A process for electrolytically coating a substrate at a preselected second voltage. The process comprises the steps of: (i) immersing the substrate in an aqueous electrolytic bath comprising at least one soluble salt, the substrate acting as a first electrode; (ii) contacting a second electrode with the aqueous electrolytic bath; (iii) passing a current through the aqueous electrolytic bath at a first voltage which is less than the second voltage, the current comprising alternating current superimposed over direct current; (iv) increasing the first voltage to a second voltage over a period of time while continuing to pass the current through the aqueous electrolytic bath; (v) keeping the second voltage substantially constant thereby allowing the current to decrease; and (vi) thereby forming an oxide coating on the substrate.
FIGURE 1
COATED SUBSTRATE AND PROCESS FOR PRODUCTION THEREOF

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to a coated substrate and to a process for production thereof. More particularly, the present invention relates to a substrate coated with a protective oxide-based film and to a process for production thereof.

[0003] 2. Description of the Related Art

[0004] It is known in art to coat various conductive substrates, such as metals, to protect them from corrosion or erosion or to act as an undercoating or base layer for organic finishes. Indeed, much of the prior art is devoted to various means by which an oxide-based film can be deposited on a metal (particularly aluminum, magnesium, and alloys thereof). Generally, oxide-based films are anodically deposited on the substrate surface.

[0005] U. S. Pat. No. 1,923,539 (Jenny et al.) teaches production of anticorrosive protective coatings on light metals such as aluminum and magnesium, including their alloys see pages 1, lines 2-5. The coatings are prepared by anodic oxidation, a process in which the coated substrate is immersed in an anodic current (AC) in an aqueous electrolyte—see page 1, lines 8-11. The anodic electrolyte can include chromic acid. The reference teaches the use, during anodization, of an alternating current (AC) which deviates from the sinus form or an alternating current on which a direct current has been superimposed—see page 3, lines 40-45.

[0006] U. S. Pat. No. 3,732,152 (Hawke) teaches anodizing magnesium metal or alloys by immersing the metal/ alloy in an aqueous bath containing sodium hydroxide and sodium hexafluorotitanate and passing AC current through the bath—see column 1, lines 28-35.

[0007] United States patent 3,996,115 (Kessler) teaches an improved bath composition for surface finishing on metal surfaces, the bath composition comprising an inorganic oxidant-etchant and an effective amount of the reaction product of a metal halide and a polyhalo-substituted alkarylamine—see column 2, lines 51-56. There is further disclosure that these metal surfaces are processed in a conventional manner—see column 2, lines 56-59. The reference further teaches that the anodizing process can utilize direct current or alternating current superimposed on direct current—see column 5, lines 63-65.

[0008] U. S. Pat. No. 4,184,926 (Kozak) teaches pretreatment of magnesium metal or alloy with aqueous hydrofluoric acid and then immersion in a bath containing an alkaline metal silicate and an alkali metal hydroxide—see column 2, lines 43-56.

[0009] U. S. Pat. No. 4,744,872 (Kobayashi et al.) teaches a purportedly novel solution for anodic oxidation of magnesium comprising a solution of: silicate, carbonate and alkali hydroxide, optionally with one or more of borate, fluoride and phosphate—see column 1, line 64 to column 2, line 6. All of the examples in this patent appear to relate to the use of alternating current only in the anodizing solution.

[0010] U. S. Pat. No. 4,976,830 (Schmeling et al.) teaches a method of preparing surfaces of magnesium and magnesium alloys by anodic oxidation. Generally, the method involves the use of an alkali-rich aqueous bath containing: (a) borate or sulphate anions, and (b) phosphate and fluoride or chloride ions, and adjusted to a pH of 8-12—see column 1, lines 55-60. The reference does teach the use of a continuous direct current with an alternating current superimposed thereon—see column 2, lines 53-68.

[0011] U. S. Pat. No. 5,240,589 [Bartak et al.] teaches a method comprising pretreatment of an article comprising a magnesium alloy in a chemical bath at a neutral pH followed by electrolytically coating the pretreated article in an aqueous solution—see column 1, lines 12-16. The specific nature of the bath and electrolysis is discussed at column 2, line 53 to column 3, line 5. Electrolysis appears to be conducted using direct current (DC) only—see column 5, lines 1-23.

