March 6, 1962 A. R. STETSON 3,024,174

ELECTROLYTIC PRODUCTION OF TITANIUM PLATE

Filed Dec. 24, 1958 3 Sheets-Sheet 1

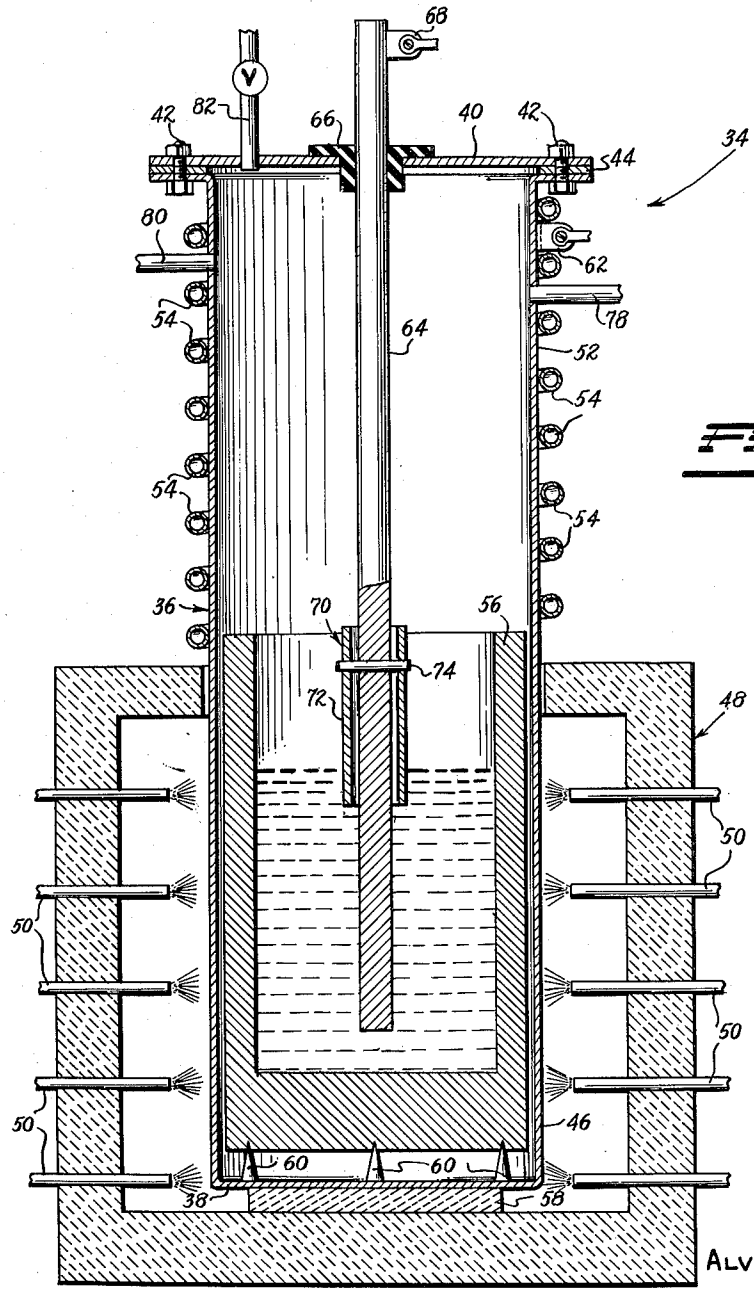


Fig. 1

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ELECTROLYTIC PRODUCTION OF TITANIUM PLATE

Filed Dec. 24, 1958 3 Sheets-Sheet 2

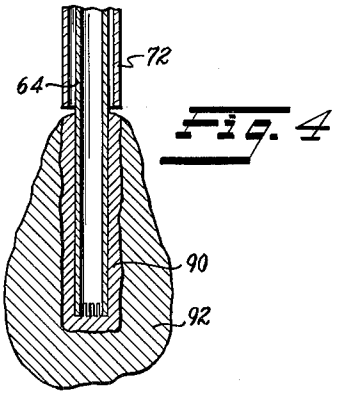


Fig. 4

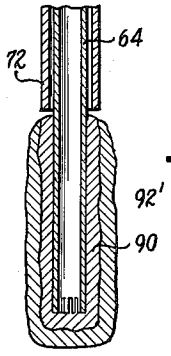


Fig. 5

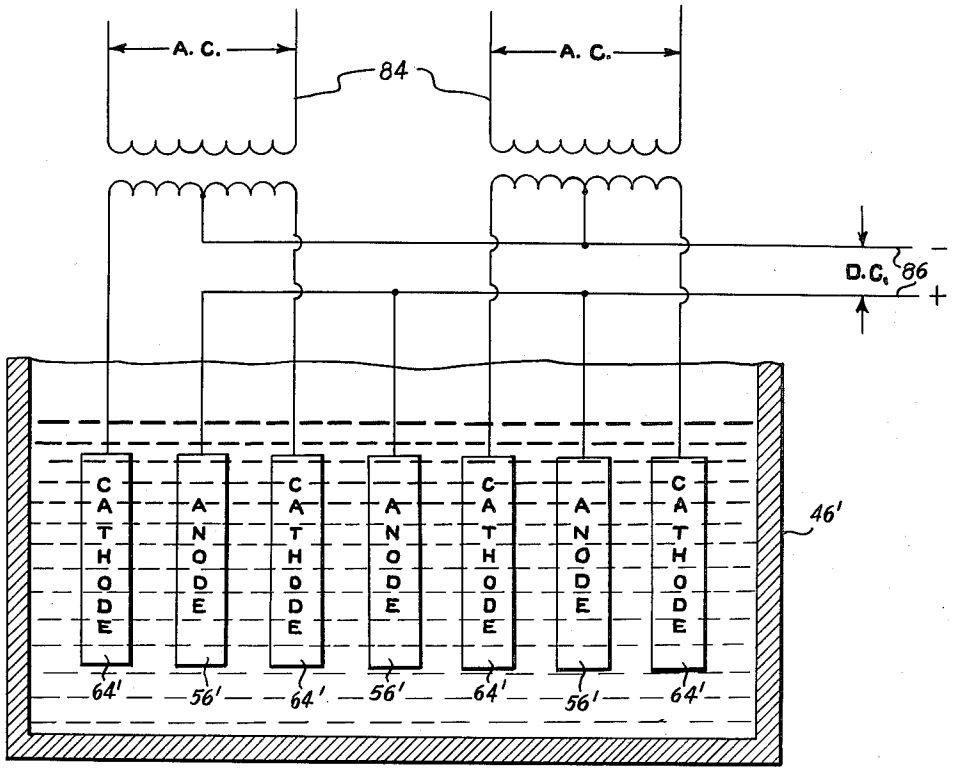


Fig. 2

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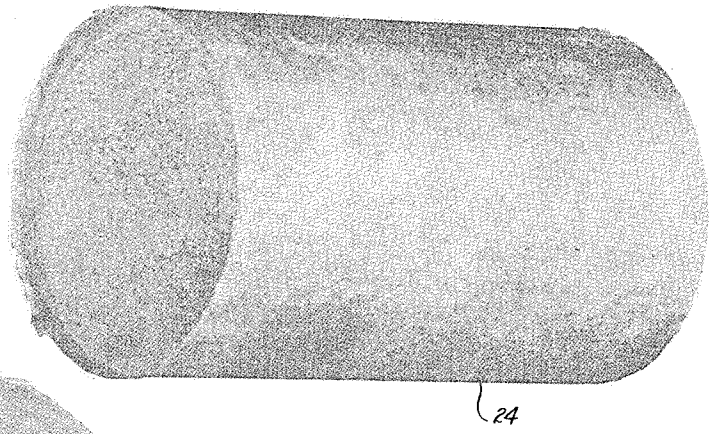
