(19)	Europäisches Patentamt European Patent Office Office européen des brevets EUROPEAN PATE	(11) EP 0 990 710 A1 NT APPLICATION
. ,	Date of publication: 05.04.2000 Bulletin 2000/14 Application number: 99117054.9	(51) Int. Cl. ⁷ : C22C 23/02 , B21J 5/00, B21K 1/20
(22)	Date of filing: 30.08.1999	
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(54) Magnesium alloy forging material and forged member, and method for manufacturing the forged member

(57) The invention provides Mg alloy forging material and forged member containing, as well as a method for manufacturing the forged member, which are superior in both mechanical characteristics and forgeability at normal temperature and high temperature and relatively low in price. The magnesium alloy forging material contains at least aluminum and calcium and has a critical upsetting rate of not less than 70% at 300°C. Also, the magnesium alloy forging material contains not less than 2 wt% and not more than 6 wt% of aluminum and not less than 0.5 wt% and not more than 4 wt% of calcium, and has a mean grain size of not more than 300 μ m. The forged member may be a valve lifter for an internal combustion engine.

Description

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BACKGROUND OF THE INVENTION

5 **[0001]** The present invention relates to magnesium alloy forging material and forged member containing at least aluminum and calcium, and a method for manufacturing the forged member.

[0002] As is well known, magnesium (hereinafter, represented by its symbol of element, Mg, appropriately) alloy is the lowest in density (most lightweight) among metallic materials that are currently in practical use. For example, in a field of automobiles that are under the demand for further improvement in the fuel efficiency, the magnesium alloy, with

10 a view to achieving further reduction in weight, has increasingly been adopted as the material of various component parts and the like in place of aluminum (hereinafter, represented by its symbol of element, AI, appropriately) as a lightweight material that has conventionally been in use.

[0003] The Mg alloy is workable by plastic working process including forging or molding process including casting and injection molding. For example, the present applicant has proposed in Japanese Patent No. 2676466 (hereinafter,

15 referred to as Prior Art 1) an Mg alloy member which is made through steps of forging a cast member formed of an Mg alloy containing 6 wt% to 12 wt% of Al, and after the forging, performing the so-called T6 heat treatment (a heat treatment of performing artificial aging treatment after solution heat treatment).

[0004] Also, the present applicant has disclosed in Japanese. Patent Laid-Open Publication HEI 9-272945 (hereinafter, referred to as Prior Art 2) a heat-resistant Mg alloy member which is obtained by injection molding, in a semi-fused state, an Mg alloy which is contains 2 - 6 wt% of Al and 0.5 - 4 wt% of calcium (hereinafter, represented by its symbol)

20 state, an Mg alloy which is contains 2 - 6 wt% of Al and 0.5 - 4 wt% of calcium (hereinafter, represented by its symbol of element, Ca, appropriately) and which has a Ca/Al ratio of 0.8 or lower, with an aim of obtaining superior moldability and elongation percentage while ensuring creep resistance characteristics.
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[0005] Further, Japanese Patent Laid-Open Publication HEI 9-263871 (hereinafter, referred to as Prior Art 3) has disclosed a hot forging product made of a high-strength Mg alloy which is obtained by hot forging of a rare earth - Ca or Y

25 base Mg alloy, with an aim of obtaining an Mg alloy part which is superior in room-temperature strength and high-temperature strength and which is applicable as an engine part for automobiles that are required to have reliabilities of the strength at both high temperature and room temperature.

[0006] This Mg alloy has already been put into practical use of as a material for wheels or the like, for example, in the field of automobiles. However, in order to apply this Mg alloy, for example, to mechanical parts associated with internal

- 30 combustion engines that are required to meet stricter conditions of use in terms of temperature or strength (e.g., valve lifters of engine air-intake/exhaust valves), the Mg alloy is required to have not only strength characteristics at normal temperature, as a matter of course, but also high tensile strength (e.g., not less than 220 MPa) and creep resistance even at high temperatures, for example, around 150°C. Further, in the case of the aforementioned valve lifter, its top-wall portion that makes sliding contact with a hole-portion wall surface of the cylinder head and the cam (or contact with an adjustment shim that makes sliding contact with the cam) is required to have a high wear-resistance property.
- an adjustment shim that makes sliding contact with the cam) is required to have a high wear-resistance property.
 [0007] In the case where there is a requirement of ensuring mechanical characteristics such as high tensile strength of a higher than specified level (e.g., not less than 220 MPa) or superior creep resistance characteristic at a high temperature level (e.g., around 150°C), molding process such as casting and injection molding would generally have difficulty in stably obtaining required characteristics, and it is the most preferable to adopt plastic working capable of
- 40 obtaining compact material structure in the working process, particularly forging at a higher than specified forging rate. [0008] Therefore, for the Mg alloy, it is necessary to ensure a successful forgeability in terms of obtaining mechanical characteristics as described above.

[0009] However, in the case of Prior Art 1, although the forgeability can be ensured, yet the Mg alloy is high in Al content and therefore low in creep resistance characteristic, unsuitable for use at high temperatures. This is because Al and

- 45 Mg, as is known, are liable to produce compounds that have adverse effects on the high-temperature characteristics such as creep resistance characteristic, so that a higher than specified level of Al content would cause a multiplicity of these harmful compounds to be deposited, making it impossible to ensure the creep resistance characteristic. [0010] Also, in Prior Art 2, because the Mg alloy member is basically an injection molded product, it is difficult to ensure high mechanical characteristics as with forged products, particularly, a stable strength at high temperatures. As
- 50 a result, the Mg alloy member is inevitably limited in the range of applicable use as compared with forged products.
 [0011] Further, in the case of Prior Art 3, because the Mg alloy also contains precious rare earth elements, it is very costly, lacking in practicability as a disadvantage.

[0012] The present invention having been accomplished in view of the above mentioned problems, an object of the invention is to provide magnesium alloy forging material and forged member which are superior in mechanical characteristics at room temperature and high temperatures, superior in forgeability, and relatively inexpensive, as well as a method for manufacturing the forged member.

[0013] The present inventors, as a result of keen studies in view of the above technical problems, have found that in a forging material made of an Mg alloy containing at least Al and Ca, the creep resistance characteristic increases with

increasing Ca content under the condition that the Ca content is not more than a specified level (not more than 4 wt%), that the creep resistance characteristic is maintained satisfactory with the Al content falling within a range of not more than a specified level (not more than 6 wt%), that a high tensile strength (not less than 220 MPa) can be ensured at a high temperature (150°C) with the Al content falling within a range of not more than 2

5 wt%), further that the ratio of occurrence of cracks in high velocity forging can be suppressed extremely low while a required forging rate is ensured, under the condition that the Ca/Al ratio (the ratio of Ca content (by weight)) to Al content (by weight)) is not more than a specified level (not more than 0.8), and furthermore that the smaller the mean grain size of the forging material is, the higher the critical upsetting rate can be ensured in the forging process.

[0014] Thus, in a first aspect of the present invention, there is provided a Mg alloy forging material characterized by containing at least Al and Ca and having a critical upsetting rate of not less than 70% at 300°C.

