A process for producing anodized aluminum with enhanced electrical conductivity, comprising anodic oxidation of aluminum alloy substrate, electrolytic deposition of a small amount of metal into the pores of the anodized aluminum, and electrolytic anodic deposition of an electrically conductive oxide, including manganese dioxide, into the pores containing the metal deposit; and the product produced by the process.

24 Claims, 1 Drawing Sheet
FIG. 1

EFFECT OF Ni DEPOSITION ON COATING RESISTIVITY

RESISTIVITY, ohm-cm x 10^-13

0.0001  0.001  0.01  0.1  1  10  100

CURRENT FOR Ni DEPOSITION, mA/cm^2

0  1  2  3  4  5  6  7

MnO_2 DEPOSITION
10 mA/cm^2 / 5 MIN
Ni DEPOSITION: 10 SEC

SAA

#2 #3 #7

-100V -35V

#10 #11
ELECTRICALLY CONDUCTIVE ANODIZED ALUMINUM COATINGS

BACKGROUND OF THE INVENTION

Conventional anodized aluminum coatings contain pores with diameters of 10–20 nm that are present at very high density, ca. $10^{10}$ cm$^{-2}$. The pores are generally aligned normal to the metal surface. These pores extend through the coating thickness, with a thin “barrier” oxide, typically 10–20 nm thick, at the pore base, and, depositing material into the pores of anodic alumina in order to change the coating properties is known in the art. For example, filling with a fluorinated hydrocarbon provides lubricity, and imbibing dye into the pores can make an attractive colored surface. Depositing a small amount of certain metals into each pore creates attractive shades from gold to bronze by a light scattering phenomenon. This is widely practiced commercially and is known as electrolytic coloring. This electrolytic coloring process consists generally of two steps: first, dc anodization to grow the porous oxide, for example, in sulfuric acid; and, second, an ac electrolysis in a bath containing the metal cation to be deposited. A general review of electrolytic coloring is given in Chapter 8 of Vol. 1 of Wernick, Pinner and Sheasby, “The Surface Treatment and Finishing of Aluminum and its Alloys, 5th ed.” Moreover, U.S. Pat. No. 3,382,160 issued to T. Asuda on May 7, 1968, and U.S. Pat. No. 4,431,489 issued to B. R. Baker, R. L. Smith and P. W. Bolmer on Feb. 14, 1984 are examples of prior art teachings of electrolytic coloring.

Anodized aluminum is widely used as the exterior surface for spacecraft because it is lightweight, easily fabricated, provides abrasion and corrosion resistance, and can be made to have a range of useful optical properties, described in terms of the coating absorptance and emittance. In a space environment the coating has a typical resistivity of $10^{12}$ ohm cm (negative bias voltage on substrate). This creates a problem during operation because an electrical charge from the space plasma builds up on the surface and cannot bleed off through this highly insulating coating. High voltages ($>100$ V) may develop across the coating which result in arcing and sporadic discharge with a frequency that depends on details of orbit, bias voltage and location on the spacecraft. The discharges and electrical noise interfere with communication and may cause structural damage.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a coating with enhanced conductivity so that an electrical charge cannot bleed off through the coating and prevent buildup of excessive voltage.

It is another object of the present invention to provide coatings with a substantial decrease in resistivity.

It is a further object of the present invention to provide a coating with decreased resistivity without degrading other coating properties.

It is also an object of the present invention to provide a coating having the ability to withstand high negative bias voltage in a vacuum plasma without arcing.

It is even a further object of the present invention to provide a coating which has corrosion resistance in ambient earth atmosphere, and suitable optical properties for thermal control in a space environment.

It has been found that the resistivity can be reduced a thousandfold by filling a fraction of the pores with MnO$_2$, an electronically conductive oxide. The filled pore fraction is controlled by a prior deposition of metal into the pores. The conditions for metal deposition are adjusted to control both the fraction of the pore population in which metal is deposited and the amount of metal deposited in each pore. These metal “nanelectrodes” are sites on which MnO$_2$ can deposit. Only those pores in which metal has deposited can be filled with MnO$_2$. The MnO$_2$ deposit grows from the pore base, and deposition is continued until this deposit reaches the outer surface of the coating. The vacuum plasma can make electrical contact with these conductive channels.

