

1

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METHOD FOR OBTAINING THICK ADHERENT COATINGS OF PLATINUM METALS ON REFRACTORY METALS

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The invention herein described and claimed may be used by or for the Government of the United States of America for governmental purposes without the payment of royalties thereon or therefor.

This invention relates to electrodeposition of metals, particularly platinum metals, on a metal substrate.

The platinum metals, i.e., palladium, ruthenium, rhodium, osmium, iridium and particularly platinum itself, are very valuable in formation of protective coatings on various metal bases. Formation of thick, adherent deposits of such metals on refractory metals such as tungsten and molybdenum are of particular value in preparation of rocket components, turbine blades, atmospheric re-entry vehicles and the like. It has been found, however, that satisfactory thick, adherent deposits of the platinum metals on refractory metal bases cannot be obtained by electrodeposition from an aqueous solution, although such deposition would be highly desirable from the standpoint of convenience and economy.

It is therefore an object of the present invention to provide a method for electrodeposition of a thick adherent deposit of a platinum metal, from an aqueous solution of the platinum metal, on a metal base, particularly a refractory metal base.

It has now been found that this objective may be achieved by treatment of the metal substrate cathodically in a fused salt bath containing ions of a platinum metal and subsequently subjecting the thus treated metal substrate to electrolysis in an aqueous solution of ions of a platinum metal.

The initial cathodic treatment of the metal substrate in the fused salt bath results in formation of a thin, adherent coating of the platinum metal in intimate contact with the metal substrate. A thick, adherent deposit of any of the platinum metals may then be applied by electrodeposition from an aqueous electrolyte.

The thickness of the initial coating from the fused salt bath is not critical, it being only necessary to develop a thickness that will insure complete coverage of the metal substrate. Suitable initial coatings may be in the thickness range of about 0.000005 to 0.0001 inch. Optimum thickness of the initial coating will depend on the substrate material and the platinum metal that is used to form the initial coating.

Suitable thickness of the final coating from the aqueous bath will depend on the application for which the coating is intended. This may extend over a thickness range of about 1 mil to 25 mils (0.001 to 0.025 inch).

Any of the platinum metals may be used as the initial or base coating for any platinum metal subsequently deposited from aqueous solution. The intended use of the coating will determine which combination of metals is most suitable. Certain combinations offer better high temperature or oxidation characteristics while other combinations offer better corrosion resistance.

Temperature, current densities and compositions of plating baths are not critical in either the initial coating or in the deposition from the aqueous bath. Optimum values of these variables will depend on the metals being deposited, desired thickness of the deposits, nature of

2

the metal substrate, etc., and are best determined empirically. A fused salt bath containing 100 percent sodium cyanide or potassium cyanide or a mixture of about equal parts of each has been found to constitute a very satisfactory bath for the initial deposition. Addition of sodium chloride in amounts up to about 50 percent by weight to the fused bath may also be desirable as shown in the examples below. About 1 to 20 parts by weight of the platinum metal salt in combination with 100 parts by weight of the above cyanide or 100 parts by weight of cyanide plus chloride fused salt bath generally gives very satisfactory results in providing an adherent initial coating of the platinum metal on the metal substrate. With the above bath compositions a temperature of about 600° to about 900° C. and a current density of about 10 to 900 ma. per cm.² give good results.

An aqueous plating bath containing about 5 to 100 grams per liter of platinum or palladium diamino dinitrite salt and about 20 to 100 grams per liter of sulfamic acid has been found very effective for aqueous deposition of these metals. For palladium, a solution of about 20 to 100 grams per liter of palladium chloride with sufficient hydrochloric acid to provide a pH of about zero to 0.5 is very effective. This solution may also contain ammonium chloride in an amount up to about 50 grams per liter. Any platinum metal salt that ionizes under the operating conditions employed in electrodeposition may be used in either the fused salt bath or the aqueous bath. Examples of salts that may be used in the fused salt bath are PdCl₂, PtCl₂, RhCl₃, H₂Pt(OH)₆, K₂IrCl₆, Na₂PdCl₄, K₂PdCl₄, Na₃RhCl₆, OsCl₃, IrCl₃ and RuCl₃. Furthermore, the platinum metal ion may be obtained from a platinum metal anode by A.C. electrolysis as in Example 1, below.

Examples of salts that may be used in the aqueous bath are Pt(NH₃)₂(NO₂)₂, Pd(NH₃)₂(NO₂)₂, H₂PtCl₆, PtCl₂, PdCl₂, Rh₂(SO₄)₃, Rh₂O₃·5H₂O and (NH₄)₂IrCl₆.

Although the process of the invention is of particular value in coating molybdenum or tungsten, it is also applicable to coating of other metals such as stainless steels, nickel, Inconel, titanium and zirconium. Furthermore, the metals forming the final coating (from aqueous solution) are not limited to the platinum metals but may comprise any metals which could normally be plated on the surface of a platinum metal.

The following examples will serve to more specifically illustrate the invention.