[0015] The critical upsetting rate set to not less than 70% above is due to the fact that it is preferable to ensure a critical upsetting rate of not less than 70% when the forged member obtained by forging the Ma alloy forging material is used for members, parts and the like that require a more than specified high strength such as a valve lifter of an engine. In this case also, the forging temperature, if set to 300°C, is lower than the temperature at which the forgeability

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15 improvement effect of an increase in the forging temperature is saturated, and it is sufficiently lower than 400°C, which would cause a problem of high temperature oxidation, so that adverse effects of oxidation at high temperatures can be avoided.

[0016] Also, in a second aspect of the present invention, the Mg alloy forging material characterized by containing not less than 2 wt% and not more than 6 wt% of Al and not less than 0.5 wt% and not more than 4 wt% of Ca, and having a mean grain size of not more than 300 μm.

- **[0017]** The lower limit of Al content set to 2 wt% in this case is due to the fact that Al contents lower than this value would make it difficult to ensure enough tensile strength (not less than 220 MPa) at a high temperature (150°C), and the upper limit of Al content set to 6 wt% is due to the fact that Al contents higher than this value would cause the creep resistance characteristic to lower.
- 25 [0018] Meanwhile, the lower limit of Ca content set to 0.5 wt% is due to the fact that Ca contents lower than this value would cause the creep resistance characteristic to lower, and the upper limit of Ca content set to 4 wt% is due to the fact that even Ca contents increased beyond this value would cause the creep-resistance characteristic improvement effect to be saturated.

[0019] Further, the mean grain size of the forging material set to not more than 300 μ m is due to the fact that mean

- 30 grain sizes greater than this value would make it difficult to ensure a required (not less than 50%) critical upsetting rate.
 [0020] Further, in a third aspect of the present invention, the Mg alloy forging material according to the first or second aspect is characterized in that a ratio of Ca content to Al content is not more than 0.8.
- [0021] The Ca/Al ratio set to not more than 0.8 in this case is due to the fact that this range of Ca/Al ratio makes it possible to ensure a required forging rate (50%) and besides to suppress the rate of occurrence of cracks to an extremely low even in high velocity forging.

[0022] Still further, in a fourth aspect of the present invention, the Mg alloy forging material according to any one of the first to third aspects is characterized in that the forging material is preformed into a specified shape by injection molding prior to forging process.

[0023] Still further, in a fifth aspect of the present invention, there is provided a method for manufacturing a Mg alloy forged member, characterized by hot forging the Mg alloy forging material according to any one of the first to fourth aspects and containing not less than 2 wt% and not more than 6 wt% of Al and not less than 0.5 wt% and not more than 4 wt% of Ca.

[0024] The lower limit of Al content set to 2 wt% is due to the fact that Al contents lower than this value would make it difficult to ensure enough tensile strength (not less than 220 MPa) at a high temperature (150°C), and the upper limit

45 of AI content set to 6 wt% is due to the fact that AI contents higher than this value would cause the creep resistance characteristic to lower.

[0025] Meanwhile, the lower limit of Ca content set to 0.5 wt% is due to the fact that Ca contents lower than this value would cause the creep resistance characteristic to lower, and the upper limit of Ca content set to 4 wt% is due to the fact that even Ca contents increased beyond this value would cause the creep-resistance characteristic improvement effect to be saturated.

50 effect to be saturated. [0026] Still further, in a sixth aspect of the present invention, the method for manufacturing a Mg alloy forged member according to the fifth aspect is characterized by hot forging the Mg alloy forging material having a ratio of Ca content to Al content (Ca/Al ratio) of not more than 0.8 at a velocity of not less than 400 [mm/sec.].

[0027] The Ca/AI ratio set to not more than 0.8 in this case is due to the fact that this range of Ca/AI ratio makes it possible to ensure a required forging rate (50%) and besides to suppress the rate of occurrence of cracks to an extremely low even in high velocity forging. Also, the forging rate set to not less than 400 [mm/sec.] is due to the fact that for manufacture of parts and the like such as mechanical parts like a valve lifter of an engine, it is desired to enhance the productivity by ensuring a forging rate of around this level.

[0028] Still further, in a seventh aspect of the present invention, the method for manufacturing a Mg alloy forged member according to the fifth or sixth aspect is characterized in that forging temperature for the hot forging is within a range of 250° C - 400° C.

- **[0029]** The lower limit of forging temperature set to 250°C is due to the fact that forging temperatures higher than this value makes it possible to ensure a satisfactory critical upsetting rate (not less than 70%) so that the Mg alloy forged member can be applied to members, parts and the like that require a more than specified high strength such as a valve lifter of an engine. Also, the upper limit of forging temperature set to 400°C is due to the fact that forging temperatures higher than this value would cause the forgeability improvement effect of increase in forging temperature to be saturated, and yet that the forged member becomes more likely to be oxidized.
- 10 **[0030]** Still further, in an eighth aspect of the present invention, the method for manufacturing a Mg alloy forged member according to any one of the fifth to seventh aspects is characterized in that the forging material is subjected to a heat treatment in which the forging material is held within a temperature range of 300°C - 500°C for 5 hours - 50 hours prior to the hot forging process.

[0031] The lower limit of heat treatment temperature set to 300°C in this case is due to the fact that heat treatment

- 15 temperatures lower than that results in only a small forgeability improvement effect of the heat treatment, and the upper limit of heat treatment temperature set to 500°C is due to the fact that heat treatment temperatures higher than that would result in a saturated forgeability improvement effect and moreover that there can occur oxidation and partial solution, hence no merits.
- [0032] On the other hand, the specified lower limit of heat-treatment temperature holding time set to 5 hours is due to the fact that time shorter than that would result in only a small forgeability improvement effect of the heat treatment, while the upper limit of heat-treatment temperature holding time set to 50 hours is due to the fact that heat treatment time longer than that would result in a saturated forgeability improvement effect.

[0033] Still further, in a ninth aspect of the present invention, the method for manufacturing a Mg alloy forged member according to any one of the fifth to eighth aspects is characterized in that forging rate in the hot forging is not less than 10%.

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[0034] The lower limit of the forging rate set to 10% in this case is due to the fact that forging rates lower than this value makes it difficult to obtain an effect for crushing microscopic defects present inside the unforged material and thereby forging the material.

[0035] Still further, in a tenth aspect of the present invention, the method for manufacturing a Mg alloy forged member according to any one of the fifth to ninth aspects is characterized in that the forged member obtained by the hot forging is subjected to a heat treatment in which the forged member is held within a temperature range of 100°C - 250°C for 5 hours - 50 hours.

[0036] The lower limit of heat treatment temperature set to 100°C in this case is due to the fact that heat treatment temperatures lower than that would result in only a small strength improvement effect of the heat treatment, and the upper limit of heat treatment temperature set to 250°C is due to the fact that heat treatment temperatures higher than

- ³⁵ upper limit of heat treatment temperature set to 250°C is due to the fact that heat treatment temperatures higher than that would result in a saturated strength improvement effect.
 [0037] On the other hand, the lower limit of heat-treatment temperature holding time set to 5 hours is due to the fact that heat-treatment temperature holding time shorter than that would result in only a small strength improvement effect of the heat treatment, and the upper limit of heat-treatment temperature holding time set to 50 hours is due to the fact
- 40 that heat-treatment temperature holding time longer than that would result in a saturated strength improvement effect.

[0038] Still further, in an eleventh aspect of the present invention, there is provided a Mg alloy forged member which is obtained by forging a Mg alloy forging material containing at least aluminum and calcium and having a tensile strength of not less than 220 MPa at 150°C.