In the use of the terms “MnO$_2$” and “manganese dioxide”, these terms are names for the deposit obtained from a manganese salt solution and not meant to specify the stoichiometry. Moreover, the deposit is likely to be a mixture of...
MnO$_2$ and suboxides of manganese with the precise composition depending on the process conditions, such as bath temperature, pH and current density.

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The particular conditions for metal deposition and MnO$_2$ deposition are critical for making a successful coating. For efficient electrical coupling with the vacuum plasma, it is necessary to get a uniform distribution of the MnO$_2$ filled pores over the coating surface. This requires that the metal sites be uniformly distributed. That is, "uniform" distribution means one for which the spatial distribution of conductive sites approaches a random, also known as a Poisson, distribution. A good distribution is obtained using ac electrolysis for the metal deposition similar to that used for prior art electrolytic coloring. There are two embodiments of the invention. One is to enhance the conductivity of a conventional anodic coating, for example, one grown in sulfuric acid and commonly known as clear anodize, and the other is to make a black anodize coating with enhanced conductivity. The first embodiment is intended to produce enhanced conductivity with minimal increase in coating absorptance, and is achieved by depositing metal into only a fraction of the pores; the amount of metal deposited being too little to impart any color to the coating. The second embodiment makes a coating with increased conductivity and with absorptance near unity, and is achieved by depositing metal into nearly all the pores, and then filling these pores with MnO$_2$. In this case, the metal and the conductive oxide strongly absorb solar radiation and impart a deep black coloration to the coating. The pores of conventional black anodize coatings are filled with a black organic dye or certain inorganic materials, such as stannous sulfide or cobalt sulfide, deposited by precipitation. Because the absorptance of these coatings is nearly one, they lose a minimal amount of energy by radiation and are used in ambient earth atmosphere for solar heat collectors, and on spacecraft to maintain an elevated temperature in some location.

Metals that can be deposited by ac electrolysis include cobalt, nickel, copper, tin, silver, iron, and gold. Cobalt, nickel and tin are the most commonly used cations in commercial electrolytic coloring baths, and nickel and tin have been found as the preferred cations for the present invention.

Although nickel baths are available commercially for ac anodization, tin baths are used more widely. Deposition of tin can be substituted for deposition of nickel, with all other process steps remaining essentially unchanged. For example, a suitable tin bath contains 5-20 g/l stannous sulfate, 10-25 g/l sulfuric acid, and may also contain a stabilizer to prevent oxidation of the tin cation from the stannous to stannic form. Examples of suitable stabilizers are phenol sulphonylic acid, cresol sulphonlic acid, and sulphophalic acid, with others used in commercial proprietary tin baths. An example of a process sequence to make a coating with tin at the pore base consists of the steps of cleaning, sulfuric acid anodizing, tin deposition, and manganese oxide deposition. More specifically, the cleaning is carried out with alkaline cleaner at 70°C for 2 minutes, the sulfuric acid anodizing at 15 V in a 15% sulfuric acid solution at 23°C for 20-30 minutes. Tin deposition is at room temperature (20-23°C), 50-60 Hz rms current of 2-8 mA/cm$^2$ for 10-15 sec. And, the manganese oxide deposition is in a 0.5M MnSO$_4$ solution, at room temperature (20-23°C), 50 Hz pulse dc with 5-20% duty cycle, pulse current density starts at 1-10 mA/cm$^2$, total charge of 0.3-0.5 C/cm$^2$.

