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(54) **Heat resistant magnesium alloy for casting**

(57) A heat resistant magnesium alloy for casting includes 6-12% by weight of aluminum, 0.05-4% by weight of calcium, 0.5-4% by weight of rare earth elements, 0.05-0.50% by weight of manganese, 0.1-14% by weight of tin, balance magnesium and inevitable impurities.

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Description

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is based on and claims priority under 35 U.S.C. § 119 to Japanese Patent Application 2003-288229 filed on August 6, 2003, and Japanese Patent Application 2004-080729 filed on March 19, 2004, the entire content of which is incorporated herein by references.

FIELD OF THE INVENTION

[0002] This invention generally relates to a heat resistant magnesium alloy for casting.

BACKGROUND

[0003] From the view-point of environmentalism for earth, weight saving for vehicle, mainly for auto mobile, is strongly required from domestic and foreign vehicle manufacturers. Employing magnesium alloy, which is most light among metals for industrial use, is most effective method for filling this requirement. Up to now, magnesium alloy was applied to members, which does not require heat resistance very much, such as a cylinder head cover, a mandrel for a steering, and a steering pedal bracket.

[0004] For further weight saving for vehicle, application of magnesium alloy for members, which require heat resistance, such as a mission case, an oil pan, and an engine block, is expected. However, magnesium alloy for current industrial use, such as AZ91D or AM60, drastically decreases the heat resistance at equal to or greater than 120 °C. The application of the magnesium alloy for the members which require heat resistance at the temperature equal to or greater than 120-150 °C is extremely difficult. Magnesium alloy with improved heat resistance is actively developed in these days as shown in following patent documents. However, problems for industrial use are remained yet in magnesium alloy disclosed in following patents.

[0005] JP2604670B discloses magnesium alloy including 0.5-5 % by weight of lanthanoid, 2-5 % by weight of calcium for improving heat resistance.

[0006] JP3229954B discloses magnesium alloy including 1.2-2.2 % by weight of calcium, 1-3 % by weight of rare earth elements and under 6% by weight of aluminum for improving heat resistance.

[0007] JP2001-316752A2 discloses magnesium alloy including 0.3-2 % by weight of calcium. Amount of added calcium is reasonable from the viewpoint of corrosion resistance and cost. However, amount of added aluminum is low (2-6 % by weight). Thus, the magnesium alloy has disadvantages in castability.

[0008] JP3326140B discloses magnesium alloy including 1-10 % by weight of aluminum, 0.2-5 % by weight of rare earth elements, 0.02-5 % by weight of calcium, 0.2-10% by weight of silicon, equal to or less than 1.5% by weight of manganese.

[0009] JPH06-172909A2 discloses magnesium alloy including 0.5-2% by weight of at least one or two of cerium, cerium series misch metal for improving heat resistance. The magnesium alloy further includes 0.5%-15% by weight of tin.

[0010] JPH07-003374A2 discloses magnesium alloy including 6.0-20.0% by weight of tin, 0.2-2.0% by weight of silicon, and further including equal to or less than 4.0% by weight of at least one of aluminum, zinc. The magnesium alloy has advantages in creep characteristics.

[0011] JPH8-020835A2 discloses magnesium alloy including 1-10% by weight of zinc, 0.3-4% by weight of silicon, 0.05-3% by weight of calcium, 0.2-1.5% by weight of manganese, and impurities such as equal to or less than 2% by weight of bismuth, lead, tin, cadmium and equal to or less than 1% by weight of antimony, rare earth elements.

[0012] JP2604670B discloses magnesium alloy including 0.5-5% by weight of lanthanoid and 2-5% by weight of calcium. However, the magnesium alloy does not include tin.

[0013] JP3229954B discloses magnesium alloy including 1.2-2.2 % by weight of calcium, 1-3% by weight of rare earth elements, equal to or less than 6% by weight of aluminum for improving heat resistance. However, the magnesium alloy includes small amount of aluminum (upper limit 6% by weight), which causes less castability (low fluidity, easiness of forming casting crack). Further, the magnesium alloy does not include tin.

[0014] JP2001-316752A2 discloses magnesium alloy including reasonable amount of calcium (0.3-2% by weight) from the viewpoint of corrosion resistance and cost performance. However, the magnesium alloy includes small amount of aluminum (2-6% by weight), which causes less castability (low fluidity, easiness of forming casting crack). Further, the magnesium alloy does not include tin.

[0015] JP3326140B discloses magnesium alloy including 1-10% by weight of aluminum, 0.2-5% by weight of rare earth elements, 0.02-5% by weight of calcium, 0.2-10% by weight of silicon, equal to or less than 1.5% by weight of manganese. Comparatively larger amount of aluminum included in the magnesium alloy causes good castability of the magnesium alloy. However, equal to or greater than 0.2% by weight of silicon included in the magnesium alloy causes crystallization of Mg_2Si phase in crystal. Mg_2Si phase is needle-like shape, and exhibits low notch toughness, which causes low toughness of the magnesium alloy. In addition, silicon forms inter metallic compound at comparatively high temperatures, as calcium and rare earth elements added for improving heat resistance does. Addition of the silicon to the magnesium alloy interferes formation of compounds of calcium and rare earth elements, which causes improvement of heat resistance of the magnesium alloy. As a result, the heat resistance of the magnesium alloy is degraded. Accordingly, it is preferable that the magnesium alloy does not include silicon. And, it is required that magnesium alloy includes rare earth elements for improving the heat resistance. However, the rare earth elements highly costs. Accordingly, cast made from the magnesium alloy including rare earth elements has problem in high cost. Further, the magnesium alloy disclosed in JP 3326140B does not include tin.

[0016] JPH6-172909A2 discloses magnesium alloy including at least any one or two of 0.5-2% by weight of cerium and 0.5-2% by weight of cerium series misch metal. The magnesium alloy further includes 0.5-15% by weight of tin. However, according to JPH6-172909A2, the magnesium alloy does not include aluminum, which contributes to improve castability and strength of host crystal (primary crystal of α-magnesium matrix). Thus, the magnesium alloy has less castability such as lower fluidity and easiness of forming casting crack. In practice, the magnesium alloy does not applicable for industrial use in casting production.

[0017] JPH07-003374A2 discloses magnesium alloy including 6.0-20.0% by weight of tin, 0.2-2.0% by weight of silicon, further at least any one of equal to or less than 4.0% by weight of aluminum, 4.0% by weight of zinc. The magnesium alloy includes tin. However, according to JPH07-003374A2, the magnesium alloy includes small amount of aluminum (equal to or less than 4% by weight) similar to the magnesium alloy disclosed in JPH6-172909. Accordingly, the magnesium alloy has less castability (low fluidity, easiness of forming casting crack).

[0018] JPH8-20835B discloses magnesium alloy including 1-10% by weight of zinc, 0.3-4% by weight of silicon, 0.05-3% by weight of calcium, and 0.2-1.5% by weight of manganese. The magnesium alloy further includes impurities such as equal to or less than 2% by weight of bismuth, lead, tin, and cadmium, and equal to or less than 1% by weight of antimony and rare earth elements. The magnesium alloy disclosed in JPH8-20835 includes tin, which is impurities. However, the magnesium alloy described in JPH8-20835 is not Mg-Al series alloy, but Mg-Zn series alloy. Accordingly, the magnesium alloy includes at most 10% by weight of zinc. The magnesium alloy including large amount of zinc forms weak Mg_7Zn_3 phase, which may causes casting crack. Further, addition of equal to or greater than 6.2% by weight of zinc is greater than solid solubility limit of the zinc for the magnesium, which causes eutectic reaction at low temperature such as 340 °C. Thus, heat resistance of the magnesium alloy is degraded.