45 **[0039]** The tensile strength at 150°C set to 220 MPa in this case is purposed to allow the Mg alloy forged member to be used for members, parts and the like that require a more than specified high strength under a high temperature of about 150°C such as a valve lifter of an engine.

[0040] Still further, in a twelfth aspect of the present invention, the Mg alloy forged member according to the eleventh aspect is characterized in that the Mg alloy forged member is a valve lifter to be incorporated into an internal combustion engine.

[0041] Still further, in a thirteenth aspect of the present invention, the Mg alloy forged member according to the twelfth aspect is characterized in that forging rate of a top-wall portion of the valve lifter is not less than 20%.

[0042] The forging rate of the top-wall portion of the valve lifter set to not less than 20% in this case is purposed to obtain an effect for crushing microscopic defects present inside the unforged material and thereby forging the material with respect to the top-wall portion that is required to have a high strength, and besides to ensure a required tensile strength (not less than 250 MPa).

[0043] Still further, in a fourteenth aspect of the present invention, the Mg alloy forged member according to the thirteenth aspect is characterized in that surface of the top-wall portion of the valve lifter is nickel plated.

[0044] Still further, in a fifteenth aspect of the present invention, the magnesium alloy forged member according to the thirteenth aspect is characterized in that surface of the top-wall portion of the valve lifter is flame-sprayed with Fe.

[0045] According to the first aspect of the present invention, since the Mg alloy forging material has a critical upsetting rate of not less than 70%, the forged member obtained by forging the Mg alloy forging material can be applied to mem-

- ⁵ bers, parts and the like that require a more than specified high strength such as a valve lifter of an engine. Also, in this case, since the forging temperature of 300°C is lower than the temperature at which the forgeability improvement effect of increase in forging temperature is saturated, the Mg alloy forging material is economical, and since the forging temperature is sufficiently lower than 400°C, which would cause a problem of high-temperature oxidation, any adverse effects of oxidation at high temperatures can be avoided.
- 10 [0046] Also, according to the second aspect of the present invention, since the Mg alloy forging material contains not less than 2 wt% of Al, a sufficient tensile strength (not less than 220 MPa) can be ensured at a high temperature (150°C), and since the Mg alloy forging material contains not less than 0.5 wt% of Ca and not more than 6 wt% of Al, a satisfactory creep resistance characteristic can be ensured. In this case, since the Ca content is not more than 4 wt%, the Mg alloy forging material is economical in terms of obtaining a creep resistance characteristic improvement effect 15 of increase in Ca content.

[0047] Further, since the mean grain size of the forging material is not more than 300 μ m, a required (not less than 50%) critical upsetting rate can be ensured.

[0048] Further, according to the third aspect of the present invention, basically, the same effects as in the first or second aspect can be produced. Still more, since the ratio of Ca content to Al content (Ca/Al ratio) is not more than 0.8, a required forging rate (50%) can be ensured and, besides, the rate of occurrence of cracks can be suppressed to an

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extremely low even in high velocity forging so that a satisfactory forgeability can be obtained.
[0049] Still further, according to the fourth aspect of the present invention, basically, the same effects as in any one of the first to third aspects can be produced. In particular, since the forging material is preformed into a specified shape by injection molding prior to forging process, and so since the forging material is molded by injection molding, the mate-

- 25 rial can be made finer in mean grain size so that the forgeability can be improved (the critical upsetting rate can be enhanced). Still, by preforming the material into a shape that is close to the final shape as a forged member by this injection molding, subsequent plastic working by forging process can be facilitated and simplified, so that the production efficiency of the forging process can be enhanced to a large extent.
- [0050] Still further, according to the fifth aspect of the present invention, since the Mg alloy forging material contains not less than 2 wt% of Al, hot forging this forging material allows a sufficient tensile strength (not less than 220 MPa) to be ensured at a high temperature (150°C), and since the Mg alloy forging material contains not less than 0.5 wt% of Ca and not more than 6 wt% of Al, a satisfactory creep resistance characteristic can be ensured. In this case, since the Ca content is not more than 4 wt%, the forging material is economical in terms of obtaining a creep resistance characteristic improvement effect of increase in Ca content.
- 35 [0051] Still further, according to the sixth aspect of the present invention, the same effects as in the fifth aspect can be produced. Still more, since the ratio of Ca content to Al content (Ca/Al ratio) is not more than 0.8, a required forging rate (50%) can be ensured and, besides, the rate of occurrence of cracks can be suppressed to an extremely low even in high velocity forging so that a satisfactory forgeability can be obtained. Also, since the forging material is hot forged at a forging velocity of not less than 400 [mm/sec.], a sufficiently high productivity can be ensured in manufacturing parts and the like such as mechanical parts like a valve lifter of an automobile engine.
- 40 parts and the like such as mechanical parts like a valve lifter of an automobile engine. [0052] Still further, according to the seventh aspect of the present invention, basically, the same effects as in the fifth or sixth aspect can be produced. In particular, since the forging temperature for the hot forging is within a range of 250°C - 400°C, a satisfactory critical upsetting rate (not less than 70%) can be ensured so that the forged member can be applied to members, parts and the like that require a more than specified high strength such as a valve lifter of an
- 45 engine. Also, since the upper limit of forging temperature is 400°C, the forged member is economical in terms of obtaining a forgeability improvement effect of increase in forging temperature and yet any adverse effects of high-temperature oxidation can be avoided.

[0053] Still further, according to the eighth aspect of the present invention, basically, the same effects as in any one of the fifth to seventh aspects can be produced. In particular, since the forging material is subjected to a heat treatment before the hot forging, the critical upsetting rate can be even more enhanced.

- **[0054]** Still further, according to the ninth aspect of the present invention, basically, the same effects as in any one of the fifth to eighth aspects can be produced. In particular, since the forging rate in the hot forging is not less than 10%, there can be obtained an effect for crushing microscopic defects present inside the unforged material and thereby forging the material effectively in terms of practical use.
- 55 **[0055]** Still further, according to the tenth aspect of the present invention, basically, the same effects as in any one of the fifth to ninth aspects can be produced. In particular, since the forged member obtained by the hot forging is subjected to a heat treatment, the tensile strength at a high temperature (150°C) can be enhanced.

[0056] Still further, according to the eleventh aspect of the present invention, since the forged member has a tensile

strength of not less than 220 MPa at 150°C, the forged member can be applied to members, parts and the like that require a more than specified high strength (tensile strength of not less than 220 MPa) under a high temperature of about 150°C such as a valve lifter of an engine.

[0057] Still further, according to the twelfth aspect of the present invention, basically, the same effects as in the eleventh aspect can be produced. In particular, since the Mg alloy forged member is a valve lifter to be incorporated into an internal combustion engine, a more than specified high strength can be imparted to the forged member under a high temperature of about 150°C in manufacturing the valve lifter by forging process.

[0058] Still further, according to the thirteenth aspect of the present invention, basically, the same effects as in the twelfth aspect can be produced. In particular, since the forging rate of the top-wall portion of the valve lifter is not less than 20%, there can be obtained an effect for crushing microscopic defects present inside the unforged material and

- 10 than 20%, there can be obtained an effect for crushing microscopic defects present inside the unforged material and thereby forging the material with respect to the top-wall portion that is required to have a high strength, and besides a required tensile strength (not less than 250 MPa at room temperature) can be ensured. [0059] Still further, according to the fourteenth aspect of the present invention, basically, the same effects as in the
- thirteenth aspect can be produced. In particular, since the surface of the top-wall portion of the valve lifter is nickel
 plated, a sufficiently high wear resistance property can be imparted to the top-wall portion that repeatedly makes sliding contact with its counterpart member.

