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Method of manufacturing magnesium alloy products
Mg-Legierung Produkt und Verfahren zur Herstellung
Procédé de fabrication des produits d’alliage à base de Mg

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- EP-A- 0 799 901
- EP-A- 0 990 710

- WATANABE H. ET. AL.: "Grain size control of commercial wrought Mg-Al-Zn alloys utilizing dynamic recrystallization” MATERIALS TRANSACTION, vol. 42, no. 7, pages 1200-1205, XP009008613 ISSN: 1345-9678
- CHINO Y. ET. AL.: “Forging characteristics of AZ31 Mg alloys” MATERIALS TRANSACTION, vol. 42, no. 3, pages 414-417, XP001146689 ISSN: 1345-9678

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Description

[Industrial Field of the Invention]

[0001] The present invention relates to a method of manufacturing magnesium alloy products comprising casting a magnesium alloy and forging the thus obtained cast semifinished product into a desired figure.

[Related Art]

[0002] Since magnesium (Mg) has a specific gravity of 1.8 which is smaller than the specific gravity of 2.7 of aluminum (Al) as a typical light metal, magnesium alloys are extremely lightweight. In addition, magnesium alloys have higher specific modulus than the that of aluminum alloys and are excel in heat conductivity. Accordingly, magnesium alloys are widely used as materials for casings and parts of electric equipments and electronics devices.

[0003] Magnesium alloys have poor formability and are therefore hardly formed into desired figures. That is, magnesium alloys have small specific latent heat of solidification and are thus fast in solidification speed. Therefore, it is difficult to cast magnesium alloy so that defects such as porosities and flow lines may be easily created in obtained cast products. Especially on appearance-conscious products, the magnesium alloy has low yield ratio. Further, because puttying should be required for such defects, the manufacturing cost should increase. Magnesium alloys have hexagonal close-packed crystal structure and have therefore low ductility. Since the work of pressing or forging a plate or rod material should be conducted at a high temperature from 300 to 500 °C, there are problems such as low processing speed, the increased number of processes, die’s short life, and the like.

[0004] To solve the aforementioned problem of poor formability of magnesium alloys, the following method has been proposed in Japanese Unexamined Patent Publication No. H7-224344. That is, in a step forming billets by continuous casting of an AZ-type magnesium alloy containing 6.2 to 7.6 wt.% aluminum, the addition of miniaturization agent and/or the control of cooling speed makes the average grain size of 200 μm or less. The billets are then forged to manufacture large-size parts. Also disclosed in this publication is a method of making the average grain size smaller than 50 μm by a combination of solution treatment and the T6 heat treatment after formed into a final product figure, thereby improving the corrosion resistance.

[0005] On the other hand, the following method is proposed in Japanese Unexamined Patent Publication No. 2001-294966. That is, a magnesium alloy is injected by a die-cast or thixo molding machine to mold a plate. After rolling the plate at a normal temperature and giving a distortion to the plate, the plate is heated at a temperature from 350 to 400 °C to recrystallize the crystal structure to be miniaturized into small grains from 0.1 to 30 μm, thereby improving the ductility. By pressing or forging the obtained magnesium alloy plate having improved ductility, products formed in an arbitrary figure can be obtained. Further, in Japanese Unexamined Patent Publication Nos. 2001-170734 and 2001-170736, a method of forming a boss part having a thickness of seven times or ten times of that of a main part of a product by forging a magnesium alloy plate and a plurality of rough forging steps and finishing forging steps.

[0006] However, to manufacture parts having complex and accurate figure from magnesium alloy, the method as disclosed in Japanese Unexamined Patent Publication No. 7-224344 is insufficient. Because forming is conducted by forging billet, there are limitations on figure and thickness. On the other hand, the methods disclosed in Japanese Unexamined Patent Publication Nos. 2001-294966, 2001-170734, and 2001-170736 are also insufficient. Because the forming is made from a magnesium alloy plate, it is possible to make thin-walled parts but it is difficult to manufacture a product having complex and accurate figure by pressing and forging the plate.

[0007] In recent years, elucidation of mechanism of superplasticity has been developed with reference to magnesium alloys, as well as aluminum alloys, to the extent that there is now important possibility that magnesium alloys having miniaturized crystal grain size can be processed at high strain rate (see, for example, “Handbook of Magnesium Technology” P119-P125).

[0008] From document JP-A-2001294966 a method is known which comprises compressing and deforming an injection-molded magnesium alloy plate and a subsequent heat treatment step. The heat treatment is carried out after the deforming step.

[0009] From "Grain Size Control of Commercial Wrought Mg-Al-Zn Alloys Utilizing Dynamic Recrystallization", by H. Watanabe et al., Materials Transactions 2001, Vol. 42, No. 7, pp. 1200 - 1205 it is known that forging properties of magnesium alloys may be improved by dynamic recrystallization. According to this document, the dynamic recrystallization process is initiated by hot forging the material. The starting materials of this process are generally extruded materials. The initial material may further be annealed. The hot forging process is characterized by the Zener-Hollomon parameter.