[0012] U. S. Pat. Nos. 5,264,113 [Bartak et al.] and 5,266,412 [Bartak et al.] teach sequential electrochemical treatment of magnesium and its alloys in a specific bath composition—see column 2, line 50 to column 3, line 10. At column 3, lines 11-12, there is a discussion of using a full wave rectified AC source. Further, the use of DC current is described at column 4, lines 8-23.

[0013] U. S. Pat. No. 5,385,662 [Kurze et al.] teaches a method of producing oxide ceramic layers on a variety of metals and alloys by plasma-chemical anodic oxidation in aqueous organic electrolytes—see column 1, lines 9-14. The specific processing conditions include: (i) the use of an electrolytic bath which has a pH of 2-8 and is substantially free of chloride, (ii) constant temperature of −30° C. to 15° C., and (iii) a current density of at least 1 A/dm²—see column 2, lines 17-34. The type of voltage and current is described as having “surprisingly no influence on the process”—see column 3, lines 23-28.

[0014] U. S. Pat. No. 5,487,823 [Kurze et al.] teaches ceramic coated metal alloys and particles of “fluorine polymers” incorporated in the ceramic layer—see column 2, lines 28-37. The method used to produce the ceramic coated metal alloys is similar to the one described in the Kurze et al. ’62 patent discussed in the previous paragraph.

[0015] Canadian patent 480,167 [Freud et al.] teaches a process for obtaining a coating for protecting metal from corrosion utilizing galvanic means. The apparent point of novelty in the process is the use of a specific bath—see column 2, line 48 to column 3, line 22.

[0016] British patent 615,848 [Haage et al.] teaches anodizing of magnesium and its alloys—see page 1, lines 10-11. The purported point of novelty in this reference appears to be the use of a specific bath—see page 1, line 70 to page 2, line 10. The reference further teaches the use of direct current on which has been superimposed alternating current—see page 2, lines 69-73.

[0017] Thus, much of the prior art has focussed on the nature of the composition of the electrolytic bath used to deposit the protective film on the substrate.

[0018] The art is constantly in need of improved coatings which will protect the underlying substrate in otherwise deleterious environments. This is especially the case for substrates that are used in extreme environments such as in aerospace applications.
SUMMARY OF THE INVENTION

[0019] It is an object of the present invention to provide a novel process for coating a substrate with a protective film.

[0020] Accordingly, in one of its aspects, the present invention provides a process for electrolytically coating a substrate at a preselected second voltage, the process comprising the steps of:

[0021] (i) immersing the substrate in an aqueous electrolytic bath comprising at least one soluble salt, the substrate acting as a first electrode;

[0022] (ii) contacting a second electrode with the aqueous electrolytic bath;

[0023] (iii) passing a current through the aqueous electrolytic bath at a first voltage which is less than the second voltage, the current comprising alternating current superimposed over direct current;

[0024] (iv) increasing the first voltage to a second voltage over a period of time while continuing to pass the current through the aqueous electrolytic bath;

[0025] (v) keeping the second voltage substantially constant thereby allowing the current to decrease; and

[0026] (vi) thereby forming an oxide coating on the substrate.

[0027] As used throughout this specification, the terms AC and alternating current are used interchangeably, and the terms DC and direct current are used interchangeably.

BRIEF DESCRIPTION OF THE DRAWING

[0028] Embodiments of the present invention will be described with reference to the attached drawing in which:

[0029] FIG. 1 illustrates a plot pH versus time for a comparative study reported in Example 2 described below.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0030] Thus, the present inventors have unexpectedly discovered that a substrate coated with a protective film or layer with enhanced resistance to corrosion can be produced if, during electrolysis, current is used at staged voltages pursuant to a specific waveform. The preferred form of the waveform has the following characteristics:

[0031] (i) a current is passed through the electrolytic cell at an initial voltage at which deposition of the protective film or layer occurs which is less than the final voltage;

[0032] (ii) as the substrate becomes coated, the voltage is then increased (preferably by a non-linear increase) to a final voltage (notionally at 1);

[0033] (iii) the final (highest) voltage is maintained substantially constant, thereby resulting in the current decreasing gradually; and

[0034] (iv) during (i), (ii) and (iii), the current comprises an alternating current superimposed over a direct current. Thus, characteristics (i) through (iv), in combination, may be considered to be an initial voltage step followed by a linear or non-linear increase in voltage to a final voltage, remaining at this final voltage for a period of time while the current decreases gradually.

