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2,828,251

## ELECTROLYTIC CLADDING PROCESS

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5 Claims. (Cl. 204—39)

This invention relates to the cladding of base metals with corrosion-resistant metals and, more particularly, to such cladding by electrolysis in a fused salt bath.

It is well known that such corrosion-resistant metals as titanium and zirconium can be electrolytically deposited on a base metal cathode immersed in fused salt bath. It is characteristic of such deposits, however, that they may be readily stripped or jarred loose from the base metal, and in fact this characteristic is relied upon to facilitate recovery of the electrolytic deposit in the production of massive shapes of the deposited metal.

In our copending United States patent application Serial No. 358,194, filed May 28, 1953, there is described and claimed a highly effective method of forming dense deposits of titanium, zirconium, hafnium, tantalum, vanadium and niobium on a base metal cathode. The method of said application is characterized by a plating-out action whereby the anode component of the metal to be deposited is caused to pass into and through a fused halide salt bath and onto a base metal cathode without significant electrolytic decomposition of any component of the bath.

We have now found that if the electrodeposition described and claimed in our aforesaid application is carried out using a combination of a specific range of relatively high bath temperatures and a specific range of cathode current densities, alloying takes place between the deposited metal and the base cathode metal with the result that there is formed on the surface of the base metal a firmly adherent layer of the deposited metal joined to the base metal by a metal-to-metal bond. The fact that this deposited metal layer is so adherent as to be virtually impossible to separate from the base metal by mere physical distortion characterizes the resulting product with the mechanical properties of the base metal and the corrosion-resistant properties of the deposited metal.

It will be seen, therefore, that we have now devised a method of cladding a base metal with a firmly adherent deposit of certain corrosion-resistant metals, to wit: titanium, zirconium, hafnium, tantalum, vanadium and niobium. This method of our invention comprises using as the anode a solid metalliferous form of such a transition metal, using as the cathode in the aforementioned plating-out procedure a base metal capable of forming an alloy with the corrosion-resistant metal, maintaining the cell voltage below that at which any bath component decomposes with the evolution of significant amount of a free halogen but sufficient to establish a cathode current density of 25 to 200 amperes per square decimeter, and maintaining the cell bath temperature between 900° to 1000° C.

The anode material which supplies the corrosion-resistant metal deposited on the base metal cathode may comprise any solid metalliferous form of the corrosion-resistant metal such as the carbide or the oxycarbide of the metal or the metal itself in pure or impure form. The corrosion-resistant metals useful in practicing our

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invention comprise titanium, zirconium, hafnium, tantalum, vanadium and niobium. The carbides and mutual solid solution of the monoxide and carbide of these metals may be produced as described in our aforementioned application. The carbides may be used either in the form of anodes of substantially 100% density as described in said application or in the form of anodes having an apparent density of about 50% of the carbide itself as described in the United States patent application of B. C. Raynes, M. E. Sibert and J. T. Burwell, Jr., Serial Number 389,191, filed December 14, 1953, and now Patent 2,813,069. All of these solid anode materials are capable of supplying the corrosion-resistant metal component which is carried into and through the bath to the base metal cathode.

The base metals which may be used as cathodes in the practice of our invention are all metals having a melting point at least as high as 1000° C. and include, but are not limited to, iron, steel, stainless steels, molybdenum-iron alloys, molybdenum-nickel alloys, nickel-chromium alloys, nickel-copper alloys, nickel, chromium and copper. All of the aforementioned base metals have melting points substantially above the operating bath temperatures which promote the firm adherence of the coating to the base metal by a metal-to-metal bond. The base metal cathode may have any suitable shape compatible with the geometry of the electrolytic cell in which it is clad with the corrosion-resistant metal.