[0019] As described above, adding aluminum is more efficient than adding zinc to the magnesium alloy for improving castability thereof. In practice, commercial AZ91 magnesium alloy includes large amount of aluminum (9% by weight), and small amount of zinc (about 1% by weight). Further, the magnesium alloy disclosed in JPH8-20835 has problems for industrial use in castability, in particular easiness of forming casting crack.

[0020] A need thus exists for magnesium alloy for casting, which has advantages in heat resistance, castability, and cost performance.

SUMMARY OF THE INVENTION

[0021] According to an aspect of the present invention, a magnesium alloy includes 6-12% by weight of aluminum, 0.05-4% by weight of calcium, 0.5-4% by weight of rare earth elements, 0.05-0.50% by weight of manganese, 0.1-14% by weight of tin, balance magnesium and inevitable impurities.

[0022] According to another aspect of the present invention, a magnesium alloy includes 6-12% by weight of aluminum, 0.05-4% by weight of calcium, 0.5-4% by weight of rare earth elements, 0.05-0.50% by weight of manganese, 0.1-14% by weight of tin. The magnesium alloy further includes at least any one of 0.05-0.2% by weight of zirconium, 0.03-0.2% by weight of carbon, balance magnesium and inevitable impurities.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] 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:

[0024] Fig. 1 shows a method for measuring an axial force of a bolt.

[0025] Fig. 2 shows a photograph of a metal structure of an alloy of an embodiment 8.

[0026] Fig. 3 shows a photograph of a metal structure of an alloy of an comparative example 8.

[0027] Fig 4 shows a photograph of a metal structure of an alloy of an embodiment 19.

DETAILED DESCRIPTION

[0028] According to Claim 1, magnesium alloy includes 6-12% by weight of aluminum, 0.05-4% by weight of calcium, 0.5-4% by weight of rare earth elements, 0.05-0.50 by weight of manganese, 0.1-14% by weight of tin. The magnesium alloy further includes balance magnesium and inevitable impurities.

[0029] According to Claim 5, magnesium alloy includes 6-12% by weight of aluminum, 0.05-4% by weight of calcium, 0.5-4% by weight of rare earth elements, 0.05-0.50% by weight of manganese, 0.1-14% by weight of tin. The magnesium alloy further includes at least any one of 0.05-0.2% by weight of zirconium, 0.03-0.2% by weight of carbon. The magnesium alloy further includes balance magnesium and inevitable impurities.

[0030] Reason of improvement of heat resistance for the magnesium alloy according to the Claims 1, 5 is assumed as follows. Tin intends to be solved by priority in primary crystal of α-magnesium matrix forming the magnesium alloy. Without addition of the tin, calcium and rare earth elements are solved in primary crystal of α-magnesium matrix. When tin is added, the calcium and the rare earth elements are crystallized on the grain boundary of the primary crystal of the α-magnesium matrix as a compound. As a result, grain boundary sliding is effectively prevented by the compound. Further, the tin solved by priority in the primary crystal of the α-magnesium matrix forming the magnesium alloy prevents transfer of dislocation in accordance with creep deformation in the crystal.

[0031] As described above, heat resistance of the alloy is improved by addition of the tin while preventing undesirable effect to castability and corrosion resistance. Accordingly, by adding tin, which is more cost effective than calcium and rare earth elements in composition in use for alloy, required amount of the calcium and the rare earth elements which highly cost is relatively reduced. Then, cost for material is also reduced.

[0032] According to Claim 1, the present invention provides the magnesium alloy for casting, which has advantages in heat resistance, castability, and cost performance. The magnesium alloy properly includes aluminum, calcium, rare earth elements, manganese, and tin.

[0033] According to Claim 5, the present invention provides the magnesium alloy for casting, which has advantages in heat resistance, castability, and cost performance. The magnesium alloy properly includes aluminum, calcium, rare earth elements, manganese, and tin. The magnesium alloy further includes zirconium and carbon.

[0034] According to Claim 1 and Claim 5, the magnesium alloy includes 6-12% by weight of aluminum, 0.05-4% by weight of calcium, 0.5-4% by weight of rare earth elements, 0.05-0.50% by weight of manganese, and 0.1-14% by weight of tin. The reasons for definition of composition are described as follows.

[0035] (6-12% by weight of aluminum) Aluminum improves castability, in particular improves fluidity of the alloy. Aluminum also improves strength of the alloy, which causes improvement of mechanical properties of the alloy. However, excess aluminum causes degradation of toughness and strength of the alloy. Lack of aluminum causes degradation of the fluidity. As considering above, amount of aluminum included in the alloy may be set to equal to or greater than 6% by weight, or may be set to greater than 6% by weight. Accordingly, the amount of aluminum included in the alloy may be set to 6-10%, 6-9%, 6-8.5% by weight. A lower limitation of the amount of aluminum may be set to 6.05% by weight, 6.1% by weight, 6.2% by weight, 6.4% by weight, 6.6% by weight as example. An upper limitation of the amount of aluminum combined with the lower limitation as described above may be set to 11.5% by weight, 10.5% by weight, 9.5% by weight as example. The amount of the aluminum is not limited to only values described above.

[0036] (0.05-4% by weight of calcium) Calcium is solved in primary crystal of α-magnesium matrix to improve heat resistance of the magnesium alloy. In addition, calcium forms compound in the grain boundary of the primary crystal of the α-magnesium matrix to prevent the grain boundary sliding, and to improve the heat resistance. However, excess calcium causes degradation of toughness, strength, and corrosion resistance of the magnesium alloy. In addition, cost is increased. As considering above, the amount of the calcium may be set to 0.05-4% by weight.

[0037] Corresponding to a requirement for property of the magnesium alloy, the amount of calcium included in the magnesium alloy may be set to 0.1-4% by weight, 0.5-3.8% by weight, 0.7-3.6% by weight. In this case, a lower limit of the calcium may be set to 0.08% by weight, 0.15% by weight, 0.2% by weight as example. An upper limit of the calcium may be set to 3.8% by weight, 3.7% by weight, 3.6% by weight as example, which is combined with the lower limit described above. The lower limit and the upper limit of the amount of the calcium is not limited to only values described above.

[0038] In case castability is key properties in addition to heat resistance, the amount of the calcium may be relatively reduced to 0.05-2% by weight. In this case, as considering above, the amount of the calcium may be reduced to equal to or less than 2% by weight, or less than 2%. The word "equal to or less than" means the value including stated value, the word "less than" means the value not including the stated value.

[0039] As considering above, the amount of the calcium may be reduced to 0.1-2% by weight, 0.5-2% by weight, 0.7-1.95% by weight in case the heat resistance and the castability are key properties. In this case, the lower limit of the amount of the calcium may be set to 0.08%, 0.15%, 0.2% by weight as example. The upper limit of the amount of the calcium may be set to 1.99%, 1.95%, 1.85% by weight as example, which is combined with the lower limit described above. The lower limit and the upper limit of the amount of the calcium are not limited to only values described above.