[0010] Also from "Forging Characteristics of AZ31 Mg Alloy" by Y. Chino et al., Materials Transactions 2001, Vol. 42, No. 3, pp. 414 - 417, it is lanown that the forging properties of the magnesium alloy material are improved by hot forging the material.
[0011] From EP 0 990 710 A1 it is known to subject a magnesium alloy material to a heat treatment both before and after forging. According to this document, the initial grain sizes before the treatment are not greater than 300 μm. The forging according to this document has the purpose of shaping the material. Forging conditions for achieving a dynamic recrystallization are not specified.

[0012] To mold an alloy into a complex and accurate figure, it is generally preferable to employ casting method such as die casting with high injection speed, i.e. high filing speed. Since magnesium alloy is easily solidified as mentioned above, however, flow lines may be easily created when molded by die casting. In addition, in some figures, it is difficult to fill the magnesium alloy in every corner. Accordingly, there are limitations on size and thickness. As the injection speed is increased, air or gas may be easily entrapped in liquid alloy, thereby creating porosities and thus reducing the reliability of properties.

[0013] On the other hand, in case of pressing a plate, it is possible to manufacture products having a size equal to or less than the width of the plate. Since magnesium alloy has low ductility and poor formability, magnesium alloy is hardly formed into a complex figure, for example, it is difficult to form a boss as formed by the casting.

[0014] In viewpoint of alloy composition, the casting property and the elongation property of magnesium alloys are in contracting relationship. Preferably employed as the material to be cast are AZ91, AM50, AM60, and the like containing a larger amount of aluminum so as to have low melting temperature. On the other hand, preferably employed as the material to be pressed and forged are AZ21 containing a smaller amount of aluminum so as to have high ductility. The larger the aluminum content is, the higher the corrosion resistance is. Accordingly, AZ31 is poor in corrosion resistance as compared to AZ91. The poor corrosion resistance is one of reasons for limited application of AZ31.

[Problems to be resolved by the Invention]

[0015] The present invention was made under the aforementioned conventional circumstances and the object of the present invention is to provide a method of manufacturing magnesium alloy products comprising a combination of casting and forging for forming a magnesium alloy of which composition allows casting and which is excellent in forgeability, thereby achieving the manufacture of products, which have complex and accurate figure and exhibit high reliability of properties and enough corrosion resistance, at sufficiently high yield.

[Means to Solve the Problems]

[0016] According to the present invention, this object is achieved by a method of manufacturing magnesium alloy products as defined in claim 1. The dependent claims define preferred and advantageous embodiments of the invention. A method of manufacturing magnesium alloy products according to the invention, comprises steps of: casting of series AZ21, AZ31, AZ41, AZ51, and AZ61 using a die casting or a thixo molding method a magnesium alloy to obtain a cast semifinished product having crystal grain size not greater than 30 μm, subjecting the cast semifinished product to solution treatment at a temperature between the solid solution temperature and the solidus curve of the composition of the alloy, after that, forging the semifinished product under conditions of a strain rate and temperature which are set to have a value of the Zener-Hollomon parameter Z in the range from 10^9 to 10^{13}, to have a forged semifinished product having crystal grain size not greater than 10 μm, and further forging the forged semifinished product to have a desired figure.

[0017] As the cast semifinished product which is made to have crystal grain size not greater than 30 μm by casting is subjected to solution treatment, the crystal grains are enlarged, but second-phase grains which are formed during the casting and are large and fragile disappear, thereby increasing the elongation and thus improving the plastic formability. The cast semifinished product having the improved plastic formability attained by the solution treatment is forged. The dynamic recrystallization according to this forging miniaturizes the crystal grain size to be 10 μm or less, thereby further improving the forgeability. According to the invention, the cast semifinished product which is made to have crystal grain size not greater than 30 μm by casting is subjected to solution treatment, after that, is forged to have crystal grain size not greater than 10 μm, and is further forged into a desired figure.

[0018] In this method, the solution treatment is preferably conducted at a temperature between 380 and 440 °C for 1 to 24 hours and and the shaping forging is preferably conducted under conditions of a strain rate and temperature which are set to have a Z value in a range from 10^9 to 10^{13}.

[0019] It should be noted that the Z value is a temperature-compensating strain rate indicating the relation between temperature and strain rate and is so-called Zener-Hollomon Parameter defined by the following equation (1) as the relational expression for the dependence of temperature and strain rate on the flow stress:

\[ Z = \varepsilon' \exp \left( \frac{Q}{RT} \right) \]  

(1)

Wherein \( \varepsilon' \) : strain rate (sec^{-1})
Q : lattice diffusion activation energy
In the method of claim 1, first, a magnesium alloy of series AZ21, AZ31, AZ41, AZ51, and AZ61 is cast to obtain a cast semifinished product having crystal grain size not greater than 30 μm. Generally employed as the value of Q is a value of 135 kJoule/mol of pure magnesium because no Q value of magnesium alloys is obtained.

