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[54] **METHOD OF FORMING PROTECTIVE COATINGS BY ELECTROLYSIS**

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[63] Continuation-in-part of Ser. No. 866,025, Oct. 13, 1969, abandoned.

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1,147,442 4/1969 Great Britain ..... 204/290 F

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[57] **ABSTRACT**

Protective ruthenium oxide coatings having desired characteristics of electrical conductivity, adherence to substrate and resistance to corrosion and heat are formed by oxidation of ruthenium in situ on the surface of the article to be protected.

12 Claims, No Drawings

METHOD OF FORMING PROTECTIVE COATINGS BY ELECTROLYSIS

This application is a continuation-in-part of U.S. application Ser. No. 866,025, filed Oct. 13, 1969 and now abandoned.

The present invention relates to methods of forming protective coatings on electrically conductive substrates and to providing coatings that protect against oxidation or other corrosion.

In the metallurgical art it is often found that articles of metal or other materials which have very useful characteristics such as strength, electrical conductivity and/or general corrosion resistance are nevertheless susceptible to special kinds of surface attack or other detrimental phenomena and, thus, special surface protection for the articles is needed.

For instance, it is well known that titanium, including commercially pure titanium and many known alloys based on titanium (wherein titanium is the major ingredient), possesses very useful corrosion resistance in many environments, e.g., moist chlorine gas, metal chloride or sulfate solutions, nitric acid and dilute alkalis, and also has very good strength, especially in relation to the light weight of the metal. However, difficulties involving certain kinds of oxidation and/or corrosion have greatly hindered full utilization of many potential advantages of titanium. Although the good resistance of titanium to attack by moist chlorine and aqueous salt solutions provides potential advantages to using titanium for inert nonconsumable anodes in electrolysis cells, it has in the past been found that when titanium anodes are used for electrolysis in various aqueous solutions, e.g., aqueous chloride or sulfate solutions, severe polarizing difficulties are encountered, such as formation of electrically insulating oxide layers on immersed surfaces of the titanium anodes, and the anodes are thus rendered inoperable or the electrical efficiency of the anodes is very detrimentally decreased. In prior efforts to overcome problems of providing titanium anodes for use in electrolysis cells, attempts have been made to coat titanium with other materials which, it was hoped, would be commercially satisfactory for providing and maintaining good electrical conductivity between titanium anodes and aqueous electrolytes. However, prior attempts at providing protectively coated titanium anodes have not been entirely successful due to, among other things, high costs of the coating materials, processing disadvantages such as necessity of heat treatment at disadvantageously high temperatures and/or poor adherence of the coating to the titanium, the latter resulting in detrimental separation of the coating from the titanium by peeling, spalling, buckling, corroding, etc.

It is also known that high strength titanium alloys suffer from a kind of corrosive attack referred to as "hot salt cracking," such as occurs when titanium is heated to elevated temperatures while having chloride salts on titanium surfaces. For instance, in the occurrence of hot salt cracking, brine salts from ocean spray become deposited on surfaces of titanium structures, e.g., aircraft engine components, and when the salt-bearing titanium surfaces are heated to elevated temperatures of about 250°C. or higher, e.g., to 550°C., cracks develop in stressed portions of the titanium. Thus, in such instances and other somewhat similar situations, even when electrical conductivity is not essential, there are needs for a commercially practical heat-resistant coating to protect titanium against attack by chlorides and other corrosive salts at elevated temperatures.

For protecting titanium and also other materials it is especially desirable to form thereon an adherent coating that has the required characteristics continuously and uniformly over the coating surface. In this regard, especially where good electrical conductivity is required, protective coatings made of two or more ingredients, such as coatings comprising mixtures of bonding materials with electrically conductive and/or corrosion resistant materials, are often unsatisfactory due to high electrical resistance of the bonding material (thus lowering average conductivity over the coated area) or due to poor heat or corrosion resistance of the bonding material.

Although many attempts were made to overcome the foregoing difficulties and other difficulties, none, as far as we are aware, was entirely satisfactory when carried into practice commercially on an industrial scale.

There has now been discovered a process that provides a continuous protective oxide coating having a particularly good combination of characteristics for electrical and/or corrosion resistant use.

It is an object of the present invention to provide a process for forming continuous, protective, electrically conductive, oxide coatings having good adherence to electrically conductive substrates.

Another object of the invention is to provide articles with special oxide coatings having durable adherence to the article and useful characteristics of electrical conductivity and protection against corrosion and heat.

Other objects and advantages will become apparent from the following description.

