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
EFFECT OF Ni DEPOSITION ON COATING RESISTIVITY

MnO₂ DEPOSITION
10 mA/cm² x 5 MIN
Ni DEPOSITION: 10 SEC

FIG. 1
ELECTRICALLY CONDUCTIVE ANODIZED ALUMINUM COATINGS

PRIORITY OF PROVISIONAL

This Patent Application claims priority based on U.S. Provisional Application Number 60/094,224 filed Jul. 27, 1998.

The U.S. Government has a paid-up license in this invention and the right in limited circumstances to require the patent owner to license others on reasonable terms as provided for by the terms of contract number NASA-40509 and contract number NASA-97134 awarded by NASA Marshall Space Flight Center.

FIELD OF THE INVENTION

This invention relates to a porous anodic aluminum oxide coating with enhanced electrical conductivity and more particularly relates to a process for the anodic oxidation of an aluminum alloy substrate.

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 impinging 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 phenomena. 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.

Whether or not a substance is deposited in the coating pores, it is common practice to “seal” the coating by reaction with hot water, or to “cold seal” in certain chemical baths. These reactions cause the coating to swell into the pores and to make it impervious to penetration by ambient atmosphere and more resistant to corrosion.

In the prior art, the pores have been used as templates to make “nano-wire arrays” by electrolytic deposition of metal or semiconductor into the pores. In this application, the deposit in a pore serves as a “wire” of a length equal to the coating thickness. The coating may either be retained as a support for the deposit or dissolved to expose the nanowires. This is described in a paper by Routkevitch et al., IEEE Trans. Electr. Dev. 43, 1646–58 (1996).

It has been found difficult to electrolytically deposit another oxide into the pores because this requires anodic conditions which will generally result in further growth of anodic aluminum oxide. For example, Baba, Yoshino and Kono (Adv. Metal Finishing Technology in Japan-1980, p. 129) found that deposition of a small amount of gold into the pores blocked anodic oxidation of aluminum during a subsequent anodic deposition of electrochromic tungsten oxide. In this way they created a layer that changed color in response to a change in voltage polarity. In order to get the strongest color change it would be necessary to fill all, or a majority, of the pores with the electrochromic oxide.

Japanese Patent JP 60,165,391 (Aug. 28, 1985) teaches electrolytically coloring anodized aluminum by directly depositing metal oxides into the pores. This reference also teaches using cationic dyes with solutions containing salts of the metal cation to be deposited, and ac with solutions containing oxyniobium of the metal (oxide) to be deposited. 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 absorbance and emittance. In a space environment the coating has a typical resistivity of 10^14 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 can 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 “nanoelectrodes” 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
MnO₄⁻ 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 MnO₂ deposition are critical for making a successful coating. For efficient electrical coupling with the vacuum plasma, it is necessary to have a uniform distribution of the MnO₂-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 MnO₂. 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 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 sulphonic acid, cresol sulphonic acid, and sulphophthalic 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 in a 0.5M MnSO₄ solution, at room temperature, pH and current density starts at 1–10 mA/cm², total charge of 0.3–0.5 C/cm². 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 wave rather than the sinusoidal wave 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 (pulse 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 MnO₂ 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 MnO₂. 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 MnO₂ before the Ni (or other metal) suboxide can be deposited.

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 nonspace 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-
5

stant for these examples. The anodized coating was grown in 15 wt % sulfuric acid at 15 V dc and a temperature of 23°C.

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
counterelectrode. This step can be done using a fixed ac
cell, 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 sinewave 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 pm
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 mea-
sured at ~35 V are reported here. The resistivity in vacuum
plasma was measured in a chamber filled with flowing argon
at a pressure of 8×10⁻³ Torr, and plasma electron densities
dr.2 to 0.83×10⁻⁶ cm⁻³. There were only small differ-
ences for the different electron densities. The values reported
here are for densities of 2.1–2.5×10⁻⁶ 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 com-
pared, 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:

| coating | Ag paint resistivity (ohm-cm) | plasma | threshold (V) | α | ε |
|---------|-------------------------------|--------|---------------|--|--|--|
| SAA only | 7.1×10⁻³ | 52×10⁻⁴ | ~300 | 0.469 | 0.72 |
| conductive | 1.6×10⁻³ | 21×10⁻¹ | ~375 | 0.608 | 0.72 |

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 con-
tventional sulfuric acid anodized coating (SAA). The arcing
threshold does not degrade with this enhanced conductivity.

