United States Patent Office 2,796,392
Patented June 18, 1957

2,796,392

PROCESS AND ELECTROLYTE FOR THE ELECTRODEPOSITION OF ZIRCONIUM

Milton H. Lietzke, Oak Ridge, Tenn., assignor to the United States of America as represented by the United States Atomic Energy Commission

No Drawing. Application August 1, 1951, Serial No. 239,847

12 Claims. (Cl. 204—1.5)

My invention relates to the application of protective coatings to metallic uranium and especially to a method and plating bath for coating uranium with zirconium by electrodeposition.

Protective coatings for metallic uranium are necessary to prevent oxidation when in contact with air or other oxidizing atmosphere, and to prevent corrosion when in contact with water or other oxidizing or corrosive liquid. Adherent electrodeposited coatings of a corrosion-resistant metal are obviously desirable for these purposes. Thin electrodeposits of such metal on uranium have also been desired as initial flash coats for subsequent electroplating operations or as blocking layers for subsequent dip-coating or cladding operations.

It has long been recognized that the oxidation-resistant and corrosion-resistant properties of zirconium make this metal particularly desirable for these coating purposes. The low neutron absorption cross section of zirconium also makes this metal especially desirable as a protective coating if the coated uranium is to be employed in nuclear reactors or the like. Zirconium-coated uranium fuel elements, for example, are useful in a nuclear reactor of the type described in the copending application of Fermi et al., S. N. 568,904, now U. S. Patent 2,708,656, issued May 17, 1955. Up to the present time, however, no method or plating bath has been found which would produce a bright adherent metallic deposit of zirconium on uranium.

An object of the present invention, therefore, is to provide a method for the application of an adherent metallic zirconium coating on metallic uranium.

Another object of this invention is to provide a method and plating bath for the electrodeposition of zirconium on uranium.

A further object of my invention is to provide a method and bath for electrodepositing on uranium thin deposits of zirconium suitable for subsequent electroplating with other metals or from other plating baths, or for subsequent dip-coating or cladding with other protective coatings.

Additional objects and advantages of my invention will be apparent from the subsequent description.

The above objects, among others, are attained in the present invention by electrodepositing zirconium, from a molten bath comprising essentially a zirconium tetrahalide and an alkyl pyridinium halide, on a uranium cathode having a freshly cleaned surface.

The uranium object to be coated in accordance with my invention must first be cleaned by any method which will provide a completely clean, bright, metallic surface, but preferably by a method which will provide a freshly etched microcrystalline surface. A suitable method, including the preferred etching step, comprises degreasing, nitric acid pickling, surface etching, again pickling with nitric acid, and finally washing and drying.

The degreasing operation may be effected by conventional trichloroethylene degreasing or by degreasing anodically in an alkaline cleaning solution.

Following the degreasing, the uranium object may optionally be subjected to shot blasting, but this is generally unnecessary.

The nitric acid pickling is preferably effected by the use of 50% nitric acid (70% HNO_3, sp. gr. 1.40–1.42). Pickling times of 3–5 minutes at temperatures of 25–35° C. will generally be satisfactory for this purpose. Following the pickling, the uranium object should be thoroughly washed with water.

The surface etching operation may be effected by any conventional etching procedure which will provide a fresh microcrystalline surface. Examples of such procedures are anodically etching with trichloroacetic acid, and hydrochloric acid etching. The anodic etching is preferably effected in aqueous solution containing 50–100% by weight of trichloroacetic acid with the addition of 0.2–0.3% by volume of hydrochloric acid (37% HCl). A 20 minute anodic etching at a temperature of 50–60° C. will generally be satisfactory at a current density of 4–7 amps./dm.^{2}, and preferably at about 5.5 amps./dm.^{2}. Equally suitable etching may be accomplished by immersing the pickled and washed uranium object in concentrated hydrochloric acid (commercial muriatic acid; 18–20° Bé.; about 32% HCl) at a temperature of 25–35° C. for a period of 1–3 minutes, or until the uranium object is completely blackened.

