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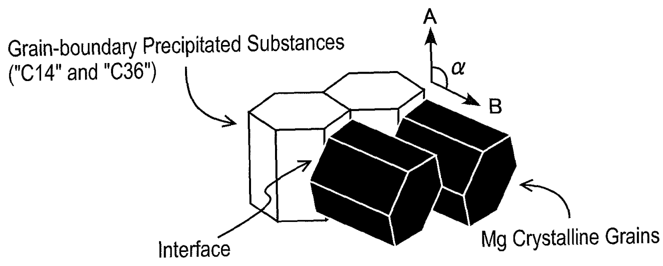
(54) HEAT-RESISTANT MAGNESIUM ALLOY

(57) A heat-resistant magnesium alloy according to the present invention has Mg as the major component, includes Al, Ca and Mg, and has a metallic structure that comprises Mg crystalline grains and grain-boundary crystallized substances being crystallized out in a grain boundary between the Mg crystalline particles. The grain-boundary crystallized substances comprise a mixed crystal phase of a Laves-phase compound with a type-"C14" crystalline structure, and another Laves-phase compound with a type-"C36" crystalline structure. Moreover, a relative angle between a normal vector to the hexagonal-system basal plane of the Mg crystalline grains and another normal vector to the hexagonal-system basal plane of the grain-boundary crystallized substances is from 88 deg. to 92 deg. at an interface between the Mg crystalline grains and the grain-boundary crystallized substances at least. The present magnesium alloy exhibits high mechanical characteristics in high-temperature atmospheres, because it has the metallic structure in which a basal-plane slip is much less likely to occur than ever before, and because the basal-plane slip is less likely to occur even at high temperatures.

Fig.3



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Description

TECHNICAL FIELD

[0001] The present invention is one which relates to a heat-resistant magnesium alloy that is capable of withstanding services under high loads and at high temperatures.

BACKGROUND ART

[0002] Magnesium alloy, which is more lightweight than aluminum alloy is, is about to be used widely for air-craft material, vehicle material, and the like, from the viewpoint of weight saving. However, magnesium alloy has been required to be furthermore upgraded in the characteristics, because it is not satisfactory in the heat resistance, as well as in the strength, depending on applications or purposes.

[0003] Hence, in Patent Literature No. 1 (Japanese Unexamined Patent Publication (KOKAI) Gazette No. 2004-162,090), and in Patent Literature No. 2 (Japanese Unexamined Patent Publication (KOKAI) Gazette No. 2004-232,060), there are disclosed magnesium alloys in which calcium (Ca) and aluminum (Al) are contained in adequate amounts, respectively. According to these literatures, the movements of dislocations are held back, because Ca-Al compounds and Mg-Ca compounds crystallize out, or deposit or precipitate, at the grain boundary between Mg crystalline particles in the magnesium alloys. As a result, the magnesium alloys exhibit good heat resistance, because they undergo creep deformations less even in high-temperature regions. In addition, the aforementioned magnesium alloys are strengthened by means of solid solution by solving Mn into the Mg crystalline grains in the magnesium alloys.

DISCLOSURE OF THE INVENTION

[0004] The metallic structure of alloy affects its characteristics greatly. Consequently, in order to obtain a magnesium alloy that shows additional heat resistance, it is necessary to control the metallic structure by adapting the types of additive elements and furthermore their addition amounts, for instance, into adequate ones. The present invention aims at providing a magnesium alloy that exhibits good heat resistance by controlling the metallic structure of the magnesium alloy with use of adequate alloying elements.

[0005] Magnesium and many magnesium alloys take on the hexagonal close-packed structure (hcp) illustrated in Fig. 1. In hep metals, deformations are likely to occur, deformations which result from a basal-plane slip (i.e., the slipping directions being <11-20>) in which the {0001} plane in the basal plane, namely, the close-packed face, makes a slipping plane. Non-basal-plane slips like the prismatic-plane slips hardly arise at room temperature. Fig. 2 is a graph that illustrates the temperature dependency of critical shear forces in a basal-plane slip, and the temperature dependency of those in a non-basal-plane slip. It has been known that the basal-plane slip, in which the {0001} plane makes a slipping plane, occurs at a smaller shear force than those at which non-basal-plane slips, in which the other planes make a slipping plane, respectively, and non-basal-plane slips become likely to occur when raising the temperature. In other words, the non-basal-plane slips do not arise as easily as the basal-plane slip does, and hence their resistances to slip are larger.

[0006] By the way, dislocations generate in a crystalline structure when a slip deformation develops. The number of dislocations that occur on this occasion (or a dislocation density) has an upper limit, and dislocations, which induce the basal-plane slip, account for a great number of it. This is because the basal-plane slip arises more easily than the other non-basal-plane slips, as having stated already. Hence, the present inventors arrived at thinking of the following: when a proportion, which dislocations stemming from non-basal-plane slips occupy in all of dislocations that occur, can be made greater, the other proportion, which dislocations stemming from a basal-plane slip exhibiting a larger deformation magnitude occupy in all of the dislocations, decreases, and eventually mechanical characteristics upgrade. Moreover, it was understood that the upgrading in mechanical characteristics by means of this mechanism is prominent at high temperatures. And, as a result of their earnest studies, a metallic structure in which non-basal-plane slips are likely to occur, and a composition for materializing that structure were found out newly; and so a heat-resistant magnesium alloy according to the present invention was invented.

[0007] Specifically, a heat-resistant magnesium alloy according to the present invention is characterized in that:

it is a heat-resistant magnesium alloy that includes:

magnesium (Mg) making the major component;
aluminum (Al);
calcium (Ca); and
manganese (Mn); and

it has a metallic structure that comprises:

Mg crystalline grains; and
grain-boundary crystallized substances being crystallized out in a grain boundary between the Mg crystalline particles;
said grain-boundary crystallized substances comprise a mixed crystal phase of a Laves-phase compound with a type-"C14" crystalline structure and another Laves-phase compound with a type-"C36" crystalline structure; and
a relative angle between a normal vector to the hexagonal-system basal plane of said Mg crystalline grains and another normal vector to the hexagonal-system basal plane of said grain-boundary crystallized substances is from 88 deg. to 92 deg. at an interface between the Mg crystalline grains and the grain-boundary crystallized substances at least.

[0008] Note that the aforementioned "type- 'C14' " and "type- 'C36' ," and later-described "type-'C15'," are codes in accordance with a magazine, "STRUKTURBERICHTE," and express three similar basic crystalline structures that are represented by $MgZn_2$, $MgCu_2$ and $MgNi_2$ of the Laves phases, respectively.

[0009] Moreover, the "heat resistance" being referred to in the present description is one which is evaluated by the mechanical properties of magnesium alloy (the creep characteristics by means of stress relaxation test and axial-force retention test, or the high-temperature strengths, and the like, for instance) in high-temperature atmospheres.

[0010] The metallic structure of the heat-resistant magnesium alloy according to the present invention comprises Mg crystalline grains, and grain-boundary crystallized substances. Since the grain-boundary crystallized substances comprise a mixed crystal phase of a Laves-phase compound with a type-"C14" crystalline structure and another Laves-phase compound with a type-"C36" crystalline structure, each of the compounds, which constitute the grain-boundary crystallized substances, becomes just about a single crystal virtually without ever undergoing phase separation. As a result, the grain-boundary crystallized substances become to be of high strength. Moreover, the mixed crystal phase is stable even at high temperatures.

[0011] Moreover, when a relative angle between a normal vector to the hexagonal-system basal plane of the Mg crystalline grains and another normal vector to the hexagonal-system basal plane of the grain-boundary crystallized substances is from 88 deg. to 92 deg. at an interface between the Mg crystalline grains and the grain-boundary crystallized substances at least, non-basal-plane slips become likely to occur instead of a basal-plane slip, and so the occurrence of the basal-plane slip with a larger deformation magnitude is inhibited. The reason for this is believed to be as follows. The Mg crystalline grains are surrounded by means of the high-strength grain-boundary crystallized substances that comprise the aforementioned mixed crystal, and additionally the crystalline orientation between the Mg crystalline grains and the grain-boundary crystallized substances is constrained in a substantially right-angled relationship at an interface between both of them at least. On this occasion, it is possible to speculate that the Mg crystalline grains are put in such a manner of constraint that deformations, which result from the basal-plane slip, become difficult to arise. Especially, at high temperatures, since the critical shear forces in the non-basal-plane slips become smaller than those at room temperature, the occurrence frequency of the non-basal-plane slips becomes so large at high temperatures that they can be of help in the inhibition of deformations resulting from the basal-plane slip.

