

METHOD TO CREATE FUNCTIONAL COATINGS ON MAGNESIUM

BACKGROUND

5 [0001] Magnesium and its alloys are widely used in automotive, structural and aerospace applications; however, without suitable functional coatings, many alloys suffer from environmental degradation due to corrosion. A number of processes have been developed to protect magnesium surfaces, including anodizing, plating, and chemical films. However, due to the reactivity of
10 magnesium, directly plating on the surface requires numerous processes generally involving toxic chemicals, anodizing is an energy intensive process, and plating on anodized films requires expensive or toxic catalysts.

[0002] Protecting the surfaces of magnesium and its alloys has been well researched and patented, with more than 400 patents granted. Processes
15 include conversion coatings, plating, organic coatings including paints, surface treatments such as thermal sprays or hot dipping, and combinations of these processes.

[0003] Conversion coatings include chromate treatments, phosphate treatments, and anodizing. Anodizing on magnesium, including the Dow17
20 process from Dow Chemicals created in the 1940s (US2313754A) and the HAE process created in the 1950's (US2723952A), requires the use of toxic chromates and fluorides. In the late 1990's, micro arc oxidation (MAO) processes were developed and patented. These processes require high power and, in some instances, hazardous chemicals (US6919012B1).

25 [0004] Magnesium has been coated using both electrodeposition and electroless coating processes, as described in US20030008471 and WO2015015524A. Such coatings rely on a complicated pre-treatment process to achieve adherent coatings, and the plating baths must be formulated specifically to minimize the replacement reaction. Certain pretreatments include
30 chrome and zinc processes which are either complex or require hazardous chemicals.

[0005] Recently, combinations of anodized and plated coatings have been developed. Such coatings are deposited from an electroless plating bath, and

the coatings require the presence of a catalyst to initiate deposition as the anodizing layer isolates the substrate from the plating bath (US20090223829A1). Despite the effective isolation of the substrate, galvanic corrosion can affect plated MAO coatings, as described in “A novel palladium-free surface activation process for electroless nickel deposition on micro-arc oxidation film of AZ91D Mg alloy”, Journal of Alloys and Compounds Volume 623, 25 February 2015.

5 [0006] US Patent Publication No. 2018/0051388 describes an approach to plate coatings through an anodized layer. However, the approach failed to
10 produce outcomes with magnesium coatings.

SUMMARY

[0007] According to aspects illustrated herein, there is provided a method for producing a coating on magnesium. One disclosed feature of the embodiments
15 is a method comprising placing a magnesium substrate into an anodizing bath, applying a voltage for a first amount of time to form a micro-porous anodizing layer having a thickness of between 1 to 50 microns on the magnesium substrate, placing the magnesium substrate with the micro-porous anodizing layer in plating bath, wherein the plating bath comprises a metal and a
20 complexing agent with a pH between 8 and 14, applying a first current to the plating bath for a second amount of time to form an interlock layer on the micro-porous anodizing layer, and applying a second current to the plating bath for a third amount of time to form a coating on the interlock layer.

[0008] Another disclosed feature of the embodiments is a method for
25 producing a coating on magnesium. The method comprises pre-treating a magnesium substrate, cleaning the magnesium substrate with de-ionized water, forming a micro-porous anodizing layer on the magnesium substrate in a anodizing bath, wherein a voltage is applied to anodizing bath for a first amount of time to form the micro-porous anodizing layer, rinsing the magnesium
30 substrate with the micro-porous anodizing layer, forming an interlock layer on the micro-porous anodizing layer in a plating bath, wherein the plating bath comprises a metal and a complexing agent with a pH between 8 and 14,

wherein a first current is applied to the plating bath for a second amount of time to form the interlock layer, and forming a coating on the interlock layer in the plating bath, wherein a second current is applied to the plating bath for a third amount of time to form the coating.

- 5 [0009] Another disclosed feature of the embodiments is a method for producing a coating on magnesium. The method comprises placing a magnesium alloy substrate into an anodizing bath, applying and maintaining a peak voltage below 75 volts for approximately 10 minutes to form a micro-porous anodizing layer having a thickness of between 5 to 15 microns on the
- 10 magnesium alloy substrate, placing the magnesium alloy substrate with the micro-porous anodizing layer in plating bath, wherein the plating bath comprises a metal and a complexing agent with a pH between 9 and 12, applying a first current that is increased over a second time period from 0 amperes per square decimeter (A/dm^2) to between 0.01 A/dm^2 to 0.5 A/dm^2 to the plating bath to
- 15 form an interlock layer on the micro-porous anodizing layer, and applying a second current that is greater than the first current and between 0.1 A/dm^2 and 2 A/dm^2 to the plating bath for a third amount of time to form a coating on the interlock layer.

