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URANIUM SURFACE PREPARATION FOR ELECTROLESS NICKEL PLATING

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ABSTRACT OF THE DISCLOSURE

The quality of nickel plating applied to uranium bodies by the electroless plating process is substantially improved if, after degreasing, pickling and etching, the uranium bodies are treated with a saturated solution of palladium chloride or a hot solution of tetrasodium pyrophosphate and rinsed before immersion in the electroless nickel plating solution.

CONTRACTUAL ORIGIN OF THE INVENTION

The invention described herein was made in the course of, or under, a contract with the United States Atomic Energy Commission.

BACKGROUND OF THE INVENTION

This invention relates to a process for plating nickel on uranium metal. More specifically, this invention relates to an improvement in a process for plating nickel on the surface of a uranium body by the electroless nickel plating process.

The nature of uranium metal is such that before it can be used in nuclear reactors it must be either alloyed or protected by cladding with another metal such as aluminum. It is important that these fuel elements exhibit certain characteristics, such as good heat transfer, dimensional and mechanical stability, resistance to corrosion and mechanical properties to withstand operating stresses. The cladding of uranium with aluminum results in the formation of solid state diffusion bonds, which are uranium and aluminum compounds having varying compositions, at the interface between the two metals. Generally, the uranium and aluminum compounds so formed do not have these desired properties. However, by plating a thin layer of nickel on the uranium prior to cladding the uranium with aluminum, the formation of these undesirable uranium-aluminum compounds is prevented and a diffusion bond is formed having the desirable characteristics.

The usual method of coating the nickel on the uranium is by means of electroplating. However, in electroplating the current density on the surface of the piece being plated is much greater in corners than on flat areas, leading to a plating which is thick on the corners and thinner in the flat areas. In addition, electroplating requires bulky electrical equipment, such as transformers, rectifiers and terminal boards, and also special plating racks which are necessary to maintain good electrical contact as well as to provide physical support for the article being plated.

Another method by which nickel can be plated on the uranium is by chemical deposition. In chemical deposition the nickel deposits are very uniform in thickness, regardless of the geometry of the article being plated. In addition, the equipment necessary for such plating need consist only of racks to provide physical support for the article to be plated and tanks for holding the plating solution. Chemical deposition of nickel is performed in hot aqueous solutions which contain nickel ions, a reducing

agent such as sodium hypophosphite, and various additives to optimize the chemical reactions which take place in the bath. Either acidic or alkaline baths may be used. However, chemical deposition of nickel on uranium often results in a plating having poor adhesion. After immersion of the uranium in the plating bath, an excessively long period of time is occasionally required before the start of plating deposition. This time interval, hereinafter called initiation time, often ranges from 10 minutes to 30 minutes or more. A long initiation time causes the uranium to turn brown, which indicates an oxidation of the surface. This oxidation prevents good adhesion of the nickel plating to the uranium metal and results in a plate which is easily removed when probed with a sharp tool.

Before nickel plating by chemical deposition can be performed on the uranium, the metal must be pretreated so that the initiation time will be short and the plating will adhere properly. The usual pretreatment consists of degreasing the uranium in trichloroethylene or in a hot caustic solution and pickling the metal in concentrated nitric acid until the surface is deoxidized. The metal is then electrolytically etched and pickled in a solution of nitric acid and rinsed in water several times prior to immersion in the electroless nickel plating bath.

SUMMARY OF THE INVENTION

We have found that, by proper pretreatment of the uranium bodies immediately prior to immersion in the plating bath, we are able to reduce substantially the initiation time of the plating of nickel on the uranium surface and are thus able to substantially improve the adhesion of the nickel plate to the uranium.

In the process of this invention, the uranium body is degreased, pickled, etched and pickled and rinsed several more times before it is dipped in a solution of palladium chloride, dipped in a solution of sodium hypophosphite, rinsed and dipped again in the sodium hypophosphite before it is immersed in the electroless nickel plating bath. The uranium body may also, after the pickling and rinsing steps, be dipped into a hot solution of tetrasodium pyrophosphate before immersion in the nickel plating bath. By the method of this pretreatment, the initiation time of plating of nickel on uranium can be reduced to as little as about 15 seconds and the adhesion of the nickel plate to the uranium metal improved substantially over that attained by the prior art methods.

