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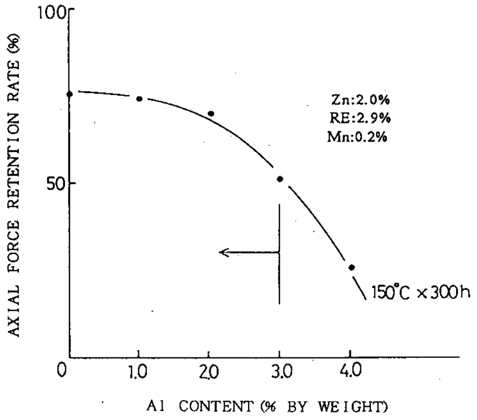
(54) Heat resistant magnesium alloy.

(57) A magnesium alloy includes 1.0 to 3.0% by weight of Al ("a"), 0.25 to 3.0% by weight of Zn ("b") and 0.5 to 4.0% by weight of R.E.: wherein when "b" is in a range, 0.25 ≦ "b" ≦ 1.0, "a" and "c" satisfy a relationship, "c" ≦ "a" + 1.0; and when "b" is in a range, 1.0 ≦ "b" ≦ 3.0, "a," "b" and "c" satisfy a relationship, "c" ≦ "a" + "b" ≦ (1/2)"c" + 4.0; in order to further improve creep properties at elevated temperatures while maintaining enhanced tensile strength at room temperature and up to 100 °C at least.

FIG. 1



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BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a heat resistant Mg-Al-Zn-rare earth element magnesium alloy which is superior in heat resistance and strength characteristics.

Description of the Related Art

Magnesium (Mg) has a specific gravity of 1.74, it is the lightest metal among the industrial metallic materials, and it is as good as aluminum alloy in terms of the mechanical properties. Therefore, Mg has been observed as an industrial metallic material which can be used in aircraft, automobiles, or the like, and which can satisfy the light-weight requirements, the fuel-consumption reduction requirements, or the like.

Among the conventional magnesium alloys, an Mg-Al alloy, for instance AM60B, AM50A, AM20A alloys, etc., as per ASTM, includes 2 to 12% by weight of aluminum (Al), and a trace amount of manganese (Mn) is added thereto. In the phase diagram of the Mg-Al alloy, there is a eutectic system which contains alpha-Mg solid solution and beta-$Mg_{17}Al_{12}$ compound in the Mg-rich side. When the Mg-Al alloy is subjected to a heat treatment, there arises age-hardening resulting from the precipitation of the $Mg_{17}Al_{12}$ intermediate phase. Further, the Mg-Al alloy is improved in terms of the strength and the toughness by a solution treatment.

Further, there is an Mg-Al-Zn alloy, for instance an AZ91C alloy or the like as per ASTM, which includes 5 to 10% by weight of Al, and 1 to 3% by weight of zinc (Zn). In the phase diagram of the Mg-Al-Zn alloy, there is a broad alpha solid solution area in the Mg-rich side where Mg-Al-Zn compounds crystallize. The as-cast Mg-Al-Zn alloy is tough and excellent in corrosion resistance, but it is further improved in terms of the mechanical properties by age-hardening. In addition, in the Mg-Al-Zn alloy, the Mg-Al-Zn compounds are precipitated like pearlite in the boundaries by quenching and tempering.

In an as-cast Mg-Zn alloy, a maximum strength and elongation can be obtained when Zn is added to Mg in an amount of 2% by weight. In order to improve the castability and obtain failure-free castings, Zn is added more to Mg. However, an Mg-6% Zn alloy exhibits a tensile strength as low as 17 kgf/mm^2 when it is as-cast. Although its tensile strength can be improved by the T6 treatment (i.e., an artificial hardening after a solution treatment), it is still inferior to that of the Mg-Al alloy. As the Mg-Zn alloy, a ZCM630A (e.g., Mg-6% Zn-3% Cu-0.2% Mn) has been available.

Furthermore, a magnesium alloy has been investigated which is superior in heat resistance and accordingly which is suitable for high temperature applications. As a result, a magnesium alloy with rare earth element (hereinafter abbreviated to "R.E.") added has been developed. This magnesium alloy has mechanical properties somewhat inferior to those of aluminum alloy at an ordinary temperature, but it exhibits mechanical properties as good as those of the aluminum alloy at a high temperature of from 250 to 300 °C. For example, the following magnesium alloys which include R.E. have been put into practical application: an EK30A alloy which is free from Zn (e.g., Mg-2.5 to 4% R.E.-0.2% Zr), and a ZE41A alloy which includes Zn (e.g., Mg-1% R.E.-2% Zn-0.6% Zr).

Among the above-described magnesium alloys, the Mg-Al or Mg-Al-Zn alloy is less expensive in the costs, it can be die-cast, and it is being employed gradually in members which are used at a low temperature of 60 °C at the highest. However, since the Mg-Al alloy has a low melting point and since it is unstable at elevated temperatures, its high temperature strength deteriorates and its creep resistance degrades considerably at high temperatures.

For example, AZ91D alloy, one of the Mg-Al-Zn alloys similar to the AZ91C alloy, is good in terms of castability, corrosion resistance and tensile strength at room temperature and up to 150 °C, but it is inferior in terms of creep resistance at temperatures of 100 °C or more. In the case that the creep resistance is low at elevated temperatures, there arises a problem in that component parts made of such alloys exhibit deteriorating tightening forces (i.e., axial forces) at the portions, for instance at the portions tightened with a bolt, when the temperature is raised during their service. When the component parts are produced by die casting, this problem is particularly notable.

The aluminum contained in the magnesium alloys forms $Mg_{17}Al_{12}$ crystals during the solidification. When the cooling rate is as fast as die casting, there arise the areas (i.e., the dendritic cells) adjacent to the grain boundaries, areas which contain the solute atoms (e.g., aluminum atoms) prior to the crystallization in high concentrations. Due to the presence of these unstable aluminum atoms, the grain boundary diffusion is active in the environment where the temperature is elevated, and accordingly it is believed that the unstable aluminum atoms facilitate the creep deformations.

SUMMARY OF THE INVENTION

The present invention has been developed in order to solve the aforementioned problems of the conventional Mg-Al magnesium alloy for die casting, e.g., their inferior creep resistance. It is therefore an object of the present invention to provide a heat resistance magnesium alloy whose creep properties are improved at 150 °C, which securely exhibits a predetermined tensile strength at room temperature and up to 100 °C, and whose castability and corrosion resistance are enhanced.

In order to achieve the object, the present inventors investigated the aluminum concentrations in magnesium alloys at which no dendritic cells are formed. As a result, they found that the dendritic cells can be inhibited from forming by restricting the aluminum concentration in a range of from 1.0 to 3.0% by weight. Further, they found that zinc can be added effectively to magnesium alloys in an amount of from 0.25 to 3.0% by weight to securely give the resulting products a predetermined tensile strength and elongation at room temperature and up to 100 °C. Furthermore, they found that a rare earth element, for example cerium (Ce) and neodymium (Nd), capable of forming crystals of high melting points in grain boundaries of magnesium alloys can be added to magnesium alloys in an amount of from 0.5 to 4.0% by weight to strengthen the grain boundaries of the resulting magnesium alloys. Moreover, they found that manganese (Mn) can be added to magnesium alloys in an amount of from 0.1 to 1.0% by weight to enhance the proof stress, and that it can be added in a limited amount of from 0.2 to 0.3% by weight thereto to enhance the corrosion resistance as well. Thus, the present inventors completed a heat resistant magnesium alloy according to the present invention.

The present heat resistant magnesium alloy has excellent elongation and strength properties, and it is expressed by a general formula, Mg-("a"% by weight)Al-("b"% by weight)Zn-("c"% by weight)rare earth element, in which:

"a" stands for an aluminum content in a range of from 1.0 to 3.0% by weight;

"b" stands for a Zinc content in a range of from 0.25 to 3.0% by weight; and

"c" stands for a rare earth element content in a range of from 0.5 to 4.0% by weight; and

when "b" is in a range, $0.25 \leqq "b" \leqq 1.0$, "a" and "c" satisfy a relationship, $"c" \leqq "a" + 1.0$; and

when "b" is in a range, $1.0 \leqq "b" \leqq 3.0$, "a," "b" and "c" satisfy a relationship, $"c" \leqq "a" + "b" \leqq -(1/2)"c" + 4.0$.

Further, the present heat resistant magnesium alloy is enhanced, if necessary, in terms of the proof stress by including Mn in an amount of from 0.1 to 1.0% by weight. Furthermore, it is improved, if required, in terms of the corrosion resistance as well by limitedly including Mn in an amount of from 0.2 to 0.3% by weight.

In the present heat resistant magnesium alloy, since the aluminum concentration is restricted in the range of from 1.0 to 3.0% by weight where no dendritic cells are formed, the resulting products made of the present heat resistant magnesium alloy are improved in terms of the creep resistance at elevated temperatures of 100 °C or more. Further, since Zn is added in the amount of from 0.25 to 3.0% by weight, the resulting products made thereof are enhanced in terms of the tensile strength and elongation at room temperature and up to 100 °C, and they are simultaneously upgraded in terms of the castability. Furthermore, since a rare earth element, for example Ce and Nd, is added in the amount of from 0.5 to 4.0% by weight, there are formed the high melting point crystals in the grain boundaries of the present heat resistance magnesium alloy so as to strengthen the grain boundaries, and thereby the resulting products made thereof are improved in terms of the creep properties at 150 °C.

In particular, when Mn is added to the present heat resistant magnesium alloy in the amount of 0.1 to 1.0% by weight, the resulting products made thereof exhibit an improved proof stress and a less degrading initial bolt tightening axial force. Mn can dissolve into grains even in a small addition amount, thereby effecting the solution strengthening or hardening. As a result, Mn improves the proof stress of the resulting products made thereof at room temperature and at elevated temperatures. Since the deterioration of the initial axial force depends on the proof stress of materials (i.e., members to be tightened), the addition of Mn is believed to result in the improvement. Moreover, when Mn is added thereto in the limited amount of 0.2 to 0.3% by weight, the resulting products made thereof exhibit enhanced corrosion resistance as well.