20 BRIEF DESCRIPTION OF THE DRAWINGS

- [0010] FIG. 1 is a flow diagram of an example method for producing a coating on magnesium;
- [0011] FIG. 2 is an example graph of the anodizing voltage showing example anodizing regions of the present disclosure;
- 25 [0012] FIGs. 3A-3B illustrates example effects of bath composition on anodizing voltage and surface morphology of the present disclosure;
- [0013] FIG. 4 is an image of an example hybrid silver coating on an AZ80 substrate of the present disclosure;
- [0014] FIG. 5 illustrate images of a cross-section of an example hybrid silver
- 30 coating on an AZ80 substrate of the present disclosure;
- [0015] FIG. 6 illustrate images of a cross-section of an example hybrid copper coating on an ZK60 substrate of the present disclosure;

[0016] FIG. 7 illustrate images of an example hybrid copper coating on an ZK60 substrate of the present disclosure;

[0017] FIG. 8 illustrate images of an example surface and cross-section of a zinc nickel coating on an AZ80 substrate of the present disclosure;

5 [0018] FIG. 9 illustrates SEM images of example anodizing films using the anodizing bath of the present disclosure;

[0019] FIG. 10 illustrates an optical image of an example surface and cross-section of a hybrid Zn-Ni coating using the anodizing bath of the present disclosure;

10 [0020] FIG. 11 illustrate an image of an example cross-section of an electroless Ni-P coating on an AZ80 substrate of the present disclosure;.

[0021] FIG. 12 illustrates a graph of the anodizing voltage for a bath for hybrid Zn-Ni coating of the present disclosure; and

15 [0022] FIG. 13 illustrates an optical image of a Zn-Ni interlock layer surface of produced with the anodizing layer of the present disclosure.

DETAILED DESCRIPTION

[0023] Examples described herein provide a process to develop functional coatings on magnesium substrates. As noted above, previous attempts to coat
20 magnesium have failed or are undesirable due to a variety of different reasons. For example, previous methods may use numerous processes generally involving toxic chemicals, may use an anodizing process that is energy intensive, and may be relative expensive.

[0024] The present disclosure provides a process to develop a plated coating
25 on a magnesium alloy substrate that eliminates the use of toxic chemicals, is less energy intensive, and is cheaper than previous methods. In an example, the process mechanically or chemically polishes and/or degreases the substrate. The substrate can be pretreated. A film of between 1 and 30
30 microns can be anodized on the substrate in an anodizing bath comprising sodium hydroxide, potassium hydroxide, disodium metasilicate, sodium tetra borate, sodium carbonate, an organic additive, other additives to produce a porous anodized layer, or any combination thereof.

[0025] In addition, a first plated layer of between 2 and 50 microns (including the anodizing film) can be deposited by electrolytically or autocatalytically adopting a voltage profile for the electro-deposition to ensure the anodizing structures are completely filled and sealed. In addition, the first plated layer can develop a surface onto which other coatings may be deposited.

[0026] The process may also deposit a second functional coating of between 0 and 100 microns on the first layer. The second functional coating can be multi-layered. The thickness of the hybrid magnesium coating may be around 10 to 100 microns.

10 [0027] FIG. 1 illustrates an example method 100 for producing a coating on magnesium. In one embodiment, the method 100 may be performed by various equipment or tools in a processing facility under the control of a processor or controller.

[0028] At block 102, the method 100 begins. At block 104, the method 100 may pre-treat a substrate. In one embodiment, the substrate may be a magnesium substrate that may be a wrought or cast alloy of magnesium. Examples of such magnesium substrates may include AZ80 or ZK60. In one embodiment, the substrate may be any suitable magnesium alloy.

20 [0029] In one embodiment, the pre-treatment may include one or more processes. The process may include chemically treating the substrate in a concentrated nitric acid bath or a dilute sulphuric acid bath, mechanically roughening the substrate through emery sandpaper or bead blasting, and/or cleaning the substrate for 3 to 15 minutes in an alkaline bath comprising 10-20 grams per liter (g/L) of sodium carbonate and 15-20 g/L of sodium phosphate, 25 10-20 g/L of sodium silicate, and 1-3 g/L of a commercial OP-10 surfactant at 60-80 degrees Celsius (°C).

[0030] Mechanically roughening the surface may produce enhanced adhesion between the anodized layer and the substrate. The adhesion may be further enhanced in the presence of tensile forces produced in later deposited functional surface layers. Mechanical roughening can be accomplished by using 30 appropriate grades of emery paper up to 1200 grit. In one embodiment, sand or bead blasting can produce an appropriate surface on which to create the

anodized layer.

[0031] At block 106, the method 100 may clean the substrate. The substrate can be cleaned prior to being anodized. The substrate may be cleaned by rinsing in de-ionized (DI) water. In one embodiment, the substrate may be
5 ultrasonically cleaned in a solution of ethanol or acetone. When the substrate is cleaned, the cleaning step should prevent the creation of any oxide layer on the surface. In other words, cleaning the substrate should not allow a new oxide layer to be created on the surface.

[0032] At block 108, the method 100 selects an anodizing bath according to
10 a substrate. For example, the composition of the anodizing bath may be selected in accordance with the composition of the magnesium substrate. The bath composition may be selected from 30-100 g/L of sodium hydroxide, 30-100 g/L of potassium hydroxide, 0-60 g/L of sodium tetra borate, 0-100 g/L of disodium meta silicate, 0-50 g/L of sodium carbonate, 0-30 g/L of phosphate
15 salt, 0-100 g/L of sodium aluminate, 0-0.05 g/L of triethanolamine, 0-20 g/L of citric acid, 0~20 g/L sodium citrate, and/or 0-20 ml/L of hydrogen peroxide.

