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PROCESS OF ELECTROPLATING METALS WITH ALUMINUM

William C. Schickner, Columbus, Ohio, assignor to the United States of America as represented by the United States Atomic Energy Commission

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This invention deals with a process of electroplating aluminum on metals, such as copper, iron, nickel, steel, zinc and brass, from a nonaqueous bath, and more particularly with a novel method of pretreating or conditioning the metal prior to the electrodeposition of the aluminum.

Aluminum coatings are frequently used to protect corrodible metals. Construction elements of aircraft engines, for instance, are frequently protected by an aluminum coating. Wave guides, too, have been formed of an aluminum-coated metal. Another instance of an aluminum-coated metal is uranium-containing fuel elements of neutronic reactors; there aluminum also is particularly advantageous on account of its low neutron capture cross section.

In all these cases it is of vital importance that the bond between the base metal and the aluminum coating be strong, continuous and impermeable, so that the base metal is sufficiently protected by the cladding against corrosion. This is particularly important for reactor fuel elements which come in contact with the cooling water, eventually at elevated temperature; corrosion of the aluminum cladding and penetration of the cooling water to the uranium core would make the fuel element swell, and this could lead to jamming and ruptured tubes. Another reason for the necessity of a strong continuous bond on fuel elements for neutronic reactors is that a good heat conductivity is required in order to obtain a good cooling effect throughout the entire element by the cooling medium.

Aluminum coatings applied to uranium elements have one disadvantage, namely, that diffusion of the aluminum into the uranium occurs at temperatures as low as 300° C. and even lower; a brittle aluminum-uranium alloy forms thereby which considerably impairs the durability of the bond of the aluminum with the uranium. This drawback has been overcome by applying an intermediate metal coat, for instance of copper, iron or nickel, to the uranium core and then plating the thus "barrier-coated" fuel element with aluminum. Nickel is the preferred barrier metal for this purpose.

One method of electroplating aluminum on metals was developed by the National Bureau of Standards and is described in an article by Couch and Brenner in the Journal of the Electrochemical Society, 99, 240–244 (1952). The method there described is based on electrolysis of a bath containing a solution of aluminum chloride and lithium hydride in absolute diethyl ether. However, that process did not produce deposits of satisfactory adherence on most metals.

It is an object of the invention to provide a process of electroplating aluminum on metals from nonaqueous solutions whereby good adherence and thus a strong bond between the metal and the aluminum are obtained.

It is another object of the invention to provide a process of electroplating aluminum on metals from nonaqueous

solutions whereby an impermeable coating is obtained so that the metal is well protected against corrosion by hot water and other corrosive agents.

It is still another object of the invention to provide a process of electroplating aluminum on metals from nonaqueous solutions by which well-coherent and well-adherent deposits of a considerable thickness can be produced.

It has been found that the adherence of aluminum coatings produced by electrodeposition from an ether solution of aluminum chloride and lithium hydride to the base metal, such as copper, nickel, iron, steel, brass and zinc, is greatly improved if said base metal is immersed in a fatty acid or an ether solution thereof before electroplating with aluminum. It has furthermore been found that a still better adhering and durable aluminum deposit is obtained if, prior to the fatty acid treatment, the base metal is immersed in an isopropyl alcohol solution of sterato chromic chloride.

The process of this invention, as applied by way of example to the plating of uranium, thus comprises the steps of plating the uranium with the barrier metal, immersing the barrier-coated uranium in fatty acid, and electrolyzing a water-free diethyl ether solution of aluminum chloride and lithium hydride while making the uranium the cathode until an aluminum deposit of the desired thickness has been formed. According to another preferred embodiment the barrier-coated uranium is immersed in an isopropyl alcohol solution of sterato chromic chloride prior to the fatty acid treatment of this invention.

The uranium is advantageously subjected to some preparatory treatment. Surface finishing is one of the preliminary steps which, in the case of uranium, was carried out satisfactorily by machine surface grinding, dry grit blasting, vapor blasting, lathe turning or shaper finishing, or by chemical or electrochemical methods known to those skilled in the art. Surface grinding, however, with a soft wheel, for instance of alundum, using a low wheel-surface speed and low table speed and good coolant flow was the preferred method.