[0012] Specifically, the heat-resistant magnesium alloy according to the present invention that includes the aforementioned alloying elements exhibits high mechanical characteristics in high-temperature atmospheres, because it has the metallic structure in which a basal-plane slip is much less likely to occur than ever before, and because the basal-plane slip is less likely to occur even at high temperatures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013]

Fig. 1 is a schematic diagram of the hexagonal close-packed structure;
Fig. 2 is a graph that illustrates the temperature dependency of critical shear forces in a basal-plane slip (e.g., the dotted line), and the temperature dependency of those in a non-basal-plane slip (e.g., the continuous line);
Fig. 3 is an explanatory diagram that schematically illustrates a relationship between a normal vector to the hexagonal-system basal plane of Mg crystalline grains and another normal vector to the hexagonal-system basal plane of grain-boundary crystallized substances;
Fig. 4 is a metallic-structure photograph in which a cross section of Test Specimen #01, one of examples, was observed with a metallograph;
Fig. 5 is a metallic-structure photograph in which an observational sample being labeled #01 was observed with a transmission electron microscope (or TEM);

Fig. 6 is a metallic-structure photograph in which another observational sample being labeled #C1, one of comparative examples, was observed with a TEM;

Fig. 7 is a dark-field scanning-transmission-electron-microscope(or DF-STEM)image of the observational sample being labeled #01;

Fig. 8 is a DF-STEM image of the other observational sample being labeled #C1;

Fig. 9 is a TEM image in which the observational sample being labeled # 01 was observed with a transmission electron microscope, and an electron-beam diffraction pattern thereof;

Fig. 10 illustrates a result of comparison between a diffraction pattern of the observational sample being labeled #01, diffraction pattern which was obtained with a TEM, and a simulated pattern thereof;

Fig. 11 is a graph that illustrates results of a stress relaxation test;

Fig. 12 is a crystal orientation mapping that displays crystal orientations in Test Specimen #01 after the stress relaxation test;

Fig. 13 is a diagram that is binarized so as to make stripe patterns likely to be viewable in one of the areas in the crystal orientation mapping of Fig. 12, and an explanatory diagram that illustrates a crystal orientation in that area;

Fig. 14 is a diagram that is binarized so as to make stripe patterns likely to be viewable in the other one of the areas in the crystal orientation mapping of Fig. 12, and an explanatory diagram that illustrates a crystal orientation in that area; and

Fig. 15 is an explanatory diagram that illustrates a deformation in which a basal-plane slip plays a major role.

BEST MODE FOR CARRYING OUT THE INVENTION

[0014] Some of best modes for enforcing the heat-resistant magnesium alloy according to the present invention (hereinafter being abbreviated to as "magnesium alloy") will be explained below.

[0015] Amagnesiumalloy according to the present invention includes magnesium making the major component, aluminum (Al), calcium (Ca), and manganese (Mg); and has a metallic structure that comprises Mg crystalline grains, and grain-boundary crystallized substances that are crystallized out in a grain boundary between the Mg crystalline grains.

[0016] The grain-boundary crystallized substances comprise a mixed crystal phase of a Laves-phase compound with a type-"C14" crystalline structure and another Laves-phase compound with a type-"C36" crystalline structure. A type-"C14" crystalline structure, and a type-"C36" crystalline structure are a hexagonal system one another, and hence they are likely to form a mixed crystal phase. Because of the fact that the Laves-phase compounds have such a crystalline structure in which their component metallic elements pack closely, respectively, the Laves-phase compounds in the mixed crystal layer come to be close to a single crystal limitlessly, respectively. Accordingly, the grain-boundary crystallized substances are continuous microscopically, and so the area of crystalline boundaries and the number of crystalline grains become a minimum, respectively. In other words, the grain-boundary crystallized substances crystallized out in the grain boundaries between the Mg crystalline grains to take on a network structure (or three-dimensional mesh structure) macroscopically, and furthermore crystals exist continuously even in the interior of networks. As a result, of the metallic structure, strengths at the grain boundaries upgrade, and hence the metallic structure is strengthened as a whole. On this occasion, it is desirable that the network structure of the grain-boundary crystallized substances can cover, of the grain boundaries between the Mg crystalline grains that are seen as linear shapes within an area with a size of about 400 μm × 600 μm in a cross section of the magnesium alloy, 70% or more of them (this value will be hereinafter abbreviated to as "a covering ratio of networks.").

[0017] The magnesium alloy possessing the aforementioned grain-boundary crystallized substances are different from conventional magnesium alloys whose grain-boundary crystallized substances take on a network structure, but in which the interior of the grain-boundary crystallized substances is constituted of small crystals and is hence discontinuous. For example, in a magnesium alloy that does not include any Mn as an alloying element, no microscopic continuity can be observed in the grain-boundary crystallized substances, although the grain-boundary crystallized substances crystallized out in the grain boundaries between the Mg crystalline grains macroscopically to form a network structure.

[0018] And, a relative angle between a normal vector to the hexagonal-system basal plane of the Mg crystalline grains and another normal vector to the hexagonal-system basal plane of the grain-boundary crystallized substances is from 88 deg. to 92 deg. at an interface between the Mg crystalline grains and the grain-boundary crystallized substances at least. Fig. 3 is an explanatory diagram that schematically illustrates a relationship between a normal vector to the hexagonal-system basal plane of Mg crystalline grains and anther vector to the hexagonal-system basal plane of grain-boundary crystallized substances in the interface between the Mg crystalline grains and the grain-boundary crystallized substances. In Fig. 3, the white hexagonal lattices are hexagonal lattices of the grain-boundary crystallized substances that comprise a Laves-phase compound with a type-"C14" crystalline structure and another Laves-phase compound with a type-"C36" crystalline structure, and the black lattices are hexagonal lattices of the Mg crystalline grains. The arrow "A" is a normal vector "A" to the basal plane of the white hexagonal lattices, and the arrow "B" is another normal vector "B" to the basal plane of the black hexagonal lattices. In the magnesium alloy according to the present invention, an angle α, which is formed by the normal vector "A" and the normal vector "B" that bisect each other at right angles virtually, is from 88 deg. to 92 deg. It is feasible to calculate the angle that the normal vectors make from the results of measurement like electron-beam diffraction methods, X-ray diffraction methods, back-scattering electron-beam diffraction methods, and so on.

[0019] When the crystalline orientations of the both of them make the aforementioned relationship at an interface between the Mg crystalline grains and the grain-boundary crystallized substances at least, the occurrence frequency of the basal-plane slip with a larger deformation magnitude reduces inside the grainy interior of the Mg crystalline grains, and so the proportion of non-basal-plane slips, which exhibit larger slip resistances and are hence smaller in the deformation magnitudes, increases. Accordingly, mechanical characteristics of the magnesium alloy according to the present invention upgrade. In particular, the effect of upgrading the mechanical characteristics is prominent at high temperatures, because the critical shear force in non-basal-plane slip becomes a half of that at room temperature approximately at high temperatures (e.g., from 150 to 200 °C) (see the area that is specified with the dotted line in Fig. 2).

[0020] Moreover, it is desirable that the grain-boundary crystallized substances can comprise an Mg-Al-Ca-system compound. Mg_2Ca has a type-"C14" crystalline structure, and so it is speculated that a mixed crystal phase, which comprises a type-"C14" crystalline structure as well as a type-"C36" crystalline structure because of Al that dissolves in Mg_2Ca, is formed. On this occasion, it is allowable that the mixed crystal phase can include a type-"C14" crystalline structure more than the type-"C36" crystalline structure.

[0021] The Mg crystalline grains exist while being surrounded by the aforementioned grain-boundary crystallized substances. Here, when the inside of a range that possesses an identical crystalline orientation substantially, that is, the inside of an area that is formed by high-angle grain boundaries, is reckoned as one Mg crystalline grain, even within the grainy interior of such an Mg crystalline grain, the relative angles between a normal vector to the hexagonal-system basal plane of the Mg crystalline grain and other normal vectors to the hexagonal-system basal plane of the grain-boundary crystallized substances fall in the range of from 88 deg. to 92 deg. substantially. It is preferable that an average diameter of such Mg crystalline grains can be 500 μm or less, further 200 μm or less. The smaller the granular diameters of the Mg crystalline grains are the more likely it is that the effect of reducing the occurrence of basal-plane slip can be demonstrated. Note that "possessing an identical crystalline orientation substantially" in the present description shall be those that possess crystalline orientations within ±2 deg. from a datum face.