The electrolytic cell baths useful in practicing our invention comprise fused halide salts composed primarily of one or more of the alkali metal halides or alkaline earth metal halides, or mixtures thereof, in admixture with a significant but generally minor proportion of a halide of the corrosion-resistant metal to be deposited from the bath. The choice of alkali metal halide or alkaline earth metal halide, or mixtures thereof, comprising the major bath constituent is governed largely by consideration of the melting point and volatility of the bath. Thus, the bath composition should be such that it is not only molten and fluid at temperatures upwards of about 850° C. but is also not excessively volatilized at temperatures up to about 1000° C. Although simple halides of the corrosion-resistant metals are suitable as the minor constituent of the bath, the alkali metal double fluorides of these metals are particularly satisfactory and are readily available in substantially pure form. For example, in the electrodeposition of titanium, which is representative of the practice of our invention, the fused salt bath may be composed, in addition to the titanium halide, of one or a mixture of the chlorides, bromides, iodides and fluorides of alkali metals such as sodium and potassium. The titanium halide may be a chloride, bromide, iodide or fluoride and may be a simple halide or a complex halide such as a double fluoride of titanium and an alkali metal (also known as an alkali metal fluotitanate). The corrosion-resistant metal halide should be present in the bath in the amount of at least about 5% by weight and generally up to about 25% by weight. The presence of fluorine in the bath in the form of such a double fluoride of an alkali metal and the corrosion-resistant metal, or in the form of a simple alkali metal fluoride, promotes the formation of larger particles of cathodically deposited corrosion-resistant metal than that which is obtained by any one or a mixture of the other halides. Except for this special effect of an added fluoride, the specific composition of the bath appears to have no effect upon the quality of the electrodeposited metal. Illustrative bath compositions which are useful in the practice of our invention for the electrodeposition of titanium, which is representative of the other corrosion-resistant metals, are set forth in the following table, the

numerical values under each salt heading representing the parts by weight or percentage of each component in the bath:

| $K_2TiF_6$ | NaCl | KCl | NaBr | KBr | NaI | KI  |
|------------|------|-----|------|-----|-----|-----|
| 5          | 95   | --- | ---  | --- | --- | --- |
| 10         | 90   | --- | ---  | --- | --- | --- |
| 10         | 45   | 45  | ---  | --- | --- | --- |
| 5          | 30   | 20  | 20   | 15  | 10  | --- |
| 10         | 20   | --- | 30   | --- | 30  | 10  |

The purity of the bath composition should be as high as possible. The alkali metal halides and alkaline earth metal halides are readily available in the substantially chemically pure state. The corrosion-resistant metal fluorides can also be obtained or prepared in substantially pure form, but the alkali metal double fluorides of these metals are particularly amenable to purification by simple recrystallization from an aqueous medium. All of these bath constituents should be used in their substantially anhydrous form, and the anhydrous quality of the bath can be further enhanced by conventional pre-electrolysis of the fused bath in situ in the cell.

Normal cell operation in the practice of our invention requires, as described in our aforementioned application, the use of a cell voltage such as to insure against the electrolytic decomposition of any bath constituent with the resulting evolution of any significant amount of a free halogen. Under such cell voltage conditions, the corrosion-resistant metal component of the solid metal-liferous anode goes into solution in the bath and is transported through the bath with ultimate deposition on the solid cathode metal. This electrolytic action is of the plating-out type as distinguished from the electrolytic decomposition type. Cell voltages useful in practicing our plating-out operation may be as low as 0.7 volt but should not exceed about 3.0 volts. However, in order to effect the cladding of the cathode metal with a metal-to-metal bond between it and the corrosion-resistant metal, the cell voltage should be so adjusted within this range as to establish a cathode current density within the range of 25 to 200, and preferably 50 to 100, amperes per square decimeter.

Within the aforementioned range of cathode current density, we have found that the deposited corrosion-resistant metal will alloy with the base metal of the cathode when the cell bath temperature is maintained within the range of 900° to 1000° C. When the cathode material is copper, the optimum bath temperature for effective cladding is about 900° C., but for all of the other base metals and alloys mentioned hereinbefore as suitable cathode materials the optimum bath temperature is any temperature within the range of 950° to 1000° C. The alloying of the deposited corrosion-resistant metal with the cathode base metal appears to take place as a result of diffusion of one metal into the other or as a result of the formation of a eutectic, or possibly by a combination of these mechanisms. Although we are not certain which of these mechanisms may be the dominant factor in the alloyage of the deposited metal with the cathode metal, it is certain that it does not result from fusion of the deposited metal or of the cathode metal because the effective bath temperatures of 900° to 1000° C. are well below the melting points of all of these metals. Regardless of the theory which may prevail, we have found it to be a fact that such alloyage does take place. The alloy composition formed immediately adjacent the cathode surface is relatively low in its content of the corrosion-resistant metal, but successive deposit layers are progressively higher in their corrosion-resistant metal content so that by the time a deposited continuous layer about one-sixteenth inch thick has been laid down its surface will be composed of the substantially pure corrosion-resistant metal.