[0035] Preferably, the initial voltage corresponds to an initial current in the range of from about 50 to about 100 mA/cm². The current then decays to a lower value, preferably in the range of from about 5 to about 35, more preferably from about 10 to about 30 mA/cm². It is preferred to increase the voltage from the initial voltage at a rate which maintains the current substantially constant. The rate of voltage increase can be substantially linear or substantially non-linear. The final voltage is not particularly restricted and will depend, inter alia, on equipment limitations, the desired final film thickness, the extent of sparking and the like. Preferably the final (or second) voltage is at least about 300 V, more preferably at least about 350 V.

[0036] Once the final (or second) voltage is reached, the process may be terminated, or the voltage may be held constant for a period of time in the range of from about 5 to about 20 minutes, to further thicken the coating.

[0037] With reference to characteristic (iv) of the waveform described above, the current is an alternating current superimposed over a direct current. Preferably, the amplitude of the applied alternating current is in the range of from about 15% to about 30% of that of the applied direct current.

[0038] The present process is useful to coat a substrate. The nature of the substrate is not particularly restricted provided, of course, that the substrate is conductive. Preferably, the substrate is a metal or an alloy thereof. More preferably, the substrate is selected from the group comprising aluminum, magnesium, lithium, beryllium, gallium, chromium, titanium, tantalum, zirconium, niobium, hafnium, antimony, tungsten, molybdenum, vanadium, bismuth and an alloy containing one or more of these metals. The most preferred substrate may be selected from magnesium and magnesium alloys.

[0039] The electrolytic bath used in the present process is not particularly restricted provided it contains at least one soluble salt.

[0040] A preferred electrolytic bath is that disclosed in U.S. Pat. No. 4,976,830 [Schmeling et al.]. Generally, this preferred electrolytic bath is an alkali-rich aqueous bath adjusted in a pH in the range of from about 8 to about 12 and comprising (a) borate or sulfate anions, and (b) phosphate and fluoride or chloride ions. Preferably, the content of the borate and sulfate ions is in the range of from about 10 to about 80 grams per liter of electrolytic bath. Preferably, the content of phosphate ions (as H₃PO₄) is in the range of from about 10 to about 70 grams per liter of electrolytic bath. Preferably, the content of fluoride or chloride ions (as HF or HCl, respectively) using in conjunction with the phosphate ions is in the range of from about 5 to about 35 grams per liter of electrolytic bath.

[0041] Another preferred electrolytic bath is that disclosed in U.S. Pat. Nos. 5,264,113 [Bartak et al.] and 5,266,412 [Bartak et al.]. Generally, the preferred electrolytic bath comprises a water soluble hydroxide compound, a water soluble fluoride compound and a water soluble silicate compound.
Preferably, the water soluble hydroxide compound is present in an amount in the range of from about 2 to about 15 g, more preferably from about 4 to about 10 g, most preferably from about 5 to about 8 g, per liter of electrolytic bath. Preferably, the water soluble hydroxide compound is selected from the group comprising alkali metal hydroxides, ammonium hydroxide and mixtures thereof. The most preferred water soluble hydroxide compound is potassium hydroxide.

Preferably, the water soluble fluoride compound is present in an amount in the range of from about 2 to about 14 g, more preferably from about 6 to about 12 g, most preferably from about 8 to about 10 g, per liter of electrolytic bath. Preferably, the water soluble fluoride compound is selected from the group consisting of alkali metal fluoride compounds ammonium fluoride, ammonium bifluoride, alkali metal fluorlosilicate compounds, hydrogen fluoride and mixtures thereof. More preferably, the water soluble fluoride compound is selected from the group consisting of alkali metal fluoride compounds, alkali metal fluorosilicate compound, hydrogen fluoride and mixtures thereof. The most preferred water soluble fluoride compound is potassium fluoride.

