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PROCESS FOR TITANIDING BASE METALS

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ABSTRACT OF THE DISCLOSURE

A titanide coating is formed on specified base metal compositions by forming an electric cell containing said metal composition as a cathode joined through an external electrical circuit to a titanium anode using a specified fused salt electrolyte maintained at a temperature of from 900° C. up to the melting point of the metal composition. This cell generates electricity, but, if desired, and external E.M.F. may be impressed providing the current density does not exceed 10 amperes/dm.^{2}. The titanium diffuses into the base metal to form a tight, adherent coating composed of titanium and the base metal. This process is useful for forming such coatings on the base metal.

This invention relates to a method for metalliding a base metal composition. More particularly, this invention is concerned with a process for titaniding a base metal composition in a fused salt bath.

It is known that titanium can be electrodeposited on certain metal compositions having melting points above 1000° C. to form a firmly adherent layer of the deposited metal joined to the metal compositions by a metal-to-metal bond by electrodeposition in a fused salt bath. This method requires, however, that high current densities be employed together with high temperatures. Current densities in the range of 25–200 amperes/dm.^{2} are not unusual.

I have now discovered that a uniform tough, adherent titanide coating can be formed on a specific group of metals employing low current densities, that is, current densities in the range of 0.05–10 amperes/dm.^{2}. This electrodeposition of titanium is possible if certain critical steps are taken to insure the substantial absence of oxygen and oxide salts in the fused salt bath.

In accordance with the process of this invention, the titanium metal is employed as the anode and is immersed in a fused salt bath composed essentially of a member of the class consisting of the alkali metal fluorides and mixtures thereof and mixtures of the alkali metal fluorides with strontium or barium fluorides and containing from 0.01–5 mole percent of titanium fluoride. Higher concentrations of titanium fluoride can be used but no commensurate advantages are obtained thereby. Excess titanium fluoride sometimes reduces the effectiveness of the salt as a fluxing solvent. The cathode employed is the base metal upon which deposit is to be made. I have found that such a combination is an electric cell in which an electric current is generated when an electrical connection, which is external to the fused bath, is made between the base metal cathode and the titanium anode. Under such conditions, the titanium dissolves in the fused salt bath and titanium ions are discharged at the surface of the base metal cathode where they form a deposit of titanium which immediately diffuses into and reacts with the base metal to form a titanide coating.

The alkali metal fluorides which can be used in accordance with the process of this invention include the fluorides of lithium, sodium, potassium, rubidium and cesium. It is preferred to employ an eutectic mixture of sodium fluoride and lithium fluoride because some free alkali metal is generated and the other alkali metals, such as potassium, rubidium and cesium are more volatile at the temperatures at which the cell is operated with the obvious disadvantages. It is particularly preferred to employ lithium fluoride as the fused salt bath in which the titanium fluoride is dissolved, because at temperatures of 900° C. to 1100° C., lithium metal is not volatilized to any appreciable extent. Mixtures of the alkali metal fluorides with strontium fluoride and barium fluoride can also be employed as a fused salt in the process of this invention. Calcium and magnesium fluorides can also be mixed with the alkali fluorides but these salts often permit the incorporation of small amounts of calcium and magnesium in the diffusion coating and thus are usually not desirable.

The chemical composition of the fused salt bath is critical for optimum titaniding results. The starting salt should be as anhydrous and as free of all impurities as is possible or should be easily dried or purified by simply heating during the fusing step. The process must be carried out in the substantial absence of oxygen since oxygen interferes with the process by forming titanium oxide, thereby preventing a firmly adhering film of titanium from being deposited on the base metal cathode. Thus, for example, the process can be carried out in an inert gas atmosphere or in a vacuum. By the term "substantial absence of oxygen" is meant that neither atmospheric oxygen nor oxides of metals are present in the fused salt bath. The best results are obtained by starting with reagent grade salts and by carrying out the process under vacuum or an inert gas atmosphere, for example, in an atmosphere of argon, helium, neon, krypton or xenon.