[0060] Still further, according to the fifteenth aspect of the present invention, basically, the same effects as in the thirteenth aspect can be produced. In particular, since the surface of the top-wall portion of the valve lifter is flame-sprayed with iron (Fe), a sufficiently high wear resistance property can be imparted to the top-wall portion that repeatedly makes sliding contact with its counterpart member.

BRIEF DESCRIPTION OF THE DRAWINGS

[0061]

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Fig. 1 is a graph showing effects of calcium content on the steady state creep rate of magnesium alloy forged members;

Fig. 2 is a graph showing effects of aluminum content on the steady state creep rate of magnesium alloy forged members;

- Fig. 3 is a graph showing effects of aluminum content on the high-temperature tensile strength of magnesium alloy forged members;
 - Fig. 4 is a graph showing effects of Ca/Al ratio on the rate of occurrence of cracks in high velocity forging;
 - Fig. 5 is a graph showing effects of after-forging heat treatment on the high-temperature tensile strength;
 - Fig. 6 is a graph showing effects of forging temperature and before-forging heat treatment on critical upsetting rate;
- Fig. 7 is a graph showing effects of forging rate on the specific gravity after forging;
 - Fig. 8 is a graph showing effects of forging rate on the tensile strength at room temperature;
 - Fig. 9 is a graph showing effects of mean grain size of a forging material on the critical upsetting rate;

Fig. 10 is a graph showing wear amount after a motoring test of a valve lifter made of a magnesium alloy forged member;

40 Fig. 11 is a perspective view of a magnesium alloy forging material according to the present embodiment;

Fig. 12 is an explanatory view schematically showing the forging process of the magnesium alloy forging material; Fig. 13 is an explanatory view of a magnesium alloy forged member sample after the forging process;

Fig. 14 is an explanatory view showing an initial state of a critical upsetting rate test on a magnesium alloy forging material according to the present embodiment;

Fig. 15 is an explanatory view schematically showing the magnesium alloy forging material during the forging process in the critical upsetting rate test; and

Fig. 16 is an partial sectional explanatory view showing an essential part of a valve lifter according to the present embodiment.

50 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0062] Embodiments of the present invention are described in detail below with reference to the accompanying drawings.

- [0063] Figs. 11 to 13 schematically shows a method for obtaining a forged member sample by using a magnesium alloy forging material according to the present embodiment. In this embodiment, a magnesium alloy forging material M1
- having a rectangular parallelopiped shape with the dimensions of A1 high × B1 wide × L1 long was prepared as shown in Fig. 11, and this material M1 was restrained, for example, in its lateral direction by sandwiching the material M1 by a pair of fixed plates P1 as shown in Fig. 12. In this state, with a compressive load applied, the material M1 was subjected

to plastic working (forging), so that a forged member sample was prepared.

[0064] As a result of the forging process, the material M1 changed in height from the initial A1 to A2 (become shorter), and changed in length from the initial L1 to L2 (become longer). In this case, the forging rate by the forging process can be calculated by the following Equation 1:

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forging rate =
$$(A1 - A2)/A1 \times 100 [\%]$$
 (Eq. 1)

[0065] In this embodiment, initial (see Fig. 11) basic dimensions of the magnesium alloy forging material M1 were so set that A1 = B1 = 12 [mm] and that L1 = 50 [mm].

[0066] By taking the forged member samples obtained in this way as sample materials, test pieces of dimensions and 10 shape adapted to various tests were cut out and prepared from these sample materials. Then various tests as described below were performed:

[0067] Table 1 shows chemical compositions and Ca/Al ratios (ratios of calcium content to aluminum content) of samples (Invention Examples 1 - 6 and Comparative Examples 1 - 4) used in various tests for determining characteristics of the magnesium alloy forging material according to this embodiment.

[0068] That is, forged member samples were fabricated by using the samples (forging materials) shown in Table 1, and subjected to various tests as described below. In Table 1, each numerical value is given in wt%, and the remainder except AI (aluminum), Ca (calcium), Mn (manganese), Si (silicon) and others (impurities) is Mg (magnesium).

20			Table ²	1			
	Chemical composition and	Ca/Al	ratio of	sample	alloys		
	(Unit: wt%)						
25		AI	Са	Mn	Si	Others	Ca/Al
	Example 1	2.9	2.8	0.34	0.24	≤ 0.01	0.97
	Example 2	3.9	0.5	0.34	0.18	≤ 0.01	0.13
30	Example 3	4.0	2.2	0.30	0.14	≤ 0.01	0.55
	Example 4	4.1	3.2	0.35	0.13	≤ 0.01	0.78
	Example 5	4.1	4.0	0.31	0.15	≤ 0.01	0.98
	Example 6	6.1	3.2	0.31	0.13	≤ 0.01	0.52
35	Example 7	2.1	3.2	0.32	0.10	≤ 0.01	1.52
	Comparative Example 1	3.9	-	0.30	0.18	≤ 0.01	0.00
	Comparative Example 2	4.0	5.1	0.30	0.21	≤ 0.01	1.28
40	Comparative Example 3	6.9	2.9	0.31	0.18	≤ 0.01	0.42
	Remainder: Mg					·	

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[0069] First, tests for determining effects of main additional-element AI (aluminum) and Ca (calcium) contents on mechanical properties at high temperatures of forged members were carried out.

[0070] Figs. 1 and 2 show results of tests for determining effects of Ca content and Al content, respectively, on the steady state creep rate of forged members. In addition, test conditions for these creep tests and set conditions of sample materials were as follows:

- test temperature: 150°C 50
 - load conditions: 100 MPa
 - forging rate of sample materials: 50%.

[0071] As shown in test results of Fig. 1, the steady state creep rate decreases with increasing Ca content if the Ca 55 content falls within a range of 0.5 wt% (Invention Example 2) to 4 wt% (Invention Example 5), making it found that the creep resistance characteristic is improved with increasing Ca content. With the Ca content beyond 4 wt% (Comparative Example 2), the steady state creep rate was almost constant, making it found that the effect of the creep resistance characteristic improvement by increase in Ca content is saturated with the Ca content beyond this value (4 wt%).

[0072] In addition, in the case of Comparative Example 1, in which Ca is not contained at all, the creep rate does not reach the steady state, and test pieces were broken in 10 hours after test start, making it found that the creep resistance characteristic considerably deteriorates.

[0073] Also, as can be well understood from test results shown in Fig. 2, the steady state creep rate, although maintained at a generally constant low value under the condition that the AI content is not more than 6 wt% (Invention Example 6), abruptly increases with the AI content beyond this value.

[0074] That is, it has been found that a satisfactory creep resistance characteristic can be obtained by setting the Al content to not more than 6 wt%.

