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ELECTROPLATING OF NIOBIUM
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Our invention is directed toward niobium and niobium alloy substrates clad with dissimilar metals.

The term niobium as used in this specification refers not only to the metal but to alloys containing a substantial proportion of niobium.

Niobium substrates are characterized by high strength at elevated temperatures. However, these substrates oxidize or corrode very readily at high temperatures, and when oxidized, become embrittled and fail. In order to retain the desirable high temperature strength while minimizing such oxidation, these substrates are often clad with dissimilar metals (such as nickel or iron) which provide a corrosion resistant layer.

The presence of an oxide film on a substrate of niobium is normally considered deleterious to the formation of an adherent electrodeposit. In contradistinction, we have discovered that the presence of an oxide film on a niobium substrate is not only permissible under certain conditions, but indeed obviates many of the difficulties (such as blistering and poor adherence) normally associated with the conventional method of plating on a clean niobium substrate.

Hence, in accordance with the principles of our invention, a yellow interference oxide film is formed on the surface of a niobium substrate, as for example by rendering the substrate anodic in an electrolytic cell containing an alkaline electrolyte. Thereafter, a coating of iron or nickel is electrolytically deposited over the film and the resulting structure is heated to bond the coating to the substrate. By virtue of the oxide film, the coating is firmly bonded and adherent, and will not blister or peel.

Illustrative embodiments of our invention will now be described with reference to the examples which follow.

Example I

A clean niobium substrate was connected as the anode in a first electrolytic cell, the electrolyte consisting of 10% concentration by weight of sodium hydroxide in aqueous solution. A voltage of 5 volts was established across the anode-solution interface and the electrolytic action was continued for a period of 1 minute. As a result a yellow (straw) colored film of niobium oxide was formed on the surface of the substrate.

The oxidized substrate was then removed from the first cell, rinsed with water and then connected as the cathode in a second electrolytic cell, the electrolyte being a nickel plating bath having the following composition:

NiCl ₂ ·6H ₂ O	grams per liter	220
HCl (specific gravity 1.18)	milliliters per lt.	125

With the bath maintained at a temperature of 25° C., the current density was adjusted to 30 amperes per square foot, and a nickel strike was applied to the substrate, this process being continued until the entire surface of the substrate was just visibly covered with nickel.

The nickel plated substrate was then removed from the second cell, rinsed, and then connected as the cathode in a third electrolytic cell, the electrolyte being a nickel plating bath having the following composition:

	Grams per liter	
NiSO ₄ ·6H ₂ O	300	
NiCl ₂ ·6H ₂ O	37.5	
H ₃ BO ₃	37.5	

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With the bath maintained at a temperature of 65° C., the current density was adjusted to a value within the range 5-10 amperes per square foot, and the substrate was plated with nickel. This process was continued until a plating of the desired thickness was obtained.

The nickel plated substrate was then removed from the third cell, rinsed, dried, and then heated to red heat in air or vacuum for a period of about two minutes. The nickel layer did not blister or peel, but instead was firmly bonded to the substrate.

Example II

A niobium substrate was first oxidized, then coated with a nickel strike in the manner set forth in Example I. The substrate so produced was then connected as the cathode in an electrolytic cell, the electrolyte being an iron plating bath having the following composition:

	Grams per liter	
FeSO ₄ ·7H ₂ O	300	
FeCl ₂ ·4H ₂ O	40	
(NH ₄) ₂ SO ₄	15	

With the bath maintained at a temperature of 60° C., the current density was adjusted to values falling within the range 10-20 amperes per square foot, and the substrate was plated with iron. This process was continued until a plating of the desired thickness was obtained.

The iron plated substrate was then removed from the cell, rinsed, dried and then heated to red heat in the same manner as in Example I. The iron layer was firmly bonded to the substrate and did not blister or peel.

Example III

Substrates of a titanium-niobium alloy containing 75% by weight of niobium and 25% by weight of titanium were processed in the manner set forth in Examples I and II with substantially identical results.

We have found that the composition of the electrolyte used in the oxidation step is not critical providing it is alkaline. For example, the sodium hydroxide can be replaced by other alkali hydroxides or alkali salts, such as alkali phosphates, carbonates and silicates, or indeed by proprietary alkaline cleaning solutions.

The oxidation step does not depend upon the concentration of the electrolyte (providing the solution remains conductive) nor upon the temperature (as long as it remains a liquid). The color of the oxide film, however, is critical, since it provides a measure of the thickness of the film. (The adherence of the nickel or iron to the substrate is adversely affected if the oxide film is too thick or too thin.) More particularly, if the film is translucent or colorless, it is too thin and the oxidation process must be continued. When the film has the proper thickness, the color will be yellow (or straw). As the film thickness is further increased, the color will change from yellow to yellowish brown to blue or purple; such colors indicate that the film is too thick and unacceptable.

In general, increased film thickness is favored by lower temperatures, higher solute concentration and higher voltage. Therefore, dependent upon the color of the film obtained, the film thickness can be varied as required by suitable adjustments of temperature, concentration and voltage.

What is claimed is:

1. A method for cladding a niobium substrate comprising the steps of connecting said substrate as the anode in an electrolytic cell containing an electrolyte of approximately 10% concentration by weight of sodium hydroxide in aqueous solution, applying a voltage across the anode-solution interface until a yellow film of niobium oxide is formed on a surface of said substrate, electrolytically depositing a first coating of nickel over said

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film, electrolytically depositing a second coating of a metal selected from the class consisting of nickel and iron over the nickel coated substrate, and heating the resultant structure to red heat to bond said coatings to said substrate.

2. A method for cladding a niobium substrate which comprises the steps of forming a yellow interference niobium oxide film on a surface of said substrate; and electrolytically depositing a coating of a metal selected from the class consisting of nickel and iron over said film.

3. A method for cladding a niobium substrate which comprises the steps of forming a yellow interference niobium oxide film on a surface of said substrate; electrolytically depositing a coating of a metal selected from the class consisting of nickel and iron over said film; and heating the resultant structure to red heat to bond said coating to said substrate.

4. A method for cladding a niobium substrate which comprises the steps of rendering said substrate anodic in an electrolytic cell containing an alkaline electrolyte to

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form a yellow interference niobium oxide film on a surface of said substrate; electrolytically depositing a coating of a metal selected from the class consisting of nickel and iron over said film; and heating the resultant structure to red heat to bond said coating to said substrate.

5. A method as set forth in claim 4 wherein a voltage of about 5 volts is applied across the substrate-electrolyte interface.

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