[0040] Further, in case the heat resistance is considered as more important properties of the magnesium alloy, the included amount of the calcium may be relatively increased. Thus, the amount of the calcium may be set from greater than 2% by weight to 4% by weight. In this case, as considering above, the amount of the calcium may be set to equal to or less than 3.8%, 3.6%, 3.3%, 3.1% by weight. Further, in case the heat resistance and the strength at high temperatures is important, the amount of the calcium is set to 2.1-3.8%, 2.2-3.6%, 2.5-3.5% by weight. In this case, a lower limit of the amount of the calcium may be set to 2.1%, 2.2%, 2.3% by weight as example. An upper limit of the amount of the calcium may be set to 3.9%, 3.8%, 3.7% by weight as example, which is combined with the lower limit described above. However, the lower limit and the upper limit of the amount of the calcium is not limited to the values described above.

[0041] (0.5-4% by weight of rare earth elements) Rare earth elements improve heat resistance by solid solution strengthening by being solved in the primary crystal of the α-magnesium matrix. The rare earth elements form compounds in the grain boundary of the primary crystal of the α-magnesium matrix. As a result, grain boundary sliding is effectively prevented, which improves the heat resistance of the magnesium alloy. However, excess rare earth elements intend to cause degradation of the toughness, strength, fluidity and corrosion resistance of the alloy. As considering above, the amount of the rare earth elements included in the magnesium alloy may be set to 0.5-3.8%, 0.6-3.5%, 0.7-3.0% by weight. A lower limits of the amount of the rare earth elements may be set to 0.6%, 0.7%, 0.8% as example. An upper limits of the amount of the rare earth elements may be set to 3.5%, 3.4%, 3.2% by weight as example, which is combined with the lower limits described above for example. The lower limit and the upper limit are not limited to only values described above. The rare earth elements are not easily obtained as elementary substance. Accordingly, misch metal substitutes for the rare earth elements. Misch metal is generally rare earth elements alloy mainly including at least any one of cerium, lanthanum, praseodymium, and neodymium. Any one of cerium series misch metal, neodymium series misch metal, and lanthanum series misch metal may be used. Elementary substance of cerium, lanthanum, praseodymium, and neodymium may be used if the occasion arises. Further, other rare earth elements may be also used. The rare earth elements are mainly solved in the primary crystal of the α-magnesium matrix forming the magnesium alloy. Further, the rare earth elements form compounds in the primary crystal of the α-magnesium matrix.

[0042] In addition, in case the amount of the calcium is relatively large (for example, the amount of the calcium is greater than 2% by weight), the castability of the magnetic alloy is somewhat degraded. Then, the amount of the calcium may be reduced to 0.5-1.9%, 0.6-1.8%, 0.6-1.7% by weight. The amount of the calcium is not limited to only values described above.

[0043] (0.05-0.50% by weight of manganese) Manganese improves corrosion resistance. However, excess amount of manganese causes degradation of the toughness and strength. As considering above, the amount of the manganese may be set to 0.08-0.45%, 0.09-0.35%, 0.1-0.4% by weight. A lower limit of the amount of the manganese may be set to 0.06%, 0.07%, 0.08% by weight as example. An upper limit of the manganese may be set to 0.45%, 0.40%, 0.35% 0.30%, 0.20%, 0.15% by weight as example. The lower limit and the upper limit of the amount of the manganese are not limited to only values described above.

[0044] (0.1-14% by weight of tin) Tin is solved in the primary crystal of the α-magnesium matrix prior to the calcium and the rare earth elements, which improve the heat resistance of the magnesium alloy by solid solution strengthening. In addition, because the tin is solved in the primary crystal of the α-magnesium matrix prior to the calcium and the rare earth elements, the compounds phase of the calcium and the rare earth elements, which prevents grain boundary sliding, are formed in the grain boundary of the primary crystal of the α-magnesium matrix. Thus, the heat resistance is improved. However, excess tin intends to degrade the toughness and the strength of the magnesium alloy. Further, tin has large specific gravity about 7.3. Then, excess amount of the tin has a disadvantage for weight saving, which is main purpose of using the magnesium alloy. However, in case requirement for weight saving of the magnesium alloy is not so strict, the amount of the tin may be increased as grater than 5%, 10% 12% by weight. In addition, according to phase diagram of magnesium-tin series, tin can be solved about 14% by weight in the primary crystal of the α-magnesium matrix at maximum.

[0045] As considering above, the amount of the tin may be set to 0.1-13%, 0.1-12%, 0.15-5%, 0.15-2.0%, 0.15-1.2% by weight. Further, for the purpose of weight saving of the magnesium alloy, the amount of the tin can be further reduced to equal to or less than 8% by weight, thus 0.1-8% by weight.

[0046] Considering further weight saving of the magnesium alloy, the amount of the tin may be set to less than 3%, 2%, 1% by weight, thus 0.1-3.0%, 0.1-2.0%, 0.1-1.0%, 0.1-0.8%, 0.1-0.5% by weight.

[0047] As considering above, a lower limit of the tin may be set to 0.15%, 0.2%, 0.3% by weight as example. An upper limit of the tin, which is combined with the lower limit described above may be set to 12%, 10%, 8%, 7%, 6%, or less than 6% by weight as example. Further, the lower limit may be set to 5%, 4%, 3% as example. The lower limit and the upper limit are not limited to the values described above.

[0048] Comparing the amount of the tin and the calcium, the amount of the tin can be less than the amount of the calcium, the amount of the tin can be greater than the amount of the calcium, the amount of the tin can be equal to the amount of the calcium, the amount of the tin can be nearly equal to the amount of the calcium. Comparing the amount of the tin and the rare earth elements, the amount of the tin can be less than the amount of the rare earth elements, the amount of the tin can be greater than the amount of the rare earth elements, the amount of the tin can be equal to the amount of the rare earth elements, the amount of the tin can be nearly equal to the amount of the rare earth elements.

[0049] According to the Claim 5, the magnesium alloy further includes at least any one of 0.05-0.2% by weight of zirconium and 0.03-0.2% by weight of carbon.

[0050] (0.05-0.2% by weight of zirconium) Zirconium contributes to form finer structure and increase strength of the magnesium alloy in normal temperature. However, excess zirconium increases crystallization of Mg-Al-Zr series compounds, AL_3Zr et. al, which causes degradation of the toughness. As considering above, the amount of the zirconium may be set to less than 0.2% by weight or equal to or less than 0.2% by weight, thus 0.06-0.19%, 0.06-0.18%, 0.06-0.17% by weight. In addition, a lower limits of the zirconium may be set to 0.055%, 0.065% by weight as example. An upper limit of the zirconium, which is combined with the lower limit described above, may be set to 0.19%, 0.18% by weight as example. However, the lower limit and the upper limit are not limited to those described above.

[0051] (0.03-0.2% by weight of carbon) Carbon contributes to form finer structure and increase strength of the magnesium alloy in the normal temperature. However, excess carbon causes high density of the carbon in the crystal, which causes degradation of the strength and the toughness of the magnesium alloy. As considering above, the amount of the carbon can be set to equal to or less than 0.2% or less than 0.2%, thus 0.03-0.19%, 0.04-0.18%, 0.05-0.17% by weight. In addition, a lower limit of the amount of the carbon mat be set to 0.04%, 0.05% by weight as example. An upper limit of the amount of the carbon, which is combined with the lower limit described above, may be set to 0.19%, 0.18% by weight as example. The lower limit and the upper limit are not limited those described above.