The reasons why the alloying elements of the present heat resistant magnesium alloy are added and the composition ranges thereof are limited as set forth above will be hereinafter described.

1.0 to 3.0% by weight of Al:

The axial force retention rate of products made of magnesium alloys decreases as the Al content increases. Figure 1 illustrates the results of an evaluation on the variation in the axial force retention rate of the test specimen made of a magnesium alloy which comprised Zn in an amount of 2.0% by weight, R.E. in an amount of 2.9% by weight, Mn in an amount of 0.2% by weight and balance of Mg and inevitable impurities, and to which Al was added in amounts of from 0 to 4.0% by weight. A target value of the axial force retention rate was designed to be 50% after degrading the test specimen at 150 °C for 300 hours. Thus, the Al content of 3.0% by weight satisfying the target value was taken as the upper limit. Figure 2 illustrates the results of an evaluation on the hot tearings occurrence rate of the test specimen made of the same magnesium alloy. As can be appreciated from the drawing, when the Al content was less than 1.0% by weight, the hot tearings were more likely to occur. Thus, the Al content of 1.0% by weight was taken as the lower limit. It is further preferred that the present heat resistant magnesium alloy includes Al in an amount of from 1.5 to 2.5% by weight.

In the evaluation of the axial force retention rate, a tensile creep test was carried out in order to measure the creep deformation amounts of the test specimens. Here, the magnesium alloys were melted and processed into a cylindrical test specimen having an inside diameter of 7 mm, an outside diameter of 15 mm and a length of 25 mm by die casting with a hot chamber at a casting temperature of 690 °C, at mold temperatures of 80 to 120 °C and under a casting pressure of 300 kgf/cm^2. This cylindrical test specimen was tightened with a bolt and a nut at the ends under a surface pressure of 6.5 kgf/mm^2 at ordinary temperature, it was held in an oven whose temperature was raised to 150 °C for 300 hours, and thereafter an elongation of the bolt was measured in order to examine for an axial force retention rate of the test specimen.

In the evaluation of the hot tearings occurrence rate, a hot tearings occurrence test was carried out in order to observe the hot tearings occurred in the test specimens. Here, the magnesium alloys were processed into a square-shaped box test specimen having corners of predetermined radii hereinafter described in detail. As illustrated in Figure 17, the test specimen 10 for die cast hot tearings occurrence test was a cylindrical body which had a square shape in a cross section, it had a thickness of 3 to 4 mm, and each of whose side had a length of 200 mm. A sprue 12 was disposed on a side 14, and a heat insulator 18 was disposed on a side 16 which was opposite to the side 14 with the sprue 12 disposed. One end of the side 16 was made into a round corner 20 having a radius of 1.0 mm, and the other end of the side 16 was made into a round corner 22 having a radius of 0.5 mm. This die cast hot tearings test specimen was intended for examining the hot tearings which were caused either in the round corner 20 or 22 by the stress resulting from the solidification shrinkage. The solidification shrinkage resulted from the solidification time difference between the portion covered with the heat insulator 18 and the other portions.

0.25 to 3.0% by weight of Zn:

Figure 4 illustrates the results of an evaluation on the variation in the room temperature tensile strength of the test specimen made of a magnesium alloy which comprised Al in an amount of 2.0% by weight, R.E. in an amount of 2.9% by weight, Mn in an amount of 0.2% by weight and balance of Mg and inevitable impurities, and to which Zn was added in amounts of from 0 to 4.0% by weight. Figure 5 illustrates the results of an evaluation on the variation in the elongation of the test specimen made of the same magnesium alloy at 100 °C. Here, the tensile strength test was carried out onto the test specimens which had a dumbbell-shaped configuration and dimensions in accordance with ASTM "80-91," paragraph 12.2.1. As can be readily seen from Figures 4 and 5, the test specimen was improved not only in the room temperature tensile strength but also in the 100 °C elongation by adding Zn in an amount of 0.25% by weight or more. In view of the room temperature tensile strength alone, Zn is added preferably in a range of 10% by weight or more. However, as can be seen from Figure 3 which illustrates the results of an evaluation on the variation in the axial force retention rate of the test specimen made of the same magnesium alloy, when Zn was added in a large amount, the axial force retention rate was deteriorated. Therefore, the Zn content of 3.0% by weight satisfying the aforementioned target axial force retention rate was taken as the upper limit. It is further preferred that the present heat resistant magnesium alloy includes Zn in an amount of from 0.5 to 1.5% by weight.

In particular, when Zn is added in a small amount, it dissolves into the grains of magnesium alloys and forms compounds of high melting points together with Mg, Al and R.E., thereby improving the tensile strength, the elongation and the creep resistance. However, when Zn is added in a large amount, there also arise compounds of low melting points which are comprised of Mg, Al and Zn but free from R.E. in the grain boundaries, thereby deteriorating the creep resistance.

0.5 to 4.0% by weight of R.E.:

Figure 6 illustrates the results of an evaluation on the variation in the axial force retention rate of the test specimen made of a magnesium alloy which comprised Al in an amount of 2.0% by weight, Zn in an amount of 2.0% by weight, Mn in an amount of 0.2% by weight and balance of Mg and inevitable impurities, and to which R.E. was added in amounts of from 0 to 4.0% by weight. As can be readily understood from Figure 6, the test specimen was sharply improved in the axial force retention rate by adding R.E. in an amount of 0.5% by weight or more. However, as can be seen from Figure 7 which illustrates the results of an evaluation on the variation in the room temperature tensile strength of the test specimen made of the same magnesium alloy, when R.E. was added in an amount of more than 4.0% by weight, the room temperature tensile strength was deteriorated. Therefore, the R.E. content of 4.0% by weight was taken as the upper limit. It is further preferred that the present heat resistant magnesium alloy includes R.E. in an amount of from 2.5 to 3.5% by weight.

As for R.E., a misch metal containing cerium (Ce) as a major component can be employed preferably, but magnesium alloys in which neodymium (Nd) substituted for the misch metal equally produced the advantageous effects.

In particular, it is furthermore preferred that R.E. is a misch metal which includes cerium (Ce) at least. It is moreover preferred that the misch metal includes Ce in an amount of 45 to 55% by weight.

0.1 to 0.1% by weight of Mn:

Mn dissolves into grains, thereby effecting the solution strengthening or hardening. As a result, the resulting products made of magnesium alloys containing Mn can be inhibited from deteriorating in the initial axial force. In order to obtain this advantageous effect, it is necessary to add Mn to magnesium alloys in an amount of 0.1% by weight or more. The advantageous effect of inhibiting the initial axial force deterioration is saturated by adding Mn thereto in an amount of around 0.4% by weight. However, when Mn is added thereto in an amount of more than 1.0% by weight, the Mn-Al-R.E. crystals are produced, thereby causing the hot tearings. Hence, the upper limit of the Mn addition is set at 1.0% by weight. In particular, when Mn is added thereto in an amount of 0.2% by weight or more, Mn and Al simultaneously operate so as to remove Fe which adversely affects the corrosion resistance of the resulting products. However, when Mn is added thereto in an amount of more than 0.3% by weight, no improvement can be appreciated in the corrosion resistance. Therefore, when improved corrosion resistance is desired, it is preferable to set the upper limit of the Mn addition at 0.3% by weight.

In addition, in the present heat resistant magnesium alloy, the aluminum content "a," the zinc content "b" and the R.E. content "c" are arranged so as to satisfy the relationship, "c" ≦ "a" + 1.0, when "b" is in the range, 0.25 ≦ "b" ≦ 1.0, and the relationship "c" ≦ "a" + "b" ≦ (1/2)"c" + 4.0, when "b" is in the range, 1.0 ≦ "b" ≦ 3.0. They are designed so as to satisfy the relationships because the resulting products are degraded in the room temperature tensile strength when R.E. is added in an amount of more than an amount calculated from the Al content, i.e., the Al content with a factor of 1.0 added thereto (e.g., "a" + 1.0), and because the resulting products are deteriorated in the creep properties at elevated temperatures when Al and Zn are added in total more than an amount calculated from the R.E. content, i.e., the R.E. content multiplied by half and a factor of 4.0 added thereto (e.g., (1/2)"c" + 4.0).

