FIG. 2 depicts voltage-time curves for various metals subjected to anodic spark reaction in aluminate solution.

FIG. 3 depicts voltage-time curves for various metals subjected to anodic spark reaction in silicate solution.

In the course of the investigation leading to the present invention, a number of metals were subjected to anodic spark reaction in various electrolytes including aqueous solutions of NaAlO₂, Na₄W₀₁₂H₂O, or Na₃SiO₃·9H₂O. The anodic reactions were carried out at a current density in the range of 0.1 to 1.0 amp./in.² with the voltage across the electrolytic cell being increased until sparks appeared on the anode surface, and thereafter increased, manually to maintain the required current as the anode film resistance increased. Electrolyte temperature was maintained in the range of 0° to 40° C., and treatment time required for coverage of the anode varied with current density, the process being more rapid as current density increased.

FIGS. 1, 2 and 3 depict the anodic voltages plotted as a function of time for the various metal parameters in 0.1 N solutions of NaAlO₂, Na₄W₀₁₂H₂O and Na₃SiO₃·9H₂O, respectively.

In obtaining the data plotted in FIGS. 1, 2 and 3, a current density of 0.16 amp./cm.² was employed in all reactions, except with Ni in Na₃SiO₃ for which the current density was 0.32 amp./cm.². The reaction cell was a glass vessel which was thermostatted at 25±1° C., and was equipped with a stirring device and a cathode comprising an inert conductor, e.g., platinum or graphite. The cathode surface area was at least equal to the anode surface area in all experiments. The power supply for this series of experiments was a rectifier having a variable D.C. output of 0 to 5000 volts. The voltage output was unregulated, but fluctuations were less than 6 percent.

Anodes were prepared in the form of cylindrical rods and mounted in tight-fitting Teflon sleeves which served to mask the anode surface at the air-electrolyte interface. Anodes varied slightly in size, but typical dimensions were 0.8 cm. dia. with a total surface area of about 6.5 cm.² exposed to the electrolyte. The only exceptions were the gold electrodes which were 2 cm. in length and 0.1 cm. dia., and the Mn electrode which was a flat plate of approximately 4 cm.² surface area. Surface preparation also varied, depending on the anode metal, but the general procedure was to degrease in an organic solvent, etch in an appropriate acid or alkaline solution and rinse in distilled water. Cleaning procedures were carried out immediately prior to anodizing.

The analyses of anodic spark reaction products were performed on insoluble material which adhered to the anode. Powder X-ray diffraction patterns were obtained (Copper Kα radiation and at 57.3 mm. camera) on products of all the anodic spark reactions shown in Table I. Chemical and spectrographic analyses were made of anode products from aluminate solutions. Spectrographic analyses were performed on the samples to provide a qualitative check on their elemental composition. These analyses showed that the only metal ions in the anode products were those of aluminum and the anode metal.

The spark reaction products adhering on anodes treated in NaAlO₂ solutions were generally light in color, very hard, and had the appearance of porous sintered powders. Chemical analyses were made of the spark reaction products obtained in NaAlO₂ solutions and the results are summarized in Table II. It is evident from the results that major components of the spark reaction products are derived from the anion constituent of the electrolyte.

X-ray analyses of the spark reaction products from NaAlO₂ solutions are given in Table III. The X-ray
products from the NaWO₄ solutions could be superimposed on a pattern for 99% pure monoclinic WO₃ which showed that the crystalline anode product was essentially this material.

Tungsten trioxide, WO₃, in its polycrystalline form is useful as a catalyst in a number of chemical syntheses, and as a high temperature corrosion protective coating for titanium. It is thus seen that the present invention provides a method of directly forming polycrystalline coatings of anhydrous WO₃ on several metals. While it has been shown in the prior art that hydrated WO₃ can be precipitated from tungstate solutions by anodic reaction, it is necessary in such cases to provide an additional dehydration step in order to obtain anhydrous material.

The anode products from reactions in Na₂SiO₃ solutions bore some resemblance to the slags which form on furnace refractories. The results of X-ray diffraction analyses of these materials are given in Table III. Crystalline phases were found on all the anodes except Cd. A very heavy background in the films for Bi, Ni, Cu, Zn, and Fe anode products pointed to the presence of amorphous material, e.g., fused silicates. The crystalline phases reported in Table III were well characterized despite the high background level and represent major anode product components. The presence of metallic Cu, Fe, and Bi in the coatings on these anodes did not impart electrical conductivity to them, and it is probable that the metallic phases were embedded in other anode products, e.g., amorphous silicates.

