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1

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METHOD OF APPLYING ADHERENT ELECTROPLATES TO ZIRCONIUM SURFACES

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The present invention relates to a method for cleaning zirconium surfaces and applying adherent electrodeposits on zirconium surfaces.

It is well known that zirconium metal readily forms a protective oxide film that resists removal by conventional methods. None of the conventional methods for cleaning other surfaces prior to electroplating, such as the conventional processes for carbon steel, stainless steel, chromium, etc., can be successfully applied to the preparation of zirconium for electroplating. Electroplates applied to zirconium after the zirconium is cleaned by conventional means for preparing the usual metals of commerce result in electroplates that can be easily peeled from the zirconium surface.

The poorly adherent quality of electrodeposits on zirconium prepared by conventional methods becomes especially apparent upon heat treatment of the composite article. The heat treatment of poorly adherent electroplated articles will result in a separation of the electroplate from the basis metal. While this may be due to several factors, one factor which it is believed contributes in a great part to this is the formation of molecular hydrogen at the interface of the basis metal and electroplate and its expansion during heat treatment which results in localized blistering or over-all separation of the electroplate from the basis metal.

It is an object of the present invention to provide a method for cleaning zirconium and zirconium alloy surfaces.

It is another object of the present invention to provide a method for plating zirconium surfaces with highly adherent metallic electroplates.

It is a further object of the present invention to provide a method of etching zirconium or zirconium alloy surfaces for electroplating with another metal so that the as-plated adhesion of the electrodeposited metal to the zirconium is maintained during heat treatment to alloy the interfacial layers of the two metals.

Other objects will be apparent from the description of the present invention which follows.

In accordance with the present invention it has been found that zirconium and zirconium alloys can be chemically cleaned by etching the surface of said metal with an aqueous solution of ammonium fluoride and hydrofluoric acid. The etching of the zirconium metal surface or zirconium alloy surface in accordance with the method described in the present application will provide a surface upon which can be electroplated an adherent coating of other metals. The etching of zirconium or zirconium alloy surfaces is an essential step in the method of applying adherent electroplates to zirconium or zirconium alloy surfaces in accordance with the process of the present invention. The complete process for applying adherent electroplates to said zirconium surfaces comprises broadly three prescribed operations: etching the surface of the basis metal with an ammonium fluoride-hydrofluoric acid bath, electroplating the plating metal on the surface of said zirconium metal and heat-treating the composite article.

2

The basis metal contemplated by the present invention includes substantially pure zirconium and zirconium alloys containing predominantly zirconium. The surface of the zirconium or zirconium alloy should be free of rolling scale or heat-treating scale, since such scales are less soluble in the etching solution than is the underlying metal. The method is applicable to zirconium surfaces which have been finished by substantially all conventional methods, such as sand or vapor blasting, shaping, surface grinding, or chemical polishing.

The etching solution of the present invention comprises an aqueous solution by hydrofluoric acid-ammonium fluoride. Although zirconium and zirconium alloys are readily soluble in aqueous solutions of hydrofluoric acid, electroplated metals onto zirconium surfaces etched in solutions containing hydrofluoric acid alone are poorly adherent and can be easily peeled. The presence of ammonium fluoride in the etchant is therefore essential to the success of this step. Furthermore, the molar ratio of ammonium fluoride to hydrofluoric acid in the etchant is important, since if the ratio is too large or too small poorly adherent electroplates will be obtained. It has been found in accordance with this invention that efficient chemical cleaning is obtained if the molar ratio of ammonium fluoride to hydrofluoric acid lies between 1.2 and 3.0.

While we do not wish to be bound by any theory advanced, it is believed that an etchant lying within these particular ratios furnishes the maximum inhibition against the adsorption by the zirconium surfaces of the hydrogen produced during the etching operation. It is presumably the adsorbed hydrogen that causes detrimental embrittlement of the interface during the subsequent electroplating of a metal upon the zirconium. It has further been found in accordance with the present invention that the addition of 0.25 to 1.0% of an aliphatic amine of the formula $C_nH_{2n+1}NH_2$, where n is a number 12 to 18 inclusive, to the etching solution extends the preferred range of NH_4F/HF molar ratios to include 1.0–3.0.

