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2,851,766

PLURAL METALLIC COATINGS ON URANIUM AND METHOD OF APPLYING SAME

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No Drawing. Application January 9, 1945
Serial No. 572,094

8 Claims. (Cl. 29—194)

This invention relates to the application of metallic coatings to chromium surfaces.

Metallic chromium has many desirable properties as a structural or coating metal. In some cases, however, its corrosion resistance is inadequate and application of other metals possessing greater resistance to the specific corrosive elements involved is desirable. In other cases the chromium exerts undesirable electro-chemical effects and application of coatings to overcome these effects may be necessary.

In the protection of metallic uranium, chromium platings have very beneficial properties for preventing diffusion of metallic uranium. However, for some purposes the metallic uranium is not adequately protected from corrosive influences by the chromium alone. Hence it is desirable to apply metallic coatings to the chromium platings. The chromium platings have been found to be particularly refractory to wetting by other coating metals. As a consequence only poor, incomplete coatings are obtained when coating of the chromium platings by low-melting hot-dip coating metals is attempted.

An object of the present invention is the application of adherent metallic coatings to chromium surfaces. A further object is the provision of corrosion-resistant protective coatings on chromium platings. A still further object is the protection of metallic uranium by means of chromium platings coated with hot-dip coatings. Other objects will appear from the following description of the invention.

In accordance with my invention chromium surfaces are coated by applying coating metals consisting of or containing aluminum. I have found that the aluminum wets the chromium and provides a firm bond between the chromium and the coating metal. The proportion of aluminum necessary to accomplish the purposes of the invention is not large. Thus zinc coatings containing as little as 1% of aluminum have been applied successfully. On the other hand coatings containing more than 99% of aluminum also may be applied. The process is particularly applicable to bright chromium electroplatings on metallic uranium. Most suitable conditions for applying the coatings will vary depending upon the composition of the coating metal employed. Thus temperatures from 450° C. or less to 750° C. or more may be used, depending upon the melting point of the metal to be applied. In the application of zinc coatings containing from 1% to 5% of aluminum, temperatures from 150° to 650° C. may be used, the lower temperatures being more suitable for alloys near the eutectic composition. Aluminum-silicon alloys having compositions approximating the eutectic may be applied at temperatures between 600° C. and 750° C.

The hot-dip coatings may be applied with or without a flux. Alkali-metal halide fluxes, especially those containing small proportions of alkali-metal fluoride, have been found to be particularly satisfactory. However, the use of such fluxes is not essential to the production of adherent coatings.

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The invention is useful for the application of hot-dip coatings to serve as final protective coatings and also to serve as bonding means to unite the chromium surfaces with other metals. Thus zinc coatings may serve as a base for solder bonds to other metals. A particularly suitable combination involves the application of low-melting aluminum-silicon alloys to metallic aluminum sheaths.

In the application of the invention to the coating of metallic uranium, the chromium may be applied directly to the uranium or over a light coating of another metal, such as nickel or copper, as described in greater detail in my U. S. patent applications, Serial No. 572,093, entitled "Nickel Coatings and Method of Applying," filed January 9, 1945, and Serial No. 571,673, entitled "Copper Coatings and Method of Applying," filed January 6, 1945.

The metallic uranium preferably is prepared for the application of the coatings by an etchant treatment of the metal surface with an aqueous etching solution containing chloride ions, i. e., a hydrochloric acid solution or a molten hydrate of ferric chloride. Particularly satisfactory treatments of this type involve anodic pickling of the metal in trichloroacetic acid solution, for example an aqueous solution containing 45% to 50% of trichloroacetic acid, or in aqueous phosphoric acid solution containing about ½% of hydrochloric acid, to remove a one-half to one mil layer of the surface metal. Prior to the etchant treatment metal may be cleaned by sand-blasting, pumice-scrubbing, treating with organic solvents to remove grease or oily impurities, or treating with a chemical solvent for the oxide film on the metal. Aqueous nitric acid solutions containing from 30% to 55% HNO₃ by weight are especially useful for this purpose. An additional short treatment with this reagent should be applied after the etchant treatment in order to remove the coating of oxide or oxychloride from the etched metal surface.

The following examples further illustrate the invention. Unless otherwise indicated, quantities are expressed in terms of weight.