While silicate coatings for the protection and decoration of metal surfaces are well known, typical processing steps in the application of such coatings are slip-casting or spraying of powdered silicate slurries to obtain soft coatings which must then be fired in order to be hardened and bonded to the underlying metal surface.

The present invention provides a method for producing hard, adherent silicate coatings on various metals by a one-step electrochemical process, which consists of
andodization of metal articles in a relatively dilute aqueous silicate electrolyte. While it is recognized that, in general, silicate solutions are not new in electrochemical processes, heretofore there has been no recognition of the critical importance of the nature and concentration of the anion constituent in determining the composition and structure of anodic reaction products.

The aforementioned results showed clearly the operability of anodic spark reaction to form useful coatings on a variety of metals when the critical nature and concentration of the anion constituent in the electrolyte is understood. These results cannot be attributed to the relatively high current density which was employed (0.16 amp/cm²) because in a number of cases, e.g., Mn in NaAlO₂, and Mg, Ni, Co, Fe, and Ag, in Na₂WO₄ solution, no such phenomena could be observed. This was true even when the current density was increased to several times the above value. Furthermore, the growth of a barrier film was found to occur in a number of cases, e.g., Ni and Co in NaAlO₂ solution, at current densities less than one tenth the above value.

Confirmation of the almost universality of the inventive process was obtained when anodic spark reaction was employed to form useful coatings on refractory metals, e.g., Ti, Zr, V, Mo, W, Nb, and Ta. Visible sparking on anodes of the refractory metals was observed in all cases at a D.C. initiation voltage in excess of 190 volts. Anodic reaction products forming coatings on the refractory metal anodes comprised corundum (α-Al₂O₃) or structurally related analogues (Mg₆Al₇O₁₆, Zr₂Al₃O₁₀, etc.), anhydrous WO₃, and fused silicates, respectively, where the anion constituent of the electrolyte employed consisted of aluminate ion, tungstate ion, and silicate ion, respectively.

Concentrations of anion constituents were varied from an effective amount up to about 0.3 N for aluminum ion and from an effective amount up to about 0.2 N for tungstate ion and silicate ion.

In accordance with another embodiment of the invention, the aforementioned coatings of corundum and structurally related analogues thereof may be formed on assembled combinations of the aforesaid metals in an electrolyte wherein the anion constituent consists of aluminate in an effective amount up to about 0.3 N. In one demonstration a bar of aluminum exposed into a 0.1 N sodium aluminate solution, the temperature of which ranged from 25 to 40°C. during treatment. The anode voltage rose from 0 to approximately 420 volts, D.C., in a period of 10 to 15 minutes at the end of which time all the metal surfaces of the assembly were covered with hard coatings of corundum or spinel, said coatings being sufficiently hard to scratch glass.

Criticality of the concentration of the aluminate anion constituent in the electrolyte employed is shown by results of anodic spark reaction attempts set forth in the following table:

<table>
<thead>
<tr>
<th>Concentration (Percent by weight)</th>
<th>Maximum Anode Voltage (volts)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>15</td>
<td>No spark reaction. Incomplete coating of anode surface. Do.</td>
</tr>
<tr>
<td>0.5</td>
<td>28</td>
<td></td>
</tr>
</tbody>
</table>

Having thus described the invention so that others skilled in the art may be able to understand and practice the same, it is expressly understood that the invention is not limited to the preferred embodiments but may be otherwise embodied or practiced within the scope of the following claims.

We claim:

1. An electrochemical process for producing a hard, adherent coating on the surface of an article comprising at least one metal selected from the group consisting of Al, Zn, Bi, Ni, Co, Fe, Cu, Ag, Au, Ti, Zr, V, Mo, W, Nb, and Ta, said process comprising subjecting said metal to anodic spark reaction in an aqueous electrolyte wherein the anion constituent consists of aluminate ion in a concentration ranging from an effective normality up to 0.3 N and maintained at a temperature between 0 and 40°C.

2. An electrochemical process according to claim 1 wherein an anodic current density between about 0.1 and 1.0 amp/in.² is maintained during said anodic spark reaction.

3. An electrochemical process according to claim 1 wherein said electrolyte is maintained at a temperature between 0 and 40°C during said anodic spark reaction.