After this surface finishing operation, the surface was advantageously cleaned, for example by wiping with trichloroethylene, or other organic solvent, followed by a cathodic electrolysis in a silicated caustic solution containing a phosphate and a wetting agent; the uranium was then rinsed with water.

Thereafter the surface was usually activated, preferably by immersion in nitric acid, followed by anodic treatment in a chloride solution, such as a solution containing hydrochloric and phosphoric acids, or trichloroacetic acid, or sodium chloride, the hydrochloric acid-phosphoric acid mixture being preferred, and subsequent immersion in nitric acid.

After this the barrier metal was applied by electroplating methods known to those skilled in the art. Nickel, the preferred barrier metal, for instance, was deposited from an electrolyte containing nickel sulfate, magnesium sulfate, ammonium chloride, boric acid and a wetting agent. The nickel surface was then dewatered either by air-drying or by immersion in alcohol, a ketone or a fatty acid.

At this point immersion in a sterato chromic chloride solution, which—as has been mentioned before—is an optional step, was carried out. A 30% solution of this compound in isopropyl alcohol yielded the best results, and an immersion time of a few seconds was sufficient. The metal was then drained.

Thereafter the nickel-plated uranium element was immersed in fatty acid at room temperature. Various saturated and unsaturated fatty acids were found opera-

tive if they had at least 10 carbon atoms in the chain. For instance, oleic, lauric and linoleic acids gave good results, also immersion into the ether solutions of these acids. The preferred agent, though, was undissolved oleic acid. The element was immersed therein for a few seconds and then drained, whereupon it was ready for aluminum plating.

The electrolyte for aluminum plating preferably contained from 265 to 400 grams of aluminum chloride and from 4 to 8 grams of lithium hydride per liter of diethyl ether solution. The optimal concentration was 332 grams of aluminum chloride and 6 grams of lithium hydride per liter of solution. Absolute ether was used because water drastically impaired the aluminum deposition. This electrolyte had been mixed in a container cooled by a dry ice-acetone bath to remove the reaction heat. The electrolyte may be stored at room temperature but advantageously is held at a temperature of −10° C. or thereabouts to avoid volatilization of ether and concentration changes connected therewith. Before application of electric current, the barrier-plated element was held immersed in the electrolyte for from 1 to 2 minutes. The element was then made the cathode and an anode of highly pure aluminum was used. Electrolysis was carried out at a temperature between 20 and 32° C., while a nitrogen atmosphere was maintained above the cell for carrying out the electrolysis. A current density between 10 and 50 amps./sq. ft. was satisfactory, but 10 amps./sq. ft. yielded the very best results. The plating rate was about 0.5 mil/hr., and current was applied for approximately 24 hours.

The aluminum coating obtained by the process just described was very firmly bonded to the nickel; the element could be twisted and bent without the aluminum layer coming loose. The aluminum cladding could also not be peeled with a knife blade.

However, a still further improvement, in particular where corrosion resistance is of prime importance, could be obtained by diffiusion-bonding the aluminum-coated element, for instance, by heating for one hour at about 510° C. in a furance in which the absolute pressure was not higher than 10μ of mercury. Where strength of the bond and corrosion resistance have to be of high quality, pressure-bonding at 510° C. for 5 minutes in a die-and-ram press using a pressure of about 9,000 p.s.i. is preferred.

In the following, an example is given showing the advantage obtained by the process of this invention. This example is not intended to limit the invention to the details given therein.

Example

A copper sheet of commercial-grade copper was degreased by immersion in trichloroethylene, dried, electrocleaned in an alkaline solution, rinsed with water, then etched by dipping it for 5 minutes in an aqueous solution containing 5% by volume of sulfuric acid (specific gravity 1.96) and 0.1% by volume of a 30% hydrogen peroxide. The sheet was then rinsed with water and thereafter immersed first in absolute ethyl alcohol and next in absolute diethyl ether. After this pretreatment the copper plate was immersed in a water-free electrolyte containing 332 grams of aluminum chloride and 6 grams of lithium hydride per liter of solution, diethyl ether being the solvent. After the copper plate had been immersed for about 2 minutes, it was made the cathode in a current of 10 amps./sq. ft. Electrolysis was carried out for 2 hours, and a 1-mil thick aluminum layer was deposited thereby. The bond of the aluminum layer was poor; it could be peeled off easily.