Following either of the above etching procedures, or any other conventional etching procedure, the uranium object is washed with water and again pickled in nitric acid as previously described. Following this pickling operation, the object is again washed with water, preferably dried by means of absorbent tissue, and then immediately immersed in the plating bath.

The plating baths which may be employed in my present invention comprise essentially fused mixtures of a zirconium tetrahalide and an alkyl pyridinium halide. Examples of suitable alkyl pyridinium halides are ethyl pyridinium bromide, ethyl pyridinium chloride, ethylene dipyridinium dibromide, and ethylene dipyridinium dichloride. Compounds having higher alkyl groups may also be employed since alkyl pyridinium halides having even very long chain alkyl groups have melting points not far removed from the melting points of the ethyl and ethylene compounds. The compounds having long chain alkyl groups, however, tend to decompose at temperatures somewhat lower than the ethyl and ethylene compounds. It is preferred, therefore, to employ the lower alkyl derivatives, and especially ethyl pyridinium bromide and ethyl pyridinium chloride.

The alkyl pyridinium halide and the zirconium halide may contain the same or different halogen atoms. Generally speaking, the chlorides and bromides are preferred, employing both as chlorides, both as bromides, or using chloride-bromide combinations.

The concentration of the zirconium halide in the alkyl pyridinium halide should preferably be as high as possible without resulting in inhomogeneity of the bath at the plating temperature. In the case of ethyl pyridinium chloride and ethyl pyridinium bromide the concentration of zirconium tetrachloride or zirconium tetrabromide should generally be from about 30 mol percent to about 40 mol percent depending upon the plating temperature, and preferably about 37 mol percent for a plating temperature of about 160–170° C. The corresponding concentration of ethyl pyridinium chloride or ethyl pyridinium bromide should be about 60–70 mol percent, and preferably about 63 mol percent for a plating temperature of about 160–170° C.

The plating temperature may vary depending upon the specific composition of the plating bath, but can generally be any temperature above the fusion point and below the decomposition temperature of the alkyl pyridinium halide employed. Temperatures in the range

100–200° C. are generally preferable, with a temperature of about 160–170° C. being preferred for ethyl pyridinium chloride or bromide and zirconium tetrachloride or tetrabromide.

The container for the plating bath may be formed of glass, porcelain, enamelled metal, or other inert material, or may be formed of zirconium in which case it may serve as the anode for the plating operation. If the container does not serve as the anode, separate zirconium anodes may be used, or platinum or other inert anodes may be employed for short plating operations or for plating with continuous or intermittent replenishment of the zirconium content of the bath.

Conforming anodes may be employed, especially if uranium objects of highly irregular shapes are to be plated. Generally speaking, however, it is unnecessary to use conforming anodes, or even to use multiple anodes, since the "throwing power" of my plating baths has been found to be especially good.

The zirconium anodes and the zirconium halide content of the plating bath are preferably prepared from purified zirconium such as the grades known in the art as "crystal bar zirconium" or "iodide zirconium." If the coated uranium is to be employed in nuclear reactors, or in other applications where low neutron absorption is desired, the zirconium should additionally be especially purified by any of the known methods for the removal of its normal hafnium impurity.

The plating operation may be effected in accordance with conventional procedures, using insulated plating racks with point contact-supports for the objects to be plated. The cathode current density employed should be in the range from about 1 to about 4 amps./dm.^{2}, preferably about 2 amps./dm.^{2}, and the anode sizes and spacings from the uranium cathodes should be chosen to minimize the voltage required to secure such cathode current density.

My invention will now be further illustrated by the following specific examples.