[0033] In one embodiment, the composition of the bath may be selected according to the composition of the substrate. In one embodiment, the magnesium substrate may be a ZK60 alloy, and the anodizing bath may
20 comprise 70 g/L of sodium hydroxide, 60g/L of sodium tetra borate, 60 g/L of disodium meta silicate, and/or 30 g/L of sodium carbonate. The ZK60 alloy is an alloy containing zinc and zirconium.

[0034] In one embodiment, the substrate may be AZ80 and the bath may comprise 70 g/L of sodium hydroxide, 60g/L of sodium tetra borate, 30 g/L of
25 sodium carbonate, and/or 10g/L of citric acid. The AZ80 is an alloy containing aluminum and zinc.

[0035] In one embodiment, the substrate may be either AZ80 or ZK60 and the bath may comprise 70 g/L of sodium hydroxide, 60 g/L of disodium meta silicate, 12 g/L of sodium citrate, 6 mL/L of hydrogen peroxide, and/or between
30 0.01 molar (M) and 0.05M sodium chloride. In one embodiment, the approximately 0.01M of sodium chloride may be included in the bath.

[0036] The presence of aluminum in the alloy has been found to be a

significant factor in selecting the bath chemistry. The exact bath composition may be a function of the magnesium alloy chemistry.

[0037] At block 110, the method 100 places the substrate in a bath comprising at least one of: sodium hydroxide or disodium metasilicate to
5 produce an anodized layer. In one embodiment, the anodizing bath may be in a heating and/or cooling apparatus to maintain a stable solution temperature. In one embodiment, the anodizing bath may include a stainless steel counter electrode. In one embodiment, a direct current (DC) power supply may provide voltage and current to perform anodizing. In one embodiment, a pulsed DC
10 power supply may provide the anodizing power.

[0038] In one embodiment, the anodizing bath may be operated between 18 °C and 30 °C. In one embodiment, the anodizing bath may be maintained at a temperature of approximately 20 °C.

[0039] In one embodiment, a constant current anodizing current may be
15 adopted. In one embodiment, the constant current may be maintained between 0.5 and 6 ampere per square decimeter (A/dm^2). In one embodiment, the current may be limited to 1 A/dm^2 .

[0040] The peak anodizing voltage may determine the structure of the anodized layer. A desired structure may be microporous. In one embodiment,
20 the peak anodizing voltage may be maintained between 60 volts (V) and 110V. In one embodiment, the peak anodizing voltage may be maintained below 75V.

[0041] The development of a micro-porous layer provides two benefits. First, the micro-porous layer limits the free magnesium surface. Second, a sufficiently thick micro-porous layer (e.g., at least 2 microns or between 4-20 microns)
25 provides a secure keying between the anodizing layer and the metal layer, which provides excellent adhesion of the metal layer with the magnesium substrate.

[0042] In one embodiment, the available magnesium accessible surface percentage may be between 1% and 25% of the magnesium substrate surface,
30 between 2% and 15% of the substrate surface area, or between 4% and 10 % of the substrate surface area. In one embodiment, approximately 8% of the substrate surface may be accessible through the anodized layer.

[0043] In one embodiment, an organic agent in the anodizing bath may be used to control the peak voltage. In one embodiment, the organic agent may be citric acid. Citric acid is a large molecule which is absorbed onto the substrate surface to limit the conductivity.

5 [0044] In one embodiment, the organic agent may be hydrogen peroxide. In one embodiment, the organic agent may be sodium citrate. In one embodiment, the organic agent may be triethanolamine. In one embodiment, any combination of the organic agents listed above may be used, or other organic agents that may provide a similar effect may be used.

10 [0045] In one embodiment, the amount of the organic agent in the bath may be selected to prevent the peak anodizing voltage from exceeding 75V. In one embodiment, the amount of citric acid used may be approximately 10 g/L. In one embodiment, the amount of hydrogen peroxide may be approximately 6 ml/L. In one embodiment, the amount of sodium citrate may be 12 g/L. In one
15 embodiment, the amount of triethanolamine may be 20ml/L.

[0046] The thickness of the anodized film in the present disclosure may be between 1 and 50 microns. However, the thickness may also be between 4 and 20 microns. In one embodiment, the thickness may be between 5 and 15 microns.

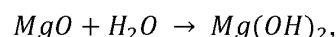
20 [0047] Anodizing for 10 minutes at the above described conditions results in an anodized film of about 6 microns. The anodized layer becomes a keying layer for a magnesium hybrid coating system allowing subsequently deposited layers to securely interlock with the anodized layer to provide superior adhesion over traditional plated solutions.

25 [0048] At block 112, the method 100 rinses the substrate. The anodized layer of the substrate may be rinsed in DI water or ultrasonically cleaned in ethanol.

[0049] At block 114 the method 100 selects an interlock layer plating bath. For example, an appropriate plating bath to deposit a metal layer in the interlock
30 layer may be selected. The characteristics of the plating bath may determine whether metal deposition is favored over dissolution of the magnesium substrate and spalling of the anodized coating.

[0050] In one embodiment, both the pH of the plating bath and the complexing agent (an anionic species) in the plating bath are characteristics that determine whether the deposition will be successful. The pH is one characteristic as shown in the reaction:

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A minimal amount of the anodized layer is dissolved at pH between 8 and 14.