I have sometimes found that even commercially available reagent grade salts must be purified further in order to operate satisfactorily in my process. This purification can be readily done by utilizing scrap metal articles as the cathodes and carrying out the initial titaniding runs with or without an additional applied voltage, thereby plating out and removing from the bath those metal impurities which interfere with the formation of high quality titanide coatings.

I have found that in order for the electrolytic cell of this process to work properly and to form a proper titanide coating which is not scaly due to the presence of titanium oxide, it is necessary to remove essentially all traces of oxygen and oxide compounds from the fused salt bath and to employ an inert atmosphere over the salt bath at all times to prevent the diffusion of oxygen into the salt bath. Although it has been possible in other metalliding situations to remove oxygen from the fused salt bath by employing a carbon anode and running the bath as an electrolytic cell to remove the oxides and oxygen by means of the carbon anode, I have found that insofar as titaniding is concerned, a carbon anode does not remove oxygen to a sufficient degree so as to enable the cells to be run without forming the undesirable titanium oxide coating. I have found that the last traces of oxygen and oxides can be removed from the fused salt bath by maintaining the fused salt bath under an inert atmosphere and placing in the bath titanium strips or chips of titanium for a period of time until the titanium strips or chips upon removal from the bath showed no evidence of pitting or other deterioration of the glossy, shiny surface of the titanium, due to the reaction of the titanium with oxygen.

I have also found that when the metal to be titanided is vanadium, niobium, tantalum, chromium, molybdenum or tungsten, it is necessary to conduct the titaniding process in the substantial absence of carbon, and carbonaceous material, because carbon forms a very stable metal carbide on the surface of such base metals thereby rendering it impossible to further titanide the base

metal and giving less firmly adhering deposits. I have found that carbon can be removed from the fused salt bath by operating it as a cell employing as a cathode, the metals such as vanadium or niobium, until the carbide coating is no longer formed on the surface of the metal. Filtering of the salt through finely woven wire cloth, especially of materials which will react with the carbon to make metal carbides, is also a satisfactory means of removing carbon from the molten salts. By the term carbonaceous material as used herein is meant elemental carbon in any of its forms and organic and inorganic compounds which contain carbon in their molecular structure. Such inorganic compounds or the metal carbides such as calcium carbide, molybdenum carbide, etc., and metal salts such as sodium carbonate, etc. Such organic compounds are hydrocarbon such as methane, ethane, dodecane, etc., and others which are readily apparent to those skilled in the art.

The base metals which can be titanided in accordance with the process of this invention includes the metals having atomic numbers 23–29, 41–47 and 73–79, inclusive. These metals are, for example, vanadium, chromium, manganese, iron, cobalt, nickel, copper, niobium, molybdenum, technetium, ruthenium, rhodium, palladium, silver, tantalum, tungsten, rhenium, osmium, iridium, platinum and gold. Alloys of these metals with each other or alloys containing these metals as the major constituent, that is, over 50 mole percent, alloyed with other metals as a minor constituent, that is, less than 50 mole percent, can also be titanided in accordance with my process, providing the melting point of the resulting alloy is not lower than the temperature at which the fused salt bath is being operated.

In order to produce a reasonably fast plating rate and to insure the fusion of the metal into the base metal to form a titanide, I have found it desirable to operate my process at a temperature no lower than about 900° C. It is usually preferred to operate at temperatures of from 900° C.–1100° C. At these temperatures, I prefer to employ lithium fluoride as the fused salt and even more preferably, from 1000°–1100° C.

When an electrical circuit is formed external to the fused salt bath by joining the titanium anode to the base metal cathode by means of a conductor, an electric current will flow through the circuit without any applied electromotive force. The anode acts by dissolving in the fused salt bath to produce electrons and the anode metal ions. The electrons flow through the external circuit formed by the conductor and the metal ions migrate through the fused salt bath to the base metal cathode to be titanided, where the electrons discharge the metal ions as the titanide coating forms. The amount of current can be measured with an ammeter which enables one to readily calculate the amount of metal being deposited on the base metal cathode and being converted to the titanide layer. Knowing the area of the article being plated, it is possible to calculate the thickness of the titanide coating formed, thereby permitting accurate control of the process to obtain any desired thickness of the titanide layer.

