



(19)

Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

EP 0 892 074 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
20.01.1999 Bulletin 1999/03

(51) Int. Cl.<sup>6</sup>: C22C 1/00, C23C 4/08,  
B22D 21/00

(21) Application number: 98113061.0

(22) Date of filing: 14.07.1998

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE  
Designated Extension States:  
AL LT LV MK RO SI

(30) Priority: 17.07.1997 JP 192261/97

(71) Applicant:  
Matsushita Electric Industrial Co., Ltd.  
Kadoma-shi, Osaka-fu, 571-8501 (JP)

(72) Inventors:  
• Nishikawa, Yukio  
Ikeda City 563-032 (JP)

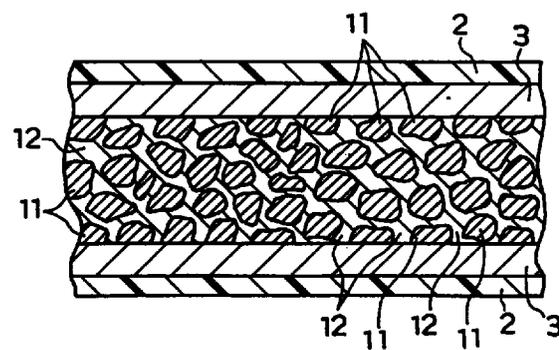
• Inoue, Takao  
Hirakata City 573-0165 (JP)  
• Taguchi, Tatsuhisa  
Katano-City 576-0051 (JP)  
• Shikata, Naohiro  
Toyono-gun, Osaka Pref. 563-0214 (JP)  
• Kondou, Yoshiaki  
Amagasaki City 661-0012 (JP)

(74) Representative:  
Dr. Elisabeth Jung  
Dr. Jürgen Schirdewahn  
Dipl.-Ing. Claus Gernhardt  
Clemensstrasse 30  
80803 München (DE)

(54) **Magnesium alloy molded product and method for producing the same**

(57) A light weight magnesium alloy molded product excellent in anti-corrosion property which makes use of a magnesium alloy capable of easily decomposing in soil is disclosed. The molded product comprises: a magnesium-aluminum alloy molded sheet containing 4 to 12 wt% of aluminum in an average alloy composition, and having an Al-poor region of grains with particle diameter of not less than 200  $\mu\text{m}$ , where Mg-content is higher than that of the average alloy composition, and Al-rich region, where Al-content is higher than that of the average composition, surrounding the grains of the Al-poor region, and a resin coating film (2) covering the surface of the molded sheet. A metal thin layer (3) composed of Al or its alloy is optionally formed between the molded sheet and the resin coating film (2).

FIG. 2



EP 0 892 074 A1

## Description

### BACKGROUND OF THE INVENTION

The present invention relates to a magnesium alloy molded product of magnesium-aluminum (Mg-Al) alloy used in exterior housings for household electric appliances and the like, and a method for producing the same.

In recent years, materials which are harmless during service and after being discarded as well as at disposal by burning, and which, after discarding, can be easily decomposed in soil are eagerly desired in viewpoints of preserving or protecting environment, for substituting the plastic products which have been widely used. For searching such materials, investigations have been conducted on an application of magnesium alloy which are light in weight and can be decomposed easily in soil.

Melting point of metallic magnesium is 650°C, and since the most of the magnesium alloys have a low melting point of 600°C or lower and thus the magnesium alloys can be molded by injection molding similar to the case of a synthetic resin, and it is thus possible to manufacture and supply injection molded products of complicated or intricated shapes.

The magnesium alloy of this kind however has a low anti-corrosion property in general and even with a normal protective paint layer, a product of the alloy cannot have an anti-corrosion property lasting for long-term. For ensuring the desired anti-corrosion property, the molded product has heretofore been usually treated with chromic acid (chromating), thereby to form a dense film of chromium oxide which is chemically stable on the whole surface of the molded product. The chromating process requires the steps of degreasing by a treatment with a weak alkaline solution, washing with hot water, descaling by an acid washing, washing with water, the treatment with chromic acid, another washing with water, and so on.

The above-mentioned surface treatment for improving the anti-corrosion property however has problems in that the chromic acid solution contains a substance demonstrating an acute toxicity and an equipment for the treatment costs much by the required countermeasure for environment protection around the periphery of the equipment involved. In addition, it costs much for the surface treatment if the process includes a number of steps for forming a plurality of painted layers and the like.

Under such circumstances, investigations have been conducted on processes for superseding the chromating process. For instance, a method for ensuring the anti-corrosion property by providing a metal layer free from pinholes on the surface of the magnesium alloy has been proposed (Japanese Patent Publication (Tokko Hei) 5-88,303). This process comprises first forming a metal film layer, for instance, an aluminum film

on the magnesium alloy molded sheet, and then applying a hydrostatic pressure on it simultaneous with heating, thereby to seal the pinholes which are responsible for reducing the anti-corrosion property at least in the vicinity of the interface between the magnesium alloy molded sheet and the metal film layer. For performing this process, a large-scale pressure applying equipment which can withstand high temperature is required for exerting a high pressure of not less than 700 kgf/cm<sup>2</sup> at 400°C, and a long time is required for the steps, and therefor cost-increase is not avoidable.

Separate from this, an investigation has also been conducted on an improvement of the anti-corrosion property of the magnesium alloy itself. For instance, a method for improving the anti-corrosion property by forming, for instance,  $\alpha$ -phase and  $\beta$ -phase in a laminated structure, and another method for dispersing particles with a particle diameter of not larger than 10  $\mu$ m of the  $\alpha$ -phase in the  $\beta$ -phase precipitate (Mg<sub>17</sub>Al<sub>12</sub>) surrounding the particles in an equilibrium state are proposed (Japanese Laid-Open Patent Publication (Tokkai Hei) 5-78,775).