[0022] It is allowable that the Mg crystalline grains can include plate-shaped deposits or precipitates inside the grainy interior. The plate-shaped precipitates prevent the transfer of dislocations within the Mg crystalline grains. Since the deformation of crystal arises from out of dislocations that transfer on a slip plane, it is permissible that the plate-shaped precipitates can have a plate shape that is parallel to the c plane of hexagonal-crystal Mg crystal, that is, they can have a plate shape that is parallel to the {001} plane of the Mg crystal. Note that the plate-shaped precipitates have from 2 to 20 nm in their thickness; and that the thicker the thickness is the more mechanical characteristics upgrade. Moreover, it is allowable that the precipitates can comprise a Laves-phase compound with a type-"C15" crystalline structure. This is because the c plane of Mg crystal and the {111} plane of type-"C15" structure are likely to forma stable interface one another crystallographically, and thereby it is possible to predict that the formation of the plate-shaped precipitates can be facilitated. It is permissible that a compound constituting the precipitates that have such a crystalline structure can be an Al-Ca-system compound and/or an Mg-Al-Ca-system compound.

[0023] Note that it is feasible to observe and measure the precipitates' configuration, crystalline structure and composition by means of elemental mapping by the observation with a transmission electronmicroscope (orTEM), anelectron-beamdiffractionandenergy dispersive X-ray spectroscopic method (or EDX).

[0024] It is even allowable that the magnesium alloy according to the present invention can further have fine particles in the grainy interior of the Mg crystalline grains. The fine particles exist inside the Mg crystalline grains, and most of them are present around the plate-shaped precipitates. It is believed that these fine particles are not those which directly contribute to upgrading strengths within the Mg crystalline grains, even if they exist inside the Mg crystalline grains. However, the existence of the fine particles has a relationship with the generation of precipitates. The fine particles can be those fine particles that include Mn like Al-Mn-system compounds, for instance.

[0025] Note that the fine particles have a substantially spherical shape, and exhibit a particle diameter of from 10 to 15 nm approximately. Note that it is possible to confirm the existence of the fine particles by means of the observation with a dark-field scanning transmission electroscope (or DF-STEM).

[0026] The magnesium alloy according to the present invention that has a metallic structure as above includes; Mg, the major component; and Al, Ca and Mn that serve as alloying elements. In particular, the magnesium alloy according to the present invention can include; Ca in an amount of from 1.235 atomic % or more to 2.470 atomic % or less; Al in an amount of from 1.34 or more to 1.63 or less by an atomic ratio of Al with respect to Ca (i.e., Al/Ca); Mn in an amount of from 0.13 atomic % or more to 0.27 atomic % or less; and that the balance can comprise Mg and inevitable impurities; when the entirety is taken as 100 atomic %.

[0027] It was understood from the cooling curve in a common solidifying process (e.g., air cooling) when casting a cast product that comprised the magnesium alloy according to the present invention that three temperature-halting points (the respective temperatures are labeled "T1," "T2" and "T3"; and "T1" > "T3, " and "T2" > "T3") appear. When the molten-metal temperature reaches a primary-crystal temperature (i.e., a temperature at which the solidification begins: "T1" = from 600 °C or more to 620 °C or less), primary-crystal Mg (or Mg crystalline grains) crystallizes out. Moreover, when it reaches "T2," it is predicted that Al and Mn react to generate fine particles of Al-Mn-system compounds, high-temperature-generated compounds. Next, when it reaches the eutectic temperature "T3," the grain-boundary crystallized substances, which form the networks, crystallize out along with eutectic Mg. However, as a result of carrying out an elementary analysis on the fine particles, it was found that Mn was included therein more than the theoretical value. Specifically, in regions of low temperatures that are much lower than "T3," it is possible to predict that Al is spewed out from the fine particles (or Al-Mn-system compounds), and that the spewed-out Al forms compounds with Ca and then precipitates being accompanied by the agglomeration of Ca that dissolves into the Mg crystalline grains.

[0028] Although Al is an element that react with Ca to form compounds and then takes on a type-"C15" Laves structure, a mixed crystal phase that is made of a type-"C14" Laves structure and a type-"C36" Laves structure is formed under such conditions that Mg_2Ca, which takes on a type-"C14" Laves structure, is dominant, because of the phenomenon that Al dissolves into Mg_2Ca.

[0029] AnAl/Ca being less than 1.34 by atomic ratio is not preferable, because the content of Ca is so great that casting properties worsen. On the other hand, an Al/Ca exceeding 1.63 by atomic ratio is not preferable, because the grain-boundary crystallized substances are less likely to turn into a mixed crystal phase, and because crystalline grains, which are constituted of a type-"C36" Lavers structure alone, are likely to be formed so that the resulting grain-boundary crystallized substances undergo phase separation. Furthermore, a type-"C36" crystalline structure is likely to undergo the phase transition to a type-"C15" crystalline structure when being exposed to high temperatures (see Scripta Materialia, vol. 51 (2004), pp. 1005-1010). Since a type-"C15" crystalline structure is likely to agglomerate as massive shapes in high-temperature regions, and since it does not form any network of crystallized substances that are continuous microscopically, mechanical characteristics at high temperatures decline remarkably. A much more preferable value of Al/Ca can be from 1.42 or more to 1.56 or less by atomic ratio.

[0030] Mn is a suitable alloying element for the magnesium alloy according to the present invention, because it does react with Al at a higher temperature than "T3," and also because it is less likely to dissolve in Mn. Moreover, Mn reacts with Al to generate compounds only between "T1" and "T3."

[0031] When a content proportion of Mn is less than 0.13 atomic %, a normal vector to the hexagonal-system basal plane of the Mg crystalline particles and a normal vector to the hexagonal-system basal plane of the grain-boundary crystallized substances are less likely to be formed so as to make a desirable angle at an interface between both of them. Moreover, it is not preferable because of the following: since a lot of Al has resided without ever reacting with Mn, crystalline grains, which possess a type-"C36" Laves structure alone that does not take a mixed crystal structure, are likely to be formed as the grain-boundary crystallized substances, and then the resulting grain-boundary crystallized substances undergo phase separation. On the other hand, a content proportion of Mn exceeding 0.27 atomic % is not preferable, because compounds that contain Mn have precipitated inside the grain-boundary crystallized substances and might possibly disconnect the networks. A much more preferable lower limit of the content proportion of Mn can be 0.15 atomic % or more. A much more preferable upper limit of Mn can be 0.25 atomic % or less.

[0032] Ca is an element that forms type-"C14" and type-"C36" Laves structures along with Mg. A content proportion of Ca being less than 1.235 atomic % is not preferable, because precipitated substances and grain-boundary crystallized substances are not generated sufficiently and so the effect of upgrading heat-resistant characteristics is not enough. On the other hand, a content proportion of Ca exceeding 2.470 atomic % is not preferable, because the generation amounts of precipitated substances and grain-boundary crystallized substances have become too much and hence problems might possibly arise in post-processing. A much more preferable content proportion of Ca can be from 1.54 atomic % or more to 2.16 atomic % or less.

[0033] The magnesium alloy according to the present invention is not limited to those made by ordinary gravity casting and pressure casting, but can even be those made by die-cast casting. Moreover, even the casting mold being utilized for the casting does not matter if it is sand molds, metallic molds, and the like. Although even the solidification rate in the solidifying step is not limited especially, it is allowable to let it stand to cool in air atmosphere.

[0034] Beginning with the fields of space, military and aviation, applications of themagnesiumalloy according to the present invention can be extended to various fields, such as automobiles and home electric instruments. In reality, however, it is all the more suitable that, taking advantage of its heat resistance, the magnesium alloy according to the present invention can be utilized in products being utilized in high-temperature environments, such as engines, transmissions, compressors for air conditioner or their related products that are put in place within the engine room of automobile, for instance. To be concrete, the following can be given: cylinder heads, cylinder blocks and oil pans of internal combustion engine; impellers for turbocharger of internal combustion engine, transmission cases being used for automobile and the like, and so forth.

[0035] So far, the embodiment modes of the heat-resistant magnesium alloy according to the present invention have been explained, however, the present invention is not one which is limited to the aforementioned embodiment modes.

It can be conducted in various modes to which modifications, improvements, and the like, which one of ordinary skill in the art can carry out, are performed, within a range not departing from the scope of the present invention.