It is most likely that nickel or tin deposition will be done using the ac line frequency, which is 50 or 60 Hz worldwide. Other frequencies may be found to provide a more uniformly dispersed metal deposit. An optimum ac frequency will be found between 10 and 120 Hz. If a frequency other than line frequency is selected, then the most readily available power sources will provide a square dissolve shape rather than the sinusoidal shape from the power lines. The square waveshape will be satisfactory. In fact, complex waveshapes composed of superimposed square waves of different amplitude and period may prove to offer particular advantages. This is by analogy with other commercial processes using pulsating dc (pulsing plating) and ac electroetching of aluminum. In these other processes the use of complex waveshapes results in more uniform deposits and more uniform etch structure. Thus, it is anticipated that use of these waveshapes may improve the uniformity of the distribution of metal deposit sites.

**Electrolytic MnO$_2$** is prepared in commercial quantities for use in batteries by anodic deposition from a warm acidified sulfate bath. For the present invention, depending on the particular metal in the pores, it was thought that these conditions could cause dissolution of the metal deposit. It has been found that a manganese sulfate bath, with no additional sulfuric acid and operated at room temperature, also can be used to deposit the MnO$_2$. Even further, it has been found that steady dc or pulse dc can be used if the current density is sufficiently high to deposit some MnO$_2$ before the Sn (or other metal) dissolves. Furthermore, it is possible to anodically deposit other conductive metal oxides into the aluminum oxide pores, but each has a limitation. For example, ruthenium, iridium and silver oxides are too expensive, whereas the bath from which lead oxide can be deposited presents a severe health hazard and disposal problem.

This coating is designed for space applications, wherein the coating must have certain optical properties and is in contact with a vacuum plasma. The plasma has a very low electron density, so the effective coating resistivity is controlled by the electrical coupling between coating and plasma. Good coupling requires that the conductive deposit extend from the pore base to the outer surface of the coating where it can contact the plasma environment, and it is improved by increasing the density of conductive channels in the coating. But the conductive deposit affects optical properties by increasing the absorptance of solar radiation. A satisfactory coating is one with the necessary balance of electrical and optical properties for the particular application.

With a metal contact, the coating resistivity is reduced 100 times from its value in vacuum plasma. This may make the conductive coating useful for non-space applications, such as to provide electrical continuity across anodized surfaces. This is needed for many applications, for example, for connections of aluminum parts to aluminum auto frames, where some of the aluminum members must be anodized for corrosion and abrasion resistance. For these applications the optical properties are not important, so the filled pore fraction may be increased to further reduce resistivity.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a graph showing the effect of nickel deposition on coating resistivity.

**EXAMPLES**

The following are examples of coating process conditions and coating properties. Certain conditions were held con-
stent for these examples. The anodized coating was grown in 15 wt % sulfuric acid at 15 V d c and a temperature of 23° C., in a cell with stainless steel mesh cathode. The ac electrolysis for Ni deposition was done in 0.2M NiSO₄+ 0.5M H₂BO₃ at room temperature in a cell with carbon counter electrode. This step can be done using a fixed ac voltage or a fixed ac current. For Examples 1 through 8, Ni deposition was done at a constant 50 Hz sine wave ac current. The ac current was monitored with an oscilloscope, and it is the current density corresponding to the ac peak current that is reported here. In Example 9, Ni deposition was done at a constant 50 Hz sine wave ac cell voltage. In Examples 1 through 8, deposition of MnO₂ was done from a 0.5M MnSO₄ solution at room temperature, using a pulse dc current, in a cell with stainless steel mesh cathode. In these examples, the pulse current is 2 ms on followed by an off period of 18 ms, except for Example 7 in which the pulse conditions were varied. The pulse conditions were set with a square wave generator and pulse time was measured using an oscilloscope. The cell voltage increased during MnO₂ deposition. The pulse current density was set at 10 mA/cm², but the available power source voltage was limited to 28 V, and when the voltage reached that value, the current dropped below 10 mA/cm². This occurred after about 1–3 minutes of deposition. This is not a necessary condition for MnO₂ deposition, but was a characteristic for the particular power source and initial current density selected. In Examples 9–10, the MnO₂ deposition conditions were substantially different, as described in those Examples. When a final seal step was used, the sealing was done in boiling water for 10 min. Unless otherwise indicated, the coatings were 12.7 µm thick and on 6061-T6 alloy.