Although the process operates very satisfactorily without impressing any additional electromotive force on the electrical circuit, I have found it possible to apply a small voltage when it is desired to obtain constant current densities during the reaction, and to increase the deposition rate of the titanium being deposited without exceeding the diffusion rate of the titanium into the base metal cathode. The additional E.M.F. should not exceed 1.0 volt and preferably should fall between 0.1 and 0.5 volt.

When it is desirable to apply additional voltage to the circuit in order to shorten the time of operation, the total current density should not exceed 10 amperes/dm.^{2}. At current densities above 10 amperes/dm.^{2}, the titanium deposition rate exceeds the diffusion rate and the base metal cathode becomes coated with a plate of titanium.

Since the diffusion rate of titanium into the cathode article varies from one material to another, with temperature, and with the thickness of the coating being formed, there is always a variation in the upper limits of the current densities that may be employed. Therefore, the deposition rate of the iding agent must always be adjusted so as not to exceed the diffusion rate of the iding agent into the substrate material if high efficiency and high quality diffusion coatings are to be obtained. The maximum current density for good titaniding is 10 amperes/dm.^{2}, when operating within the preferred temperature ranges of this disclosure. Higher current densities can sometimes be used to form coatings with titanium but in addition to the formation of a metallide coating, plating of the iding agent occurs over the diffusion layer.

Very low current densities (0.01–0.1 amp/dm.^{2}) are employed when diffusion rates are correspondingly low, and when very dilute surface solutions or very thin coatings are desired. Often the compostiion of the diffusion coating can be changed by varying the current density, producing under one condition a composition suitable for one application and under another condition a composition suitable for another application. Generally, however, current densities to form good quality titanide coatings fall between 0.5 and 5 amperes per dm.^{2} for the preferred temperature ranges of this disclosure.

If an applied E.M.F. is used, the source—for example, a battery or other source of direct current—should be connected in series with the external circuit so that the negative terminal is connected to the external circuit, terminating at the metal being titanided and the positive terminal is connected to the external circuit terminating at the metal anode. In this way, the voltages of both sources are algebraically additive.

As will be readily apparent to those skilled in the art, measuring instruments such as voltmeters, ammeters, resistances, timers, etc., may be included in the external circuit to aid in the control of the process.

Because the tough adherent corrosion resistant properties of the titanide coatings are uniform over the entire treated area, the titanide coated metal compositions prepared by my process have a wide variety of uses. They can be used to fabricate reaction vessels for chemical reactions, to make gears, bearings and other articles requiring hard, wear-resistant surfaces. Other uses will be readily apparent to those skilled in the art as well as other modifications and variations of the present invention in light of the above teachings.

In the specification and claims I use the term "titanide" to designate any solid solution or alloy of titanium and the base metal regardless of whether the base metal does or does not form an intermetallic compound with titanium in definite stoichiometric proportions which can be represented by a chemical formula.

The following examples serve to further illustrate my invention. All parts are by weight unless otherwise stated.

EXAMPLE 1

Lithium fluoride (9534 grams) was charged into a Monel liner (5½" diameter x 17¾" deep) and the liner placed in a mild steel pot 6" in diameter x 18" deep. The pot was sealed with a cover of nickel plated steel 11" x 1", containing a water channel for cooling, two ports (2¼" in diameter) for glass electrode towers, and two 1" holes for a thermocouple probe and a gas bubbler. The steel pot was then placed in a 7" diameter x 20" deep electric furnace in which an inert gas atmosphere could be maintained to prevent oxidation of the steel pot. The lithium fluoride was then melted under vacuum. Argon was introduced into the cell and with an argon flush and bypass to prevent air from diffusing back into the cell, 0.3 mole percent of titanium trifluoride was added to the lithium fluoride.

