

1

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ELECTROLYTIC CLADDING

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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.

The quest for an effective and economical method of producing transition elements such as titanium and zirconium in pure metallic form has been spurred by their mechanical properties as well as by their corrosion-resistant properties. Where the advantage in constructing a device of such a transition element is predicated primarily upon the corrosion-resistance of the transition element, this objective could be attained by forming the device from a less expensive and more readily available base metal having a surface coating of the corrosion-resistant transition element. A similar coating arrangement would be effective where the strength versus weight characteristics of titanium and the corrosion-resistance of zirconium are desired. It will be apparent, accordingly, that many of the contemplated applications of the corrosion-resistant transition elements to structural devices can be substantially completely satisfied if only the surface of the device possesses the corrosion-resistant characteristic of the transition element.

Although a number of metals can be readily electrodeposited on a base metal in the form of an adherent thin film by aqueous electrolytic methods, such aqueous electrodeposition of the transition elements including titanium, zirconium, hafnium, vanadium, niobium and tantalum has not been successfully achieved. The classic method of electrodepositing these transition elements is through the medium of a fused halide salt bath, but it is characteristic of such electrodeposition from a fused bath that the deposited transition element is obtained on the cathode in the form of a relatively loosely adhering granular deposit.

In the copending application of Merle E. Sibert and John T. Burwell, Jr., Serial Number 383,401 filed simultaneously herewith, there is described a method of cladding base metals with the aforementioned transition elements in the form of a firmly adherent layer of the deposited metal joined to the base metal by a metal-to-metal bond. The aforesaid method depends upon a combination of a specific range of relatively high temperatures for the fused salt bath and a specific range of cathode current densities in conjunction with the supplying of the metal to be deposited by means of a consumable anode comprising a solid metalliferous form of the transition element. Although this method is effective, it requires relatively high bath temperatures with consequent complications including volatilization of bath constituents.

I have now found that a base metal may be clad with a corrosion-resistant metal such as the aforementioned transition elements at considerably lower temperatures by supplying the corrosion-resistant metal component of the fused salt bath in the form of its alkali metal double fluoride and by further incorporating in the bath from about 1/4 to 10% by weight of water. Thus, my method

2

of cladding a base metal with a corrosion-resistant metal by electrolysis in a fused salt bath comprises establishing and maintaining a fused salt bath comprising (a) a major amount of a halide of one or more of the alkali metal and alkaline earth metal halides, (b) about 15 to 50% by weight of a double fluoride of an alkali metal and the corrosion-resistant metal, and (c) about 1/4 to 10% by weight of water. The bath is maintained at an elevated temperature above its melting point, and electrolysis of the molten bath is carried out between a solid anode and a solid cathode composed of a base metal having a melting point substantially above the melting point of the bath. The base metal cathode is thus clad with the corrosion-resistant metal by a metal-to-metal bond, and the clad base metal may be then further fabricated if necessary to shape it for its intended use.

The base metals which may be clad by the practice of my invention are all metals having a melting point at least as high as 600° 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, and further include one of the corrosion-resistant metals other than that which is to be deposited, to wit, one of the corrosion-resistant metals titanium, zirconium, hafnium, tantalum, vanadium, niobium, chromium, molybdenum and tungsten. All of the aforementioned base metals have melting points substantially above the melting points of the fused halide salt baths which are used in the practice of my invention. The base metal is clad with the electrodeposited metal by providing the former in the form of a cathode having any suitable shape compatible with the geometry of the electrolytic cell in which it is clad with the corrosion-resistant metal.

The corrosion-resistant metals which may be deposited on the aforementioned base metals in the form of a firmly adherent layer include not only the transition elements titanium, zirconium, hafnium, tantalum, vanadium and niobium but also chromium, molybdenum and tungsten. Each of these corrosion-resistant metals may be readily electrodeposited from an alkali metal double fluoride of the metal in a fused halide salt bath.

