amount of aluminum or the Ca/Al ratio is not proper in those comparative examples. Consequently, overall judgements for the comparative examples are $\times$ (unsatisfactory). The bolt-load retention rate is high in comparative examples 1-7 and 1-8, however, the casting cracks occur and the overall judgment is $\times$ (unsatisfactory).

[0055] Compared to the comparative examples, the amount of aluminum, the amount of calcium, and the Ca/Al ratio are properly set for the series of the examples of the embodiment 1. As shown in Table 1, the magnesium alloys comprehensively excels in terms of the β phase ratio, the bolt-load retention rate, and the prevention of the casting cracks. The reason for the excellence is inferred that the occurrence of the β phase is restrained and boundary sliding

is effectively prevented in the high temperature range.

[0056] The bolt-load retention rate is obtained for the series of the examples of the embodiment 2 as well as the series of the examples of the embodiment 1. O is filled in evaluation column if the alloy has the bolt-load retention rate exceeding 80 and × is filled in the evaluation column if the bolt-load retention rate does not exceed 80. The amount of aluminum and the Ca/Al ratio is properly set for the series of the examples of the embodiment 2. As shown in Table 2, the magnesium alloys for the series of the examples of the embodiment 2 are excellent in the β phase ratio and the bolt-load retention rate. In addition, the alloys are excellent in the prevention of the cast cracks. As shown in Table 2, the bolt-load retention rate is low and the overall judgment is X (unsatisfactory) for comparative examples 2-1, 2-1 and 2-3.

[0057] Furthermore, a creep resistance test at a range of high temperature is conducted. The test is conducted under the following condition. The measured temperature is 180 degrees C, the initial stress is 104Mpa, the shape of the test piece is a cylinder rod (parallel portion: six millimeter diameter), and the measurement time is 300 hours. The results of the minimum strain rate are shown in Fig.5. As shown in Fig.5, the strain rate is considerably large in a comparative example 3 (Ca/Al = 0.43, Mg-7%Al -3%Ca-0.3%Mn). On the other hand, the strain rate is excellent in the order of an example 3-1 (Ca/Al= 0.71, Mg-7%Al-5%Ca-0.3%Mn), an example 3-2 (Ca/Al = 0.71, Mg-7%Al-5%Ca-0.3%Mn-0.5%Sr), and an example 3-3 (Ca/Al = 0.75, Mg-12%Al-9%Ca-0.3%Mn-0.5%Sr). Comparison of the amount of Sr between the example 3-1 and the example 3-2 shows that addition of Sr is effective for reduction of the strain rate in the creep resistance test.

(metal structure)

[0058] In Figs.6-13, photographs (SEM) of metal structures are shown. In Figs. 10 and 13, the photographs of the metal structures of the examples of the embodiment 1 are shown. In the photographs, the portions indicated by black triangles exhibit the β phase. The metal structures are observed after being etched with 10 weight% aqueous solution of acetate. As it is understood from the photographs, the β phase is formed in the grain boundary for the alloys of the comparative examples of the embodiment 1. In some cases, the β phase is formed in crystal grains. On the other hand, the formation of the β phase is prevented by the compositions used for the examples of the embodiment 1 and the β phase is practically 0%. It is inferred that the enhancement of the heat resistance (the creep resistance and the likes) of the magnesium alloy is possible because the formation of the β phase is restrained to effectively prevent boundary sliding. The β phase is identified by a device (SEM-EDX) having an electron scanning microscope function and an energy dispersive X-ray analysis function.

[0059] The embodiments of the invention are not to be considered limited to what are shown in the drawings and described above. It is possible to make appropriate modifications as necessary. For example, it may use one or more than one of scandium, gadolinium, terbium, samarium, holmium, thulium, erbium, europium, and ytterbium as rare earth elements as well as cerium, lanthanum, neodymium, and praseodymium. The amounts of each alloying element described in Table 1 can be stated as upper limits and lower limits which define the compositions described in each claim.