Any of these methods intends to ensure the anti-corrosion property of the molded sheet as a whole by stopping growth of a corrosion nucleus generated at the  $\alpha$ -phase and development of the corrosion nucleus with an intermetallic compound of  $\beta$ -phase having a high anti-corrosion property.

The former method however involves a modification of the once molded sheet into a layered pearlite structure by a liquefying treatment and an aging treatment. The method requires a large-scale thermal treating equipment and the liquefying treatment process performed at not less than 400°C takes as long as 10 hours, and thus involves a high manufacturing cost.

Since the latter method involves dispersing the  $\beta$ -phase precipitate in the equilibrium state, it is believed that, in a case where the thickness of the molded sheet is small and not thicker than 5 mm, and the cooling speed at the injection molding process becomes as large as 10<sup>4</sup> °C/sec. or larger, the alloy becomes a supersaturated solid solution, thereby to reduce the anti-corrosion property of the molded sheet.

### BRIEF SUMMARY OF THE INVENTION

In view of the above-mentioned problems, an object of the present invention is to provide a magnesium alloy molded product having a satisfactory anti-corrosion property with the treatment of low cost which entails no harmful substances.

Another object of the present invention is to provide a method for producing such magnesium alloy molded product.

The present invention provides a magnesium alloy molded product comprising:

a magnesium-aluminum alloy molded sheet con-

taining 4 to 12 wt% of aluminum in its average alloy composition, and having an Al-poor region of grains with particle diameter of not less than 200  $\mu\text{m}$ , where Mg-content is higher than that of the average alloy composition, and Al-rich region, where Al-content is higher than that of the average alloy composition, surrounding the grains of the Al-poor region, and

a resin coating film covering the surface of said molded sheet.

The present invention also provides a method for producing magnesium alloy molded product comprising the steps of:

heating a magnesium-aluminum alloy containing 4 to 12 wt% of aluminum to a temperature exceeding at least the solidus temperature of the alloy, exerting a shearing force which is sufficient for breaking at least portion of the dendritic structure of the alloy on said heated alloy in a screw extruder, at a temperature higher than the solidus temperature and lower than the liquidus temperature of the alloy, thereby to create a liquid-solid alloy composition, injecting said liquid-solid alloy composition into a cavity formed between metal dies, thereby to obtain a molded sheet, applying a resin paint on the surface of said molded sheet released from the metal dies, thereby to form a layer of resin coating film, and subjecting said resin coating film to a thermal treatment, thereby to cure the resin coating film.

In a preferred mode of the present invention, the above-mentioned molded sheet has a thickness of 0.3 to 3 mm.

In another preferred mode of the present invention, the above-mentioned resin coating film is transparent, and the method comprises a step of mechanically working the surface of the molded sheet, thereby to prevent a metallic luster surface, prior to the above-mentioned step of applying the resin paint.

In still another preferred mode of the present invention, a metal thin layer having a higher anti-corrosion property than that of the above-mentioned molded sheet is interposed between the above-mentioned molded sheet and the above-mentioned resin coating film.

It is preferable that the above-mentioned metal thin film comprises Al or its alloy.

A preferred method for forming the metal thin film composed of Al or its alloy is a process of thermally spraying Al or its alloy on the surface of the above-mentioned molded sheet.

Another preferred method for forming the metal thin film composed of Al or its alloy is a process of forming a metal thin film on the surface of the above-mentioned molded sheet in a vacuum vessel of a thin film-forming

equipment.

In any method, it is preferable to mechanically work the surface of the above-mentioned molded sheet prior to the formation of the metal thin film.

In a preferred mode of the present invention, the above-mentioned resin film is transparent, and the method comprises a step of mechanically working the above-mentioned metal thin film, thereby to present a metallic luster surface, prior to the above-mentioned step of applying the resin paint.

A preferred magnesium-aluminum alloy used in the present invention comprises 4 to 12 wt% of Al, not more than 2 wt% of Zn, and Mg for the rest.

In a preferred mode of embodying the present invention, the method further comprises a step of preparing the above-mentioned magnesium-aluminum alloy, and the step comprises the steps of:

exerting a plastic deformation on the above-mentioned alloy to an extent of not less than a rupture elongation of the alloy, thereby to produce tips of the alloy, and selecting the ruptured tips by the predetermined sizes.

While the novel features of the invention are set forth particularly in the appended claims, the invention, both as to organization and content, will be better understood and appreciated, along with other objects and features thereof, from the following detailed description taken in conjunction with the drawings.

#### BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

FIG. 1 is a schematic view of a cross-section of the magnesium alloy molded product in accordance with an embodiment of the present invention.

FIG. 2 is a schematic view of a cross-section of the magnesium alloy molded product in accordance with another embodiment of the present invention.

FIG. 3A is a schematic view of a microstructure of the magnesium alloy molded sheet in a casting die at the cross-section, for illustrating a process of casting the alloy by an injection molding.

FIG. 3B is a schematic view of a microstructure of the obtained magnesium alloy molded sheet.

FIG. 4 is a longitudinal cross-sectional view showing schematically an injection process step in an injection molding machine.

FIG. 5 is an equilibrium diagram for illustrating Mg-Al alloy.