[0075] Fig. 3 shows effects of AI content on high-temperature tensile strength. Test conditions for these high-temperature tensile strength tests and set conditions of sample materials were as follows:

- test temperature: 150°C
- forging rate of sample materials: 50%.
- 15 **[0076]** As can be well understood from test results of Fig. 3, with the Al content not less than 3 wt% (Invention Example 1), the high-temperature tensile strength is maintained at a generally constant high value. However, when the Al content decreases below this value to 2 wt% (Invention Example 7), the high-temperature tensile strength shows a slight decreasing tendency, but holds a still high value (not less than 220 MPa).

[0077] Consequently, it has been found that if the Al content is not less than 2 wt%, enough tensile strength can be ensured even at a high temperature (150°C), and that, more preferably, if the Al content is not less than 3 wt%, even higher tensile strengths can be maintained more stably.

[0078] With regard to this high-temperature tensile strength, when the forged member is used for members, parts and the like that require a more than specified high strength under an about 150°C high-temperature atmosphere, such as a valve lifter of an engine, it is preferable to ensure a strength of not less than 220 MPa from the viewpoint of practical

25 use. In any case of the samples used in the high-temperature tensile test of Fig. 3, a tensile strength not less than 220 MPa can be ensured under the 150°C high-temperature atmosphere, so that the forged member is enough applicable to members, parts and the like that require a more than specified high strength.

[0079] Next, a test for determining the effects of the Ca/Al ratio on the forgeability of Mg alloy forging material, was carried out.

30 [0080] Fig. 4 is a graph showing effects of Ca/AI ratio on the rate of occurrence of cracks in high velocity forging. It is noted that the terms "high velocity forging" refer to a forging process performed at a forging velocity of approximately 100 mm/sec. or more.

[0081] Test conditions for the high velocity forging test shown in Fig. 4 and set conditions of sample materials were as follows:

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- forging temperature: 350°C
- forging velocity: 400 mm/sec.
- forging rate: three kinds of rate; 10%, 25%, 50%.
- 40 [0082] As can be well understood from test results shown in Fig. 4, with the Ca/AI ratio falling within a range of not more than 0.8 (Invention Example 4), the rate of occurrence of cracks can be suppressed to an extremely low value not more than, at most, 0.1%, whatever the forging rate is. With the Ca/AI ratio beyond 0.8 (Invention Example 5), on the other hand, the rate of occurrence of cracks abruptly increases in the case of the sample materials with 25% and 50% forging rates. However, no occurrence of cracks were recognized in the sample material with the 10% forging rate, as in the case of 0.8 or lower Ca/AI ratios.

[0083] From these results, it has been found that with the sample material having the forging rate of 10%, which indeed exhibits a relatively low practicability, but shows no cracks even in the high velocity forging, whatever the Ca/AI ratio is, and that the sample materials with the forging rate not less than 25% (25% and 50%) is capable of ensuring enough forgeability by suppressing the rate of occurrence of cracks in the high velocity forging to an extremely low level.

50 **[0084]** In addition, as a result of performing a forging test at a low velocity of about 10 mm/sec. separately from the above high velocity forging test, no occurrence of cracks were recognized, whatever the Ca/AI ratio was, even with the sample materials having the 25% and 50% forging rates as well as, needless to say, the sample material having the 10% forging rate.

[0085] That is, it has been found that with low forging velocities, there occurs no occurrence of cracks regardless of the forging rate and the Ca/AI ratio, hence no problem forgeability.

[0086] Next, tests for determining effects of heat treatment on high temperature strength (tensile strength) and forgeability (critical upsetting rate) of sample materials were carried out.

[0087] Fig. 5 shows effects of after-forging heat treatment on the high-temperature tensile strength. Test conditions

for the high-temperature tensile test shown in Fig. 5 and set conditions of sample materials were as follows:

test temperature: 150°C

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- type of sample material: Invention Example 4
- forging rate of sample materials: 50%
- heat treatment conditions of sample materials: no heat treatment / air cooling after holding at 150°C for 30 hours after the forging.
- **[0088]** As can be well understood from results of this test, the sample material, by being subjected to heat treatment after the forging, showed a greatly increased tensile strength at a high temperature (150°C), as compared with cases in which the sample material was not subjected to heat treatment. Thus, effects of after-forging heat treatment on an improvement in high-temperature tensile strength was able to be verified.

[0089] With regard to this high-temperature tensile strength, when the forged member is used for members, parts and the like that require a more than specified high strength under an about 150°C high-temperature atmosphere, such as

15 a valve lifter of an engine, it is preferable to ensure a strength of not less than 220 MPa from the viewpoint of practical use. In the case of the sample of Invention Example 4 shown in the test of Fig. 5, a tensile strength, not less than 220 MPa was enough ensured under the 150°C high-temperature atmosphere, whether the sample is subject to after-forg-ing heat treatment or not. And thus it has been verified confirmatively that the forged member is enough applicable to members, parts and the like that require a more than specified high strength under the high-temperature atmosphere as described above.

[0090] With regard to the heating temperature and holding time for the after-forging heat treatment, a forged member obtained by hot forging is preferably held within a temperature range of 100 - 250°C for a period of 5 - 50 hours.

[0091] The above specified lower limit of heat treatment temperature of 100°C in this case is attributable to the fact that temperatures lower than that would result in only a small strength-improvement effect of heat treatment, while the

- above specified upper limit of heat treatment temperature of 250°C is attributable to the fact that temperatures higher than that would result in a saturated strength-improvement effect of heat treatment. On the other hand, the above specified lower limit of heat-treatment temperature holding time of 5 hours is attributable to the fact that time shorter than that would result in only a small strength-improvement effect of the heat treatment, while the above specified upper limit of heat-treatment temperature holding time of 50 hours is attributable to the fact that time longer than that would result in a saturated strength-improvement effect.
 - **[0092]** Fig. 6 shows effects of forging temperature and before-forging heat treatment on critical upsetting rate during the forging process. Test conditions for the critical upsetting rate test shown in Fig. 6 and set conditions of sample materials were as follows:
- *type of sample material: Invention Example 4*
 - heat treatment conditions of sample materials: no heat treatment / air cooling after holding at 410°C for 16 hours before the forging.

[0093] The terms "critical upsetting rate" refer to a critical upsetting rate at which cracks occur to a test piece M2 when, with the test piece M2 prepared as a diameter D × length L3 cylindrical-shaped one, a compressive load is applied to the test piece M2 longitudinally as schematically shown in Fig. 14 so that the test piece is compressively deformed as schematically shown in Fig. 15 (with the after-deformation length of L4).

[0094] In the example of Figs. 14 and 15, assuming that micro cracks occur when the test piece M2 having an initial length L3 is deformed to a length L4, the critical upsetting rate in this case can be calculated by the following Equation 2:

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critical upsetting rate =
$$(L3-L4)/L3 \times 100$$
 [%] (Eq.2)

[0095] In addition, in this embodiment, initial (see Fig. 14) basic dimensions of the test piece M2 were set as D = 16 [mm] and L3 = 24 [mm].

50 **[0096]** As can be well understood from test results shown in Fig. 6, the critical upsetting rate increases with increasing forging temperature under the condition that the forging temperature is not more than about 400°C, whether the sample is subject to heat treatment or not. Thus, within this range, a forgeability improvement effect of increasing the forging temperature was able to be verified.

[0097] With the forging temperature beyond 400°C, the forgeability improvement effect is saturated and, still more, oxidation becomes more likely to occur. Accordingly, the forging temperature is preferably not more than 400°C, more preferably, not more than 350°C from the viewpoint of preventing oxidation.

