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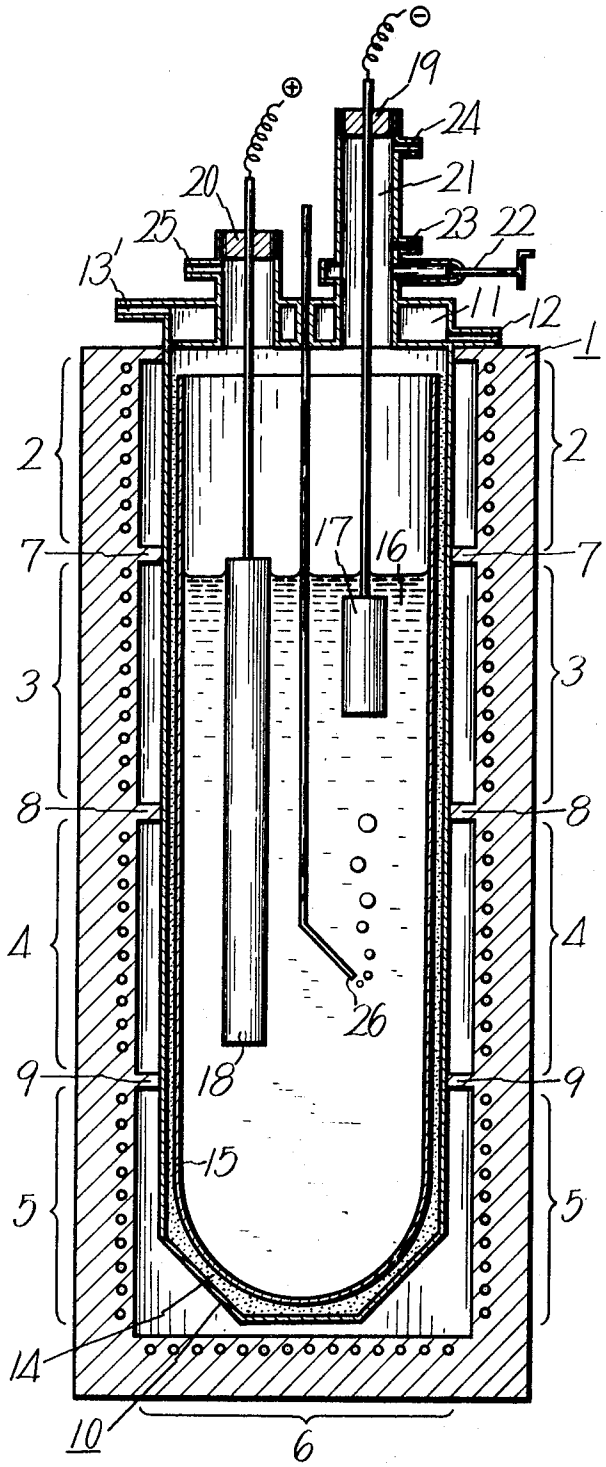

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ELECTRODEPOSITION METHOD

Shin-ichi Tokumoto and Eiji Tanaka, Kanagawa, Japan, assignors to Sony Corporation, Shinagawa-ku, Tokyo, Japan

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ABSTRACT OF THE DISCLOSURE

A method for the electrodeposition of titanium or its alloys is shown. A fused salt electrolytic bath containing (1) a mixture of the chloride salts of barium, magnesium, sodium and calcium having a freezing point of less than 600° C., and (2) titanium dichloride, and if desired, (3) a source of a suitable alloy metal is electrolyzed. The electrolytic bath is maintained at a temperature of 400° C. to 580° C. and under such conditions as will maintain the molar ratio of titanium trichloride to titanium dichloride less than 0.5 in the vicinity of the electrode to be electrodeposited. A portion of the bath is desirably maintained at a temperature above 500° C. to convert titanium trichloride to titanium dichloride to maintain the above molar ratio near the cathode. A unique polarized region is formed about the cathode as magnesium is simultaneously electrodeposited with titanium or its alloy and then rehalogenized into the electrolyte. The plate product is smooth in surface and numerous capital and operating efficiencies are achieved.

This invention relates to an electrodeposition method for producing titanium metal or its alloys having a smooth surface through the use of a fused salt electrolytic bath consisting of metal chlorides.