The electrolysis is carried out under purified argon in which all oxygen, hydrogen, water vapor, nitrogen, and the like have been eliminated by conventional cleaning techniques well known in the art. When anodes composed of the carbides of one of the corrosion-resistant metals are properly made and are used in the form of the densely sintered rods or other shapes as described hereinbefore, a condition evidenced by a silvery white appearance at a fracture, the electrolytic reaction proceeds quietly as long as a significant amount of metal carbide remains in the anode structure. In view of the frangible nature of the residual carbon structure, it can be removed readily from the upper unused portions of a long anode by rapping it sharply. Then the unused portion of the same anode is inserted in the bath and the electrolysis is continued. Most efficient utilization of the metal carbide dictates a physical shape such as to provide a relatively large surface area-to-volume ratio. With these conditions properly observed, at least 90% of the corrosion-resistant metal content of the metal carbide will be deposited on the cathode.

The following specific examples are illustrative of the practice of our invention:

#### Example I

An anode of titanium carbide was prepared by milling substantially oxygen-free titanium carbide from which a mixture was then prepared consisting of 100 parts of the milled carbide, 1.5, parts of methyl cellulose having a viscosity of 4000 centipoises, and approximately 12 parts of water, all parts being by weight. The ingredients were thoroughly mixed until completely dispersed. Rods  $\frac{5}{8}$  inch in diameter were produced by extruding the resulting plastic mass through an extrusion orifice. After air drying for 24 hours, the rods were placed in a graphite crucible which was induction heated under vacuum conditions to a temperature of about 2000°–2100° C. for a period of one hour. Within a few minutes after reaching this temperature, the vacuum conditions within the heating furnace had reached a steady state and these vacuum conditions were maintained during the remainder of the one-hour heat treatment.

The electrolytic cell consisted of a graphite container in the center portion of which a baffle was positioned, the baffle being pierced with a multiplicity of fine holes over an area which extended to the bottom of the crucible. The cell was fitted with electrical connections and inlets for pure argon gas so that the operation could be carried out under a controlled atmosphere. The cell bath consisted of 100 parts of sodium chloride and 16 parts by weight of potassium titanium fluoride. These constituents were purified and vacuum dried so as to be free of oxygen and water. The dried and purified salt mixture was charged to the cell after the latter had been heated to approximately 850° C. Thereupon the heating of the cell was continued under the controlled atmosphere until the salt fused and reached a temperature of 1050° C. At this stage a graphite rod was inserted into the bath, and pre-electrolysis of the bath was begun by applying a voltage of 1.5 volts between the rod as the cathode and the container as the anode. The cell current was initially approximately 15 amperes, but within one to two hours it fell rather abruptly to about  $\frac{1}{3}$  of this value, thus indicating that most of the oxygen-containing impurities had been discharged from the bath. The voltage was then raised to and held at 3.2 volts for about 45 minutes, following which this pre-electrolysis was stopped and the graphite cathode rod was withdrawn.

The bath was then in anhydrous molten condition for electrolytic cladding pursuant to the practice of our invention. Accordingly, the temperature of the cell was dropped to 950° C., and pellets of the aforementioned titanium carbide were introduced into the annular space between the baffle and the container wall until the space