The present invention contemplates a process for forming a protective, adherent and electrically conductive oxide coating on an article, or on a portion thereof at a place where protection is desired, comprising oxidizing an outer surface of ruthenium in situ in an aqueous solution of potassium permanganate. The ruthenium oxide composition of the coating produced with the process of the invention is usually nonstoichiometric and is referred to herein as an RuO_x composition. Usually the mean value of x is at least about 1.0. Where the article is made of an electrically conductive material, the ruthenium can be applied on the article, prior to oxidation, by electroplating. Also, when the ruthenium is on an electrically conductive article, the ruthenium layer can be oxidized anodically with electric current passing through the potassium permanganate bath. The bath solution usually contains at least about 0.01 molecular weight or mole per litre (M/1) potassium permanganate, and the bath can also contain potassium dichromate to promote adherence of the oxide. The bath is effective for the oxidation of ruthenium with electric current and also without electric current. Thus, the invention includes a process of electrolytically forming a protective, adherent and electrically conductive ruthenium oxide coating on an electrically conductive substrate comprising anodically oxidizing ruthenium in situ on an anode immersed in an aqueous solution containing at least about 0.01 M/1 potassium permanganate and up to about 0.2 M/1 potassium dichromate or a greater amount up to the solubility limit of potassium dichromate in the bath. For performing the anodic oxidation process, an electrically conductive substrate having a ruthenium surface,

e.g., a titanium sheet having an electro deposited ruthenium coating, is provided as an anode in an electrolytic cell having one or more inert cathodes, e.g., two symmetrically placed platinum cathodes, and a potassium permanganate electrolyte bath in accordance with the invention. A direct current is passed between the cathode(s) and the ruthenium-surfaced anode while at least a portion of the anode is immersed inthe bath to anodically oxidize ruthenium in situ on the immersed anode surface and thereby form a continuous RuO_x coating adhering on the anode. To provide a continuous protective coating, sufficient electric current should be passed between cathode and anode in the present process to oxidize the ruthenium surface to an RuO_x composition with a mean value of x of at least 1.0. Accordingly, it is to be understood that the RuO_x may include a minor atomic proportion of elemental ruthenium. Also, the coating can usually contain very small amounts of the plating bath ingredients, e.g., manganese, and be satisfactory. Particularly useful characteristics of oxide coatings provided by the invention include good electrical conductivity, protective resistance to many corrosive media, e.g., alkali metal chloride salts, and also resistance to polarization and to anodic dissolution in aqueous electrolysis baths. Thus, the present process forms ruthenium oxide coatings that are satisfactory for use on inert (nonconsumable; insoluble; nonsacrificial) anodes in electrolytic processes, including processes for electrolytic extraction of elements from aqueous electrolyte solutions, e.g., electrolytic production of chlorine gas from brine and electrowinning of copper from copper sulfate solutions.

In carrying the invention into practice, the anodic oxidation process is usually controlled to have the electrolyte bath temperature at least about 20°C., the bath pH at least about 0.1 and the current density at least about 0.1 milliamperes per square centimeter (ma/cm²) of immersed anode surface. As aforementioned, the electrolyte bath contains at least 0.1 M/1 of potassium permanganate ($KMnO_4$) and may also contain up to about 0.2 M/1 or more potassium dichromate ($K_2Cr_2O_7$). The $KMnO_4$ concentration in the bath can be up to the solubility limit of $KMnO_4$ in the bath, e.g., up to about 0.2 M/1 $KMnO_4$ in aqueous solution. Presence of 0.01 M/1 to about 0.2 M/1 $K_2Cr_2O_7$, advantageously at least about 0.5 M/1 $K_2Cr_2O_7$, in the bath electrolyte is desirable for obtaining good adherence characteristics in the anodically oxidized coating. Usually, the bath temperature is not greater than about 95°C., the pH is not greater than about 9 and the current density is not greater than about 15 ma/cm². Advantageously, the bath temperature is 40°C. to 60°C. or somewhat higher, e.g., 65°C. or 80°C., and the pH is at least 0.5. Relatively high temperatures of about 40°C. to 80°C. e.g., 60°C. or 65°C., are particularly advantageous for oxidizing the ruthenium without passing electric current through the bath. Of course, when metals are anodized there are usually two competing tendencies, to wit, a tendency to anoidically dissolve the anode metal and a tendency to oxidize the metal in situ on the anode; in the present invention, the anodizing conditions are controlled to obtain oxidation without detrimental dissolution. For instance, conditions of very high current densities, especially at low pH values, e.g., 40 ma/cm² at 1.0 pH or 20 ma/cm² at 0.5 pH should be avoided in order to prevent detrimental anodic dissolution of ruthenium from the surface and/or cracking, spalling, exfoliation, etc., of any RuO_x coating that may be formed. Current density during the anodic oxidation can be conveniently maintained at 0.1 ma/cm² to 15 ma/cm² to obtain satisfactory anodic oxidation and good adherence of the coating.

For obtaining advantageously good quality of coating and good economy in commercial practice, the invention achieves special advantages of rapid anodic oxidation, electrical efficiency and especially well oxidized and adherent coatings with an advantageous anodic oxidation process wherein a ruthenium coating on another metal is anodically oxidized with an anode current density of 8 to 12 ma/cm² in an aqueous solution containing 0.05 to 0.15 or 0.20 M/1 $KMnO_4$ and up to 0.2 M/1 $K_2Cr_2O_7$, or the solubility limit, at a pH OF 0.5 to 6 and a temperature of 40°C. to 80°C.