[0052] Further according to Claim 1 and Claim 5, the magnesium alloy may include at least any one of equal to or less than 0.4% by weight (less than 0.4% by weight) of silicon, equal to or less than 0.4% by weight (less than 0.4% by weight) of strontium, equal to or less than 0.4% by weight (less than 0.4% by weight) of titanium, equal to or less than 0.4% by weight (less than 0.4% by weight) of titanium boride (TiB), equal to or less than 0.8% by weight (less than 0.8% by weight) of zinc.

[0053] Further according to the Claim 1 and Claim 5, the magnesium alloy may includes at least any one of equal to or less than 0.2% by weight (less than 0.2% by weight) of silicon, equal to or less than 0.2% by weight (less than 0.2% by weight) of strontium, equal to or less than 0.2% by weight (less than 0.2% by weight) of titanium, equal to or less than 0.2% by weight (less than 0.2% by weight) of titanium boride (TiB), equal to or less than 0.5% by weight (less than 0.5% by weight) of zinc.

[0054] Further, the amount of the silicon may set to 0.05-0.2% by weight, the amount of the strontium may set to 0.005-0.2% by weight, the amount of the titanium may be set to 0.05-0.2% by weight, the amount of the titanium boride (TiB) may be set to 0.05-0.2% by weight, the amount of the zinc is set to 0.05-0.5% by weight.

[0055] Greater amount of the silicon than the values described above causes the large amount of the crystallization of Mg_2Si compounds, which causes degradation of the toughness and the strength of the magnesium alloy. Greater amount of the strontium than the values described above causes the large amount of formation of Mg-Al-Sr and Al_4Sr, which causes the degradation of the toughness of the magnesium alloy. Greater amount of the titanium than the values described above causes crystallization of Al-Ti series compounds, which causes the degradation of the toughness of the magnesium alloy. Greater amount of the titanium boride (TiB) than the values described above causes large amount of the formation of the TiB compounds in the crystal, which causes the degradation of the toughness of the magnesium alloy. Greater amount of the zinc than the values described above causes the large amount of crystallization of Mg-Zn series compounds, which increases a frequency of forming casting crack.

[0056] The magnesium alloy according to Claim 1 or Claim 5 is appropriate for die casting, gravity die casting, sand casting and the like, because of castability thereof. In die casting, either one of cold chamber method and hot chamber method is applicable. The magnesium alloy according to Claim 5, which including zirconium and/or carbon, which has function for forming finer structure, is appropriate for gravity die casting, sand casting, high pressure die casting. However, the magnesium alloy according to the Claim 5 is also applicable for the die casting.

[0057] The magnesium alloy according to Claim 1 or Claim 5 is applicable for components, which requires both weight saving and heat resistance. For example, the magnesium alloy is applicable for a cylinder head cover, a cylinder block, a piston, a transmission case for a vehicle. The application of the magnesium alloy is not limited to those described above.

[0058] The embodiment of the invention will be explained as follows. Each ingot, which has composition indicated in Table 1, is melted at a gas melting furnace using a flux free method. Temperature of molten metal is held at 690 °C. The molten metal is charged into a molding cavity of a die casting mold of 7.8 MN die casting machine. An oil pan used in vehicle engine (2.8 kg in weight, box shaped component) is practically formed from the molten metal as a casting specimen. In order to stabilize condition of temperature of the mold, the specimen is made after about tenth shot of casting. The specimens are measured as follows. The composition indicated in Table 1 is analyzed composition of the specimen.

[0059] Table 1.

	Composition of magnesium alloy % by weight (analyzed value)							Preservation of axial strain	Casting crack	Burning frequency	Fluidity	Corrosion resistance
	Al	Ca	RE	Mn	Sn	others	Mg					
Comparative example 1	8.7	-	-	0.18	-	0.98% Zn	balance	17	NO	0/56	1	1
Comparative example 2	7.1	0.0	0.0	0.21	-	-	balance	22	NO	0/28	1	2
Comparative example 3	5.2	2.3	2.2	0.19	-	-	balance	80	Entire surface	20/50	5	4
Comparative example 4	6.9	2.5	0.0	0.19	-	-	balance	67	Subtle	3/50	4	5
Comparative example 5	7.2	0.0	2.6	0.18	-	-	balance	60	NO	0/18	3	2
Comparative example 6	7.2	2.6	1.1	0.20	-	-	balance	76	Subtle	6/20	4	4
Comparative example 7	7.1	1.3	1.5	0.20	-	-	balance	62	NO	0/50	3	2
Comparative example 8	7.0	1.8	1.1	0.19	-	-	balance	65	NO	0/50	3	2
Comparative example 9	8.1	1.3	1.4	0.19	-	-	balance	60	NO	0/50	3	2
						-						
Embodiment 1	7.1	0.9	1.1	0.19	0.43	-	balance	61	NO	0/12	3	2
Embodiment 2	7.0	1.3	1.4	0.19	0.42	-	balance	67	NO	0/40	3	2
Embodiment 3	7.0	1.8	2.7	0.20	0.40	-	balance	75	NO	0/14	3	2
Embodiment 4	8.0	1.0	0.9	0.21	0.43	-	balance	58	NO	0/15	2	2
Embodiment 5	8.1	1.3	1.5	0.21	0.44	-	balance	65	NO	0/40	2	2
Embodiment 6	8.0	1.9	2.8	0.20	0.42	-	balance	72	NO	0/19	2	2
Embodiment 7	7.2	1.8	0.9	0.20	0.18	-	balance	69	NO	0/10	3	2
Embodiment 8	7.1	1.9	1.1	0.19	0.42	-	balance	71	NO	0/40	3	2
Embodiment 9	7.1	1.8	1.0	0.18	0.91	-	balance	73	NO	0/16	3	2
Embodiment 10	7.2	1.9	0.9	0.17	0.38	0.11% Zr	balance	72	NO	0/40	3	2
Embodiment 11	7.0	1.9	0.9	0.17	0.44	0.10% C	balance	72	NO	0/40	3	2
Embodiment 12	7.2	1.8	1.0	0.19	0.42	0.20% Si	balance	71	NO	0/40	3	2
Embodiment 13	7.2	1.8	1.0	0.21	0.40	0.22% Sr	balance	71	NO	0/40	3	2
Embodiment 14	7.2	1.9	0.9	0.20	0.39	0.15% Ti	balance	70	NO	0/40	3	2
Embodiment 15	6.9	1.8	1.1	0.18	0.41	0.12% TiB	balance	71	NO	0/40	3	2
Embodiment 16	6.9	1.8	1.0	0.19	0.41	0.15% Y	balance	72	NO	0/40	3	2
Embodiment 17	7.0	1.9	0.9	0.18	0.43	0.45% Zn	balance	71	NO	0/40	3	2
Embodiment 18	7.0	2.5	0.9	0.15	0.45	-	balance	77	NO	1/30	3	3
Embodiment 19	6.9	2.9	1.1	0.12	0.48	-	balance	81	NO	0/18	4	3
Embodiment 20	6.9	3.8	1.2	0.20	0.51	-	balance	85	NO	1/12	4	4
Embodiment 21	6.8	3.0	1.2	0.14	0.98	-	balance	82	NO	1/17	4	3
Embodiment 22	7.0	3.0	1.0	0.16	1.52	-	balance	83	NO	1/30	4	3

*Fluidity, corrosion resistance are evaluated in 5 grades. Superior is evaluated as 1, inferior is evaluated as 5.