**Brief Explanation of the drawings**

**[0020]**

Fig. 1 is a graph showing crystal grain sizes of thixo molding cast articles (after solution treatment) in Example 1.

Figs. 2(a), 2(b) are graphs showing results of tensile strength tests of solution-treated articles at 300 °C and ε = 1.0 × 10⁻² s⁻¹ in Example 1.

Fig. 3 is a graph showing crystal grain sizes of die cast articles (before and after solution treatment) in Example 2.

**[Embodiments for carrying out the Invention]**

**[0021]** Hereinafter, embodiments of a method of manufacturing magnesium alloy products according to the present invention will be described.

**[0022]** First, an embodiment of the method of manufacturing magnesium alloy products of the invention will be described.

**[0023]** In the method of claim 1, first, a magnesium alloy of series AZ21, AZ31, AZ41, AZ51, and AZ61 is cast to obtain a cast semifinished product having crystal grain size not greater than 30 μm.

**[0024]** If the aluminum content of the magnesium alloy is less than 2 mass %, the corrosion resistance should be poor and the melting temperature is high so that it is not suitable for casting. If the aluminum content of the magnesium alloy is more than 10 mass %, it is impossible to obtain enough increase of plastic formability obtained by solution treatment as the following step and it is impossible to obtain products after solution treatment having excellent forgeability. Therefore, the aluminum content of the magnesium alloy is from 2 to 10 mass %, preferably, from 2.5 to 6 mass %.

**[0025]** For obtaining a cast product having crystal grain size not greater than 30 μm, a die casting method or a thixo molding method is employed because their cooling/solidification speed is relatively high and the crystal grains can be miniaturized. In gravity casting method, the obtained cast product has generally large thickness so that the solidification of melt magnesium alloy is slow. Therefore, crystals should grow during the cooling/solidification so as to have large crystal grain size to the extent of 200 μm. On the other hand, in the die casting method and the thixo molding method in which the alloy is injected in a die in the melt state or the semi-melt state, the cooling/solidification speed is fast so that crystal grains are miniaturized to have crystal grain size not greater than 30 μm.

**[0026]** Generally, the casting is conducted to have crystal grain size from 15 to 30 μm depending on the employed casting method and the composition of used alloy. The thus obtained cast product having crystal grain size not greater than 30 μm is then subjected to solution treatment.

**[0029]** The temperature of the solution treatment may be in a range between the solid solution temperature and the solidus curve of the composition of the used alloy and the suitable temperature is from 380 to 430 °C. When the temperature of the solution treatment is lower than the solid solution temperature or lower than 380 °C, huge compounds of aluminum and magnesium may be deposited, impairing the plastic formability. When the temperature of the solution treatment exceeds the solidus curve or 430 °C, liquid phase may be generated, thus impairing the plastic formability. The time period of the solution treatment is from 1 to 24 hours. It is preferable to increase the time period when the temperature is low and to decrease the time period when the temperature is high. By the solution treatment, β-phase deposited in crystal grain boundary of α-phase as the parent phase are dissolved in the parent phase, thereby enlarging crystal grains in the parent phase. However, because of decrease in β-phase grains impairing the grain boundary sliding in the plastic forming, effect improving the formability is obtained.

**[0030]** After the solution treatment, the semifinished product is forged to obtain a forged semifinished product having crystal grain size not greater than 10 μm (hereinafter, the forging for miniaturizing crystal grains will be sometimes referred to as “grain-miniaturizing forging”). The forged semifinished product is further forged for shaping the semifinished product into a desired figure, thereby obtaining a product (hereinafter, the forging for shaping a semifinished product into a desired figure will be sometimes referred to as “shaping forging”).

**[0031]** The grain-miniaturizing forging is conducted for miniaturizing crystal grains of cast semifinished product by
dynamic recrystallization. The grain-miniaturizing forging and the shaping forging should be conducted under conditions allowing forging process depending on the composition of magnesium alloy.

[0032] The conditions of the grain-miniaturizing forging depend on the composition of magnesium alloy. However, the conditions of strain rate and temperature for the grain-miniaturizing forging are set to have a Z value in a range from \(10^8\) to \(10^{13}\), preferably, in a range from \(10^{10}\) to \(10^{13}\).

[0033] The conditions of the forging shaping also depend on the composition of magnesium alloy. However, the conditions of strain rate and temperature for the shaping forging are preferably set to have a Z value of \(10^{13}\) or less, preferably in a range from \(10^8\) to \(10^{13}\), more preferably, in a range from \(10^9\) to \(10^{12}\).

