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NICKEL COATED URANIUM ARTICLE

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This invention relates to the application of protective coatings on metallic uranium. The products produced in practicing this invention are useful in a neutronic reactor of the type described in the copending application of Fermi et al., Serial Number 568,904, filed December 19, 1944, which became U. S. Patent Number 2,708,656 on May 17, 1955.

Metallic uranium is an easily oxidizable metal which is readily corroded by atmospheric oxygen and by aqueous solutions. In order to protect the metal from the injurious effects of such media, it is desirable to provide a coating of some material which is less easily acted upon.

Many common protective coating materials are unsuitable for coating uranium; lead forms a pyrophoric alloy with uranium and for this reason its use is objectionable; some metals, such as tin, permit diffusion of the uranium through coatings of these metals with consequent impairment of their protective value; other metals form very brittle alloys with the uranium, containing many cracks and crevices which reduce their effectiveness.

It is an object of the present invention to provide protective coatings for uranium which are not subject to the defects enumerated above. A further object is to provide a barrier coating for uranium over which it is possible to apply various protective coatings that normally would be unsuitable because of their behavior toward the base metal. A further object of the invention is to provide highly protective electrodeposited coatings on metallic uranium.

In accordance with the present invention metallic uranium is protectively coated with nickel, preferably but not necessarily applied to the uranium directly.

The metallic uranium preferably is prepared for the application of the nickel coating by an etchant treatment of the metal surface with an aqueous etching solution containing chloride ions, for example, a hydrochloric acid solution or a molten hydrate of ferric chloride. Particularly satisfactory preparatory treatments of this type involve anodic pickling of the metal in aqueous trichloracetic acid solution, or aqueous phosphoric acid solution containing about ½% of hydrochloric acid, to remove a ½ to one mil layer of the surface metal. Prior to the etchant treatment the metal may be cleaned by sand-blasing, pumic-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% HNO_3 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 surfaces.

The nickel coating may be applied by electroplating from a conventional acidic nickel electroplating bath, such as an aqueous nickel sulfate bath.

The nickel coatings of the invention may vary from

exceedingly thin coatings, of the order of 0.000015 inch, up to 0.001 inch or thicker. The thickness of the coating may be varied to suit the subsequent treatment of the metal. Thus the thinnest coatings have been found to be especially suitable as bases for chromium electro-deposits. Nickel electroplating baths have much higher throwing power than chromium electroplating baths and consequently are more effective for coating fissures such as cracks, pipes and other surface irregularities. Electroplated nickel coatings protect the uranium from the adverse effects of chromic acid so that more satisfactory chromium platings are obtainable from the standpoint of uniformity and completeness of protection. Since the nickel is required for only transitory protection of the uranium during the chromium plating operation, very thin coatings are suitable for accomplishing the purpose.

The nickel platings retard the diffusion of uranium into aluminum or aluminum-silicon brazing alloys and are therefore valuable in preventing the formation of the brittle uranium-aluminum alloys which normally are formed at the interface of the uranium and aluminum or aluminum-silicon when no barrier is provided. The nickel platings are accordingly of benefit in the application of such metals as protective coatings or as bonding means, for example, in the bonding of aluminum sheaths to the uranium. They serve a similar purpose when zinc or zinc-tin solder is used as the bonding agent. For use in this manner heavier nickel electroplatings are more desirable, such as platings between 0.0003 inch and 0.001 inch thick. In applying such coatings by hot-dipping, the nickel plated article should be immersed at a temperature and for a time just long enough to wet and uniformly coat the surface.

While very adherent nickel electrodeposits may be produced upon uranium when a suitable preparatory treatment is employed for etching the uranium, their adherence may be still further improved by subjecting them to an alloying treatment. Such a treatment involves heating the electroplated uranium for a short time at a temperature above 662° C. The heating may be effected by immersion of the electroplated article in a molten bath such as a bath of molten sodium chloride, potassium chloride, or lithium chloride, or a mixture thereof maintained at a temperature between 700° C. and 800° C. The alloying may also be effected by inductive heating or by radiant heating in a vacuum or in an inert gas. By appropriate control of the time and temperature of heating, the extent of alloying and depth of penetration of the nickel may be controlled to provide nickel alloy layers at the uranium-nickel interface varying all the way from exceedingly thin layers up to layers many times the thickness of the plating. Thus by appropriate heat treatment it is possible to provide straight nickel protective platings bonded to the uranium by nickel-uranium alloy layers of various thicknesses, or to provide very thick layers composed entirely of alloy. By the application of alternate platings of copper and nickel on top of the initial nickel platings and subsequent heat treatment, coatings may be prepared comprising a bonding layer of uranium-nickel alloy beneath a cupro-nickel alloy layer firmly bonded thereto.

The nickel electrodeposits of the invention may be used as bases for subsequent zinc, tin, or lead hot-dip coatings or electroplatings. Composite platings may be rendered highly impervious by a short heat treatment slightly above the melting point of the secondary plating to promote diffusion into the pores of the underlying nickel layer. Heat treatments below the melting point of the secondary plating also may be used to improve the coatings. Thus zinc platings on the nickel may be treated by immersion in Silicone #700 at 300° C. for 2 or 3 hours.