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ELECTROLYTIC PRODUCTION OF TITANIUM PLATE

Filed Dec. 24, 1958 3 Sheets-Sheet 3

Fig. 6



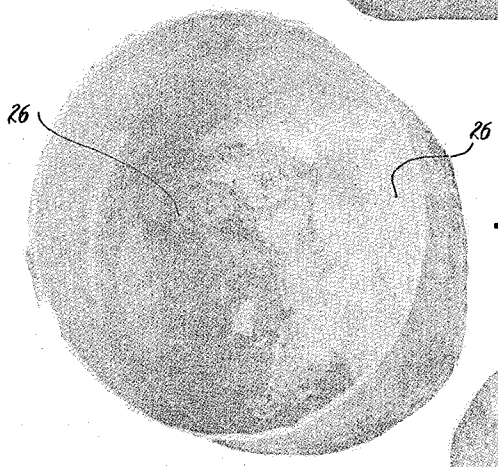


Fig. 7

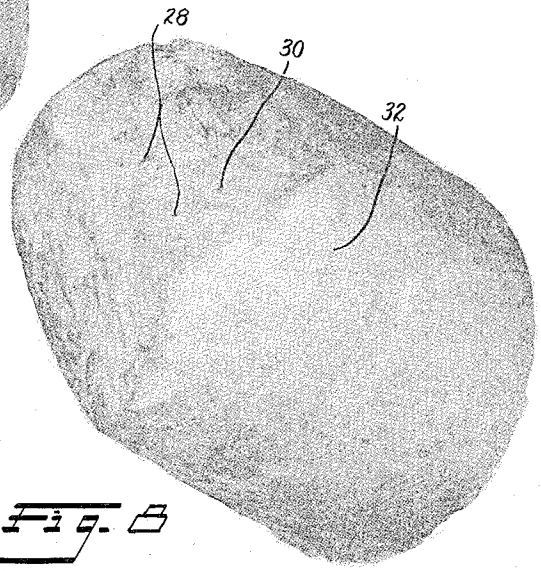


Fig. 8



Fig. 3

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United States Patent Office

3,024,174

Patented Mar. 6, 1962

3,024,174
ELECTROLYTIC PRODUCTION OF TITANIUM PLATE

Alvin R. Stetson, San Diego, Calif., assignor to Solar Aircraft Company, San Diego, Calif., a corporation of California