Example 1

A metallic uranium rod is pickled in aqueous 15% trichloroacetic acid solution at about 55° C. while a current is passed through the solution with the rod connected as anode for 10 minutes at a current density of 50 amperes per square foot. The rod is then rinsed with cold water, dipped for four minutes in aqueous 35% HNO₃ solution, rinsed again and electroplated in a chromic acid bath containing 400 grams per liter of chromic acid at 50° C. and 250 amperes per sq. ft. current density until a chromium layer about 0.001" thick is formed (about 1 hour). A conforming lead anode spaced about one inch from the rod is used. The freshly plated rod is then dipped into a molten zinc bath containing 1% of aluminum at 600° C. for approximately 100 seconds. The rod is removed from the bath, shaken to free it from excess molten metal, placed on smooth Transite (asbestos cement) rollers and rolled slowly in air until the coating solidifies. A firmly adherent zinc-aluminum coating is obtained on the chromium-plated rod.

Example 2

A rod plated and coated as in Example 1, upon removal from the zinc bath, is spun at high speed for 5 seconds to remove excess metal and is then dipped for 10 seconds into a molten aluminum-silicon alloy comprising 88 parts of aluminum and 12 parts of silicon at 638° C. The rod is withdrawn and cooled on rollers as in Example 1. A firmly adherent coating of aluminum-silicon alloy over zinc is obtained on the chromium-plated uranium rod.

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In this example the zinc bath has an important function of heating the rod to a temperature approaching that of the aluminum-silicon bath and thus facilitating application of this alloy.

Example 3

A chromium-plated rod prepared as in Example 1 is dipped through a halide flux (prepared by first mixing 53 parts of potassium chloride, 42 parts of lithium chloride and 5 parts of sodium chloride and adding to the mixture 10 parts of sodium fluoride) into a zinc bath of 99% zinc and 1% aluminum at a temperature of about 660° C. The rod is held in this bath for 1 minute, then removed, spun to remove excess metal, and dipped for 4 seconds directly into an aluminum-silicon alloy containing 88% aluminum and 12% silicon at 640° C. for 4 seconds. The rod is removed from this alloy and rolled until cool as in the preceding examples.

Example 4

A rod, chromium plated as in Example 1, is dipped through a halide flux of the same composition as used in Example 3 into a molten zinc bath consisting of 95% zinc and 5% aluminum at 650° C. The rod is held in this bath for about 75 seconds, withdrawn, centrifuged for 5 seconds, and passed through a flux of the same composition into an 88% aluminum 12% silicon alloy at 640° C. After 2 seconds in this bath the rod is withdrawn and plunged into a preheated aluminum can containing a small amount of aluminum-silicon at 600° C. Upon cooling the assembly the aluminum can is firmly united by the aluminum-silicon alloy and zinc to the chromium-plated rod.

Example 5

A uranium rod, electroplated as in Example 1, is dipped for 30 seconds into molten aluminum 2S at a temperature of about 750° C. The molten aluminum is covered by a flux prepared by adding 15 parts of NaF to 100 parts of a 53% KCl, 42% LiCl, 5% NaCl mixture. The coating is cooled on rollers as in Example 1. A continuous aluminum coating on the chromium-plated rod is thus obtained.

Example 6

A machined cylindrical uranium rod about 8 inches long and 1 1/8 inches in diameter is prepared for electroplating by dipping in trichlorethene to remove grease, sand-blasting lightly, dipping in aqueous 35% HNO₃ at 30° C. for 4 minutes, rinsing with cold water, etching by anodic treatment in aqueous 50% trichloroacetic acid solution at between 50° C. and 60° C. for 10 minutes at 50 amperes per square foot current density, rinsing with cold water, dipping for 4 minutes in cold aqueous 35% HNO₃ solution to clean the etched metal surface, and rinsing in cold water.

The cleaned, etched metal rod is immediately electroplated in a copper pyrophosphate electroplating bath, comprising 75 grams per liter of copper as pyrophosphate, at a current density of 25 amperes per square foot at 60° C. with air agitation until a copper plating about 0.0005 inch thick is formed (about 30 minutes). The copper-plated rod is rinsed with water and then electroplated in a chromic acid bath, containing 400 grams per liter of chromic acid and 4 grams per liter of sulfuric acid at 50° C. and 250 amperes per sq. ft. current density until a chromium layer 0.0005 inch thick has formed (about 30 minutes). For the chromium plating step a concentric lead anode comprising an expanded metal cylinder having a diameter about 2 inches greater than the rod is used.