The fused salt baths useful in practicing my invention comprise fused halide salts composed primarily of one or more of the alkali metal halides and alkaline earth metal halides, and mixtures thereof. The useful halides include the chlorides, bromides, iodides and fluorides, and the choice of specific salt or mixture of salts is wholly dependent upon the desired melting point for the bath. For example, if sodium chloride is used as the sole constituent of the carrier bath other than the alkali metal double fluoride of the corrosion-resistant metal and the water, the resulting mixture of the sodium chloride with the double fluoride will have a melting point within the range of about 700° C. On the other hand, if a eutectic mixture of potassium and sodium chlorides is used, the double fluoride-containing bath will have a melting point below 550° C. Similarly, other bath melting points may be achieved by using mixtures of the halides of potassium, sodium and lithium and the halides of calcium, magnesium, strontium and barium. For example, mixtures of calcium and sodium chlorides and mixtures of calcium, sodium and potassium chlorides have been used satisfactorily as the carrier components of the fused salt baths wherein my invention is practiced. The aforementioned halide components of the bath comprise a major constituent of the bath, the other constituents being generally restricted to the double fluoride of the corrosion-resistant metal to be electrodeposited and a small but significant amount of water.

The alkali metal double fluoride of the corrosion-

3

resistant metal comprises the source of the corrosion-resistant metal which is electrodeposited. Although this double fluoride can be produced in situ in the bath by electrolysis of a solid metalliferous anode composed of the corrosion-resistant metal, I presently prefer to establish the corrosion-resistant component of the bath by the direct addition thereto of the alkali metal double fluoride. In general, I prefer to use the sodium and potassium double fluorides of the aforementioned corrosion-resistant metals, and I have found that amounts of these double fluorides ranging from about 15 to 50% by weight of the total bath constituents are satisfactory in practicing the method of my invention.

The effective cladding of the corrosion resistant metal on the surface of the base metal cathode at fused salt bath temperatures below the melting point of any alloy of the corrosion-resistant metal and the base metal of the cathode, pursuant to my invention, is predicated upon the presence in the bath of a small but significant amount of water. In general, I have found that from ¼% to 10% of water by weight of the total bath constituents is effective for this purpose, and within this range I presently prefer to use from ½% to 5% of water by weight of the bath. The water may be incorporated in the bath either in an indigenous form, such as the water of hydration of one of the bath constituents, or it may be added from an extraneous source.

The effectiveness of the water component of the bath in promoting cladding pursuant to my invention appears to be a result of its presence as water and not by virtue of any oxide or oxides which may be formed in the bath as a result of the presence of the water in the hot halides. The presence of such oxides, in the absence of a significant amount of water pursuant to my present invention, appears to be wholly ineffective in promoting the formation of a metal-to-metal bond between the electrodeposited corrosion-resistant metal and the base metal cathode. However, the presence of such an extraneous oxide in a bath containing a significant amount of water in accordance with the invention does not adversely affect the quality of the cladding bond nor does it appear to have any pronounced advantageous effect upon the cladding.

The cladding operation is performed simply by electrolyzing the aforementioned bath composition between a solid anode and a solid cathode composed of the base metal to be clad. This electrolysis takes place readily at cell voltages of at least 4.5 volts and preferably at cell voltages within the range of about 5 to 8 volts. The choice of cell voltage within this range is based upon the cell geometry and upon the shape and size of the cathode, the voltage being such as to establish and maintain a cathode current density within the range of about 100 to 500 amperes per square decimeter. The cell atmosphere above the bath should be maintained free of oxygen, nitrogen and carbon, and for this purpose I have found it suitable to maintain either vacuum conditions above the molten bath or to sweep the cell with an inert gas such as argon. In general, the cell operation may be continued without interruption for a period sufficient to effect the desired cladding of the base metal cathode with an impervious layer of corrosion-resistant metal, but when the amount of water initially present in the bath mixture is low it has been found to be advantageous in some instances to replenish the water component of the bath either continuously or intermittently during the electrolysis. The electrolytic cell design and structure are not critical, although due care should be taken to use cell components which are not attacked by the fused salt bath during electrolysis. Graphite is wholly satisfactory as a cell wall material, and the graphite cell either may be used as the anode or it may remain electrically neutral whereupon a graphite rod or plate (or other solid material not attacked by chlorine at the prevailing cell temperature) is used as the anode.

4

After cladding of the cathode base metal has been effected, the cathode is withdrawn from the bath and into a cooling chamber associated with the cell where it is permitted to cool to room temperature in an inert atmosphere without being exposed during the interim to the ambient atmosphere. The cooled cathode is then removed from the cooling chamber and the salt cake which has frozen around the metal is leached by conventional means so as to expose the clad layer.