It is therefore one object of this invention to provide an improved method for the plating of nickel on uranium.

It is another object of this invention to provide a method for decreasing the initiation time of plating nickel on uranium.

Finally, it is an object of this invention to provide a method of plating nickel on uranium which results in better adhesion of the nickel.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

These and other objects of this invention may be attained by degreasing the uranium body to be nickel plated in trichloroethylene or in a caustic such as 5% NaOH at 80 to 90° C., pickling the body in 8 to 12 M HNO_3 at 70 to 90° C. for 1 to 5 minutes until deoxidized, rinsing in water, etching the body by passing 50 to 70 amps/sq. ft. of current through it for 5 to 6 minutes while in a solution of 5.2 to 6.0 M H_3PO_4 and 0.25 to 0.3 M HCl, rinsing in water, pickling in 8 to 9 M HNO_3 at 40 to 45° C. for 2 to 3 minutes, rinsing in water, pickling in 8 to 9 M HNO_3 at 15 to 25° C. for 2 to 3 minutes, rinsing in water and then further treating the uranium body by dipping it for 30 seconds in a 0.4 M tetrasodium pyrophosphate solution at 70° C. or by dipping the body for 15 seconds in a saturated solution of palladium chloride,

followed by a 30-second dip in 0.225 M sodium hypophosphite solution, a rinse and another dip in the hypophosphite solution immediately prior to immersion of the uranium body in the electroless nickel plating bath.

It is important that the bodies to be plated are thoroughly rinsed to prevent any carry-over of palladium chloride to the nickel plating solution, since the smallest amount of palladium chloride or palladium will cause a rapid disintegration of the plating solution.

A plating bath with which excellent results have been attained has the following composition:

$Ni(C_2H_3O_2)_2 \cdot 4H_2O$	M	0.121
$NaH_2PO_2 \cdot H_2O$	M	0.600
$Na_3C_6H_5O_7 \cdot 5½H_2O$	M	0.287
$HC_2H_3O_2$	M	0.65
Add NH_4OH to give pH 9.0.		
Sodium lauryl sulfate	gm./l.	0.1

The initiation of plating of uranium bodies treated with palladium chloride in the above nickel plating bath at 70° C. was within 15 seconds and the uranium does not change color before plating commences.

When plating uranium bodies which have been treated with pyrophosphate, initiation is increased to about 2 minutes and the bodies turn to a yellow-brown color before plating commences; however, adhesion of the nickel plate to the uranium substrate was found to be as good as that attained by the use of the palladium chloride dip.

Samples of uranium metal plated with nickel which have been prepared by the above method have been tested by boiling in water for 16 hours after being plated. No spalling can be induced on the samples by probing with a sharp tool before or after fracturing the samples. When sufficient force is exerted, the nickel can be pried off, but it leaves a clean uranium surface, indicating that the uranium substrate is broken, indicating a good metal-to-metal bond has been established.

The following examples are given as illustrative of the process of this invention and are not to be taken as limiting the scope or extent of the invention.

Example I

Four washer-shaped uranium bodies labeled BP, BQ, BR and BT were nickel plated by the following method: degreased in a 5% solution of NaOH at 80° C. for 2 minutes; pickled in 10 M HNO_3 for 3 minutes; rinsed in tap water; etched in a solution of 5.5 M. H_3PO_4 and 0.25 M HCl by passing 12 amps through the bodies for 5 minutes and 25 amps for 20 minutes; rinsed in tap water; pickled in 8 M HNO_3 at 40° C. for 1 minute; rinsed in tap water; pickled in 8 M HNO_3 at 20° C. for 1 minute; alkaline rinse (a tap water rinse is now considered to be sufficient); dipped in a saturated solution of $PdCl_2$ for 15 seconds; dipped in 0.225 M sodium hypophosphite for 30 seconds; and rinsed in tap water and again dipped in 0.225 M NaH_2PO_4 for 30 seconds.