It has been proposed to electrolyze fused salt baths and thereby electrodeposit a metal or an alloy in the form of a tight and smooth plated layer or in the compact form of a plate or a cake. Japanese Patents Nos. 212,080 entitled "Method of Electrolysis Using Intermittent Current" and 229,381 entitled "Method of Electrodeposition in Waterless Electrolytic Bath Using Electrolytic Corrosion at the Same Time," both relate to such electrodeposition and No. 294,943 entitled "Method of Electrodepositon of Metallic Titanium or Its Alloy(s) of Good Quality" relates to electrolysis using a fused bromide bath. United States Patent No. 2,935,454, British Patent No. 963,743 and West German Patent No. 1,202,990 likewise are relevant to the subject of this invention.

With the methods disclosed in the above patents, the electrodeposit can be produced in a desired form, for example, in the form of a plate or a cake by using the electrolytic polarization in the fused salt bath. These methods, however, necessitate the use of a bromide electrolytic bath, an expensive bath component such as cesium chloride and intermittent application of an electrodepositing current high enough to electrodeposit positive elements other than the desired metal.

In the conventional electrodeposition methods a polarized region or "polarization" of the bath compoistion in contact with the electrode is created. This "polarization" effects the electrodeposition of the titanium or alloy within itself and serves to smooth or polish the surface of the deposited titanium or alloy by permitting those portions of the electrodeposited metal which project beyond the "polarization" to be selectively corroded by the thermochemical action of the trivalent titanium compound in the electrolyte. In conventional processes where magnesium metal is codeposited on the cathode with titanium or its alloy, the magnesium deposited on the cathode reduces the titanium compound of higher valency to a compound of lower valency, the magnesium returning to the bath in the form of its compound. In such processes the polarized region or "polarization" must be formed and maintained so as to limit the quantity of trivalent titanium compound therein to less than that of divalent titanium compound, even if larger amounts were dissolved in the original electrolytic bath. This end is only in part accomplished by the presence of the magnesium compound in the polarized region in amounts greater than in the original bath, which excess decreases the solubility of the trivalent titanium compound.

The prior methods thus require the conversion of a higher-valency compound of the desired metal to a lower-valency one for the formation and maintenance of the "polarization" on the cathode, and this in turn requires fulfilment of difficult conditions which are extremely uneconomical and disadvantageous in operation. Specifically, these methods require addition of cesium chloride or rubidium chloride for adjustment of the polarization. In the application of the electrodeposition mechanisms of the above conventional methods to the fused chloride salt electrolytic bath, it is necessary to add to the bath a substantial amount of cesium chloride or rubidium chloride for adjustment of the "polarization." In the event that the cesium chloride added to the bath is replaced with another chloride, the electrodeposit, even under optimum conditions, becomes increasingly porous and dendritic. It is difficult to obtain the electrodeposit in a compact form with a substitute chloride and consequently, this additive cannot be dispensed with.

Still a further problem exists in the mechanisms for smoothing the surfaces of the electrodeposit during operation of the electrolytic call. The electrodeposition mechanism of the conventional methods although extremely suitable for smoothing the surface of the electrodeposit when using a bromide electrolytic bath is not always effective when using a chloride electrolytic bath. The differences are primarily due to the difference in solubility between titanium chloride(s) and titanium bromide(s), the raw materials for electrodeposition, the difference in intensity of corrosive actions of the respective electrolytic baths on the electrodeposited metals, the difference in stability between divalent titanium chloride and divalent titanium bromide in the electrolytic baths at operating temperatures and the difference in phase diagram between the respective compositions. Accordingly, the electrodeposition mechanism which is suitable for use with the bromide bath is not always adequate for the chloride bath.

It is thus the primary object of this invention to provide an electrodeposition method for producing titanium or its alloy by electrolysis which is economical and well suited for use in industry.

It is a related object of this invention to provide a method for electrodepositing titanium or its alloy in a compact form, i.e., in the form of a plate or an ingot or to plate titanium or its alloy on the surface of another object.

It is still a further object of this invention to provide an electrodeposition method whereby a metallic member containing at least a desired metal is placed in the electrolytic bath in order to use at least the desired metal therein as a source of the metal desired to be electrodeposited.