[0034] In either of the grain-miniaturizing forging and the shaping forging, the forging conditions outside of the range of Z value may create defects such as cracks and splits, not allowing the forging.

[0035] Normally, the condition for conducting the grain-miniaturizing forging is determined according to the composition of the alloy to have a Z value in the suitable range within a range from \(10^{-3}\) to \(10^{-1}\) sec\(^{-1}\) of the strain rate and a range from \(200\) to \(500\) °C of the temperature. On the other hand, the condition for conducting the shaping forging is determined according to the composition of the alloy to have a Z value in the suitable range within a range from \(10^{-3}\) to \(10^{-1}\) sec\(^{-1}\) of the strain rate and a range from \(200\) to \(400\) °C of the temperature.

[0036] The crystal grains are miniaturized to have crystal grain size not greater than \(10\) μm by grain-miniaturizing forging, thereby improving the plastic formability as an effect of the forging, thus allowing the product to be subjected to the shaping forging. The crystal grain size not greater than \(10\) μm is allowed. Generally, the range of crystal grain sizes to be obtained by the grain-miniaturizing forging is from 1 to \(10\) μm.

[0037] Hereinafter, a further example of manufacturing magnesium alloy products will be described.

[0038] In this method first, a magnesium alloy of series AZ21, AZ31, AZ41, AZ51 and AZ61 is cast to obtain a cast semifinished product having crystal grain size not greater than \(10\) μm.

[0039] If the aluminum content of the magnesium alloy is less than \(2\) mass %, the corrosion resistance should be poor. If the aluminum content of the magnesium alloy is more than \(10\) mass %, it is impossible to obtain enough increase of plastic formability to be attained by solution treatment as the following step and it is impossible to obtain products after solution treatment having excellent forgeability. Therefore, the aluminum content of magnesium alloy is from \(2\) to \(10\) mass %, preferably, from \(2\) to \(6\) mass %.

[0040] The contents of materials other than aluminum in the magnesium alloy to be used are the same as those of the aforementioned method of claim 1.

[0041] Preferably employed are die casting method because its cooling/solidification speed is relatively high and the crystal grains can be significantly miniaturized.

[0042] The crystal grain size of the cast semifinished product is preferably smaller and may be \(10\) μm or less. Generally, the range of crystal grain size of the semifinished product obtained by the casting is from \(5\) to \(10\) μm.

[0043] The thus obtained cast semifinished product having crystal grain size not greater than \(10\) μm is then subjected to solution treatment at a temperature between the solid solution temperature and the solidus curve of the composition of the used alloy. Because of the same reasons of the solution treatment as the method of claim 1, the suitable temperature is from \(380\) to \(430\) °C and the suitable time period of the solution treatment is from \(1\) to \(24\) hours. After the solution treatment, the cast semifinished product is forged to obtain a product of a desired figure.

[0044] The forging should be conducted under conditions allowing forging process depending on the composition of magnesium alloy similarly to the forging processes of the method of claim 1.

[0045] The conditions of the forging depend on the composition of magnesium alloy. However, the conditions of strain rate and temperature for the forging are preferably set to have a Z value less than \(10^{13}\), more preferably in a range from \(10^6\) to \(10^{12}\). The Z value of \(10^{13}\) or more may create defects such as cracks and chaps, not allowing the forging.

[0046] In this case, the conditions for conducting the forging is determined according to the composition of the alloy to have a Z value in the suitable range within a range from \(10^{-3}\) to \(10^{-1}\) sec\(^{-1}\) of strain rate and a range from \(200\) to \(500\) °C of temperature.

[Examples]

[0047] The present invention will be further specifically described with reference to the following examples.

[0048] By using commercially available AZ91 alloy ingots, Mg alloy ingots used for the following examples were prepared by adding magnesium and zinc to the AZ91 alloy ingots and governing the qualities of the ingots. In this manner, Mg alloy ingots having compositions from AZ81 to AZ 21 were prepared. Table I shows results of componental analysis of the used AZ91 alloy ingot and prepared ingots.
Example I

(1) Casting and Solution Treatment

[0049] The ingots from AZ91 to AZ21 were ground to make chips for thixo molding. The chips were used in casting process. By using a thixo molding machine JMG-450 manufactured by the Japan Steel Works, Ltd., the injection speed was set at 4 m/sec that is the maximum under the idling condition and the die temperature was set at 250 °C. Under the conditions, cast articles of a box shape of 181 mm length \times 255 mm width \times 10 mm height having a bottom and no lid and 1.5 mm thickness were obtained. The casting process was conducted with finding a mold-allowing condition by controlling the temperature of a barrel and a nozzle of the molding machine because each ingot has each melting point. Table 2 shows the temperatures of the barrel tips during casting process of the respective alloys.

