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METAL SURFACE TREATMENT

Lowell D. Eubank, Richland, Wash., assignor to the United States of America as represented by the United States Atomic Energy Commission

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This invention relates to the application of metal coatings to uranium. It is especially concerned with the hot dipping process in accordance with which such coatings are applied by dipping the article to be coated into a molten metal bath of the coating metal.

The application of metal coatings to uranium by dipping the uranium in molten metal baths is hindered by the rapidity with which uranium forms an oxide film and by the difficulty of completely eliminating this film once it has formed. While the surface may be improved by various pickling treatments, oxide forms on the metal while it is being transferred from the pickling bath to the coating bath. The conventional fluxing materials used in the treatment of iron and steel and various other metals react violently with uranium and the reaction products prevent wetting of the metal by the coating bath. As a consequence, the metal coatings which have been applied by the hot dipping method have not been uniformly adherent.

It is an object of the invention to prepare metallic uranium surfaces for the application of coatings by the hot dipping process. Further objects are to improve the adherence of the coating metal and to assist the flow of coating metal over the uranium surface so as to provide uniform and firmly adherent coatings. Further objects are the elimination of oxide film from metallic uranium to be coated and the prevention of oxide formation upon the surface of the molten metal coating bath. Further objects will appear from the following description.

In accordance with the present invention a molten alkali-metal halide of the group consisting of alkali-metal chlorides and bromides is used as a flux for the application of metal coatings to uranium.

In addition to the alkali-metal chloride or bromide, other alkali-metal halides or alkaline earth metal halides may be present. Thus the fluorides and iodides of the alkali-metals and alkaline earth metals as well as the chlorides and bromides of the latter metals may be present. By varying the proportions of the salts, fluxes of melting points (minimum temperatures at which solids are absent) varying as desired from about 320° to 800° C. may be prepared. The alkali-metal halide fluxes have been found to be applicable to the coating of uranium with metals by the hot dipping method in general. Examples of such coating metals are zinc, aluminum, and alloys such as solder, bronze, brass, and aluminum-silicon.

Lithium chloride contributes to alkali-metal halide fluxes very desirable properties of increased activity and reduced melting point. The greater activity makes possible rapid and complete coverage of uranium with coating metal. The reduced melting point makes possible the use of alkali-metal chloride fluxes at lower coating temperatures and hence under a wider variety of coating conditions. This property is especially important in the application of low-melting coating metals, such as zinc.

The coating may be effected in conventional dipping apparatuses employing an appropriately heated vessel for

containing the molten metal bath and the alkali-metal halide flux. If a graphite pot is employed, those surfaces at the level of the flux may be protected by a liner of porcelain or other material resistant to lithium halides when lithium is present in the flux.

Especially suitable mixtures are mixtures of lithium chloride and potassium chloride melting between 350° and 400° C., to which the chlorides, bromides, fluorides or iodides of sodium, rubidium, calcium, barium, strontium or caesium may be added. Compositions containing potassium, lithium and sodium chlorides in approximately the proportions of the triple eutectic are highly satisfactory.

Sodium and potassium chlorides and bromides become more effective as the metal bath temperature is increased, and consequently may be used satisfactorily without lithium for the application of high-melting coating metals.

Mixtures of the chlorides of sodium, potassium, and barium, liquid at about 550° C. have been used satisfactorily for the application of copper alloy coatings. Since these fluxes do not attack graphite or silicon-carbide-bonded graphite, for instance, "Tercod," they have an advantage over lithium-chloride-containing fluxes in that vessels of such materials can be used to contain a flux-covered metal without the necessity of using a liner of porcelain or other especially flux-resistant material.

Mixtures of the chlorides of calcium, barium, and sodium, liquid below 600° C. have been used satisfactorily for the application of aluminum alloy coatings.

In addition to the advantages enumerated above, the alkali-metal halide fluxes have the ability to maintain the content of uranium in molten metal dipping baths at a low value. This advantage has been particularly noticeable in the application of bronze coatings such as copper-tin eutectic and speculum metal.

In the application of coatings from baths containing aluminum as the principal component, for example, aluminum and aluminum-silicon eutectic mixture, alkali-metal halide fluxes containing a fluoride render the application easier than fluxes of chlorides alone. Thus the addition of 5% to 15% of sodium fluoride to a triple eutectic alkali-metal chloride mixture or to a calcium, barium, sodium chloride mixture has proved especially beneficial.