Filed Dec. 24, 1958, Ser. No. 782,978
11 Claims. (Cl. 204—39)

The present invention relates to an electrolytic process, and more particularly to electrolytic plating processes for applying a titanium plate coating or layer to a metallic surface.

This application is a continuation-in-part of my application Serial No. 431,484, filed May 21, 1954, now abandoned.

While the metallic element titanium is a highly attractive addition to metals and alloys now used in industry, titanium is seldom, if ever, found in the pure state, but rather, generally as the oxide, and methods of extraction or reduction are so costly and complex as to discourage the general use of titanium metal. A number of processes of electrically winning titanium metal are known, but all except the present invention produce powder, granules, dendrites or sponge, which are recovered from the bath in particle form and then must be subjected to expensive and extensive operations to produce commercially useful massive and continuous sheet or plate.

For many contemplated uses, a fabrication of pure titanium is not required. In these cases it is sufficient to provide a structure of some readily available metal or alloy such as steel and to protect only the exposed surfaces of such structure with a permanently bonded coating or layer of titanium or an alloy composed predominately of titanium. Prior art methods of accomplishing this have generally proven to be commercially unsatisfactory.

The known processes for obtaining titanium by the reduction of halide compounds to the metal produce powder, granules, dendrites, or sponge. It has been discovered that certain compounds containing titanium may, under proper conditions, be made to give up their metal, not as an impure sponge, powder, granules or dendrites, but rather as a dense layer of uniform thickness bonded to a metallic surface. The novel process of this invention is essentially an electrolytic one whereby a compound containing a titanium hexafluoride radical ($TiF_6^=$) can be caused to release its metal atoms, and these atoms can be collected as a solid, firmly bonded coating on the cathode of the electrolytic system.

Superficially my novel process may appear similar to such known electrolytic processes for extracting metallic titanium from halide compounds of titanium as those described by Cordner and Worner in an article appearing in the Australian Journal of Applied Science, 2, pp. 358–367 (1951), that disclosed in U.S. Patent No. 1,835,025 to Driggs, or those of British Patent No. 678,807, or German Patent No. 615,951. However, closer examination will reveal the similarity if any resides only on the standard equipment common to all, the methods employed and end result being decidedly different. The processes described in the first three of the foregoing sources produce individual particles of titanium metal dispersed in the electrolyte, while that of the instant invention provides a dense uniform coating or layer of titanium metal or alloy permanently bonded to the cathode workpiece. The process of German Patent No. 615,951, produces titanium, if at all, heavily loaded with embrittling impurities and requires operating conditions which would not be usable in a commercially practicable operation.

Accordingly, it is a primary object of this invention to provide novel methods of electroplating titanium and titanium alloy on metallic surfaces.

Other objects of this invention are:

(1) To provide novel methods of electroplating titanium and its alloys on metallic surfaces;

(2) To provide a metallic surface coated with titanium or a titanium alloy which coating is of uniform thickness and is permanently bonded to said surface;

(3) To provide novel methods for the electrolytic production of titanium and titanium alloy coatings while avoiding the production of impure titanium or titanium alloy sponge, powder, granules or dendrites;

(4) To provide titanium or titanium alloy coatings of different thicknesses and contours on metallic bases of various sizes, shapes and compositions;

(5) To provide novel methods for producing titanium and titanium alloy coatings bonded to metallic workpieces directly by electrolysis of fused halide salts of titanium; and

(6) To provide electrolytic methods such as those above wherein an all-fluoride electrolyte is utilized.

These and other objects and advantages of my invention will become more apparent by reference to the appended claims and the following detailed description taken in conjunction with the accompanying drawings, wherein:

FIGURE 1 is a sectional view in side elevation of a simple electrolysis cell for use in carrying out the process of the invention;

FIGURE 2 is a diagrammatic illustration of a more complex cell and power supply arrangement providing increased productive capacity;

FIGURE 3 is a reproduction of a photograph of a cathode after an uncontrolled run, as will be explained fully hereinafter;

FIGURE 4 is a diagrammatic sectional drawing of a cathode after an uncontrolled run;

FIGURE 5 is a diagrammatic sectional drawing of a cathode after a controlled run;

FIGURES 6, 7, and 8 are reproductions of photographs of articles formed by plating from which the cathode workpieces have been removed by dissolving in acid.

