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2,881,119

TITANIUM PLATING

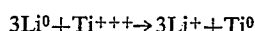
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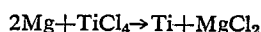
8 Claims. (Cl. 204—39)

This invention relates to electroplating of titanium upon a metallic base. More specifically it relates to the electrodeposition of an impermeable plate of pure titanium upon an iron surface.

In recent years workers in the art have expended considerable time and money in efforts to successfully electrodeposit pure titanium in massive form upon a base surface. It is well known in the art that one of the serious problems in titanium technology stems from the necessity for attaining an oxygen-free titanium product. Even the presence of a few tenths of one percent of oxygen is sufficient to render titanium brittle and unworkable. For this and other reasons electrodeposition of titanium from an aqueous electrolyte has been generally unsuccessful. An example of such prior art efforts is the Fink et al. Patent 1,885,701. On the other hand deposition of titanium from an electrolyte of fused salts such as sodium chloride and lithium chloride also fails. The reasons are not too clear. It is postulated that the comparatively high solubility of the sodium and the lithium in their molten halides interferes with the process by encouraging side reactions like



to occur inside the electrolyte so that any titanium metal deposits out as a fine powder or sludge along the cell walls. As a result of these difficulties titanium is commercially produced at high cost and in relatively small quantities by the Kroll process using the reaction



However, many of the uses suggested for titanium have been predicated upon its resistance to certain types of corrosion. For these uses a thin plate of titanium on a less expensive metal like iron, nickel, copper, etc. will serve as a satisfactory substitute for pure titanium. Titanium plate offers the advantage that the small weight of titanium actually deposited would not unduly increase the cost of the final object.

Accordingly the prime object of this invention is the provision of a technically operative process for securing an adherent titanium plate upon a base metal.

Briefly stated, the process of this invention comprises the electroplating of titanium upon a base metal using a fused salt as electrolyte and using relatively pure titanium as the anode. The fused salt is predominantly an alkali or alkaline earth halide, the metal of which is substantially insoluble therein.

A major criterion for the technical feasibility of titanium plating lies in the anhydrous, more specifically the oxygen-free, nature of the electrolyte during plating operations. As aforementioned, even very small percentages of oxygen in titanium metal are detrimental, and this holds true even in a thin film of titanium as is normally present on a plated surface. Substantial presence of oxygen in the fused salt electrolyte will result

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in oxygen occlusion on the titanium plate. At a rough estimate it appears that more than one percent oxygen in the electrolyte during plating operations is undesirable, and below 0.25% is preferable. As hereinafter used, the term "substantially oxygen-free" should be understood to intend an oxygen content of not more than about 1%.

There are three major sources of oxygen in the plating process. One is the atmosphere above the plating bath. Free oxygen or moisture in the atmosphere may dissolve directly into the bath, or react with the bath surface. To prevent or reduce the possibility of atmospheric contamination a dry inert atmosphere may be maintained above the bath. Argon or helium are preferred gases for an inert atmosphere. Oxygen in some form may be initially present in the salts which become the electrolyte. Entry of oxygen from this source may be prevented by starting with anhydrous, oxide-free halides. Oxygen may also be initially present in the anode and cathode. The surface of the cathode should be substantially free of an oxide film, and the anode should be relatively oxygen free. For the titanium anode, considering oxygen as the sole impurity, anodes containing less than about 90% titanium are not relatively oxygen-free titanium; they are undesirable because oxygen carried over onto the plate along with the titanium metal. Titanium of better than 99% purity is preferred, Kroll process grade or ductile titanium being best. In any event, during plating whether the oxygen enters from the atmosphere or is initially present in the electrolyte or the anode, the electrolyte should be kept substantially oxygen free to avoid detrimental effects on the titanium plate, going if necessary to the extent of blanketing the electrolyte with argon or helium, and/or starting with completely oxygen-free salts, and/or using ductile titanium for the anode, and/or any other suitable expedients.