FIG. 6 is a schematic view of a cross-section of a conventional magnesium alloy molded sheet.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a magnesium alloy

molded product widely applicable to household electric appliances and the like. The present invention uses an alloy of thixotropic type as specifically disclosed in U.S. Patents No. 4,694,881, 4,694,882 and 5,040,589 to produce a thin magnesium alloy molded sheet by injection molding and forms a mono-layered resin coating film on the surface of the resultant molded plate directly or via a thin film of a metal with an excellent corrosion property, such as aluminum or an aluminum alloy.

In the present invention, a magnesium-aluminum alloy with an aluminum content of 4 to 12 wt% as its average alloy composition is used. If the aluminum content is less than 4 wt%, a satisfactory anti-corrosion property cannot be obtained, whereas if the aluminum content exceeds 12 wt%, an intermetallic compound is liable to precipitate on the grain boundaries and causes brittleness of the alloy, and thus the both extremes are not preferable. As shown by the equilibrium diagram of FIG. 5, the alloy having such composition is composed of an  $\alpha$ -phase and an  $\alpha$ - $\beta$ -phase of eutectic crystals in the vicinity of room temperature.

The above-mentioned alloy preferably contains zinc (Zn) in a range of not more than 2 wt%. Although Zn improves strength of the alloy, ductility of the alloy is reduced if Zn content exceeds 2 wt%.

In a case wherein an alloy in this composition range is heated to a temperature higher than the liquidus temperature of the alloy, and the molten alloy is gradually solidified at a small cooling speed in a casting die under a state where the flow of the molten alloy is not permitted, a thermal flow is created in a direction perpendicular to the surface of the casting die and thus a temperature gradient is established along this direction. In that state, the  $\alpha$ -phase is preferentially precipitated from the molten alloy, starting at the surface of the casting die to the direction of the temperature gradient, whereby a number of pillar-shaped crystals are grown.

During the process of solidification whose microstructure is schematically shown by FIG. 6, a portion of the molten alloy, which is concentrated and enriched with aluminum by the growth of the pillar-shaped crystals, occupies gaps among the pillar-shaped crystals 11a, and at the final step of the solidification, the molten alloy enriched with aluminum is solidified into an aluminum-rich phase 12a among the pillar-shaped crystals 11a. The thus obtained cast alloy becomes a typical pillar-shaped structure. In this figure and FIGs. 3A and 3B, numeral 7 indicates layers of a mold release agent.

According to the present invention by contrast, a liquid-solid alloy composition is created by exerting a shearing force sufficient for breaking at least portion of dendritic crystal structure of the alloy on the structure by a screw extruder, at a temperature higher than the solidus temperature and lower than the liquidus temperature of the alloy. That is, as shown by FIG. 3A, a molten alloy 10 wherein subdivided solids of  $\alpha$ -phase 11 are being dispersed is prepared, and is then solidified in a

narrow cavity 50 formed between the metal dies 5, 5 in a fluidized state at a relatively large cooling speed.

According to this method, the portion of the molten alloy enriched with aluminum is solidified around the crystals of  $\alpha$ -phase 11, before they are grown into the pillar-shaped crystals. As shown by FIG. 3B, the cast microstructure of the magnesium alloy molded sheet 1 thus obtained becomes a mesh-like structure composed of a number of granular Al-poor regions 11, each consisting mainly of the  $\alpha$ -phase as it is, and the Al-rich region 12 having a larger aluminum content than that of the average alloy composition and being formed for surrounding the respective Al-poor regions.

As previously-described, since the Al-poor region has a poor anti-corrosion property, the Al-poor region surrounded by the Al-rich region is preferentially corroded under a corrosive environment, but possible development and growth of the corrosion is inhibited by the Al-rich region. By this means, the anti-corrosion property of the whole is ensured. For that reason, it is preferable that the grains of the Al-poor region 11 are as small as possible. From this point, it is required to make the particle size of the granular crystals of the Al-poor region not larger than 200  $\mu\text{m}$ . As shown by FIG. 3B, it is preferred to adjust the particle size of smaller grains 11 in the Al-poor region to 5 to 20  $\mu\text{m}$ , and that of larger grains 111 to 50 to 150  $\mu\text{m}$ , and further to adjust the average particle size to not larger than 50  $\mu\text{m}$ .

The magnesium alloy molded product having such mesh-like structure is obtained by a concurrent use of the preparation of the above-mentioned liquid-solid alloy composition and the rapid cooling of the composition. As the manufacturing method, although a die casting of the molten alloy, a direct casting and roll-pressing from the molten alloy and the like can also be employed, an injection molding whereby the molten alloy is injected into a narrow cavity formed between the metal dies is particularly preferable.

The magnesium alloy molded sheet obtained in the above-mentioned manner is released from the metal dies, then formed with a resin coating film on its surface by applying a paint, and thereafter subjected to a baking step for curing the coating film by heating.

The injection molding is composed of the steps of preparing a liquid-solid alloy composition by exerting a shearing force on the alloy at a specified temperature and casting by injection. For which, any conventional equipment can be employed as the injection molding equipment. An example of the injection molding equipment is shown in FIG. 4. The injection molding equipment is, for instance, composed of a screw extruder 8 which heats the starting material of the alloy and feeds or discharges the molten alloy at a high pressure, and a pair of metal dies 5 (5a, 5b) having a cavity 50 of a desired pattern in their inside surfaces 51, which communicates through a discharge end 80 of the extruder 8. The metal dies 5 can be split or separated into a die 5a and a die 5b for unloading the molded product.