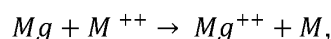
In one embodiment, the pH of the plating bath may be between 9 and 12. In

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one embodiment, the pH of the plating bath may be approximately 10.

[0051] The bath complexing agent (an anionic species) may control the solubility product (Ksp) of magnesium. Minimizing the Ksp may be desirable. In one embodiment, the anionic species includes a complexing agent to slow a displacement reaction between the metal ion in the plating bath and the

15 magnesium substrate. Since any metal ion of interest is more noble than magnesium, the following reaction occurs at the exposed surface:



20 where M is the metal in the plating bath. Due to the high negative galvanic voltage of magnesium (e.g., -1.75V) and the relatively low voltage of metal coatings of interest (e.g. Ni -0.3V) this reaction can be extreme, resulting in dissolution of the substrate and spalling of the anodized layer.

[0052] In one embodiment, complexing agents, in particular anionic species or organic species, may be selected to form stable chelates with the metal ions in the plating bath. Examples of anionic species that may be selected as complexing agents include cyanide, pyrophosphate, hydroxide, and the like. It should be noted that the anionic species listed are provided as examples, and that other complexing agents may work with metal ions of interest, such as

25 certain organic species, glycerin, citric acid, lactic acid, malic acid, pyrroles and

30 EDTA. It is to be appreciated that other methods to select complexing agents that work well with metal ions of interest may also be deployed.

- [0053] In one embodiment, the metal in the plating bath may be silver, and the complexing agent may be cyanide. The bath may contain silver cyanide, potassium cyanide, and potassium hydroxide with a pH of 12.5. In one embodiment, the metal may be copper, the complexing agent may be pyrophosphate, and the bath may be copper pyrophosphate, commercially available from Atotech Corporation, which includes copper pyrophosphate, potassium pyrophosphate, ammonia, and proprietary ingredients. The pH may be 9. In one embodiment, the bath may be a commercial Zn-Ni bath, commercially available from Atotech Corporation, the complexing agent may be a proprietary complexing agent, and the pH may be 13.
- [0054] In one embodiment, high pH autocatalytic baths are also suitable. For example, high pH may include pHs in a range of 8 to 11. The autocatalytic bath may include an electroless nickel bath comprising 25g/L of nickel sulphate, 25 g/L of sodium hypophosphite, 50 g/L of sodium pyrophosphate, and 1 g/L of thiourea. Here, the pyrophosphate may be the complexing agent, and the thiourea serves to moderate the reaction speed. The autocatalytic bath may have a pH of 11, and ammonia may be added to achieve the pH of 11.
- [0055] At block 116, the method 100 places the substrate in an autocatalytic or galvanic deposition bath for plating the substrate. For example, the substrate may be placed in the galvanic deposition bath that follows a plating current profile for a predetermined period. For example, the current may be gradually increased in accordance with the plating current profile.
- [0056] In one embodiment, a first electrodeposited coating is applied to the anodizing film from a bath selected from a range of possible baths as described herein. The electrical parameters pertaining to the first electrodeposited coating are controlled, where a first plating current or current profile is applied for a first plating period comprising a first plating stage, and a second plating current is applied for a second plating period comprising a second plating stage. The first electro-deposited layer forms an interlock layer, completely filling the pores in the anodized layer to securely lock the first electroplated layer to the surface of the anodized layer.
- [0057] In one embodiment, the substrate is placed in a high pH autocatalytic

bath, for example an electroless nickel phosphorous bath or an electroless nickel boron bath, at a temperature that is dependent on the bath chemistry. The substrate may be placed in the bath for a time that is selected to ensure that the pores of the anodizing layer are at least completely filled. In one

5 embodiment, the substrate may be placed in the bath for a time to ensure that the entire anodizing layer is encapsulated in the electroless coating.

[0058] At block 118, the method 100 plates at a second current for a second time period. For example, the plating current can be increased to a recommended bath plating current and held constant at the recommended bath
10 plating current to produce a plating (e.g., a metal coating or metal layer) having a desired initial coating thickness. The second current may be greater than the first current.

[0059] For example, once the pores are filled to a particular level (e.g., less than completely filled, completely filled, more than completely filled, and the
15 like), then the second plating stage commences. During the second stage, the current may remain the same as during the first plating stage, or the current may be immediately increased to the recommended bath plating current. The second plating period is selected to be sufficient to ensure complete coverage of the anodizing film, to develop the required plating thickness, to develop the
20 required surface morphology, and/or to achieve other desirable characteristics for the first electrodeposited layer. In one embodiment, the thickness of the second plating state may be 5 to 50 microns. At block 120, the method 100 ends.

[0060] In one embodiment, the first electrodeposited layer may be between
25 15-50 microns thick. In one embodiment, the thickness may be achieved if the first electrodeposited layer is the only electro-deposited layer providing all the functional attributes of the plated surface.

[0061] In one embodiment, a silver cyanide bath from Technic Corporation is used, and a first plating current profile ramps for 0 A/ dm² to between 0.01 and
30 0.5 A/dm². In one example, the first plating current profile may be 0.2A/dm² over a first plating period of between 20 and 60 minutes. In one example, the first plating period may be 40 minutes.