Thus, the present heat resistance magnesium alloy is expressed by the general formula, Mg-("a"% by weight)Al-("b"% by weight)Zn-("c"% by weight) rare earth element, in which: "a" stands for an aluminum content in a range of from 1.0 to 3.0% by weight; "b" stands for a zinc content in a range of from 0.25 to 3.0% by weight; and "c" stands for a rare earth element content in a range of from 0.5 to 4.0% by weight; and when "b" is in a range, 0.25 ≦ "b" ≦ 1.0, "a" and "c" satisfy a relationship, "c" ≦ "a" + 1.0; and when "b" is in a range, 1.0 ≦ "b" ≦ 3.0, "a," "b" and "c" satisfy a relationship, "c" ≦ "a" + "b" ≦ (1/2)"c" + 4.0. Since the aluminum content is restricted in the range of from 1.0 to 3.0% by weight where no dendritic cells are formed, the resulting products made of the present heat resistant magnesium alloy can be improved in terms of the creep resistance at elevated temperatures of 100 °C or more. Since Zn is added in the amount of from 0.25 to 3.0% by weight, the resulting products made thereof can securely exhibit the tensile strength and elongation at room temperature and up to 100 °C and it can be simultaneously enhanced in terms of the castability. Since a rare earth element, for example Ce and Nd, is added in the amount of from 0.5 to 4.0% by weight, there are formed the high melting point crystals in the grain boundaries of the present heat resistance magnesium alloy so as to strengthen the grain boundaries, and thereby the resulting products made thereof are upgraded in terms of the creep properties at 150 °C. In the case that Mn is further added in the amount of from 0.1 to 1.0% by weight, the resulting products can be inhibited from deteriorating in terms of the initial axial force, and, in particular, in the case that Mn is further added in the limited amount of from 0.2 to 0.3% by weight, the resulting products can be further enhanced in terms of the corrosion resistance as well.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the present invention and many of its advantages will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings and detailed specification, all of which forms a part of the disclosure:

Figure 1 is a graph illustrating the relationship between the axial force retention rate and the Al contents of the present heat resistant magnesium alloy;

Figure 2 is a graph illustrating the relationships between the hot tearings occurrence rate and the Al contents of the present heat resistant magnesium alloy;

Figure 3 is a graph illustrating the relationship between the axial force retention rate and the Zn contents of the present heat resistant magnesium alloy;

Figure 4 is a graph illustrating the relationship between the tensile strength at room temperature and the Zn contents of the present heat resistant magnesium alloy;

Figure 5 is a graph illustrating the relationship between the elongation at 100 °C and the Zn contents of the present heat resistant magnesium alloy;

Figure 6 is a graph illustrating the relationship between the axial force retention rate and the R.E. contents of the present heat resistant magnesium alloy;

Figure 7 is a graph illustrating the relationship between the tensile strength at room temperature and the R.E. contents of the present heat resistant magnesium alloy;

Figure 8 is a scatter diagram illustrating the compositions of the present heat resistant magnesium alloys which contain Zn in an amount of 1.0% by weight and which exhibit a tensile strength and axial force retention rate of a predetermined value or more;

Figure 9 is a scatter diagram illustrating the compositions of the present heat resistant magnesium alloys which contain Zn in an amount of 2.0% by weight and which exhibit a tensile strength and axial force retention rate of a predetermined value or more;

Figure 10 is a scatter diagram illustrating the compositions of the present heat resistant magnesium alloys which contain Zn in an amount of 3.0% by weight and which exhibit a tensile strength and axial force retention rate of a predetermined value or more;

Figure 11 is a scatter diagram illustrating the compositions of the present heat resistant magnesium alloys which contain Zn in an amount of 0.25% by weight and which exhibit a tensile strength and axial force retention rate of a predetermined value or more;

Figure 12 is a trace of a microphotograph showing a comparative magnesium alloy containing Al and Zn more than the composition range of the present heat resistant magnesium alloy;

Figure 13 is a trace of a microphotograph showing the present heat resistant magnesium alloy;

Figure 14 is a graph illustrating the results of the tensile creep test to which the present heat resistant magnesium alloy, a comparative magnesium alloy and a conventional magnesium alloy were subjected;

Figure 15 is a graph illustrating the relationship between the initial axial force retention rate and the Mn contents of the present heat resistant magnesium alloy;

Figure 16 is a graph illustrating the relationships between the hot tearings occurrence rate and the Mn contents of the present heat resistant magnesium alloy; and

Figure 17 is a perspective view of the test specimen which was prepared for the die cast hot tearings occurrence test.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Having generally described the present invention, a further understanding can be obtained by reference to the specific preferred embodiments which are provided herein for purposes of illustration only and are not intended to limit the scope of the appended claims.

Preferred embodiments of the present heat resistant magnesium alloy will be hereinafter described together with the conventional magnesium alloys or comparative examples in order to demonstrate the advantageous effects of the present invention.

First Preferred Embodiment

The following four magnesium alloys were prepared:

a first magnesium alloy containing Zn in an amount of 1.0% by weight, Al in an amount of from 0 to 4.0% by weight, R.E. in an amount of from 0 to 4.0% by weight, and balance of Mg and inevitable impurities (hereinafter referred to as "Alloys "A"");

a second magnesium alloy containing Zn in an amount of 2.0% by weight, Al in an amount of from 0 to 4.0% by weight, R.E. in an amount of from 0 to 5.0% by weight, and balance of Mg and inevitable impurities (hereinafter referred to as "Alloys "B"");

a third magnesium alloy containing Zn in an amount of 3.0% by weight, Al in an amount of from 0 to 4.0% by weight, R.E. in an amount of from 0 to 5.0% by weight, and balance of Mg and inevitable impurities (hereinafter referred to as "Alloys "C""); and

a fourth magnesium alloy containing Zn in an amount of 0.25% by weight, Al in an amount of from 0 to 4.0% by weight, R.E. in an amount of from 0 to 5.0% by weight, and balance of Mg and inevitable impurities (hereinafter referred to as "Alloys "D"").

The four alloys, i.e., the Alloys "A" through "D," were melted and processed into the aforementioned cylindrical test specimens and the dumbbell-shaped test specimens designated in ASTM "80-91," paragraph 12.2.1. The cylindrical test specimens were examined for their axial force retention rate after they were left in the 150 °C oven for 300 hours, and the dumbbell-shaped test specimens were examined for their tensile strength at room temperature. The obtained results are illustrated in Figures 8, 9, 10 and 11 on the Alloys "A," "B," "C" and "D," respectively. In the drawings, magnesium alloys are marked with "x" which produced the cylindrical test specimens exhibiting an axial force retention rate of 50% or less, magnesium alloys are marked with solid triangles (▲) which produced the dumbbell-shaped test specimens exhibiting a room temperature tensile strength of 200 MPa or less, and magnesium alloys are marked with solid circles (●) which produced the cylindrical test specimens exhibiting an axial force retention rate of 50% or more and the dumbbell-shaped test specimens exhibiting a room temperature tensile strength of 200 MPa or more.

Figure 8 illustrates the examination results on the Alloys "A" which are expressed by a general formula, Mg-("a"% by weight)Al-("b(=1.0)"% by weight)Zn-("c"% by weight)R.E. In Figure 8, among the Alloys "A," alloys which are marked with solid circles (●) and whose aluminum content "a," zinc content "b" and R.E. content "c" satisfied the following conditions: $1.0 \leqq$ "a" $\leqq 3.0$; $1.0 \leqq$ "b" $\leqq 3.0$; $0.5 \leqq$ "c" $\leqq 4.0$; and "c" $\leqq$ "a" + "b" $\leqq (1/2)$"c" + 4.0; lie in the area enclosed by the quadrangle "ABCD" thereof, and they produced the cylindrical test specimens and the dumbbell-shaped test specimens which exhibited an axial force retention rate of 50% or more, and a room temperature tensile strength of 200 MPa or more, respectively. On the other hand, among the Alloys "A," alloys which are marked with "x" or solid triangles (▲) and whose aluminum content "a," zinc content "b" and R.E. content "c" did not satisfy the aforementioned conditions lie outside the quadrangle "ABCD" area, and they produced the cylindrical test specimens and the dumbbell-shaped test specimens which exhibited an axial force retention rate of 50% or less, or a room temperature tensile strength of 200 MPa or less, respectively. Thus, the alloys whose compositions satisfied the aforementioned conditions were verified to effect the advantageous effects of the present invention.

Figure 9 illustrates the examination results on the Alloys "B" which are expressed by a general formula, Mg-("a"% by weight)Al-("b(=2.0)"% by weight)Zn-("c"% by weight)R.E. In Figure 9, among the Alloys "B," alloys which are marked with solid circles (●) and whose aluminum content "a," zinc content "b" and R.E. content "c" satisfied the following conditions: $1.0 \leqq$ "a" $\leqq 3.0$; $1.0 \leqq$ "b" $\leqq 3.0$; $0.5 \leqq$ "c" $\leqq 4.0$; and "c" $\leqq$ "a" + "b" $\leqq (1/2)$"c" + 4.0; lie in the area enclosed by the hexagon "ABCDEF" thereof, and they produced the cylindrical test specimens and the dumbbell-shaped test specimens which exhibited an axial force retention rate of 50% or more, and a room temperature tensile strength of 200 MPa or more, respectively. On the other hand, among the Alloys "B," alloys which are marked with "x" or solid triangles (▲) and whose aluminum content "a," zinc content "b" and R. E. content "c" did not satisfy the aforementioned conditions lie outside the hexagon "ABCDEF" area, and they produced the cylindrical test specimens and the dumbbell-shaped test specimens which exhibited an axial force retention rate of 50% or less, or a room temperature tensile strength of 200 MPa or less, respectively. Thus, the alloys whose compositions satisfied the aforementioned conditions were verified to effect the advantageous effects of the present invention.

Figure 10 illustrates the examination results on the Alloys "C" which are expressed by a general formula, Mg-("a"% by weight)Al-("b(=3.0)"% by weight)Zn-("c"% by weight)R.E. In Figure 10, among the Alloys "C," alloys which are marked with solid circles (●) and whose aluminum content "a," zinc content "b" and R.E. content "c" satisfied the following conditions: $1.0 \leqq$ "a" $\leqq 3.0$; $1.0 \leqq$ "b" $\leqq 3.0$; $0.5 \leqq$ "c" $\leqq 4.0$; and "c" $\leqq$ "a" + "b" $\leqq (1/2)$"c" + 4.0; lie in the area enclosed by the quadrangle "ABCD" thereof, and they produced the cylindrical test specimens and the dumbbell-shaped test specimens which exhibited an axial force retention rate of 50% or more, and a room temperature tensile strength of 200 MPa or more, respectively. On the other hand, among the Alloys "C," alloys which are marked with "x" or solid triangles (▲) and whose aluminum content "a," zinc content "b" and R.E. content "c" did not satisfy the aforementioned conditions lie outside the quadrangle "ABCD" area, and they produced the cylindrical test specimens and the dumbbell-shaped test specimens which exhibited an axial force retention rate of 50% or less, or a room temperature tensile strength of 200 MPa or less, respectively. Thus, the alloys whose compositions satisfied the aforementioned conditions were verified to effect the advantageous effects of the present invention.