[0098] Also, when heat treatment is performed before the forging, the critical upsetting rate increased, as compared with cases in which the heat treatment was not performed. Thus, an effect of before-forging heat treatment on an

improvement in the critical upsetting rate was able to be verified.

[0099] As this critical upsetting rate, it is generally preferable to ensure not less than, at least, 50% for practical use. In particular, when the forged member is used for members, parts and the like that require a more than specified high strength such as a valve lifter of an engine, it is more preferable to ensure a critical upsetting rate of not less than 70%.

5 In the case of the sample of Invention Example 4, a critical upsetting rate of not less than 70% can be ensured even under a forging temperature below 250°C without performing the heat treatment before the forging, and thus the forged member is applicable also to members, parts and the like that require a more than specified high strength as described above.

[0100] With regard to the heating time and holding time for the heat treatment before forging, the forging material is preferably heat treated within a temperature range of 300 - 500°C for 5 - 50 hours.

- **[0101]** The above specified lower limit of heat treatment temperature of 300°C in this case is attributable to the fact that temperatures lower than that would result in only a small forging formability improvement effect of heat treatment, while the above specified upper limit of heat treatment temperature of 500°C is attributable to the fact that temperatures higher than that would result in a saturated forging formability improvement effect and moreover that there can occur
- 15 oxidation and partial solution, hence no merits. On the other hand, the above specified lower limit of heat-treatment temperature holding time of 5 hours is attributable to the fact that time shorter than that would result in only a small forging formability improvement effect of the heat treatment, while the above specified upper limit of heat-treatment temperature holding time of 50 hours is attributable to the fact that time longer than that would result in a saturated forging formability improvement effect.
- [0102] Figs. 7 and 8 show effects of forging rate on specific gravity and tensile strength at room temperature, respectively, after forging. In these tests, the sample of Invention Example 4 was used as the kind of sample material.
 [0103] As can be well understood from test results shown in Fig. 7, the specific gravity becomes higher with rising forging rate in a forging rate range of not more than about 25%, whereas the effect of increase in forging rate on
- increase in specific gravity is saturated with the forging rate beyond this value (25%). Also, with the forging rate lower than 10%, there can be obtained only a low effect for crushing microscopic defects present inside the unforged material and thereby forging the material. Therefore, generally, it is preferable to ensure a forging rate of at least not less than 10% for practical use, and in particular, when the forged member is used for members, parts and the like that require a more than specified high strength such as a valve lifter of an engine, it is more preferable to ensure a forging rate of not less than 20%.
- 30 **[0104]** Also, as shown in test results of Fig. 8, the tensile strength at room temperature increases with increasing forging rate and, in particular, within a forging rate range of not more than about 25%, the tensile-strength improvement effect of increase in the forging rate is enhanced more than the cases of the range beyond this value.
- [0105] When the forged member is used for members, parts and the like that require a more than specified high strength such as a valve lifter of an engine, it is preferable to ensure a tensile strength of not less than 250 MPa at normal temperature, and therefore it is preferable to ensure a forging rate of not less than 20%.
- **[0106]** Further, Fig. 9 shows effects of mean grain size of a Mg alloy forging material on the critical upsetting rate during forging process. Test conditions for the critical upsetting test of Fig. 9 and set conditions of sample materials were as follows:
- 40 forging temperature: 400°C

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• type of sample material: Invention Example 4

[0107] As can be well understood from test results shown in Fig. 9, the critical upsetting rate becomes higher with decreasing mean grain size of the forging material, so that the mean grain size may appropriately be set to not more than 300 [µmm] in order to ensure a critical upsetting rate of 50%.

[0108] As has already been known, in refining the grain size of Mg alloy forging material, it is very effective to mold the material by injection molding. Molding the material by injection molding makes the mean grain size of the material finer so that the forgeability can be improved (critical upsetting rate can be made higher). Still, by preforming the material into a shape that is close to the final shape as a forged member by this injection molding, subsequent plastic work-

⁵⁰ ing by forging process can be facilitated and simplified, so that the production efficiency of the forging process can be enhanced to a large extent.

[0109] Referring to a case in which the forged member using an Mg alloy forging material according to this embodiment is applied to a valve lifter of an engine, as shown in Fig. 16, in a top-wall portion Wa of a valve lifter W, its side surface repeatedly makes sliding contact with a cylinder head Hc at high speed, and its crest portion also makes con-

55 tact with an adjustment shim Cm that makes sliding contact with a cam S, thus the forged member being required to have a high wear resistance. Therefore, a surface Wf, including side surface and top surface, of the top-wall portion Wa of the valve lifter W formed by forging the Mg alloy forging material was subjected to surface treatment such as plating or flame spray coating ,then, incorporated into an engine, and thereafter, subjected to a so-called motoring test. Test

conditions for this motoring test and set conditions of sample materials were as follows:

- engine rotating speed: 3000 [rpm] (cam shaft rotating speed: 1500 [rpm])
- test duration: 100 hours

content is not more than 0.8.

• surface treatment of valve-lifter top-wall portion: no surface treatment / Ni plating / Fe flame spray coating

[0110] Test results of the motoring test are shown in Fig. 10. In the graph of Fig. 10, the amount of wear in the case where the valve-lifter top-wall portion was subjected to Ni plating or Fe flame spray coating is displayed relative to a reference value (1) for amount of wear which is in the case where no surface treatment was performed.

- [0111] As can be well understood from test results shown in Fig. 10, by subjecting the valve-lifter top-wall portion to Ni plating or Fe flame spray coating, the amount of wear remarkably reduced and the wear resistance property was greatly improved, compared with the case in which no surface treatment was performed.
 [0112] In performing surface treatment as described above, the plating process may be either electroplating or elec-
- troless plating, and besides, Ni-P plating with a high content of P (phosphorus) may be performed.
 [0113] In addition, the present invention is not limited to the above embodiments and various modifications or design changes may be made without departing from the gist of the invention.

Claims

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- 20 **1.** A magnesium alloy forging material characterized by containing at least aluminum and calcium and having a critical upsetting rate of not less than 70% at 300°C.
 - **2.** A magnesium alloy forging material characterized by containing not less than 2 wt% and not more than 6 wt% of aluminum and not less than 0.5 wt% and not more than 4 wt% of calcium, and having a mean grain size of not more than 300 μm.
 - 3. The magnesium alloy forging material according to Claim 1 or 2, wherein a ratio of calcium content to aluminum
- 30 4. The magnesium alloy forging material according to any one of Claims 1 to 3, wherein the forging material is preformed into a specified shape by injection molding prior to forging process.
 - 5. A method for manufacturing a magnesium alloy forged member, characterized by hot forging the magnesium alloy forging material according to any one of Claims 1 to 4 and containing not less than 2 wt% and not more than 6 wt% of aluminum and not less than 0.5 wt% and not more than 4 wt% of calcium.
 - 6. The method for manufacturing a magnesium alloy forged member according to Claim 5, characterized by hot forging the magnesium alloy forging material having a ratio of calcium content to aluminum content of not more than 0.8 at a velocity of not less than 400 [mm/sec.].
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- **7.** The method for manufacturing a magnesium alloy forged member according to Claim 5 or 6, wherein forging temperature for the hot forging is within a range of 250°C 400°C.
- The method for manufacturing a magnesium alloy forged member according to any one of Claims 5 to 7, wherein the forging material is subjected to a heat treatment in which the forging material is held within a temperature range of 300°C 500°C for 5 hours 50 hours, prior to the hot forging.
 - **9.** The method for manufacturing a magnesium alloy forged member according to any one of Claims 5 to 8, wherein forging rate in the hot forging is not less than 10%.
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- **10.** The method for manufacturing a magnesium alloy forged member according to any one of Claims 5 to 9, wherein the forged member obtained by the hot forging is subjected to a heat treatment in which the forged member is held within a temperature range of 100°C 250°C for 5 hours 50 hours.
- **11.** A magnesium alloy forged member which is obtained by forging a magnesium alloy forging material containing at least aluminum and calcium and having a tensile strength of not less than 220 MPa at 150°C.
 - 12. The magnesium alloy forged member according to Claim 11, wherein the magnesium alloy forged member is a

valve lifter to be incorporated into an internal combustion engine.