Example 2

In this example it is demonstrated that sealing does not
degrade the electrical and optical properties of the conduc-
tive 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>plasmas resistivity (ohm-cm)</th>
<th>arcing</th>
<th>optical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>not sealed</td>
<td>41×10⁻³</td>
<td>~300</td>
<td>0.691</td>
</tr>
<tr>
<td>10 min seal</td>
<td>33×10⁻³</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
absorbance. Only the emittance was increased by a small
amount.

Example 3

In this example it is demonstrated that conductive coat-
ings 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- MnO₂</th>
<th>resistivity (ohm-cm)</th>
<th>optical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>6061-T6</td>
<td>1.25 um 10 min</td>
<td>32×10⁻³ beyond ~450 V</td>
<td>0.678</td>
</tr>
<tr>
<td>clad</td>
<td>1.7</td>
<td>1.5</td>
<td>15×10⁻³ beyond ~450 V</td>
</tr>
<tr>
<td>clad</td>
<td>1.7</td>
<td>3.0</td>
<td>92×10⁻³ beyond ~450 V</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

This example demonstrates the effect of MnO₂ deposition conditions on coating resistance and optical properties. The Ni conditions were constant at 5 mA/cm² peak current for 10 s. The MnO₂ time was varied. The samples were unsealed.

<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 10⁶</td>
<td>78 x 10⁶</td>
<td>−400</td>
<td>0.547</td>
<td>0.71</td>
</tr>
<tr>
<td>5.0 min</td>
<td>10 x 10⁷</td>
<td>30 x 10⁷</td>
<td>−340</td>
<td>0.574</td>
<td>0.72</td>
</tr>
<tr>
<td>10 min</td>
<td>16 x 10⁸</td>
<td>21 x 10⁸</td>
<td>−375</td>
<td>0.608</td>
<td>0.72</td>
</tr>
</tbody>
</table>

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

This example demonstrates a feature of the present invention in that only a fraction of the pores are filled with MnO₂. This satisfies the condition where an increase in conductivity is required but only a small increase in absorptance is allowed. This condition was verified by determining the concentration of Mn in a coating using ICP (inductively coupled plasma analysis), from which the amount of MnO₂ was calculated. A coating was processed with ac deposition of Ni at a peak current of 7 mA/cm² followed by MnO₂ deposition for 3 min. The amount of Mn in the coating corresponded to 15.6 µg/cm² of MnO₂. The coating thickness is 12.7 µm. The nominal coating properties are a pore density of 4x10¹⁵ cm⁻² with pore diameter of 22 nm, based on measurements of SAA coatings reported in the scientific literature. Using these figures and assuming the MnO₂ deposit has the density of bulk MnO₂, 4.4 g/cm³, one calculates that the amount of MnO₂ found in the coating filled about 2% of the pores. This is not a precise figure, but the magnitude is correct.

In another experiment, the fraction of pores filled with MnO₂ was estimated from the density of MnO₂ modules seen on the surface using the scanning electron microscope. This was about 4x10⁸ cm⁻², corresponding to about 10% filled pores.

Example 7

Table I

Conditions studied for MnO₂ deposition which gave uniform coatings.

A listing is given in Table I of pulse dc (and dc) conditions that have been found to produce uniform MnO₂ deposits as judged by visual inspection. In all cases the initial current was set at 10 mA/cm², but the power supply voltage output was limited to 28 V, and when this was reached the current dropped. The voltage limit was reached within a few seconds with steady dc and 50 Hz pulses with 95% duty cycle, whereas with 50 Hz and 5% duty cycle, 10 mA/cm² was held for the full 10 min process time. The amount of MnO₂ in the coating depends on the deposition charge, as well as the current efficiency. Estimates of the charge for several coupons prepared at these conditions are given in the table. Coupons with similar depth of coloration were found to have resistivity of about 10¹¹ ohm-cm in vacuum plasma. A charge of 0.3 to 1.0 C/cm² at these process conditions deposits a suitable amount of MnO₂ for conductive oxide.