According to the invention, metallic titanium and titanium alloy coatings are provided by subjecting an all-fluoride electrolyte containing a titanium hexafluoride radical ($TiF_6^=$) to electrolysis under the conditions described hereinafter.

Electrolytes I have found satisfactory for my use are of two general groups, one composed solely of a double fluoride of titanium, the other of a double fluoride of titanium combined with alkali metal fluorides. In the first group, I have found useful potassium titanium fluoride (K_2TiF_6) and sodium titanium fluoride (Na_2TiF_6). These double fluorides may be used singly or in combination with one another. The second group consists of the above recited double fluorides with one or more of the following alkali metal fluorides: sodium fluoride (NaF), lithium fluoride (LiF), and potassium fluoride (KF). It will be noted that each of the titanium-containing compounds recited includes the negative titanium hexafluoride radical ($TiF_6^=$).

Examples of electrolytes I have found satisfactory are listed in Table I, wherein the compositions of the different electrolytes are given in terms of the percentage of each constituent in parts by weight of the total.

Table I

Compound	1	2	3	4	5	6	7
K_2TiF_6*	100	90	90	50	80	90	70
NaF	0	10	5	50	10	0	15
LiF	0	0	5	0	10	0	15
KF	0	0	0	0	0	10	0

*The K_2TiF_6 may be replaced in whole or in part by Na_2TiF_6 as recited supra.

I have found that for best results the melt should contain from 10 to 25 percent by weight in the aggregate of the alkali metal fluorides, with the balance of the melt consisting of the selected fluotitanate compound or compounds. Melts containing more than 25 percent of the metal fluorides may successfully be used; the 50 percent fluotitanate–50 percent alkali metal fluoride mixture listed in column 4 of Table I is one example of a melt having high metal fluoride content which has been found to yield satisfactory results, but at a much higher electrolyte melting point, and the 50–50 ratio is considered the maximum fluoride content. The melting point of the electrolyte increases as the percentage of alkali metal fluorides is increased above the desired range, however, and it therefore is desirable to limit the metal fluoride content to within the preferred range of 10 to 25 percent of the total bath.

A number of electrolytic systems are feasible for carrying out my process, as will be understood by those skilled in the art from the following disclosure, and these are not limited to the comparatively simple systems illustrated in the drawings and which will now be described in detail.

The electrolytic system generally indicated at **34** in FIGURE 1 comprises a cell **36** which may be fabricated of any heat and corrosion resistant metal or alloy such, for example, as Inconel. Cell **36** is closed at its lower end by bottom wall **38** and is provided at its upper end with a removable cover plate **40** secured in place thereon by any suitable means such as the nut and bolt assemblies **42**. A gasket **44** is preferably interposed between the abutting surfaces of cell **36** and cover plate **40** to provide a more gas-tight seal therebetween.

The lower portion **46** of cell **36** is positioned on furnace block **58** within a furnace **48** provided with fuel burner tubes **50** as shown, or with other heating means capable of raising the temperature of the cell to and beyond the melting point of the electrolyte contained therein. The upper portion **52** of cell **36** extends above the top wall of furnace **48** and is provided with cooling means such as the cooling coils **54** shown encircling the cell **36**. This upper portion **52** of cell **36** constitutes a cooling chamber into which the cathode workpiece may be withdrawn and cooled after electrolysis is completed. While no partition is shown between the melt and cooling chambers, it will be understood that for production purposes such a partition will be desirable.

A graphite crucible **56**, which may serve as the anode of the system, is positioned in the lower portion of cell **36** in close mating engagement with conical contact members **60** which in turn are attached to the bottom wall **38** and provide a positive and low resistance electrical connection between the crucible **56** and the cell **36**. A connector lug such as shown at **62** may be provided on cell **36** to facilitate electrical connection to the cell and, through contacts **60**, to the graphite crucible **56** within the cell.

As shown in FIGURE 1, cathode workpiece **64** is positioned within crucible **56**, the cathode being maintained in this position by its tight sliding fit in seal **66** or by a suitable clamping device mounted on cover plate **40**. The seal **66** is fabricated of electrically insulating material and is interposed between the cathode and cover plate to seal the sliding joint therebetween and to electrically insulate these elements from each other. Cathode **64** is preferably provided with a lug **68** to facilitate electrical connection thereto, and may if desired also be provided with an anode gas shield assembly **70** to prevent corrosion of the cathode by gases liberated at the anode during electrolysis. This shield assembly comprises a tubular shield element **72** supported in place on the cathode **64** by means of a carbon or metal pin **74** which passes through the shield and cathode to lock these elements securely together.