- **13.** The magnesium alloy forged member according to Claim 12, wherein forging rate of a top-wall portion of the valve lifter is not less than 20%.
- **14.** The magnesium alloy forged member according to Claim 13, wherein surface of the top-wall portion of the valve lifter is nickel plated.
- **15.** The magnesium alloy forged member according to Claim 13, wherein surface of the top-wall portion of the valve lifter is flame-sprayed with iron.

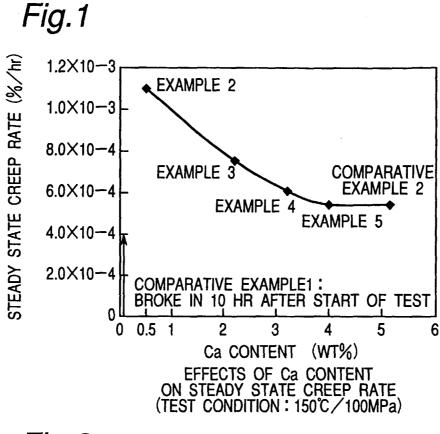
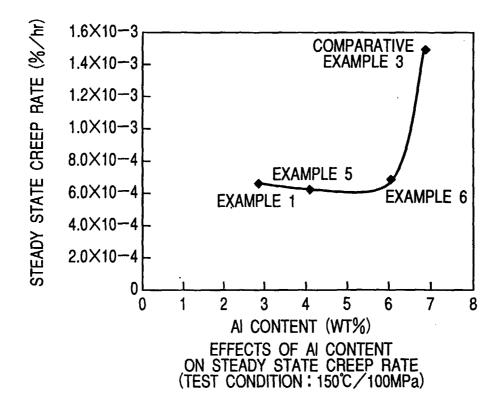


Fig.2





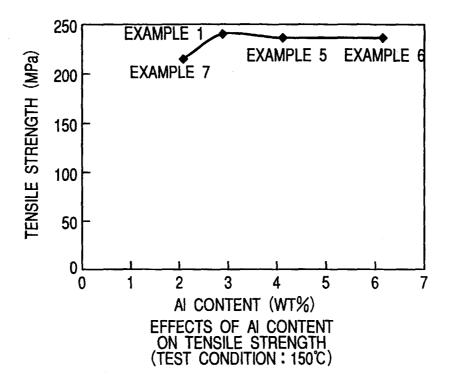
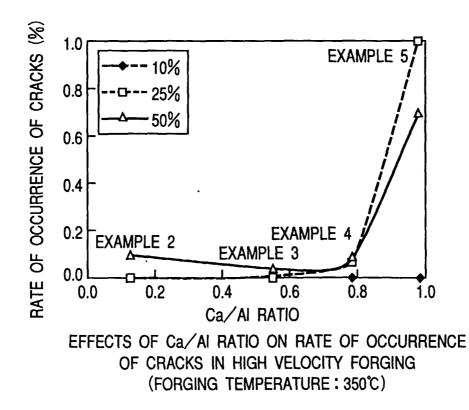
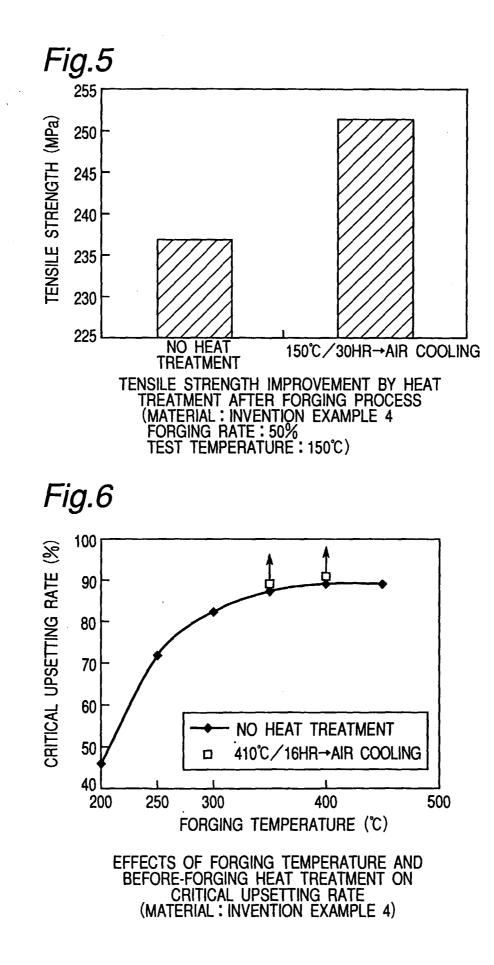
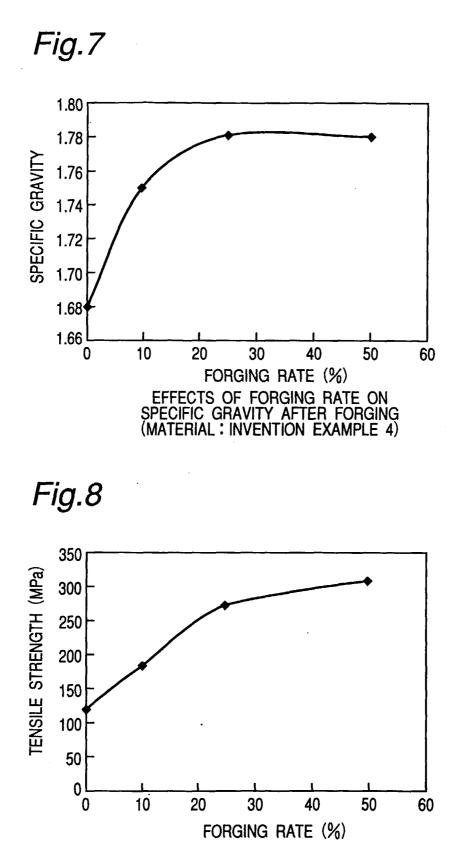