The following examples, in which quantities are expressed as parts by weight, further illustrate the invention:

Example 1

A solid metallic uranium rod 1.1 inches in diameter and 4 inches in length was cleaned by dipping for 20 seconds in aqueous 50% HNO_3 solution containing 1% HCl and was then coated with zinc by dipping it through a molten flux comprising 30% lithium chloride, 50% potassium chloride and 20% sodium chloride into a molten zinc (Horsehead Special, 99.99+percent zinc) bath at a temperature of 532° C. The rod was held in the molten metal for one minute during which the temperature of the metal dropped to 522° C. The rod was removed from the bath, shaken briskly to remove excess metal, and promptly placed in the trough formed by a pair of smooth asbestos cement (Transite) rollers, each 5½ inches in diameter, and spaced ⅝ inch from each other and rotated at a speed of 130–140 R. P. M.

The coated metal rod was rotated in this manner until the zinc coating had solidified. It was then cooled to normal temperature by quenching in water. The resulting coating was smooth and uniform throughout the length of the rod and over both ends of the rod.

Example 2

A metal rod, the surface of which had been machined,

was pickled for three minutes in 50% nitric acid at about 70° C., rinsed in water and dried. It was then dipped into a molten metal bath protected by a molten alkali-metal halide flux in such a manner that the rod was completely contacted with the flux as it passed into the metal bath and as it was withdrawn from the metal bath. The metal bath, consisting of 94% zinc and 6% aluminum, was at a temperature of 490° C. The protective flux consisted of a mixture of 42 parts of lithium chloride, 53 parts of potassium chloride and 5 parts of sodium chloride. The period of contact of the uranium rod with the metal bath was four minutes.

Upon withdrawal from the bath, the rod was rotated on smooth asbestos cement rollers for two minutes to cause the coating to cool and solidify. It was then placed in an annealing oven maintained at a temperature of about 250° C. for three hours and was then further cooled in air to room temperature in about 40 minutes.

The coating was smooth, uniform and free from pinholes. The coating was tested by maintaining it in air heated to 200° C. It was found to be free of defects after 70 days of such exposure.

Example 3

A uranium rod was pickled for 2½ minutes at 60° C. in aqueous 50% nitric acid solution, rinsed, and wiped dry. It was then passed through a molten protective flux into a molten metal bath at 600° C. and maintained in the bath for 2½ minutes. The molten bath consisted of 85% zinc and 15% aluminm. The protective flux had the same composition as that of Example 2.

After the rod had remained in the molten metal for 2½ minutes, it was withdrawn through the flux, rolled for 2½ minutes on smooth asbestos cement rollers in air to cool and solidify the coating and then annealed at 250° C. for 2½ hours, after which it was cooled in air.

The coating was dull, smooth and free from defects. When tested by heating in air at 200° C., it was found to be unimpaired at the end of 70 days.

Example 4

A clean metallic uranium rod was dipped through a molten protective flux of the composition 56% potassium chloride and 44% sodium chloride into a molten metal bath comprising 67 parts of copper and 33 parts of tin maintained at a temperature of about 815° C. The rod was allowed to remain in the metal bath for about 1 minute and then was withdrawn through the protective flux, centrifuged for 10 seconds to remove surplus coating metal, and allowed to cool by exposure to air.

A uniform coating of bronze (speculum metal) on the uranium was thus obtained.

Example 5

A clean metallic uranium rod was dipped for 15 seconds into a molten alkali-metal halide flux comprising 42% sodium chloride, 6% potassium chloride, and 52% calcium chloride on a molten metal bath comprising 82 parts of tin and 18 parts of nickel at a temperature of about 950° C. and then into the molten metal for 60 seconds. The rod was withdrawn from the bath through the flux and cooled in air.

The rod was completely coated with the tin-nickel alloy.

Example 6

A metallic uranium rod, after a 10 minute cleaning in 50% HNO_3 at about 70° C. and a water rinse, was preheated for 5 minutes in a molten flux consisting of 58 parts of lithium chloride and 42 parts of potassium chloride and then passed directly into an underlying molten metal bath consisting of about 52½% tin, 46½% copper and 1% nickel, maintained at a temperature of 720° C. The uranium rod was maintained in this metal bath for 30 seconds, withdrawn through the molten flux and cooled in air.

The rod was completely and uniformly coated with the bronze coating alloy.

Example 7

A metallic uranium rod was cleaned in 50% HNO_3 at room temperature, rinsed with water and then dipped through a flux comprising 37% LiCl, 53% KCl, and 10% NaCl into a molten zinc bath (99.99+% Zn) at 433° C. The rod was coated completely with an adherent coating of zinc about 3 mils thick.