The cathode workpiece can be of Inconel, nickel, any of the so-called super alloys, any of the stainless steels, any of the mild steels, and many non-ferrous metals and alloys. My experience has been that superior coatings are achieved on high nickel-bearing alloys, such alloys apparently increasing the efficiency of the electrolytic process, possibly with the nickel acting as a catalyst during the process. However, the mild steels, copper, and other metals and alloys can be satisfactorily coated by my novel process.

Ratios of cathode workpiece area to anode area of from 1:2 to 1:6 have proven satisfactory with cathode workpiece current densities within the range of 0.1 to 5.0 amperes per square inch and a preferred range of .3–2 amperes for best quality plating. Polarization may become troublesome if current density is made excessively high. Further, at high current densities it appears that the alkali metals are produced concurrently with titanium metal. These alkali metals, being above their melting points, disperse rapidly into the melt and react with the titanium fluorides to produce titanium metal in powder and dendritic form, thus interfering with and decreasing the desired plating process.

Cell **36** may be provided with inlet and outlet fittings **78** and **80** respectively for connection into an argon or other inert gas supply system which, by maintaining the cell filled with inert gas, protects the materials in the cell against contamination by the oxygen, nitrogen, and other impurities present in the atmospheric air outside the cell. Inlet **78** may be connected through a manually or automatically controlled valve to a source of inert gas under pressure. Outlet **80** may be connected into a two-way valve (not shown) which may be manipulated to place the cell either in communication with a vacuum pump for evacuating the cell, or in communication with the atmosphere through the secondary line.

The cell may, if desired, be provided with a third fitting **82** through which additional electrolyte or particular constituents thereof may be added to the cell without removal of cover plate **40**.

In using the electrolysis cell of FIGURE 1, the graphite crucible **56** is filled with any of the compounds named above as suitable for use in my process, the compound having first been thoroughly dried and mixed. Cover plate **40** is then put in place and the valve on outlet **80** manipulated to connect the cell to the vacuum pump which should be capable of evacuating the cell to a pressure of about 25 microns. With the cell thus evacuated, it may be heated as by burners **50** to approximately 300° F. to further dry and out-gas the electrolyte. The valves may then be adjusted to disconnect the vacuum pump from the cell and to provide a controlled flow of argon to and through the cell for excluding atmospheric air therefrom. The argon within the cell should be maintained at a pressure at least slightly greater than atmospheric so that any leakage will be of inert gas outwards rather than of atmospheric air into the cell. Since commercial grades of argon generally include at least traces of water vapor and of oxygen and nitrogen, it may be desirable to include a purification train in the argon supply system to remove these contaminants from the argon entering the cell.

Once the cell and its contents have been thoroughly dried and proper argon flow has been established, the temperature of the cell may be raised, as by increasing the rate of flow of fuel to burners **50**, until complete melt-

ing and clarification of the electrolyte is obtained. I have found that the titanium compounds when used alone will require a temperature of approximately 1550° F. to achieve clarity of the melt, while the addition of the listed fluorides as indicated in Table I will allow complete clarity at temperatures up to 400° F. lower. Therefore, in general, a range of from 1080° F. to 1800° F. will be found adequate.

It will be found that the conductivity of the melt increases with temperature rise. Variation of the melt temperature may, therefore, be used as one method of controlling the current through the cell. The temperature of the electrolyte should not be permitted to exceed the melting point either of the metal of the cathode workpiece or of titanium and titanium alloys with the metal of the cathode, since no plate can be achieved at such temperatures and excessive volatilization of the electrolyte will occur. The optimum temperature for any one melt composition may readily be determined through analysis of the results obtained at different temperatures. For example 1500° F. has been found to be an optimum temperature for the K_2TiF_6-NaF mixture listed in column 2 of Table I, although satisfactory results have been obtained at temperatures ranging between 1200° F. and 1700° F.

For purposes of illustration, the production run by which the titanium plating shown in the photographs of FIGURES 6–8 were produced will be briefly summarized. For this run, a mixture consisting of 90% by weight of potassium fluotitanate and 10% by weight of sodium fluoride (compound No. 2 in Table I) was heated to approximately the 1500° F. temperature mentioned above as optimum for this electrolyte. The graphite crucible was the anode and a stainless steel cathode workpiece was used. A protective layer of inert gas was provided. During the 630 ampere hours of the process, the voltage range was from 3.5 to 4.7 volts and the cathode current density was about 1.2 amperes per square inch. Following the run, the cathode workpiece was withdrawn from the melt and found to look much like FIGURE 3. The outer cathode deposit, composed of occluded salts and compounds of lower fluorides of titanium, as will be explained infra, was removed by first breaking off chunks with a hammer, loosening the remainder by water soak, and final cleaning by light sandblast. Removal of the outer cathode deposit revealed the exterior of the titanium coating to be a deep, closed end tube sheathing the cathode workpiece. To establish the characteristics of the titanium coating per se, the stainless steel workpiece then was dissolved by immersing it, with its titanium coating, in aqua regia. The tube of titanium which resulted was cut into the open-ended tube of FIGURE 6 and the cup of FIGURES 7 and 8.

