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[54] **METHOD FOR ELECTRODEPOSITION OF NICKEL-CHROMIUM ALLOYS AND COATING OF URANIUM**

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[58] **Field of Search** ..... 204/1.5, 43 R, 43 T

[56] **References Cited**

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[57] **ABSTRACT**

High-quality electrodeposits of nickel-chromium binary alloys in which the percentage of chromium is controlled can be obtained by the addition of a complexing agent such as ethylenediaminetetraacetic disodium salt to the plating solution. The nickel-chromium alloys were found to provide an excellent hydrogen barrier for the protection of uranium fuel elements.

7 Claims, No Drawings

METHOD FOR ELECTRODEPOSITION OF NICKEL-CHROMIUM ALLOYS AND COATING OF URANIUM

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 method for the electrodeposition of nickel-chromium binary alloys. More specifically, this invention relates to a method for the electro-deposition of a nickel-chromium binary alloy on a nuclear reactor fuel element.

The nature of the actinide metals such as uranium is such that, before they can be used in nuclear reactors, they must be either alloyed or protected by cladding with another metal such as aluminum or stainless steel. 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 stress. 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. One method to prevent this is to plate a thin layer of nickel on the uranium prior to cladding the uranium with aluminum. The nickel plate acts as a diffusion and secondary corrosion barrier, prevents the formation of undesirable aluminum-uranium compounds, and the uranium-nickel-aluminum bond found in the cladding operation provides good heat transfer. One problem associated with the use of nickel plating is that it is permeable to hydrogen, thus it is not dependable as a secondary corrosion barrier for the uranium fuel element. When the aluminum cladding fails and only the nickel coating is left to protect the fuel element from failure, a galvanic reaction can occur which makes the nickel the cathode and the aluminum cladding and the reactor process tubes the anode. In this system, the area of the anode can be many orders of magnitude higher than the area of the cathode. Consequently, the current density of the nickel cathode can be very high and substantial quantities of hydrogen can be liberated at the exposed nickel surface. The hydrogen migrates through the nickel to the uranium and forms uranium hydride which, in turn, can rupture the nickel coating.

One method which has been proposed to control the permeability of the nickel plate to hydrogen was to co-deposit chromium with the nickel to form a binary nickel-chromium alloy on the surface of the fuel element before cladding the element with aluminum. A comprehensive discussion of nickel-chromium binary alloys may be found in an article by C. U. Chisholm, "The Electrodeposition of Nickel-Chromium Alloys," Plating, Vol. 55, pp. 735–739 (1968). The article indicates that, while there are many solutions and processes available for the electrodeposition of nickel-chromium binary alloys, apparently none of the processes is presently in use commercially.

SUMMARY OF THE INVENTION

We have developed a process in which we add a complexant such as ethylenediaminetetraacetic disodium salt to the plating solution for the electrodeposition of nickel-chromium binary alloys which provides a good quality plating in which the chromium content of the binary alloy can be controlled and which is impermeable to the hydrogen ion. In the process of this invention for the electrodeposition of a nickel-chromium binary alloy on a substrate, the substrate, which is the cathode, is immersed in an aqueous plating bath consisting eseentially of about 0.08 to 0.19 molar disodium salt of ethylenediaminetetraacetic acid; about 0.5 to 1.0 molar of chromium potassium sulfate; about 0.25 to 0.5 molar nickel sulfate; and about 0.3 to 0.5 molar boric acid; at a pH of about 1.5 to 2.5 and a temperature of about 45° to 55°C.; and a current of from 125 to 330 milliamps/cm^2 is passed through the solution to the cathodic substrate, thereby depositing a binary nickel-chrominum alloy on the substrate.

It is therefore one object of the invention to provide a process for depositing a coating on uranium fuel elements which is impermeable to hydrogen.

It is a further object of this invention to provide a process for the electrodeposition of a chromium-nickel binary alloy on a substrate.

It is another object of the invention to provide a process for the electrodeposition of a chromium-nickel alloy on a uranium substrate.

Finally, it is the object of the invention to provide a process for the electrodeposition of a chromium-nickel alloy on a uranium substrate.

DESCRIPTION OF THE PREFERRED EMBODIMENT

These and other objects of the invention for the electro-deposition of a nickel-chromium binary alloy on a substrate can be met by immersing the cathodic substrate in an aqueous plating solution containing about 0.13 M ethylenediaminetetraacetic acid disodium salt, about 0.76 M chromium potassium sulfate, and about 0.40 M boric acid having a pH of about 2.3 and a temperature of about 50°C., and agitating the plating solution while passing a current of about 230 mA/cm^2 through the solution to the cathodic substrate whereby a nickel-chromium alloy is deposited on the substrate.

The ethylenediaminetetraacetic acid disodium salt (EDTA) which may be present in a concentration of from about 0.08 to about 0.19 M, acts as a complexant and affects the plating solution by shifting the depositing potential of the metal ions in the solution. It is expected that complexing agents such as other EDTA-type compounds will give satisfactory results in the plating solution, although EDTA was the only compound which was tried.

The concentration of the chromium potassium sulfate may vary from about 0.5 to 1.0 M while that of the nickel sulfate may range from about 0.25 to 0.5 M and the boric acid from about 0.3 to 0.5 M.

Best results are obtained when the temperature is between about 45° and 55°C. and the pH is from 1.5 to 2.5. Agitation of the solution is necessary to insure an even electroplating deposition. A convenient method for agitating the solution was to rotate the cathodic substrate at from about 90- 150 rpm which resulted in a high-quality evenly applied alloy plate.