[0062] The current and time are chosen to ensure that the porous anodized layer is filled with silver and depends on the thickness of the anodized layer and the low current deposition rate of the silver bath. The current is then raised to between 0.1 and 2 A/dm² (e.g., in one example 1 A/dm²) for a second plating period between 10 and 30 minutes (e.g., in one example 20 minutes) to develop a total coating thickness of 25 microns.

[0063] In one embodiment, a pyro-copper bath commercially available from Atotech Corporation may be used to deposit the interlock layer. In the example with the pyro-copper bath, the plating current profile ramps from 0 A/dm² to between 0.01 and 1 A/dm². In one example, the plating current profile may ramp to 0.2 A/dm². The plating current may ramp over a period between 10 and 70 minutes. In one example, the plating current may ramp over a period of 20 minutes. This current and time may be chosen to ensure that the porous anodized layer is filled with copper. The plating current profile and time may depend on the thickness of the anodized layer and the low current deposition rate of the copper bath. The current is then raised to between 0.1 and 3 A/dm². In one example, the current may be raised to 1 A/dm². The plating current may be raised for a second plating period between 5 and 90 minutes. In one embodiment, the second plating period may be approximately 70 minutes to develop a total coating thickness of 20 microns.

[0064] In one embodiment, a zinc-nickel bath commercially available from Atotech Corporation may be used to deposit the interlock layer. In the example with the zinc-nickel bath, the plating current profile ramps from 0 A/dm² to between 0.01 and 0.5 A/dm². In one example, the plating current profile may ramp to 0.2 A/dm². The plating current profile may ramp over a first plating period of between 20 and 90 minutes. In one embodiment, the first plating period is 50 minutes. This plating current and time is chosen to ensure that the porous anodized layer is filled with Zn-Ni. The plating current profile and time may depend on the thickness of the anodized layer and the low current deposition rate of the zinc-nickel bath. The current is then raised to between 0.1 and 2 A/dm². In one embodiment, the current may be raised to 1 A/dm². The plating current may be raised for a second plating period between 10 and 90

minutes. In one embodiment, the second plating period is 50 minutes. The plating current may be raised for the second plating period to develop a total coating thickness of 50 microns.

[0065] In one embodiment, an autocatalytic deposition is used from a high
5 pH electroless nickel phosphorous bath in a single process. Here, the anodized pores may be completely filled by Ni-P, and an 8-micron layer may be deposited over the anodizing layer deposited over a period of between 10 and 180 minutes. In one embodiment, the period is 30 minutes. The electroless nickel phosphorous bath may comprise 25 g/L of nickel sulphate and 25 g/L of sodium
10 hypophosphate. 50g/L of sodium pyrophosphate was used as a complexing agent, and 1 mg/L of thiourea was used to moderate the reaction speed. The bath pH is maintained at 11 ± 0.5 using ammonia and operated at a temperature of between 40 and 75 degrees Celsius. In one embodiment, the bath is operated at 60 degrees Celsius to minimize dissolution of the substrate.

15 [0066] In one embodiment, the first metal layer interlocks securely with the anodizing layer and provides a strong foundation for the deposition of further metal layers. The strength of the interlock may be measured by many means well known in the art. In one embodiment, the interlock strength is measured according to the American Society for Testing and Materials (ASTM) D3359
20 standard by completely cutting through the anodizing layer and first metal layer in a grid pattern, with lines on 1 millimeter (mm) centers and using tape to assess the adhesion. In one embodiment, the adhesion is assessed as 4B-5B. In one example, the adhesion is assessed as 5B.

[0067] In one embodiment, the first electrolytically or autocatalytically-
25 deposited layer may provide a first functional component of the overall coating system. In particular, the first deposited layer may provide both corrosion protection and a low conductivity path to the substrate. In this case the first electro-deposited layer may have a conductivity of <0.1 milliohms (m Ω) when measured using the procedure specified in Mil DTL 81706.

30 [0068] In one implementation, the first deposited layer may be deposited from a commercial bath, such as those proposed above, to which a sol of a ceramic phase has been added in a manner described in U.S. Application

13/381,487, incorporated herein by its entirety, to provide enhanced functional attributes to the coated surface.

[0069] In one embodiment, further electrolytically or autocatalytic deposited layers can be applied over the first electrodeposited layer to provide additional
5 functional aspects of the coating. Such a layer or layers may enhance the appearance, hardness, wear resistance, conductivity, etc., of the coating system.

[0070] In one embodiment, due to the high open circuit potential (OCP) of magnesium (-1.75V), a multilayer coating system is deposited to provide
10 corrosion protection to the surface. Here, the composition of the coating system is designed to direct corrosion away from the surface through appropriate selection and ordering of the coating materials for each layer to have a specific OCP.

[0071] In one embodiment the Zn-Ni is selected for the interlock layer due to
15 its ability to form a compact coating with an OCP of about -1.3V. A thick layer of Zn-Ni of between 10 and 30 micron provides a barrier layer that directs corrosion away from the substrate. A second layer of semi-bright nickel is selected due hardness, and OCP of about -0.3V and about 6 microns is deposited as a sacrificial coating. Finally, a decorative or functional surface
20 layer is selected to have an OCP of higher than the semi-bright nickel.