Particularly significant in the production run described above is the fact that the stainless steel cathode workpiece which was used had a cap section welded over its end, which welding was purposely crudely carried out to develop a rather complex surface with machine marks, irregularities, holes, and scores to illustrate the covering, throwing and sealing power of the bath and of the resulting titanium coating. As can readily be seen in FIGURES 7 and 8, the titanium, in plating to the stainless steel cathode workpiece, has faithfully followed the contour of the cathode and has covered each individual puddle, projection and depression of the weld pattern. The articles shown in FIGURES 6, 7 and 8 are shown as produced without finishing or polishing, and are illustrative of the complex configurations or articles that may readily be obtained by the instant invention.

As used hereinafter, to simplify discussion, $TiF_6^=$ will be assumed to be composed of TiF_4 and two fluoride ions.

It is my theory that prior to the introduction of the electric current, the titanium tetrafluoride (TiF_4) tends to react with the metal of the cathode workpiece to produce titanium trifluoride (TiF_3) and an ion of the workpiece metal, and possibly the TiF_4 also reacts with the carbon of the anode to form TiF_3 and carbon tetrafluoride (CF_4). It is also possible that both of these reactions may be in process simultaneously, thus setting up conditions for electrolysis when anode and cathode are connected to a voltage source through connections 62 and 63 respectively, and current passes through the cell. TiF_3 could also be produced by direct reduction of TiF_4 at the cathode workpiece. I believe the following half-cell reactions are typical of what takes place:

Cathode workpiece: $Ti^{2+}+2e^- \rightarrow Ti$
Anode: $2F^- - 2e^- \rightarrow F_2$
Secondary anode: $2F_2+C \rightarrow CF_4$

As CF_4 is evolved at the anode, part of the titanium metal plates to the cathode workpiece and part reacts with TiF_4 to give TiF_3 or TiF_2. If the latter, the TiF_2 combines with TiF_4 to give TiF_3 which again goes:

$$TiF_3+3e^- \rightarrow Ti \text{ (metal)}$$

Accordingly, I believe the cathode reaction progresses in the following manner:

A. TiF_4 in contact with the cathode is reduced to TiF_3 by corrosion or electrolytic reduction.
B. $Ti^{3+}+e^- \rightarrow Ti^{2+}$
C. $Ti^{2+}+2e^- \rightarrow Ti$
D. $Ti+3Ti^{4+} \rightarrow 4Ti^{3+}$
E. $4Ti^{3+}+4e^- \rightarrow 4Ti^{2+}$
F. $4Ti^{2+}+8e^- \rightarrow 4Ti$

This process continues with the deposition of titanium plate on the cathode workpiece, and the production of TiF_3 and probably TiF_2 more rapidly than the titanium metal is reduced. These lower fluorides are fairly insoluble in the bath, and form over the titanium plate an outer "cathode deposit." This outer deposit appears to be essential in this electroplating process. I theorize that the outer deposit acts as a porous separator which restricts the amount of $TiF_6^=$ available at the cathode and consequently decreases the attack on the titanium plate by the excessively available oxidizing agent. The outer deposit also isolates the plate from the anode gases such as CF_4 and F_2.

In utilizing the cell of FIGURE 1 and the electrolytes of Table I, I have found that the outer cathode deposit, clearly seen in FIGURE 3, develops in two distinct phases which, for this discussion, may be termed the purple phase and the black phase, due to the fact that on the cooled cathode workpiece following a run, the two phases have these distinctive colors. The outer cathode deposit has little or no effect on the conductivity of the bath, and therefore it may be assumed that said deposit in the molten bath is spongy and porous with molten salt throughout, and that the whole is in an unstable condition with chemical reactions taking place continually. However, when the cathode workpiece is cooled, the outer cathode deposit solidifies into a hard, dense mass, practically insoluble in water and most acids. From a careful examination of this material, it is believed that the purple phase probably is substantially titanium trifluoride (TiF_3), and that the black phase is either titanium difluoride (TiF_2) or TiF_3 impregnated with a small amount of titanium metal which has been dissolved or dispersed throughout. It has been found that the black phase is present to at least three or four times the amount of the purple phase and that while the two phases are more or less mixed, there is a preponderance of the purple phase toward the outside of the outer cathode deposit mass, with the black phase concentrated nearer the titanium plated to the cathode workpiece. This fact would seem to bear out the theory of cathode protection provided by the outer cathode deposit, as discussed supra.