[Industrial applicability]

[0060] The invention can be used for vehicles and components of industrial machineries, which are expected to reduce weight. In the vehicles, the invention is used for engine components, for example, an oil pan, a transmission case, a cylinder block, a cylinder head, a piston or the components which requires both lightweight properties and the heat resistance.

[0061] The principles, of the preferred embodiments and mode of operation of the present invention have been described in the foregoing specification. However, the invention, which is intended to be protected, is not to be construed as limited to the particular embodiment disclosed. Further, the embodiment described herein are to be regarded as illustrative rather than restrictive. Variations and changes may be made by others, and equivalents employed, without departing from the spirit of the present invention. Accordingly, it is expressly intended that all such variations, changes and equivalents that fall within the spirit and scope of the present invention as defined in the claims, be embraced thereby. A magnesium alloy containing aluminum, manganese and calcium, characterized in that the magnesium alloy includes 6~12% by weight of aluminum, 0.1~1.5% by weight of manganese, a calcium/aluminum mass ratio being 0.55~1.0, and balance being magnesium and inevitable impurities.

Claims

1. A magnesium alloy containing aluminum, manganese and calcium, **characterized in that** the magnesium alloy comprises 6~12% by weight of aluminum;

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0.1~1.5% by weight of manganese;
a calcium/aluminum mass ratio being 0.55~1.0; and
balance being magnesium and inevitable impurities.

- 5 **2.** A magnesium alloy according to claim 1, further comprising;
at least one of equal to or less than 1.5% by weight of strontium, equal to or less than 2.5% by weight of rare earth
element, equal to or less than 1 % by weight of silicon; and equal to or less than 2% by weight of tin.
- 10 **3.** A magnesium alloy according to claim 1, wherein the calcium/aluminum mass ratio is 0.60~0.88.
- 4.** A magnesium alloy according to claim 1, wherein the manganese is equal to or less than 0.2~1.0% by weight.
- 5.** A magnesium alloy according to claim 1, wherein the calcium is equal to or greater than 4% by weight.
- 15 **6.** A magnesium alloy according to claim 1, wherein the calcium is equal to or greater than 5% by weight.
- 7.** A magnesium alloy according to claim 1, wherein the magnesium alloy includes a β phase ($\text{Mg}_{17}\text{Al}_{12}$) and the β
phase ($\text{Mg}_{17}\text{Al}_{12}$) is equal to or less than 0.5% in an area ratio.
- 20 **8.** A casting **characterized in** being formed from a magnesium alloy according to claim 1.

