Title: COATING OF SUBSTRATES MADE OF LIGHT METALS OR LIGHT METAL ALLOYS

Abstract: The present invention relates to a method for the production of coated workpieces made of light metal or light metal alloy, said method comprising the steps of: a) electrodeposition of one or more layers containing at least one metal and/or metal alloy selected from the group of aluminum, magnesium, zinc on a substrate of light metal or light metal alloy, the substrate and the layer apply thereto or, in the event of multiple layers, two adjacent layers not consisting of the same metal or the same metal alloy; b) heat treatment of the coated substrate at a temperature between 200°C and 800°C so that at least the surface layer of the substrate and the layer/layers applied in step a) undergo partial and/or complete interdiffusion; and to the coated workpieces produced using said method.
Coating of Substrates Made of Light Metals or Light Metal Alloys

The invention is directed to a method for the production of coated workpieces made of light metal or light metal alloy and to the workpieces thus produced.

In many technical fields, efforts are now being made to use lightweight materials to the largest possible extent in order to achieve weight minimization in this way. In the past, the use of light metals was of predominant importance in the field of aerospace industry, but is gaining more and more importance today in the fields of automotive industry, offshore technology and other technical fields as well where energy can be saved by reducing weight.

More recently, the metal magnesium in particular has gained major importance. Magnesium has a density of 1.7 g/cm³, thus once more being considerably lower in weight even when compared to other light metals already commonly used in construction, such as aluminum with a density of 2.7 g/cm³ and titanium with a density of 4.5 g/cm³.

Especially in the automobile industry, efforts are therefore being made to make increasing use of magnesium, and this industry already uses magnesium in the sector of drive assemblies to a greater extent today.

Indeed, one major drawback of light metals is that they are non-noble to a high degree, making them highly susceptible to corrosion. However, most light metals form a passivation layer of the corresponding metal oxide in ambient air by reaction with oxygen. While the passivation layer protects from corrosion, it can nonetheless be disadvantageous to further treatment of the light metal because the nature of the surface is changed. For this reason, the passivation layer of ox-
ides is frequently undesirable, and other systems must be used for corrosion protection.

Consequently, there is a need in new systems to improve the corrosion protection of light metals.

In this context, a first well-known aspect of the prior art is to improve corrosion protection by reinforcing the natural oxide layer of light metals using anodization. However, this is practicable only in those cases where there is no interference by the respective oxide layer.

Another way of protecting from corrosion is providing the light metals with metallic coatings, in which case metals less noble than the base material are usually employed. In this way, the coatings can function as sacrificial anode on damaged spots, providing cathodic protection for the base material. With magnesium, however, this option applies to only a very limited extent because Mg is pronouncedly non-noble, so that no common metal is available as sacrificial anode. Thus, owing to its non-noble properties, Mg itself is frequently used as sacrificial anode in steel vessels.

However, in metal coating with zinc or aluminum using magnesium as base material, it should be noted that magnesium is a pronouncedly non-noble metal, being considerably less noble even when compared to aluminum and zinc. Therefore, when coating magnesium base material with aluminum, the electrochemical compatibility requires special attention because otherwise, there would be a risk of bimetallic corrosion between the base material and the coating material, resulting in corrosion of the base material. This is critical particularly with magnesium because it has an extremely negative electric potential. As a consequence, magnesium is attacked by bimetallic corrosion much more violently than aluminum or zinc when in contact with virtually any common metallic construction and coating material. Thus, magnesium undergoes corrosion to form alkaline corro-
sion products having a pH value of more than 11. These corrosion products attack aluminum which dissolves from a pH value of about 9.4 on.

The strong alkalinity of the corrosion products represents another problem in magnesium corrosion. The alkaline corrosion products of magnesium can do damage to paint films, but also to other amphoteric contact metals such as aluminum or zinc. For this reason, the paint adhesion on magnesium component parts is difficult to handle, and the lifetime of pure aluminum coatings on magnesium materials is extremely short.

In the context with corrosion protection for light metals, it must also be considered that when coating metallic layers, attention must be paid to the fact that the corrosion resistance substantially depends on the adhesion of the protective layer coated on the workpiece. In the event of insufficient adhesion of the protective layer on the workpiece, the protective layer will easily be removed or damaged, e.g. when screwing a screw constituting a workpiece and provided with such a metallic protective layer into a second workpiece. As a result of the damage of the protective layer, there will be increased corrosion in these areas.

In the prior art, there have been various attempts of improving the adhesive strength of corrosion protecting layers by using various measures.