Figure 11 illustrates the examination results on the Alloys "D" which are expressed by a general formula, Mg-("a"% by weight)Al-("b(=0.25)"% by weight)Zn-("c"% by weight)R.E. In Figure 11, among the Alloys "D," alloys which are marked with solid circles (●) and whose aluminum content "a," zinc content "b" and R.E. content "c" satisfied the following conditions: 1.0 ≦ "a" ≦ 3.0; 0.25 ≦ "b" ≦ 1.0; 0.5 ≦ "c" ≦ 4.0; and "c" ≦ "a" + 1.0; lie in the area enclosed by the quadrangle "ABCD" thereof, and they produced the cylindrical test specimens and the dumbbell-shaped test specimens which exhibited an axial force retention rate of 50% or more, and a room temperature tensile strength of 200 MPa or more, respectively. On the other hand, among the Alloys "D," alloys which are marked with "x" or solid triangles (▲) and whose aluminum content "a," zinc content "b" and R.E. content "c" did not satisfy the aforementioned conditions lie outside the quadrangle "ABCD" area, and they produced the cylindrical test specimens and the dumbbell-shaped test specimens which exhibited an axial force retention rate of 50% or less, or a room temperature tensile strength of 200 MPa or less, respectively. Thus, the alloys whose compositions satisfied the aforementioned conditions were verified to effect the advantageous effects of the present invention.

Second Preferred Embodiments

Magnesium alloys having the following chemical compositions as set forth in Table 1 below were melted and processed into the aforementioned cylindrical test specimens and the dumbbell-shaped test specimens designated in ASTM "80-91," paragraph 12.2.1 by die casting with a cold chamber. I.D. No. 1 is the present heat resistant magnesium alloy. I.D. No. 2 is a comparative magnesium alloy which included Al and Zn in amounts more than the present composition range. I.D. No. 3 is a conventional magnesium alloy which is equivalent to the AZ91D alloy.

Figures 12 and 13 are traces of microphotographs showing the comparative magnesium alloy and the present heat resistant magnesium alloy, respectively. As illustrated in Figure 12, in the comparative magnesium alloy, there existed the areas containing the solute atoms, which did not produce the crystals, in high concentrations adjacent to the grain boundaries, because the cooling rate was faster. When these areas are present, the solute atoms are facilitated to diffuse in the vicinity of the grain boundaries, and the high temperature creep properties are believed to be adversely affected. On the other hand, as illustrated in Figure 13, in the present heat resistant magnesium alloy, there existed no such areas, because the Al and Zn concentrations were kept low. Accordingly, the present heat resistant magnesium alloy are superior in terms of the high temperature creep properties.

The cylindrical test specimens were examined for their axial force retention rate after they were left in the 150 °C oven for 300 hours, and the dumbbell-shaped test specimens were examined for their tensile strength at room temperature. The results obtained are summarized in Table 1 below and illustrated in Figure 14.

TABLE 1

Classification	I.D. No.	Alloying Elements (% by weight)				Axial Force Retention Rate after 300 hrs. at 150 °C (%)	R.T. Tensile Strength (MPa)
		Al	Zn	R.E.	Mn		
Pref. Embodiment	1	2	2	3	0.2	70	220
Comp. Ex.	2	4	4	2	0.2	30	220
Conventional Alloy	3	9	1	0	0.2	30	260

As can be appreciated from Table 1 and Figure 14, the dumbbell-shaped test specimens made of the comparative magnesium alloy exhibited a room temperature tensile strength of 220 MPa which was almost equivalent to that of the dumbbell-shaped test specimens made of the conventional AZ91D alloy. However, the cylindrical test specimens made of the comparative magnesium alloy were inferior in the bolt loosening characteristic which was associated with the high temperature creep properties, and thereby they exhibited an axial force retention rate of 30%.

Likewise, in the conventional AZ91D alloy, there were the areas containing the solute atoms, which did not produce the crystals, in high concentrations adjacent to the grain boundaries, because the conventional AZ91D alloy was processed into the cylindrical test specimens by die casting. Accordingly, the cylindrical test specimens made thereof exhibited an axial force retention rate of 30%.

On the other hand, the dumbbell-shaped test specimens made of the present heat resistant magnesium alloy also exhibited a room temperature tensile strength of 220 MPa which was almost equivalent to that of the dumbbell-shaped test specimens made of the conventional AZ91D alloy. Moreover, the cylindrical test specimens made thereof exhibited an axial force retention rate of 70%. Thus, the present heat resistant magnesium alloy was improved in terms of the high temperature creep properties without loss of the tensile properties.

Third Preferred Embodiments

A magnesium alloy was melted which comprised 2% by weight of Al, 2% by weight of Zn, 3% by weight of R.E., and balance of Mg and inevitable impurities, and Mn was added to the resulting molten metal in an amount which varied in a range of 0 to 1.0% by weight. The thus prepared magnesium alloys were processed into the aforementioned cylindrical test specimens by die casting with a cold chamber. The resulting test specimens were subjected to the bolt loosening test, in which they were left in the 150 °C oven for 1 hour, in order to examine for their initial axial force retention rates. The results obtained are illustrated in Figure 15 as a relationship between the Mn contents and the initial axial force retention rates.

Further, except that the amount of Mn addition was varied in a range of 0 to 1.6% by weight, the magnesium alloys prepared as above were melted and cast into the square-shaped box test specimens for the die cast hot tearings occurrence test illustrated in Figure 17. The resulting test specimens were subjected to the die cast hot tearings occurrence test in order to examine for their hot tearings occurrence rates at the round corner 20 having a radius of 1.0 mm as set forth above. The results obtained are illustrated in Figure 16 as a relationship between the Mn contents and the hot tearings occurrence rates.

Furthermore, another magnesium alloy was melted which comprised 3% by weight of Al, 2% by weight of Zn, 3% by weight of R.E., and balance of Mg and inevitable impurities, and Mn was added to the resulting molten metal in an amount which varied in a range of 0 to 1.6% by weight. The thus prepared another magnesium alloys were cast into the square-shaped box test specimens for the die cast hot tearings occurrence test, and they were similarly examined for their hot tearings occurrence rates at the round corner 20 having a radius of 1.0 mm. The results obtained are also illustrated in Figure 16 as another relationship between the Mn contents and the hot tearings occurrence rates.

It is apparent from the results illustrated in Figure 15 that the initial axial force retention rate was improved appreciably when Mn was added in an amount of 0.1% by weight or more, and that the effect of the initial axial force improvement saturated when Mn was added in an amount of up to 0.4% by weight. However, as can be seen from Figure 16, the hot tearings occurred when the Mn content exceeded 1.0% by weight, because there were formed the Mn-Al-R.E. crystals. According to these results, it was verified that the present heat resistant magnesium alloy could produce the advantageous effects more favorably when it contained Mn in an amount of from 0.1 to 1.0% by weight.

Having now fully described the present invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the present invention as set forth herein including the appended claims.

A magnesium alloy includes 1.0 to 3.0% by weight of Al ("a"), 0.25 to 3.0% by weight of Zn ("b") and 0.5 to 4.0% by weight of R.E.: wherein when "b" is in a range, $0.25 \leqq "b" \leqq 1.0$, "a" and "c" satisfy a relationship, $"c" \leqq "a" + 1.0$; and when "b" is in a range, $1.0 \leqq "b" \leqq 3.0$, "a," "b" and "c" satisfy a relationship, $"c" \leqq "a" + "b" \leqq (1/2)"c" + 4.0$; in order to further improve creep properties at elevated temperatures while maintaining enhanced tensile strength at room temperature and up to 100 °C at least.

Claims

1. A heat resistant magnesium alloy expressed by a general formula, Mg-("a"% by weight)Al-("b"% by weight)Zn-("c"% by weight)rare earth element, in which:

"a" stands for an aluminum content in a range of from 1.0 to 3.0% by weight;

"b" stands for a zinc content in a range of from 0.25 to 3.0% by weight; and

"c" stands for a rare earth element content in a range of from 0.5 to 4.0% by weight; and

when "b" is in a range, $0.25 \leqq "b" \leqq 1.0$, "a" and "c" satisfy a relationship, $"c" \leqq "a" + 1.0$; and

when "b" is in a range, $1.0 \leqq "b" \leqq 3.0$, "a," "b" and "c" satisfy a relationship, $"c" \leqq "a" + "b" \leqq -(1/2)"c" + 4.0$.

2. The heat resistant magnesium alloy according to claim 1, wherein said heat resistant magnesium alloy further includes manganese (Mn) in an amount of from 0.1 to 1.0% by weight.

3. The heat resistant magnesium alloy according to claim 2, wherein said heat resistant magnesium alloy includes said manganese in an amount of from 0.2 to 0.3% by weight.

4. The heat resistant magnesium alloy according to claim 1, wherein said heat resistant magnesium alloy includes said aluminum in an amount of from 1.5 to 2.5% by weight.

5. The heat resistant magnesium alloy according to claim 1, wherein said heat resistant magnesium alloy includes said zinc in an amount of from 0.5 to 1.5% by weight.

6. The heat resistant magnesium alloy according to claim 1, wherein said heat resistant magnesium alloy includes said rare earth element in an amount of from 2.5 to 3.5% by weight.

7. The heat resistant magnesium alloy according to claim 1, wherein said heat resistant magnesium alloy is free from dendritic cells in metallic structure thereof.

8. The heat resistant magnesium alloy according to claim 1, wherein a cylindrical test specimen made of said heat resistant magnesium alloy exhibits an axial force retention rate of 50% or more after it is left in a 150 °C oven for 300 hours, and a dumbbell-shaped test specimen made thereof exhibits a tensile strength of 200 MPa or more at room temperature.