[0050] As a result, AZ91 through AZ31 were allowed to be cast. However, since the melting point of AZ21 was 645 °C that was over the heating limit of the barrel of the molding machine, AZ21 was not allowed to be cast. Therefore, the limit of AZ alloys allowing the casting by the thixo molding machine is 2.5% aluminum content.

[0051] To measure the crystal grain sizes of the cast articles obtained by the thixo molding casting, specimens were taken from middle portions of the respective articles and were embedded in resin and polished. After that, the specimens were etched by picric or acetic etching agent of which selection depends on the composition of the specimens. Electron micrographs of 500X of the respective specimens were taken. The crystal grain sizes were measured according to the section method of JIS G0522 "Ferritic Grain Size Test of Steel" and were expanded 1.74 times.

[0052] To check the effects attained by the solution treatment, the cast articles were subjected to heat treatment at 430 °C for 1 hour and, after that, the crystal grain size were measured again in the same manner.

[0053] The results are shown in Table 3 and Fig. 1.
As apparent from Table 3 and Fig. 1, while differences in crystal grain size according to the compositions were small before the solution treatment, the crystal grain size was enlarged by the solution treatment. This is attributed to the fact that the solution treatment makes $\beta$-phase existing at the grain boundaries to be resolved in $\alpha$-phase as parent phase so as to enlarge the crystal grains. It is believed that the crystal grain size is smaller as the speed of solidifying liquid alloy by quenching is higher. Therefore, the following results were obtained. That is, in the order from AZ91 to AZ31, the aluminum content decreases so that the melting point increases. Accordingly, the barrel temperature of the barrel tip of molding machine is raised. However, the quenching effect is created by temperature difference between the liquid alloy and the die. Therefore, AZ91 has crystal grain size of 28 $\mu$m, i.e. relatively large grain size, because of small temperature difference, while AZ51 has crystal grain size of 14 $\mu$m, i.e. relatively small grain size, because of large temperature difference. However, contrariwise, AZ41, ZA31 have grain size from 18 to 20 $\mu$m because cooling delay effect is attained in high-temperature liquid alloy.

To measure the plastic formability of the solution-treated articles, specimens were taken from the respective articles and were subjected to solution treatment at 420 °C for 1 hour. After that, the tensile tests were made at 300 °C at strain rate $1.0 \times 10^{-2}$ sec$^{-1}$. The results are shown in Figs. 2(a), 2(b).

As apparent from Figs. 2(a), 2(b), AZ91 through AZ71 as aluminum-rich alloys have lower elongation from 15 to 24%, while AZ61 through AZ31 have elongation of 40% or more, significantly improving the plastic formability.

Therefore, the aluminum content of cast article to be forged is equal to or more than 25 mass % in view of castability and equal to or less than 6 mass % in view of plastic formability.

In the above (1), the cast articles of AZ61 through AZ31 cast by thixo molding were subjected to solution treatment at 420 °C for 1 hour. After that, samples of 20 mm $\times$ 20 mm were taken out. Each specimen was heated uniformly by an electric furnace and put on a mold which was held at a predetermined forging temperature shown in Table 4. The forging was conducted under a fixed condition of strain rate of $3.3 \times 10^{-2}$ sec$^{-1}$. Specimens were cut and taken from the samples after the forging. For the specimens, the measurement of crystal grain size was carried out in the same manner as the above (1). $Z$ values obtained by substituting the aforementioned strain rates in the aforementioned equation (1) are shown in Table 1. The value for $Q$ in this equation was 135Kjoule/mol. Table 4 also shows crystal grain sizes of the respective samples before forging process (after solution treatment).
The following are apparent from Table 4.

That is, it is found that, at the same temperature, larger amount of aluminum content of the alloy facilitates the miniaturization of crystals by forging. On the other hand, as for the aluminum-rich alloys, cracks were created during forging when the temperature was low. In the strain rate tests, the forging of AZ61 was allowed at 300 °C or more, while the forging of AZ31 was allowed even at 200 °C, obtaining effect of crystal grain miniaturization.

As a result, in case of AZ61 through AZ31, the forging conditions for miniaturizing crystal grain size to be 10 μm or less allowing superplasticity forging are Z value ranging from $10^9$ to $10^{13}$, preferably from $10^{10}$ to $10^{13}$.

Samples in which crystal grain miniaturization by the aforementioned forging was sufficient and samples in which crystal grain miniaturization was insufficient were selected. Plate-like specimens of 20 mm × 20 mm × 1.5 mm thickness were cut and taken from these selected samples. Each specimen was inserted into a cavity of 20 mm × 2 mm as a drag of a casting mold. Each specimin was forged under conditions shown in Table 5 until the true strain reaches -1.1 by using a cope having a cylindrical concave of 3 mm diameter and 10 mm height and was formed into a boss shape. The respective forgeabilities during the forging process were evaluated. The evaluation results are shown in Table 5.