[0060] In the embodiments, a misch metal is used for the rare earth elements. The misch metal includes 50% by weight of cerium, 27% by weight of lanthanum, 11% by weight of neodymium, 5% by weight of praseodymium, and other rare earth elements for balance, relative to the 100% by weight of misch metal. The major constituents such as cerium, lanthanum, neodymium, and praseodymium occupy 93% by weight relative to the 100% by weight of misch metal used in the embodiments.

[0061] In the embodiments, the amount of the cerium, lanthanum, neodymium, and praseodymium included in the magnesium alloy by weight are analyzed. Total amount of the cerium, lanthanum, neodymium, and praseodymium by weight is obtained by adding these analyzed value. The amount of the misch metal by weight is obtained by applying 100/93 to the total amount of the cerium, lanthanum, neodymium, and praseodymium by weight. The amount of the misch metal is defined as RE (rare earth elements), indicated in column RE (rare earth elements) in Table 1. Accordingly, the amount of the included RE exhibited in Table 1 does not directly corresponds to the amount of cerium, lanthanum, neodymium, and praseodymium. The RE exhibited in Table 1 corresponds to the amount of misch metal including not only cerium, lanthanum, neodymium, and praseodymium, but also other rare earth elements. According to the embodiments, as shown in Table 1, the amount of the tin is generally set less than the amount of the calcium, the amount of the tin is generally set less than the amount of the rare earth elements (in embodiment 22, the amount of the tin is set greater than the amount of the rare earth elements exceptionally), or the amount of the tin is generally set nearly equal to the amount of the rare earth elements.

[0062] Magnesium alloy are measured in characteristics evaluation for preservation ratio of an axial force, easiness of forming casting crack, burning frequency, fluidity, and corrosion resistance. Measurement results are shown in Table 1 with the compositions of the specimens.

[0063] As a test sample, a bolt tightening portion of a flange of the oil pan formed from the magnesium alloy (flange outer diameter 20 mm, inner diameter (bolt through hole) 9-9.5 mm, thickness about 10 mm) is used. As shown in Fig. 1, a bolt 200 is inserted into the bolt through hole 101 of the test sample 100 and tightened to a screw hole 301 at a counter member 300 via a washer 105 (outer diameter 18 mm, thickness 3 mm, A6061-T6). The bolt 200 is made from steel, M8 $\times$ 25, strength grade 10.9 (JIS B1051). The counter member 300 is aluminum die casting alloy, ADC 12 in JIS (Japanese Industrial Standards). The bolt 200 is tightened with 7.8 KN of initial axial force. The axial force is measured by using a strain gauge 400 attached to the bolt 200. After that, the evaluating members including the test sample 100 tightened by the bolt 200 and the counter member 300 are inserted into an air atmosphere furnace to be held at high temperature (150 °C), in 300 hours, and to be cooled down to room temperature. After that, the axial force is re-measured. The preservation ratio of the axial force relative to the initial axial force is measured. The preservation ratio of the axial force is measured as average value from plural measured values. 76% of the preservation ratio of the axial force means that the axial force of the test peace 100 held at high temperature in above condition is reduced to the axial force 7.8 KN (the initial axial force) $\times$ 0.76. The axial force of the bolt 200 measured by ultrasonic axial force measurement exhibits similar result to the axial force measured by the strain gauge 400.

[0064] In casting crack evaluation, the oil pan is visually examined whether the specimen includes casting crack or not.

[0065] In burning frequency evaluation, the mold cavity surface is examined when the mold is opened and the casting product is taken out from the mold cavity whether a part of the casting product is burned to the mold cavity. The burning ratio is measured.

[0066] In evaluation of the fluidity of the magnesium alloy, amount of the over flowing molten metal and amount of the charged molten metal into a chillvent space into which molten metal charged is measured. The fluidity is evaluated in 5 grades. Superior in fluidity is evaluated as 1, inferior in fluidity is evaluated as 5.

[0067] For evaluating corrosion resistance, salt splay test (compliance with JIS Z 2371, spraying in 6 hours) is conducted for the cast oil pan. Relative merit is visually examined. The corrosion resistance is evaluated in 5 grades. Superior in corrosion resistance is evaluated as 1, inferior in corrosion resistance is evaluated as 5.

[0068] Comparative examples 1-9 described above are magnesium alloy not including tin. As shown in table 1, the magnesium alloy of the comparative example 1 (commercial AZ91D) and 2 do not substantially include calcium and rare earth elements. Thus, the heat resistance is low, and the preservation ratio of the axial force is extremely low. The magnesium alloy in the comparative example 3 includes the calcium and the rare earth elements. Thus, the heat resistance is improved. In addition, the preservation ratio of the axial force is substantially high (80%). However, the magnesium alloy in the comparative example 3 includes substantially low amount of aluminum, 5.2% by weight. Then, the fluidity of the magnesium alloy is degraded. Further, casting crack is easily formed and burning frequently occurs. The castability of the magnesium alloy in comparative example 3 is extremely degraded. Further, the magnesium alloy in the comparative example 3 is inferior in corrosion resistance, which is evaluated as 4.

[0069] The magnesium alloy in the comparative example 4 includes 6.9% by weight of aluminum. Then, the castability (small amount of the casting crack, low frequency of the burning, good fluidity) is superior. However, the magnesium alloy in the comparative example 4 is inferior in corrosion resistance, which is evaluated as 5.

[0070] The magnesium alloy in the comparative example 5 includes the rare earth elements. However, the magnesium alloy in the comparative example 5 does not include the calcium. Therefore, the preservation ratio of the axial force is low. The magnesium alloy in the comparative example 6 includes the rare earth elements and the calcium. Therefore, the preservation ratio of the axial force is superior. However, the corrosion resistance is inferior, which is evaluated as 4. The magnesium alloy in the comparative example 7, 8, 9 includes reasonable amount of the aluminum, calcium, rare earth elements, and manganese. Therefore, the magnesium alloy in this example does not frequently exhibits casting crack, and is superior in fluidity and corrosion resistance. However, the preservation ratio of the axial stress is not so high (60-65%) because the magnesium alloy in this example does not include the tin.

[0071] On the contrary, the magnesium alloy in the embodiments 1-22 includes reasonable amount of the aluminum, calcium, rare earth elements, manganese, and tin. Therefore, the magnesium alloys in these embodiments are totally superior in the heat resistance and the castability (small amount of the casting crack, good fluidity). Further, the tin substitutes function of the costly calcium and rare earth elements. Therefore, the heat resisting magnesium alloy for casting at low cost becomes available. The amount of the calcium is set to 0.9-1.9% by weight for the magnesium alloy in the embodiments 1-17, and the amount of the calcium is set to 2.5-3.8% by weight for the magnesium alloy in the embodiments 18-22.

[0072] The alloy in the embodiments 2, 8, 5 correspond to the alloy added about 0.4% by weight of the tin to the alloy in the comparative examples 7, 8, 9. The alloy in embodiment 2 corresponds to the alloy obtained by adding about 0.4% by weight of the tin to the alloy in the comparative example 7. The alloy in the embodiment 8 corresponds to the alloy obtained by adding 0.4% by weight of the tin to the alloy in the comparative example 8. The alloy in the embodiment 5 corresponds to the alloy obtained by adding 0.4% by weight of the tin to the alloy in the comparative example 9.