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FIG. 1

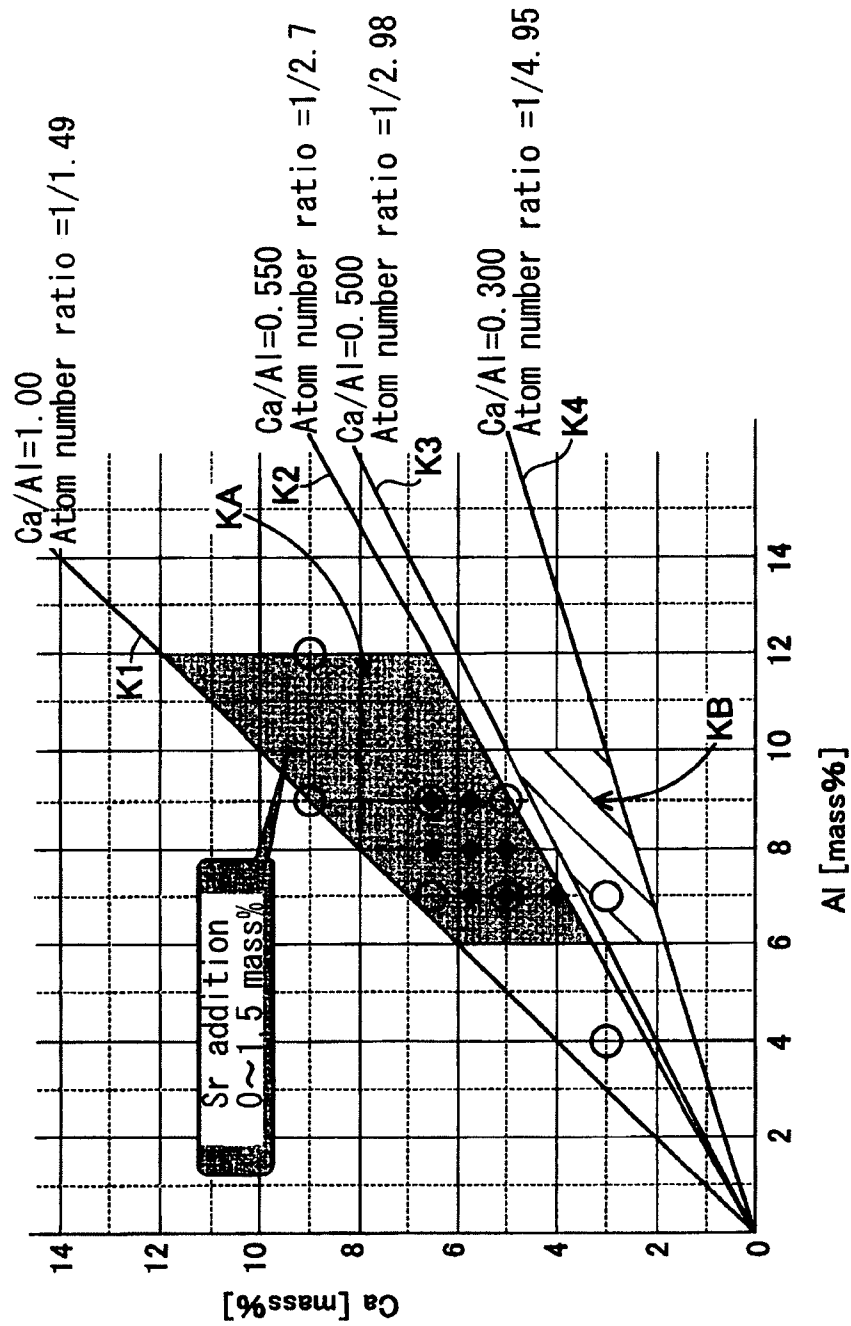


FIG. 2

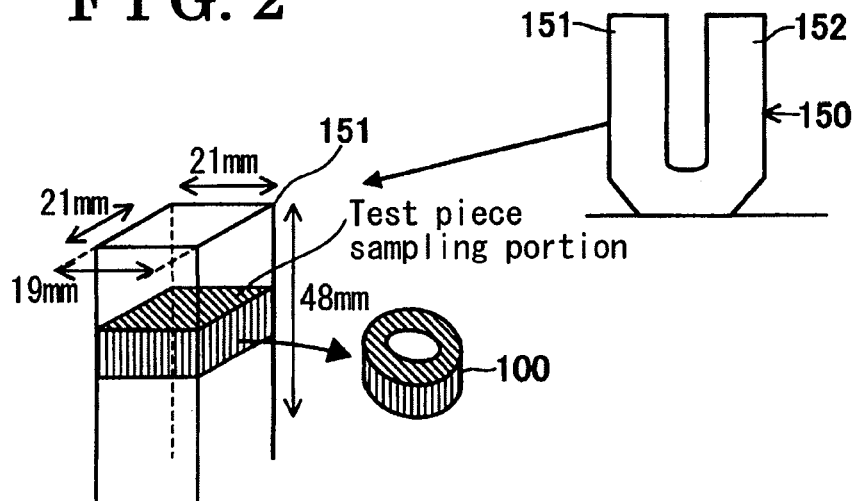


FIG. 3