4. An electrochemical process for producing a hard, adherent coating comprising a substance selected from the group consisting of corundum and structurally related analogues thereof on the surface of a metal selected from the group consisting of Al, Zn, Bi, Ni, Co, Fe, Cu, Ag, Au, Ti, Zr, V, Mo, W, Nb, and Ta, said process comprising subjecting said metal to anodic spark reaction while maintaining anodic current density between about 0.1 and 1.0 amp/in.² in an electrolyte consisting of an aqueous solution of sodium aluminate ranging in concentration from an effective normality up to 0.3 N and maintained at a temperature between 0 and 40°C.

5. An electrochemical process for producing a hard, adherent coating on the surface of an assembly of different metals, said process comprising subjecting said assembly to anodic spark reaction in an electrolyte wherein the anion constituent consists of aluminate ion in a concentration ranging from an effective normality up to 0.3 N.

6. An electrochemical process according to claim 5 wherein said coating comprises a substance selected from the group consisting of corundum and structurally related analogues thereof.

7. An electrochemical process according to claim 5 wherein the anodic current density between about 0.1 and 1.0 amp/in.² is maintained during said anodic spark reaction.

8. An electrochemical process according to claim 5 wherein said electrolyte is maintained at a temperature between 0 and 40°C during said anodic spark reaction.

9. An electrochemical process for producing a hard, adherent coating comprising a substance selected from the group consisting of Mg, Al, Zn, Bi, Ni, Co, Fe, Cu, Ag, Au, Ti, Zr, V, Mo, W, Nb, and Ta, said process comprising subjecting said assembly to anodic spark reaction while maintaining anodic current density between about 0.1 and 1.0 amp/in.² in an electrolyte consisting of an aqueous solution of sodium aluminate ranging in concentration from an effective normality up to 0.3 N and maintained at a temperature between 0 and 40°C.

10. The method of coating the surface of a metal selected from the group consisting of Al, Cd, Zn, Bi, Cu, Ti, Zr, W, Nb, and Ta, which comprises electrolytically treating which comprises electrolytic treatment of an anode of said metal in an electrolyte consisting of an aqueous tungstate solution at a voltage sufficiently high to cause sparking on the anode surface, the concentration of tungstate anion in said solution ranging from an effective normality up to 0.2 N.

11. The method of claim 10 wherein the electrolyte temperature during treatment is maintained between 0 and 40°C.

12. The method of claim 10 wherein the anodic current density is maintained between 0.1 and 1.0 amp/in.².
13. The method of producing an anhydrous tungsten trioxide coating on the surface of a metal selected from the group consisting of Al, Cd, Zn, Bi, Cu, Ti, Zr, V, Mo, W, Nb, and Ta, which comprises electrolytically treating said metal at a voltage sufficiently high to cause sparking on said surface and at a current density between 0.1 and 1.0 amp/in.² in an aqueous tungstate solution maintained at a temperature between 0 and 40°C, the concentration of tungstate anion in said solution ranging from an effective normality up to 0.2 N.

14. The method of producing a silicate coating on the surface of a metal selected from the group consisting of Al, Zn, Bi, Ni, Fe, Cu, Ti, Zr, V, Nb, Ta, Mo, and W, which consists of the electrolytic treatment of an anode of said metal in an electrolyte consisting of an aqueous silicate solution at a voltage sufficiently high to cause sparking on the anode surface, the concentration of silicate anion in said solution ranging from an effective normality up to 0.2 N.

15. The method of claim 14 in which the electrolyte temperature is in the range 0 to 40°C.

16. The method of claim 14 in which the anodic current density is in the range 0.01 to 1.0 amp/in.².

17. The method of producing a silicate coating on the surface of a metal selected from the group consisting of Al, Zn, Bi, Ni, Fe, Cu, Ti, Zr, V, Nb, Ta, Mo, and W, which comprises electrolytically treating said metal at a voltage sufficiently high to cause sparking on said surface and at a current density between 0.1 and 1.0 amp/in.² in an aqueous silicate solution maintained at a temperature between 0 and 40°C, the concentration of silicate anion in said solution ranging from an effective normality up to 0.2 N.

18. A coated article produced by the process of claim 1.

19. A coated article comprising an assembly of different metals produced by the process of claim 5.

20. A coated article produced by the process of claim 10.

21. A coated article produced by the process of claim 14.

References Cited by the Examiner

UNITED STATES PATENTS

1,954,000 4/1937 Tuesdale et al. 204—56
2,196,161 4/1940 Frasch 204—56
2,215,167 9/1940 Summer et al. 204—56 X
2,313,755 3/1943 Loose 204—56
2,348,826 5/1944 Krause et al. 204—56
2,364,964 12/1944 Frasch 204—58
2,780,591 2/1957 Frey 204—56 X

FOREIGN PATENTS


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