[0036] Hereinafter, while giving specific examples of the heat-resistant magnesium alloy according to the present invention, the present invention will be explained concretely.

[0037] Two kinds of test specimens whose contents (or addition amounts) of Al, Ca and Mn in magnesium alloys were varied were made, and then not only their metallic structures were observed and analyzed but also a stress relaxation test was carried out.

(Manufacture of Test Specimens)

[0038] A chloride-system flux was coated onto the inner surface of a crucible being made of iron that had been preheated within an electric furnace, and then a weighed pure magnesium base metal, pure Al, and an Mg-Mn alloy, if needed, were charged into it and were then melted. Further, weighed Ca was added into this molten metal that was held at 750 °C (i.e., a molten-metal preparing step).

[0039] After fully stirring this molten metal to melt the raw materials completely, it was held calmly at the same temperature for a while. During this melting operation, a mixture gas of carbon dioxide gas and SF_6 gas was blown onto the molten metal's surface in order to prevent the burning of Mg, and the flux was sprayed whenever being deemed appropriate.

[0040] The various alloy molten metals that were obtained by the aforementioned procedure were poured into a metallic mold with a predetermined configuration (i.e., a molten-metal pouring step), and were then solidified in air atmosphere (i.e., a solidifying step). Thus, test specimens with 30 mm × 300 mm × 40 mm were made by means of gravity casting. The obtained test specimens were labeled #01 (an example including Mn), and #C1 (a comparative example not including Mn). The chemical compositions of the respective test specimens were specified in Table 1. Note that, in the magnesium-alloy compositions being given in Table 1, the balances are Mg, respectively.

(TABLE 1)

Test Specimen	Magnesium-alloy Composition (atomic %)					Al/Ca
	Al	Zn	Ca	R.E.	Mn	
#01	2.75	-	1.85	-	0.23	1.49
#C1	2.75	-	1.85	-	-	1.49
AZ91D	8.23	0.38	-	-	-	-

[0041] Note that, in Table 1, "atomic %" is used as the units for the alloy compositions being labeled #01 and #C1. Inthemolten-metal preparing step, the values of the "atomic %" in Table 1 were converted into those of the "% by mass" to weigh the raw materials. Moreover, the composition of AZ91D (according to the ASTM standard) is set forth therein additionally.

(Observation and Analysis on Metallic Structure)

(1. Observation on Mg Crystalline Grains and Grain-boundary Crystallized Substances)

[0042] Test specimen #01 being thus made was observed with a metallographic microscope. Fig. 4 is a metallic-structure photograph in which a cross section of the test specimen being labeled #01 was observed with a metallographic microscope. The Mg crystalline grains (dark parts), and the grain-boundary crystallized substances (bright parts) that existed like networks at the grain boundaries between the Mg crystalline grains were observed. Note that, although not being shown diagrammatically, a metallic-structure photograph being similar to Fig. 1 was obtained even when a cross section of the test specimen being labeled #C1 was observed. In other words, in either one of the test specimens, network-shaped grain-boundary crystallized substances were observed.

(2. Observation on Grain-boundary Crystallized Substances)

[0043] In order to observe micro-fine constructions of the grain-boundary crystallized substances that had been observed with a metallographic microscope, Test Specimens #01 and #C1 were adapted into a flake-shaped observational sample, respectively, and were then observed using a transmission electron microscope (or TEM).

[0044] Fig. 5 and Fig. 6 are metallic-structure photographs in which the observational samples according to #01 and

#C1 were observed with a TEM. In both of them, crystalline grain boundaries in which two or more crystalline grains of primary-crystal Mg neighbor to each other were observed. In Fig. 5 (#01), the grain-boundary crystallized substances (black parts) were grown as a lamellar shape (or layered shape), and were continuous. In Fig. 6 (#C1), the grain-boundary crystallized substances were interrupted partially, and were discontinuous. Note that the covering ratio of networks in #01 was about 90%.

[0045] Moreover, Fig. 7 and Fig. 8 are a dark-field scanning-transmission-electron-microscope (or DF-STEM) images in which the grain-boundary crystallized substances in the observational samples according to #01 and #C1 were observed, respectively. In the test specimen being labeled #01, no phase separation was seen as shown in Fig. 7; whereas, in the test specimen being labeled #C1, phase separation was seen as shown in Fig. 8. When an elementary mapping was carried out with respect to the DF-STEM images of Fig. 7 and Fig. 8 by means of energy dispersive X-ray spectroscopy (or EDX), Mg, Al and Ca were distributed uniformly in Fig. 7 (#01); whereas the concentration of Al was high in the crystalline grains, which were agglomerated granularly to undergo phase separation, in Fig. 8 (#C1). And, the electron diffraction of type-"C36" crystalline structure was obtained from the crystalline grains with high Al concentrations. On the other hand, the electron-diffraction pattern of type-"C14" crystalline structure was obtained mainly from the crystals in which each of Mg, Al and Ca was distributed uniformly in Fig. 7 and Fig. 8; however, the diffraction spot of type-"C36" crystalline structure, which coincided with the double period to type-"C14" crystalline structure, appeared partially, even though they did not undergo any phase separation. Specifically, it was understood that the crystals in which Mg, Al and Ca were distributed uniformly were a mixed crystal phase of type-"C14"crystalline structure and type-"C36" crystalline structure, and were virtually single crystals visually. Therefore, in the test specimens being labeled #01, the grain-boundary crystallized substances forming the networks were continuous microscopically, and they virtually represented single crystals visually. On the contrary, in the test specimen being labeled #C1, although the grain-boundary crystallized substances formed networks macroscopically, the networks were discontinuous microscopically, and the Laves-phase compounds, which comprised type-"C36" crystalline structure alone and had undergone phase separation, were present.

[0046] Note that, on a magnesium alloy as well in which the Mn content in #01 was changed to 0.09 atomic %, the grain-boundary crystallized substances were observed with a TEM, though not being shown diagrammatically. According to the obtained DF-STEM image, the massive agglomerations that were seen in #C1 (Fig. 8) decreased so that compounds extending as band shapes came to account for it greatly when the Mn amount increased; however, it was understood that no continuity that was observed in #01 (Fig. 7) was seen when the Mn content was 0.09 atomic %.

(3. Measurement on Orientations of Mg Crystalline Grains and Grain-boundary Crystallized Substances)

[0047] In order to measure crystalline orientations of the Mg crystalline grains and grain-boundary crystallized substances, Test Specimen #01 was observed using a TEM. The results are illustrated in Fig. 9. Fig. 9 is a TEM image and an electron-beam diffraction pattern that were obtained by observing an observational sample being according to #01 with a TEM. Moreover, the diffraction pattern is a selected-area diffraction pattern in a predetermined area that covers (or bridges over) the interface between the Mg crystalline grains and the grain-boundary crystallized substances (or corresponding to the part that is enclosed with the dotted line on the TEM image).

[0048] Next, indexing of the obtained diffraction pattern, and a geometric calculation thereon were carried out. In Fig. 10, results of the comparison between the diffraction pattern and a simulated pattern that was obtained from a theoretical calculation are illustrated. Note that the diffraction pattern being illustrated in Fig. 10 is one that is the same as the diffraction pattern in Fig. 9. Moreover, in Fig. 10, the forbidden reflections are illustrated with "× ." It was understood that the obtained diffraction pattern was made by superimposing the diffraction from Mg in the Mg crystalline grains and the diffraction from Mg compounds in the grain-boundary crystallized substances.

[0049] As a result of analyzing the diffraction pattern in more detail, the Euler angles (Φ, Θ, Ψ) that represent the crystalline orientation of the grain-boundary crystallized substances were (90, 51.2, 0); whereas the Euler angles (Φ, Θ, Ψ) that represent the crystalline orientation of the Mg crystalline grains were $\Phi = 0$, $\Theta = -90 \pm 2$, and $5 \leqq \Psi \leqq 10$. In other words, a relative angle between a normal vector to the hexagonal-system basal plane of the Mg crystalline grains and another normal vector to the hexagonal-system basal plane of the grain-boundary crystallized substances was from 88 deg. to 92 deg. Note that, in the present description, the Euler angles are those being converted about the z-y-z axes, and that the reference rotational axes are illustrated in Fig. 1. In Fig. 1, the downward arrow (i.e., the x-axis) extends toward the viewer along the hexagonal {0001} plane (that is, in the <11-20> direction).