More specifically, the injection molding is performed in the following procedure. Namely, a description will be made by selecting an alloy (liquidus temperature of about 530°C) composed of 9 wt% aluminum, about 1 % zinc and the balance of magnesium as the alloy. Tips of the alloy of this composition are charged into a hopper 86 of the extruder 8, fed or transferred into a cylinder 81 of the extruder 8 by a screw 83.

And, the tips are molten at a temperature (about 550°C for the above-mentioned alloy of 9 wt% Al) which is slightly higher than the liquidus temperature, by heating action of a heater 84 for the cylinder 81. Immediately before the injection, by adjusting the temperature of the molten alloy to that between the liquidus temperature and the solidus temperature (about 620 to 650°C), the molten alloy is brought to a state where Mg-rich granular crystals are caused to precipitate and dispersed in the Al-rich molten alloy. Alternatively, the temperature to which the alloy is heated is adjusted to a temperature between the liquidus temperature and the solidus temperature.

The metal dies 5 used for the injection molding is usually made of steel.

The cooling speed during the casting process by the injection can be adjusted in compliance with the width of the cavity formed between the metal dies and with the temperature of the metal dies before the injection. It is therefore possible to adequately reduce the cooling speed by heating the metal dies. It is usually preferable for improving the fluidity of the molten alloy to previously heat the metal dies to a temperature range of 50 to 300°C

An example of operation in the injection molding will be described. First, the split dies are set as the metal dies, the discharge end of the screw extruder is connected to an injection opening of the metal dies, the screw 83 is revolved in the cylinder 81, while it is retreated back, thereby to feed or transfer the above-mentioned molten alloy 10 containing the dispersed Mg-rich granular crystals to a front part of the cylinder 81 and to form a molten alloy reserve 82. Thereafter, the screw is advanced by a pressing means 85, thereby to inject the molten alloy into the casting cavity 50 formed between the metal dies at a high speed. The molten alloy 10 in a state of being fed to the casting cavity 50 by the injection is gradually cooled while being kept in contact with the inside surface of the cavity, and solidification of the molten alloy proceeds in its fluidized state in compliance with the above-mentioned procedure. Until the solidification is completed, the molten alloy 10 is cooled while being kept under pressure of the screw 85 pushed by the pressing means 85, thereby to ensure spreading the molten alloy 10 all over the cavity 50 of the dies, by being pressed against the inside surface of the cavity, while compensating its shrinkage due to the solidification by further supply. After the solidification is completed, the dies are split for unloading the molded sheet 1 which is then left to be cooled.

It is preferable to previously apply a mold release agent to the inside surface of the cavity 50 of the metal dies 5. As the mold release agent, a mixed material of waxes of, for instance, aliphatic acid esters is used. The application of the mold release agent is usually performed by spraying a liquid mold release agent on the inside surface 51 of the cavity 50 of the metal dies in their split state through a spray nozzle and then drying. In this manner, a film of the mold release agent 7 with a thickness of about 100 μm is formed on the inside surface 51 of the cavity 50 of the metal dies 5a, 5b. By the use of the mold release agent, it is possible to prevent seizure of the molded sheet to the casting dies and to make the releasing of the molded sheet from the die easy. In a case of using the mold release agent, it is preferable to remove it from the injection molded sheet by washing with a degreasing agent, blasting or surface grinding, prior to the formation of the coating film on the injection molded sheet which will be described later.

In a case of the thickness of the obtained injection molded sheet is about 2mm, it becomes a meshlike structure comprising the Al-poor region of a number of granular crystals with a diameter from several μm to 20 μm and the Al-rich region surrounding the respective granular crystals of the Al-poor region. In this case, the cooling speed during the solidification process is 100 to 2000°C/sec., and the Al-poor region and the Al-rich region are in a non-equilibrium state where the composition is not constant and the boundary between the both region is not necessarily clear.

On the surface of the magnesium alloy molded sheet 1 after the injection molding, a coating film 2 is formed as shown by FIG. 1. This coating film is formed for coloring the molded sheet for ornament and for giving an anti-humid property thereon. The thickness of the coating film is suitably 10 to 30 μm. If the coating film is thinner than this, a satisfactory anti-humid effect cannot be obtained. If the coating film is thicker than the above-mentioned range, no metallic texture attributable to the use of the magnesium alloy is obtained and its appearance becomes worse, even in a case of using a transparent coating film.

Formation of the coating film 2 is composed of the steps of applying a resin paint on the surface of the molded sheet released from the metal dies and baking the paint by heating the applied molded sheet. Although the baking conditions vary depending on the resin for configuring the coating film, it is suitable to heat the molded sheet at 120 - 220°C for 10 to 60 minutes. This heating condition does not substantially influence on the above-mentioned non-equilibrium structure composed of the Al-poor region and the Al-rich region of the magnesium alloy.

An examination for evaluating the anti-corrosion property was conducted on the molded product, which had been obtained by the injection molding of the above-mentioned magnesium alloy containing 9 wt% aluminum, thereby to produce a molded sheet with a

thickness of 2 mm and by applying a colored paint composed of a mixture of an epoxy resin and an polyester resin for forming a coating film with a thickness of about 80  $\mu\text{m}$  on the molded sheet by baking. The examination was conducted under a protocol of a salt water spraying test comprising a repetition of a spraying 5 wt% salt water at 35°C for 8 hours and a standing for 16 hours for 3 cycles. Thereafter, adhesion of the paint and surface corrosion of the magnesium alloy were investigated by peeling of the coating film. Although only one layer of the coating film was applied, the adhesion of the coating film and the anti-corrosion property of the substrate alloy were found to be preferable.