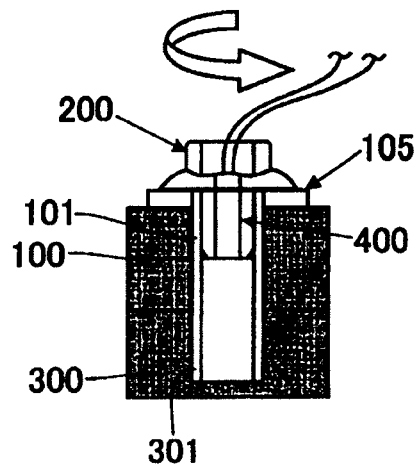


FIG. 4

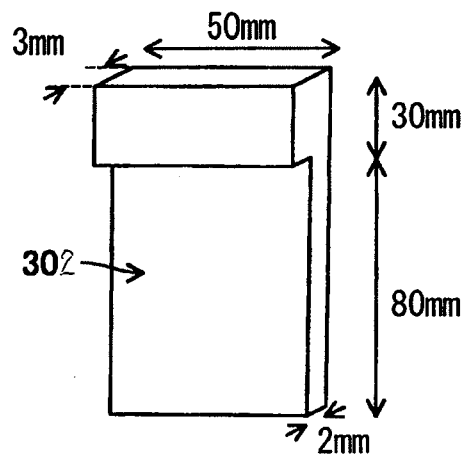


FIG. 5

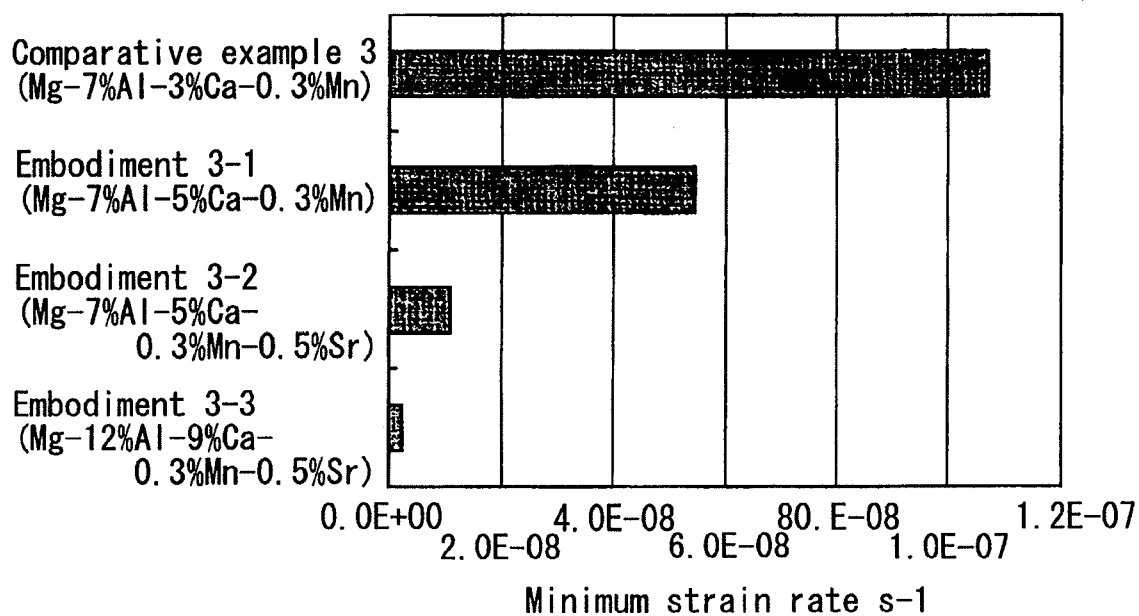
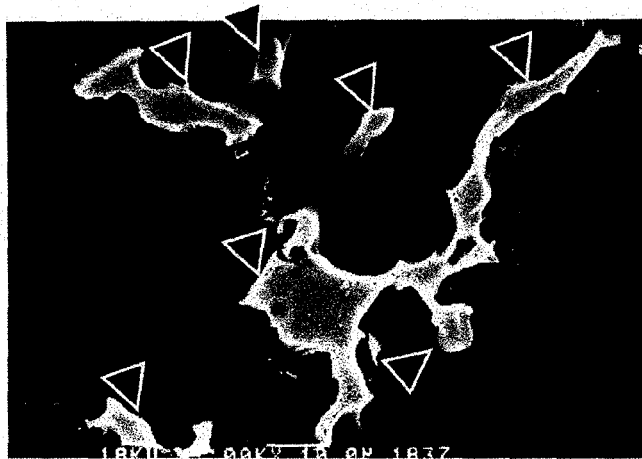