Another copper sheet was treated identically with the exception that, after immersion in diethyl ether and before the immersion in the aluminum bath, the sample was immersed in oleic acid and drained thereafter for 15 seconds. In this instance the aluminum coating obtained was well bonded and could not be peeled off.

The same favorable results were obtained when linoleic acid was substituted for the oleic acid, and a still better bond was accomplished when an immersion in a 30% isopropanol solution of sterato chromic chloride and subsequent draining for a few seconds were carried out prior to the immersion in the fatty acid.

Similarly good results were also produced by plating the aluminum on nickel, iron, and on uranium that had been coated with one of these metals.

It will be understood that the process is applicable not only to aluminum plating which has been described in detail herein, but that it is also useful for other electroplating processes in which the electrolyte is a non-aqueous organic solvent solution.

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

What is claimed is:

1. A process of electroplating aluminum on a base metal selected from the group consisting of copper, iron, nickel, steel, zinc and brass from a water-free organic solvent solution of a salt of said plate metal comprising immersing the base metal in water-free condition in a fatty acid having a chain of at least 10 carbon atoms and room temperature, immersing the thus pretreated base metal in said organic solution for a short period of time, and applying electric current to said organic solution while making the base metal the cathode whereby a coating is deposited on said base metal.

2. A process of electroplating aluminum on a base metal selected from the group consisting of copper, iron, nickel, steel, zinc and brass from a water-free diethyl ether solution of aluminum chloride and lithium hydride comprising immersing the base metal in water-free condition in a fatty acid having a chain of at least 10 carbon atoms and room temperature, immersing the thus pretreated base metal in said ether solution for a short period of time, and applying electric current to said ether solution while making the base metal the cathode whereby a coating is deposited on said base metal.

3. The process of claim 2 wherein the fatty acid is selected from the group consisting of oleic acid, lauric acid and linoleic acid.

4. The process of claim 2 wherein the fatty acid is oleic acid.

5. The process of claim 2 wherein the fatty acid is dissolved in diethyl ether.

6. The process of claim 2 wherein the aluminum-coated base metal is subjected to heating at about 510° C. and reduced pressure for about one hour.

7. The process of electroplating aluminum on a base metal selected from the group consisting of copper, iron, nickel, steel, zinc and brass from a water-free diethyl ether solution of aluminum chloride and lithium hydride comprising immersing the base metal in a solution of sterato chromic chloride in isopropyl alcohol, immersing the base metal in water-free condition in a fatty acid having a chain of at least 10 carbon atoms and room temperature, immersing the thus pretreated base metal in said ether solution for a short period of time, and applying electric current to said ether solution while making the base metal the cathode.

8. The process of claim 7 wherein the sterato chromic chloride solution has a concentration of about 30%.

9. A process of plating a uranium element, comprising immersing said element in a nickel sulfate-containing electrolyte, applying current to said electrolyte while making said element the cathode whereby a nickel layer is deposited on the surface of said element, removing said element from said electrolyte, drying the surface of said electrolyte, immersing the element in oleic acid, immersing the element in a water-free diethyl ether solution containing about 332 grams of aluminum chloride and 6 grams of lithium hydride per liter of solution, applying an electric current to said diethyl ether solution

of a density of about 10 amperes per square foot while making said element the cathode until an aluminum layer of the desired thickness has been formed, removing said element from said diethyl ether solution, and heating said aluminum-plated element to about 510° C. for one hour at a maximum absolute pressure of 10 microns.

10. The process of claim 9 wherein said element, after surface drying and before immersion in oleic acid, is immersed in a 30% isopropyl alcohol solution of sterato chromic chloride.

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