Example 1

A fused salt electrolyte was prepared using two platinum electrodes immersed in 100 grams of sodium cyanide at 615° C. with 2 to 2.5 amperes A.C. The electroplating was done in a platinum crucible which was placed in an argon filled Inconel furnace tube. The tube was heated by resistance rods placed in a refractory brick framework. A positive flow of argon was maintained around the crucible during operation of the molten cyanide plating bath, to prevent undue amounts of moisture or oxygen from reacting with the molten electrolyte. Thirty grams of sodium chloride were added to the electrolyte and a molybdenum cathode was substituted for one of the platinum electrodes. Electroplating was continued for one-half hour at 800° C. and a current density of 112 ma./cm.². The molybdenum was then allowed to cool to room temperature in the inert atmosphere. It was washed in water and plated in an aqueous platinum electrolyte consisting of platinum diamino dinitrite, 65.7 grams per liter, and sulfamic acid, 90 grams per liter, at a current density of 15 amperes per square foot and a temperature of 75° C. A platinum anode at a current density of 7.5 amperes per square foot was employed. An adherent deposit of

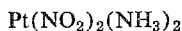
platinum 1.5 mils thick was made in 400 minutes. The source of platinum ion in the fused salt bath in this example was pure platinum metal which was dissolved from the anode during electrolysis by the A.C. current.

Example 2

Molybdenum was treated cathodically in a fused electrolyte containing 100 grams of sodium cyanide, 30 grams of sodium chloride and about 0.1 gram platinum ions in the form of PtCl_2 for one hour at 816°C . at a current density of 400 ma./cm.². An adherent coating of palladium, 2.2 mils thick, was then electroplated on the cathodically treated molybdenum from an aqueous bath of PdCl_2 . The initial plating with Pt in this example was applied in a pot furnace exposed to air rather than in an inert atmosphere as in Example 1.

Example 3

In this example an adherent coating of platinum was plated on molybdenum after treating the molybdenum cathodically in a fused salt bath consisting of 100 grams of KCN and 2 grams of PtCl_2 at 816°C . and a current density of 40 amperes per square foot per 120 minutes. The platinum was plated from an aqueous bath of



In this example the initial coating of Pt was also applied in a pot furnace exposed to air.

Example 4

In this example an adherent deposit of platinum, 4.9 mils thick, was electroplated on molybdenum after first treating the molybdenum cathodically at 816°C . for 123 minutes at a current density of 41 amperes per square foot in an electrolyte consisting of 100 grams of KCN and 2 grams of PdCl_2 . The platinum was again plated from an aqueous solution of $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$. A pot furnace was used for the initial deposition (of Pd) as in Examples 2 and 3.

Obviously many changes can be made in the details of operation of the process of the invention without departing from the essential spirit and scope of the invention, e.g., temperatures, current densities and compositions of both the fused salt and aqueous baths may be varied widely; optimum conditions can be determined readily by one of ordinary skill in the art.

Since the process of the invention results in greatly improved adhesion of the electroplate to the basis metal, the reliability of the composite coating is greatly enhanced. As a result effective protective coatings can be applied to the aforementioned components such as rocket components, turbine blades and re-entry vehicles, which are subject to severe conditions of temperature and friction.

What is claimed is:

1. A method for depositing an adherent coating of a metal on a metal substrate by electrodeposition of the metal from an aqueous solution of a compound of the metal comprising forming an initial coating of a platinum metal on the metal substrate by electrodeposition from a fused salt bath containing ions of the platinum metal and

subsequently subjecting the thus coated metal substrate to electrodeposition of the metal from aqueous solution.

2. The method of claim 1 in which the substrate is a refractory metal.

3. The method of claim 2 in which the substrate is molybdenum.

4. The method of claim 2 in which the substrate is tungsten.

5. The method of claim 1 in which the substrate is a metal selected from the group consisting of stainless steel, nickel, Inconel, titanium and zirconium.

6. The method of claim 1 in which the initial coating is of platinum.

7. The method of claim 1 in which the initial coating is of palladium.

8. The method of claim 1 in which the metal deposited from aqueous solution is a platinum metal.

9. The method of claim 8 in which the metal deposited from aqueous solution is platinum.

10. The method of claim 9 in which the platinum is deposited from a solution of platinum diamino dinitrite.

11. The method of claim 10 in which the aqueous solution additionally contains sulfamic acid.

12. The method of claim 8 in which the metal deposited from aqueous solution is palladium.

13. The method of claim 12 in which the palladium is deposited from a solution of PdCl_2 .

14. The method of claim 1 in which the fused salt bath comprises an electrolyte from the group consisting of NaCN, KCN and a mixture of the two.

15. The method of claim 14 in which the fused bath additionally contains sodium chloride.

16. The method of claim 1 in which the ions of a platinum metal in the fused salt bath are derived by dissolution from the anode by A.C. electrolysis.

17. The method of claim 1 in which the ions of a platinum metal in the fused salt bath are supplied by addition of a compound of the platinum metal.

18. The method of claim 17 in which the platinum metal compound is PtCl_2 .

19. The method of claim 17 in which the platinum metal compound is PdCl_2 .

20. The method of claim 1 in which the deposition from the fused salt bath is conducted at a temperature of about 600° to 900°C . and a current density of about 10 to 900 ma. per cm.².

References Cited by the Examiner

UNITED STATES PATENTS

2,093,406	9/1937	Atkinson	204—39
2,457,021	12/1948	Wise et al.	204—47
2,719,797	10/1955	Rosenblatt et al.	204—40 X
2,739,107	3/1956	Ricks	204—40 X
2,805,192	9/1957	Brenner	204—40 X
2,929,766	3/1960	Withers et al.	204—39 X
2,984,604	5/1961	Duva et al.	204—47
3,007,855	11/1961	Ellwood	204—40 X

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