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METHOD OF FORMING TITANIUM COATING ON REFRACTORY BODY

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This invention relates to the formation of metallic coatings and is a continuation-in-part of my co-pending application, Serial No. 116,217, filed September 16, 1949, now abandoned. More particularly, it relates to titanium alloy coatings and to the bath and method or process for forming such coatings.

For many years, attempts have been made to coat surfaces with metals which have the ability to resist corrosion and which are characterized by an appreciable degree of passivity. A coating of titanium or a titanium alloy, hardened by a nitriding process, has been found to have excellent resistance to heat, acids, corrosion and wear. However, the lack of a commercially practicable coating procedure has deterred its general use.

The process of coating articles with titanium has presented an additional problem since titanium tends to oxidize in air. Consequently, in the prior art it has been necessary to operate a titanium coating process which involves high temperature in a vacuum or in an inert atmosphere.

The coating of ceramic ware by elementary zirconium and titanium is disclosed in U. S. P. 2,292,026 to Horace W. Gillett and the process is useful in the decoration of ceramic bodies. This method makes use of the ability of ductile titanium or zirconium to seize or adhere to glass and ceramic ware in general when the metal is rubbed against the surface. Kelley in U. S. P. 2,570,248 has also made use of titanium as a bonding agent between ceramic bodies and metal by a unique method wherein titanium hydride and a soldering metal are heated together on the surface of the ceramic article. Each of these prior art processes provide a method for bonding metals to ceramics, but certain disadvantages have been demonstrated which have hindered commercial adoption.

In the prior art it has also been customary to use metallic silver to form conductive coatings. One of the objections to the use of silver is that the adherence of its metallic film has not been completely satisfactory. In addition, the relatively high cost of silver has resulted in a correspondingly high cost in the coated article.

The problem of corrosion and wear has frequently been made by making entire articles from a suitable metal such as stainless steel. However, since corrosion begins as a surface reaction, a large portion of the costly metals in such articles serves no useful purpose in preventing the corrosion or wear. The titanium or titanium alloy coating of this invention eliminates such waste by localizing the protection to the surface of the article. As a result, the thickness of the coating need only be great enough to allow for normal wear.

Another problem which has been encountered with surface coatings has been the difficulty of coating internal parts of structures or small bores. Also, the coating may increase the dimensions of articles or alter the contours of intricate shapes. As a result, the articles must be remachined after coating or the dimensions of the base material must be decreased and the coating closely controlled.

It is, accordingly, one of the objects of this invention to provide a titanium or titanium alloy coating which is resistant to heat, acids, corrosion and wear. A further object of this invention is to provide an economical coating which is an integral part of the base material and which will not peel off. Another object is to provide an economical conductive coating firmly joined to a non-conductor. An additional object is to provide a novel and improved coating for non-conductors for titanium, in which the coating bath also serves as a flux to protect the titanium from oxidation and as a heating medium. Still another object is to provide a conductive coating which is serviceable at relatively high temperatures and is resistant to corrosion. Yet another object is to provide a method of coating a non-conductor with a strong basis metal which may be plated with other metals. Various other objects and advantages will be apparent as the nature of this invention is more fully disclosed.

The above objects are realized by my novel process which comprises immersing solid bodies into a molten salt bath of one or more alkali or alkaline earth halides and divalent titanium. During such immersion a coating of titanium is deposited on the surface of the immersed article. The thickness of the coating will depend upon the temperature of the bath and also on the time of immersion as well as the concentration of the titanium salt in the bath. The process is useful in coating of diverse materials such as glass, carbon and porcelain and it has also been found to apply to metallic surfaces such as iron, steel, nickel, brass, silver, copper, chromium, and the like. It is, therefore, possible to completely change the nature of the surface of solid bodies by the simple procedure of immersion in the indicated molten salt bath.