DE 31 12 919 A1 suggests providing metal-coated iron workpieces with an adhesion-promoting intermediate layer made of cobalt, cobalt alloys or cobalt containing nickel and electroplating an aluminum layer thereon. The intermediate layer serving as adhesion promoter is electroplated from an aqueous medium. Following coating of the electro-aluminum layer on the adhesion-promoting layer, the electro-aluminum layer optionally can be chromatized. In this way, the corrosion resistance is further improved.
DE 38 04 303 A1 suggests a method of improving the adhesion of electrodeposited aluminum layers on metal workpieces by applying an adhesion-promoting layer. A non-aqueous electrolyte is used to apply the adhesion-promoting layer of iron, iron and nickel, nickel, cobalt, copper, and alloys of the above-mentioned metals, or tin-nickel alloys. Following the application of the intermediate layer as adhesion-promoting layer on a metal workpiece, an electro-aluminum layer is applied to the intermediate layer. In doing so, it is essential to apply the intermediate layer from a non-aqueous electrolyte, because otherwise, i.e., when using an aqueous electrolyte, embrittlement of the metal workpiece will occur due to the hydrogen being formed during electrolysis. As a result, the high-strength low-alloy steels frequently being used are adversely affected. Embrittlement of the workpieces is avoided by using a non-aqueous electrolyte to apply the metallic intermediate layer.

Both in DE 31 21 919 A1 and in DE 38 04 303 A1 pure electro-aluminum layers are applied to workpieces provided with an intermediate layer. Neither of the above printed documents describes the application of aluminum/magnesium alloys on workpieces.

EP 1 141 447 B1 discloses electrolytes for coating workpieces with layers of an aluminum/magnesium alloy. In particular, such coating is necessary in those cases where joints with magnesium parts are to be generated, because the corrosion products of magnesium are alkaline, attacking the aluminum surface coatings. By using aluminum/magnesium alloys, contact corrosion is avoided and long-term resistance of the coating is provided. It is suggested to coat steel fastening elements intended to contact magnesium component parts, especially in the automobile industry, with aluminum/magnesium alloy. EP 1 141 447 B1 fails to disclose any metallic intermediate layers interposed between workpiece and corrosion-reducing layer of aluminum/magnesium alloy.
Corrosion protection of light metals, especially of magnesium, further requires considering the fact that the material magnesium is a very soft substance. In comparison, workpieces coated with aluminum or aluminum/magnesium layers tend to be very hard and brittle. When using such workpieces as fastening means, e.g. as screws, to fasten component parts made of magnesium, there is a risk in that the screws would cause superficial roughening of the component parts, destroying them in the worst case. As a result of such superficial destruction of the component part, the latter may be exposed to increased corrosion which may lead to the destruction of said component part.

The prior art has seen various proposals of coating the base material magnesium with metal layers of aluminum. Thus, for example, US 4,148,204 describes coating of cylinders of a magnesium-containing alloy, "Electron", consisting of 90% magnesium and more and various other metals, with an aluminum layer to improve the workability and protect from corrosion. However, it has been determined that aluminum layers coated in this way, being subject to bimetallic corrosion and, in addition, lacking sufficient adhesive strength, fail to provide sufficient corrosion protection for magnesium.

The technical object of the invention is therefore to provide a corrosion protection system for light metals as base materials, particularly magnesium, which system has extremely low bimetallic corrosion sensitivity, good adhesion and permanent protection of the base material for a long time even under corresponding mechanical load.

The above technical object is accomplished by means of a method for the production of coated workpieces made of light metal or light metal alloy, said method comprising the steps of:

a) electrodeposition of one or more layers containing at least one metal and/or metal alloy selected from the group of aluminum, magnesium, zinc
on a substrate of light metal or light metal alloy, the substrate and the layer coated thereon or, in the event of multiple layers, two adjacent layers not consisting of the same metal or the same metal alloy;

b) heat treatment of the coated substrate at a temperature between 200 and 800°C so that at least the surface layer of the substrate and the layer/layers coated in step a) undergo partial and/or complete interdiffusion.

Surprisingly, it has been determined that the method specified above forms intermetallic phases representing an ideal corrosion protection system for light metals. Thus, for example, in the event of the system magnesium with zinc coating or magnesium with aluminum coating respectively, it has been determined that the subsequent heat treatment results in the formation of different intermetallic phases which become higher in zinc or aluminum in the direction of the surface of the coated base material and higher in magnesium in the direction of the base material. In particular, this results in a substantial reduction of the bimetallic corrosion because several layers of different alloys are formed. As a result, there are lower gradations of the electric potential with respect to the base material and, as a consequence, lower corrosion susceptibility when compared to simple coating with no subsequent heat treatment.