The electrical resistivity was calculated from current readings at different dc voltages. Most measurements were made with negative bias, as these are most important for space applications. Resistivity with a silver paint contact was measured under bone dry conditions, after equilibration in nitrogen atmosphere over P₂O₅ desiccant. Values measured at -35 V are reported here. The resistivity in vacuum plasma was measured in a chamber filled with flowing argon at a pressure of 8x10⁻⁴ Torr, and plasma electron densities from 2.3 to 0.83x10¹⁴ cm⁻³. There were only small differences for the different electron densities. The values reported here are for densities of 2.1–2.3x10¹⁴ cm⁻³ and a 60 V negative bias voltage.

Solar absorptance was calculated from reflectance using a spectral reflectometer which integrates over the 250–2500 nm wavelength range. Total emittance was determined from total reflectance.

**Example 1**

In this example the resistivity and optical properties of a conventional coating and a conductive coating are compared, each in the unsealed state. The Ni deposition was for 10s at 5 mA/cm² followed by a 10 min MnO₂ deposition. The coating properties were as follows:

<table>
<thead>
<tr>
<th>resistivity (ohm-cm)</th>
<th>arcing</th>
<th>optical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>coating</td>
<td>Ag paint</td>
<td>plasma</td>
</tr>
<tr>
<td>SAA only</td>
<td>7.1 x 10¹³</td>
<td>52 x 10¹³</td>
</tr>
<tr>
<td>conductive</td>
<td>1.6 x 10¹⁰</td>
<td>21 x 10¹¹</td>
</tr>
</tbody>
</table>

The resistivity of the conductive coating is more than 3 orders smaller with metal contact, and more than 2 orders smaller with plasma contact in comparison with a conventional sulfuric acid anodized coating (SAA). The arcing threshold does not degrade with this enhanced conductivity. The absorptance (α) is higher for the conductive coating, but the emissivity (ε) is not changed. The optical properties of the conductive coating are suitable for thermal control applications in space.

**Example 2**

In this example it is demonstrated that sealing does not degrade the electrical and optical properties of the conductive coating. Two conductive coatings were prepared at the same conditions as for Example 1. One coating was sealed for 10 min in boiling water, and the other was left unsealed. Coating properties were as follows:

<table>
<thead>
<tr>
<th>coating</th>
<th>resistivity (ohm-cm)</th>
<th>arcing</th>
<th>optical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>not sealed</td>
<td>41 x 10¹⁰</td>
<td>~300</td>
<td>0.691</td>
</tr>
<tr>
<td>10 min seal</td>
<td>33 x 10¹⁰</td>
<td>~375</td>
<td>0.642</td>
</tr>
</tbody>
</table>

The sealed coating had superior properties of lower resistivity, higher threshold voltage, and lower optical absorptance. Only the emittance was increased by a small amount.

**Example 3**

In this example it is demonstrated that conductive coatings can be made on different alloys, and with different thickness coatings. Coatings were prepared on two alloys, with different thickness coating on each alloy. The same Ni deposition conditions were used for both, 8.8 mA/cm² for 10 s, but the MnO₂ deposition time was adjusted to scale with the coating thickness. All coatings were sealed in hot water.

<table>
<thead>
<tr>
<th>alloy</th>
<th>thick-</th>
<th>MnO₂</th>
<th>resistivity (ohm-cm)</th>
<th>arcing</th>
<th>optical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>6061-T6</td>
<td>12.5 µm</td>
<td>10 min</td>
<td>32 x 10¹⁰ beyond ~450 V</td>
<td>0.678</td>
<td>0.76</td>
</tr>
<tr>
<td>clad</td>
<td>1.7</td>
<td>1.5</td>
<td>15 x 10¹⁰ beyond ~450 V</td>
<td>0.478</td>
<td>0.55</td>
</tr>
<tr>
<td>clad</td>
<td>1.7</td>
<td>3.0</td>
<td>92 x 10¹⁰ beyond ~450 V</td>
<td>0.623</td>
<td>0.56</td>
</tr>
</tbody>
</table>

The resistivities of the thin coatings on clad alloy are 3–5 times higher than for the coating on 6061-T6, but still orders smaller than for conventional anodized coating.