(Stress Relaxation Test)

[0050] A stress relaxation test was carried out onto each of the test specimens that comprised Test Specimens #01 and #C1 and AZ91D, respectively, thereby examining the magnesium alloys' heat resistance (e.g., the creep property). In the stress relaxation test, a process was measured, process in which the stress, which was needed when a load was applied to a test specimen until it exhibited a predetermined deformation magnitude, decreased with time in the course of testing time. To be concrete, in 150 °C air atmosphere, a compression stress of 100 MPa was loaded to the test specimens, and then the compression stress was lowered in agreement with the elapse of time so as to keep the displacements of the test specimens at that time constant.

[0051] In Fig. 11, the respective test specimens' alloy compositions, and their stresses after 40 hours since the stress relaxation test started are illustrated. Test Specimen #01 exhibited a decrease proportion of the loaded stress especially less, compared with those of the other test specimens, and therefore showed higher creep resistance even under high temperatures. Hence, the crystalline orientation of Test Specimen #01 after the test was analyzed by means of electron backscatter diffraction (or EBSD, or being called EBSP as well), thereby examining the mode of dislocations. An EBSD is an apparatus that measures the crystalline orientation of polycrystalline material and the state of its distribution. For the analysis, an SEM/EBSD apparatus was used, SEM/EBSD apparatus which comprised: an SEM main unit, that is, JSM-6490LA produced by NIHON DENSHI Co. , Ltd.; an EBSD analysis system, that is, HighSpeed EBSD Detector produced by TSL Corporation (or TexSEML Laboratories, Inc.); and an OIM automatic analysis system. As a pretreatment, an observational face of Test Specimen #01 was subjected to polishing by means of Ar ion beam with use of SM-09010 produced by NIHON DENSHI Co., Ltd. A result of the measurement on the test specimen being labeled #01, which had undergone the pretreatment, with the aforementioned SEM/EBSD apparatus is illustrated in Fig. 12.

[0052] Fig. 12 is a crystalline-orientation mapping that displays crystalline orientations in Test Specimen #01 after the stress relaxation test. Note that a crystalline-orientation mapping is one in which only angles, which fall within a predetermined range fromapredeterminedplane (e.g., ±2 deg. in the present measurement), are displayed with identical colors, respectively. Specifically, Fig. 12 is displayed intrinsically in a color for each of distinct crystalline orientations. The crystalline-orientation mapping on Test Specimen #01 that is illustrated in Fig. 12 is divided into seven major areas, and those that possess stripe patterns, which are specified with different colors, were observed within the areas. Moreover, even when observing the other parts, many areas were seen to possess stripe patterns or lattice patterns.

[0053] Fig. 13 is a diagram that is binarized so as to make the strip patterns more likely to be viewable in one of the areas of the crystalline-orientation mapping in Fig. 12. For example, in Fig. 13, the region being enclosed with the dotted line was an area in which pinkish stripe patterns were seen in a green color originally, and the binarizing resulted in turning the green color into white, and in turning the strip patterns into black. Hence, when the respective crystalline orientations in white and black are expressed in a drawing on the basis of numerical data of the crystalline orientations according to the EBSD, they make a relationship in the right diagram of Fig. 13. The white hexagonal lattices, and the black hexagonal lattice correspond to the white parts, and to the black part, respectively. Although the hexagonal lattices with substantially the same crystalline orientations one another are arranged regularly before the stress relaxation test, the black hexagonal lattice is made by rotating one of them by β = 88 deg. about an axis, which is taken in the <-1-120> direction, by means of the compression-stress loading. When this change between the relative orientations is represented in the Euler angles, it makes (80.6, 17.2, 25.4), and so all of the components of (Φ, Θ, Ψ) possess a value, respectively.

[0054] Moreover, Fig. 14 is a diagram that is binarized so as to make the strip patterns more likely to be viewable in another one of the areas of the crystalline-orientation mapping in Fig. 12. In Fig. 14, the region being enclosed with the dotted line was an area in which dark purple-colored stripe patterns were seen in a light purple color originally, and the binarizing resulted in turning the light-purple-colored region into white, and in turning the strip patterns into black. Here, when the respective crystalline orientations in white and black are expressed in a drawing on the basis of numerical data of the crystalline orientations according to the EBSD, they make a relationship in the left diagram of Fig. 14. The white hexagonal lattices, and the black hexagonal lattice correspond to the white parts, and to the black part, respectively. Although the hexagonal lattices with substantially the same crystalline orientations one another are arranged regularly before the stress relaxation test, the black hexagonal lattice is inclined by γ = 4 deg. about another axis, which is taken in the <10-10> direction, by means of the compression-stress loading. When a relationship that results from this change between the relative orientations is represented in the Euler angles, it is expressed in (0, 0, 52.4), that is, $(0, 0, \Psi)$, and so only one of the components, Ψ, possesses a value.

[0055] Here, in such a case as well where the change between the relative orientations in a deformed structure in which only basal-plane slips have occurred is expressed by Euler angles, it becomes $(0, 0, \Psi)$. However, a slipping interface that is formed on this occasion is formed parallelly with respect to the basal plane of hexagonal crystal. It is evident that the change between the relative orientations in the structure after the stress relaxation test (namely, the change being illustrated in Fig. 13) is different from the deformation that results from a basal-plane slip alone, because it is a change whose components, ϕ and Θ, possess a value, respectively. On the other hand, the stripe patterns in the area that is illustrated in Fig. 14 are analogous to a change that is expressed by a basal-plane slip alone, according to the representation by Euler angles. But, since a slipping interface in this instance is confirmed to appear in one of the hexagonal-system side faces, it is less likely to believe that the slipping interface can lead to the deformation that results from a basal-plane slip alone (namely, the deformation illustrated in Fig. 15) that occurs in the basal planes. In other words, it is indicated that both the stripe patterns, which appeared in the crystalline orientation mapping in the present measurement, are deformed structures to which non-basal-plane slips had contributed. And, although similar strip patterns were observed over a wide region of Test Specimen #01, no areas were observed, areas in which the change between the relative orientations was expressed by (0, 0, Ψ), and in which a slipping interface was parallel to the basal plane of hexagonal crystal. Specifically, Test Specimen #01 exhibited high creep resistance, because non-basal-plane slips, in place of a basal-plane slip, become likely to occur under high temperatures and then the occurrence of basal-plane slip can be inhibited as a consequence.

Claims

1. A heat-resistant magnesium alloy being **characterized in that**:

   it is a heat-resistant magnesium alloy that includes:

      magnesium (Mg) making the major component;
      aluminum (Al);
      calcium (Ca); and
      manganese (Mn); and

   it has a metallic structure that comprises:

      Mg crystalline grains; and
      grain-boundary crystallized substances being crystallized out in a grain boundary between the Mg crystalline particles;

   said grain-boundary crystallized substances comprise a mixed crystal phase of a Laves-phase compound with a type-"C14" crystalline structure and another Laves-phase compound with a type-"C36" crystalline structure; and
   a relative angle between a normal vector to the hexagonal-system basal plane of said Mg crystalline grains and another normal vector to the hexagonal-system basal plane of said grain-boundary crystallized substances is from 88 deg. to 92 deg. at an interface between the Mg crystalline grains and the grain-boundary crystallized substances at least.

2. The heat-resistant magnesium alloy as set forth in claim 1, wherein said grain-boundary crystallized substances comprise an Mg-Al-Ca-system compound.

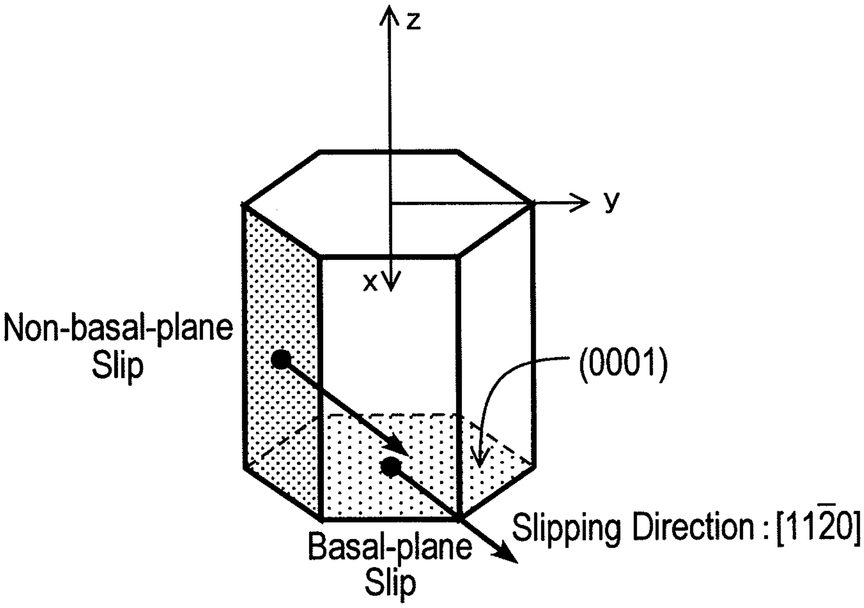
3. The heat-resistant magnesium alloy as set forth in claim 1, wherein said mixed crystal phase includes the type-"C14" crystalline structure more than the type-"C36" crystalline structure.