Furthermore, it has been discovered that the determined thicknesses of the corrosion protection layer are substantially greater because part of the base material is also involved in the formation of the corrosion protection layer. In addition, this achieves improved adhesive strength because there is improved anchoring of the applied corrosion protection layer in the base material as a result of such heat treatment.

In a preferred embodiment the substrate is constituted of magnesium or magnesium alloy. More specifically, the magnesium alloys include alloy compositions with aluminum, wherein the aluminum content can be from greater than zero to
10 wt.-% aluminum, and wherein minor amounts of zinc, manganese, silicon, rare earths and of the elements scandium and yttrium related to the rare earths can be included.

The layer of step a) is applied to the substrate material from a non-aqueous electrolyte or from an aqueous electrolyte.

The method according to the invention relates to light metals and light metal alloys. Light metal is understood to be a collective term used for metallic elements of low density. In addition to alkali and alkaline earth metals, light metals include metals such as aluminum, scandium, yttrium and titanium. Amongst those, light metals of technical importance - also preferred within the scope of the invention - are aluminum, magnesium, zinc, titanium or alloys thereof.

Various layer systems of substrate and corrosion protection layer are included within the bounds of the invention. Firstly, this includes a system wherein the substrate consists of magnesium or magnesium alloy and the layer consists of aluminum, zinc or alloys thereof. Another system included in the present invention is a system wherein the substrate consists of aluminum or aluminum alloy and the layer consists of magnesium, zinc or alloys thereof.

Another preferred embodiment also includes systems consisting of three or more layers, i.e., including one or more intermediate layers. In a particularly preferred fashion this includes a system wherein the substrate consists of magnesium or magnesium alloy, the first layer (intermediate layer) consists of aluminum, zinc or alloys thereof, and the second layer (surface layer) consists of aluminum, magnesium, zinc or alloys thereof, the first layer and the second layer not being made of the same metal.

Another preferred system is a system wherein the substrate consists of aluminum or aluminum alloy, the first layer (intermediate layer) consists of magne-
sium, zinc or alloys thereof, and the second layer (surface layer) consists of aluminum, magnesium, zinc or alloys thereof. Similarly, the metals of the first and second layers are not the same.

With respect to temperature as well as duration, the heat treatment is preferably effected in such a way that an alloy containing metal of the surface layer of the substrate and metal or metal alloy of the applied layer will be formed at least in the boundary area between substrate and applied layer. In a preferred fashion the temperature of the heat treatment ranges between 250°C and 700°C, preferably between 300°C and 650°C, and more preferably between 250°C and 600°C.

The duration of heat treatment is preferably between 1 second and 5 hours, preferably between 30 seconds and 2 hours, and most preferably between 1 minute and 1 hour.

Furthermore, the layer preferably can be subjected to an additional treatment subsequent to applying the layer to the substrate material and prior to performing the heat treatment. In a preferred fashion this can be anodic oxidation, preferably anodization of the layer.

Each applied layer preferably has a layer thickness of from 0.1 to 100 μm. In another preferred embodiment the layer thickness is from 0.5 μm to 70 μm, more preferably from 1 μm to 50 μm, preferably from 2 μm to 40 μm, more preferably from 3 μm to 30 μm, more preferably from 4 μm to 28 μm and most preferably from 5 μm to 25 μm.

If the layer or one of the layers is electrodeposited from an aqueous electrolyte, solutions of the above-mentioned metals can be used as possible electrolytes. More specifically, the metals can be present as halides, sulfates, sulfonates or fluoborates. The electrolytes may contain further additives such as complexing
substances. Furthermore, a layer deposited from an aqueous electrolyte or any portion of such a layer can also be deposited in an electroless fashion.

If the layer or one of the layers of step a) is electrodeposited from a non-aqueous electrolyte, it is possible to use any non-aqueous electrolyte well-known to those skilled in the art.

When depositing aluminum, magnesium or alloys thereof, organoaluminum compounds are preferably employed. More specifically, the electrolyte preferably includes organoaluminum compounds of general formulas (I) and (II):

\[ M[(R^1)_2Al-(H-Al(R^2)_2)_n-R^3] \quad (I) \]

\[ Al(R^4)_3 \quad (II) \]

wherein \( n \) is equal to 0 or 1, \( M \) is sodium or potassium, and \( R^1, R^2, R^3, R^4 \) can be the same or different, \( R^1, R^2, R^3, R^4 \) being a C<sub>1</sub>-C<sub>4</sub> alkyl group, and a halogen-free, aprotic solvent being used as solvent for the electrolyte.