The container in which the bath is prepared must be able to withstand operating temperatures and to resist any large-scale reaction with the titanium or with the halide salts. A carbon crucible has proven very satisfactory and glass vessels may be used at lower temperatures. When using the latter, a titanium deposit will be formed on the glass and in this case, one is really using a titanium plated glass vessel. We soon arrive at a condition where the rate of deposition of titanium onto the glass becomes negligible. Needless to say, it is also possible to use titanium vessels. Iron and other metals may be used and these too become coated in time with titanium and then behave as titanium vessels. Unglazed ceramic containers are not ordinarily suitable for use as they are porous enough to alloy the salt bath to pass through the walls of the container. However, if the bath is heated by internal electrodes with the cooled exterior wall, a solid salt crust will form on the interior walls and prevent the fused salt bath from leaking out.

The salt bath as used in this process is particularly desirable because of its stability at high temperatures. The bath is composed of the halide salts of alkali or alkaline earth metals. A single salt may be used, or two or more of the salts may be mixed together. Usually a mixture will fuse at a lower temperature than any one of its components. The salts are heated to a temperature sufficiently high to fuse them; that is, higher than the melting point but less than the boiling point. The exact temperature range, of course, will vary with the composition of the salt bath.

Although any of the halide salts may be suitable for the bath, it is preferable not to use a bath composed solely of fluorides when the bath is to be used in contact with glass and ceramics since fluoride salts attack these mate-

rials of construction. In such a case, special treatment would be necessary to protect the container and specimen from the actions of the fluoride salts, but a simpler solution is to select vessels which are not subject to attack by fluoride salts. However, the presence of a small percentage of a fluoride salt in the bath would be beneficial in cleaning and etching the surface of ceramic articles which are to be coated.

The container for the salt bath may be heated externally by conventional heating methods such to raise the bath to the required temperature. If desired, the bath can be heated by internal resistance heating using titanium electrodes and alternating current. The molten salt baths useful in the invention may have a melting point as low as 900° F. or lower and when using such baths, glass is suitable as a container. For the higher temperature operations other structural bodies must be used due to the inability of glass to maintain its shape at the elevated temperatures which may reach as high as 1500° F. or higher.

The divalent titanium may be introduced into the fused salt bath in several different ways. The bath may be electrolyzed by passing a direct current between a titanium anode and a titanium cathode. The cathode may also be constructed of other substances, such as carbon or copper, or the crucible itself, if made of a conductive material, may serve as a cathode. Another method of securing divalent titanium is by the addition to the salt bath of a divalent titanium compound, such as titanium dichloride, titanium-di-iodide, or titanium dibromide, etc. These divalent salts are pyrophoric and must be handled with care. The divalent titanium may also be formed by electrolytically reducing tetravalent titanium compounds. Other procedures to secure the divalent titanium will suggest themselves to those skilled in the art.

The divalent salt bath may also be prepared by the partial reduction of titanium tetrahalides by metals such as sodium, potassium, lithium, calcium and magnesium. These reducing elements yield the subhalides of titanium when the tetrahalide of titanium is present in excess. The reaction product comprising the halide of the reducing metal and the titanium subhalide may readily be dissolved in a molten salt to give a bath suitable for use in this invention.

The surfaces to be coated by immersion within the titanium containing salt bath comprise diverse objects of a non-metallic nature such as glass, porcelain, silica, alundum, magnesia and the like, as well as metallic surfaces such as steel, copper, brass, etc. It is simply necessary to lower the object regardless of whether it is an oxidic body of the type mentioned or a metal body such as those which have been referred to above. Where the surface to be coated is smooth, the coating will consist of a brilliant film of titanium. If the surface is rough and irregular the coating will be dull gray in color.

Prior to immersion to obtain the coating, any surface dirt or grease should be removed from the object. This may be accomplished by washing, brushing or treatment with the solvent and then drying completely. When delicate ceramics are to be coated it may be necessary to preheat before immersing in the salt bath in order to prevent the material from cracking or shattering as a result of the quick change in temperature. This preheating is easily accomplished by suspending the article immediately above the bath for a short time since the heat rising from the bath will be sufficient for this purpose. No such precautions have been found necessary for the treatment of metal surfaces as damage is not encountered by use of the temperatures found useful in my coating operation.