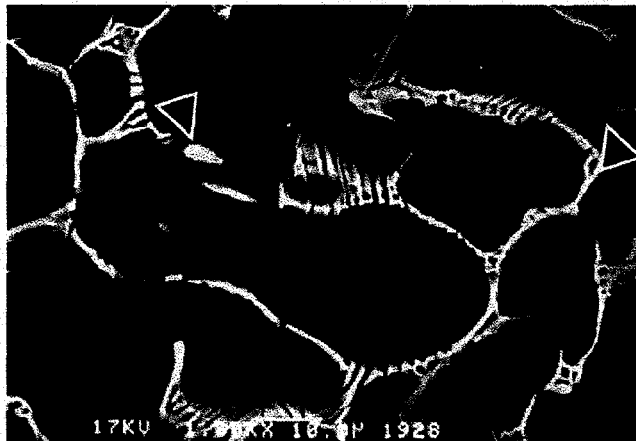
FIG. 6



Ca: not contained

Mg-7%Al-0.3%Mn alloy

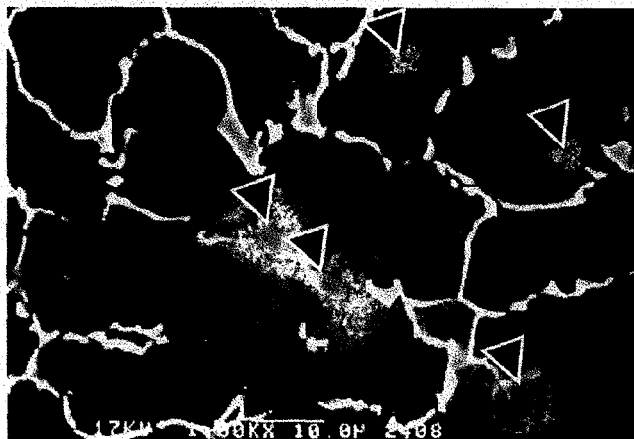
FIG. 7



Ca/Al $\cong$ 0.43

Mg-7%Al-0.3%Ca-0.3%Mn alloy

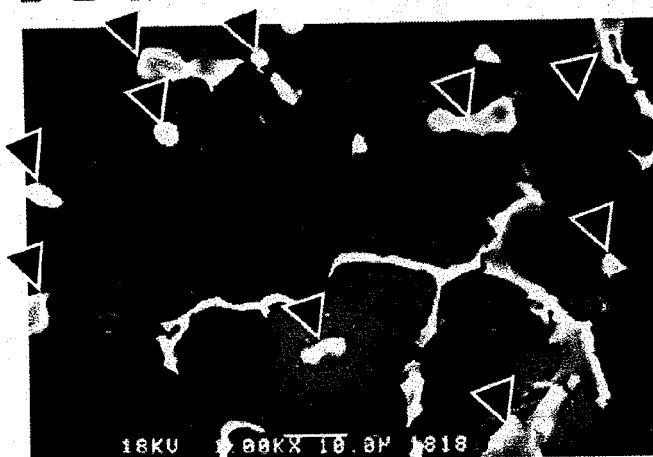
FIG. 8



Ca/Al $\cong$ 0.25

Mg-8%Al-2%Ca-0.3%Mn alloy

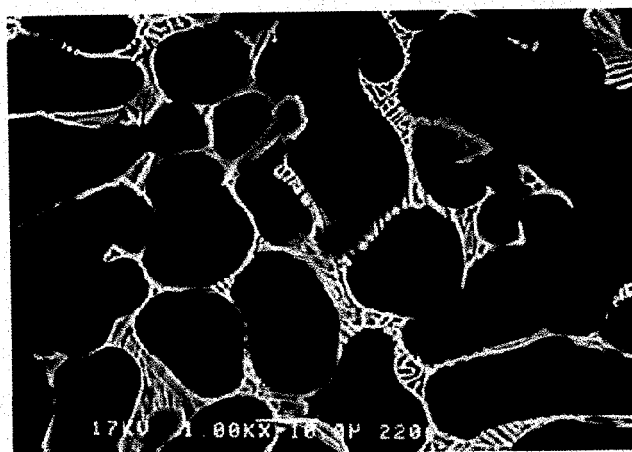
FIG. 9



$\text{Ca/Al} \doteq 0.14$

Mg-7%Al-1%Ca-0.3Mn alloy

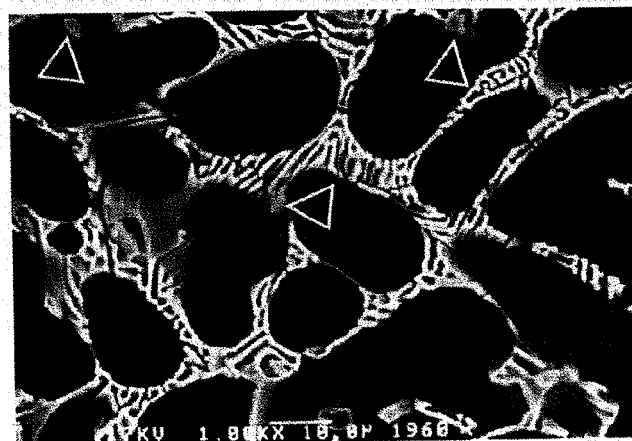
FIG. 10



The invention