While the etching can be applied under whatever occasion it is desired to chemically clean zirconium or zirconium alloy surfaces, it is particularly desirable as a step in a process for applying an adherent electroplated metallic coating to a zirconium or zirconium alloy surface. Where the etching is to be a step in a zirconium electroplating process, between about 0.2 and 0.6 mil of the zirconium surface are preferably removed by the etchant before the electroplating step. The amount of zirconium removed by etching will depend upon the time of immersion in the etching solution and the temperature of the etching solution. Immersion times of 10 to 240 seconds and solution temperatures of 70 to 120° F. are satisfactory for the pretreatment of zirconium objects to be electroplated with metals. However, an immersion time of 30 to 90 seconds and a solution temperature of 100° F. are preferred.

The efficiency of the etching step as a step in the process of electroplating metals to zirconium surfaces has been tested for various molar ratios of ammonium fluoride/hydrogen fluoride by carrying out the etching step, then electroplating a metal such as nickel on the surface and determining the stress (in pounds per square inch) required to separate the plating from the basis metal at the interface. The following examples illustrate the difference in the as-plated adhesion versus the composition of the etching solution in detail.

Example Number	NH_4F Mole/Liter	HF, Mole/Liter	NH_4F/HF, Molar Ratio	As-plated Adhesion, p. s. i.
1	0.00	0.50	0	1,000
2	0.44 to 0.88	0.44 to 0.88	1.0	1,000
3	0.48 to 0.96	0.40 to 0.80	1.2	6,000
4	0.66 to 1.32	0.22 to 0.44	3.0	6,000
5	0.83	0.05	16.6	1,000
6	1.67	0.09	18.5	1,000

As shown by Examples 3 and 4, the best as-plated adhesion (6000 p. s. i.) was obtained on zirconium etched in solutions with NH_4F/HF molar ratios of 1.2 to 3.0.

After the surface of the metal is etched the metal is then rinsed. This may be accomplished in an aqueous rinse or other conventional rinsing baths.

The surface preparation of zirconium and zirconium alloy objects by etching in accordance with the foregoing procedure is sufficient preparation for electroplating most metals upon the zirconium from conventional baths for electroplating the particular plating metal. The above etching step is particularly suitable for preparing zirconium and zirconium alloy surfaces for subsequent plating by a metal of the transition group of the fourth period of the periodic table, such as iron, cobalt or nickel. Conventional nickel and iron plating baths may be used to electroplate the zirconium object. The as-plated adhesion of the electroplated transition metal is greatly improved by heat treatment to diffuse the plating metal and the zirconium or zirconium alloy and thereby produce strong alloy bonds which will resist stresses as great as 40,000 to 50,000 p. s i. Diffusion-bonded nickel or iron to zirconium is a satisfactory basis for subsequent electroplating of the composite object with other metals.

The alloy bonds between zirconium and the electroplating are formed by heating the plated zirconium object to elevated temperatures for a substantial time; for example a transitional metal-plated zirconium object can be heated from 5 to 60 minutes at temperatures from 1250 to 1600° F. The strongest alloy bonds between electroplated nickel and zirconium are formed in 10 to 45 minutes at 1300° F. The strongest alloy bonds between electroplated iron and zirconium are formed in 10 to 45 minutes at 15000° F. Alloying was not apparent at 1100° F. and diffusion at higher temperatures is difficult to control.

It is desirable to pretreat the composite electroplated article before subjecting it to high temperatures. For example, zirconium-electroplated nickel or iron composites are prebaked at 400° F. for more than one hour in order to remove codeposits of hydrogen. Storing the composite at room temperature for several weeks is also an effective pretreatment to prevent blistering during subsequent diffusion heat treatment.

Now that we have described the process of the present invention, it may be further illustrated by the following examples.