[0073] The castability (small amount of the casting crack, low frequency of the burning, good fluidity) and the corrosion resistance of the alloy in embodiments 2, 8, 5 are approximately similar to the alloy in the comparative example 7, 8, 9. However, the preservation of the axial force of the alloy in embodiments 2, 8, 5 are about 5-6% superior to the alloy in the comparative examples 7, 8, 9. Thus, the alloy in the embodiments 2, 8, 5 exhibit improved heat resistance.

[0074] The alloy in the embodiments 4, 5, 6 exhibit superior fluidity to other embodiments because the alloy in embodiments 4, 5, 6 include large amount of the aluminum.

[0075] As stated above, the reasons of the improvement of the heat resistance of the alloy in the embodiments are assumed as follows. The tin intends to be solved in the primary crystal of the α-magnesium matrix by priority to the calcium and the rare earth elements. Thus, the crystallized calcium and the crystallized rare earth elements under the condition without the tin are crystallized as compounds at the grain boundary of the primary crystal of the α-magnesium matrix under the condition with the tin. Therefore, magnesium-calcium series compound phase, aluminum-calcium series compound phase, magnesium-rare earth elements series compound phase, and magnesium-aluminum-calcium series compound phase, or the like, which prevents grain boundary sliding in the crystal, are increased in the alloy, to which the tin is added (embodiments 1-22), to effectively prevent the grain boundary sliding. Further, the tin solved in the primary crystal of α-magnesium matrix forming the magnesium alloy prevents a transfer of a dislocation along with a creep deformation in the crystal.

[0076] Thus, the addition of the tin improves the preservation ratio of the axial force of the bolt at the high temperature, while preventing the degradation of the castability and the corrosion resistance of the magnesium alloy. Therefore, in case the required characteristics of the axial force is determined in advance, by adding the tin, which is relatively lower cost to the composition of the magnesium alloy in use, the required amount of the calcium and the rare earth elements can be relatively reduced. Accordingly, a material cost for the magnesium alloy can be reduced relative to the known magnesium alloy. Thus, the magnesium alloy of lower cost becomes available.

[0077] The embodiments of the magnesium alloy will be further explained. The magnesium alloy in the embodiment 10 is the alloy obtained by adding 0.11 % by weight of zirconium to the based alloy in the embodiment 8. The magnesium alloy in the embodiment 11 is the alloy obtained by adding 0.10% by weight of carbon to the based alloy in the embodiment 8. The magnesium alloy in the embodiments 10,11 does not exhibit difference in the preservation ratio of the axial force from the magnesium alloy in the embodiment 8. However, the increase of strength in the normal temperature is exhibited. The formation of the finer structure formed by the zirconium and the carbon is assumed to improve the strength.

[0078] In the embodiment 12, 0.20% by weight of silicon is added to the alloy of the embodiment 8. In the embodiment 13, 0.22% by weight of strontium is added to the alloy of the embodiment 8. In the embodiment 14, 0.15% by weight of titanium is added to the alloy of the embodiment 8. In the embodiment 15, 0.12% by weight of titanium boride (TiB) is added to the alloy of the embodiment 8.

[0079] In the embodiment 16, 0.15% by weight of yttrium is added to the alloy of the embodiment 8. 0.15% by weight of yttrium is not included in the RE concentration shown in the table 1. In the embodiment 17, 0.45% by weight of zinc is added to the alloy of the embodiment 8.

[0080] The alloy in the embodiments 12-17 does not show differences from the alloy in the embodiment 8 on the preservation ratio of the axial force. In other words, these elements (silicon, strontium, titanium, titanium boride, yttrium, and zinc) can be added in the alloy without problem if the included ratio is set in the range described above. Accordingly, an operation for removing of these elements, which is conducted when the molten metal is purified, can be abolished or reduced. This leads to reduction of material cost.

[0081] As shown in Table 1, in the embodiments 18-22, the alloy includes large amount of the calcium (equal to or greater than 2% by weight). The amount of the rare earth elements is somewhat reduced corresponding to the somewhat large amount of the calcium. In the embodiments 18-22, the casting crack, which troubles the mass production, does not occur in the alloy. Further, the alloy has high preservation ratio of the axial force at the high temperature, and good heat resistance. In particular, in the embodiment 19-22, the preservation ratio of the axial force at the high temperature is further increased, showing equal to or greater than 80%. As stated above, because the amount of the calcium is high, the compounds of the calcium, and the rare earth metal solved in the primary crystal of α-magnesium matrix in case the tin is not added, are crystallized in the host crystal in case the tin is added to the alloy. The grain boundary sliding is effectively prevented by this.

[0082] (metal structure) Fig. 2 shows a photograph of a metal structure of the alloy of the embodiment 8. Fig. 3 shows a photograph of a metal structure of the alloy of the comparative example 8. Fig. 4 shows a photograph of a metal structure of the alloy of the embodiment 19. Each photograph shows 95 μm $\times$ 73 μm in view. The metal structures of the alloy are observed after etched by glycol liquid. A basic structures of the metal structure of the alloy in the comparative example 8, in the embodiment 8, and in the embodiment 19 are similar. In the comparative example 8, the alloy does not include the tin. In the embodiment 8, the alloy includes 0.42% by weight of the tin. In the embodiment 19, the alloy includes 0.48% by weight of the tin.

[0083] Comparing Fig. 2-Fig. 4, according to the metal structure in the embodiment 8 shown in Fig. 2, the grain size of the primary crystal of the α-magnesium matrix is about 30-35 μm. The grain size is more miniaturized than that of the metal structure in the comparative example 8 (about 40-50 μm). Similarly, the size of the primary crystal of the α-magnesium matrix in the embodiment 19 is about 20-30 μm as shown in Fig.4. The metal structure of the embodiment 19 is more miniaturized than that of the metal structure in the comparative example 8. It is assumed that the tin contributes finer metal structure.

[0084] Further, a formation of Mg_2Sn in the primary crystal of the α-magnesium matrix is observed in the metal structure of the alloy of the embodiment 8 as shown in Fig. 2. A compound of magnesium-calcium-aluminum series, a compound of magnesium-rare earth elements-aluminum series are formed in the crystal of the alloy of the embodiment 8, which includes the greater amount of the tin than the alloy of the comparative example 8 shown in Fig. 3, as shown in Fig. 2. Similar tendency is observed in the metal structure of the embodiment 19 shown in Fig. 4.

[0085] It is assumed that these phases of compounds contribute to prevent the grain boundary siding effectively, and to improve the heat resistance of the magnesium alloy. These phases of compounds are identified using an apparatus including a scanning electron microscope and an apparatus for energy dispersion X-ray analysis (SEM-EDX).

[0086] The embodiments of the invention are not restricted to the embodiment explained and shown in drawings. A change can be made corresponding to requirement. For example, the applicable rare earth elements include not only the cerium, lanthanum, neodymium, and praseodymium but also any one of scandium, gadolinium, terbium, samarium, holmium, thulium, erbium, europium, and ytterbium. The included amount of the elements of the alloy shown in Table. 1 may be used as an upper limit or a lower limit in claims.

[0087] The present invention can be utilized in parts of vehicles and industrial machines, which expect weight saving. The present invention can be utilized in engine related parts such as an oil pan, a transmission case, a cylinder block, a cylinder head, and a piston, or the like. The present invention can be utilized in parts, which requires both weight saving and heat resistance.

[0088] According to Claim 1, the present invention provides the magnesium alloy for casting having advantages in heat resistance, castability, and cost performance. The magnesium alloy properly includes aluminum, calcium, rare earth elements, manganese, and tin.