 $\text{Ca/Al} \doteq 0.57$

Mg-7%Al-4%Ca-0.3Mn alloy

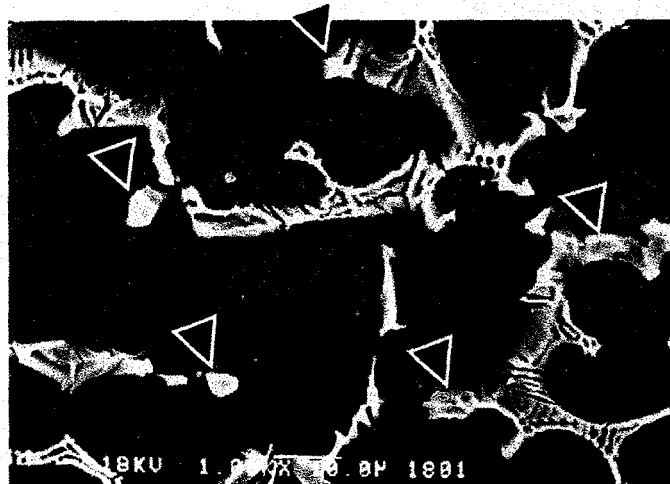
FIG. 11



$\text{Ca/Al} \doteq 0.5$

Mg-8%Al-4%Ca-0.3Mn alloy

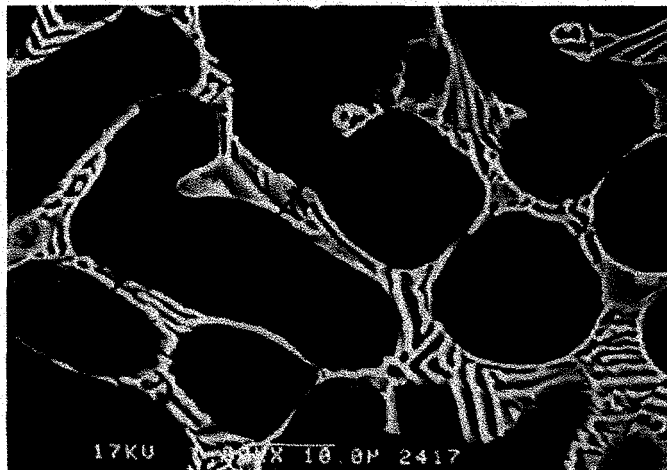
FIG. 12



$\text{Ca/Al} \doteq 0.29$

Mg-7%Al-2%Ca-0.3Mn alloy

FIG. 13



The invention
 $\text{Ca/Al} \doteq 0.71$

Mg-7%Al-5%Ca-0.3Mn alloy



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
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