Preferably, the water soluble silicate compound is present in an amount in the range of from about 5 to about 40 g, more preferably from about 10 to about 25 g, most preferably from about 15 to about 20 g, per liter of electrolytic bath. Preferably, the water soluble silicate compound is selected from the group comprising alkali metal silicate compounds, alkali metal fluorosilicate compounds and mixtures thereof. The most preferred water soluble silicate compound is sodium silicate.

While the electrolytic bath taught in the Bartak et al. patents is the preferred electrolytic bath for use in the present process, those of skill in the art will appreciate that the composition and properties of the electrolytic bath are not particularly restricted. Preferably, the substrate is pretreated prior to immersion in the electrolytic bath. For example, the substrate may be initially ultrasonically treated in ethanol and degreased in an alkaline solvent. The next pretreatment step preferably is conducted at a temperature of from about 40° to about 1 DOOC and comprises immersion of the substrate in an aqueous solution comprising from about 0.2 to about 5.0 M ammonium fluoride having a pH of from about 5 to about 8. This pretreatment serves to clean the article and creates an ammonium fluoride-containing layer at the surface of the substrate.

Thus, in a preferred embodiment of the present process, electrochemical anodization is used to apply an anodic potential or current to the metal (or other substrate) to form an oxide film (compact and/or porous film) on the anode surface. Optionally, this treatment may be followed by various post-treatments steps to seal or cure the oxide film, thereby further enhancing its corrosion resistance. For aluminum-based substrates, care should be exercised to conduct the anodization in a relatively acidic electrolytic bath, whereas for magnesium-based substrates, the anodization should be conducted in a relatively alkaline electrolytic bath. There are two useful anodization methods for oxidation of alloy surfaces. First, there is a non-spark method in which the alloy surfaces are anodized at lower DC density and voltage. The other is an anodic spark deposition process, also known as “silicodizing” (when carried out in a silicate solution). The film grows through the dielectric breakdown of the oxide layer, causing visible sparks or scintillation over the anodic substrate. It is believed that the sparking action results from the applied voltage being greater than the dielectric breakdown voltage of the oxide layer that is produced during anodization. Sparking is a relatively complicated process and its mechanism is still not understood completely, because the high temperatures reached (up to 1000° C, on the anode surface) result in a complex series of processes, including reactions between the substrate being coated, oxygen, the electrolytes, the solvent and other components of the anodizing bath. Also, physical processes, such as fusion, can occur at these high temperatures. The process is clearly very complex, and the variables that contribute to spark film formation are difficult to isolate and analyze.

Embeddings of the invention will be described with reference to the following Examples which are for illustrative purposes only and should not be used to limit the scope of the invention.

In the Examples, electrochemical methods were utilized to evaluate various anodized substrates in aqueous saline solutions and in hydrocarbon fuel media, with the use of conventional three-electrode circuitry. The analytical methods employed in Examples include an AC impedance technique, combined with Scanning Electron Microscope (SEM) analysis. Also, salt fog tests were carried out on oxide-coated substrates in accordance with ASTM B117.

Instrumentation

The AC impedance measurements were carried out using a Solartron 1255 frequency response analyzer connected to a Solartron 1286 electrochemical interface. In this work, the frequencies ranged from 65 kHz to 0.1 Hz, 12 points per decade, with a polarization amplitude of 10 mV (root mean square). The sensing resistor was set to the “auto” mode in the low frequency range and 1.5m in the high frequency range. With all the features engaged, data gathering over the entire frequency range at a single potential required about 4 minutes. An IBM 8088 PC with installed Z-plot software (Scribner Associates, Inc.) was interfaced to the Solartron system and used to gather AC impedance data.

Most of the AC impedance measurements were carried out at the open-circuit potential (OCP), while others were at potentials positive of the OCP. Therefore, the OCP versus time was recorded simultaneously while gathering ac impedance data. The OCP data was stored in a batch file of Z-plot and then read or printed out.