[0089] According to Claim 5, the present invention provides the magnesium alloy for casting having advantages in heat resistance, castability, and cost performance. The magnesium alloy properly includes aluminum, calcium, rare earth elements, manganese, tin. The magnesium alloy further includes zirconium and carbon.

[0090] The principles, preferred embodiment 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 embodiments disclosed. Further, the embodiments 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 sprit of the present invention. Accordingly, it is expressly intended that all such variations, changes and equivalents which fall within the spirit and scope of the present invention as defined in the claims, be embraced thereby.

A heat resistant magnesium alloy for casting includes 6-12% by weight of aluminum, 0.05-4% by weight of calcium, 0.5-4% by weight of rare earth elements, 0.05-0.50% by weight of manganese, 0.1-14% by weight of tin, balance magnesium and inevitable impurities.

Claims

1. A heat resistant magnesium alloy for casting **characterized in that** the magnesium alloy comprises
6-12% by weight of aluminum;
0.05-4% by weight of calcium;
0.5-4% by weight of rare earth elements;
0.05-0.50% by weight of manganese;
0.1-14% by weight of tin;
balance magnesium; and
inevitable impurities.

2. The heat resistant magnesium alloy for casting according to Claim 1, wherein the calcium is 0.05-2% by weight.

3. The heat resistant magnesium alloy for casting according to Claim 1, wherein the calcium is greater than 2% and equal to or less than 4% by weight.

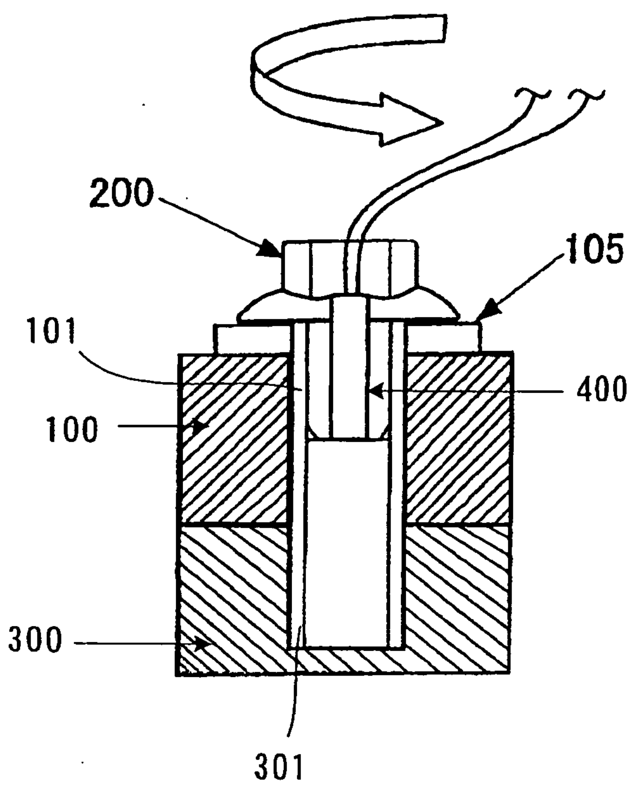
4. The heat resistant magnesium alloy for casting according to any one of Claims 1-3, wherein the rare earth elements are 0.5-2 % by weight.

5. A heat resistant magnesium alloy for casting **characterized in that** the magnesium alloy comprises
6-12 by weight of aluminum;
0.05-4% by weight of calcium;
0.5-4% by weight of rare earth elements;
0.05-0.50% by weight of manganese;
0.1-14% by weight of tin;
at least any one of 0.05-0.2% by weight of zirconium and 0.03-0.2% by weight of carbon;
balance magnesium; and
inevitable impurities.

6. The magnesium alloy according to any one of Claims 1-5, wherein the tin is 0.1-8% by weight.

7. The magnesium alloy according to any one of Claims 1-6, wherein the magnesium alloy is utilized in any one of a die casting, a gravity die casting, a sand casting, and a high pressure die casting.