[0072] In one embodiment, a final layer may be deposited, which may be a bright Ni layer with an OCP of -0.4V. It should be noted that that many metals may be chosen for the final layer, provided that the corrosion is directed by the OCP potential of each layer to the sacrificial layer. Such a multi-layer hybrid
25 coating system can provide in excess of 150 hours of Neutral Salt Spray testing performance according to the ASTM specification B117.

EXAMPLES

[0073] The following examples point out example operating conditions and
30 provide examples for creating functional coatings on a magnesium substrate as described in the present disclosure. However, these examples are not to be considered as limiting the scope of the disclosure. The examples are selected

to illustrate aspects of the anodizing bath development, the features of the metallic interlock layer, and the production of a coating stack-up providing good corrosion protection to the magnesium substrate.

5 **EXAMPLE 1 – Development of Magnesium Anodized Layer for Hybrid Coating**

[0074] Anodizing was performed on AZ80 and ZK60 magnesium alloy substrates. Each substrate was cut to 2 cm x 3 cm x 1 cm. Electrical
10 connection to the substrate was made by drilling and taping a 4 mm hole in one edge and screwing a threaded aluminum wire into the hole. The connection point was electrically protected by coating the top edge with epoxy and taping the aluminum wire.

[0075] Substrates were pre-treated by manually grinding the surface to
15 remove the natural oxide layer. A series of emery papers was used from 400 grit to 1000 grit. The substrate was washed in DI water to remove residue. No further pre-treatment was adopted since the alkaline anodizing bath was enough to remove any oils and greases, and the sanded surface provided bonding for the anodizing layer.

[0076] It was discovered that a low power anodizing system from a non-toxic bath can produce relatively thick porous anodizing layers suitable for depositing metallic coatings through electrolytic or autocatalytic deposition. As with hybrid coatings on aluminum described in previous disclosures, the structure of this anodizing layer can determine whether successful coatings are produced.

[0077] FIG. 2 shows a graph of the anodizing voltage against time while
25 anodizing an AZ80 magnesium substrate from a bath comprising 70g/L of sodium hydroxide, 60g/L of sodium tetra borate, 60 g/L of disodium metasilicate, 30 g/L of sodium carbonate, and 12 g/L of citric acid. The bath temperature is 19°C, and constant current anodizing is performed at 1A/dm². Once power is
30 applied, the voltage rapidly climbs to 53.1V and remains below 54V with little observable change on the surface (201) as an oxide barrier forms. The voltage then rises rapidly, associated with the appearance of many small arcs covering

the surface, anodizing can be observed on the surface (202). After about 150 seconds, the voltage stabilizes at 80V when the surface is covered by an anodized layer (204). Growth of the anodizing layer is associated with the presence of larger arcs over the entire surface (203), and a slow growth in the voltage to 86V. After 10 minutes, 15-20 microns of anodizing will be formed (204). The total amp hours (AH) to develop this coating is 0.133 AH/dm², while the power is ~12Wh/dm², i.e., two orders of magnitude less than that required for the MAO process.

[0078] It has also been discovered that the structure of the anodizing layer is controlled by the peak anodizing voltage as shown in graph 302 illustrated in FIG. 3A. Here, the graph 302 illustrates the anodizing voltage over time for constant current anodizing at 1A/dm² with different bath compositions. The table 301 shows the two bath compositions and the substrate type. The surface 303 illustrated in FIG. 3B is created with a high final voltage, (92.3V) and the presence of large sparse arcs during anodizing layer growth, and is characterized by surface features with large pores which do not plate well. The surface 304, also illustrated in FIG. 3B, is created with a lower final voltage, (73.3V) and has small surface features and many small pores, which provides a satisfactory interlock layer for the plating process.

EXAMPLE 2 – Electro Deposition of Silver in the Interlock Layer

[0079] A hybrid coating comprising a 15-micron anodized interlock layer combined with a silver first functional layer provides uniform coverage and provides a good substrate for the deposition of further functional layers.

[0080] Anodizing was performed on AZ80 magnesium alloy substrates cut to 2 cm x 3 cm x 1 cm. Electrical connection to the substrate was made by drilling and taping a 4 mm hole in one edge and screwing a threaded aluminum wire into the hole. The connection point was electrically protected by coating the top edge with epoxy and taping the aluminum wire.

[0081] Substrates were pre-treated by manually grinding the surface to remove the natural oxide layer. A series of emery papers was used from 400

grit to 1000 grit. The substrate was washed in DI water to remove residue.

[0082] The substrates were placed in an anodizing bath comprising 70g/L of sodium hydroxide, 65g/L of sodium tetra borate, and 30 g/L of sodium carbonate at 22°C using constant current anodizing at 1A/dm² for 10 minutes. A 6-micron structured anodized layer was formed.

[0083] The substrates were rinsed in DI water and placed in a silver cyanide bath with a pH of 12. The silver cyanide bath was procured from Technic Corporation and comprised silver cyanide, potassium cyanide, and proprietary ingredients. DC plating was performed for a total period of 60 minutes following a current profile to ensure pore filling as previously disclosed. The current was 0.036A/dm² for 40 minutes followed by 0.18A/dm² for 20 minutes. A 25-micron uniform silver layer was formed as shown in FIG. 4.