Example I

A zirconium article was first sandblasted to remove all scale. An aqueous etching bath was then prepared by adding 0.66 mole per liter ammonium fluoride and 0.33 mole per liter anhydrous hydrofluoric acid to an aqueous bath. The bath was heated to about 100° F. and the zirconium article was then dipped in the bath for 60 seconds. The article was then removed from the bath and washed with tap water. Following the rinsing with tap water, the zirconium article was immersed in a nickel plating bath containing the following ingredients:

Ingredients	Ounces per gallon
Nickel sulfate, $NiSO_4 \cdot 7H_2O$	44
Nickel chloride, $NiCl_2 \cdot 6H_2O$	6.1
Boric acid, H_3BO_3	5.0
H_2O_2 added as needed to prevent pitting	

at a pH of 2.0, a temperature of 140° F. and a current density of 40 amperes per square foot. The composite article was pre-baked at 400° F. for 1½ hours. It was then heat-treated for 45 minutes at 1300° F.

Example II

A zirconium article was treated by surface grinding to remove all scale. The article was then immersed in an etching bath comprised of 0.49 moles per liter NH_4F, 0.49 mole per liter HF, 0.50% $C_{12}H_{25}NH_2$, and water for 30 seconds at a temperature of 80° F. The etched article was then rinsed with water. The article was then plated in an iron plating bath consisting of the following ingredients:

Ingredients	Ounces per gallon
Ferrous sulfate, $FeSO_4 \cdot 7H_2O$	40
Ferrous chloride, $FeCl_2 \cdot 4H_2O$	5.4
Boric acid, H_3BO_3	4.0
Ammonium sulfate, $(NH_4)_2SO_4$	2.0
Sodium formate, HCOONa	2.0
Wetting agent (sodium lauryl sulfate), $C_{12}H_{25}OSO_3Na$	0.13

at a pH of 4.0, a temperature of 140° F. and a current density of 40 amperes per square foot. Upon completion of the plating operation, the composite article was removed from the bath and stored for two weeks at room temperature. It was then heat-treated for 30 minutes at 1500° F.

The foregoing process, while it has been described as applying to zirconium metal and zirconium alloys, is of course equally applicable to hafnium. In all steps of the present method hafnium and hafnium alloys react in exactly the same manner as zirconium and zirconium alloys, so that hafnium and hafnium alloys may be cleaned and plated in exactly the same manner as zirconium.

The foregoing disclosure and examples are merely illustrative of the process of the present invention, but the scope of the present invention is not to be limited thereby but only by the scope of the claims appended thereto.

What is claimed is:

1. A zirconium material etchant comprising an aqueous solution containing 0.44 to 1.32 moles per liter ammonium fluoride and 0.44 to 0.88 moles per liter hydrofluoric acid, the ammonium fluoride to hydrofluoric acid ratio lying between 1 and 3, inclusive, and 0.25 to 1 per cent of an aliphatic amine having the formula

$$C_nH_{2n+1}NH_2$$

where n lies between 12 and 18, inclusive.

2. The method of applying an adherent metal coating to a zirconium material object which comprises physically cleaning the surface of said object, then immersing said object in a zirconium etching composition comprising an aqueous solution containing ammonium fluoride and hydrogen fluoride in a molar ratio of between 1.2 and 3.0, inclusive, for 10 to 240 seconds at a temperature of 70 to 120° F., then removing said article from the etching solution and rinsing the surface of said object with water, then electroplating said zirconium object with a metal, then heat-treating the composite object by heating for 10 to 45 minutes at a temperature between 1200 and 1600° F.

3. The process of claim 2 wherein the electroplated metal is an iron group metal.

4. The process of claim 2 wherein the electroplating metal is nickel.

5. The process of claim 2 wherein the electroplating metal is iron.

6. A method of chemically cleaning zirconium material surfaces comprising immersing the article to be cleaned in a bath containing between 0.25 and 1.0% of an aliphatic amine having the formula $C_nH_{2n+1}NH_2$, where n has a value of 12 to 18 inclusive, and ammonium fluoride and hydrofluoric acid in a molar ratio of ammonium fluoride to hydrogen fluoride of 1 to 3 for at least 10 seconds at a temperature of 70 to 120° F.

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