Usually the bath is not agitated, although slow agitation can be employed if it is desired.

The subject oxidation process can be performed anodically and also without electric current on practically any electrically conductive article having a good adherent exterior surface of ruthenium. Thus, the process is applicable to anodic oxidation of ruthenium surfaces on electrically conductive substrates generally, including ruthenium coatings applied by electrochemical deposition, chemical deposition, pressure bonding, diffusion bonding and/or vapor deposition, provided that the ruthenium has good adherence to the substrate. Also, ruthenium surfaces on nonconducting substrates, e.g., nonconducting ABS polymer plastics, can be oxidized by the process without requiring electric current.

To produce ruthenium oxide coatings over titanium substrates in accordance with the invention it is especially advantageous for obtaining good adherence of the oxide coating, particularly for use in chloride environments, to provide the titanium substrate with a ruthenium coating by the Reddy-Taimsalu (R-T) electrodeposition method, described in U.S. Pat. No. 3,576,724, wherein ruthenium is electrodeposited from an aqueous acidic plating bath solution containing a reddish brown ruthenium sulfamate complex obtained by heating an aqueous solution of ruthenium chloride with an excess of sulfamic acid to hydrolyze the sulfamate.

Titanium surfaces that are to be electroplated with ruthenium for anodic oxidation in the present invention can be prepared for electroplating with ruthenium by etching in hot, preferably boiling, hydrochloric acid (37 percent by weight HCl). Another good, but not necessarily required, surface preparation of titanium for electroplating is obtained by etching the titanium with nitric acid and hydrofluoric acid, e.g., by etching in a hot aqueous solution containing, by volume, 1 percent HNO_3 and 18.5 percent HF.

The substrate for the process can be a continuous solid metal, such as strip or plate, or a ceramic or plastic, or can be an expanded metal grid or a combination of materials, e.g., a powder metallurgical compact or a laminated composite. Thus, the substrate can comprise a thin outer layer of another metal that is advantageous for adherently retaining ruthenium and/or ruthenium oxide on the substrate or for providing corrosion resistance or other desired characteristics. For instance, the substrate can be titanium having a thin outer layer of gold or nickel to promote adhesion of the ruthenium for the coating.

In the subject process, the oxidation is understood to proceed from the exterior of the ruthenium surface toward the interior surface of the ruthenium nearest the substrate. Accordingly, it is understood that the oxygen content of the resultant coating can, and usually does, vary across the thickness of the coating and the highest oxygen content is at the exterior portion of the coating. In this connection it is noteworthy that the oxidation process of the invention has advantages of enabling production of RuO_x coatings having preselected oxygen contents within a broad range of x values, e.g., from RuO_1 to about $RuO_{3.7}$, and the invention provides RuO_x coatings having high x values greater than 2, e.g., 2.1 or 2.3 or higher, such as, x values of 2.5 to 3.7.

The oxidation in the potassium permanganate bath is normally continued (either continuously or intermittently) sufficiently to oxidize the ruthenium at the exterior of the article to a depth of at least about 5 microinches. Thus, with the mean value of x being at least 1, the invention provides a ruthenium oxide coated article having an exterior layer or stratum consisting essentially of ruthenium and oxygen in an RuO_x composition wherein the amounts of ruthenium and oxygen are in an average atomic weight ratio of oxygen to ruthenium of at least 1:1 or greater, e.g., 2.7:1 or 3.7:1, across an exterior thickness of at least 5 microinches. Advantageouly for inert anode use in electrolytic processes the ruthenium oxide coating thickness is 20 to about 100 microinches and for use in protection against corrosive attack by hot salts the coating thickness is 5 to about 40 microinches. Usually the ruthenium oxide coating thickness is not greater than about 300 microinches in order to avoid excessive cost, although the coating thickness can be greater if needed, e.g., for protection against especially severe corrosive media and/or very prolonged exposure.

Thicknesses of ruthenium coatings, layers, strata, etc., initially provided on conductive substrates and there-after oxidized for purposes of the invention are usually at least about 40 percent of the required oxidized thickness. Thus, articles whereon ruthenium oxide coatings of at least 5 microinch thickness are to be formed have an exterior stratum of ruthenium at least about 2 microinches thick, or greater.

Ruthenium oxide coatings provided by the invention are continuously of the ruthenium oxide composition RuO_x referred to herein and are essentially devoid of interruption by presence of other materials. It is especially important to avoid having electrically nonconductive or highly resistive materials in the coating inasmuch as presence of such poorly conductive materials is detrimental to electrical efficiency in use of the coated article as an inert anode. Also, presence of foreign materials having inferior resistance to corrosion and/or dissolution is to be avoided in order to have good duration of protection of the substrate. (It is to be understood, of course, that reference to "continuous" in connection with the ruthenium oxide coating does not exclude ruthenium oxide coatings that continuously surround areas that are not coated with ruthenium oxide, such as where coating is deliberately avoided by masking certain areas for some special purpose.)