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was filled up to the bath level. The steel part to be plated, supported by a clamp and shank made of nickel, was inserted into the bath as the cathode. A voltage of 1.8 volts was applied between this cathode and the carbide pellets which functioned as the anode. The cell current was about 50 amperes and corresponded to a cathode current density of approximately 100 amperes per square decimeter. Electrolysis was conducted for a total of about 30 ampere-hours after which the clad cathode was withdrawn to cool in a closed chamber above the cell through which purified argon was also kept flowing. The cathode removal chamber was closed with a gate valve so that when the cathode had been removed from the top of the cell a second cathode article to be plated could be immediately inserted into the cell, and the cladding of this second article was thus begun with a minimum loss of time. By this procedure and by using the aforementioned bath it was possible to clad in this manner 30 such articles before the carbide anode pellets were so depleted of metal that the operation had to be discontinued. At this stage the titanium carbide rods were removed from the cell, the carbon regulus on the surface of the rods was removed by tumbling, and the remaining solid titanium carbide cores were used as the carbide pellets charged to the same bath.

Each of the clad cathodes was then soaked in water for about 10 minutes, and thereafter the outer layer of salt and small amounts of loose granular metal were easily stripped off to disclose a shiny smooth continuous layer of substantially pure metallic titanium of about  $\frac{1}{32}$  inch thickness adhering to the underlying steel body by a metal-to-metal bond.

#### Example II

The operation described in Example I was repeated with the exception that the anode consisted of several of the aforementioned titanium carbide rods mounted at equally spaced positions around the cathode. These rods, like the cathode, were inserted in the molten bath after the pre-electrolysis was completed. The results were the same as in Example I.

#### Example III

The operation described in Example I was again repeated except that the anode material consisted of metallic titanium in the form of an anode-shaped ingot obtained by melting under an argon atmosphere of finely divided metallic titanium obtained by a previous but dissimilar electrolytic operation. This anode contained 98% titanium. The results were the same as in Example I.

#### Example IV

The operation described in Example I was again repeated with the only change being that the cathode shape to be clad was copper, and that the electrolytic cladding bath temperature was maintained at about 900° C.

#### Example V

The operation described in Example I was repeated to effect the cladding of a base metal cathode with each of the metals zirconium, hafnium, tantalum, vanadium and niobium. For each of these cladding metals the carbide and the double fluoride were those of the corresponding cladding metal, and in each operation the base metal was clad with a tightly adhering and continuous layer of the cladding metal.

We claim:

1. A method of forming an electrodeposited coating of a coating metal of the group consisting of titanium, zirconium, hafnium, vanadium, tantalum and niobium on a metal base in which the coating is bonded to the metal base by an alloy consisting of the base metal and the coating metal which comprises: providing an anhydrous fused salt electrolyte consisting essentially of at least 5% by weight of a halide of the coating metal and at least

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one halide of the group consisting of the alkali metal halides and the alkaline earth metal halides; immersing in said molten electrolyte a metalliferous anode of said coating metal and a cathode of a base metal different from the coating metal and selected from the group consisting of metals having a melting point of at least 1000° C.; passing an electrolyzing current between said anode and said cathode sufficient to establish a cathode current density of 25 to 200 amperes per square decimeter and to maintain a cell voltage below that at which any bath component decomposes with the evolution of a significant amount of a free halogen and cladding the cathode with an alloy bonded adherent coating of said coating metal by maintaining the electrolyte temperature above 900° C. and at least sufficient to form an alloy between the coating metal and the base metal and below the temperature at which a liquid alloy forms between the base metal and the coating metal and not above 1000° C. during said electrolysis.

2. A method of forming an electrodeposited coating of a coating metal of the group consisting of titanium, zirconium, hafnium, vanadium, tantalum and niobium on a metal base in which the coating is bonded to the metal base by an alloy consisting of the base metal and the coating metal which comprises: providing an anhydrous fused salt electrolyte consisting essentially of at least 5% by weight of a halide of the coating metal and at least one halide of the group consisting of the alkali metal halides and the alkaline earth metal halides; immersing in said molten electrolyte (1) a metalliferous anode of said coating metal and (2) a cathode of a base metal different from the coating metal and selected from the group consisting of iron, steel, molybdenum-iron alloys, molybdenum-nickel alloys, nickel and chromium; passing an electrolyzing current between said anode and said cathode sufficient to establish a cathode current density of 25 to 200 amperes per square decimeter and to maintain a cell voltage below that at which any bath component decomposes with the evolution of a significant amount of a free halogen and cladding the cathode with an alloy bonded adherent coating of said coating metal by maintaining the electrolyte temperature above 950° C. and at least sufficient to form an alloy between the coating metal and the base metal and below the temperature at which a liquid alloy forms between the base metal and the coating metal and not above 1000° C. during said electrolysis.