It is to be understood that the titanium plated to the cathode workpiece is not itself visible in FIGURE 3, the

coating being completely hidden by the overlying cathode deposit, which contains little titanium metal. As the titanium metal collects as plate on the cathode workpiece, the outer surface of the titanium becomes in effect the outer face of the cathode workpiece, and the outer cathode deposit collects around this outer face and is in no way mixed with the titanium coating itself. The clear line of division between the outer cathode deposit and underlying metallic titanium is clearly illustrated in FIGURES 4 and 5, to which reference will now be made.

FIGURES 4 and 5 are diagrammatic showings of the cold cathode workpiece, titanium coating, and outer cathode deposit after two runs, that of FIGURE 4 during which there was no attempt to control the growth of the outer cathode deposit, and that of FIGURE 5 during which careful conrol was exerted, and the growth of the outer cathode deposit was substantially limited, allowing only enough deposit to be present to protect the titanium coating.

As can been in FIGURE 4, and as discussed above, the outer cathode deposit 92 develops around the cathode workpiece 64 concurrently with the growth of the titanium plate 90. If uncontrolled, the outer deposit tends to continue growth throughout the plating cycle.

However, by incorporating into the system a means of controlling the growth of the outer cathode deposit, the deposit will be limited to its growth as shown in FIGURE 5. As seen in FIGURE 5, the titanium plate 90 has developed, while growth of the outer cathode deposit 92' has been limited to a value which will provide protection to the titanium plate, but will not be excessive.

Agitation of the bath during the electrolytic cycle by external means provides an excellent method of controlling development and growth of the outer cathode deposit. The external agitation may be induced by use of high frequency waves and could be carried out with no mechanical connections to the cell or internal parts of the cell, as is well known in the art. Various means of internal agitation are feasible. For example, agitation can be created by the introduction of inert gas through the bottom of the cell; or a suitably sealed stirring rod may be introduced into the electrolyte; or the anode or cathode or both may be made movable in the bath and actuated by mechanical means (not shown) from outside the cell.

I prefer carbon or graphite as the anode material, but other anode materials may be useful in specified cases, as will be apparent to those skilled in the art.

The voltage applied to the cell must be greater than the breakdown potential of the titanium salt for electrolytic separation of metallic titanium to occur. As long as the applied voltage is greater than this breakdown potential, which is on the order of 2 volts, plating can be successfully accomplished at any voltage consistent with proper current density. As hereinbefore pointed out, however, excessive current densities will produce dendritic deposits, granules or powder, thus defeating the purpose of the invention. For a given voltage, the current density may be varied by varying the conductivity of the melt, which may be accomplished either by raising or lowering the temperature of the melt as discussed supra.

While the cell of FIGURE 1 is satisfactory for laboratory processes, other arrangements are desirable for large scale production. A cell useful in large scale production is diagrammatically illustrated in FIGURE 2, with a plurality of anodes 56' and cathode workpieces 64' arranged in spaced relation from each other in the electrolyte. While FIGURE 2 shows only the lower portion of the cell 46', the counterpart of the lower portion 46 of cell 36 of FIGURE 1, it will be understood that the remainder of the cell 46' would follow the general pattern of cell 36 in FIGURE 1, with an upper chamber preferably divided by partition from the lower cell, with a protective atmosphere of inert gas provided for both sections of the cell. The arrangement of cathode workpieces to anodes would be such as to gain optimum use of the gases evolved at the anode to control formation of outer cathode deposit. The direct current source 86 would be attached by such means as attachments 62 and 68 of FIGURE 1 to the anodes and cathode workpieces, respectively. It will be further understood that anodes and cathode workpieces would be provided with means to remove them from the electrolyte into the upper chamber individually.

Also shown in FIGURE 2 is a source 84 of alternating current supply. The alternating current may be superimposed on the direct current system to improve the plating efficiency, apparently by heating the cathode workpieces and decreasing polarization.

When the electrolysis is complete, the cathode workpieces are withdrawn into the upper chamber of the cell and allowed to cool in the argon atmosphere therein until the workpiece temperature has fallen to about 600° F., at which point the argon flow may be discontinued and the plated workpiece removed from the cell.

The residual outer cathode deposit may be readily removed without damage to the titanium coating, as discussed supra.

As will be apparent, many variations within the scope of the present invention may be made. For example, titanium tetrafluoride (TiF_4) may be added to the bath during plating in any suitable manner with cathode workpieces individually removable from the melt when each is plated to the desired thickness. Further, the cathode workpiece may be in the form of an interior mold of any desired configuration upon which the titanium metal is plated to a desired thickness. Or, the cathode workpiece may be hollow and the anode and electrolyte arranged to plate the inner surface of the cathode workpiece.