A series of six runs at 1000° C. were then made in

order to clean up the fused salt bath of oxides which greatly interfere with the formation of the titanide diffusion coatings. These runs were made employing nickel strips (6" x 1" x 0.025") as cathodes and titanium strips as anodes. The improvement in the operation of this cell is readily apparent from the following table, in which coulombic efficiences are based on a valence change of three for titanium.

TABLE I

Run No.	Time (Min.)	Volts (anode polarity)	Amps	Ti Gain, Grams	Percent Coulombic Efficiences
1	60	−0.5 to +0.55	5.0	0.350	14
2	60	−0.5 to +0.5	5.0	0.453	18
3	60	−0.5 to +0.3	0.2	0.500	42
7 ampere hours of clean-up, no measure of efficiency of titaniding.					
4	30	−0.5 to −0.25	0.25	0.082	110
5	60	−0.5 to −0.02	1.0	0.609	103
6	30	−0.5 to +2.25	2.0	0.546	93

The operational data of runs 4 and 5 is given in the following two tables.

Time (min.)	Volts (anode polarity)	Amps	Remarks
0	−0.475	0.1	Operating as a battery.
1	−0.330	0.25	Extermal EMF applied.
5	−0.300	0.25	
30	−0.250	0.25	Current off.
30:10	−0.380	0	
31	−0.400	0	

Run #5

Time (min.)	Volts (anode polarity)	Amps	Remarks
0	−0.500	0.13	Operating as a battery.
1	−0.260	1.0	External EMF applied.
5	−0.125	1.0	
60	−0.016	1.0	Current off.
60:10	−0.112	0	
61	−0.120	0	

The data clearly show the battery characteristics of the process and the ease with which titanium diffuses into nickel.

The titanide coating on the nickel strip of Run #5 was 4 mils thick, very shiny, smooth, flexible and measured 700 in Knoop hardness. It was strongly resistant to the corrosive action of concentrated nitric acid. X-ray emission analysis showed both titanium and nickel on the surface of the coating with no other materials present.

In the first three runs of Table I, the cathode samples were very black and were similar in appearance to the titanium anode strips. In each subsequent run, both the cathodes and the anodes became progressively cleaner until by Run #6, both the nickel cathode strips and the titanium anode strips were quite shiny and smooth. After removing the crust from the anode strips (Runs 1–3), the anode strips were found to have sustained weight losses greatly in excess of the theoretical, but when the anodes kept their shiny appearance (Runs #5 and 6), weight losses were essentially theoretical. X-ray analysis of the encrusted layers showed Ti_20 and TiO, which demonstrates the deleterious effects of oxygen in the system, because the formation of the titanium oxides causes the poor titaniding results. It has been found that after the bath has been cleaned electrolytically, the reintroduction of only a few cubic centimeters of air into the cell will seriously affect the ability to make quantitative runs, or good titanide coatings. It was found that oxygen, in the salt as oxides, could not be removed from the titanium-containing bath by electrolysis employing a carbon anode.

A large number of other metals were titanided in accordance with the procedure given in Example 1 and the results are given in Table II along with a description of the coatings. Most of the coatings are diffusion coatings but by the proper adjustment of temperature and current density, different thicknesses of diffusion and plating can be obtained.