The process of this invention is useful to provide a nickel-chromium plating on any substrate which can normally be plated by electrodeposition such as, for example, copper, brass or nickel. However, certain substrates which are difficult to plate such as, for example, uranium must first be provided with a layer of a platable metal such as, for example, nickel or copper before attempting to deposit the nickel-chromium alloy. The platable metal may be deposited by any method known to those skilled in the art, such as, for example, by electrodeposition or by electroless plating.

The amount of time required to deposit a coating of nickel-chromium binary alloy will depend upon the composition of the solution, the current density and the thickness of coating desired. It was found, for example, that about 15 minutes was sufficient to provide a 0.4 mil layer of alloy containing about 9% chromium on a brass cylinder cathode.

The percentage of chromium which is being codeposited with the nickel can be controlled by varying the current density and the pH of the plating solution. Example I below is given to illustrate the process of the invention and to demonstrate how the chromium content of the alloy can be controlled.

EXAMPLE I

% chromium in binary alloy	0.5%	9.0%	56%	88%
Disodium salt of ethylene diaminetetraacetic acid (EDTA)	0.15M	0.15	0.15	0.22
$CrK(SO_4)_2 \cdot 12H_2O$	0.76	0.76	0.76	0.76
$NiSO_4 \cdot 6H_2O$	0.40	0.40	0.40	0.40
H_3BO_3	0.40	0.40	0.40	04.0
Temperature	50°C	50°C	50°C	50°C
Current density	230 mA/cm²	230	330	330
pH	1.5	2.4	2.5	2.1
Cathode agitation	120 rpm	120	120	120

The test sample cathodes were ¼ inch diameter, 2 inches long solid brass cylinders which fit upon a stirring rod attached to a small electric motor.

The plating obtained by the process in all examples was semi-bright, of good flaw-free quality with good adherent properties. The plate was tested for adherence by immersion in hot nitric acid.

EXAMPLE II

To demonstrate that the alloy electroplates were impermeable to hydrogen, a two-compartment cell separated by a bipolar electroplated membrane and filled with appropriate solution was set up. The membrane was prepared by depositing a 5 mil thick membrane of nickel on a flat piece of aluminum about 3 by 3 inches and which was then removed from the aluminum. A second membrane of nickel-chromium alloy containing about 10 percent chromium and about 0.4 mil in thickness was also prepared by the above process. Hydrogen gas was cathodically discharged at one side of the compartment consisting of an anode and the cathodic side of the bipolar membrane. If hydrogen diffuses through the membrane, it is oxidized at the anode side of the bipolar membrane by applying a potential across the other cell compartment consisting of the anodic side of the membrane and a cathode. The current conducted in this electrolysis is a direct measure of the rate of hydrogen diffusion through the electroplated membrane. When the pure nickel membrane was tested, the hydrogen oxidation current became very high within a period of less than 1 minute, showing that substantial quantities of hydrogen were migrating through the membrane. By substituting the 10% chromium-nickel alloy film for the nickel membrane, the rate of hydrogen diffusion was lowered to a very low level so that a hydrogen level only sightly above background was noted through the foil in a period of over 3 hours.

As can be seen from the previous discussion and examples, the process of this invention produces a high-quality chromium-nickel binary alloy in which the chromium content is controllable and also produces a binary alloy which is impervious to hydrogen ion migration.

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

1. A process for the electrodeposition of a nickel-chromium binary alloy on a cathodic substrate comprising:

immersing the substrate in an aqueous plating bath consisting essentially of about 0.08 to 0.19 M disodium salt of ethylenediaminetetraacetic acid, about 0.5 to 1.0 M chromium potassium sulfate, about 0.25 to 0.5 M nickel sulfate and about 0.3 to 0.5 M boric acid;

adjusting the pH of the solution to about 1.5 to 2.5 and the temperature to between about 45° and 55°C.; and

agitating the solution while passing a current of from about 125 to about 330 mA/cm² through the solution to the cathodic substrate, thereby depositing a binary nickel-chromium alloy on the substrate.

2. The process of claim **1** wherein the substrate is selected from the group consisting of nickel, brass and copper.

3. The process of claim **2** wherein the plating solution contains about 0.15 M disodium salt of ethylenediaminetetraacetic acid, about 0.76 M chromium potassium sulfate, about 0.40 M nickel sulfate, about 0.40 M boric acid, the temperature of the solution is 50°C., current density is about 230 mA/cm² and the pH is about 1.5, whereby the nickel-chromium alloy is about 0.5 percent chromium.

4. The process of claim **3** wherein the pH is 2.4, whereby the nickel-chromium alloy is about 9.0 percent chromium.

5. The process of claim **3** wherein the current density is about 330 mA/cm² and the pH is about 2.5, whereby the nickel-chromium alloy is about 56 percent chromium.

6. The process of claim **5** wherein the pH is about 2.1 and the concentration of the disodium salt of ethylenediaminetetraacetic is about 0.22 M, whereby the nickel-chromium alloy is about 88% chromium.

7. In the process for protecting uranium metal from corrosion by applying a layer of nickel to the outer surface of the metal, the improvement comprising immersing the nickel-plated uranium metal in an aqueous plating bath consisting essentially of about 0.08 to 0.19 M disodium salt of ethylenediaminetetraacetic acid, about 0.5 to 1.0 M chromium potassium sulfate, about 0.25 to 0.5 M nickel sulfate and about 0.3 to 0.5 M boric acid;

adjusting the pH of the solution to about 1.5 to 2.5 and the temperature to between about 45° and 55°C.; and

agitating the solution while passing a current of from about 125 to about 330 mA/cm² through the plating solution to the nickel-plated uranium metal, thereby depositing a layer of a binary nickel-chromium alloy on the nickel-plated uranium metal.

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