**Example 4**

The effect of Ni deposition on coating resistivity is demonstrated in FIG. 1. The Ni deposition current density was varied while holding the deposition time constant at 10 s. The MnO₂ process conditions were the same for all samples. The electrical measurements were made with Ag paint at two voltages, ~35 and ~100 V. The amount of Ni deposited depends on the charge, which is proportional to peak current density times deposition time. There is a threshold, at about 4 mA/cm², beyond which the resistivity rapidly decreases with increasing Ni deposition to a level 4 orders smaller than for SAA coating. This illustrates the importance of proper selection of Ni deposition conditions in order to get high enough density of sites for subsequent MnO₂ deposition.
Ni deposition can also be done at fixed ac voltage. A 15 V SAA coating was treated in the same bath using a 9 V ac voltage. A current peak on the cathodic half-cycle showed Ni deposition was occurring and the specimen visibly darkened after 30 seconds processing due to the Ni deposit.

Example 5

MnO₂ deposition starts at the bottom of a pore, and with increasing deposition time the height of the MnO₂ column in the pore increases. The sharp decrease in resistivity between 5 to 10 minutes MnO₂ deposition time in this example is thought to be due to a large increase in the number of pores in which the columns of conductive MnO₂ have reached the outer oxide surface and hence make contact to the Ag paint or vacuum plasma.

Example 6

MnO₂ deposition was limited to 28 V, and when this was reached the current was set at 10 mA/cm², but the power supply voltage output was no evidence of corrosion on any of the conductive coatings, designated as B1, B2 and B4, are given in Table II. After 240 hr exposure there was no evidence of corrosion on any of the conductive coupons. In contrast, one SAA coupon had one corrosion spot, and the other SAA coupon had two corrosion spots, each spot ≤ 0.4 mm diameter. Whereas the results with SAA are acceptable, the corrosion resistance of the conductive coating is superior.

TABLE I

<table>
<thead>
<tr>
<th>MnO₂ time (min)</th>
<th>Ag paint</th>
<th>plasma</th>
<th>threshold (V)</th>
<th>α</th>
<th>ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 min</td>
<td>10 x 10⁻²</td>
<td>78 x 10⁻³</td>
<td>400</td>
<td>0.547</td>
<td>0.71</td>
</tr>
<tr>
<td>5.0 min</td>
<td>10 x 10⁻²</td>
<td>30 x 10⁻³</td>
<td>340</td>
<td>0.574</td>
<td>0.72</td>
</tr>
<tr>
<td>10 min</td>
<td>16 x 10⁻²</td>
<td>21 x 10⁻³</td>
<td>375</td>
<td>0.608</td>
<td>0.72</td>
</tr>
</tbody>
</table>

TABLE II

<table>
<thead>
<tr>
<th>Pulse time, ms</th>
<th>Frequency, Hz</th>
<th>approx charge C/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>500</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>500</td>
<td>0.5</td>
</tr>
<tr>
<td>1.0</td>
<td>50</td>
<td>0.6</td>
</tr>
<tr>
<td>2.0</td>
<td>50</td>
<td>1.0</td>
</tr>
<tr>
<td>4.0</td>
<td>50</td>
<td>1.0</td>
</tr>
<tr>
<td>8.0</td>
<td>50</td>
<td>1.0</td>
</tr>
<tr>
<td>30</td>
<td>dc</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Example 8