[0084] FIG. 5 shows an optical cross-section 502 and scanning electron microscope (SEM) cross-section 501 of the silver interlock layer formed on a substrate 503. The coating thickness is about 25 microns. The SEM cross-section 501 clearly shows the silver 506 penetrating the anodized layer 504.

EXAMPLE 3 – Electro Deposition of Copper in the Interlock Layer

[0085] A hybrid coating comprising an 8-micron anodized interlock layer combined with a copper first functional layer provides uniform coverage and provides a good substrate for the deposition of further functional layers.

[0086] Anodizing was performed on ZK60 magnesium alloy substrates cut to 2 cm x 3 cm x 1 cm. Electrical connection to the substrate was made by drilling and taping a 4 mm hole in one edge and screwing a threaded aluminum wire into the hole. The connection point was electrically protected by coating the top edge with epoxy and taping the aluminum wire.

[0087] Substrates were pre-treated by manually grinding the surface to remove the natural oxide layer. A series of emery papers was used from 400 grit to 1000 grit. The substrate was washed in DI water to remove residue.

[0088] The substrates were placed in an anodizing bath comprising 70g/L of sodium hydroxide, 60g/L of sodium tetra borate, 60g/L of di sodium silicate, 30

g/L of sodium carbonate, and 12 g/L of citric acid at 22°C using constant current anodizing at 1A/dm² for 10 minutes. An 8-micron structured anodized layer was formed.

[0089] The substrates were rinsed in DI water and placed in a pyro copper bath with a pH of approximately 10. The pyro copper bath was procured from Atotech Corporation and comprised copper pyrophosphate, potassium pyrophosphate, citric acid, and proprietary ingredients. DC plating was performed for a total period of 48 minutes following a current profile to ensure pore filling as previously disclosed. The current was ramped to 0.15A/dm² over 28 minutes, followed constant current at 0.15A/ dm² for 10 minutes, followed by constant current at 0.3A/ dm² for 10 minutes. A copper layer of approximately 40 microns was formed as shown in FIG. 7 and disclosed below.

[0090] FIG. 6 shows an optical cross-section 602 and SEM cross-section 601 of the copper interlock layer on a substrate 603. The coating thickness is about 40 microns. The anodizing was performed with unconstrained voltage leading to an anodized surface with large pores. This surface is not ideal for plating the interlock layer. As may be seen from SEM cross-section 601, the copper 606 penetrates the anodized layer 604; however, the copper is discontinuous, featuring disconnected nodules approximately 100 microns in diameter.

[0091] FIG. 7 shows an image 701 of a copper layer formed on a substrate, as described above. Image 702 shows that the copper layer adheres well to the anodizing layer, as demonstrated by the crosshatch adhesion test performed according to ASTM D3359, which passes with no delamination (5B).

[0092] Image 703 shows a simple measurement of the conductivity of the coating through to the substrate, clearly demonstrating that the copper is directly connected to the magnesium.

EXAMPLE 4 – Electro Deposition of Zinc Nickel in the Interlock Layer with an Improved Anodizing Bath

[0093] A hybrid coating comprising a 10-micron anodized interlock layer combined with a zinc nickel first functional layer provides uniform coverage and

provides a good substrate for the deposition of further functional layers.

[0094] Anodizing was performed on AZ80 magnesium alloy substrates cut to 2 cm x 3 cm x 1 cm. Electrical connection to the substrate was made by drilling and taping a 4 mm hole in one edge and screwing a threaded aluminum wire
5 into the hole. The connection point was electrically protected by coating the top edge with epoxy and taping the aluminum wire.

[0095] Substrates were pre-treated by manually grinding the surface to remove the natural oxide layer. A series of emery papers was used from 400 grit to 1000 grit. The substrate was washed in DI water to remove residue.

10 [0096] The substrates were placed in an anodizing bath comprising 70g/L of sodium hydroxide, 60g/L of sodium tetra borate, 60g/L of di sodium silicate, 30 g/L of sodium carbonate, and 12 g/L of citric acid at 20 °C using constant current anodizing at 1A/dm² for 10 minutes. A 10-micron structured anodized layer was formed.

15 [0097] The substrates were rinsed in DI water and placed in a zinc nickel bath with a pH of 13.2. The zinc-nickel bath was procured from ATOTECH Corporation and comprised sodium hydroxide, zinc oxide, complexing agent, and several proprietary ingredients. DC plating was performed for a total period of 60 minutes following a current profile 0~0.1A/ dm² to ensure pore filling as
20 previously disclosed. The current was 0.1A/dm² for 40 minutes followed by 0.3A/ dm² for 20 minutes.

[0098] FIG. 8 shows a sample image 801, an optical microscope surface image 802, and optical microscope cross-section image 803 of the hybrid Zn-Ni coating developed on the anodizing layer produced from the original bath. The
25 coatings 802 and 803 are quite rough, with large nodules 804 visible on the surface. The nodules 804 are larger than is common for a Zn-Ni coating and are generated by preferential coating growth where current paths are available to the substrate through the anodizing film. By manipulating the anodizing bath chemistry, temperature, and conductivity, the number of and size of the pores
30 may be modified such that the Zn-Ni coating becomes uniform and continuous. The cross-section image 803 shows a substrate 805 and an anodizing film 806 of about 22 microns penetrated by a Zn-Ni interlock layer 807.