A mixture of the complexes \( K[AlEt_4], \ Na[AlEt_4] \) and \( AlEt_3 \) can be employed as electrolyte. The molar ratio of those complexes to \( AlEt_3 \) is preferably from 1:0.5 to 1:3, more preferably 1:2.

Electrolytic deposition of the layer can be performed using a soluble anode including the metals to be deposited. This anode either can include the above-mentioned metals intended for deposition in the form of a metal alloy, or multiple soluble anodes of the respective pure metals can be used. If a layer including an aluminum/magnesium alloy is to be deposited, it is possible to use a soluble aluminum anode and a likewise soluble magnesium anode or an anode of an aluminum/magnesium alloy. Electrolytic deposition can also be effected using an insoluble anode.
Electrolytic coating from a non-aqueous electrolyte is preferably performed at a temperature of from 80 to 105°C. Preferred is an electroplating bath temperature of from 91 to 100°C.

In a preferred embodiment an electroconductive layer is applied to the substrate prior to electrodepositing the layer in step a). The electroconductive layer can be applied to the substrate using any method known to those skilled in the art. In a preferred fashion the electroconductive layer is applied to the substrate by means of metallization.

In step b) of the method according to the invention the temperature and/or duration of the heat treatment is selected in such a way that an alloy containing metal of the surface layer of the substrate and metal and/or metal alloy of the coated layer will be formed at least in the boundary area between substrate and applied layer of step a). Here, temperature and/or duration of the heat treatment must be selected in a way so as to be adjusted to the properties of the substrate and to the specific applied layer.

As a result of such heat treatment, an intermetallic phase will generally form on the surface of the coated workpiece, wherein the layer applied in step a) is converted either partially or completely into the intermetallic phase.

Alternatively, the coated substrate can be annealed below/along the liquidus line of the material mixture being formed. The liquidus line is the melting temperature of the resulting material mixture as a function of the specific composition. When applying an aluminum layer on a magnesium substrate, the initial proportion of aluminum in the surface layer will be 100%. During heat treatment, a magnesium/aluminum alloy is formed which has a specific melting point. Now, when selecting the temperature during heat treatment in a way so as to precisely reach or fall just below the melting point of the alloy being formed, such heat treatment
is understood to be a heat treatment below/along the liquidus line of the material mixture being formed.

Alternatively, the heat treatment of the coated substrate can be carried out in such a way that a liquid phase will form on the surface of the coated substrate. This is achieved by performing the treatment at a temperature which is higher than the melting temperature of the surface layer being formed.

Heat treatment can be effected under a protective gas atmosphere. In this context, it is preferred to use a protective gas that would not undergo reaction with the coated material. Preferably, the protective gas is a noble gas such as argon. However, it is not necessary that heat treatment be performed in a protective gas atmosphere. Alternatively, heat treatment can also be effected in air.

Subsequent to applying the layer in step a) and prior to performing the heat treatment of step b), the layer is subjected to further treatment in a preferred embodiment. Any treatment procedure known to those skilled in the art can be used. In particular, the treatment can be anodic oxidation, preferably anodization of the layer. Such treatment is recommendable in those cases where a layer including aluminum has been applied in step a).

The coated workpiece employed in the method of the present invention is preferably a rack article, bulk material, continuous product or molded article. The coated workpiece is preferably a wire, a band, a screw, a nut, a concrete anchorage, a machine component part, an engine, an engine part, or a turbine blade.

The workpieces produced according to the method of the invention have a strongly adhering corrosion protection layer which has very low tendency to undergo bimetallic corrosion and is permanently stable. Thus, corrosion protection for corrosion-sensitive light metals has been found, especially for aluminum al-
loys and magnesium materials, with a rest potential largely adapted to the base material.

In the event of magnesium, contact corrosion is avoided by providing the magnesium with a coating that does not represent an active anode towards the substrate material and, at the same time, is compatible with zinc, aluminum, as well as zinc/aluminum alloys and aluminum/magnesium alloys, neither attacking the latter, nor being attacked by the same.