Working Electrodes (WE)

The chemical composition of the alloy used in these Examples is provided in Table

1. The working electrode was in the shape of a cylinder or a disc (i.e. WE43 disc electrode), the latter being referred to in the Examples.
The coated WE43 alloy was assessed in the JP-8 fuel medium. The JP-8 fuel, supplied by AlliedSignal Inc., was additized with 0.01 vol % (H₂O - 5 wt % NaCl), consistent with these used in the typical contaminated fuel testing for a fuel control. The fuel provided was thermally degraded fuel, which was subjected to thermal exposure in a bomb at 177°C (350°F) for 72 hours. It is believed that the degraded fuel is more acidic than the fresh fuel. Although the fuel contained certain conductive and anti-static agents, and 4 vol % (H₂O - 5 wt% NaCl) was added to achieve a conductivity of 50 to 450 pico Siemens, it was necessary to perform the tests in an aqueous solution periodically while the samples were immersed in the fuel medium. In order to compare with the results obtain in the 0.86 M NaCl solution, the same solution was employed for the testing of coatings as a function of time of exposure to the degraded fuel medium. Therefore, the same electrochemical cell, CE, RE and AE were used and the experiment was carried out in the identical way.

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[0065] Analysis

The AC impedance data were analyzed using a nonlinear least squares fit program, “Equivert” (Equivalent Circuit, version 3.97), written by B.A. Boukamp, University of Twente, Netherlands.

[0067] The oxide films formed at WE43 alloys were examined using scanning electron microscopy (SEM) techniques to determine the film thickness, morphology and porosity of the oxide. The SEM work was performed using

<table>
<thead>
<tr>
<th>Solution pH</th>
<th>Component 1</th>
<th>Component 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>x ml 0.5 M H₂BO₃</td>
<td>y ml 0.025 M Na₂B₂O₅</td>
</tr>
<tr>
<td>7</td>
<td>50 ml 0.1 M KH₂PO₄</td>
<td>25 ml 0.1 M NaOH</td>
</tr>
<tr>
<td>7.5</td>
<td>50 ml 0.1 M KH₂PO₄</td>
<td>45 ml 0.3 M NaOH</td>
</tr>
</tbody>
</table>

### Table 1

<table>
<thead>
<tr>
<th>Y</th>
<th>Nd</th>
<th>Zr</th>
<th>HRE</th>
<th>Re</th>
<th>Zn</th>
<th>Li</th>
<th>Mn</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min.</td>
<td>3.70</td>
<td>2.00</td>
<td>0.40</td>
<td>1.50</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>Max.</td>
<td>4.30</td>
<td>2.50</td>
<td>1.00</td>
<td>1.25</td>
<td>0.20</td>
<td>0.20</td>
<td>0.15</td>
<td>0.03</td>
<td>0.01</td>
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</tr>
</tbody>
</table>

HRE = Heavy Rare Earths, principally Ytterbium, Erbium, Dysprosium and Gadolinium. The HRE fraction is directly related to the Yttrium content of the alloy (i.e., Yttrium is present as a nominal 80% Y, 20% HRE mixture).
a HITACHI S-4500 Scanning Electron Microscope at the Electron Microscope Unit of the Health Sciences Center, the Faculty of Medicine, University of Calgary, or a JSM 6300V (JOEL). Accelerating voltages of 20 kV were employed throughout.

**EXAMPLE 1**

[0068] Formation of Oxide Coating on WE43 Disc Samples

[0069] In this Example, the process was used to coat a series of WE43 disc electrodes. Thus, the WE43 disc sample surfaces were prepared by single point lath machining, in order to obtain reproducible surface conditions for all experiments.

[0070] Prior to coating, the WE43 alloy was pre-treated to provide a clean and smooth base for anodic oxidation. Thus, the WE43 disc sample was first subjected to 5 minutes of ultrasonic cleaning in ethanol. Then, the WE43 disc sample surface was chemically cleaned for 5 minutes at 70°C in an alkaline solution having a pH of 10.5, and thereafter rinsed with triply distilled water. The composition of the alkaline solution is provided in Table 3.

| Table 3 |
|-------------------|-----------------|----------|
| Sodium pyrophosphate, Na₂P₂O₇ | 50 g/L | 0.2 M |
| Sodium borate, Na₂BO₂ | 10 g/L | 0.1 M |
| Sodium fluoride, NaF | 1 g/L | 0.02 M |

[0071] After the WE43 sample surface was cleaned, the sample was chemically treated in ammonium fluoride solution (0.50 M, pH =6-7) for 30 minutes at 70°C and then rinsed with triply distilled water. This results in the formation of a MgO and MgF₂ layer on the surface, which provides a good base for the following anodization step.