After the objects, particularly ceramic objects, have been coated with the titanium film it may be desirable to electrodeposit a layer of copper on the titanium by means of a conventional cyanide copper plating bath or other suitable means. This copper coating will serve as an excellent base for plating other metals.

The following examples illustrate applications of the process, whereby a coating of titanium was applied.

Example I

A mixture of sodium chloride, potassium chloride and lithium chloride was fused in a glass beaker at 1000° F., in the following proportions:

Sodium chloride ..... 37 g. (6.4 mol per cent).
Potassium chloride ..... 396 g. (53.2 mol per cent).
Lithium chloride ..... 171 g. (40.4 mol per cent).

With the temperature maintained at 1000° F., a titanium anode and a titanium cathode were placed in the bath and a direct current of 48 amperes per square foot at 2 volts was then passed through the bath between the electrodes to introduce divalent titanium into the bath. When the bath turned black (indicating the presence of the divalent titanium) a strip of glass plate was immersed in it. During the coating process the electrolytic current was maintained for the purpose of assuring a suitable concentration of the divalent titanium in the molten salt. At the end of 20 minutes the strip was removed and was found to be coated with a briliant film 0.001 inch in thickness. The strip was then washed to remove all traces of the salt.

Example II

A mixture of calcium chloride and magnesium chloride was fused in a carbon crucible at 1250° F., in the following proportions:

Calcium chloride ..... 218 g. (39 mol per cent).
Magnesium chloride ..... 290 g. (61 mol per cent).

A direct current of 60 amperes per square foot at 3 volts was used between a titanium anode and a titanium cathode to produce divalent titanium. A piece of glass suspended in this bath acquired a dense titanium film in 20 minutes.

Example III

A mixture of sodium chloride and calcium chloride was fused in an iron crucible at 1100° F., in the following proportions:

Sodium chloride..... 143 g. (48.5 mol per cent).
Calcium chloride..... 285 g. (51.5 mol per cent).

A direct current of 60 amperes per square foot at 2.5 volts was used between a titanium anode and a titanium cathode. A glazed porcelain tube immersed in this bath acquired a dense titanium film after 20 minutes.

Example IV

A mixture of sodium chloride, potassium chloride, and sodium fluoride was fused in a carbon crucible at 1300° F., in the following proportions:

Sodium chloride..... 366 g. (62.5 mol per cent).
Potassium chloride ..... 93 g. (25.0 mol per cent).
Sodium fluoride..... 105 g. (12.5 mol per cent).

A direct current of 50 amperes per square foot at 2 volts was passed between a titanium anode and the carbon crucible serving as a cathode. A glazed porcelain tube acquired a bright metallic film after being suspended in the bath for 10 minutes.

Example V

A mixture of potassium chloride, lithium chloride, and sodium iodide was fused in a glass beaker at 900° F., in the following proportions:

Potassium chloride..... 276 g. (37 mol per cent).
Lithium chloride..... 224 g. (53 mol per cent).
Sodium iodide..... 150 g. (10 mol per cent).

A direct current of 40 amperes per square foot at 2 volts was passed between a titanium anode and an iron cathode

suspended in the bath. A plate of glass was completely covered with a bright metallic film after it had been immersed in the bath for 15 minutes.

Example VI

A mixture of sodium fluotitanate and potassium fluotitanate was fused in a zircon crucible at 1300° F., in the following proportions:

Sodium fluotitanate _____ 208 g. (50 mol per cent).
Potassium fluotitanate _____ 240 g. (50 mol per cent).

Using a carbon anode and a nickel cathode the cell was electrolyzed at 150 amperes per square foot at 3 volts until the bath turned black, indicating the presence of divalent titanium. A slab of polished Alundum was suspended in the bath and the electrolysis continued for 20 minutes. The Alundum was completely covered with a bright metallic film.