Microexamination of a cross section of a specimen of a coating formed by the invention, without heat treatment, at a magnification of 75 diameters (75X) showed the coating was continuously and uniformly of high density and free from porosity, voids and foreign materials; the oxide was of such a fine structure that no grains were discernible at 75X. Electron probe analysis of an RuO_x coating produced by the subject process indicated the coating contained at least 66 percent ruthenium and at least 17 percent oxygen and indicated manganese was definitely present, the proportion of manganese being estimated as less than 1 percent.

Characteristics of the RuO_x coating, especially the adhesion to the substrate and the life of the coating in anodic use at high current densitites, can be enhanced by heat treatment. Heat treatment of the ruthenium oxide coating is advantageously done in air or possibly a higher oxygen content atmosphere and can be at about 800°C. to about 500°C. or at lower temperatures down to about 350°C. for periods of about 5 minutes to about 10 hours or longer. At relatively high temperatures the heat treatment period should be relatively short and vice versa, for instance, 5 minutes to 1 hour at about 800°C. to about 500°C., or 2 hours to 10 hours at about 480°C. to 350°C., or 7 hours at 430°C. to 370°C., e.g., 4 hours at 370°C. plus 3 hours at 430°C.

The ruthenium (metal) surfaced substrate may be heat treated, e.g., heated at least 5 minutes at 550°C. or higher, in an inert atmosphere to obtain improved bonding of the ruthenium, and also of the subsequently formed RuO_x, to the substrate and/or to stress-relieve and/or recrystallize the ruthenium. Heat treatment of the ruthenium (before oxidation) on titanium substrates can be at about 1,000°C. to 800°C. for about 5 minutes to 60 minutes, e.g., about 15 minutes. Heat treatment can also be employed for stress relief and/or diffusion bonding when the substrate is a composite having an intermediate layer between the ruthenium and the basis metal of the substrate.

A specially recommended practice for producing protective, electrically conductive, oxide coatings on titanium that is deemed advantageous for obtaining long enduring adherence of the coating to the titanium, especially for anode operation at high current densities, is: electroplate ruthenium on etched titanium by the R-T method; heat treat the electroplated ruthenium on the titanium in an inert atmosphere at 1,000°C. to 800°C. for 5 to 60 minutes, e.g., about 15 minutes; then oxidize the ruthenium to an RuO_x coating in the potassium permanganate bath as soon as possible or practical after heat treating the ruthenium; and thereafter heat treat the RuO_x coated article at about 480°C. to 350°C., in air for about 2 to 10 hours.

For the purpose of giving those skilled in the art a better understanding of the invention and a better appreciation of the advantages thereof, the following illustrative examples are given:

EXAMPLE I

A sheet of commercially pure titanium having on both sides a ruthenium coating of 56-microinch thickness provided by the R-T electrodeposition method was introduced as the anode in an electrolytic cell containing an aqueous solution consisting essentially of water and 0.1 M/1 $KMnO_4$ as the electrolyte. The cell had two platinum cathodes spaced symmetrically apart from the ruthenium-coated titanium. The electrolyte bath temperature was about 40°C. and the pH of the bath was about 9. The bath was not agitated. A direct current voltage of about 0.5 volts and an anode current density of about 1.5 to 1.9 ma/cm² was established and

maintained between the anode and the cathodes and the ruthenium coating was thus anodically oxidized. At anodizing time intervals cumulatively totaling 15, 30 and 60 minutes, the coated titanium anode was removed from the cell, dried, and weighed to determine the gain in wieght by the anodic oxidation in the cell. The cumulative weight gains by the thus-accomplished anodic oxidation for 15, 30 to 60 minutes were about 0.2, 0.4 and 0.5 milligrams per square centimeter (mgm/cm²) of immersed anode surface, respectively. At the end of the 60 minute treatment the anode surface had a deep blue-black color. The color and weight gain indicated that the coating was an RuO_x composition with an x value of about 1.8. Inspection of the thus-produced oxide coating confirmed that the coating had good adherence to the titanium and was very satisfactorily continuous and free from cracks, fissures and foreign substances. Moreover, electrical conductivity measurements showed that the coating had a highly satisfactory electrical conductivity of 10^3oh-$m^{-1}cm^{-1}$.

The ruthenium metal coating on the titanium substrate in the foregoing Example I was provided by the R-T method with the following procedures. A solution of 50 grams of ruthenium trichloride ($RuCl_3 \cdot 3H_2O$) and 300 grams of sulfamic acid was diluted to a volume of 2 liters with distilled water, refluxed for 30 hours, condensed to one-fourth the original volume and cooled to room temperature. Concentrated hydrochloric acid was added until the solution turned black and then, after holding at room temperature for 4 hours, the solution was filtered and a reddish-brown precipitate of a ruthenium sulfamate complex was obtained. To provide the ruthenium electroplating bath, a solution was made of 16 grams of the thus-obtained refluxed ruthenium sulfamate complex per liter of hot water and then acidified to a pH of 1.5 by addition of sulfamic acid. Ruthenium was electrodeposited on the titanium substrate, which had been cleaned by degreasing and then etching in hot HCl, with the foregoing plating bath solution at 70°C. using a cathode current density of 0.3 ma/cm² and two platinum anodes symmetrically spaced about each side of the substrate.