[0072] Using the electrolytic cell described above, the WE43 samples were then anodized in an electrolytic bath (pH =12.5-13; see Table 4 for composition) by using a range of combinations of current density, voltage and time, to produce oxide films of different thickness and other properties. During the anodization process, the bath temperature was maintained at 8-20°C using an ice water bath.

| Table 4 |
|-------------------|-----------------|----------|
| Potassium hydroxide, KOH | 5-7 g/L | 0.09-0.12 M |
| Potassium fluoride, KF | 8-10 g/L | 0.14-0.17 M |
| Sodium silicate, Na₂SiO₃ | 15-20 g/L | 0.11-0.15 M |

[0073] The circuit employed in the anodization coating process involved the application of a continuous DC voltage with superimposed AC voltage at a frequency of 60 Hz. The AC amplitude was set to be 15 - 30 % of the DC, adjusted with a variable transformer.

[0074] The initial voltage, V₀, applied between the anode and the cathode, was ca. 200 V DC and 40 V AC in all cases. After ca. 30-60 seconds, during which initially relatively high current densities of up to 50 to 100 mA/cm² passed at short times but then decayed quite rapidly, the current density was maintained constant at i₀ by increasing the DC voltage (and proportionally, the AC voltage) for a period of time, t₁. In most cases, when the applied DC voltage reached values in the range of 240 to 370 (V2) DC at t₀, it was maintained at close to constant at V₂ for another period of time, t₂ - t₁, during which the current density slowly decayed. The applied voltage was switched off at t₂.

[0075] A stainless steel disc served as the counter electrode, large enough in area to provide an even current distribution at the anode.

[0076] After the oxide film was formed on the surface of the WE43 alloy, it was rinsed with triply distilled water and air dried before it was analyzed in the 0.86 M NaCl solution.

[0077] Analysis of Oxide Coatings Formed On WE43 Discs Samples Coatings formed using the anodization parameters given in Table 5 were assessed using the AC impedance technique, as well as by SEM examination. Only one face of the coated disc specimens was exposed to solution, yielding an active surface area of 0.77 cm² in each case. AC impedance data were used to yield Rf values, the low frequency resistance (inversely relates to susceptibility of specimen to corrosion; and also inversely proportional to corrosion rate) at the open circuit potential as a function of time in 5% (0.86 M) NaCl solution in these experiments. SEM analysis was used for some samples to determine barrier and porous oxide film thickness, and the diameter and number of pores in the coatings.

[0078] Table 5 compares coating performance in terms of the initial Rf values in the NaCl solution, and at various longer times of immersion. Table 5 shows that the key factors in yielding good coatings is a higher i₀ value and the existence of the period of time after the application of i₀ over which the current drops, i.e., the existence of the t₁ to t₂ time period. The length of this t₂ - t₁ period also plays a role in coating performance. The best coating in Table 5 is that where i₀=30 mA/cm², t₁ is 5 min, V₂ is greater than 320 V, and t₂ is greater than 10 min.

[0079] Those specimens for which i₀ was maintained constant throughout the anodization time, i.e., when t₁=t₂, and the current was not allowed to decay with time before switching off the applied voltage, clearly exhibit inferior properties.

[0080] The SEM results shown in Table 5 indicate that the overall coating thickness increases with i₀, hence explaining the observed better performance of the higher current density coatings. The longer the time of anodization, i.e. both larger t₁ and t₂ values, the thicker the film also. Coatings which were formed with a substantial length of time, t₁ to t₂, over which the current decayed showed evidence for pores which were partially sealed deeper inside the coating. Coatings formed without the current decay period may contain pores which penetrate deeper into the film.
<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>Vc (V)</th>
<th>i0 (mA/cm²)</th>
<th>t1 (min.)</th>
<th>t2 (min.)</th>
<th>V (V)</th>
<th>t (min.)</th>
<th>t (min.)</th>
<th>NaCl, x 10³</th>
<th>R (Ω) - 5 min. in NaCl, x 10³</th>
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<th>R (Ω) - 36 hrs. in NaCl, x 10³</th>
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**EXAMPLE 2**

[0081] In this Example, a coating (i.e., CCM-A coating), provided by AlliedSignal Inc., was deposited on the identical WE43 disc specimens (single point machined followed by hand grinding on abrasive paper). It is believed that the CCM-A coating was achieved using the methodology of the Bartak et al. patents discussed above—i.e., using a conventional AC/DC voltage program. The CCM-A coating was used for comparison of coating resistance with the coating described in Example 1 in the aqueous media. All experimental conditions were kept without any change exactly the same as used before.