Furthermore, an improvement in paintability of magnesium materials is achieved by providing them with a substrate-compatible coating which can be phosphated in the low-zinc process, including the bi- and trication processes. When providing substrates thus coated with fastening means, there is, unexpectedly, no impairment of the coated substrates. Particularly when using fastening means coated with aluminum/magnesium alloys, thereby being rendered very hard, brittle and sparingly ductile, the coating will not be damaged during assembly and will tightly adhere to the coated material. Thus, because there is no damage done to the corresponding corrosion protection layer, the coated material is permanently protected from corrosion, particularly contact corrosion, even subsequent to assembly.

Workpieces made of magnesium coated merely with an aluminum layer, as well-known from the prior art, fail to offer such advantages. As a result of low adhesive strength, the surface layer is liable to be destroyed or attacked during assembly. Moreover, there is more contact corrosion due to the higher electric potential occurring at the boundary surface between magnesium material and aluminum layer as compared to the intermetallic phases according to the invention. Similarly, this results in increased contact corrosion on the material and destruction of the aluminum layer by the basic corrosive medium.
The invention will be illustrated in more detail with reference to the following examples.

Examples

Samples were produced at various temperatures, the material consisting of magnesium and the coating consisting of aluminum or zinc respectively.

Following appropriate heat treatment, the layers obtained were characterized using solid electron microscopy and subjected to quantitative analysis using an electron beam microprobe.

Heat treatment of the samples was effected in normal atmosphere chamber furnaces under argon atmosphere.

In the event of the magnesium/aluminum system, the samples were aluminized using aprotic solutions. In the event of the magnesium/zinc system, a zinc layer was applied using 20% electroless plating and 80% electroplating.

Example 1  The electro-aluminized magnesium system

An aluminum layer about 12 µm in thickness was electrodeposited on a magnesium substrate consisting of AZ91 magnesium alloy.

Example 1 A  Test series at 460°C

Multiple samples of aluminum-coated magnesium were heated to a temperature of 460°C for 30 minutes. The samples were subsequently investigated as described above. It was found that a concentration equilibration between magnesium and aluminum had taken place in the transitional area between coating and
base material. The overall layer thickness had increased to 20 μm. An aluminum content of 37 atom % was detected in the above alloy layer, roughly corresponding to the Al₄Mg₁₇ intermetallic phase.

**Example 1 B**  Test series at 465°C

The samples were heated in the same way as in Example 1 A, but this time to 465°C for a period of 9 minutes. An investigation of the cooled samples showed that diffusion had taken place between magnesium material and aluminum layer. Layer growth of more than 50 μm with an aluminum content of about 35 atom % was determined, indicating an Al₄Mg₁₇ intermetallic phase.

The tests show that pure aluminum coatings can be deposited on magnesium and converted into alloy coatings by subsequent heat treatment.

**Example 2**  Zinc-electroplated magnesium system

These tests were performed using magnesium base material and a coating of zinc. As base material, an AZ91 magnesium alloy was used, conventionally coated with a zinc layer using 20% electroless plating and 80% electroplating. The layer thickness on the sample was 12 μm.

In all diffusion tests described below a multilayered structure of the sample outer zone was determined depending on the composition. The following categories will be used for the various layers below.

The originally deposited pure zinc layer is characterized as layer A. Following diffusion treatment, the composition thereof may contain a magnesium percentage of up to 14 atom %. Consequently, the composition thereof may vary between virtually pure zinc across the two-phase range zinc/Mg₃Zn₁₁ and up to pure Mg₃Zn₁₁.
Layers having the approximate composition MgZn$_2$ will be regarded as layer B hereinbelow.

A characterization as layer C applies to layers having a zinc content of about 60 atom % zinc, roughly corresponding to a composition of Mg$_2$Zn$_3$.

Where layers are depleted down to values between 28 atom % and 52 atom % zinc, these layers will be designated as C'. This corresponds to a composition range which may include the intermetallic phases MgZn and Mg$_2$Zn$_3$ or the high-magnesium eutectic.

A system having less than 8 atom % zinc, which is formed from the substrate material by zinc incorporation, with no complete formation of intermetallic phases being observed, will be characterized as layer D. Consequently, it may consist of a mixed crystal (MC), which may include a maximum of 2.4 atom % zinc, and, in addition, some percentage of low-zinc intermetallic phases.