Example 1

An extruded uranium rod about ⅜ inch in diameter is first dipped for one minute in aqueous 50% HNO_3 solution at 25° C., and then rinsed with water. It is immediately dipped in aqueous 36% HCl solution until the surface is completely black (about 40 seconds). It is then removed from the HCl solution, rinsed with water and dipped for 5 seconds in 50% HNO_3 solution.

The rod, which now has a gray, uniformly etched appearance, is again rinsed briefly with water and then immediately electroplated by placing it in an aqueous electroplating bath, which contains per liter, 240 grams of $NiSO_4.7H_2O$, 45 grams of $NiCl_2.6H_2O$, and 30 grams of H_3BO_3, and is at a temperature of 40° C., and passing a current through the solution with the rod as cathode at an initial current density of 75 amperes per square foot for one minute and then at a current density of 20 amperes per square foot for 3 minutes.

A smooth, uniform, firmly adherent nickel plating is formed on the surface of the metal.

The nickel electroplating may be alloyed with the uranium rod by heating for a few minutes in an induction furnace to raise the surface temperature to 800° C. and form an integral uranium-nickel alloy coating on the rod.

Example 2

A machined uranium rod about 8 inches long and 1⅓ inches in diameter is prepared for electroplating by dipping in trichloroethene to remove grease, sand-blasting lightly, dipping in aqueous 35% HNO_3 by weight at 30° C. for 4 minutes, rinsing with cold water, etching by anodic treatment in aqueous 50% trichloracetic acid solution at between 50° 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% HNO_3 solution to clean the etched metal surface, then rinsing in cold water.

The cleaned etched metal rod is immediately electroplated in a nickel sulfate electroplating bath of the composition employed in Example 1 at a current density of 25 amperes per square foot at 40° C. until a nickel plating about 0.0005 inch thick is formed (about 25 minutes).

The nickel-plated rod is dipped directly in a sodium-modified alloy of 88% aluminum and 12% silicon at 640° C. for 50 seconds and then brazed by an alloy of the same composition to an aluminum sheath at about 600° C. A firm bond is formed between the rod and the sheath with no noticeable brittleness.

Example 3

An extruded uranium rod prepared for plating in the manner described in Example 2 is electroplated in a nickel sulfate electroplating bath of the same composition for about 5 minutes.

The lightly plated rod is then rinsed in water and electroplated in an aqueous electroplating bath containing 400 grams per liter of chromic acid, at 50° C. until a chromium plating 0.0001 inch thick has been built up (about 6 minutes). A concentric lead anode comprising an expanded metal cylinder having a diameter about 2 inches greater than the rod is used. A smooth uniform adherent coating is thus produced over the entire cylindrical surface of the rod with all of the fine crevices on the metal surface covered by a continuous coating of chromium on nickel.

Example 4

A uranium specimen nickel electroplated as in Example 1 is rinsed with water, electroplated in an aqueous copper

electroplating bath comprising 75 grams per liter of copper as pyrophospate at 60° C. for 20 minutes, then rinsed again, electroplated for 20 minutes in the nickel sulfate electroplating bath described in Example 1, rinsed again, electroplated for 10 minutes in the copper bath, rinsed, and again electroplated in the nickel bath for 10 minutes.

This coating provides good protection for the metallic uranium. However, by immersing it in a molten bath of potassium chloride lithium chloride eutectic at 750° C. for between 1 and 2 minutes, an alloyed coating of cupro-nickel over uranium-nickel alloy is obtained having excellent adherence and the corrosion resistance characteristic of cupro-nickel alloys. The copper improves the barrier effect of the coating to diffusion of uranium as described in greater detail and claimed in my U. S. patent application Serial No. 571,673 entitled "Copper Coatings and Method of Applying," filed January 6, 1945.

Example 5

A uranium rod is nickel electroplated and then electroplated with a single layer of copper as in the first two electroplating steps of Example 4. The rod is then rinsed and rolled in an evacuated tube at 750° C. for 2 hours. The nickel is thus alloyed with the uranium and copper to form a nickel-uranium alloy bond between the uranium and a cupro-nickel alloy protective coating. The copper in this case serves the additional function of preventing uranium-nickel alloy, which at the rolling temperature is relatively soft, from adhering to the tube.

The novel coating methods described in this application are being claimed in my copending divisional application, Serial Number 190,671, filed on October 17, 1950.

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. A metallic uranium article having an integral protective coating of corrosion-resistant cupro-nickel alloy bonded to the uranium by a uranium-nickel alloy bond.

2. A metallic uranium article having a protective coating of chromium over an intermediate nickel coating directly on the metallic uranium.

3. A metallic uranium article having an aluminum-silicon coating thereon separated from the uranium by an intermediate nickel barrier layer.

4. A metallic uranium article having a protective coating comprising a nickel layer directly on the uranium, a copper layer directly on the nickel layer and a second nickel layer directly on the copper layer.

5. A metallic uranium article having a protective coating comprising a nickel layer directly on the uranium followed by successive layers of copper, nickel, copper, and nickel.

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