A preferred magnesium alloy molded product in accordance with the present invention comprises, as shown by FIG. 2, the injection molded sheet 1, a metal thin layer 3 formed on the molded sheet and a coating film 2 formed thereon. As the metal thin layer 3, the use of a metal having a better anti-corrosion property than that of the magnesium alloy of the above-mentioned composition is preferable, and in particular, the use of aluminum or an aluminum alloy is preferable. As the metal other than aluminum for the layer, a metal such as zinc having a small potential difference with magnesium, i.e., a metal or its alloy which is near to Mg or nobler than Mg in the electrochemical series may be used.

For forming the film of aluminum or its alloy as the metal thin layer 3, a process of thermally spraying Al on the molded sheet is utilized. The thermal spraying process has a feature capable of forming a metal thin layer of a large adhesion, because it involves a spraying of molten metal particles which are firmly stuck to the surface of the magnesium alloy even with any foreign matters such as fatty oil remaining on the surface of the molded product which are destroyed at the time of the spraying. When aluminum or an aluminum alloy is used as the metal thin layer, aluminum in the metal thin layer diffuses into the magnesium alloy molded sheet at the time of baking the resin coating film, thereby to raise a bonding strength between them.

The aluminum layer as the metal thin layer may alternatively be formed by any other process in a thin-film forming equipment using, for instance, sputtering in a vacuum chamber, plasma CVD, or the like process. In a case of forming the metal thin layer by the thin film-forming equipment, it is preferable to mechanically grinding the surface of the magnesium alloy molded sheet and thereafter form the metal thin layer. In a case of forming the layer by using a thin-film forming equipment, the thickness of the metal thin layer 3 is suitably 0.05 to 1.0  $\mu\text{m}$ . A satisfactory anti-corrosion property is demonstrated with the thickness of the film of not less than 0.05  $\mu\text{m}$ , but if the thickness exceeds 1.0  $\mu\text{m}$ , an unduly long time is taken for the film forming which represents a high manufacturing cost.

On the metal thin layer 3, the coating film is formed by the previously-mentioned procedure. Although the

thermally sprayed aluminum film as the metal thin layer has a number of pinholes, the pinholes are sealed with the coating film, and thus it is possible to prevent the invasion of water by sealing effect of the coating film.

In order to give an ornamental effect having a metallic texture to the magnesium alloy molded product in accordance with the present invention, it is preferable to use a transparent material, for instance, a paint composed mainly of an acrylic resin and a melamine resin, available from Honney Chemicals Co. Ltd., under a trade name "Honneyceran", as the material for the resin coating film and to finish the substrate of the molded sheet or the metal thin layer to appear a metallic luster surface by machine tooling with a bite, grinding with a grindstone, and the like.

The magnesium alloy molded product in accordance with the present invention can improve its anti-corrosion property by forming a mesh-like structure composed of the Al-poor region and the Al-rich region in the alloy molded sheet itself. Further, since it realizes the water-proof property of the surface and improves the anti-corrosion property of the molded product as a whole by forming a coating film on the surface of the molded sheet.

Moreover, the anti-corrosion property of the magnesium alloy molded sheet can further be enhanced by forming the metal thin layer on the magnesium alloy molded sheet and forming the coating film thereon.

The method for producing the magnesium alloy molded product in accordance with the present invention is performed by casting process using an injection molding machine with the conventional screw. Since the coating film of the resin can demonstrate a satisfactory anti-corrosion property with only one layer of the film, it is possible to easily obtain a thin molded product excellent in practical anti-corrosion property, without requiring a particularly large-scale equipment or apparatus and without inviting a high manufacturing cost. Further, since the metal thin layer can easily and rapidly be formed by the thermal spraying process or a thin film-forming process, it is possible to realize a high grade anti-corrosion property without inviting a high manufacturing cost.

The magnesium alloy tips to be fed to the molding machine, as the starting material for the magnesium alloy molded product of the present invention, are frequently finished to have the size ranging from 2 mm to 10 mm for ensuring safety such as prevention of igniting. In addition, it is desirable that the sizes are approximately uniform for facilitating the flow of the tips in the cylinder of the molding machine. As a process for preparing such tip material, there is known a cutting or a liquid phase rapid cooling process.

The cutting process requires a previous preparation of the material which permits easy handling in the cutting and has constant shapes such as cylindrical and the like shapes, by for instance, casting, and thus it is difficult to obtain tips directly from waste material having

nonuniform or irregular shapes. In contrast, the liquid phase rapid cooling process requires a melting step and also invites a high manufacturing cost.

In the present invention, it is preferable to break the magnesium alloy into the tips by exerting a plastic deformation on the magnesium alloy to the extent of not less than the rupture elongation of the alloy and to select the broken tips into the tips having the intended sizes.

As a method for causing the starting material to be plastically deform, there is a process of charging the alloy starting material into a compressible container and compressing the alloy by a high pressure applying machine to be plastically deformed. The alloy material is broken in a manner whereby the tips are ripped off from its surface as they cleave in compliance with the magnitude and the speed of the deformation.

An alternative method is a process of plastically deform the alloy material by feeding the starting material to a gap formed between a pair of rotating pressure rolls. One or two steps of the pressure rolls are used.

In any case, it is preferable to perform the plastic deformation of the alloy at a temperature of not higher than 300°C. If the temperature exceeds 300°C, the ductility of the alloy is made high and the tipping of the alloy by the plastic deformation is made difficult.