Example 8

A metallic uranium rod ⅜ inch in diameter and 2 inches in length was dipped in aqueous 50% HNO_3 solution at about 65° C. for 3 minutes. It was then dipped through a molten flux of the composition 37% LiCl, 53% KCl and 10% NaCl into a molten metal bath containing 94 parts of zinc (Prime Western Spelter) and 6 parts of aluminum at 485° C.

The rod was withdrawn from the coating bath and rolled in air on carbon rollers for 2 minutes to allow the coating to solidify. It was then dipped in cold water to cool the rod to normal temperature.

The rod was then placed in an oven through which air at 200° C. was circulated, to determine its resistance to corrosion. After 135 days of this treatment, the rod was still in perfect condition.

Example 9

A metallic uranium rod cleaned by immersing for five minutes in aqueous 50% HNO_3 at 65° C. was dipped through a molten flux of about 565° C. melting point, prepared by adding to 90 parts of flux of 53% KCl, 42% LiCl and 5% NaCl, 10 parts of NaF, and into a molten metal bath comprising 88% aluminum and 12% silicon at 620° C. After 3 minutes in the aluminum-silicon alloy bath the rod was withdrawn and rolled on cold, smooth steel rolls until the coating solidified. The rod was completely coated with a smooth, even coating of the aluminum alloy.

Example 10

A uranium rod was pickled for five minutes in 50% nitric acid solution at 60–70° C., rinsed and dried. It was then passed through a protective flux layer consisting of 48% barium chloride, 31% potassium chloride and 21% sodium chloride into a molten metal bath held at 705–715° C. and was maintained in the bath for 40 to 50 seconds. The molten metal bath was composed of 53 parts tin and 47 parts copper. After 40 to 50 seconds in the bath the rod was withdrawn and quenched in water. A complete coating of bronze was obtained.

Example 11

A uranium rod was pickled for five minutes in 50% nitric acid solution at 60–70° C., rinsed and dried. The rod was then passed through a flux layer consisting of 45% calcium chloride, 30% barium chloride, 20% sodium chloride and 5% sodium fluoride into a molten metal bath at 600° C. and maintained in the bath for 30 seconds. The molten metal bath consisted of 88 parts aluminum and 12 parts silicon. After 30 seconds the rod was removed from the molten metal bath and quenched in water. A complete coating of aluminum-silicon alloy was obtained.

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. In the application of a metal coating to uranium by dipping in a molten metal bath, the improvement which comprises passing the uranium article to be coated through a molten alkali-metal halide protective flux into

the molten metal bath, said flux consisting of lithium chloride.

2. In the application of a low-melting metal coating to uranium by dipping in a bath of the molten coating metal, the improvement which comprises passing the uranium article to be coated through a molten alkali-metal halide protective flux into the molten metal bath, said flux consisting of a mixture of lithium and potassium chlorides having a melting point between 350° and 400° C.

3. In the application of a metal coating to uranium by dipping in a molten metal bath, the improvement which comprises passing the uranium article to be coated through a molten alkali-metal halide protective flux into the molten metal bath, said flux consisting of potassium, lithium, and sodium chlorides in approximately the proportions of the triple eutectic.

4. In the application of a metal coating to uranium by dipping in a molten metal bath, the improvement which comprises passing the uranium article to be coated through a molten alkali-metal halide protective flux into the molten metal bath, said flux consisting of at least one alkali-metal chloride and up to 10% of alkali-metal fluoride.

5. In the application of a metal coating to uranium by dipping in a molten metal bath containing aluminum as its principal component, the improvement which comprises passing the uranium article to be coated through a molten alkali-metal halide protective flux into the molten metal bath, said flux consisting of at least one alkali-metal chloride and up to 10% of alkali-metal fluoride.

6. A process for coating uranium by immersion into a molten metal bath, comprising passing the uranium article to be coated through an alkali metal halide-containing flux selected from the group consisting of alkali metal chloride, a mixture of alkali metal chloride and alkali metal fluoride, and a mixture of alkali metal chloride and alkaline earth metal chloride.

7. In the application of a metal coating to uranium by dipping in a molten metal bath, the improvement which comprises passing the uranium article to be coated into said molten metal bath through a molten flux consisting of about 48% barium chloride, 31% potassium chloride, and 21% sodium chloride.

8. In the application of a metal coating to uranium by dipping in a molten metal bath, the improvement which comprises passing the uranium article to be coated into said molten metal bath through a molten flux consisting of alkali metal halide at least 90% of which is alkali metal chloride.

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