4. The heat-resistance magnesium alloy as set forth in either one of claims 1 through 3, the heat-resistance magnesium alloy including:

   Ca in an amount of from 1.235 atomic % or more to 2.470 atomic % or less;
   Al in an amount of from 1.34 or more to 1.63 or less by an atomic ratio of Al with respect to Ca (i.e., Al/Ca);
   Mn in an amount of from 0.13 atomic % or more to 0.27 atomic % or less; and
   the balance comprising Mg and inevitable impurities;
   when the entirety is taken as 100 atomic %.

5. The heat-resistance magnesium alloy as set forth in claim 4, the heat-resistance magnesium alloy including Mn in an amount of from 0.15 atomic % or more to 0.25 atomic % or less.

Fig.1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y
x
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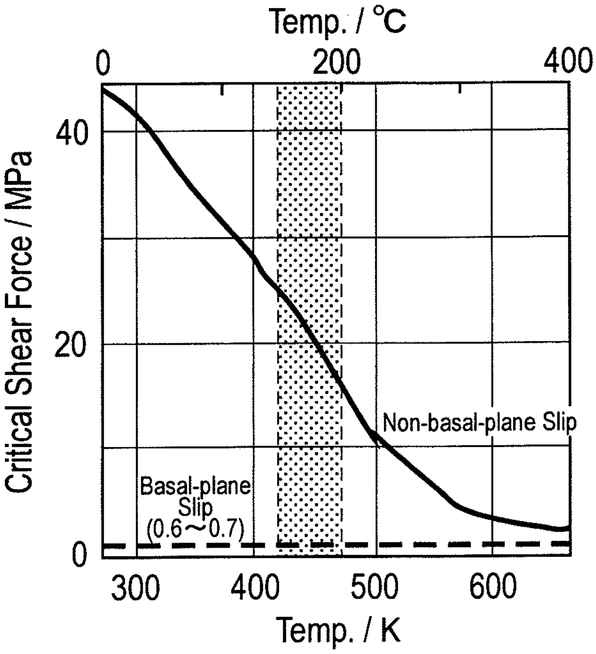
(0001)
Slipping Direction : [11$\bar{2}$0]
Basal-plane Slip

Fig.2


Temp. / °C
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200
400
Critical Shear Force / MPa
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20
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Basal-plane Slip (0.6〜0.7)
300
400
500
600
Temp. / K

Fig.3

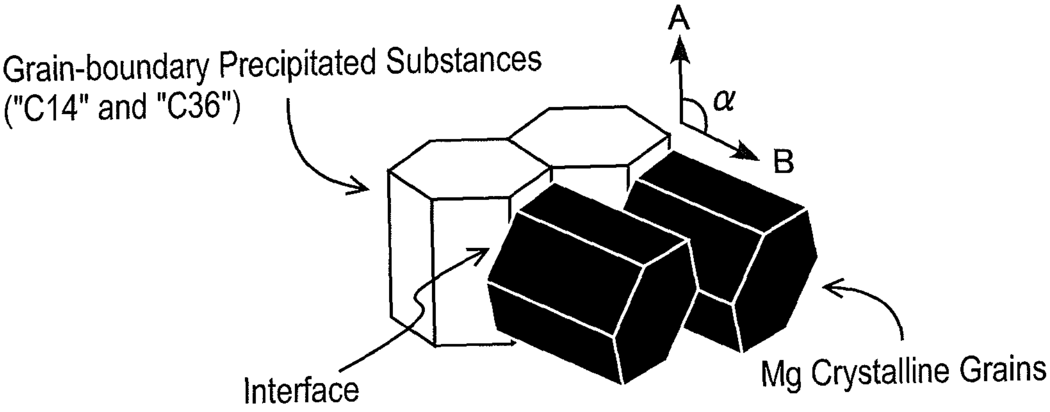

Grain-boundary Precipitated Substances
("C14" and "C36")
A
α
B
Interface
Mg Crystalline Grains

Fig.4

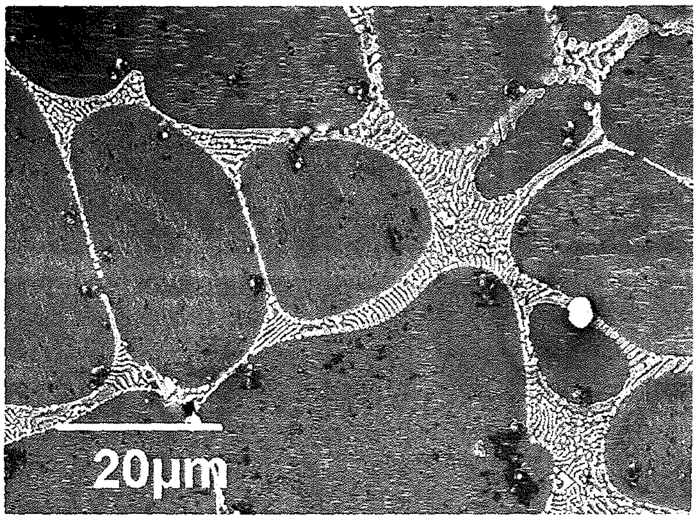

20μm

Fig.5

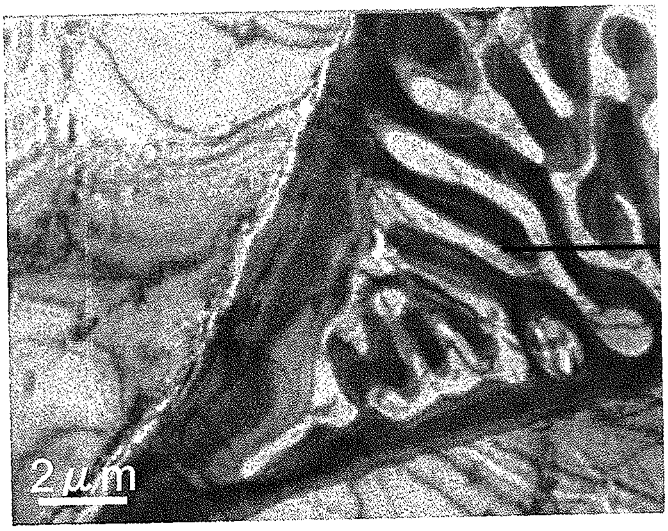


Fig.6

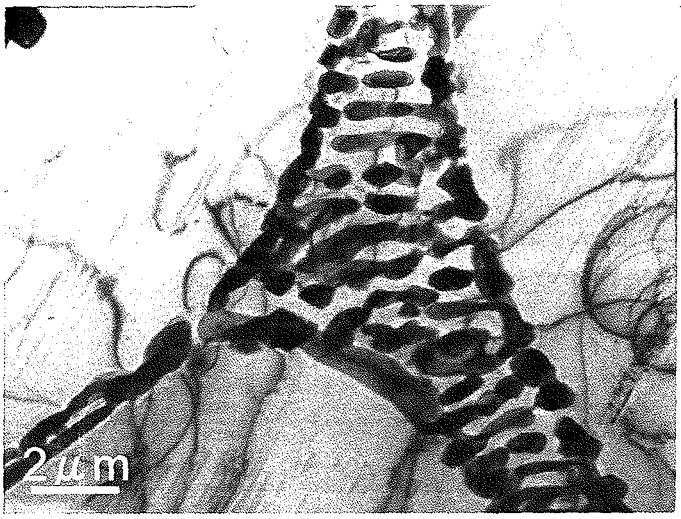
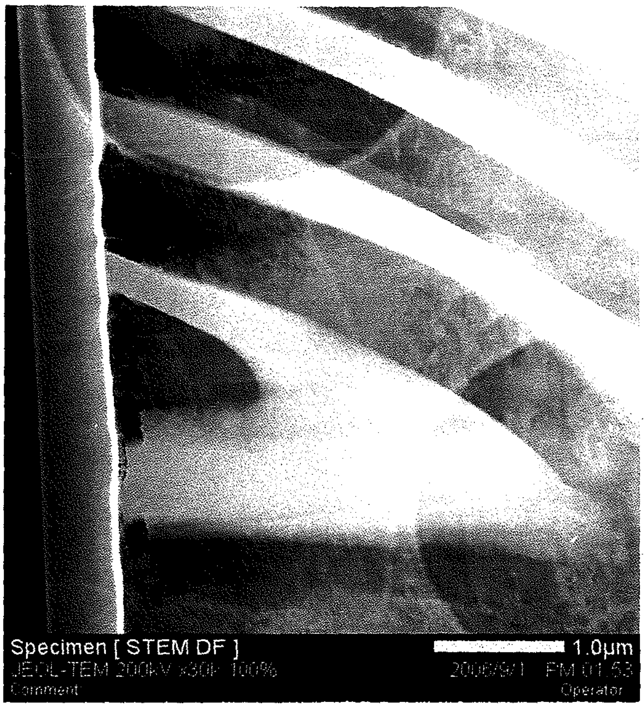