It is a further and more specific object of this invention to provide an electrodeposition method wherein a positive element other than the desired metal, as for example magnesium, is electrodeposited on the electrode surface concurrently with the desired metal and is then rehalogenized and returned into the electrolytic bath to create and

maintain one the electrode surface a special polarized region or "polarization" which inhibits the growth of the deposit at projections on its surface and promotes the growth at depressions in its surface.

It is still a further object of this invention to provide a method of electrolysis whereby it is no longer necessary to use the chemical polishing technique of earlier processes and to adjust the "polarization" on the cathode by addition of expensive components such as cesium and rubidium chloride to the electrolytic bath.

It is another object of this invention to obviate the necessity of intermittently applying electrolysis current to the electrodes.

These and other objects of this invention are achieved in an electrodeposition method wherein a fused salt electrolytic bath containing (1) a mixture of the chloride salts of barium, magnesium, sodium and calcium, said mixture having a freezing point of less than 600° C., and (2) titanium dichloride is electrolyzed at a temperature above 400° C. but below 580° C. and under such conditions that the molar ratio of titanium trichloride to titanium dichloride in the vicinity of the electrode to be deposited is less than 0.5. The process can be used to electrodeposit alloys of titanium if a source of a suitable alloy metal is present in the electrolyte.

It has been found that predetermined cathode coating can be formed and maintained on the cathode surface to be electrodeposited via a simultaneous electrodeposition of a desired metal (i.e., titanium or a titanium alloy) and magnesium metal from the above described fused salt electrolytic bath containing the four-component mixture and titanium dichloride. Deposition is followed by rehalogenation of the deposited magnesium into the electrolytic bath. Magnesium chloride contained in the electrolytic bath is relatively easy to electrolyze due to its low decomposition voltage to metallic magnesium. Since magnesium, once deposited on the cathode surface is electrochemically more base than the metal desired to be produced, it reduces a compound of the desired metal in the bath and returns into the bath near the cathode in the form of a salt. The amount of magnesium salt gradually increases in the neighborhood of the cathode. Titanium is of course electrochemically nobler than magnesium and any metals desired in the titanium alloy are limited to those which are also electrochemically nobler than magneisum in the electrolytic bath at the operating temperature.

The fundamental concept underlying this invention is similar to those disclosed in the aforementional patents in that a fused electrolytic bath is employed for the electrodeposition of titanium or its aloy and in that the polarization of the bath formed on the surface of the deposit is effectively used for smoothing the surface of the deposit. The electrodeposition method of this invention employs a chloride electrolytic bath which is more economical than the bromide electrolytic bath. As compared with bromide baths this method also lowers the cost of the equipment required, provides for an increased amount of electrodeposits per unit time, facilitates operations and ensures attainment of the object of smoothing the surface of an electrodeposited layer, and of controlling the shape of an electrodeposit as compared with the bromide electrolytic bath.

The electrodeposition method of this invention is entirely different in the mechanism of smoothing the surface of the electrodeposit from the fused salt electrodeposition method proposed in the aforesaid patents. A "polarization" which is different from conventional processes, in hibits the growth of the deposit at projections on the surface thereof but promotes the growth at the depressions and thereby plays an important role in the electrodeposition mechanism. In order to distinguish this polarization from the usual one, it is hereinafter referred to as "cathode coating." With "cathode coating" it is no longer necessary to use the thermochemical smoothing mechanism of conventional methods.

There are numerous advantages in using this method. Intermittent application of the electrodepositing current is no longer absolutely indispensable and expensive bath components such as cesium and rubidium chlorides are not always required. Instead new restrictive process conditions are imposed on the composition of the electrolytic bath and upon the temperature of operation which controls those conditions.

The method of this invention is illustrated by the following example.