TABLE I

| Ni deposition: Bath: 0.2M NiSO₄ + 0.5M H₂BO₃ Sinusoidal wave; 50 Hz; peak current 5 mA/cm² process time 15 seconds |
| MnO₂ deposition: initial pulse current 10 mA/cm², maximum supply V = 28 V process time 10 minutes |
| Pulse time, ms | Frequency, Hz | approx charge C/cm² |
| 0.1 | 500 | |
| 0.5 | 500 | 0.3 |
| 1.0 | 50 | 0.3 |
| 2.0 | 50 | |
| 4.0 | 50 | 0.6 |
| 8.0 | 50 | 1.0 |
| 19 | 50 | 1.0 |
| 1000 | dc | 1.0 |
judged that 14 minute deposition time filled the pores black. At this low current density the cell voltage stayed at which is equivalent to a Ni deposit of 0.4 mg/cm². Assuming was deposited at the same conditions as in Example 9. The voltage is raised, there is a narrow voltage window in which waveshape with an oscilloscope. If the voltage is too low, maintained at pH 3 by periodic addition of H₂SO₄. Pulse dc deposits are about 0.3 µm thick, about 2.5% of the coating stated in Example 6 and with Ni in all the pores, the Ni the pores have the same dimensions and distribution as deposition is estimated from the peak area to be 1.35 C/cm², evolution which degrades the coating and interferes with Ni deposition. These voltages are measured versus the stainless steel cathode of the cell.

Ni was deposited at 17 Vpk for 15 min. The charge for Ni deposition is estimated from the peak area to be 1.35 C/cm², which is equivalent to a Ni deposit of 0.4 mg/cm². Assuming the pores have the same dimensions and distribution as stated in Example 6 and with Ni in all the pores, the Ni deposits are about 0.3 µm thick, about 2.5% of the coating thickness. This deposit appears black or very dark bronze. MnO₂ was deposited from 1M MnSO₄ at 23º C. and maintained at pH 3 by periodic addition of H₂SO₄. Pulse dc with a pulse current density of 0.68 mA/cm², 60 ms on and 60 ms off was run for several times. These coatings were examined in cross-section in an optical microscope at 1000x, and the progress of pore-filling was followed. It was judged that 14 minute deposition time filled the pores without significant spillover to the outer surface, and this time was used to prepare specimens. The coatings were dead black. At this low current density the cell voltage stayed at about 17 V and there was no clipping of the current pulse as reported in previous examples. The charge for MnO₂ deposition was 2.9 C/cm².

### Example 10

It was found useful to add a step to enhance the Ni deposition and so assure achieving a deep dead black appearance for the final coating. The same SAA coating was deposited as in Example 9, and then a Cu strike was deposited in the pores by immersing the workpiece in 15% H₂SO₄+4.18 g/l CuSO₄ at room temperature and electrolyzing for 15 seconds with 50 Hz sinewave voltage with 12 V peak amplitude. This was followed by Ni deposition for 10 minutes at the same conditions as in Example 9. The MnO₂ was deposited at the same conditions as in Example 9. The final coating had a deep dead black appearance.

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 2.2×10⁻⁸–1.2×10⁻⁶ ohm-cm. This is 10 to 100 times lower than for the conductive oxide coatings in the previous examples, and at much as 10⁶ 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 by varying the bath composition. For example, on 5657 alloy the conductive oxide has a much lower optical absorbance 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 the 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 so 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 absorbance, 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 the pores, or in most of the pores. The peak voltage should 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.

### TABLE II-continued

<table>
<thead>
<tr>
<th>Coating conditions for B1, B2, and B4</th>
<th>B1</th>
<th>B2</th>
<th>B4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seal</td>
<td>10 min boiling water</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 (20°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 conventional upper limit for bath concentration is 4 M. Observations made during the processing of black anodizing 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 is 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. electrolysing deposition of a metal into the surface pores of said porous anodic oxide,
   c. electrolysing 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 a 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 process 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 deposition is selected from the group consisting of: cobalt, nickel, copper, tin, silver, iron and gold.

7. The process of claim 2, 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. C., and wherein the electrolysing 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 sine wave 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%, with 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 electric current.

14. The process produced by the process of claim 13.

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

16. The process 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 II, 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