9. A mold-cast structure formed of the heat resistant magnesium alloy according to claim 1.

10. The heat resistant magnesium alloy according to claim 1, wherein said rare earth element is a misch metal.

11. The heat resistant magnesium alloy according to claim 10, wherein said misch metal includes cerium (Ce) at least.

12. The heat resistant magnesium alloy according to claim 11, wherein said misch metal includes said cerium in an amount of 45 to 55% by weight.

FIG. 1

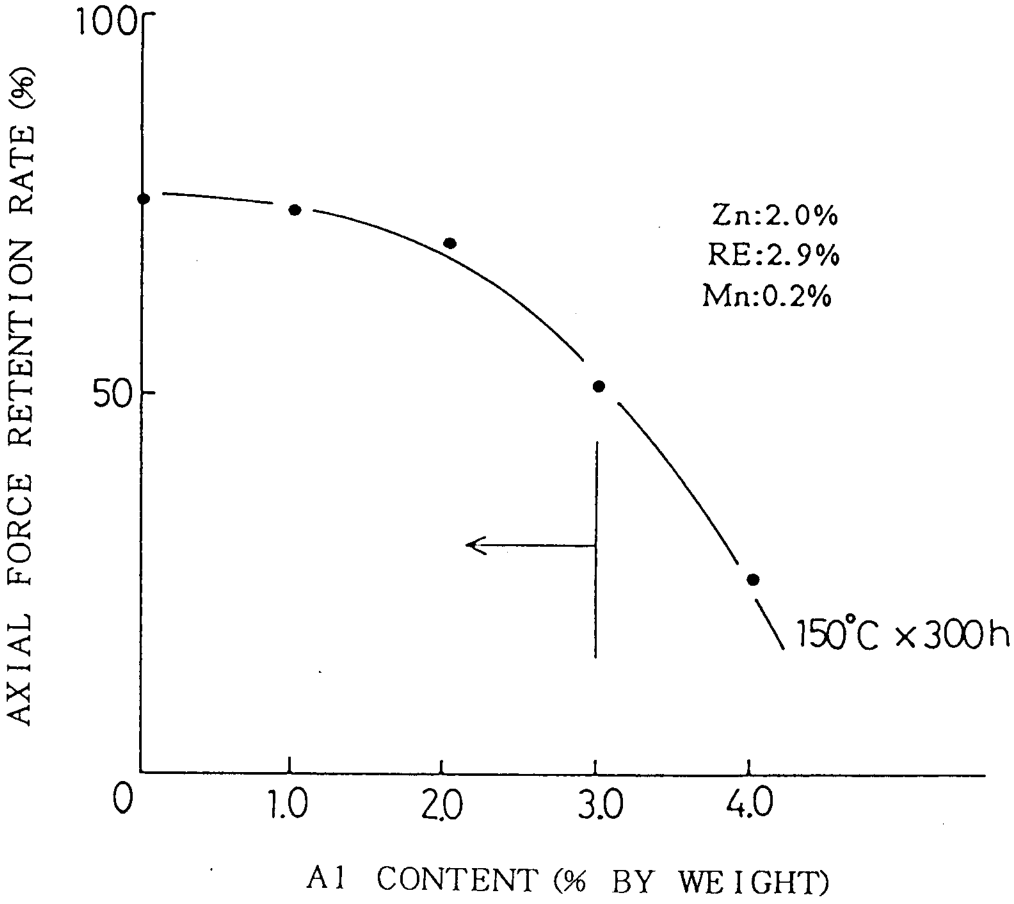

100
50
0
AXIAL FORCE RETENTION RATE (%)
Zn:2.0%
RE:2.9%
Mn:0.2%
150°C x 300h
1.0
2.0
3.0
4.0
Al CONTENT (% BY WEIGHT)

FIG. 2

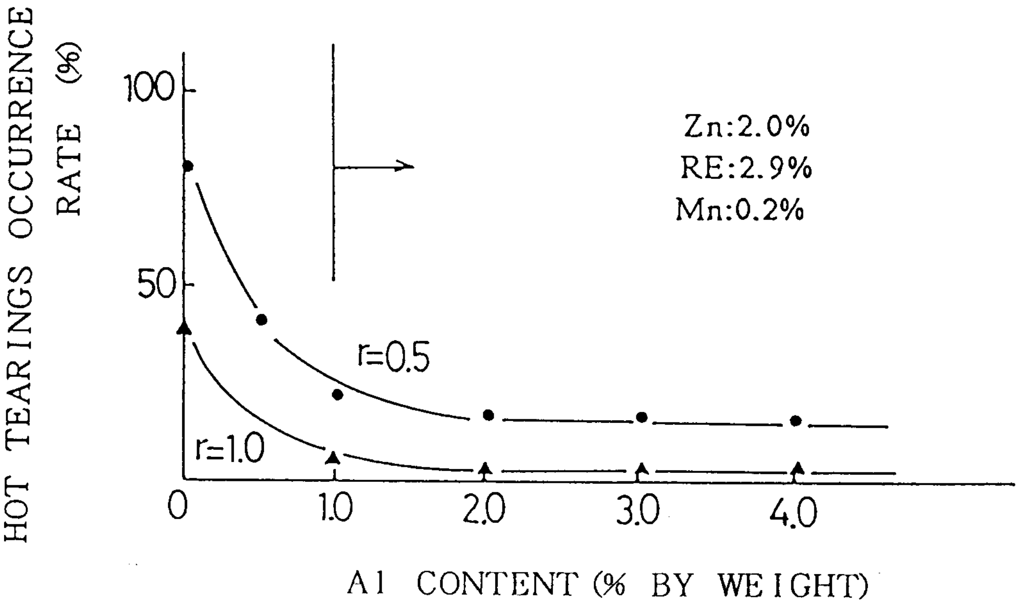

HOT TEARINGS OCCURRENCE RATE (%)
100
50
0
Zn:2.0%
RE:2.9%
Mn:0.2%
r=0.5
r=1.0
1.0
2.0
3.0
4.0
Al CONTENT (% BY WEIGHT)

FIG. 3

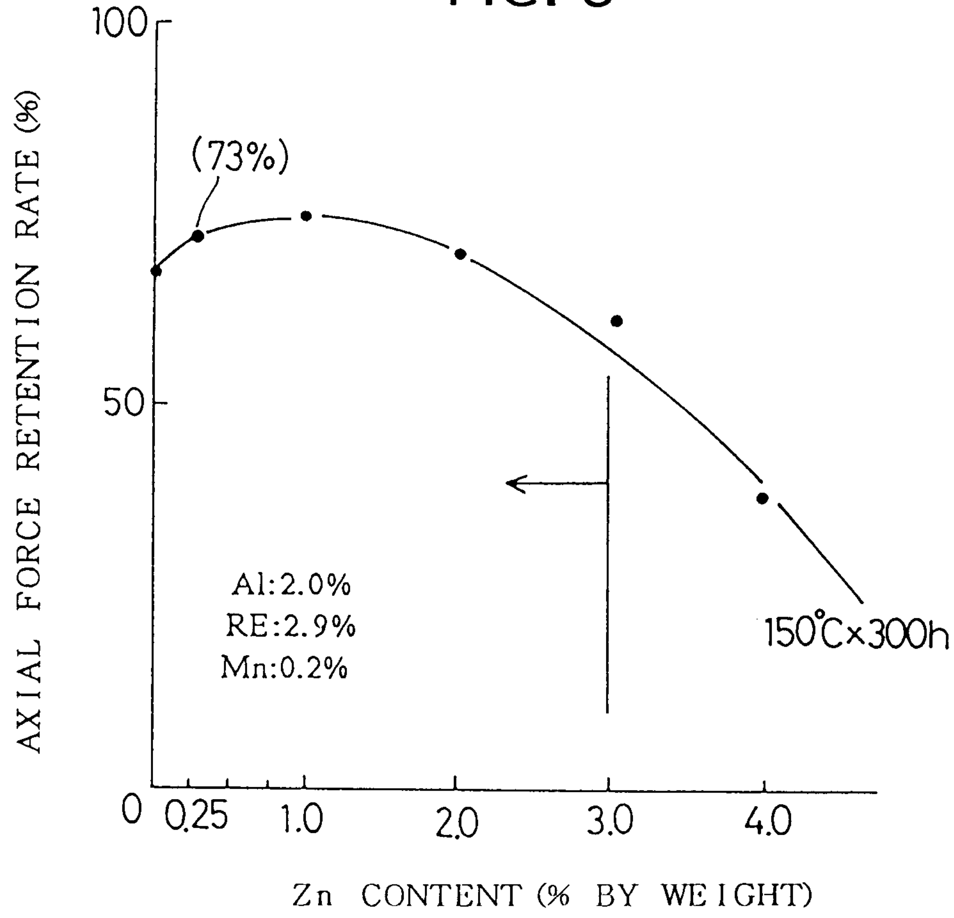

100
50
0
AXIAL FORCE RETENTION RATE (%)
(73%)
Al:2.0%
RE:2.9%
Mn:0.2%
150°C×300h
0
0.25
1.0
2.0
3.0
4.0
Zn CONTENT (% BY WEIGHT)