[0099] When developing the Zn-Ni interlock layer 807, it has been discovered that the bath containing sodium citrate and hydrogen peroxide produces improved results. ZK60 samples were pre-treated as described above and anodized in a bath comprising 70g/L NaOH, 60g/L of Na₂SiO₃, 12g/l of citric acid, 6 ml/l of hydrogen peroxide, and between 0.01M and 0.05M NaCl. FIG. 12 shows the voltage time curve, 1201, during anodizing using this bath. As may be seen in contrast to the curve in FIG. 3, the more controlled conductivity in this bath produces a flatter voltage curve and limits the peak voltage below 75V. It has been found that the bath improves the density and uniformity of pores in the anodized layer, which works better with the Zn-Ni coating and other interlock layer metals.

[00100] FIG. 9 shows images 901, 902, and 903 of anodized samples created using the new bath. A surface SEM 904 is of the surface developed using the new bath. The surface SEM 904 shows a surface that has a well-defined pore structure with an improved surface morphology that provides superior grip for the interlock layer. An area SEM 905 and associated EDS data 906 shows higher magnesium and oxygen in the dark areas, around box 908 in the area SEM 905, suggesting a porous structure supporting electrical conductivity to the substrate. The lighter areas, around box 910 in the area SEM 905 and the last line of the EDS table 906, show more oxygen and silicon, suggesting a robust silicon dioxide framework for depositing an interlock layer.

[00101] FIG. 13 also shows an optical image of the Zn-Ni interlock layer surface that may be produced with the anodizing layer of the present disclosure. The surface 1302 shows a dense nodular structure typical of a Zn-Ni coating. FIG. 10 shows the surface and cross section images of a hybrid Zn-Ni coating produced using the new bath. A sample image 1001 shows a fine uniform surface. The optical microscope image shows a finer and more uniform surface nodule structure than the example in FIG. 8, discussed above, that was developed using the original anodizing bath. A cross-section SEM image 1002 shows the Zn-Ni interlock layer well integrated with the anodizing structure and demonstrates a more uniform Zn-Ni surface. A SEM line scan 1003 and associated EDS data 1004 shows that the Zn-Ni coating penetrates the

anodizing layer. The dotted circle 1005 shows the coating composition as the Zn-Ni interlock penetrates the anodizing layer. The increase in silicon, oxygen, and magnesium is characteristic of the anodizing structure developed with the new bath

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EXAMPLE 5 –Deposition of Ni-P in the Interlock Layer

- [00102] A hybrid coating comprising a 4-micron anodized interlock layer combined with a Ni-P first functional layer provides uniform coverage and provides a good substrate for the deposition of further functional layers.
- [00103] Anodizing was performed on AZ80 magnesium alloy substrates cut to 2 cm x 3 cm x 1 cm. Electrical connection to the substrate was made by drilling and taping a 4 mm hole in one edge and screwing a threaded aluminum wire into the hole. The connection point was electrically protected by coating the top edge with epoxy and taping the aluminum wire.
- [00104] Substrates were pre-treated by manually grinding the surface to remove the natural oxide layer. A series of emery papers was used from 400 grit to 1000 grit. The substrate was washed in DI water to remove residue.
- [00105] The substrates were placed in an anodizing bath comprising 70g/L of sodium hydroxide, 60g/L of sodium tetra borate, and 30 g/L of sodium carbonate at 20°C using constant current anodizing at 1A/dm² for 10 minutes. A 4-micron structured anodized layer was formed.
- [00106] The substrates were rinsed and ultrasonically cleaned in an alcohol bath for 1-5 minutes.
- [00107] The cleaned anodized specimens were placed in an alkaline nickel phosphorous bath comprising 25 g/L of nickel sulphate and 25 g/L of sodium hypophosphate. 50g/L of sodium pyrophosphate was used as a complexing agent, and 1 mg/L of thiourea was used to moderate the reaction speed. The bath was heated to 70 °C, and pH of the bath adjusted to 11 using ammonia.
- [00108] The plating time of 3 hours was enough to fill the pores and deposit a uniform layer over the surface of the anodizing.
- [00108] FIG. 11 depicts SEM images of the coating produced. An image 1102

of the surface shows a nodular Ni-P surface morphology. Here, nodules 1106 shown in the image 1102 do not completely cover the surface, and some voids 1107 exist. By carefully controlling the anodizing bath chemistry, temperature, and conductivity, the density of pores in the anodizing layer may be optimized to
5 ensure that the Ni-P coating is contiguous. An image 1101 shows a SEM image of the coating cross section. Here, a substrate 1103 is anodized to a thickness of about 3-5 microns, and the Ni-P coating is 10-20 microns. The Ni-P clearly penetrates an anodizing layer 1104.

[00109] It will be appreciated that variants of the above-disclosed and other
10 features and functions, or alternatives thereof, may be combined into many other different systems or applications. Various presently unforeseen or unanticipated alternatives, modifications, variations, or improvements therein may be subsequently made by those skilled in the art which are also intended to be encompassed by the following claims.