A second major criterion for the technical feasibility of titanium plating is the characteristics of the fused salt electrolyte. As previously mentioned, tests have shown the sodium and lithium chlorides to be unsatisfactory electrolytes. It is believed that this result has been due to the comparatively high solubility of these metals in their molten halides. Anhydrous magnesium chloride has been found eminently satisfactory and is the specifically preferred electrolyte. It appears, however, from analysis of the experimental data that any molten halide of any alkali or alkaline earth metal in which that alkali or alkaline earth metal is soluble to an extent less than 2 mole percent may be satisfactory, provided: (A) that the halide is stable at the plating temperatures to an extent that there is less than about 2 mole percent dissociation into the free metal; (B) that the ionic titanium anodic reaction product is soluble in the halide; and (C) that titanium metal is not insoluble in the halide. At a rough estimate the titanium should be soluble to 0.5 mole percent or more in the halide. Generally speaking the requirements B and C are invariably met in halides which are otherwise satisfactory. Even so it is realized that this multiple criterion of stability and solubility eliminates many of the possible halides, but there are however halides which satisfactorily satisfy all these criteria, specifically magnesium chloride which is stable and has a magnesium solubility in the chloride of only about 1 mole percent. Mixed halides and complex salts are contemplated within the limits of the above criteria in the sense of the term stable halide.

At the start up of a plating cell where no titanium halide is initially present in the electrolyte, there is a short induction period during which titanium ions build up in the electrolyte. Measurements of the decomposition potential of the cell indicate that at first there is

decomposition of the electrolyte with concomitant deposition of the alkali or alkaline earth metal. Polarization, as well as the relative insolubility of the alkali or alkaline earth metal in the electrolyte, cause the decomposition voltage to vary during the induction period, but after a while the induction period ends, the decomposition potential having leveled off at about the zero potential of the titanium-titanium cell and plating of the titanium on the cathode occurs. Obviously this induction period may be shortened or even eliminated by initially introducing a minor proportion of the appropriate titanium halide into the electrolyte, e.g. $TiCl_3$ in an $MgCl_2$ electrolyte.

During the actual plating operation the cathode current densities must be within plating limits ranging, for example, from substantially 0 to 100 or even 200 amps. per square foot, a preferred range being between 5 and 50 amps. per square foot. It has been noted that the throwing power in titanium electroplating is good; it is apparently of the order of or better than nickel electroplating in aqueous medium. Therefore it is quite possible to plate titanium on an irregular metallic base without great concern for conforming the shape of the anode to that of the cathode.

Plating temperatures, of course, must exceed the melting point of the halide which forms the electrolyte. In actuality, however, it is preferred to operate far above this minimum level. Suitably the temperature should exceed the transformation point of the alpha titanium to beta titanium, i.e. about $880^\circ C.$ for pure titanium. Even temperatures of $1000^\circ C.$ may be attained or exceeded without detrimental effects. In fact in plating of mild steel a particularly retentive plate is obtainable at $1000^\circ C.$, apparently because at this elevated temperature titanium is soluble in the steel so that the plating process appears to proceed as follows. At first the titanium being plated on to the steel dissolves directly into the surface of the steel; as the plating continues the percentage of titanium in the outermost surface layer gradually increases until an actual plate of titanium is established at the surface layers. In the final product the titanium plate appears to be bonded to a titanium-iron alloy which in turn merges into the ferrous material of the steel base. This type of plate is tenaciously held on the base object. Repeated heating and cooling cycles, and bending of a test specimen failed to dislodge the titanium plate.

The upper temperature limit for plating is both theoretical and practical—the melting point of the cathode, the boiling point of the electrolyte, or the point at which the dissociation of the electrolyte begins to greatly exceed the 2 mole percent level. In any event it would not be desirable to operate above about $1500^\circ C.$ if only because of the problems involved in constructing a cell to withstand such temperatures.

Among the possible applications of this invention is the direct electroplating of pure titanium on less expensive base metals. It may even become desirable to plate titanium on a titanium base. It may be desirable on occasion to co-plate an alloy of titanium much in the manner that brass is plated. The titanium may be plated on an undercoat metal, e.g. copper, nickel, in lieu of directly plating on the base metal. Also contemplated is electroforming in which a massive coating of titanium is plated on a metallic base and then, if desired, stripped. All of these contemplated applications are to be understood as falling within the sense of the term plating as used in the claims, and the term titanium as used in the claims should also be understood to include alloys thereof with other metals.

Zirconium is so closely allied to titanium that it has been called a non-identical twin of titanium. It, too, may be plated under the same conditions as herein above delineated for titanium and is expressly contemplated as falling within the scope of this invention.

The following specific examples are included as illustrative of this invention.

Example 1

A cell was constructed using a four-inch iron pipe, welded shut at its bottom. Anhydrous magnesium chloride electrolyte filled the cell to a depth of four inches. A one-half inch circular bar of Kroll grade titanium was centrally positioned in the cell, extending to within $1\frac{1}{2}$ inches from the bottom. The cell was placed inside an electric furnace and an argon atmosphere was maintained during the entire run. Once operating temperature was attained, flow of direct current through the cell was initiated, the titanium forming the anode and the pipe the cathode. The applied voltage was periodically varied to maintain current flow at desired levels. From time to time the current level was shifted. The open current voltage or decomposition potential was measured to give an indication of cell operation. The following tabulation shows the operational characteristics of the run.