The freshly chromium-plated rod is rinsed to remove electroplating solution, dried, and dipped directly into a sodium-modified 88% aluminum 12% silicon alloy at 640° C. for 50 seconds. It is then removed from the alloy, shaken free of excess metal, and placed on smooth

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Transite rollers where it is rolled in contact with air at room temperature until it has cooled.

Example 7

The process of the preceding example is repeated except that the copper electroplating step is conducted for only about 2 minutes to produce a copper coating about 0.00003 inch thick and the uranium rod covered with this flash coating is electroplated in a chromic acid bath, to a thickness of 0.0008 inch chromium and then hot dipped as in Example 6. An equally adherent aluminum-silicon alloy coating affording adequate protection for the uranium rod is obtained.

Example 8

A metallic uranium rod prepared for electroplating as in Example 6 is electroplated in a nickel sulfate electroplating bath, comprising 240 grams of NiSO₄·7H₂O, 45 grams of NiCl₂·6H₂O, and 30 grams of H₃BO₃, at a current density of 25 amperes per sq. ft. at 40° C. until a nickel plating about 0.0001 inch thick is formed (about 5 minutes). The plated rod is then rinsed in water and electroplated in an aqueous solution containing 400 grams per liter of chromic acid and 4 grams per liter of sulfuric acid at 50° C. until a chromium plating 0.0005 inch thick has been built up. A concentric lead anode comprising an expanded metal cylinder having a diameter about 2 inches greater than the rod is used. The chromium-plated rod is rinsed, dried and dipped in aluminum-silicon as in Example 6. After rolling and cooling, a uniform adherent coating is obtained on the rod.

Example 9

The process of the preceding example is repeated except that the nickel electroplating step is conducted for only about 45 seconds to apply a nickel coating 0.000015 inch thick and the chromium electroplating step is conducted for about one hour to apply a chromium plating 0.001 inch thick. As in the preceding example a firmly adherent coating is obtained affording adequate protection for the uranium rod.

In a similar manner hot-dip coatings of other aluminum alloys such as copper-modified aluminum and magnesium-aluminum alloys may be applied to chromium platings on uranium and other metals.

It will be understood that I intend to include variations and modifications of the invention and that the preceding examples are illustrations only and in no wise to be construed as limitations upon the invention, the scope of which is defined in the appended claims, wherein:

I claim:

1. The method of protectively coating uranium, which comprises applying a chromium plating to the uranium and bonding the chromium plating by means of molten aluminum-silicon alloy to an aluminum sheath.

2. The method of protectively coating uranium, which comprises applying a flash coating of a metal of the group consisting of copper and nickel, applying a chromium plating thereover, and bonding the chromium plating by means of molten aluminum-silicon alloy to an aluminum sheath.

3. A uranium article having a chromium plating on a flash plating of the group consisting of nickel and copper and bonded to an aluminum sheath by means of an aluminum-silicon alloy containing about 12% of silicon.

4. The method of protectively coating a chromium article which comprises applying a chromium plating thereto by electrolysis from a chromic acid bath and then applying to the chromium surface of said plated article a molten metal of the group consisting of aluminum and aluminum-containing alloys by passing said chromium plated article thru a molten halide flux containing from 10 to 15 parts of NaF added to 100 parts of a 53% KCl, 42% LiCl, 5% NaCl mixture into a bath of said molten metal.

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5. The method of protectively coating a uranium article which comprises applying a chromium plating thereto by electrolysis from a chromic acid bath, passing said chromium plated article thru a molten halide flux containing from 10 to 15 parts of NaF added to 100 parts of a 53% KCl, 42% LiCl, 5% NaCl mixture into a molten metal bath consisting of 99% to 95% zinc and 1% to 5% aluminum, and then applying to the surface of said coated article molten aluminum containing a minor proportion of silicon by passing said coated article thru a molten halide flux containing from 10 to 15 parts of NaF added to 100 parts of a 53% KCl, 42% LiCl, 5% NaCl mixture into a molten bath of an 88% aluminum 12% silicon alloy.

6. A uranium article having a chromium plating over which is firmly bonded a metal coating of the group consisting of aluminum and aluminum-containing alloys.

7. A uranium article having a chromium plating over which is firmly bonded an adherent metal coating con-

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sisting of an alloy of aluminum with a minor proportion of silicon.

8. A uranium article having a chromium plating over which there is a bonding layer consisting of an aluminum-silicon alloy containing about 12% of silicon and an aluminum sheath, said bonding layer lying between said chromium plating and said aluminum sheath.

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