Example VII

A mixture of sodium chloride, potassium chloride, and lithium chloride was fused in a carbon crucible at 1200° F. The salts were present in the following proportions:

Sodium chloride_____ 37 g. (6.4 mol per cent).
Potassium chloride _____ 396 g. (53.2 mol per cent).
Lithium chloride _____ 171 g. (40.4 mol per cent).

With the temperature maintained at 1200° F., a titanium anode and a titanium cathode were placed in the bath, and a direct current having a density of 240 amperes per square foot at 3 volts was then passed through the bath between the electrodes to introduce divalent titanium into the bath. When the bath turned black (indicating the presence of divalent titanium), a strip of steel was immersed in it. During the coating process the electrolytic current was continued for the purpose of assuring a suitable concentration of the divalent titanium in the molten salt. After one hour of immersion in the bath, during which time the bath was maintained at a temperature of 1200° F., the steel strip was withdrawn from the bath and all salt was washed from the surface. The surface was coated with a gray film which was found to be resistant to corrosion from the air.

Example VIII

A mixture of sodium chloride and calcium chloride was fused in a carbon crucible at 1500° F., in the following proportions:

Sodium chloride_____ 143 g. (48.5 mol per cent).
Calcium chloride_____ 285 g. (51.5 mol per cent).

A direct current of 240 amperes per square foot at 3 volts was passed between a titanium anode and the carbon crucible serving as a cathode. After immersion in this bath for one-half hour, a strip of copper was found to have acquired a shiny metallic coating on the portion which had been immersed in the bath.

Example IX

A mixture of sodium fluotitanate and potassium fluotitanate was fused in a carbon crucible at 1500° F., in the following proportions:

Sodium fluotitanate _____ 208 g. (50 mol per cent).
Potassium fluotitanate _____ 240 g. (50 mol per cent).

Using a carbon anode and a nickel cathode the cell was electrolyzed at 200 amperes per square foot at 3 volts for six hours. A strip of brass acquired a shining metallic coating after being suspended in the bath for one-half hour.

Example X

A salt bath of the following composition was fused in a carbon crucible at 1000° F.:

	G.
Sodium chloride	37
Lithium chloride	171
Potassium chloride	396

While the bath was maintained at 1000° F., a direct current of 48 amperes per square foot at 2 volts was passed between a titanium anode immersed in the bath and the carbon crucible, serving as the cathode.

A magnesium oxide body (20 per cent porous) was heated to 1000° F. at a rate of about 300° F. per hour, and then immersed in the salt bath for one hour. After the body had been cooled slowly, it was washed in water and all of the exposed surfaces were found to be coated with a grayish-black film.

The above examples illustrate the use of various molten salts as vehicles for the dihalide of titanium. I have also shown the use of various structural materials as containers for the salt bath and it is understood that other combinations may be used in the practice of my invention. It is obviously necessary that the melting point or softening point of the container should be substantially above the salt bath temperature and it is also essential that the object to be coated should be a solid under the operating conditions. The container may first react with the bath to give a titanium coating thereon and after this has happened the container is essentially a titanium container.

The exact reaction which occurs during the deposition of a coating on a surface cannot be stated with any certainty and it is possible that the oxides of a glass or ceramic body may react with the halide of the salt bath to give a titanium film containing interstitially held oxygen. The exact mechanism is regarded as relatively unimportant since the refractory body then has an electrically conducting coating on which other metals may be plated if such is desired. The presence or absence of oxide in the film does not interfere with plating and soldering operations.

When metal bodies, such as steel, are immersed in the bath, it seems plausible that some iron will enter the bath with titanium being plated on the surface of the metal. This titanium deposit may be transformed to an iron titanium alloy under suitable temperature conditions and it is possible to vary the nature of this surface considerably by variations in concentration of the titanium in the salt bath, in temperature of operation as well as time of contact. As mentioned above various alkali metal and alkaline earth metal halides may be used in the formation of the plating bath. For economical reasons, the chlorides are particularly interesting and for commercial reasons the chlorides of sodium, potassium, lithium, magnesium and calcium are of a greatest interest. The titanium halide may be dissolved in the other salts either before or after reduction of the titanium to the divalent state.