TABLE II

Run No.	Metal	Temp., ° C.	Time, Mins.	Current Density, Amp/dm.^{2}	Wt. Gain, Grams	Percent Coulombic Efficiencies	Description of Coating
7	Co	1,000	60	0.5	0.063	100	Shiny, smooth, very hard, moderately flexible, 0.5 mil. coat, resistant to HNO_3, all diffusion.
8	Mild Steel	1,000	120	0.5	0.465	80	Bright mat finish, smooth, very hard, moderately flexible 0.5 mil. coat, all diffusion. Improved resistance to hot HNO_3.
9	do	1,000	6	5.5	0.126	100	Shiny, smooth, hard. Improved resistance to hot HNO_3.
10	V	1,100	120	3.0	0.108	73	Very shiny, smooth and hard, ½ mil. thick, all diffusion, very resistant to HNO_3.
11	Cr	1,100	30	2.9	0.023	39	Moderately shiny, smooth, extremely hard, 0.25 mil. thick, all diffusion.
12	Cu	900	120	0.7	0.158	43	Dull finish, poorly defined, soft coating, all diffusion.
13	Ta	1,100	10	5.0	0.030	51	Shiny, smooth, hard, ½ mil. coat, improved high temperature oxidation resistance.
14	Mo	1,090	6	6.25	0.164	91	Shiny, smooth, slightly hard, ½ mil., some diffusion coating, mostly plating, very flexible.
15	Mo	1,100	60	0.6	0.213	72	Bright mat finish, smooth, hard 0.5 mil. diffusion coat, no plating, brittle.
16	Nb	1,100	3	6.5	0.125	84	Bright mat finish, smooth, soft, flexible 0.5 mil. thick, some diffusion, mostly plating.
17	Nb	1,100	60	2.0	0.201	68	Shiny, smooth, moderately hard, very flexible, 0.5 mil. thick, mostly diffusion.
18	Rodar	1,000	60	0.5	0.101	85	Shiny, smooth, very hard, 1 mil. thick, flexible, resistant to HNO_3, all diffusion.
19	304 S.S	1,000	60	1.6	0.495	84	Shiny, smooth, very hard, moderately flexible, 1 mil. coat, mostly diffusion.
20	Pd	1,000	6	4.3	0.056	94	Bright mat finish, smooth, flexible, 1 mil. thick, all diffusion.
21	Pt	1,000	15	4.4	0.060	81	Bright, mat finish, smooth, flexible, 0.8 mil. thick, all diffusion.

It will, of course, be apparent to those skilled in the art that modification other than those set forth in the above examples can be employed in the process of this invention without departing from the scope thereof.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A method of forming a titanide coating on a metal composition having a melting point greater than 900° C., at least 50 mole percent of said metal composition being at least one of the metal selected from the class consisting of metals whose atomic numbers are 23–29, 41–47 and 73–79, said method comprising (1) forming an electric cell containing said metal composition as the cathode, joined through an external electrical circuit to a titanium anode and a fused salt electrolyte which consists essentially of a member of the class consisting of lithium fluoride, sodium fluoride, mixtures thereof and mixtures of said fluorides with strontium fluoride or barium fluoride, and from 0.01–5 mole perecent of titanium fluoride, said electrolyte being maintained at a temperature of at least 900° C. but below the melting point of said metal composition in the substantial absence of oxygen, (2) controlling the current flowing in said electric cell so that the current density of the cathode does not exceed 10 ameres/dm.^{2} during the formation of the titanide coating, and (3) interrupting the flow of electrical current after the desired thickness of the titanide coating is formed on the metal object.

2. The process of claim 1 wherein said fused salt electrolyte consists essentially of lithium fluoride and titanium fluoride.

3. The method of claim 1 which is also conducted in the substantial absence of carbonaceous materials.

4. The process of claim 1 wherein the absence of oxygen is obtained by using an inert atmosphere and by allowing titanium metal to be in contact with the fused electrolyte prior to carrying the the process of claim 1 until the oxygen has been depleted from the electrolyte bath.

5. The method of claim 1 wherein the metal composition is nickel.

6. The method of claim 1 wherein the metal composition is cobalt.

7. The method of claim 1 wherein the metal composition is vanadium.

8. The method of claim 1 wherein the metal composition is molybdenum.

9. The method of claim 1 wherein the metal composition is niobium.

10. The method of claim 1 wherein the metal composition is iron.

11. A product produced in accordance with the process of claim 1.

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