FIG. 4

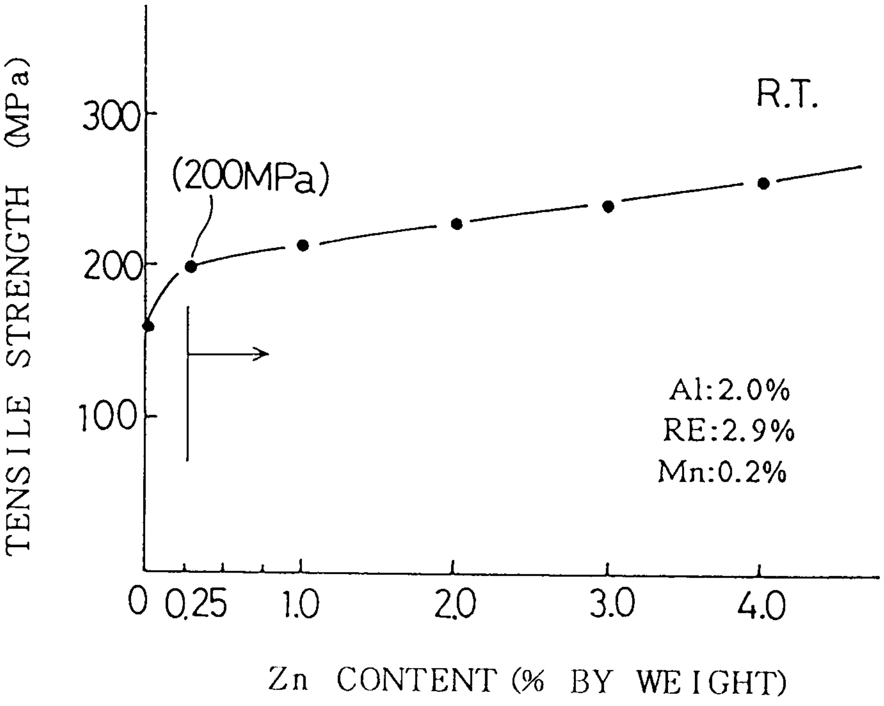

300
200
100
TENSILE STRENGTH (MPa)
R.T.
(200MPa)
Al:2.0%
RE:2.9%
Mn:0.2%
0
0.25
1.0
2.0
3.0
4.0
Zn CONTENT (% BY WEIGHT)

FIG. 5

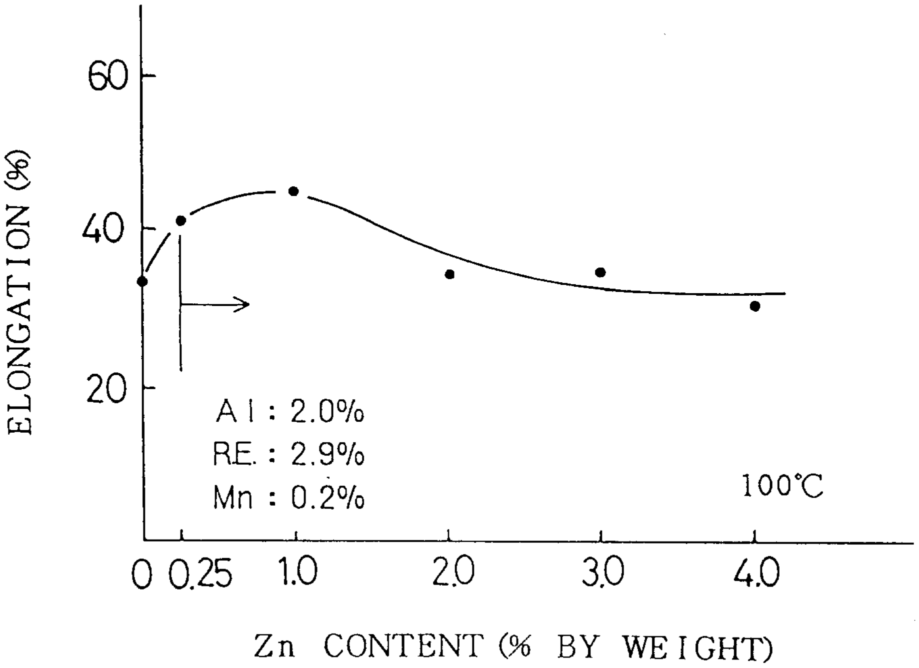

ELONGATION (%)
60
40
20
Al : 2.0%
R.E. : 2.9%
Mn : 0.2%
100℃
0
0.25
1.0
2.0
3.0
4.0
Zn CONTENT (% BY WEIGHT)

FIG. 6

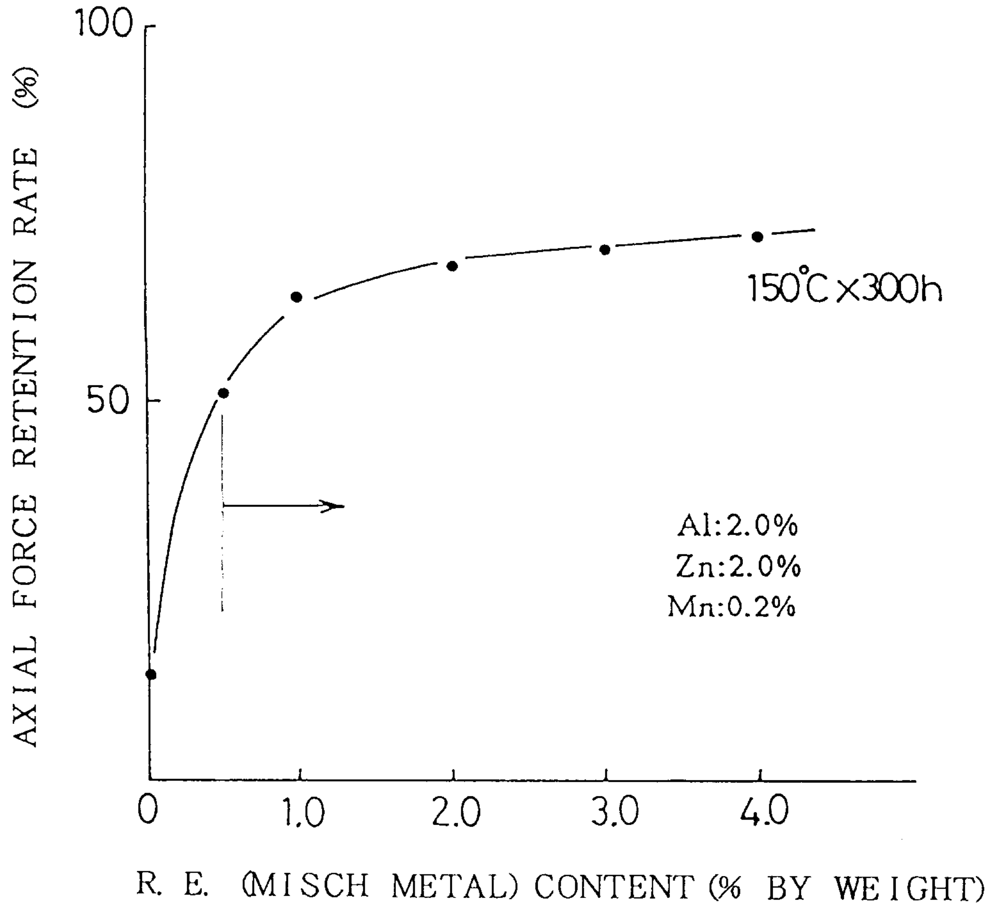

100
50
AXIAL FORCE RETENTION RATE (%)
150°C×300h
Al:2.0%
Zn:2.0%
Mn:0.2%
0
1.0
2.0
3.0
4.0
R. E. (MISCH METAL) CONTENT (% BY WEIGHT)

FIG. 7

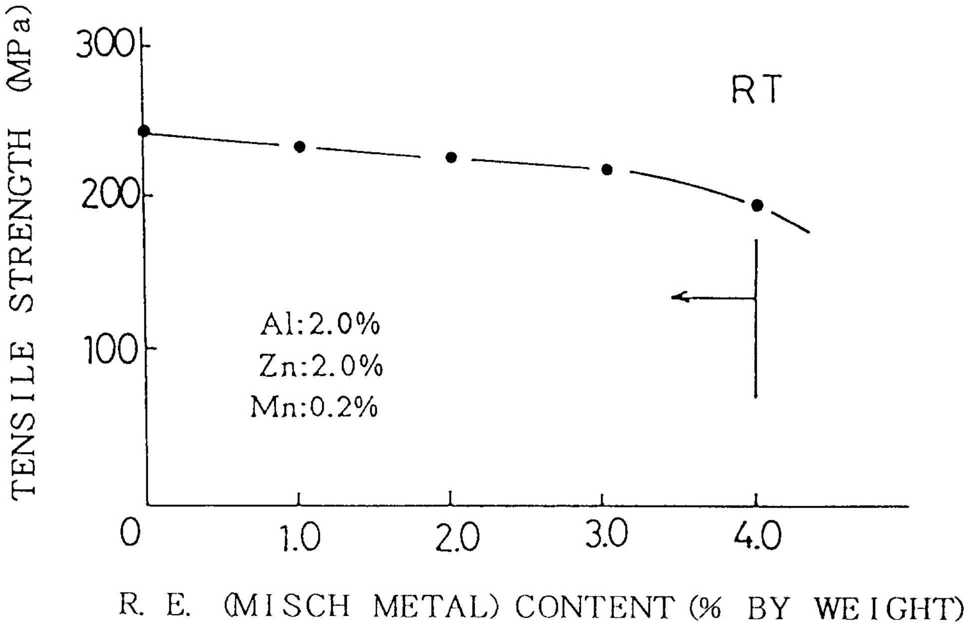

300
200
100
TENSILE STRENGTH (MPa)
RT
Al:2.0%
Zn:2.0%
Mn:0.2%
0
1.0
2.0
3.0
4.0
R. E. (MISCH METAL) CONTENT (% BY WEIGHT)