**Example 2 A**  Test series at 350°C

The samples were heated to 350°C for a period of 30 or 90 or 180 minutes respectively in the manner described above. Following cooling, the layer structures obtained were investigated, the following Table 1 showing the composition and thickness of the layers found.
Table 1

<table>
<thead>
<tr>
<th>Time [minutes]</th>
<th>Layer A</th>
<th>Layer C</th>
<th>Layer C'</th>
<th>Layer D</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>90 atom % Zn</td>
<td>60 atom % Zn</td>
<td>43 atom % Zn</td>
<td>MC</td>
</tr>
<tr>
<td></td>
<td>8 µm</td>
<td>2 µm</td>
<td>3 µm</td>
<td>15 µm</td>
</tr>
<tr>
<td>90</td>
<td>88 atom % Zn</td>
<td>60 atom % Zn</td>
<td>52 atom % Zn</td>
<td>MC</td>
</tr>
<tr>
<td></td>
<td>5 µm</td>
<td>2 µm</td>
<td>10 µm</td>
<td>15 µm</td>
</tr>
<tr>
<td>180</td>
<td>84 atom % Zn</td>
<td>layer C completely converted into layer C'</td>
<td>43 atom % Zn</td>
<td>MC</td>
</tr>
<tr>
<td></td>
<td>5 µm</td>
<td></td>
<td>15 µm</td>
<td>45 µm</td>
</tr>
</tbody>
</table>

The table shows that diffusion of zinc into the magnesium, especially along the grain boundaries, takes place during such heat treatment. As a result of magnesium diffusion from the base material, the outer layer A has a lower content of pure zinc. The layers B and C are formed by diffusion of zinc situated at the surface into the substrate, as well as by outward magnesium diffusion in the reverse direction. As a result of such mixing, there is a layer growth of about 300%.

Example 2 B

The same test series as in Example 2A was performed at a temperature of 380°C, using heating periods between 15 minutes and 90 minutes. The following Table 2 shows the structure of the resulting layers.
Table 2

<table>
<thead>
<tr>
<th>Time [minutes]</th>
<th>Layer A</th>
<th>Layer B</th>
<th>Layer C’</th>
<th>Layer D</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>78 - 90 atom % Zn</td>
<td>ca. 25 atom % Zn 4 µm</td>
<td>1-3 atom % Zn 8 µm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6 µm porous Mg₂Zn₁₁</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>87 atom % Zn</td>
<td>26 + 32 atom % Zn 4 µm</td>
<td>1-3 atom % Zn 8 µm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6 µm porous Mg₂Zn₁₁</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>8 µm porous</td>
<td>35 atom % Zn 6 µm</td>
<td>&lt; 2 atom % Zn 8 µm</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>8 µm porous</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>conversion of layer A into layer B</td>
<td>72 atom % Zn 8 µm porous</td>
<td>35-37 atom % Zn 10 µm</td>
<td>2 atom % Zn 10 µm</td>
</tr>
<tr>
<td>90</td>
<td>conversion of layer A into layer B</td>
<td>38 atom % Zn 8 µm highly porous MgZn₂</td>
<td>32 atom % Zn 20 µm</td>
<td>2 atom % Zn 20 µm</td>
</tr>
</tbody>
</table>

As can be seen from the table, the outer layer A is depleted in zinc from a maximum of 90 atom % to 66 atom % with increasing migration time, thus being converted into layer B. The course of porosity is approximately proportional to zinc depletion. The layer decreases in thickness with increasing migration time. Obviously, layer B is formed from layer A by conversion.

Following a primary accumulation phase, the portion characterized as layer C’ is also depleted in zinc with time. After reaching a maximum layer thickness, this portion turns thinner again. Further enlargement thereof predominantly proceeds along the grain boundaries. Layer D was invariably found to have a zinc concen-
tration of less than or equal to 3 atom % and thus should be homogeneous. Furthermore, this layer shows a smooth transition to the zinc content of the substrate so that a maximum in layer thickness as a function of time can be expected.

In summary, it is noted that formation of alloy layers by heat treatment of zinc coatings on magnesium substrates is easily possible. Intermediary liquid phases occur during the process, which, at the time of completing the heat treatment, cause the resultant alloy layers to be present in a solid or at least partially solid form.

It has also been found that, due to the wide variety of possible intermetallic phases, the layer composition is highly complex. Furthermore, it has been determined that the alloy layers, compared to the pure zinc layers originally present, substantially gain in volume and thickness as a result of magnesium incorporation and the associated decrease in density.
Claims:

1. A method for the production of coated workpieces made of light metal or light metal alloy, said method comprising the steps of:

   a) electrodeposition of one or more layers containing at least one metal and/or metal alloy selected from the group of aluminum, magnesium, zinc on a substrate of light metal or light metal alloy, the substrate and the layer applied thereto or, in the event of multiple layers, two adjacent layers not consisting of the same metal or the same metal alloy;

   b) heat treatment of the applied substrate at a temperature between 200°C and 800°C so that at least the surface layer of the substrate and the layer/layers applied in step a) undergo partial and/or complete interdiffusion.