Information illustrating further examples of the anodic oxidation proces of the invention is set forth in the following Table I, which pertains to anodic oxidation of commercially pure titanium substrates having coatings of ruthenium applied by the R-T electrodeposition method. Specimen No. 11 was electroplated with 25 microinches of gold and subsequently annealed in vacuum at 700°C. for about 15 minutes, before electroplating with ruthenium. In Table I, moving across the columns from left to right: initial thicknesses of the ruthenium (metal) coatings (Ru Coat) on the titanium specimens are in microinches; bath compositions (Comp.) are aqueous solutions wherein bath A contains 0.1 M/1 $KMnO_4$ and bath B contains 0.1 M/1 $KMnO_4$ plus 0.1 M/1 $K_2Cr_2O_7$ and bath C contains 0.158 M/1 $KMnO_4$; bath temperatures (Temp.) are in degrees Centrigrade; pH conditions of 1.0 are with adjustment with H_2SO_4; V refers to direct-current anode-to-cathode voltages (two symmetrically spaced platinum cathodes were used in each example); Id refers to current density in milliampees per square centimeter of immersed anode (titanium coated with ruthenium) surface; "Time" is total minutes of anodization, or cumulative total where two time periods are shown; "percent Wt. Gain" is the weight gain during anodization divided by the total of the initial weight of the ruthenium metal coating plus the gain in weight, expressed in per cent, and thus illustrates the weight per cent gain in oxygen by the anodic oxidation; and the x value shows the mean value of x in the RuO_x coatings produced in these examples of anodic oxidation processes in accordance with the invention. EAch of the examples referred to in Table I produced satisfactory continuous ruthenium oxide coatings having good adherence to the substrate.

TABLE I

Example No.	Ru coat (micro-inch)	Bath Comp.	Bath Temp. °C.	Bath pH	V	Id	Time (min.)	Percent weight gain	x value
2	50	B	60	1.0	0.1	2.0	50	24.0	2
3	50	B	60	1.0	0.1	2.0	50	20.5	1.7
4	50	B	60	1.0	0.1	2.0	50	17.4	1.5
5	50	B	60	1.0	0.1	2.0	50	18.9	1.6
6	56	A	23	9	0.5	4.7	60	14.1	1.2
.....		A	23	9	0.5	4.8	120	21.2	1.8
7	25	A	40	9	0.5	0.4–0.3	45	22.8	1.9
8	25	A	40	9	0.5	0.4–0.3	30	32.5	2.7
9	100	A	40	9	0.5–0.7	2.0	60	25.2	2.1
10	11	A	40	9	0.5	1.0	25	27.0	2.2
.....		A	40	9	0.5	1.0	50	38.0	3.2
11	25	A	40	1.0	0.1–0.2	2	60	30.1	3.05
12	25	C	60	1.0	N.R.	10	3	24.0	2
13	25	C	65	1.0	none	none	1.25	24.3	2.03
14	25	C	66	1.0	none	none	2.00	35.3	3.4

N.R. = not recorded.

Success of the process of the invention in forming coatings having good electrical conductivity characteristics, including resistance to polarization and other useful characteristics including durable adherence and resistance to corrosion, dissolution and cracking is illustrated with the following examples of the invention.

Coatings of ruthenium oxide prepared in accordance with the invention enabled electrolytic release of chlorine from chloride solutions, such as brine, when speci-

mens of titanium with the subject ruthenium oxide coating were operated as anodes in brine at current densities up to 200 amperes per square foot (amp./ft.^{2}) and higher, e.g., 1,000 amp./ft.^{2}. Portions of specimens with ruthenium oxide coatings (Examples 11, 12 and 13 of Table I) were anodically operated in electrolytic cells which each had a nickel cathode and a brine electrolyte (22 percent sodium chloride in water) at about room temperature in a nonconducting corrosion-resistant tank. The Example 11 ruthenium oxide-coated specimen was heat-treated in argon at about 700°C. for 20 minutes and then anodically operated to release chlorine from brine for 2¾ hours at an anode current density of 1,000 amp./ft.^{2}; anode potential measurements were less than 2.5 volts and the coating remained in good condition. The specimen with the ruthenium oxide coating formed in Example 12 was heat treated in air at 480°C. for 3 hours and a portion of the heat treated specimen was exposed as an anode in the brine solution of a chloride electrolysis cell. The thus heat treated coating of Example 12 functioned satisfactorily in releasing chlorine for about 95 hours and an anode current density of 1,000 amp./ft.^{2} and anode potentials were less than 2.5 volts; after 95 hours the anode potential rose higher. The specimen having the nonelectrolytically formed coating (Example 13 in Table I) was heat treated for 4 hours at 370°C. plus 3 hours at 427°C. and then a portion of the heat treated coating was exposed to the brine solution of a chloride electrolysis cell for over 390 hours at an anode current density of 1,000 amp./ft.^{2}. Chlorine was released at the coating and the anode potentials at the heat treated coating of Example 13 remained less than 2.5 volts for up to 393 hours with the anode potentials being less than 2 volts during the operating period from 128 hours to 393 hours, whereafter the anode potential rose higher. After over 400 hours and functioning at 1,000 amp./ft.^{2} in electrolysis of brine, the specimen of Example 13 was removed from the cell and visual examination showed the coating still had good adherence to the titanium substrate and was in good physical condition.