Fig.7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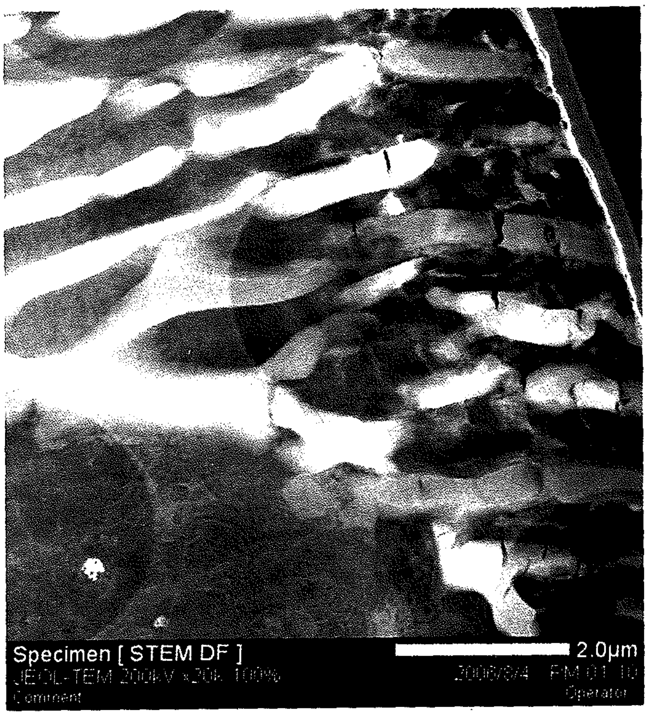
2006/9/1 PM 01:53
Comment
Operator

Fig.8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Comment
Operator

Fig.9

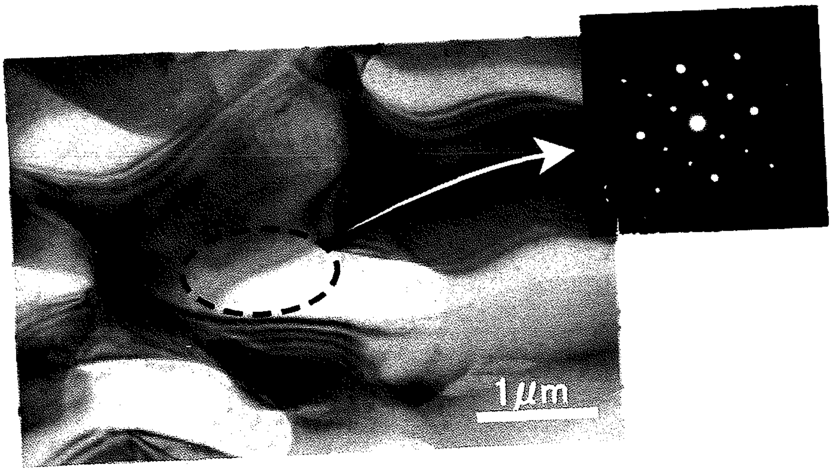
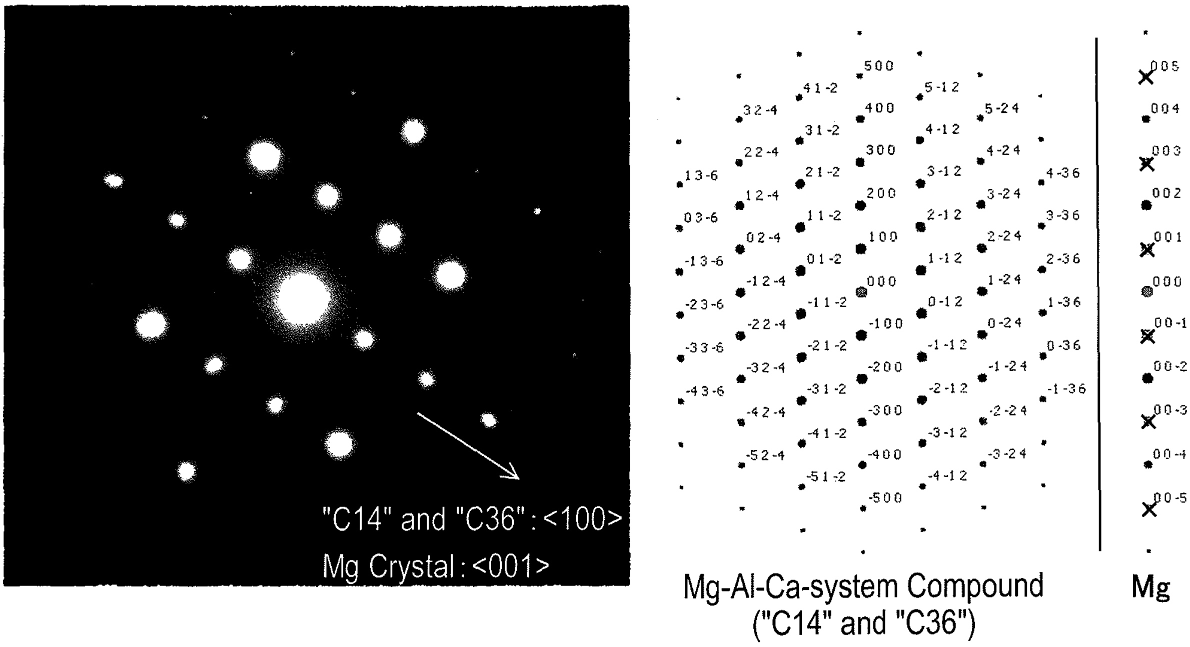


Fig.10



Mg-Al-Ca-system Compound ("C14" and "C36")