The particles of the alloy broken into the tips in the previously mentioned manner are preferably selected continuously by being charged into a mesh-like selecting machine equipped with a vibrator for facilitating the selection. The sizes of the tips are preferably not less than 1 mm and not more than 20 mm at the maximum length.

It is also preferable, in advance to the plastic deformation of the alloy material, to degrease the alloy material by treating it with an alkaline solution, and to remove an oxide or the like layer formed on the surface of the alloy by washing with an acid.

As previously-described, by applying the mentioned process for preparing the magnesium-aluminum alloy, it is possible to improve the productivity of the method as a whole including the later molding steps.

It is understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the scope and spirit of this invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the description as set forth herein, but rather that the claims be construed as encompassing all the features of patentable novelty that reside in the present invention, including all features that would be treated as equivalents thereof by those skilled in the art to which this invention pertains.

## Claims

1. A magnesium alloy molded product comprising:

a magnesium-aluminum alloy molded sheet

containing 4 to 12 wt% of aluminum in an average alloy composition, and having an Al-poor region of grains with particle diameter of not less than 200  $\mu\text{m}$ , where Mg-content is higher than that of the average alloy composition, and Al-rich region, where Al-content is higher than that of the average alloy composition, surrounding the grains of the Al-poor region, and a resin coating film covering the surface of said molded sheet.

2. The magnesium alloy molded product in accordance with claim 1, wherein a thickness of said molded sheet is 0.3 to 3 mm.

3. The magnesium alloy molded product in accordance with claim 1, further comprising at least one thin layer of metal having a higher anti-corrosion property than that of said molded sheet, formed between said molded sheet and said resin coating film.

4. The magnesium alloy molded product in accordance with claim 3, wherein said thin layer of the metal comprises aluminum or an aluminum alloy.

5. The magnesium alloy molded product in accordance with claim 3, wherein the surface of said thin layer of the metal has a metallic luster and said resin coating film is transparent.

6. The magnesium alloy molded product in accordance with claim 3, wherein said thin layer of the metal has a thickness of 0.05 to 1.0  $\mu\text{m}$ .

7. The magnesium alloy molded product in accordance with claim 1, wherein said magnesium-aluminum alloy contains not more than 2 wt% of zinc.

8. A method for producing magnesium alloy molded product comprising the steps of:

heating a magnesium-aluminum alloy containing 4 to 12 wt% of aluminum to a temperature exceeding at least the solidus temperature of the alloy,

exerting a shearing force which is sufficient for breaking at least portion of the dendritic structure of the alloy on said heated alloy in a screw extruder, at a temperature higher than the solidus temperature and lower than the liquidus temperature of the alloy, thereby to create a liquid-solid alloy composition,

injecting said liquid-solid alloy composition into a cavity formed between metal dies, thereby to obtain a molded sheet with a thickness of 0.3 to 3 mm,

applying a resin paint on the surface of said

molded sheet released from the metal dies, thereby to form a layer of resin coating film, and subjecting said resin coating film to a thermal treatment, thereby to cure the resin coating film.

rolls.

5

9. The method for producing magnesium alloy molded product in accordance with claim 8, further comprising a step of mechanically working the surface of said molded sheet of the alloy, thereby to present a metallic luster surface, prior to said step of applying the resin paint. 10
10. The method for producing magnesium alloy molded product in accordance with claim 8, further comprising the steps of forming a metal thin layer on the molded sheet of the alloy and mechanically working the surface of said metal thin layer, thereby to present a metallic luster surface, prior to said step of applying the resin paint. 15  
20
11. The method for producing magnesium alloy molded product in accordance with claim 10, wherein said step of forming the metal thin film is performed by thermally spraying aluminum or an aluminum alloy on the surface of the molded sheet of the alloy. 25
12. The method for producing magnesium alloy molded product in accordance with claim 10, wherein said step of forming the metal thin film comprises the steps of mechanically working the surface of the molded sheet of the alloy and forming a metal thin film on the surface of said molded sheet in a vacuum vessel of a thin film-forming equipment. 30  
35
13. The method for producing magnesium alloy molded product in accordance with claim 8, further comprising a step of preparing said magnesium-aluminum alloy, wherein said step comprises the steps of: 40
- exerting a plastic deformation on said alloy to an extent of not less than a rupture elongation of said alloy, thereby to produce tips of the alloy, and 45
- selecting the ruptured tips by the predetermined sizes.
14. The method for producing magnesium alloy molded product in accordance with claim 13, wherein said step of exerting the plastic deformation comprises a process of compressing said alloy by a high pressure press. 50
15. The method for producing magnesium alloy molded product in accordance with claim 13, wherein said step of exerting the plastic deformation comprises a process of pressing said alloy by a pair of rotating 55

FIG. 1

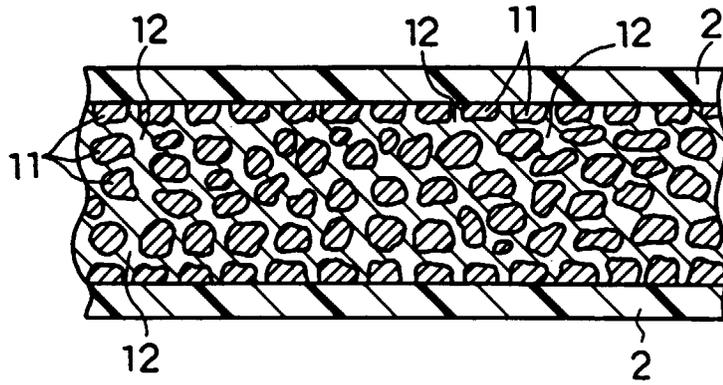


FIG. 2

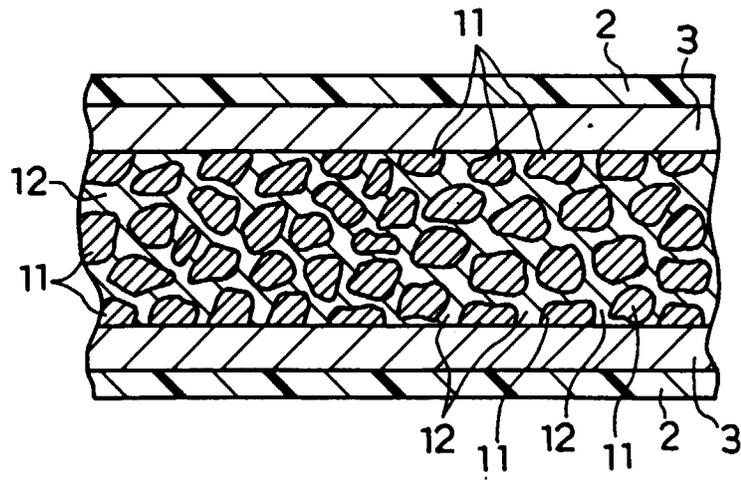


FIG. 3A

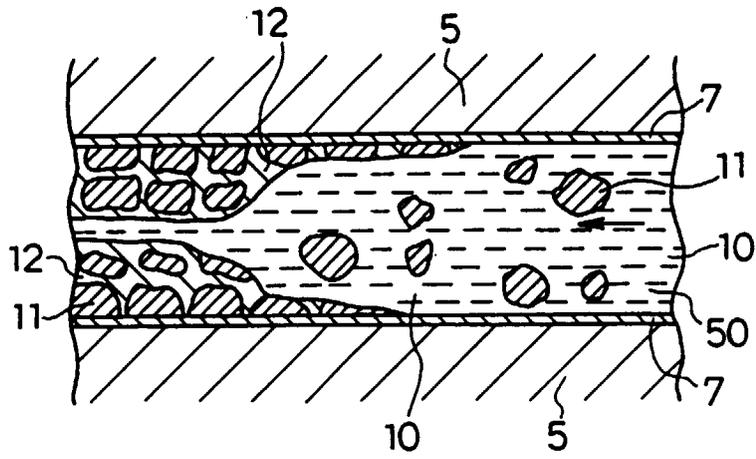


FIG. 3B

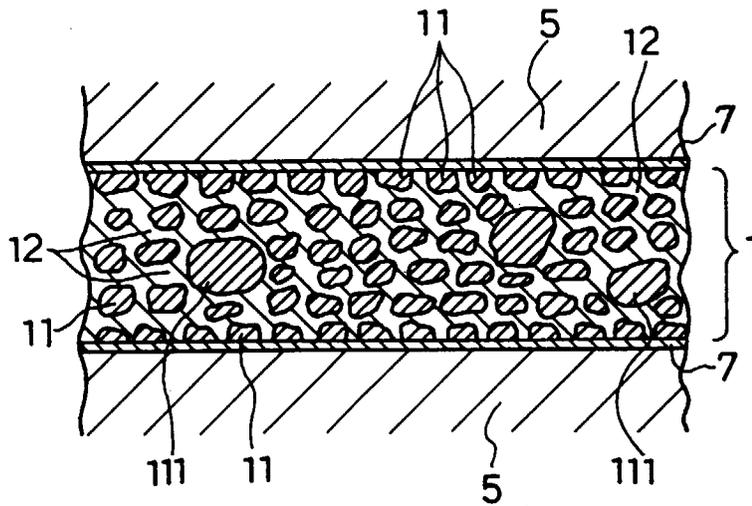


FIG. 6

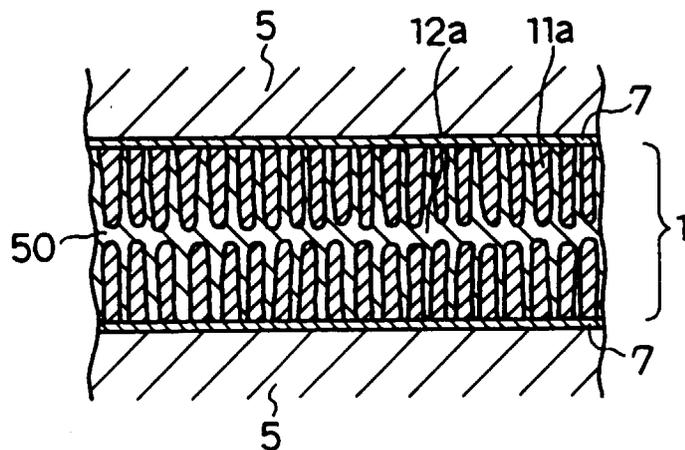


FIG. 4

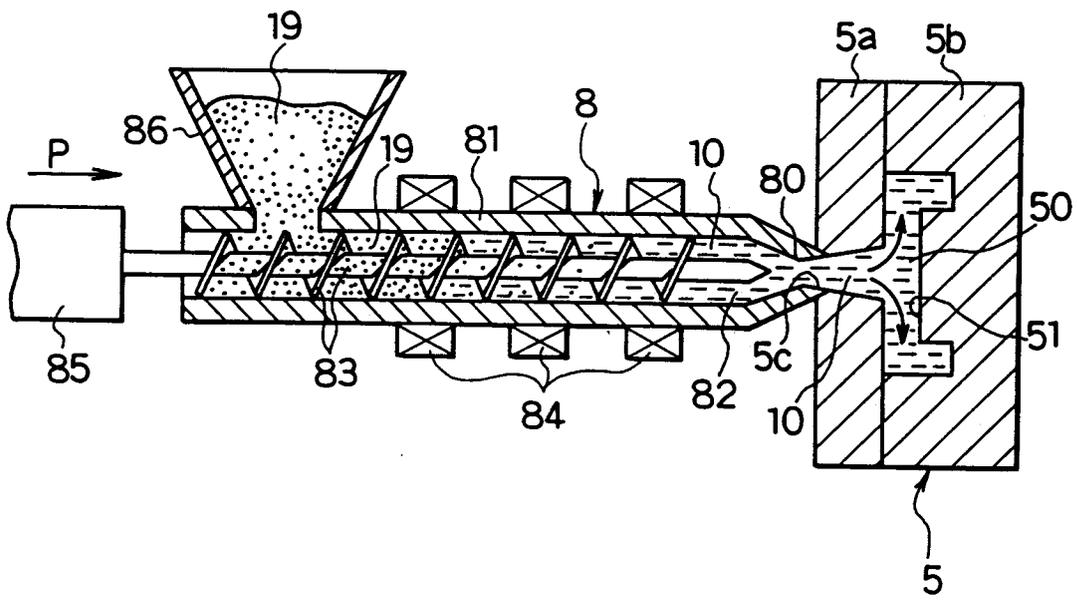
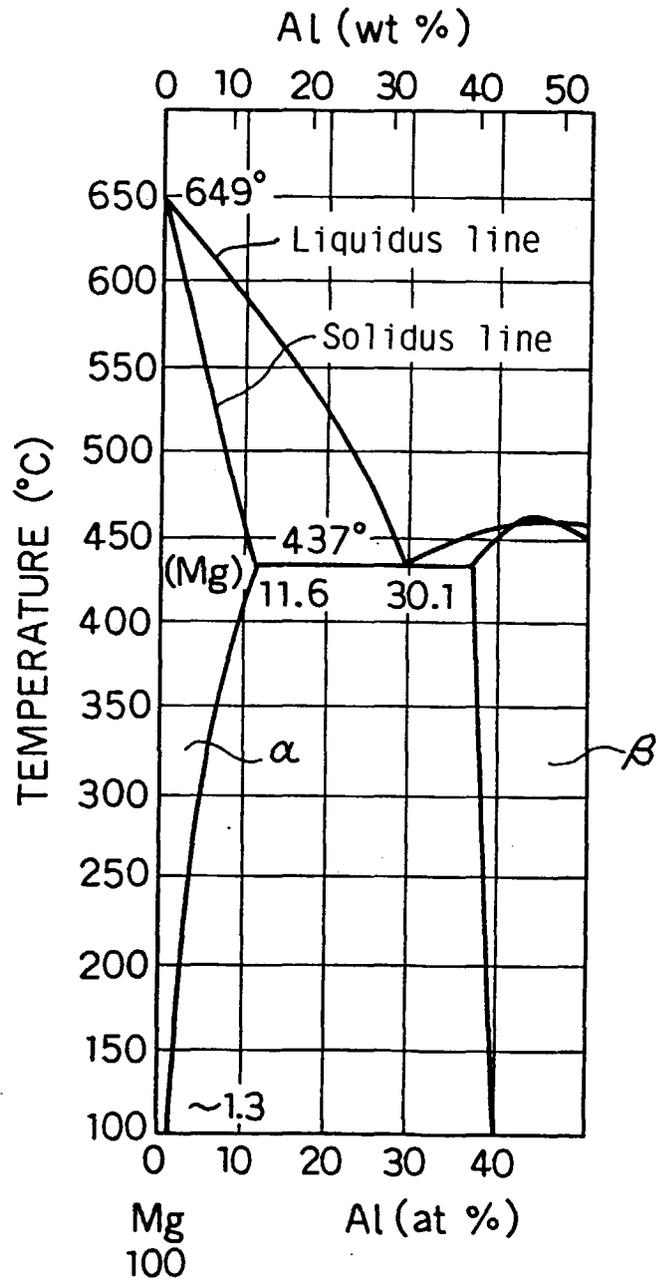


FIG. 5





European Patent  
Office

EUROPEAN SEARCH REPORT

Application Number  
EP 98 11 3061

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)
A,D	PATENT ABSTRACTS OF JAPAN vol. 17, no. 406 (C-1090), 29 July 1993 & JP 05 078775 A (TOYOTA MOTOR CORP.), 30 March 1993 * abstract *	1,8	C22C1/00 C23C4/08 B22D21/00
A	EP 0 575 796 A (NORSK HYDRO TECHNOLOGY ) 29 December 1993 * the whole document *	1,8	
A	US 3 650 312 A (ALLEN) 21 March 1972 * the whole document *	1,8	
A	GB 826 038 A (COAL INDUSTRY (PATENTS) LIMITED) * the whole document *	1,3,8	
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 434 (M-875), 28 September 1989 & JP 01 166874 A (AKIO NAKANO), 30 June 1989 * abstract *	8	
A	TISSIER ET AL.: "MAGNESIUM RHEOCASTING: A STUDY OF PROCESSING-MICROSTRUCTURE INTERACTIONS" J.OF.MAT.SCI., vol. 25, no. 2, February 1990, pages 1184-1196, XP000541387 LONDON,GB	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C22C C23C B22D B32B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20 October 1998	Examiner Lippens, M
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	

EPO FORM 1503 03 R2 (PC4C01)