F I G. 1



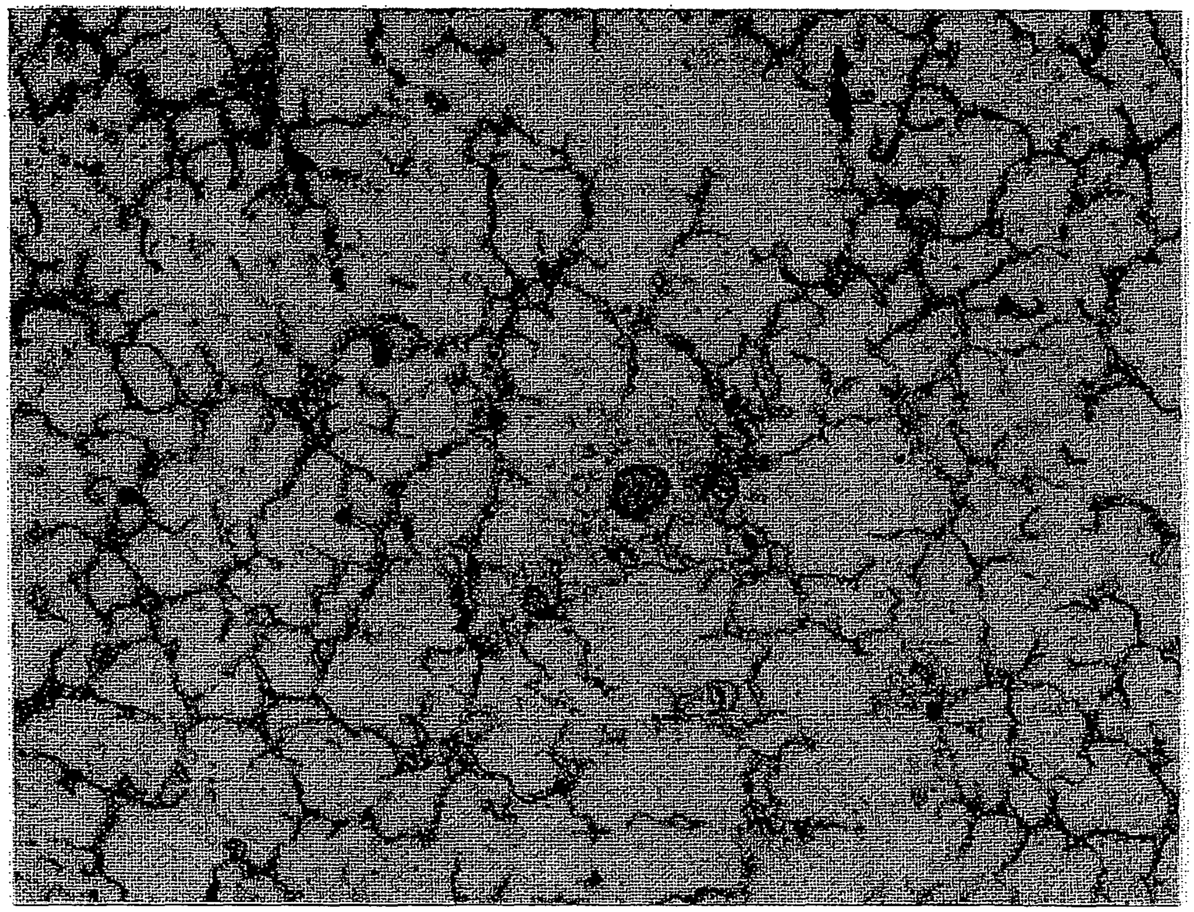


FIG.2

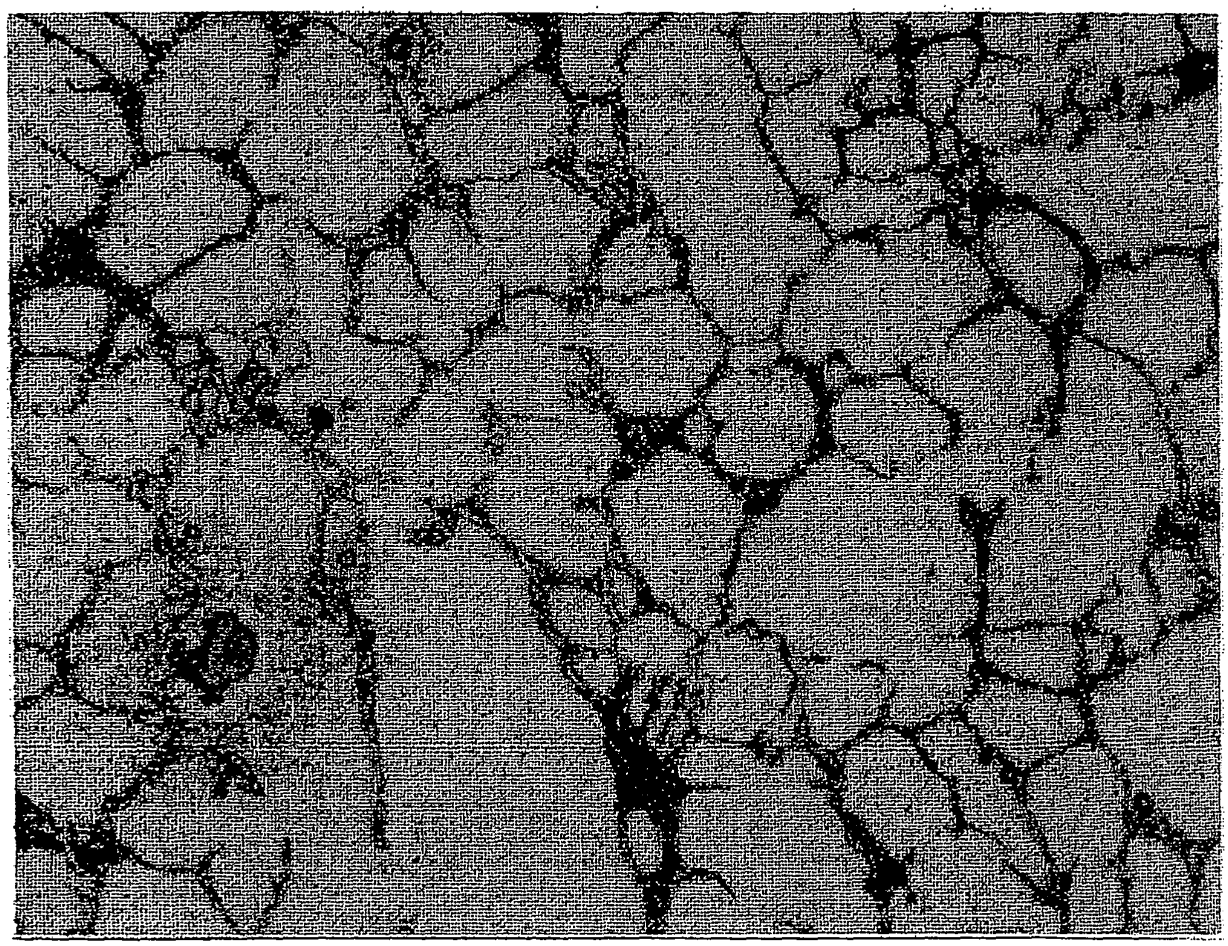


FIG.3

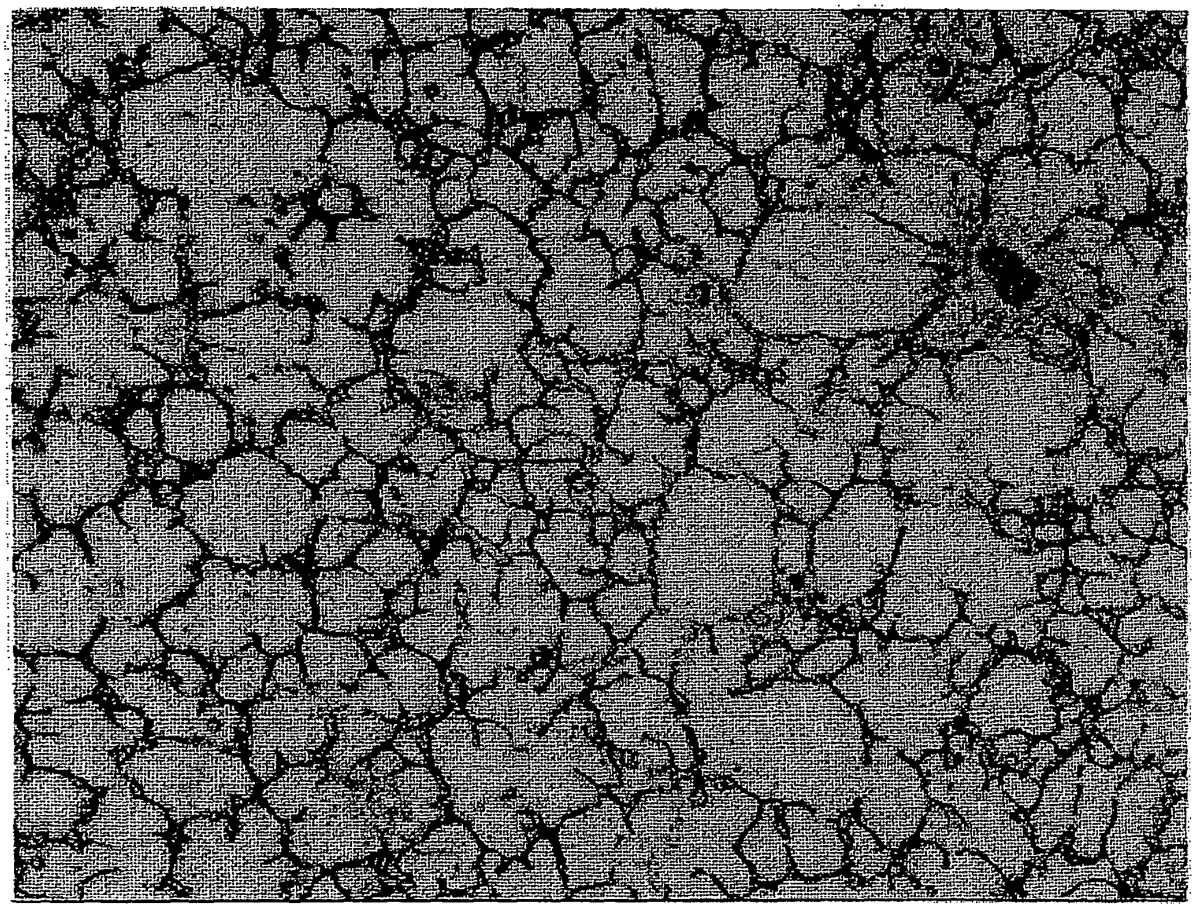


FIG.4