FIG. 8

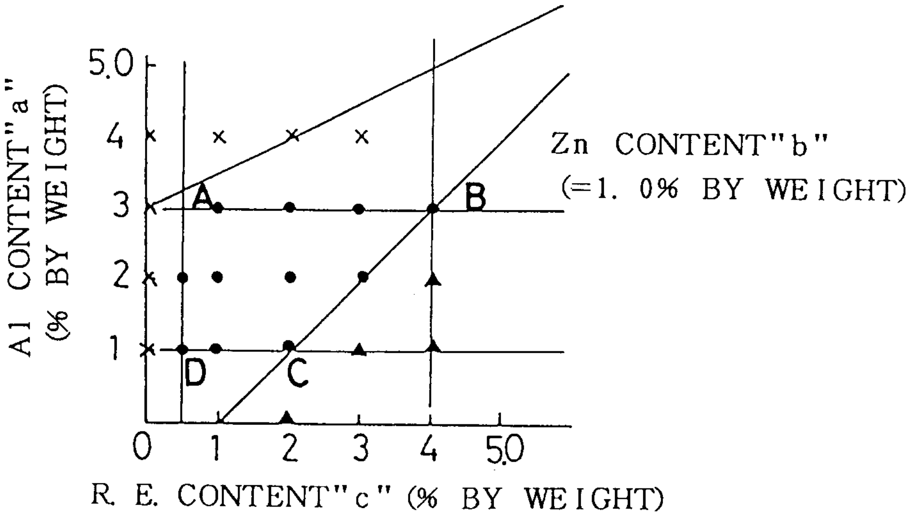


FIG. 9

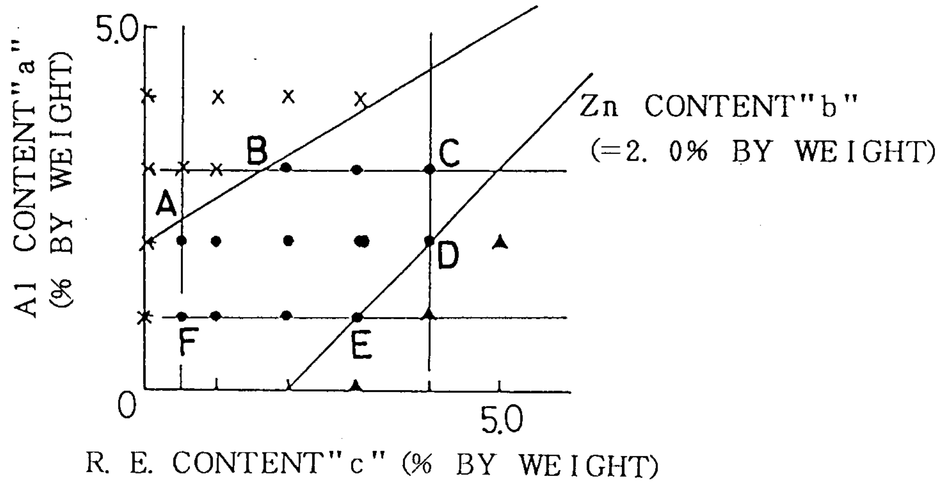


FIG. 10

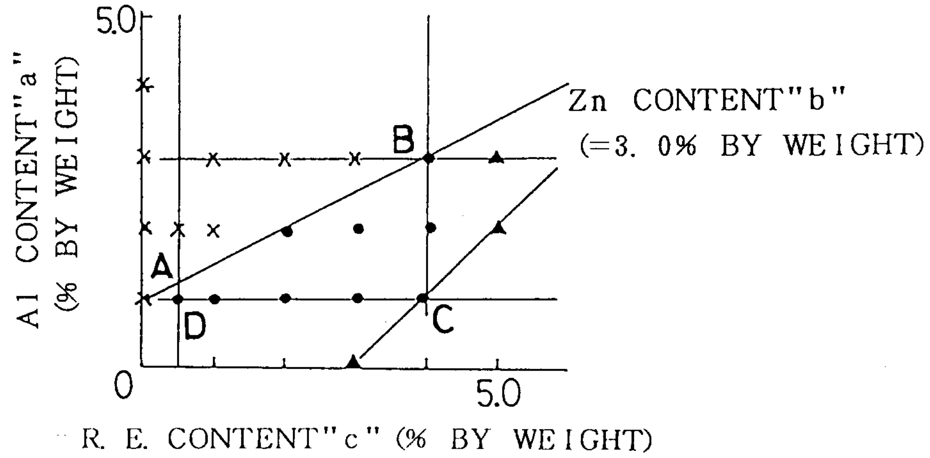


FIG. 11

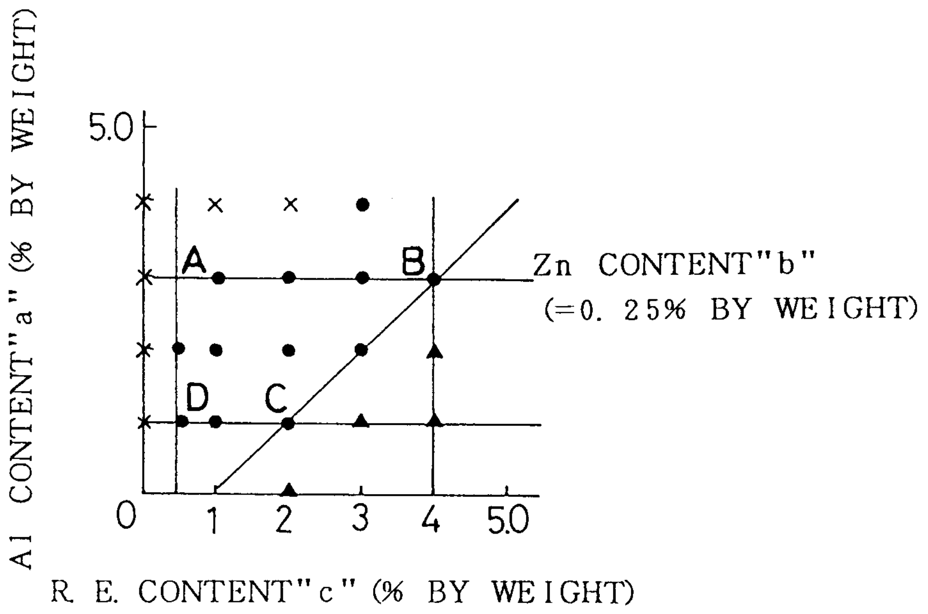
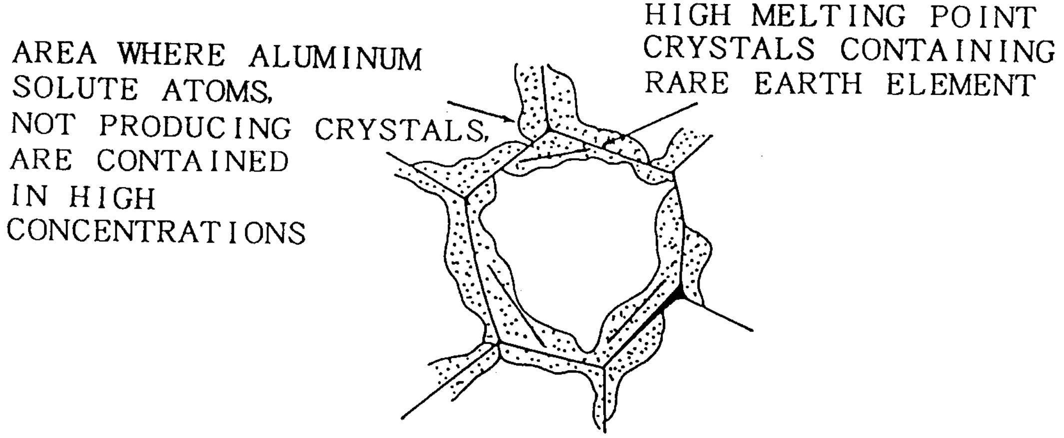
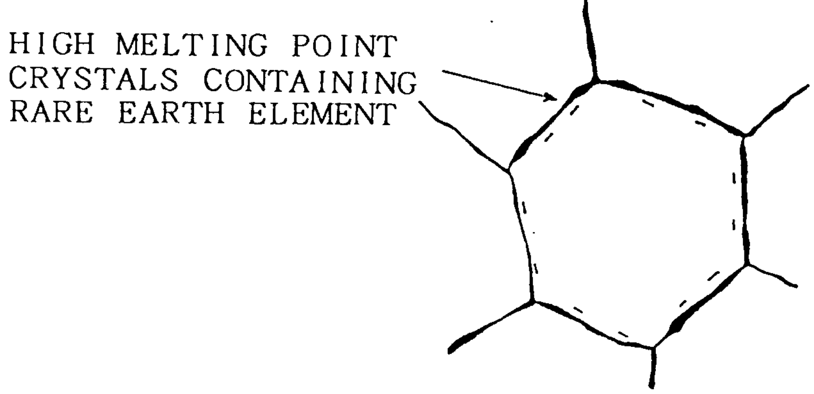

5.0
A
B
D
C
Zn CONTENT"b"
(=0. 25% BY WEIGHT)
0
1
2
3
4
5.0
Al CONTENT"a" (% BY WEIGHT)
R. E. CONTENT"c" (% BY WEIGHT)

FIG. 12



(Al:4% Zn:4% RE:2%)

FIG. 13



(Al:2% Zn:2% RE:3%)