Conductive coatings were prepared which provide corrosion resistance equal to that of conventional anodized coatings. Five coupons of 6061-T6 alloy, three with conductive coatings and two with conventional SAA coatings, each 12.5 µm thick and sealed in hot water, were given a standard salt spray test in accordance with ASTM B117. Preparation conditions for the conductive coatings, designated as B1, B2 and B4, are given in Table II. After 240 hr exposure there was no evidence of corrosion on any of the conductive coupons. In contrast, one SAA coupon had one corrosion spot, and the other SAA coupon had two corrosion spots, each spot ≤ 0.4 mm diameter. Whereas the results with SAA are acceptable, the corrosion resistance of the conductive coating is superior.
The electrical resistivity of the black anodize coatings of Examples 9 and 10 were measured in dry atmosphere with Ag paint contact. The resistivities for three coatings at ~35 V bias were in the range 2.2×10⁹–1.2×10⁹ ohm-cm. This is 10 to 100 times lower than for the conductive oxide coatings in the previous examples, and as much as 10⁴ times less than conventional SAA.

Whereas these examples are limited to certain process conditions, it is understood that a wide range of conditions are likely to produce useful coatings.

CONCLUSIONS AND RAMIFICATIONS

Various embodiments are possible without departing from the scope of the invention. The Examples and Tables are illustrations of possible embodiments and are not restrictive.

Examples have been mostly for coatings on 6061T6 alloy. Any aluminum alloy onto which a porous anodic oxide coating can be deposited also can be coated with conductive oxide. Different properties may be obtained when the alloy influences the porous structure and other coating properties. For example, on 5657 alloy the conductive oxide has a much lower optical absorptance than on 6061T6.

Only three coating thicknesses were used in the Examples, ranging from 1.7 to 17.5 μm. It is likely that conditions can be found to render any porous oxide conductive, regardless of thickness. It is estimated that the coating thickness range of commercial interest will be from 1 to 75 μm.

The metal deposited at the pore base serves to block further aluminum oxide growth during deposition of MnO₂ and serves as a substrate for the MnO₂. As long as only a small fraction of pores is filled, the metal deposit does not contribute directly to coating properties, so any metal that will not dissolve during the anodic deposition of MnO₂ can be used for this purpose. Nickel and tin baths are suggested because they are used in commercial two-step anodizing processes and are readily available. Some commercial baths contain combinations of these cations, in addition to cobalt salts and these will also be satisfactory.

The decrease in resistivity depends on the fraction of pores with MnO₂ and that depends on the fraction of pores with a metal deposit. In Example 6, it is estimated that two coatings had 2% and 10% of pores filled. To get a significant (~100×) reduction in resistivity, without large increase in optical absorptance, pore fraction filled with conducting material should be between 1–15%. There may be particular applications for which larger change in optical properties is allowed, or desirable, and then larger fraction of filled pores can be used.