3. A method of forming an electrodeposited coating of a coating metal of the group consisting of titanium, zirconium, hafnium, vanadium, tantalum and niobium on a metal base in which the coating is bonded to the metal base by an alloy consisting of the base metal and the coating metal which comprises: providing an anhydrous fused salt electrolyte consisting essentially of at least 5% by weight of a halide of the coating metal and at least one halide of the group consisting of the alkali metal halides and the alkaline earth metal halides; immersing a metalliferous anode of said coating metal and a steel cathode in said molten electrolyte; passing an electrolyzing current between said anode and said cathode sufficient to establish a cathode current density of 25 to 200 amperes per square decimeter and to maintain a cell voltage below that at which any bath component decomposes with the evolution of a significant amount of a free halogen and cladding the steel cathode with an alloy bonded adherent coating of said coating metal by maintaining the electrolyte temperature above 950° C. and at least sufficient to form an alloy between the coating metal and the cathode metal and below the temperature at which a liquid alloy forms between the cathode metal and the coating metal and not above 1000° C. during said electrolysis.

4. A method of forming an electrodeposited titanium coating on a metal base in which the coating is bonded to the metal base by an alloy consisting of the base metal and the coating metal which comprises: providing an

anhydrous fused salt electrolyte consisting essentially of at least 5% by weight of a halide of the coating metal and at least one halide of the group consisting of the alkali metal halides and the alkaline earth metal halides; immersing a metalliferous anode of titanium and a steel cathode in said molten electrolyte; passing an electrolyzing current between said anode and said cathode sufficient to establish a cathode current density of 25 to 200 amperes per square decimeter and to maintain a cell voltage below that at which any bath component decomposes with the evolution of a significant amount of free halogen and cladding the cathode with an alloy bonded adherent coating of said coating metal by maintaining the electrolyte temperature above 950° and at least sufficient to form an alloy between the titanium and the cathode metal and below the temperature at which a liquid alloy forms between the cathode and the titanium and not above 1000° C. during said electrolysis.

5. A method of forming an electrodeposited coating of a coating metal of the group consisting of titanium, zirconium, hafnium, vanadium, tantalum and niobium on a metal base in which the coating is bonded to the metal base by an alloy consisting of the base metal and the coating metal which comprises: providing an anhydrous fused salt electrolyte consisting essentially of at least 5% by weight of a halide of the coating metal and at least one halide of the group consisting of the alkali metal halides and the alkaline earth metal halides; immersing a metalliferous anode of said coating metal and a cathode of

copper in said molten electrolyte; passing an electrolyzing current between said anode and said cathode sufficient to establish a cathode current density of 25 to 200 amperes per square decimeter and to maintain a cell voltage below that at which any bath component decomposes with the evolution of a significant amount of a free halogen and cladding the cathode with an alloy bonded adherent coating of said coating metal by maintaining the electrolyte temperature above 900° C. and at least sufficient to form an alloy between the coating metal and the cathode metal and below the temperature at which a liquid alloy forms between the cathode metal and the coating metal and not above 1000° C. during said electrolysis.

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U. S. DEPARTMENT OF COMMERCE  
PATENT OFFICE  
**CERTIFICATE OF CORRECTION**

Patent No. 2,828,251

March 25, 1958

Merle E. Sibert et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 50, for "corrosion-resitant" read -- corrosion-resistant --; line 62, before "significant" insert -- a --; column 2, line 11, for serial number "389,191" read -- 398,191 --; column 4, line 5, for "carbides" read -- carbide --; line 29, after "1.5" strike out the comma; column 5, line 48, for "titainum" read -- titanium --; column 6, line 13, for "alley" read -- alloy --; line 49, for "tatalum" read -- tantalum --.

Signed and sealed this 20th day of May 1958.

(SEAL)

Attest:

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Commissioner of Patents