Mg

Fig.11

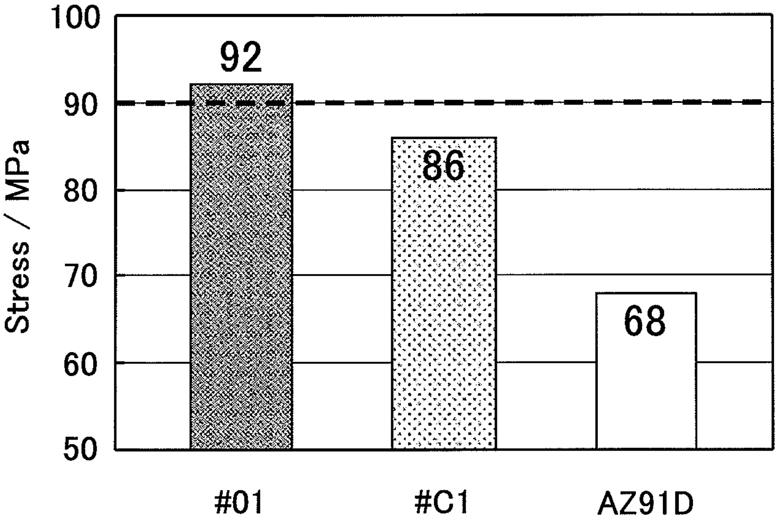


Fig.12

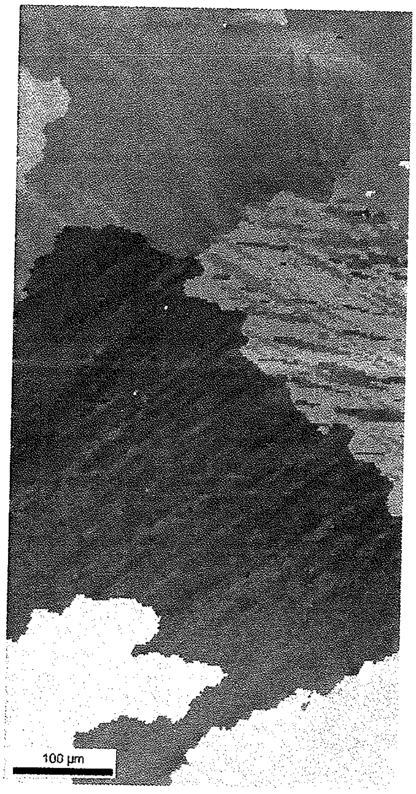


Fig.13

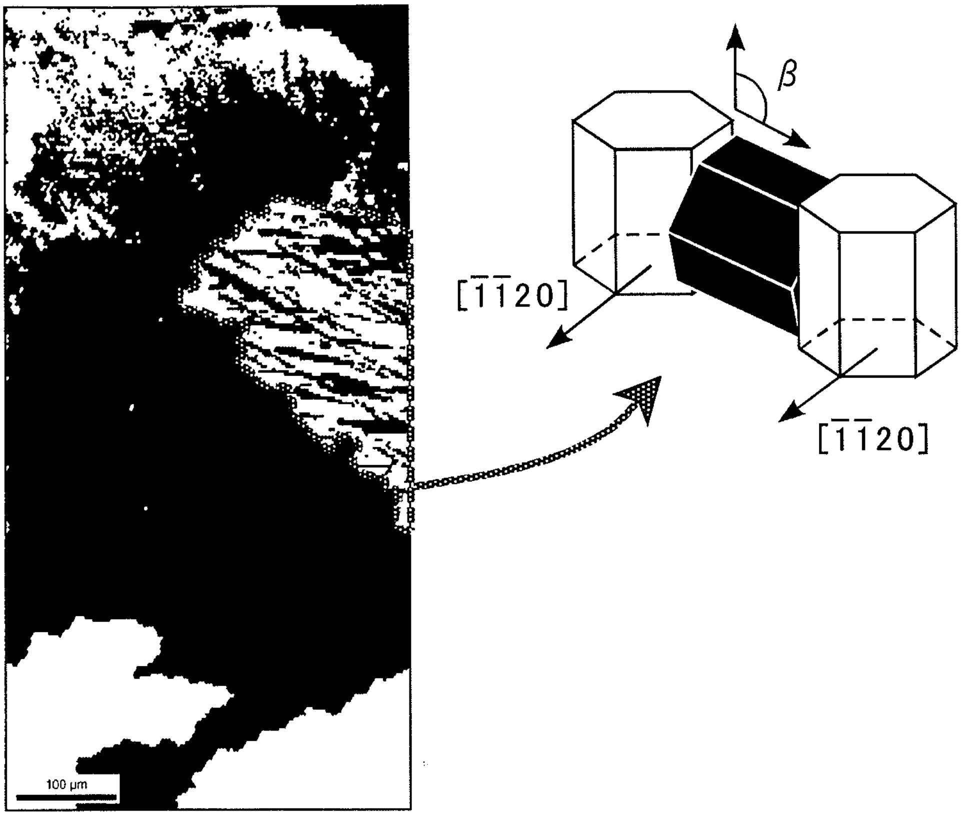


Fig.14

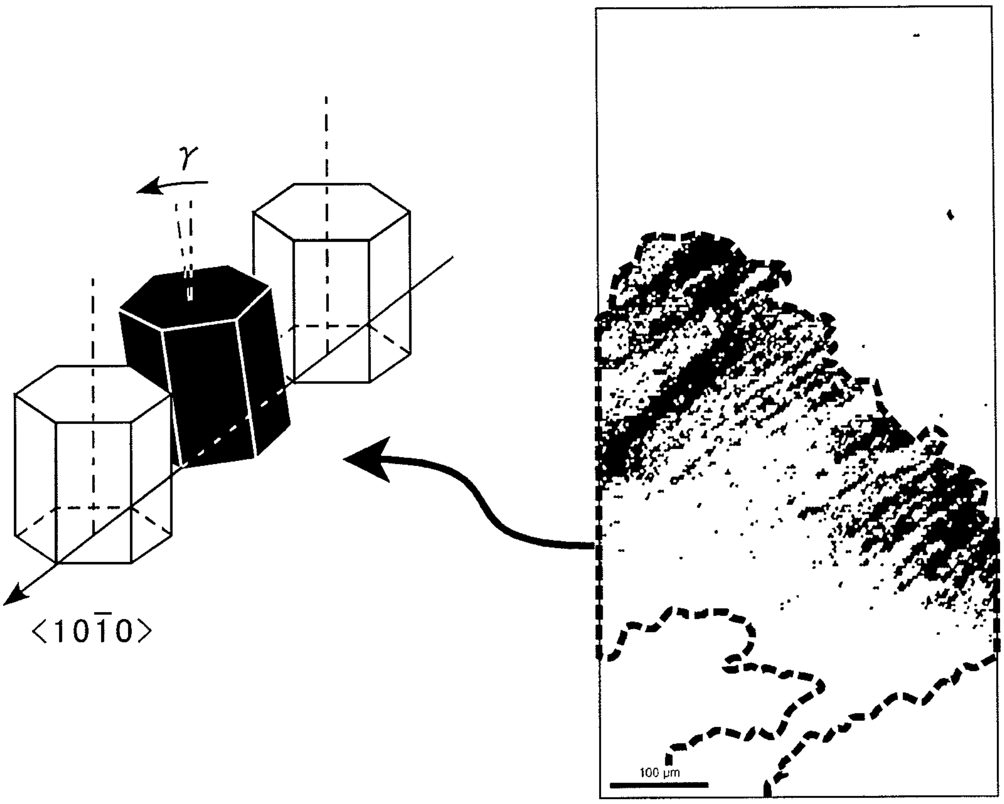
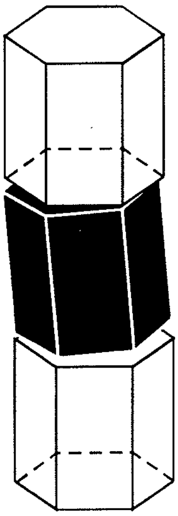


Fig.15



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2009/067318

A. CLASSIFICATION OF SUBJECT MATTER
C22C23/02(2006.01)i, *C22C23/00*(2006.01)i, *C22F1/00*(2006.01)n, *C22F1/06*(2006.01)n

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C23/00-23/06, C22F1/00, C22F1/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2009
Kokai Jitsuyo Shinan Koho	1971-2009	Toroku Jitsuyo Shinan Koho	1994-2009

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2000-104137 A (Mazda Motor Corp.), 11 April 2000 (11.04.2000), claims 2, 3; table 1 & EP 990710 A1 & KR 10-2000-0023503 A & CN 1249355 A	1-5
A	JP 06-025790 A (Mitsui Mining & Smelting Co., Ltd., Metallgesellschaft AG.), 01 February 1994 (01.02.1994), claims; table 1 (Family: none)	1-5
A	JP 2001-316753 A (The Japan Steel Works, Ltd.), 16 November 2001 (16.11.2001), table 1 (Family: none)	1-5

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 11 December, 2009 (11.12.09)	Date of mailing of the international search report 22 December, 2009 (22.12.09)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2007)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2009/067318

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 09-271919 A (Mitsui Mining & Smelting Co., Ltd., Mazda Motor Corp.), 21 October 1997 (21.10.1997), table 1 (Family: none)	1-5
A	JP 2004-232060 A (Toyota Industries Corp.), 19 August 2004 (19.08.2004), claims 1 to 4; table 1 & US 2004/0151613 A1 & US 2008/0187454 A1 & DE 102004004892 A1 & FR 2850672 A1	1-5
A	JP 2004-162090 A (Toyota Industries Corp.), 10 June 2004 (10.06.2004), claims 1 to 2; table 1 & EP 1418248 A1	1-5

Form PCT/ISA/210 (continuation of second sheet) (April 2007)

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Patent documents cited in the description

- JP 2004162090 A **[0003]**
- JP 2004232060 A **[0003]**

Non-patent literature cited in the description

- *Scripta Materialia,* 2004, vol. 51, 1005-1010 **[0029]**