The Ni deposition can be run at a constant ac cell voltage or constant current. With constant ac voltage, the peak voltage can be set so deposition occurs in only a small fraction of pores, or in most of the pores, and this can be less than the anodization voltage to make sure that deposition occurs only in a fraction of the pores. For example, for a 15 V SAA coating a peak voltage of 9 V resulted in an initial Ni deposition current of 3.7 mA/cm² and this decreased to 1.2 mA/cm² after 5 seconds. An acceptable range for the cell peak voltage is 50 to 100% of the anodization voltage. The peak voltage should be greater than the anodization voltage, by about 1–2 volts, for metal to deposit in the majority of pores. Operating with fixed ac current, we do not have a similar diagnostic for determining a suitable current density. The Ni (or Sn) bath composition and temperature are not critical; conditions in the examples are acceptable, as are other conditions used in commercial anodizing baths.
In the manufacture of electrolytic MnO₂, it is found that the oxide conductivity and density are increased by deposition at low pH and at high temperature. The same relation is expected for the deposits in pores. Because deposition is on an aluminum oxide substrate, the pH cannot be too low, nor the temperature too high, or the aluminum oxide will dissolve. We find that a pH range of 3–4 works well, and the temperature can be between ambient (21 °C) and 40 °C. There is no reason to operate at a bath concentration lower than 0.5 M MnSO₄ and, since saturation at room temperature is about 4.7 M, a convenient upper limit for bath concentration is 4 M. Observations made during the processing of black anodize concerning the deposition of MnO₂ are probably relevant to the case of fractional pore filling, since the basic process of depositing MnO₂ onto the metal substrate is the same. It was observed that good results were obtained if the voltage during MnO₂ deposition remained between 17 and 20 V for a 15 V SAA coating. A current density of 0.68 mA/cm² at 50% duty cycle generally produced a voltage in this range. If the voltage increased during deposition, then reducing the current to keep the voltage less than 20 V resulted in a good coating. Too high a voltage caused a dark coating to become lighter, indicating loss of MnO₂. For black anodize, the best voltage for MnO₂ deposition is 2–5 V above the cell voltage for growth of the anodic oxide, e.g., 17–20 V for the 15 V SAA coatings used in the Examples. For Examples 1–8, where only a minimal pore fraction was filled with MnO₂ in order to not increase absorbance too much, the voltage rose to 28 V and the current density decreased from its initial value of 10 mA/cm² during deposition. Use of a pulsed current did not prevent this voltage change. Best practice for MnO₂ deposition for this type coating has not been determined, but it is likely that 10 mA/cm² or an upper limit and a current as low as 0.5 mA/cm² will be suitable. Too low a current density would lengthen process time which would increase the possibility of dissolution of aluminum oxide in the acidic manganese bath. Pulse current is observed to widen the envelope for acceptable pH and temperature. It has been demonstrated that both steady dc and pulse dc currents are acceptable, with duty cycle varying from 5 to 100%. Only two frequencies, 50 Hz and 8.3 Hz have been used, and both gave good MnO₂ deposits.

A necessary condition for low coating resistivity is for the MnO₂ deposit to reach the outer surface where it can make electrical contact. This can be detected in several ways. The outer surface of the coating can be examined in plan view in a scanning electron microscope, and the deposition condition when nodules of the MnO₂ are first detected can be identified. Alternatively, a coating can be examined in cross-section in an optical microscope and, if the density of pores with MnO₂ is great enough, the coating will appear dark over the coating thickness in which the pores contain the conducting oxide. The conditions for which the dark zone extends over the full coating thickness can be identified. In these ways suitable current density, time, and duty cycle can be determined.

The hot water seal can be for a time acceptable to commercial practice, which is likely to be in the range of 5 to 40 minutes, but depends on water temperature and coating thickness. It is common to use chemical additives such as nickel salts in the seal bath, and there are "cold seals" which operate near ambient temperature and rely on other chemical reactions, e.g., precipitation of nickel hydroxide, to close the pores to the atmosphere. These processes have not been evaluated. Whether or not a particular seal process can be used is not crucial to this invention.

The scope of the invention should not be determined by the embodiments illustrated but by the appended Claims and their legal equivalents.

We claim:

1. A process for producing anodized aluminum with increased electrical conductivity, comprising the steps of:
   a. anodic oxidation of the surface of an aluminum alloy substrate to deposit a porous anodic oxide,
   b. electrolytic deposition of a metal into the surface pores of said porous anodic oxide, and
   c. electrolytic anodic deposition of an electrically conductive oxide into said pores containing the metal deposit, wherein said electrically conductive oxide fills said pores so that it extends to the outer surface of said porous anodic oxide, and wherein said electrically conductive oxide comprises manganese dioxide or a mixture of different oxides of manganese.

2. The process of claim 1, wherein the metal is deposited into said pores essentially randomly distributed over the surface of the aluminum alloy, and wherein the metal is deposited in a range of 1 to 15 percent of the pores, and wherein the thickness of the metal deposit in said pores is small compared to pore length and is in a range of one-tenth micron, whereby the optical properties of said anodized aluminum are in the desirable ranges for space applications.