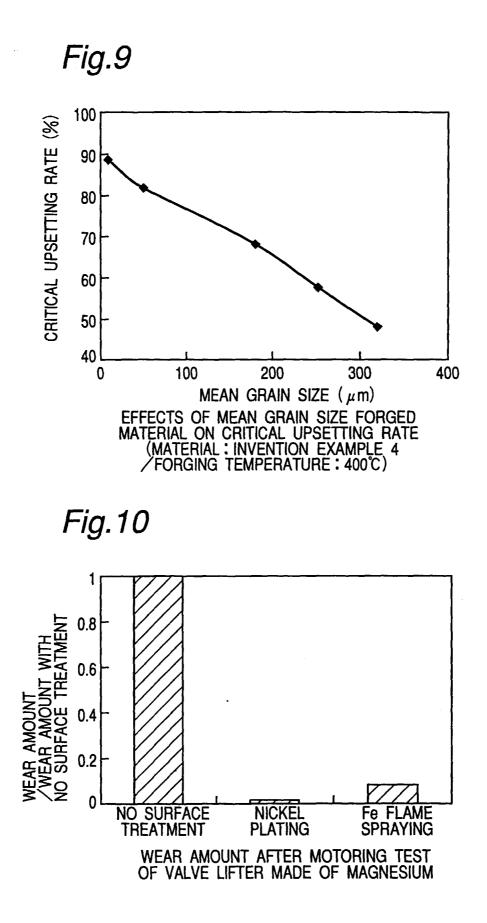
Fig.4











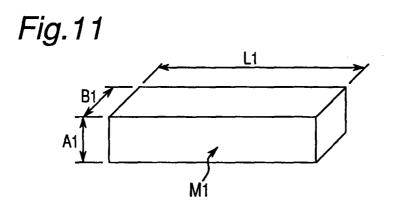


Fig.12

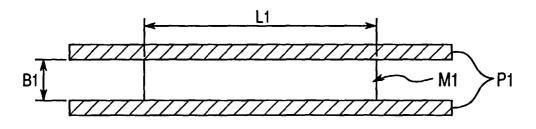


Fig.13

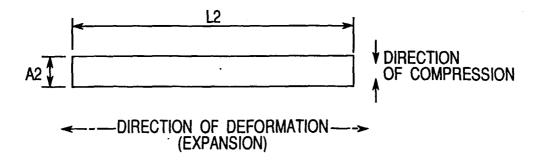


Fig.14

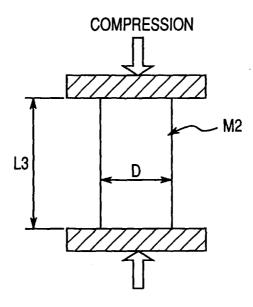
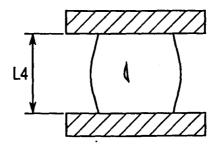


Fig.15





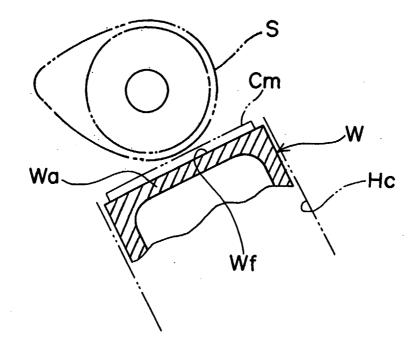


Fig. 16



European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 99 11 7054

l	DOCUMENTS CONSIDI	ERED TO BE RELEVANT				
Category	Citation of document with in of relevant pass	dication, where appropriate, ages	Releva to claim			
X	PATENT ABSTRACTS OF vol. 1998, no. 02, 30 January 1998 (19 -& JP 09 279286 A (28 October 1997 (19	98-01-30) UBE IND LTD),	1-3,5	C22C23/02 B21J5/00 B21K1/20		
Y	* abstract *		4,6-11	L		
x	US 4 997 622 A (REG. 5 March 1991 (1991-	AZZONI GILLES ET AL) 03-05)	1-3,5			
Y		6-11; Col.3, 1.65-68;	4,6-11			
x	WO 96 25529 A (INST		1-3			
Y	MAGNESI) 22 August * Tables 2,3,4 *	1990 (1990-08-22)	4,6-11	1		
Y	1998 , WERKSTOFF-IN MBH , FRANKFURT, GE	nd their Applications" FORMATIONSGESELLSCHAFT	4	TECHNICAL FIELDS SEARCHED (Int.CL7) C22C B21J B21K		
Y,D	US 5 409 555 A (FUJ 25 April 1995 (1995 * Claim 1; Col.5, l l.19-20 *		6–10	DZIK		
X,D	EP 0 799 901 A (MAZ 8 October 1997 (199 * Table 1, examples	7-10-08)	1–3			
A	US 5 239 951 A (RAO 31 August 1993 (199 * Claim 1 *		12			
	The present search report has	been drawn up for all claims				
	Place of search	Date of completion of the search		Examiner		
	MUNICH	21 January 2000		Bjoerk, P		
X:per Y:per doo A:tec	CATEGORY OF CITED DOCUMENTS ticularly relevant if taken alone ticularly relevant if combined with ano sument of the same category hnological background	E : earlier patent o after the filing ther D : document cite L : document cite	iocument, but late d in the applic i for other rea	published on, or ation sons		
	n—written disclosure ermediate document	& : member of the document	& : member of the same patent family, corresponding document			



European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 99 11 7054

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		ERED TO BE RELEVANT				
Category	Citation of document with in of relevant pass	idication, where appropriate, ages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CL7)		
A	PATENT ABSTRACTS OF vol. 1995, no. 02, 31 March 1995 (1995 & JP 06 322582 A (R 22 November 1994 (1 * abstract *	-03-31) IKEN CORP),	14			
A	PATENT ABSTRACTS OF vol. 1996, no. 01, 31 January 1996 (19 & JP 07 243307 A (F 19 September 1995 (* abstract *	96-01-31) UJI 00ZX INC),	15			
A	US 4 431 445 A (FUR 14 February 1984 (1 * Col.4, 1.32-33 *	USAWA SADAYOSHI ET AL) 984–02–14) 	1			
				TECHNICAL FIELDS SEARCHED (Int.Cl.7		
	The present search report has					
	Place of search	Date of completion of the search		Examiner		
	MUNICH	21 January 2000	Bjo	oerk, P		
X:par Y:par doc A:tecl	ATEGORY OF CITED DOCUMENTS loularly relevant if taken alone loularly relevant if combined with ano ument of the same category mological background	E : earlier patent d after the filing d ther D : document cited L : document cited	ocument, but publiate I in the application for other reasons	lahed on, or		
A : technological background O : non-written disclosure P : intermediate document		& : member of the	& : member of the same patent family, corresponding document			

ANNEX TO THE EUROPEAN SEARCH REPORT **ON EUROPEAN PATENT APPLICATION NO.**

EP 99 11 7054

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

21-01-2000

NE
2627780 A 01-0 9
2642439 A 03-08
68909544 D 04-11
68909544 T 27-01
0357743 A 14-03
) 8908154 A 08-09-
2651245 A 01-03
2503331 T 11-10
J 4617796 A 04-09
2213550 A 22-08
2676466 B 17-11
6172949 A 21-06
5 5902424 A 11-05
9272945 A 21-10
I 1174243 A 25-02
A 2102574 A,C 13-05
DNE
69311302 D 10-07
E 69311302 T 08-01
° 0618040 A 05-10
5 5455078 A 03-10
2 1267261 C 10-06
2 57019357 A 01-02
59047024 B 16-11
P 1040104 B 25-08
P 1609794 C 15-07
2 57019365 A 01-02
E 3126984 A 25-03
JP JP JP DE

FORM PO469

Tor more details about this annex : see Official Journal of the European Patent Office, No. 12/82