EXAMPLE A

A fused chloride salt electrolytic bath was heated to and maintained at a temperature ranging from 442° C. to 445° C. The bath composition at this temperature in molar ratio was:

$BaCl_2$	15.18
$MgCl_2$	20.66
NaCl	34.70
$CaCl_2$	14.02
KCl	3.77
$TiCl_2$	10.87
$TiCl_3$	0.80
Total	100.00

The above numerical values were obtained by analysis when the bath was held at room temperature as is further described below. A square-shaped magnesium metal rod having a cross sectional area of 8 mm. x 8 mm. was electrically connected with a titanium metal rod of similar shape and both rods were immersed into the bath to a depth of about 2.5 cm. After one hour the magnesium rod was pulled from the bath, rinsed with a 2% aqueous solution of hydrochloric acid to wash away the salts adhering to it and was again rinsed with water. Thereafter it was dried. The rod was found to have metallic titanium deposited on the portion that had been immersed, in substitution for magnesium. When the rod was replaced in the 2% aqueous solution of hydrochloric acid, magnesium was dissolved and the titanium was obtained in the form of a frame.

The analysis of titanium dichloride and titanium trichloride contained in the electrolytic bath was according to the method disclosed by S. Mellgrem and W. Opie (J. Metals, 266, 1957). This method is based upon the fact that titanium dichloride gives off quantitatively, a constant amount of hydrogen gas in a dilute acid solution

$$(Ti^{+2}+H^{+}\rightarrow Ti^{+3}+\tfrac{1}{2}H_2)$$

This method is thus referred to as a hydrogen method. A sample of the fused chloride salt electrolyte at the operating temperature is quenched and then placed in a 0.7% aqueous solution of hydrochloric acid. The amount of hydrogen gas emitted is measured in order to define the quantity of titanium dichloride in the electrolytic bath on the assumption that the emission of hydrogen gas results from the presence of titanium dichloride. The analysis for titanium trichloride proceeds as follows. A sample of electrolyte is quenched and then dissolved in a 5% aqueous solution of hydrochloric acid. Barium salt is removed from the solution with 10% aqueous sulfuric acid, and then titanium ions reducible by zinc amalgam are reduced to trivalent titanium ions. The resulting solution is titrated with a standard aqueous solution containing ferric ions in order to measure the quantity of titanium salt as titanium trichloride. Then the quantity of titanium dichloride as measured by the hydrogen method is subtracted from the total amount of titanium salt to obtain the amount of titanium trichloride in the electrolytic bath.

The method of this invention is not operative when a large amount of titanium trichloride is contained in the electrolytic bath. The reaction $Ti+2TiCl_3\rightarrow 3TiCl_2$ takes place and efficient electrodeposition is not achieved. How-

ever, with a suitably controlled amount of titanium trichloride in the salt bath near the cathode, i.e., in the proportion to titanium dichloride discussed above, good results are obtained.

Example a demonstrates that a magnesium metal rod, if immersed in a fused chloride salt bath having a composition usable in the electrodeposition method of this invention, is plated with titanium. It can also be shown however that, if magnesium is electrodeposited on the cathode, and, if the amount of the compound of the desired metal in the bath around the cathode exceeds that of the electrodeposited magnesium metal on the cathode, and, if the latter reacts well with the former, a similar phenomenon to that above described in Example A will occur on the cathode surface.

Several mechanisms are responsible for the smoothing of the surface of the plate. At projections on the cathode surface the current density is likely to be higher than that at depressions, so that the amount of magnesium electrodeposited on the projections exceeds that on the depressions. Consequently, the amount of magnesium chloride resulting from rehalogenation of the electrodeposited magnesium on the projections is larger than that on the depressions. In the event that the composition ratio of the component salts of the electrolytic bath is such that the freezing point is relatively low, the magnesium chloride resulting from the application of the electrodepositing current and the rehalogenation causes the bath composition at the projections to deviate more from the original bath composition than at the depressions. Consequently, the freezing point of the composition at the projections exceeds the electrolytic temperature earlier than at the depressions. This produces a greater amount of solid-phase or highly viscous portion at the projections than at the depressions and the electrolytic resistance at the projections becomes higher than that at the depressions. This automatically tends to uniformly distribute the current density over the entire surface area of the electrode. This phenomenon is referred to as an electrolytic resistance difference effect.

The solid-phase or highly viscous portion which gradually increases during the application of the electrodepositing current also serves as a high electrolytic resistance at the projections of the cathode surface and, at the same time inhibits diffusion and supply of the compound(s) or ions of the desired metal to the projections. This is referred to as a diffusion velocity difference effect. When the desired metal component in the electrolytic bath has been consumed by electrodeposition and the freezing point of the bath rises and increases in viscosity, the above two effects are simultaneously produced.