In a further example, the subject anodic oxidation process formed an RuO_x coating that served successfully in use as a protective electrically conducting coating on an anode used in electrowinning copper. In accordance with the invention, a ruthenium stratum which had been electro-deposited over a titanium substrate using the R-T method was anodically oxidized in an aqueous solution containing 0.1 M/1 $KMnO_4$ and 0.1 M/1 $K_2Cr_2O_7$ and maintained at 45°C. and 1.0 pH while passing an electric current of about 2.0 ma/cm^2 at 1.0 volt (direct-current) from the anode to two platinum cathodes to thereby form an adherent RuO_x coating about 25 microinches thick with an x value of 1.4. The thus-prepared anode was used successfully at an anode current density of 30 amp./ft.^{2} to electrodeposit copper in an electrolytic cell having a copper cathode and an aqueous acidic copper sulfate bath. From visual examination of the anode coating it was evident that the RuO_x coating did not crack, spall or otherwise deteriorate and endured very satisfactorily during use in electrowinning of copper.

Anodically formed ruthenium oxide coatings produced by the process of the invention provide good protection of metals against corrosive attack by hot salts. For example, a strip of solution-treated and aged 6A1-4V titanium (a commercially produced high-strength titanium alloy nominally containing, by weight, 6 percent aluminum, 4 percent vanadium and the balance titanium) having thereon an 11-microinch ruthenium layer electrodeposited by the R-T method was anodically oxidized in accordance with the invention in an aqueous electrolyte bath containing 0.1 M/1 $KMnO_4$, at 40°C. and 7.6 pH, with an anode current density of about 1 ma/cm^2 at 0.7 to 1.0 volts for a time of about 50 to 75 minutes to form a bluish black RuO_x coating with an x value greater than 2 and a thickness of about 25 microinches. Good protection provided by the oxide coating of the invention against hot salt cracking was confirmed by applying a layer of sodium chloride to the middle of the ruthenium oxide coated strip and heating the thus-treated strip to about 540°C. for 20 hours while maintaining an elastic stress (at or above the yield point) on the strip. For comparison, a layer of sodium chloride was also applied to the middle of a control specimen of an uncoated strip of the same 6A1-4V titanium alloy, also in the solution treated and aged condition, and the uncoated control specimen was heated to the same temperature and subjected to the same elastic stress as the aforementioned oxide coated strip of the invention. The uncoated titanium strip failed by cracking in less than 4 hours whereas, in contrast, the ruthenium oxide coated strip was not cracked after completion of the aforedescribed 20-hour exposure to hot salt and stress. In longer time tests at 510°C., under essentially comparable stress-corrosion conditions, the titanium coated with RuO_x by the process of the invention survived without cracking in a 150-hour test whereas the uncoated titanium cracked in less than 24 hours.

In contrast to the good results of obtaining continuous adherent coatings of ruthenium oxide by oxidation of ruthenium layers on titanium substrates in aqueous potassium permanganate baths in accordance with the invention, unsatisfactory results, including losses of metal from the specimens, formation of nonadherent oxides and/or failure to change the weight or appearnace of the specimen, were obtained when attempts were made to oxidize ruthenium layers on titanium substrates in sulfuric acid. Data in the following Table II pertain to anodization conditions that were tested and to results of changes in weight and visual appearance (and other visible phenomena) that were observed when specimens of titanium having exterior layers of ruthenium were anodically treated in acid baths not in accordance with the invention. The ruthenium layers were applied to the titanium substrates by the R-T electrodeposition method used to prepare specimens for examples of the invention. For each treatment the specimen was connected as an anode in the acid electrolyte bath with two platinum cathodes and a direct-current power source. The baths were not agitated. In Table II, moving from left to right, the prime (') marks, after the specimen identification letters, e.g., XA, XB, etc., indicate the same specimen was tested again for the second and third time; numbers under "Initial Ru Surface" are weights of ruthenium metal per unit area in milligrams per square centimter; "Bath Electrolytes" are aqueous acid solutions of the indicated weight percentages; "Current Densities" are anode current densities in milliamperes per square centimeter; "Times" are the minutes of each treatment; "Weight Changes" are weight changes per unit area of specimen anode surface exposed in the bath and are cumulative where

shown for second and third treatments of the same specimen. After each treatment the specimen was washed in running water without abrasive rubbing, dired, and then weighed to determine weight change. From the experimental data referred to in Table II it was concluded that the subject treatments did not result in formation of continuous adherent ruthenium oxide coatings on any of the specimens.