### MINIATURIZING OF CRYSTAL GRAINS BY FORGING

<table>
<thead>
<tr>
<th>FORGING CONDITION</th>
<th>CRystal Grain Size (μm) AFTER FORGING</th>
<th>SOLUTION TREATMENT (BEFORE FORGING)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FORGING TEMPERATURE (°C)</td>
<td>150</td>
<td>200</td>
</tr>
<tr>
<td>STRAIN RATE (sec⁻¹)</td>
<td>3.3×10⁻²</td>
<td>3.3×10⁻²</td>
</tr>
<tr>
<td>Z VALUE</td>
<td>1.5×10¹⁵</td>
<td>2.7×10¹³</td>
</tr>
<tr>
<td>AZ61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AZ51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AZ41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AZ31</td>
<td></td>
<td></td>
</tr>
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</table>

1. Sample cracked during forging, not allowing the forging.

[0059] The following are apparent from Table 4.

[0060] That is, it is found that, at the same temperature, larger amount of aluminum content of the alloy facilitates the miniaturization of crystals by forging. On the other hand, as for the aluminum-rich alloys, cracks were created during forging when the temperature was low. In the strain rate tests, the forging of AZ61 was allowed at 300 °C or more, while the forging of AZ31 was allowed even at 200 °C, obtaining effect of crystal grain miniaturization.

[0061] As a result, in case of AZ61 through AZ31, the forging conditions for miniaturizing crystal grain size to be 10 μm or less allowing superplasticity forging are Z value ranging from $10^9$ to $10^{13}$, preferably from $10^{10}$ to $10^{13}$.

[0062] Samples in which crystal grain miniaturization by the aforementioned forging was sufficient and samples in which crystal grain miniaturization was insufficient were selected. Plate-like specimens of 20 mm × 20 mm × 1.5 mm thickness were cut and taken from these selected samples. Each specimen was inserted into a cavity of 20 mm × 20 mm as a drag of a casting mold. Each specimin was forged under conditions shown in Table 5 until the true strain reaches -1.1 by using a cope having a cylindrical concave of 3 mm diameter and 10 mm height and was formed into a boss shape. The respective forgeabilities during the forging process were evaluated. The evaluation results are shown in Table 5.
The following are apparent from Table 5.

Alloys, containing larger amount of aluminum in which β-phase is easily deposited at grain boundaries so as to easily impair the grain boundary sliding, should require higher processing temperature, that is, higher Z value to form boss. On the other hand, even when the crystal grain size exceeds 10 μm, some alloys are allowed to form boss by setting the temperature high.

However, from the industrial point of view, the mold temperature of 400 °C or more impairs the durability of mold so that it is not practical. It is possible to improve the heat resistivity of the mold by applying heat resistance material or treating the surface. However, since the cost of the mold is increased, it is not preferable.

### Table 5

**FORGEABILITIES OF THIXO MOLDING CAST ARTICLES**

<table>
<thead>
<tr>
<th>FORGING CONDITION</th>
<th>FORGING TEMPERATURE (°C)</th>
<th>150</th>
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<th>300</th>
<th>350</th>
<th>400</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filling condition</td>
<td>STRAIN RATE (sec⁻¹)</td>
<td>3.3×10⁻²</td>
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<td>3.3×10⁻²</td>
<td>3.3×10⁻²</td>
<td>3.3×10⁻²</td>
<td>3.3×10⁻²</td>
</tr>
<tr>
<td>Z VALUE</td>
<td></td>
<td>1.5×10¹⁵</td>
<td>2.7×10¹³</td>
<td>6.7×10¹⁰</td>
<td>6.9×10⁹</td>
<td>9.9×10⁸</td>
<td>4.4×10⁷</td>
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<tr>
<td>AZ61</td>
<td>6.1 *1</td>
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</table>

*1 Crystal grain size after forging for miniaturizing crystal grains (value shown in Table 4)

*2 Evaluation of forgeability

○: No defects were created after forging, i.e. complete formation of boss

■: Fine cracks were created after forging, i.e. incomplete formation of boss

×: Serious cracks were created after forging

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[0063] The following are apparent from Table 5.

[0064] Alloys, containing larger amount of aluminum in which β-phase is easily deposited at grain boundaries so as to easily impair the grain boundary sliding, should require higher processing temperature, that is, higher Z value to form boss. On the other hand, even when the crystal grain size exceeds 10 μm, some alloys are allowed to form boss by setting the temperature high.

[0065] However, from the industrial point of view, the mold temperature of 400 °C or more impairs the durability of mold so that it is not practical. It is possible to improve the heat resistivity of the mold by applying heat resistance material or treating the surface. However, since the cost of the mold is increased, it is not preferable.
It is found from the results that, in case of AZ61 through AZ31, the forging condition for forming alloy into a desired figure is a Z value of $10^{13}$ or less, preferably in a range from $10^8$ to $10^{13}$.