FIG. 14

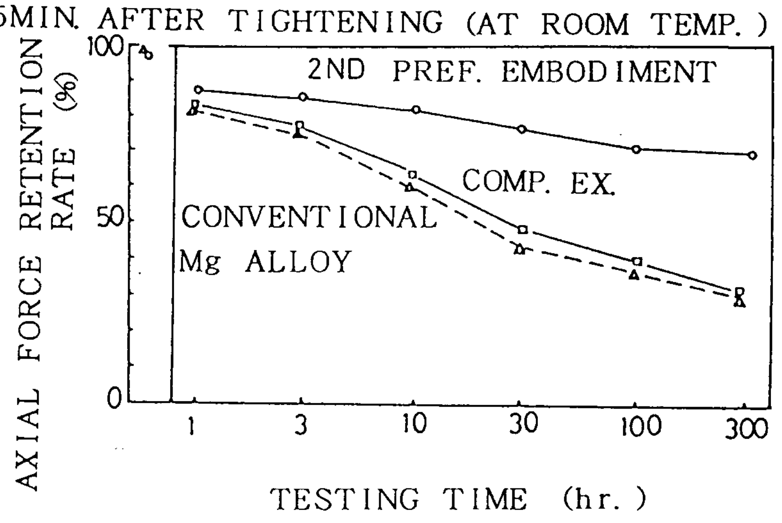


FIG. 15

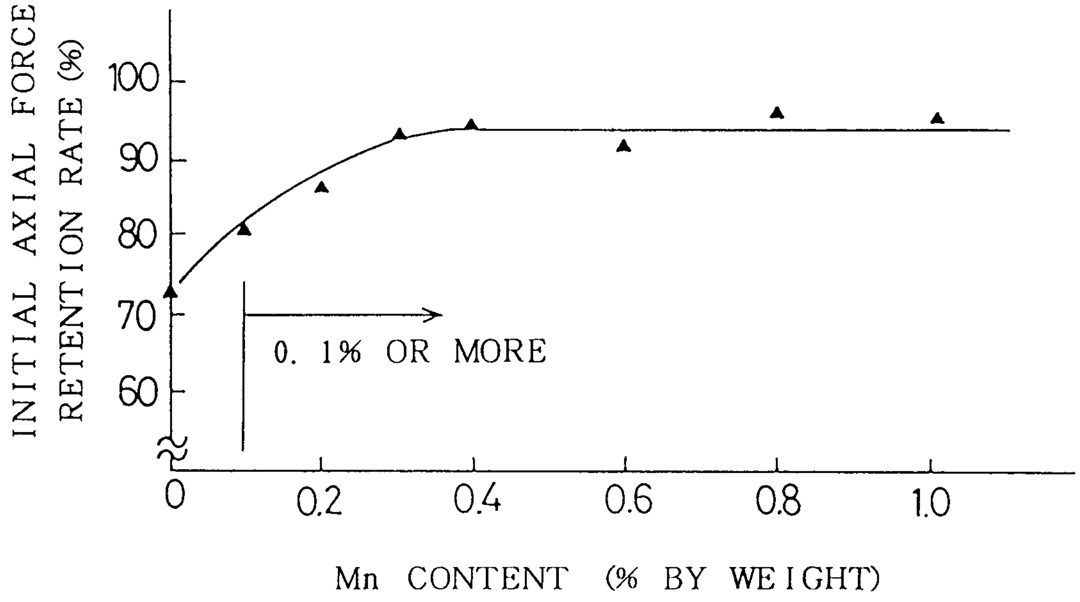

INITIAL AXIAL FORCE RETENTION RATE (%)
100
90
80
70
60
0. 1% OR MORE
0
0.2
0.4
0.6
0.8
1.0
Mn CONTENT (% BY WEIGHT)

FIG. 16

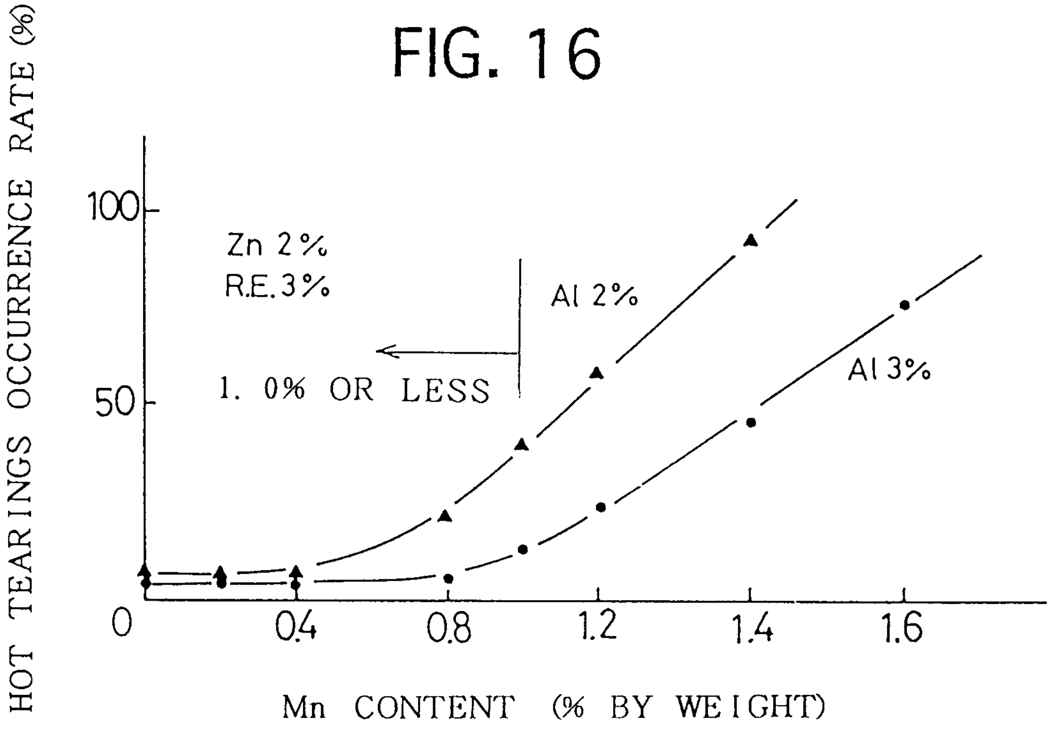
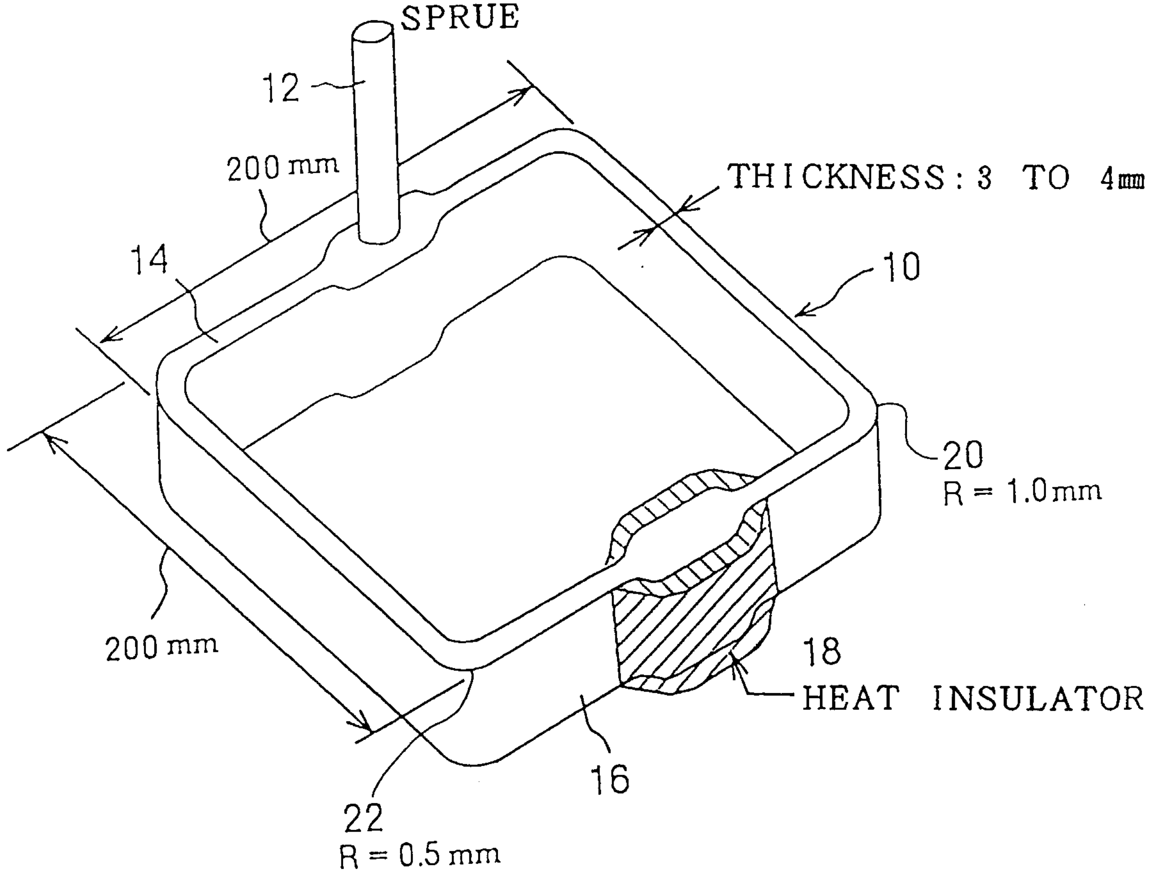

HOT TEARINGS OCCURRENCE RATE (%)
100
50
0
Zn 2%
R.E.3%
1. 0% OR LESS
Al 2%
Al 3%
0.4
0.8
1.2
1.4
1.6
Mn CONTENT (% BY WEIGHT)

FIG. 17


SPRUE
12
200 mm
14
THICKNESS : 3 TO 4mm
10
20
R = 1.0mm
200 mm
18
HEAT INSULATOR
16
22
R = 0.5 mm

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 10 8544

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 524 644 (TOYOTA JIDOSHA KK) 27 January 1993 *Page 5, line 17 - page 12, line 35, claims and Figures* ---	1,4-12	C22C23/00 C22C23/02 C22C23/04 C22C23/06
A	EP-A-0 470 599 (YOSHIDA KOGYO KK) 12 February 1992 *Table Nr. 17 and claims* ---	1-12	
A	US-A-5 139 077 (ALLIED-SIGNAL INC.) 18 August 1992 *Col.2, lines 1-9, col.3, lines 9-30, Table 1 and claims* -----	1-12	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C22C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	9 November 1994	Badcock, G

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document