[0082] The CCM-A coating and one of the better performing coatings produced in Example 1 (30 mA/cm²; Vc = 320 V; t1 = 5 min.; t2 = 10 min.) were both tested for their impedance response as a function of time in the 5% (0.86 M) NaCl solution.

[0083] FIG. 1 illustrates a plot of Rf versus time of immersion in solution for these two coatings. It is seen that the results of the comparative study are as follows:

[0084] (i) The coating of Example 1 yield a 10:500 fold increase in corrosion resistance compared to the CCM-A coating.

[0085] (ii) The coating of Example 1 can survive in the 0.86 M NaCl solution for over one hundred hours without any sign of pitting. In contrast, the CCM-A samples fail quickly in the NaCl solution. The CCM-A coatings showed inductive character at very early immersion time in the NaCl solution, where coatings of Example 1 did not. Normally, inductors shown in AC impedance data correlate with pitting on the surface. The coating of Example 1 is clearly more resistive to pitting than are the CCM-A coatings in the NaCl solution.

[0086] The salt fog test was conducted, pursuant to ASTM B 117, on the two coated (CCM-A and the coating of Example 1) WE43 disc specimens, for comparison. The results indicated that the two coatings appeared similar after 24 hours, both that the CCM-A coating suffered significantly more pitting after 120 hours of exposure compared to the coating of Example 1.

**EXAMPLE 3**

[0087] A coating of Example 1 (30 mA/cm²; Vc = 320 V; t1 = 5 min.; t2 = 10 min.) and the CCM-A coating were also evaluated in the degraded fuel medium using AC impedance technique. Although 5% of NaCl solution was added to the fuel, it is still too resistive to allow carrying any electrochemical experiments in it directly. Increasing the conductivity of the fuel will definitely alters the fuel properties, thus the specimens are not tested in the fuel media. Instead, the samples were tested electrochemically in an aqueous solution after they were immersed in the fuel for a certain period of time. The aqueous solution chosen for this purpose is the same NaCl solution used in this work, i.e., 0.86 M NaCl solution. The samples were tested using AC impedance technique and by tracking OCP changes simultaneously. The samples were carefully cleaned before and after they were coated in the aqueous NaCl solution.

[0088] The coatings in this Example were formed using conditions similar to those in previous Examples, i.e., anodized at 30 mA/cm² for 5 minutes followed by current density decay for 15 minutes. Table 7 shows that the coating of Example 1 showed virtually no indication of any deterioration, even after almost 1600 hours in the degraded fuel medium. Also, no visual changes were seen, i.e., no pits and no change in colour. In contrast, while the CCM-A coating exhibits good initial resistance, it failed much sooner than the coating of Example 1. Finally, it is noteworthy that the coatings in this Example were not pre-treated or post-treated in any way, illustrating the advance corrosion protection of the coating of Example 1.
embodiments of the invention, will be apparent to persons skilled in the art upon reference to this description. It is therefore contemplated that the appended claims will cover any such modifications or embodiments.

[0090] All publications, patents and patent applications referred to herein are incorporated by reference in their entirety to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated by reference in its entirety.

What is claimed is:
1. A process for electrolytically coating a substrate at a preselected second voltage, the process comprising the steps of:
   (i) immersing the substrate in an aqueous electrolytic bath comprising at least one soluble salt, the substrate acting as a first electrode;
   (ii) contacting a second electrode with the aqueous electrolytic bath;
   (iii) passing a current through the aqueous electrolytic bath at a first voltage which is less than the second voltage, the current comprising alternating current superimposed over direct current;
   (iv) increasing the first voltage to a second voltage over a period of time while continuing to pass the current through the aqueous electrolytic bath;
   (v) keeping the second voltage substantially constant thereby allowing the current to decrease; and
   (vi) thereby forming an oxide coating on the substrate.