2. The method according to claim 1, characterized in that the substrate consists of magnesium or magnesium alloy.

3. The method according to at least one of claims 1 or 2, characterized in that the layer of step a) is applied from a non-aqueous electrolyte or from an aqueous electrolyte.

4. The method according to at least one of claims 1 to 3, characterized in that the substrate consists of aluminum, magnesium, zinc, titanium or alloys thereof.
5. The method according to at least one of claims 1 to 4, characterized in that the substrate consists of magnesium or magnesium alloy and the layer of step a) consists of aluminum, zinc or alloys thereof.

6. The method according to at least one of claims 1 to 4, characterized in that the substrate consists of aluminum or aluminum alloy and the layer of step a) consists of magnesium, zinc or alloys thereof.

7. The method according to at least one of claims 1 to 4, characterized in that the substrate consists of magnesium or magnesium alloy, the first layer (intermediate layer) of step a) consists of aluminum, zinc or alloys thereof, and the second layer of step a) consists of aluminum, magnesium, zinc or alloys thereof.

8. The method according to at least one of claims 1 to 4, characterized in that the substrate consists of aluminum or aluminum alloy, the first layer (intermediate layer) of step a) consists of magnesium, zinc or alloys thereof, and the second layer of step a) consists of aluminum, magnesium, zinc or alloys thereof.

9. The method according to one or more of claims 1 to 8, characterized in that the temperature and/or duration of the heat treatment of step b) are selected in such a way that an alloy containing metal of the surface layer of the substrate and metal and/or metal alloy of the applied layer will be formed at least in the boundary area between substrate and applied layer of step a).

10. The method according to one or more of claims 1 to 9, characterized in that the temperature of the heat treatment of step b) ranges between 250°C and 700°C, preferably between 300°C and 650°C, and most preferably between 320°C and 550°C.
11. The method according to one or more of claims 1 to 10, characterized in that the duration of heat treatment in step b) is between 1 second and 5 hours, preferably between 30 seconds and 2 hours, and most preferably between 1 minute and 1 hour.

12. The method according to one or more of claims 1 to 11, characterized in that subsequent to applying the layer in step a) and prior to performing the heat treatment of step b), said layer is subjected to an additional treatment.

13. The method according to claim 12, characterized in that said treatment is anodic oxidation which preferably is anodization of the layer.

14. The method according to at least one of claims 1 to 13, characterized in that the coated workpiece is a rack article, bulk material, continuous product or molded article, the coated workpiece preferably being a wire, a band, a screw, a nut, a concrete anchorage, a machine component part, an engine, an engine part, or a turbine blade.

15. A coated workpiece which can be obtained according to one or more of claims 1 to 14.

16. The coated workpiece according to claim 15, characterized in that the coated workpiece is a rack article, bulk material, continuous product or molded article, the coated workpiece preferably being a wire, a band, a screw, a nut, a concrete anchorage, a machine component part, an engine, an engine part, or a turbine blade.
### INTERNATIONAL SEARCH REPORT

**International Application No**

PCT/EP2005/053676

### A. CLASSIFICATION OF SUBJECT MATTER

|-----|----------|----------|----------|

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

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

<table>
<thead>
<tr>
<th>IPC</th>
<th>C25D</th>
</tr>
</thead>
</table>

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

Electronic database consulted during the international search (name of database and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 2 437 612 A (HANS OSBORG) 9 March 1948 (1948-03-09) column 1, paragraph 1</td>
<td>1-5, 9-12, 14-16</td>
</tr>
<tr>
<td></td>
<td>column 3, lines 30-32, 47-55 column 8, lines 34, 35, 58-68 column 11, lines 16-30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>column 13, line 73 - column 14, line 3 column 14, lines 29-40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>--/--</td>
<td></td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of box C.