3. The process of claim 2 further comprising, after the last step, the step of sealing the anodized aluminum by immersion in water at 90 to 100°C for 5 to 40 minutes.

4. The product produced by the process of claim 3.

5. The process produced by the process of claim 2.

6. The process of claim 1, wherein the metal deposited is selected from the group consisting of: cobalt, nickel, copper, tin, silver, iron and gold.

7. The process of claim 6, wherein the metal deposition is by alternating current electrolysis of a bath containing a salt of one of said metals.

8. The process of claim 7 further comprising, after the last step, the step of sealing the anodized aluminum by immersion in water at 90 to 100°C for 5 to 40 minutes.

9. The product produced by the process of claim 7.

10. The process of claim 6 further comprising, after the last step, the step of sealing the anodized aluminum by immersion in water at 90 to 100°C for 5 to 40 minutes.

11. The product produced by the process of claim 6.

12. The process of claim 1, wherein said porous anodic oxide is produced in an aqueous sulfuric acid bath, comprising 10 to 20 weight % sulfuric acid solution at 18 to 30°C, and wherein the electrolytic deposition of said metal into said pores comprises nickel deposition and is produced by alternating current electrolysis in a solution comprising 0.2M nickel sulphate and 0.5 M boric acid at a temperature of 18 to 30°C, with a sinusoidal frequency of 50–60 Hz and a peak current density of 2 to 8 mA/cm² for 5 to 30 seconds, and wherein the electrically conductive oxide deposition comprises MnO₂ deposition is produced by pulsed direct current deposition in a solution comprising 0.5 to 4.0 M MnSO₄ at a temperature of 18 to 40°C with a pulse frequency of 50 to 60 Hz, a duty cycle of 5 to 50%, and a current density selected to pass a total charge of 0.3 to 1.0 C/cm² within about 10 minutes.

13. The process of claim 12, wherein the nickel deposition is at a controlled voltage.


15. The process of claim 12, wherein the MnO₂ deposition is with steady dc current.

16. The product produced by the process of claim 15.

17. The product produced by the process of claim 12.
18. The process of claim 1, wherein the second step of metal deposition is at sufficient peak ac voltage to cause the metal to be deposited in substantially all of said pores, whereby after the third step of electrolytic deposition of said electrically conductive oxide, the porous anodic oxide is substantially darkened to a black appearance.

19. The product produced by the process of claim 18.

20. The process of claim 18, further comprising, after the first step of anodic oxidation and before the second step of electrolytic deposition of metal, the step of depositing copper into said pores by immersing the anodically oxidized aluminum alloy in a bath of sulphuric acid and copper sulphate and electrolyzing with an ac voltage.

21. The process of claim 1 further comprising, after the last step, the step of sealing the anodized aluminum by immersion in water at 90 to 100° C. for 5 to 40 minutes.

22. The product produced by the process of claim 21.

23. The product produced by the process of claim 1.

24. A process for producing anodized aluminum with increased electrical conductivity, comprising the steps of:

a. anodic oxidation of the surface of an aluminum alloy substrate to deposit a porous anodic oxide,
b. deposition of copper into said pores by immersing the anodically oxidized aluminum alloy in a bath of sulphuric acid and copper sulphate and electrolyzing with an ac voltage,
c. electrolytic deposition of a metal into the surface pores of said porous anodic oxide at sufficient peak ac voltage to cause the metal to be deposited in substantially all of said pores, and
d. electrolytic anodic deposition of an electrically conductive oxide into said pores containing the metal deposit, wherein said electrically conductive oxide fills said pores so that it extends to the outer surface of said porous anodic oxide, and wherein the porous anodic oxide is substantially darkened to a black appearance.
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 8,
Line 60/61, Table 11, under "Ni deposition" heading, row "Deposition time", right-hand column "B4", delete "10 s" and insert instead -- 15s --.

Signed and Sealed this
Sixteenth Day of July, 2002

Attest:

JAMES E. ROGAN
Attesting Officer
Director of the United States Patent and Trademark Office