If desired, the cathode workpiece may be dissolved out in an acid bath, leaving a substantially finished article of titanium somewhat alloyed with cathode metal, as was done with the subjects of FIGURES 6, 7 and 8.

If desired, controlled titanium alloys may be formed by co-depositing other metals with titanium. This is accomplished by employing secondary anodes of the desired alloying metals and by introducing into the melt the respective fluorides of the desired metals. These secondary anodes are maintained at current densities sufficient to maintain the desired percentage of the metal fluorides in the bath. Variation of these current densities will change the concentration of the metal fluorides in the bath and will thereby change the rate at which the metals are plated. Uniform alloys may be obtained by accurately controlling the percentage of the metal fluorides added and the current densities on the secondary anodes.

By controlling the time of reaction, the process may be discontinued when the exact desired thickness for coating is obtained. For example, I have been able to control plating thickness to within one mil.

From the foregoing disclosure it will be readily understood that I have developed new and novel and highly advantageous methods for obtaining titanium layers or coating on metallic items.

I have described my invention in conjunction with preferred embodiments, but it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention. Therefore, such modifications and variations are considered to be within the purview and scope of the appended claims.

When used in the appended claims, the word "titanium" is to be understood to include both titanium and alloys predominantly of titanium with other metals.

What I claim and wish to have protected by United States Letters Patent is:

1. A process for producing a titanium plate on a metal-

lic base which comprises: providing an electrolyte consisting essentially of at least 50% by weight of at least one salt from the group consisting of sodium fluotitanate and potassium fluotitanate and 0% to 50% by weight of at least one salt from the group consisting of sodium fluoride, lithium fluoride, and potassium fluoride; heating said salts in a non-consumable vessel of an electrically conductive material to dry and out-gas said electrolyte, and maintaining said electrolyte as a melt at a temperature between 1080° F. and 1800° F.; immersing at least a portion of said metallic base in said electrolyte; shielding said electrolyte and said metallic base from exposure to the atmosphere; and passing an electrical current between said vessel and said metallic base through said electrolyte with said vessel serving as a non-consumable anode and said metallic base as a cathode, and maintaining a cathode current density of 0.1 to 5.0 amperes per square inch of immersed cathode surface with an impressed voltage potential in excess of the breakdown potential of the electrolyte for a sufficient time to decompose said electrolyte and free titanium metal therefrom and cause said freed titanium metal to form a plate coating on the immersed surface of said metallic base.

2. The process defined in claim 1, wherein said electrolyte consists essentially of salt from the group consisting of sodium fluotitanate and potassium fluotitanate.

3. The process defined in claim 1, wherein the electrolyte is agitated during deposition of the titanium on the cathode.

4. The process defined in claim 1, wherein said anode vessel is carbonaceous so that fluoride liberated at the anode may react therewith.

5. A process as defined in claim 1, wherein titanium tetrafluoride is added to the electrolyte as the electrolytic deposition progresses.

6. The process recited in claim 1, wherein the metallic base cathode is composed of a high nickel-bearing alloy.

7. The process defined in claim 1, wherein the anode has a surface area at least twice as great as the surface area of the metallic base cathode immersed in the electrolyte.

8. A process for producing titanium plate on a metallic base which comprises: providing an electrolyte consisting essentially of 75–90% by weight of at least one salt from the group consisting of sodium fluotitanate and potassium fluotitanate and 25 to 10% by weight of at least one salt

from the group consisting of sodium fluoride, lithium fluoride, and potassium fluoride; heating said electrolyte salts in a non-consumable vessel of electrically conductive material to dry and out-gas said electrolyte, and maintaining said electrolyte as a melt at a temperature between 1080° F. and 1800° F.; immersing at least a portion of said metallic base in said electrolyte; providing a protective atmosphere of inert gas to shield said electrolyte and said metallic base from exposure to air; and passing an electrical current between said vessel and said metallic base through said electrolyte with said vessel serving as a non-consumable anode and said metallic base as a cathode, and maintaining a cathode current density of 0.1 to 5.0 amperes per square inch of immersed cathode surface with an impressed voltage potential in excess of the breakdown potential of the electrolyte for a sufficient time to decompose said electrolyte and free titanium metal therefrom and cause said freed titanium metal to form a plate coating on the immersed surface of said metallic base.

9. The process defined in claim 8, wherein the electrolyte is maintained at a temperature above the melting point of the electrolyte but below the melting point of said metallic base cathode and of the titanium formed on the cathode.

10. The process defined in claim 8, wherein the metallic base cathode is shielded from exposure to air by enclosure in a larger vessel containing argon under pressure in excess of ambient atmospheric pressure.

11. The process defined in claim 8, wherein the cathode current density is 0.3 to 2 amperes per square inch of immersed cathode surface.

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