Although the baths described above have been found to produce the desired results, it will, of course, be clear to those skilled in the art that variations may be made without departing from the scope of this invention, and the invention is to be limited only as required by the following claims.

What is claimed is:

1. A method of forming a titanium coating on the surface of a refractory solid inert body which comprises immersing said solid body in a fused salt bath consisting essentially of a divalent titanium halide and not less than one of the group of halides selected from the group consisting of alkali and alkaline earth metals for a period of time and at a temperature sufficient to deposit a coating of titanium on said body.

2. A method of forming a titanium coating on a metal surface which comprises immersing a metal body in a fused salt bath consisting essentially of a divalent titanium halide and not less than one of the group of halides selected from the group consisting of alkali and alkaline earth metals for a period of time and at a temperature sufficient to deposit a coating of titanium on said body.

3. A method of forming a titanium coating on a surface which comprises immersing an iron body in a fused salt bath consisting essentially of a divalent titanium

halide and not less than one of the group of halides selected from the group consisting of alkali and alkaline earth metals for a period of time and at a temperature sufficient to deposit a coating of titanium on said body.

4. A method of forming a titanium coating on a glazed silica-containing ceramic which comprises fusing not less than one of the group of halide salts selected from the group consisting of the alkali and alkaline earth metals, introducing a divalent titanium halide into the fused salt, mechanically cleaning the surface of the ceramic to remove dirt and grease, and immersing the ceramic in the salt for a period of time and at a temperature sufficient to deposit a coating of titanium on said ceramic.

5. A method of forming a conductive coating on a glazed silica-containing ceramic comprising cleaning the surface of the ceramic and immersing said ceramic in a fused salt bath consisting essentially of a divalent titanium halide and not less than one of the group of halide salts selected from the group consisting of alkali and alkaline earth metals for a period of time and at a temperature sufficient to deposit a coating of titanium on said ceramic.

6. A method of forming a conductive coating on a glazed silica-containing ceramic comprising fusing at least one of the group of halide salts selected from the group consisting of the alkali and alkaline earth metals, forming divalent titanium in said fused salt by passing an electric current between two titanium electrodes in contact with the fused salt, cleaning the surface of the ceramic, and immersing said ceramic in the bath for a period of time and at a temperature sufficient to deposit a coating of titanium on said ceramic.

7. A method of forming a titanium coating on a cleaned, glazed, silica-containing ceramic comprising fusing not less than one of the group of halide salts selected from the group consisting of the alkali and alkaline earth metals, adding at least one divalent titanium halide, and immersing said ceramic in the bath for a period of time and at a temperature sufficient to deposit a coating of titanium on said ceramic.

8. A method of forming a conductive coating on a glazed silica-containing ceramic which comprises mechanically cleaning the ceramic, preheating the ceramic, and immersing said ceramic in a fused salt bath consisting essentially of a divalent titanium halide and at least one of the group of halide salts selected from the group consisting of the alkali and alkaline earth metals for a period of time and at a temperature sufficient to deposit a coating of titanium on said ceramic.

9. The method of forming a titanium coating on a glazed silica-containing ceramic comprising cleaning the surface of the ceramic and immersing said ceramic in a fused salt bath consisting essentially of a divalent titanium chloride and not less than one of the group of chlorides selected from the group consisting of alkali and alkaline earth metals for a period of time and at a temperature sufficient to deposit a coating of titanium on said ceramic.

10. A method of forming a titanium coating on a glazed silica-containing ceramic comprising cleaning the surface of the ceramic and immersing said ceramic in a fused salt bath consisting essentially of a divalent titanium halide and an alkali metal halide for a period of time and at a temperature sufficient to deposit a coating of titanium on said ceramic.

11. A method of forming a titanium coating on a glazed silica-containing ceramic comprising cleaning the surface of the ceramic and immersing said ceramic in a fused salt bath consisting essentially of a divalent titanium chloride and an alkali metal chloride for a period of time and at a temperature sufficient to deposit a coating of titanium on said ceramic.

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