Portions of specimens XA'', XB'' and XC'', after the foregoing teatments in sulfuric acid, were electrically connected as anodes, each with two platinum cathodes, in electrolysis cells with brine solutions containing 22 percent sodium chloride. Voltages of about 15 volts DC were applied across the anodes and cathodes. With specimen XA'' no current passed through the cell; with specimen XB'' the anode current density was initially about 650 amp./ft.^{2} but dropped to zero within 30 seconds; and with specimen XC'' the anode curent rose to about 580 amp./ft.^{2} but dropped to less than 30 amp./ft.^{2} within 80 seconds. Chlorine was not released, at least not in substantial visually detectable quantities. In view of these three trials in brine solutions and the failures to obtain substantial increases in weight on any of the specimens treated in sulfuric acid solution, it was concluded that treatments XA through XC'' of Table II were not satisfactory for producing ruthenium oxide coatings.

The present invention, in addition to providing anodes for electrowinning, electrorefining and electrodeposition of copper and for extraction of nonmetallic elements such as chlorine, provides ruthenium oxide coated, inert anodes for electrowinning, electrorefining and electro-deposition of nickel, manganese, chromium or other metals that can be electrolytically extracted from aqueous solution, or possibly, for fused salt baths.

Furthermore, ruthenium oxide coated articles provided by the invention can also be used as nonsacrificial anodes for cathodic protection of metal in structures and products exposed to aqueous environment corrosion, e.g., ships, underground pipelines, tunnel casings, off-shore oil drilling or mining platforms or other articles.

The oxidation process of the invention is widely applicable to providing continuous coatings of ruthenium oxide on most, or practically all, other solid materials, e.g., copper, stainless steel, powder metallurgical compacts or graphite, or on nonconductors, such as, plastics or ceramics. While the coating has very good adherence it is of course to be understood that in general the substrate should have sufficient rigidity to avoid being excessively distorted, e.g., bent, twisted or stretched, in use so as to avoid excessively straining and cracking the coating, unless specially supported. The substrate can be a corrosion resistant metal (including commercially pure metals and alloyed metals) such as titanium, tantalum, molybdenum, zirconium, silver, gold, platinum and platinum-group metals, stainless steel, e.g., austenitic nickel-chromium stainless steel, or nickel, including nickel-base alloys, e.g., nickel-chromium alloys and nickel-chromium-molybdenum alloys wherein nickel is the major ingredient. Thus, protectively coated articles contemplated in the invention include ruthenium oxide coated titanium alloys, ruthenium-oxide coated nickel-chromium-molybdenum alloys and ruthenium-oxide coated stainless steels, especially anodes thereof. Further, the invention includes anodic and nonelectrolytic formation of ruthenium oxide coatings on articles consisting of ruthenium or ruthenium alloys and oxidation of ruthenium articles, e.g., sheet or strip, across the entire thickness of the article to provide articles consisting essentially of the subject RuO_x composition. Also, the substrate can be of copper (including brass and bronze), zinc, lead, iron (incuding steels), aluminum, tungsten or other metal.

The invention is further applicable to providing protectively coated electrodes in electric process cells such as electroplating cells, electrowinning and/or electrorefining cells, fuel cells, batteries and catalytic electrosynthesis cells, and to providing ruthenium oxide resistance components. Moreover, it is also important to observe that the invention provides articles having ruthenium oxide coatings which protect against stress-corrosion cracking and other corrosion and thus is applicable to providing protectively coated articles for use under stress at elevated temperatures in chloride-containing environments, particularly including turbine engine components, e.g., compressor blades or vanes, made of titanium-base alloys and subjected in use to temperatures of 250°C. and higher while in contact with chlorides from ocean water.

Although the present invention has been described in conjunction with preferred embodiments, it is to be un-

TABLE II

Specimen	Initial Ru surface (mgm/cm^2)	Bath: Electrolyte (wt.%)	Bath: Temp. ° F.	Current density (Ma/cm^2)	Time; min.	Weight change (mgm/cm^2)	Observations
XA	0.62	80%H_2SO_4	140	1	15	0.0	
XA'		80%H_2SO_4	140	25	15	− 0.68 (loss)	Copious gas evolution. Surface black but washed off.
XA''		80%H_2SO_4	140	12.5	15		Specimen turned to light brown color.
		(would not pass higher current)					All Ru dissolves off specimen in this acid solution.
XB	0.78	50%H_2SO_4	140	1	15	− 0.02 (loss)	
XB'		50%H_2SO_4	140	25	15	− 0.27 (loss)	Center dark brown edges deep blue.
XB''		50%H_2SO_4	140	50	15	− 0.39 (loss)	Specimen black but most of coating washed off.
XC	0.78	50%H_2SO_4	122	10	2	− 0.03 (loss)	Copious gas evolution.
XC'		50%H_2SO_4	122	10	15	− 0.12 (loss)	Copious gas evolution edges of specimen dark.
XC''		50%H_2SO_4	122	50	15	− 0.51 (loss)	Copious gas evolution specimen partially blue-black in center.