Example 2

(1) Casting and Solution Treatment

Casting tests were conducted in the die casting method instead of thixo molding of Example 1. Die having the same shape as that for the thixo molding was used. Used alloys were ingots of the same batch as those used for the thixo molding machine, but not processed to be chips. By using a cold chamber die casting machine DC650tCLS available from Toshiba Machine Co., Ltd., articles were sequentially formed by casting under conditions that the temperature of liquid alloy was 700°C, the injection speed was set at 5.0 m/sec at the highest, and the die temperature was set at 250°C. The cast articles had the same size and shape as those of Example 1.

Even AZ21, impossible to be cast by the thixo molding method, could be cast by the die casting method. This is attributed to the fact that the material was melted by a metal heater provided separately from the casting machine, unlike the thixo molding machine in which material is melted in the barrel provided therein, so that the melting temperature could be raised to 700°C, thereby melting even AZ21 of which melting temperature was high.

As for the respective articles, the crystal grain sizes after solution treatment were measured in the same manner as that of Example 1 and the results are shown in Table 6 and Fig. 3. It should be noted that the solution treatment was conducted at 430°C for 1 hour.

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>CRYSTAL GRAIN SIZE (µm)</th>
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<tr>
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<td>BEFORE SOLUTION TREATMENT</td>
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<tr>
<td>AZ91</td>
<td>7.3</td>
</tr>
<tr>
<td>AZ81</td>
<td>6.4</td>
</tr>
<tr>
<td>AZ71</td>
<td>7.0</td>
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<td>AZ61</td>
<td>7.8</td>
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<tr>
<td>AZ51</td>
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<td>5.7</td>
</tr>
<tr>
<td>AZ21</td>
<td>5.8</td>
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</table>

As apparent from Table 6 and Fig. 3, the crystal grain sizes of the die cast articles were smaller than the crystal grain sizes of the thixo molding cast articles. Even before the solution treatment, the crystal grain sizes were below 10 µm so that the grain-miniaturizing forging is not required. This is attributed to the fact that the cooling effect could be attained because the molding machine was so fast in filling speed.

(2) Forging

Since the obtained cast articles already had fine crystal grains, casting was conducted under the same conditions as those for grain-miniaturizing forging which had been conducted for the thixo molding articles in Example 1. For giving indication of forgeability of the respective cast articles, it was checked whether cracks were formed or not. As for the samples before the solution treatment, preliminary forging tests were conducted with the result that cracks were easily formed. This may be because the β-phase was thick so that the grain boundary sliding was hardly occurred. This tendency was enhanced as the aluminum content increased. Therefore, only for the samples after solution treatment, tests were conducted. The results are shown in Table 7. The tests were conducted with plate-like specimens of 20 mm × 20 mm × 1.5 mm thickness which were cut and taken from these samples. Each specimen was forged at a constant strain rate. The true strain for the forging was -1.1.
The following are apparent from Table 7.

That is, similar to the samples before the solution treatment, the higher the aluminum content was, the worse the forgeability was. Under condition of strain rate of $3.3 \times 10^{-2}$, AZ91 through AZ71 created serious cracks during forging even when the processing temperature was raised to 350 °C. On the other hand, the lower the aluminum content was, the better the forgeability was. Accordingly, AZ91 created serious cracks at any temperature, AZ81 created no serious cracks but fine cracks when forged at a temperature of 300 °C or more (that is, when $Z$ value was below $6.7 \times 10^{10}$), and AZ71 created no serious cracks but created fine cracks when forged at a temperature of 250 °C or more (that is, when $Z$ value was below $1.0 \times 10^{12}$).

With reduced aluminum content, casting was conducted without cracks so that AZ61, AZ51, and AZ41 created no defects when forged at a temperature of 250 °C or more (that is, when $Z$ value was below $1.0 \times 10^{12}$), and AZ31 and AZ21 created no defects when forged at a temperature of 200 °C or more (that is, when $Z$ value was below $1.0 \times 10^{13}$). In these ranges, excellent forgeabilities were exhibited.

It is found from the results that composition suitable for forging alloy cast to have crystal grain size not greater than 10 μm is aluminum content ranging from 2 to 6 mass % corresponding to magnesium alloy of series AZ21, AZ31,
AZ41, AZ51 and AZ61 and the forging condition is a Z value of $1.0 \times 10^{13}$ or less.

**[Effects of the Invention]**

As described in the above, according to the method of manufacturing magnesium alloy products of the present invention, a combination of casting and forging is employed for forming magnesium alloy of which composition allows casting and which is excellent in forgeability, thereby achieving the manufacture of products, which have complex and accurate figure and exhibit high reliability of properties and enough corrosion resistance, at sufficiently high yield ratio.