The treated bodies were then immersed in a nickel plating solution at a temperature of 70° C. which had the following composition:

$Ni(C_2H_3O_2)_2 \cdot 4H_2O$	M	0.121
$NaH_2PO_2 \cdot H_2O$	M	0.600
$Na_3C_6H_5O_7 \cdot 5½H_2O$	M	0.287
$HC_2H_3O_2$	M	0.65
Add NH_4OH to give pH 9.0.		
Sodium lauryl sulfate	gm./l.	0.1

Initiation of plating commenced at about 15 seconds and the bodies remained in the plating solution for 2 hours and 25 minutes. When removed, the surfaces of the samples were very smooth with little or no lustre.

Sample BP was boiled in water for 16 hours with no sign of plating failure.

Samples BP and BR were also heated in a muffle furnace at 600° C. for 30 minutes in an air atmosphere with no sign of plating failure at the end of that period.

Example II

Three unmarked samples were treated as described in Example I, except that after the alkaline rinse the samples were dipped in 0.40 M tetrasodium pyrophosphate rinse for 30 seconds, dried for 30 seconds and then dipped again into the 0.4 M tetrasodium pyrophosphate solution at 70° C. for 30 seconds before being immersed in the nickel plating bath previously described at 70° C.

The samples turned brown almost immediately upon entering the bath and plating did not start to appear upon the samples for 2 minutes. A full covering was not attained on the samples for 4 minutes after entry into the bath. The samples remained in the plating bath for 2 hours and 15 minutes, after which they were removed for inspection. The samples were dull gray in color with streaks that had some lustre and smoothness.

The plating was tested by boiling the samples in water for 16½ hours. The only noticeable effect was discoloration of the plate, which varied between the samples. There was no sign of water penetration. One sample which was broken showed no sign of spalling and quite excellent plate adhesion to the uranium substrate. The samples were then tested by placing them into a muffle furnace and heating them in air to 600° C. for 30 minutes. At the end of this period, one sample had several small blisters about the inside hole which were throught to be due to stress points. The other sample had a large number of small bubbles on the sides which may have been caused by a poor sample.

It can be seen from the above examples that quite good nickel platings can be attained on uranium substrates by the method of this invention.

It will be understood that the invention is not to be limited to the details given herein but that it may be modified within the scope of the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of pretreating uranium bodies for improved electroless nickel plating comprising:
degreasing said bodies;
pickling said bodies in 8–12 M nitric acid;
rinsing said bodies in water;
electrolytically etching said bodies in solution containing 5.2 to 6.04 M H_3PO_4 and 0.25 to 0.3 M HCl;
rinsing said bodies in water;
pickling said bodies in hot 8–9 M nitric acid;
rinsing said bodies in water;
pickling said bodies in cold 8–9 M nitric acid;
rinsing said bodies in water; and
contacting said bodies with a solution selected from the group consisting of palladium chloride and tetrasodium pyrophosphate, wherein said bodies are pretreated for plating and further treating said bodies contacted with palladium chloride by contacting said bodies with sodium hypophosphite, rinsing said bodies in water, and contacting said bodies with sodium hypophosphite to remove any palladium chloride continued thereon.

2. The method of claim **1** wherein said bodies are degreased in trichloroethylene, pickled in 8 to 12 M nitric acid at 70 to 90° C., etched by passing 50 to 70 amp/sq. ft. of current through said bodies for 5 to 6 minutes, said hot nitric acid solution is at 40 to 45° C., said cold nitric acid solution is at 15 to 25° C., said palladium chloride solution is a saturated solution and said bodies remain therein for 15 seconds, said solution of sodium hypophosphite is an aqueous solution containing 0.225 M sodium hypophosphite and said bodies remain therein for 30 seconds.

3. The method of claim **1** wherein said bodies are degreased in trichloroethylene, pickled in 8–12 M nitric acid at 70 to 90° C., etched by passing 50 to 70 amp/sq. ft. of current through said bodies for 5 to 6 minutes, said hot nitric acid solution is at 40 to 45° C., said cold nitric

acid solution is at 15 to 25° C., and wherein the tetrasodium pyrophosphate solution is at 70° C., contains 0.4 M tetrasodium pyrophosphate and the body is immersed therein 30 seconds.

References Cited

UNITED STATES PATENTS

3,341,350	9/1967	Anderson et al.	117—50
3,275,535	9/1966	Lundquest et al.	204—1.5
3,574,664	4/1971	Feldstein	117—47 R
2,854,738	10/1958	Gray	204—1.5 X
3,573,120	3/1971	Waldrop et al.	204—32 RX

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