2. The process defined in claim 1, wherein the substrate is a metal or an alloy thereof.

3. The process defined in claim 1, wherein the metal is selected from the group comprising aluminum, magnesium, lithium, beryllium, gallium, chromium, titanium, tantalum, zirconium, niobium, hafnium, antimony, tungsten, molybdenum, vanadium, bismuth and an alloy containing one or more of these metals.

4. The process defined in claim 2, wherein the metal is magnesium or an alloy containing magnesium.

5. The process defined in claim 1, wherein the substrate acts as an anode and the second electrode acts as a cathode.

6. The process defined in claim 1, wherein the second voltage is at least about 300 V.

7. The process defined in claim 1, wherein the second voltage is at least about 350 V.

8. The process defined in claim 1, wherein the second voltage is at least about 400 V.

9. The process defined in claim 1, wherein Step (iv) comprises increasing the first voltage to the second voltage in a substantially non-linear manner.

10. The process defined in claim 1, wherein Step (iv) comprises increasing the first voltage to the second voltage in a substantially linear manner.

11. The process defined in claim 1, wherein the electrolytic bath comprises a water soluble hydroxide, a water soluble fluoride compound and a water soluble silicate.

12. The process defined in claim 11, wherein the water soluble hydroxide is present in an amount in the range of from about 4 to about 10 g per liter of electrolytic bath.

13. The process defined in claim 11, wherein the water soluble hydroxide is present in an amount in the range of from about 4 to about 10 g per liter of electrolytic bath.

14. The process defined in claim 11, wherein the water soluble hydroxide is present in an amount in the range of from about 5 to about 8 g per liter of electrolytic bath.

15. The process defined in claim 11, wherein the water soluble hydroxide is selected from the group comprising alkali metal hydroxides, ammonium hydroxide and mixtures thereof.

16. The process defined in claim 11, wherein the water soluble hydroxide is potassium hydroxide.

17. The process defined in claim 11, wherein the water soluble fluoride compound is present in an amount in the range of from about 2 to about 14 g per liter of electrolytic bath.

18. The process defined in claim 11, wherein the water soluble fluoride compound is present in an amount in the range of from about 6 to about 12 g per liter of electrolytic bath.

19. The process defined in claim 11, wherein the water soluble fluoride compound is present in an amount in the range of from about 8 to about 10 g per liter of electrolytic bath.

20. The process defined in claim 11, wherein the water soluble fluoride is selected from the group consisting of alkali metal fluorides, ammonium fluoride, ammonium bifluoride, alkali metal fluorosilicates, hydrogen fluoride and mixtures thereof.

21. The process defined in claim 11, wherein the water soluble fluoride is selected from the group consisting of alkali metal fluorides, alkali metal fluorosilicates, hydrogen fluoride and mixtures thereof.

22. The process defined in claim 11, wherein the water soluble fluoride is potassium fluoride.

23. The process defined in claim 11, wherein the water soluble silicate is present in an amount in the range of from about 5 to about 40 g per liter of electrolytic bath.

24. The process defined in claim 11, wherein the water soluble silicate is present in an amount in the range of from about 10 to about 25 g per liter of electrolytic bath.

25. The process defined in claim 11, wherein the water soluble silicate is present in an amount in the range of from about 15 to about 20 g per liter of electrolytic bath.

26. The process defined in claim 11, wherein the water soluble silicate is selected from the group comprising alkali metal silicates, alkali metal fluorosilicates and mixtures thereof.

27. The process defined in claim 11, wherein the water soluble silicate is sodium silicate.

28. The process defined in claim 1, wherein the electrolytic bath has a pH of at least about 11.

29. The process defined in claim 1, wherein the electrolytic bath has a pH in the range of from about 11.5 to about 13.

30. The process defined in claim 1, wherein the electrolytic bath is maintained during the process at a temperature in the range of from about 5° to about 35° C.

31. The process defined in claim 1, wherein the electrolytic bath is maintained during the process at a temperature in the range of from about 50° to about 25° C.

32. The process defined in claim 1, wherein the electrolytic bath is maintained during the process at a temperature in the range of from about 5° to about 20° C.

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