Total Transfer of Electrical Charge Ampere, Minutes	Current during Period, Amps.	Open Circuit Voltage at End of Period, Volts	Applied Voltage during Period, Volts
0-15	0.5	-0.4	0.45
15-55	0.5-3.0 Step-wise Rise.	0	0.5-2.50.
55	0.5-5.0 Step-wise Rise.	0.16 Linear Rise.	2.50±0.50.
55-105	5.0	0.70 Sharp Rise.	3.65 Sharp Rise.
105-157	5.0	.80	4.0±0.8.
157-227	7.0	.85	3.1±0.1.
227-287	9.5±0.5	0.03	3.1-1.6.
287-335	9.5±0.5	0.70	1.7±0.1.
335-670	9.5±0.5	0.70	1.9±0.1.
670-1,200	9.5±0.5	0.10	1.8±0.4.
		0.00	2.2±0.3.

The induction period ended at about the 600 ampere minute point when within the limits of the experimental error substantially the zero potential of a titanium-titanium cell was attained. Thereafter titanium plating occurred. During this entire run the cathode current densities ranged from 1.2 amperes per square foot at the beginning to 23 amperes per square foot at the end, anode current density respectively ranging from 19 to 360 amperes per square foot.

Example 2

Using the same cell and conditions but changing electrolyte, a second run was made; fresh $MgCl_2$ electrolyte was used, and 3 grams of $TiCl_3$ added to it. The induction period was shortened to about 300 ampere minutes, but otherwise the operational characteristics of the cell were substantially the same.

After the runs of Examples 1 and 2 the cell was disassembled and the pipe cut up for examination. A photomicrograph showed that a titanium plate about 2 mils thick had formed on the pipe wall and about an equal depth of a titanium-iron transition zone underlay the plate. Repeated heating and cooling (to $1000^\circ C.$), and a bending test failed to dislodge the plate.

Example 3

In a similarly constructed cell, operated at $500^\circ C.$, using an electrolyte of the lithium chloride, potassium chloride eutectic, no significant titanium plate was obtained on the cathode.

What is claimed is:

1. The process of plating a metal from the group of titanium and zirconium which comprises passing direct current through a cell composed of a relatively oxygen-free anode made of said metal, a substantially oxygen-free fused salt electrolyte, and a basis metal cathode at plating cathode current densities not exceeding 200 amperes per square foot, said molten salt electrolyte consisting essentially of magnesium chloride, and a plating

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temperature above the alpha-beta transition point of the metal selected from said group being maintained.

2. The process of claim 1 wherein said electrolyte and said anode each have less than 1% oxygen therein.

3. The process of plating a metal from the group of titanium and zirconium which comprises passing direct current through a cell formed of a relatively oxygen-free anode formed from said metal, a substantially oxygen-free molten magnesium chloride electrolyte and a basis metal cathode, the cathode current densities not exceeding 100 amperes per square foot and the temperature exceeding the alpha-beta transition point of the metal selected from said group.

4. The process of claim 3 wherein said electrolyte and said anode each have less than 1% oxygen therein, and an inert atmosphere is maintained above said cell.

5. The process of plating titanium which comprises passing direct current through a cell maintained at a temperature above the alpha-beta transformation point of titanium, said cell being formed of a ductile titanium anode, a substantially oxygen-free magnesium chloride electrolyte and a basis metal cathode, the current density at the cathode falling in the range of 5 to 50 amperes per square foot.

6. The process of plating titanium which comprises passing direct current through a cell maintained at a temperature in the range of about 880° C. to about 1500° C., said cell being formed of a ductile titanium anode, a substantially oxygen-free electrolyte essentially consisting of magnesium chloride, and a metallic cathode, the current density at the cathode falling in the range of

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5 to 50 amperes per square foot and said cell being blanketed with argon.

7. The process of plating a metal selected from the group consisting of titanium and zirconium which comprises passing direct current through a cell composed of an anode made of a metal selected from said group having less than 10% oxygen therein, a basis metal cathode, and a fused salt consisting essentially of anhydrous magnesium chloride at a cathode current density not exceeding 200 amperes per square foot, and maintaining the temperature above the alpha-beta transformation point of the metal selected from said group.

8. The process of claim 1 wherein the electrolyte initially contains a minor proportion of titanium halide therein.

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