Example I

A strip of uranium metal was cleaned in accordance with the procedures previously described, by degreasing with trichloroethylene, pickling in 50% nitric acid for 3–4 minutes, washing with cold water, etching with concentrated hydrochloric acid until completely black, washing again with cold water, pickling in 50% nitric acid until the uranium surface appeared bright, washing again with cold water, and drying with absorbent tissue. The cleaned uranium strip was then immediately immersed in a plating bath consisting of 37 mol percent of anhydrous zirconium tetrachloride dissolved in 63 mol percent of ethylene pyridinium bromide. The plating was effected at a temperature 160–170° C. for a period of 1 hr., using a platinium anode and employing a cathode current density of 1.6 amps./dm.^{2}. The resulting coating was found to be bright and metallic in nature, strongly adherent, and to have a thickness of 1.2×10^{-5} cm.

The following example illustrates the effect of cathode current density on the type of deposit obtained:

Example II

Strips of metallic uranium were cleaned and plated as in Example I, utilizing different cathode current densities as shown in the following table, which also shows the nature of the deposit obtained.

Cathode Current Density	Nature of Deposit
0.9 amp./dm.^{2}	Bright, silvery.
1.6 amps./dm.^{2}	Do.
3.5 amps./dm.^{2}	Do.
5.2 amps./dm.^{2}	Dark gray.

It is to be understood of course, that the above examples are illustrative only, and are not to be construed as limiting the scope of my invention. Other plating baths and plating conditions within the purview of the preceding description may be substituted for those employed in the examples, and the scope of my invention should be understood to be limited only as indicated in the appended claims.

I claim:

1. A process for coating uranium with zirconium which comprises electrodepositing zirconium, from a molten bath consisting essentially of about 30 mol percent to about 40 mol percent of a zirconium tetrahalide and about 60 mol percent to about 70 mol percent of an alkyl pyridinium halide, onto a uranium cathode having a freshly cleaned surface.

2. The process of claim 1 in which the zirconium tetrahalide is zirconium tetrachloride.

3. The process of claim 1 in which the alkyl pyridinium halide is ethyl pyridinium bromide.

4. The process of claim 1 in which the zirconium tetrahalide is zirconium tetrachloride and the alkyl pyridinium halide is ethyl pyridinium bromide.

5. A process for coating uranium with zirconium which comprises electrodepositing zirconium, from a molten bath consisting essentially of about 30 mol percent to about 40 mol percent of a zirconium tetrahalide and about 60 mol percent to about 70 mol percent and an alkyl pyridinium halide maintained at a temperature within the range 100–200° C., onto a uranium cathode having a freshly cleaned surface, at a cathode current density within the range 1–4 amps./dm.^{2}.

6. The process of claim 5 in which the zirconium tetrahalide is zirconium tetrachloride.

7. The process of claim 5 in which the alkyl pyridinium halide is ethyl pyridinium bromide.

8. The process of claim 5 in which the zirconium tetrahalide is zirconium tetrachloride, the alkyl pyridinium halide is ethyl pyridinium bromide, the temperature is 160–170° C., and the cathode current density is about 2 amps./dm.^{2}.

9. A nonaqueous electrolyte for use in the deposition of zirconium as a bright, adherent deposit, consisting essentially of a fused mixture of 30–40 mol percent of a zirconium tetrahalide and 60–70 mol percent of an ethyl pyridinium halide.

10. The composition of claim 9 in which the zirconium tetrahalide is zirconium tetrachloride.

11. The composition of claim 9 in which the ethyl pyridinium halide is ethyl pyridinium bromide.

12. The composition of claim 9 in which the zirconium tetrahalide is zirconium tetrachloride, the ethyl pyridinium halide is ethyl pyridinium bromide, the concentration of zirconium tetrachloride is about 37 mol percent, and the concentration of ethyl pyridinium bromide is about 63 mol percent.

References Cited in the file of this patent

UNITED STATES PATENTS

2,446,331	Hurley	Aug. 3, 1948
2,510,128	Miner et al.	June 6, 1950

OTHER REFERENCES

Chipman: "Metallurgy in the Development of Atomic Power," U. S. A. E. C. document No. MDDC–539, dated October 1946, declassified November 25, 1946, entire publication of 20 pages, pages 15 and 16 relied upon.