**Patent family members are listed in annex.**

* Special categories of cited documents:
  - "A" document defining the general state of the art which is not considered to be of particular relevance
  - "E" earlier document but published on or after the international filing date
  - "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  - "O" document referring to an oral disclosure, use, exhibition or other means
  - "P" document published prior to the international filing date but later than the priority date claimed

**Dates:**

- Date of the actual completion of the international search: 26 September 2005
- Date of mailing of the international search report: 07/10/2005

**Name and mailing address of the ISA**

European Patent Office, P.O. Box 5816 Patentlaan 2 NL - 2280 HV Rijswijk
Tel. (+31-70) 940-2040, Tx. 31 651 epo nl,
Fax (+31-70) 940-3016

Authorized officer: Zech, N
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>CA 1 285 857 C (CANADA MINISTER DEFENCE) 9 July 1991 (1991-07-09) page 1, lines 1-4 page 2, lines 13-27 page 3, line 13 - page 5, line 17 page 7, lines 1-4</td>
<td>1, 3, 4, 6, 9-11, 14-16</td>
</tr>
<tr>
<td>X</td>
<td>DATABASE WPI Section Ch, Week 199317 Derwent Publications Ltd., London, GB; Class M14, AN 1993-140710 XP002308041 &amp; JP 05 078888 A (NIPPON STEEL CORP) 30 March 1993 (1993-03-30) abstract</td>
<td>1, 3, 4, 6, 9-11, 14-16</td>
</tr>
<tr>
<td>X</td>
<td>PATENT ABSTRACTS OF JAPAN vol. 0180, no. 82 (C-1164), 10 February 1994 (1994-02-10) &amp; JP 05 287469 A (SKY ALUM CO LTD), 2 November 1993 (1993-11-02) abstract</td>
<td>1, 3, 4, 6, 9-11, 14-16</td>
</tr>
<tr>
<td>X</td>
<td>PATENT ABSTRACTS OF JAPAN vol. 0102, no. 03 (C-360), 16 July 1986 (1986-07-16) &amp; JP 61 044194 A (MITSUBISHI ALUM CO LTD), 3 March 1986 (1986-03-03) abstract</td>
<td>1, 3, 4, 6, 9-10, 14-16</td>
</tr>
<tr>
<td>X</td>
<td>PATENT ABSTRACTS OF JAPAN vol. 0181, no. 50 (C-1179), 14 March 1994 (1994-03-14) &amp; JP 05 320951 A (NIPPON STEEL CORP), 7 December 1993 (1993-12-07) abstract</td>
<td>1, 3, 4, 6, 9-11, 14-16</td>
</tr>
<tr>
<td>Category</td>
<td>Citation of document, with indication, where appropriate, of the relevant passages</td>
<td>Relevant to claim No.</td>
</tr>
<tr>
<td>----------</td>
<td>---------------------------------------------------------------------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>X</td>
<td>DE 102 57 737 B (THYSSEN KRUPP STAHL AG) 26 February 2004 (2004-02-26)</td>
<td>1,3,4, 9-12, 14-16</td>
</tr>
<tr>
<td></td>
<td>paragraphs ‘0003’, ‘0013’, ‘0014’, ‘0019’, ‘0025’ – ‘0027’ claims 1,7,8</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>DE 874 101 C (STANDARD STEEL SPRING COMPANY) 20 April 1953 (1953-04-20)</td>
<td>1,7-12</td>
</tr>
<tr>
<td></td>
<td>page 1, line 1 – page 3, line 13 claims 1-3</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>GB 356 443 A (EDWARD SMITH; AUTOMATIC TELEPHONE MFG CO LTD; CHARLES ALOYSIUS VELARDE) 10 September 1931 (1931-09-10) claims 1,3</td>
<td></td>
</tr>
<tr>
<td>Patent document cited in search report</td>
<td>Publication date</td>
<td>Patent family member(s)</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>----------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>EP 1533401</td>
<td>A</td>
<td>25-05-2005</td>
</tr>
<tr>
<td>US 2437612</td>
<td>A</td>
<td>09-03-1948</td>
</tr>
<tr>
<td>JP 2000239862</td>
<td>A</td>
<td>05-09-2000</td>
</tr>
<tr>
<td>CA 1285857</td>
<td>C</td>
<td>09-07-1991</td>
</tr>
<tr>
<td>JP 6179997</td>
<td>A</td>
<td>28-06-1994</td>
</tr>
<tr>
<td>JP 5078888</td>
<td>A</td>
<td>30-03-1993</td>
</tr>
<tr>
<td>JP 61044194</td>
<td>A</td>
<td>03-03-1986</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JP 05320951</td>
<td>A</td>
<td>07-12-1993</td>
</tr>
<tr>
<td>DE 10257737</td>
<td>B</td>
<td>26-02-2004</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE 874101</td>
<td>C</td>
<td>20-04-1953</td>
</tr>
<tr>
<td>GB 356443</td>
<td>A</td>
<td>10-09-1931</td>
</tr>
</tbody>
</table>