10 The following specific examples are illustrative of the practice of my invention:

Example I

Six hundred parts by weight of potassium fluozirconate and 12 parts by weight of water were mixed with 1800 parts by weight of sodium chloride. The resulting mixture was then placed in a graphite crucible and was heated and maintained at a temperature of 750° to 850° C. in an atmosphere of argon. After fusion of the salt mixture occurred an iron base metal shape was completely immersed in the fused bath. A voltage of about 6 volts was applied between the graphite crucible as the anode and the base metal shape as the cathode in order to maintain a cathode current density of about 420 amperes per square decimeter. The electrolysis was continued for 20 minutes, at the end of which period a deposit of metallic zirconium ¼ inch thick was obtained on the base metal shape. Upon completion of the electrolysis, the cathode shape was withdrawn from the bath and cooled in an argon atmosphere to room temperature. The clad piece was removed from the cooling chamber and was leached free of residual salts. Metallographic examination of the resulting product showed that the zirconium-base metal bond was continuous and not intermittent, the base metal adjacent the bond exhibiting an intermediate region approximately equal in thickness to that of the zirconium layer.

Example II

40 The fused salt bath of sodium chloride and potassium fluozirconate described in Example I but with no addition of water failed to produce a clad layer of zirconium at bath temperatures of 770°–800° C. when attempts were made to deposit the zirconium on cathodes of steel, ingot iron, molybdenum, nickel and copper in the same cell and under the same electrolysis conditions prevailing in Example I.

Example III

50 A fused salt bath consisting of carefully purified and pre-electrolyzed mixture of sodium chloride (1800 parts by weight) and potassium fluotitanate (345 parts by weight) was electrolyzed at a cathode current density of 380 amperes per square decimeter on a steel cathode at 885° C. under the cell conditions reported in Example I. No addition of water was made. There was no evidence of a cladding layer of titanium, the titanium deposit being granular and loosely adhering to the cathode.

Example IV

60 A fused bath consisting of 1800 parts by weight of sodium chloride and 400 parts by weight of potassium fluotitanate, the latter containing 20% water of crystallization, was electrolyzed at 770° C. under the cell conditions set forth in Example I and resulted in a clad layer of titanium adhering to an ingot iron cathode by a metal-to-metal bond.

It will be seen, accordingly, that the method of my invention effectively clads a wide variety of base metals with a firmly adherent layer of a corrosion-resistant metal. Inasmuch as the resulting product may frequently be used without further deformation during subsequent fabrication, the ductility of the clad layer is not important. As a matter of fact, the tendency of the electrodeposited metal to exhibit a hardness greater than that compatible

with cold rollability, as is generally exhibited by these metals in their electrodeposited form, becomes a virtue inasmuch as it enhances the durability of the corrosion-resistant surface on the basic metal object. Thus, the purity of the clad layer is relatively unimportant except for any influence which such impurities may have on the corrosion-resistance of the cladding metal. Nevertheless, clad layers produced in the manner of my invention have exhibited fabrication properties which permit the clad specimens to be deformed readily in subsequent fabrication.

I claim:

1. The method of cladding a base metal with a corrosion-resistant metal of the group consisting of titanium, zirconium, hafnium, vanadium, tantalum, niobium, chromium, molybdenum and tungsten by electrolysis in a fused salt bath which comprises establishing a fused salt bath consisting essentially of (a) a major amount of a halide of the group consisting of alkali metal and alkaline earth metal halides, (b) about 15 to 50% by weight of a double fluoride of an alkali metal and the corrosion-resistant metal and (c) about ¼ to 10% by weight of water, maintaining said bath at an elevated temperature above its melting point, and then electrolyzing the bath at said elevated temperature between a solid anode and a solid cathode composed of a base metal having a melting point substantially above the melting point of the bath, and recovering the resulting base metal cathode clad by a metal-to-metal bond with the corrosion-resistant metal.