derstood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A process for providing an electrically conductive article having a protective electrically conductive oxide coating comprising:

a. providing an electrically conductive article;

b. applying a layer of ruthenium metal at least about 2 microinches thick adherent to an exterior surface of said article;

c. providing an electrolytic cell having at least one inert cathode and an aqueous electrolyte bath solution at a temperature of about 20°C. to about 95°C. and containing potassium permanganate in an amount of at least about 0.01 mole per liter and up to the solubility limit;

d. immersing at least a portion of said ruthenium metal layer in said bath;

e. connecting said cathode and said electrically conductive article having said ruthenium layer immersed in the bath to a direct-current electric power source with said article in anodic relationship to said cathode; and

f. passing unidirectional electric current through said cell at a current density of about 0.1 to 15 milliamperes per square centimeter of immersed anode surface to anodically oxidize the exterior of said immersed ruthenium layer to a coherent RuO_x composition characterized by an x value of at least 1.0, resistance to chloride corrosion, electrical conductivity and adherence to the article.

2. A process as set forth in claim **1** wherein the solution is characterized by a potassium permanganate content of 0.05 to 0.20 mole per liter, a pH of 0.5 to 6 and a temperature of 40°C. to 80°C. and the anode current density is 8 to 12 milliamperes per square centimeter.

3. A process as set forth in claim **1** wherein the ruthenium layer is applied by electrodeposition.

4. A process as set forth in claim **1** wherein the ruthenium layer is applied by electrodeposition from an aqueous acidic plating bath solution containing the reddish brown ruthenium sulfamate complex resulting from heating an aqueous solution of ruthenium trichloride with an excess of sulfamic acid to hydrolyze the sulfamate.

5. A process as set forth in claim **1** wherein at least a major proportion of the electrically conductive article is titanium.

6. A process as set forth in claim **1** wherein the passage of electric current through the bath is continued until the exterior of the immersed ruthenium layer is anodically oxidized to an RuO_x composition characterized by an x value greater than 2.0.

7. A process as set forth in claim **6** wherein the exterior of the ruthenium layer is anodically oxidized to an RuO_x composition characterized by an x value of 2.5 to 3.7.

8. A process as set forth in claim **1** which additionally comprises heat treating the anodically oxidized coating for at least 5 minutes at about 350°C. to about 800°C.

9. A process for forming a protective electrically conductive ruthenium oxide coating over an electrically conductive substrate having an adherent exterior stratum of ruthenium comprising anodically oxidizing an outer surface of the ruthenium stratum on the substrate while said substrate having the ruthenium stratum is connected as an anode at least partially immersed in the bath of an electrolytic cell comprising a cathode and an aqueous electrolyte bath solution containing potassium permanganate in an amount of at least 0.01 mole per litre and up to the solubility limit of potassium permanganate in the bath, said bath being at a temperature sufficient to dissolve at least 0.01 mole per litre potassium permanganate and not greater than about 95°C., and passing between the anode and the cathode a unidirectional electric current at a current density sufficient to promote adherent oxidation of the immersed ruthenium surface to provide a continuous coherent, adherent, RuO_x composition characterized by an x value of at least 1.0 and meanwhile controlling the current density to not exceed 15 milliamperes per square centimeter of immersed anode surface.

10. A process in accordance with claim **9** wherein the potassium permanganate solution is characterized by a potassium permanganate content of at least 0.05 mole per litre, a pH of at least 0.5 and a temperature of at least 40°C. and the anode current density is at least 8 milliamperes per square centimeter.

11. A process in accordance with claim **9** wherein the substrate is titanium and the ruthenium stratum is an electroplate on the titanium, which comprises heat treating the ruthenium on the titanium in an inert atmosphere at 1,000°C. to 800°C. for 5 minutes to 60 minutes before oxidizing the ruthenium in the potassium permanganate solution and thereafter heat treating the ruthenium oxide coating in air at 480°C. to 350°C. for 2 hours to 10 hours.

12. A protectively coated article having a ruthenium oxide coating produced by the process set forth in claim **9** and having manganese in the coating.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,763,002 Dated October 2, 1973

Inventor(s) Robert Max Skomoroski and Gaylord Darrel Smith

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 46, for "0.5" read --0.05--.

Column 4, line 15, for "OF" read --of--.

Column 7, line 8, for "to" read --and--.

Signed and sealed this 28th day of January 1975.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents