TITLE: METHOD FOR MANUFACTURING MAGNESIUM ALLOY SHEET CLADDED WITH ALUMINUM SHEET AND MAGNESIUM ALLOY SHEET USING THE SAME

ABSTRACT: Provided is a method of manufacturing a magnesium alloy sheet cladded with an aluminum alloy sheet, which reduces manufacturing cost through a simple process and secures perfect adhesion between magnesium and aluminum. The method includes strip casting a magnesium alloy sheet by injecting molten magnesium alloy between two rotating cooling rolls of a twin roll strip caster with supplying an aluminum sheet to one or both of the cooling rolls, so that one or both surfaces of the strip cast magnesium alloy sheet is cladded with the aluminum sheet.
Invention Title

METHOD FOR MANUFACTURING MAGNESIUM ALLOY SHEET CLADDED WITH ALUMINUM SHEET AND MAGNESIUM ALLOY SHEET USING THE SAME

Technical Field

The present disclosure relates to a method for manufacturing a magnesium alloy sheet cladded with an aluminum alloy sheet, and particularly, to a method for manufacturing a magnesium alloy sheet cladded with aluminum, capable of improving adhesion of magnesium alloy and aluminum and simplifying the process by cladding magnesium alloy with an aluminum sheet while casting the magnesium alloy by a twin roll strip caster, and a magnesium alloy sheet cladded with aluminum manufactured by the method.

Background Art

Magnesium (Mg) is a very light metal having a specific gravity of 1.74 g/cm³, and has high specific strength, high vibration absorption, high thermal/electrical conductivity, and excellent machinability.

There are increasing demands for light weight vehicles in view of oil prices and environments. Accordingly, there are also increasing demands for magnesium alloy for the light weight vehicles. However, only a few magnesium alloy sheet products have satisfied the strength and the formability requirements of automobile industry.

Recently, with the development of the twin roll strip casting technology, it becomes possible to obtain, at low price, magnesium alloy having mechanical properties as good as the magnesium alloy manufactured by typical ingot casting.

However, substantial improvement of corrosion resistance is required for the application of the magnesium alloy manufactured by the twin roll strip casting to a variety of fields.

A number of researches have been done on the addition of various alloying elements to the magnesium alloy to improve its corrosion resistance. However, the magnesium alloys added with alloying elements for improving
their corrosion resistance still have much lower corrosion resistance than aluminum alloys.

Another typical method for improving corrosion resistance of the magnesium alloy is to clad the magnesium alloy with aluminum sheet by using welding and the like. However, the typical cladding method has the drawback of increasing the manufacturing cost due to the addition of the cladding step. Furthermore, the typical cladding method also has the drawbacks of deteriorating adhesion or mechanical properties because of poor adhesion between the magnesium alloy base metal and the aluminum clad, and formation of brittle intermetallic compounds along the interface between the magnesium alloy and the aluminum clad.

[Disclosure]

[Technical Problem]

The present invention addresses the above mentioned drawbacks of the related art. The present invention provides a method for manufacturing a magnesium alloy sheet cladded with an aluminum sheet, which reduces manufacturing cost through a simple process and secures perfect adhesion between magnesium and aluminum.

[Technical Solution]

In accordance with an exemplary embodiment of the present invention, there is provided a method for manufacturing a magnesium alloy sheet with high corrosion resistance, the method including strip casting a magnesium alloy sheet by injecting molten magnesium alloy between two rotating cooling rolls of a twin roll strip caster with supplying an aluminum sheet to one or both of the cooling rolls, so that one or both surfaces of the strip cast magnesium alloy sheet is cladded with the aluminum sheet.

One of the significances of the above mentioned method for manufacturing a magnesium alloy sheet is to perform casting using twin roll strip casting. In the twin roll strip casting, casting and hot rolling are simultaneously performed in a single process. Accordingly, the process is very cost-effective in comparison to the typical ingot casting. Further, cooling is
performed at a cooling rate of \(10^2\) K/s to \(10^3\) K/s, which is very rapid in comparison to the typical ingot casting.

Such a rapid cooling results in refined microstructure and decreased segregation. In addition, while slow cooling rate of the typical ingot casting results in a coarse intermetallic compounds, which would decrease the tensile property, the rapid cooling rate of the strip casting disperses the intermetallic compounds more finely and thus improves the tensile property.

Another significance of the method is to use strip casting, instead of ingot casting, and to supply an aluminum sheet to a surface of a magnesium alloy melt during the strip casting. As such, it is possible to perform the manufacturing of the sheet and the cladding at the same time.

Accordingly, because there is no need for an additional cladding process, and the magnesium sheets are manufactured continuously through the strip casting, it is possible to obtain an Al-cladded sheet at very low cost. In addition, because the aluminum sheet adheres the magnesium alloy sheet while magnesium alloy is molten, adhesion between aluminum and the magnesium alloy can be significantly improved in comparison to the typical cladding methods.

After the strip casting, solution treatment is usually needed because the strip casting may cause segregation of alloying elements and thus cause lack of property uniformity in the casting. In view of the secondary dendrite arm spacing (SDAS) of the manufactured magnesium alloy sheet and the oxidation number analyzed by DTA/DSG, it is preferable that the solution treatment is performed at 250 °C to 450 °C for 1 hour to 24 hours.

Thereafter, a variety of subsequent heat treatments such as thermomechanical treatment and aging treatment may be performed according to the use of the solution treated sheet.

The aluminum sheet used in the exemplary embodiment may have any thickness as long as it can be used in the strip caster. However, if the thickness is greater than 5 mm, adhesion is significantly lowered and thus the aluminum sheet needs to be heated, which result in increased
manufacturing cost and sophisticated apparatuses. Accordingly, in view of manufacturing cost and process easiness, it is preferable that the thickness of the aluminum sheet is 5 mm or less.

In addition, the aluminum sheet may be formed of various aluminum alloys as well as pure aluminum.

It is preferable that the molten magnesium alloy is kept at a temperature ranging from 650 °C to 750 °C. This is because, below 650 °C, the molten magnesium alloy is solidified before it contacts the rolls and thus cannot pass between the rolls, and, above 750 °C, liquid phase still remains after passing between the rolls, thus producing solidification defects or cracks in the surface.

It is preferable that the cooling rate of the molten magnesium alloy ranges from $10^2$ K/s to $10^3$ K/s. This is because, below $10^2$ K/s, the inventive method is not quite different in microstructure from the typical mold casting, and, above $10^3$ K/s, the process is difficult to perform commercially except the rapid solidification technique providing a very thin ribbon shape.

In addition, it is preferable for the rapid cooling rate that the distance between the two cooling rolls is 10 mm or less, and the rotation speed of the cooling rolls is 10 m/min or less.

When supplying the aluminum sheet, tension may be selectively applied to the aluminum sheet to improve adhesion thereof to the molten magnesium alloy when it contacts the cooling roll.

In addition, when supplying the aluminum sheet, the aluminum sheet may be selectively preheated by heating apparatus before being inserted between the cooling rolls.

In accordance with another exemplary embodiment of the present invention, there is provided a magnesium alloy sheet with high corrosion resistance, wherein one or both surfaces of the magnesium alloy sheet are cladded with an aluminum sheet by injecting molten magnesium alloy between two rotating cooling rolls of a twin roll strip caster with supplying the
aluminum sheet to one or both of the cooling rolls.

The magnesium alloy may have any composition as long as it can be strip cast. However, a magnesium alloy including Mg-Zn based alloy, which is a precipitation-hardenable alloy, and the Mg-Zn based alloy added with one or more alloying elements such as Mn, Al, Cu, Y and Ca may be advantageously applied to a sheet for automobiles because they have high strength and high elongation by the use of strip casting and subsequent heat treatment.

[Advantageous Effects]

In accordance with the exemplary embodiments of the present invention, cladding a magnesium alloy sheet with an aluminum sheet is performed simultaneously with strip casting process instead of being performed in a separate process as in the related art. Accordingly, it is possible to simplify the process and significantly reduce the manufacturing cost.

In accordance with the exemplary embodiments of the present invention, an aluminum sheet adheres to a surface of molten magnesium alloy. Accordingly, it is possible to improve adhesion of aluminum and the magnesium alloy.

In accordance with the exemplary embodiments of the present invention, it is possible to prevent the formation of intermetallic compounds on an interface between magnesium alloy and aluminum. Accordingly, it is possible to prevent the formation of defects caused by the intermetallic compounds.

[Description of Drawings]

Fig. 1 is a schematic view illustrating a method for manufacturing a magnesium alloy sheet cladded with aluminum by injecting magnesium alloy melt between rotating twin rolls, and at the same time, inserting an aluminum foil to a surface of the magnesium alloy melt.

Fig. 2 is a scanning electron micrograph of a cross section of a magnesium alloy sheet cladded with aluminum, which is manufactured by strip casting in accordance with an exemplary embodiment of the present invention.

Fig. 3 is a photograph illustrating result of SEM-EDS surface mapping of a cross section of a magnesium alloy sheet cladded with aluminum, which is
manufactured by strip casting and subsequent heat treatment in accordance with an exemplary embodiment of the present invention.

Fig. 4 illustrates a photograph and a graph showing result of SEM-EDS surface mapping of a cross section of a magnesium alloy sheet cladded with aluminum, which is manufactured by strip casting and subsequent heat treatment in accordance with an exemplary embodiment of the present invention.

Fig. 5 illustrates a transmission electron micrograph of a cross section of a magnesium alloy sheet cladded with aluminum, and X-ray diffraction patterns for respective phases therein, the magnesium alloy sheet being manufactured by strip casting in accordance with an exemplary embodiment of the present invention.

Fig. 6 illustrates a transmission electron micrograph of a cross section of a magnesium alloy sheet cladded with aluminum and, X-ray diffraction patterns for respective phases, the magnesium alloy sheet being manufactured by strip casting and subsequent heat treatment in accordance with an exemplary embodiment of the present invention.

Fig. 7 illustrates a transmission electron micrograph of a cross section of a magnesium alloy sheet cladded with aluminum, and X-ray diffraction patterns for respective phases, the magnesium alloy sheet being manufactured by strip casting, heat treatment, and subsequent rolling with a reduction ratio of 25% in accordance with an exemplary embodiment of the present invention.

Fig. 8 illustrates a scanning electron micrograph of a surface of a strip cast magnesium sheet, and a result of EDS composition analysis of the surface.

Fig. 9 illustrates a scanning electron micrograph of a surface of the magnesium sheet of Fig. 8, which is taken after the magnesium sheet is subjected to 97 hours of corrosion test using 5% NaCl solution, and a result of EDS composition analysis of the surface.

Fig. 10 illustrates a scanning electron micrograph of a surface of a
magnesium alloy sheet cladded with aluminum, and a result of EDS composition analysis of the surface, the magnesium alloy sheet being manufactured by strip casting in accordance with an exemplary embodiment of the present invention.

Fig. 11 illustrates a scanning electron micrograph of a surface of the magnesium sheet cladded with aluminum of Fig. 10, and a result of EDS composition analysis of the surface, which are taken after the magnesium sheet is subjected to 97 hours of corrosion test using 5% NaCl solution.

[Best Mode]

Hereinafter, the present invention will be described in detail with reference to exemplary embodiments. The present invention may, however, be embodied in many different forms and should not be construed as being limited to the exemplary embodiments set forth herein.

Pure Mg (99.9%), pure Zn (99.995%o), pure Al (99.99%), and pure Ca (99.99%) were melted under a gas mixture of CO₂ and SF₆ in an induction melting furnace to prepare a magnesium alloy melt having the composition as listed in Table 1.

[Table 1]

<table>
<thead>
<tr>
<th>No.</th>
<th>Zn</th>
<th>Al</th>
<th>Ca</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.0</td>
<td>1.0</td>
<td>0.7</td>
<td>Bal</td>
</tr>
</tbody>
</table>

The molten magnesium alloy having the above composition was kept at a temperature of 700 °C and transported to a tundish as shown in Fig. 1. Then, the molten magnesium alloy was injected between two water-cooled cooling rolls provided to a twin roll strip caster. Here, the tundish was kept at the same temperature as that of the molten magnesium alloy in the melting furnace.

While the molten magnesium alloy was injected between the two cooling rolls, aluminum sheets coiled in a roll form were supplied to the upper roll and the lower roll, respectively.

The distance between the two cooling rolls was kept at 2 mm and the
rotation speed of the cooling rolls was kept at 4 ra/min to 4.5 m/min, so that the molten magnesium alloy may be cast with a cooling rate of 100 K/s to 400 K/s. Resultant Iy, a magnesium alloy sheet cladded with an aluminum sheet of 5 m length, 70 mm width, and 2 mm thickness was obtained.

The cast magnesium alloy sheet was subjected to a solution treatment (T4 heat treatment) at 300 °C for 1 hour.

The cast magnesium alloy sheet requires a solution treatment and a rolling process to obtain more uniform microstructure and to control internal defects. In the exemplary embodiment, the cast magnesium alloy sheet was subjected to a solution treatment at 300 °C for 1 hour, and rolled at 300 °C with a reduction ratio of 25%.

Then, the bonding strength between a clad layer and a base metal and the corrosion resistance of the magnesium alloy sheet in accordance with the exemplary embodiment were examined.

Fig. 2 is a scanning electron micrograph of a cross section of the magnesium alloy sheet cladded with aluminum, which is manufactured by strip casting in accordance with the exemplary embodiment. As shown in Fig. 2, it is possible to obtain excellent interfacial bonding between a magnesium alloy base metal layer and a clad layer without defects such as a porosity.

Figs. 3 and 4 illustrate the result of SEM-EDS mapping of a magnesium alloy sheet manufactured by strip casting and subjected to 1 hour of heat treatment at 300 °C in accordance with an exemplary embodiment. As shown in Figs. 3 and 4, intermetallic compounds, which are brittle phases, do not form between the magnesium alloy base metal layer and the aluminum clad layer. Instead, a portion of the magnesium diffuses into the aluminum clad layer. Accordingly, it is possible to solve the problem of deterioration of physical properties due to the formation of intermetallic compounds.

Figs. 3 and 4 illustrate the result of SEM-EDS mapping of a magnesium alloy sheet manufactured by strip casting and subjected to 1 hour of heat treatment at 300 °C in accordance an exemplary embodiment. As shown in Figs. 3 and 4, gradual diffusion of magnesium and aluminum occurs between the
magnesium alloy base metal and the aluminum clad layer, which means the formation of bondings between different materials.

A cross section of the magnesium alloy sheet manufactured in accordance with the exemplary embodiment was observed using a transmission electron microscope (TEM) to analyze interfacial products in the magnesium alloy sheet. As a result, Mg$_2$Al$_3$ phase was observed at the interface of the cast magnesium alloy sheet as shown in Fig. 5. After the solution treatment, Mg$_{7}$Al$_{12}$ phase having higher Al content was also observed as shown in Fig. 6. After the rolling with a reduction ratio of 25%, it was observed that the width of the interface was reduced.

To investigate the corrosion resistance of the magnesium alloy sheet manufactured in accordance with the exemplary embodiments, a magnesium alloy sheet and a magnesium alloy sheet cladded with an aluminum sheet were cast by strip casting, and then subjected to 97 hours of corrosion test by the use of 5% NaCl solution.

As a result, for the magnesium alloy sheet that is not cladded with an aluminum sheet, the surface of the magnesium alloy sheet was quite different before and after the corrosion test, as shown in Figs. 8 and 9. The SEM-EDS analysis of the surface also told us that alloying elements of the magnesium alloy combined with oxygen to form oxides in the surface of the magnesium alloy after the corrosion test, resulting in severe corrosion.

On the contrary, for the magnesium alloy sheet cladded with an aluminum sheet, the surface of the magnesium alloy sheet was not quite different before and after the corrosion test, as shown in Figs. 10 and 11. As shown in Fig. 11, although aluminum oxide was also observed in the experimental magnesium alloy sheet, the amount of aluminum oxide was quite lower than that of the comparative magnesium alloy sheet.
[CLAIMS]

[Claim 1]
A method for manufacturing a magnesium alloy sheet with high corrosion resistance, the method comprising strip casting a magnesium alloy sheet by injecting molten magnesium alloy between two rotating cooling rolls of a twin roll strip caster with supplying an aluminum sheet to one or both of the cooling rolls, so that one or both surfaces of the strip cast magnesium alloy sheet is cladded with the aluminum sheet.

[Claim 2]
The method of claim 1, further comprising, after the strip casting of the magnesium alloy sheet, performing a heat treatment on the magnesium alloy sheet cladded with the aluminum sheet.

[Claim 3]
The method of claim 1 or 2, wherein the aluminum sheet has a thickness of 5 mm or less.

[Claim 4]
The method of claim 1 or 2, wherein the molten magnesium alloy is kept at a temperature ranging from 650 °C to 750 °C, and, after being injected between the cooling rolls, the molten magnesium alloy is cooled with a cooling rate ranging from 10 K/s to 10 K/s.

[Claim 5]
The method of claim 2, wherein the heat treatment comprises performing a solution treatment at 250 °C to 450 °C for 1 hour to 24 hours, on the magnesium alloy sheet cladded with the aluminum sheet.

[Claim 6]
The method of claim 4, wherein a distance between the two cooling rolls is kept at 10 mm or less, and a rotation speed of the two cooling rolls is kept at 10 m/min or less.

[Claim 7]
The method of claim 4, wherein a predetermined tensile stress is applied to the aluminum sheet during the supplying of the aluminum sheet to improve
adhesion of the aluminum sheet to the molten magnesium alloy when it contacts
the cooling rolls.

[Claim 8]

The method of claim 1 or 2, wherein the aluminum sheet is preheated by a
heating apparatus before being supplied to the cooling rolls.

[Claim 9]

A magnesium alloy sheet with high corrosion resistance, wherein one or
both surfaces of the magnesium alloy sheet are cladded with an aluminum sheet
by injecting molten magnesium alloy between two rotating cooling rolls of a
twin roll strip caster with supplying the aluminum sheet to one or both of
the cooling rolls.

[Claim 10]

The magnesium alloy sheet of claim 9, wherein the thickness of the
aluminum sheet is 5 mm or less.

[Claim 11]

The magnesium alloy sheet of claim 10 or 11, wherein the magnesium alloy
comprises Mg-Zn based alloy.