2. The method of cladding a base metal with a corrosion-resistant metal of the group consisting of titanium, zirconium, hafnium, vanadium, tantalum, niobium, chromium, molybdenum and tungsten by electrolysis in a fused salt bath which comprises establishing a fused salt bath consisting essentially of (a) a major amount of a halide of the group consisting of alkali metal and alkaline earth metal halides, (b) about 15 to 50% by weight of a double fluoride of an alkali metal and the corrosion-resistant metal and (c) about ½ to 5% by weight of water, maintaining said bath at an elevated temperature above its melting point, and then electrolyzing the bath at said elevated temperature between a solid anode and a solid cathode composed of a base metal having a melting point substantially above the melting point of the bath, and recovering the resulting base metal cathode clad by a metal-to-metal bond with the corrosion-resistant metal.

3. The method of cladding a base metal with a corrosion-resistant metal of the group consisting of titanium, zirconium, hafnium, vanadium, tantalum, niobium, chromium, molybdenum and tungsten by electrolysis in a fused salt bath which comprises establishing a fused salt bath consisting essentially of (a) a major amount of a halide of the group consisting of alkali metal and alkaline earth metal halides, (b) about 15 to 50% by weight of a double fluoride of an alkali metal and the corrosion-resistant metal and (c) about ¼ to 10% by weight of water, maintaining said bath at an elevated temperature above its melting point but below the melting point of any alloy of the corrosion-resistant metal with the base metal, and then electrolyzing the bath at said elevated temperature between a solid anode and a solid cathode composed of a base metal having a melting point substantially above the melting point of the bath, and recovering the resulting base metal cathode clad by a metal-to-metal bond with the corrosion-resistant metal.

4. The method of cladding a base metal with a corrosion-resistant metal of the group consisting of titanium, zirconium, hafnium, vanadium, tantalum, niobium, chromium, molybdenum and tungsten by electrolysis in a fused salt bath which comprises establishing a fused salt bath consisting essentially of (a) a major amount of a halide of the group consisting of alkali metal and alkaline earth metal halides, (b) about 15 to 50% by weight of a double fluoride of an alkali metal and the corrosion-resistant metal and (c) about ¼ to 10% by weight of water, maintaining said bath at an elevated temperature above its melting point, and then electrolyzing the bath at said elevated temperature between a solid anode and a solid cathode composed of a base metal having a melting point substantially above the melting point of the bath and with a cathode current density within the range of about 100 to 500 amperes per square decimeter, and recovering the resulting base metal cathode clad by a metal-to-metal bond with the corrosion-resistant metal.

5. The method of cladding a base metal of the group consisting of titanium, zirconium, hafnium, vanadium, tantalum, niobium, chromium, molybdenum and tungsten with another metal of said group by electrolysis in a fused salt bath which comprises establishing a fused salt bath consisting essentially of (a) a major amount of a halide of the group consisting of alkali metal and alkaline earth metal halides, (b) about 15 to 50% by weight of a double fluoride of an alkali metal and of the metal with which the base metal is to be clad, and (c) about ¼ to 10% by weight of water, maintaining said bath at an elevated temperature above its melting point, and then electrolyzing the bath at said elevated temperature between a solid anode and a solid cathode composed of a base metal having a melting point substantially above the melting point of the bath, and recovering the resulting base metal cathode clad by a metal-to-metal bond with the corrosion-resistant metal.

6. The method of cladding a base metal with a corrosion-resistant metal of the group consisting of titanium, zirconium, hafnium, vanadium, tantalum, niobium, chromium, molybdenum and tungsten by electrolysis in a fused salt bath which comprises establishing a fused salt bath consisting essentially of (a) a major amount of a halide of the group consisting of alkali metal and alkaline earth metal halides, (b) about 15 to 50% by weight of a double fluoride of an alkali metal and the corrosion-resistant metal and (c) about ¼ to 10% by weight of water, maintaining said bath at an elevated temperature above its melting point under a cell atmosphere substantially free of oxygen-, nitrogen- and carbon-containing gases, electrolyzing the bath at said elevated temperature between a solid anode and a solid cathode composed of a base metal having a melting point substantially above the melting point of the bath, and recovering the resulting base metal cathode clad by a metal-to-metal bond with the corrosion-resistant metal.

References Cited in the file of this patent

UNITED STATES PATENTS

1,535,339	Peacock	Apr. 28, 1925
1,845,978	Hosenfeld	Feb. 16, 1932
1,933,319	Driggs et al.	Oct. 31, 1933
2,715,093	Senderoff et al.	Aug. 9, 1955