**Claims**

1. A method of manufacturing magnesium alloy products comprising the steps of:

   casting a magnesium alloy of series AZ21, AZ31, AZ41, AZ51, and AZ61 using a die casting or a thixo molding method to obtain a cast semifinished product having crystal grain size not greater than 30 $\mu$m,

   subjecting the cast semifinished product to solution treatment at a temperature between the solid solution temperature and the solidus curve of the composition of the magnesium alloy,

   after that, forging the semifinished product under conditions of a strain rate and temperature which are set to have a value of the Zener-Hollomon parameter $Z$ in a range from $10^9$ to $10^{13}$, to obtain a crystal-grain miniaturized forged semifinished product having crystal grain size not greater than 10 $\mu$m, and

   further forging the forged semifinished product to have a desired figure.

2. A method of manufacturing magnesium alloy products as claimed in claim 1, wherein the solution treatment is conducted at a temperature between 380 and 440 °C for 1 to 24 hours.

3. A method of manufacturing magnesium alloy products as claimed in claim 1 or 2, wherein the crystal grain-miniaturized forged semifinished product is forged under conditions of a strain rate and temperature which are set to have a value of the Zener-Hollomon parameter $Z$ of $10^{13}$ or less, to have a desired figure.

**Patentansprüche**

1. Verfahren zur Herstellung von Magnesiumlegierungsprodukten, das die folgenden Stufen umfasst:

   Gießen einer Magnesiumlegierung der Reihen AZ21, AZ31, AZ41, AZ51 und AZ61 unter Verwendung eines Druckguß- oder eines Thixoformverfahrens, um ein gegossenes Halbfertigprodukt mit einer Kristallkorngröße von nicht größer als 30 $\mu$m zu erhalten,

   Unterziehen des gegossenen Halbfertigprodukts einer Lösungsbehandlung bei einer Temperatur zwischen der Temperatur einer festen Lösung und der Soliduskurve der Zusammensetzung der Magnesiumlegierung,

   danach Schmieden des Halbfertigprodukts unter Bedingungen einer Formänderungsgeschwindigkeit und einer Temperatur, die so eingestellt sind, dass ein Wert des Zener-Hollomon-Parameters $Z$ in einem Bereich von $10^9$ bis $10^{13}$ erhalten wird, um ein geschmiedetes Halbfertigprodukt mit verkleinertem Kristallkorn und einer Kristallkorngröße von nicht größer als 10 $\mu$m zu erhalten, und

   weiteres Schmieden des geschmiedeten Halbfertigprodukts, um eine gewünschte Gestalt zu erhalten.

2. Verfahren zur Herstellung von Magnesiumlegierungsprodukten nach Anspruch 1, wobei die Lösungsbehandlung bei einer Temperatur zwischen 380 und 440 °C 1 bis 24 Stunden lang durchgeführt wird.

3. Verfahren zur Herstellung von Magnesiumlegierungsprodukten nach Anspruch 1 oder 2, wobei das geschmiedete Halbfertigprodukt mit verkleinertem Kristallkorn unter Bedingungen einer Formänderungsgeschwindigkeit und einer Temperatur geschmiedet wird, die so eingestellt sind, dass ein Wert des Zener-Hollomon-Parameters $Z$ von $10^{13}$ oder weniger erhalten wird, um eine gewünschte Gestalt zu erhalten.

**Revendications**

1. Procédé de fabrication de produits en alliage de magnésium comprenant les étapes de:
EP 1 347 074 B1

- mouluer un alliage de magnésium de la série AZ21, AZ31, AZ41, AZ51 et AZ61 à l’aide d’un procédé de coulage sous pression ou de moulage thixo pour obtenir un produit moulé semi-fini ayant une dimension de grain de cristal pas plus grande que 30 µm.
- soumettre le produit moulé semi-fini à un traitement par une solution à une température entre la température de solution solide et la courbe de solidus de la composition de l’alliage de magnésium.
- après quoi, forger le produit semi-fini sous des conditions de contrainte et de température qui sont déterminées pour avoir une valeur de paramètre Z de Zener-Hollomon dans la gamme allant de $10^9$ à $10^{13}$, pour obtenir un produit semi-fini forgé à grain de cristal miniaturisé, ayant une dimension de grain de cristal pas plus grande que 10 µm, et
- forger encore le produit semi-fini pour obtenir la forme souhaitée.

2. **Procédé de fabrication de produits en alliage de magnésium selon la revendication 1, dans lequel le traitement par solution est effectué a une température comprise entre 380 et 440° C pendant 1 à 24 heures.**

3. **Procédé de fabrication de produits en alliage de magnésium selon l’une des revendications 1 ou 2, dans lequel le produit semi-fini forgé à grain de cristal miniaturisé est forgé sous des conditions de taux de contrainte et de température qui sont déterminées pour avoir une valeur du paramètre Z de Zener-Hollomon de $10^{13}$ ou moins, pour avoir la forme souhaitée.**
Fig. 1
Fig. 2
Fig. 3