The solid-phase or highly viscous portion is constantly dissolved into the electrolytic bath. The removal of the solid-phase or highly viscous portion from the electrode surface is dependent upon the degree of stirring of the electrolytic bath or vibration of the electrode. Accordingly, a periodic change in the degree of stirring of the bath or vibration of the electrode causing alternate and repeated formation and removal of the solid-phase or highly viscous portion ensures the electrolytic resistance difference effect. Consequently these two steps are of particular utility in the electrodeposition method of this invention.

The solid-phase or highly viscous portion may also be removed by periodically passing an electrodepositing current high enough to deposit an element other than the desired metal. While the electrodepositing current ceases at least a portion of the polarized region disappears and subsequent application of the current again causes deviation of the bath composition and provides a new solid-phase or highly viscous portion.

Even if the difference in the viscosity of the electrolytic bath at the projections and at the depressions of the electrode surface is not great and the current distribution is not uniform, calcium chloride is used as a bath component and the bath temperature is selected to be as low as possible so as to suppress migration of the desired metal compounds or ions in the bath. The desired metal compound whose decomposition voltage is lower than that of the other bath components is consumed by electrodeposition more rapidly at those areas of relatively higher current density than at those areas of lower current density during the supply of the electrodepositing current. Thus there is less desired metal compound at the projections than at the depressions. This leads to uniformity of the curernt distribution due to lack of current carrier at the projections. According to experimental results, it appears that this is effective for microscopic brightening of the deposit rather than macroscopic controlling of the shape of the deposit. In any case, the desired metal compound or ions are deficient at the projections more than at other sites during the application of the electrodepositing current.

When the electrolytic bath at the projections is intermingled with or dissolved into the original bath of low viscosity by violent stirring of the bath or violent shaking of the cathode or interruption of the electrodepositing current, the projections are corroded more easily than the depressions, because the osmotic pressure of the bath at the projections is low due to the deficiency of the desired metal compound or ions. This preferential dissolution of the projections due to a potential difference of the bath at projections and depressions caused by the differences in concentration of the desired metal compound(s) or ions between those sites is referred to as the dissolution velocity difference effect.

The electrolytic resistance difference effect, the diffusion velocity difference effect and the dissolution velocity difference effect are the several mechanisms in the "cathode coating" electrodeposition method of this invention. These three effects inhibit the growth of the projections of the electrodeposit and promote the growth at depressions.

The bath composition must be maintained so that the amount of titanium trichloride is less than ½ of the amount of titanium dichloride in the vicinity of the electrode to be electrodeposited with the desired metal. Where titanium dichloride and titanium trichloride coexist in the same bath, the reaction reducing titanium trichloride to titanium dichloride occurs more readily than that of the electrolytic reduction of titanium dichloride to titanium metal. A similar phenomenon occurs in the case where reduction of titanium compounds with metallic magnesium is promoted by the electromotive force of a battery established between metallic magnesium and titanium in the bath. An increase in the amount of titanium trichloride dissolved in the electrolytic bath intensifies the corrosive attack on titanium metal thereby creating titanium dichloride. According to experiments, the corroding and dissolving velocities of metallic titanium where an appreciably large amount of titanium trichloride is dissolved n the bath are several times and sometimes more than ten times as high as those encountered when substantiall yno titanium trichloride is dissolved in the bath. Corroding speed is, however, dependent upon the degree of stirring of the bath. Consequently, when a large amount of titanium trichloride exists together with titanium dichloride in the bath near the cathode, it is possible to form so much titanium dichloride by the reduction of titanium trichloride on the cathode surface as will exceed the solubility of the bath. The excess of titanium dichloride becomes solid, clings to the surface and becomes containe din the electrodeposit or causes the electrodeposit to form powder-like masses of dendrites. It has been found, through experiments, that the tolerable limit of titanium trichloride in the fused chloride salt in the vicinity of the cathode is, on a molar basis, less than one half of the titanium dichloride, in order to avoid this unsatisfactory effect.

Experimental studies on the composition of the fused chloride salt electrolytic bath have shown that the fol-

lowing four component mixture is most effective in electrodepositing titanium or its alloys in compact form with smooth surfaces. In molar ratio:

	Parts
$BaCl_2$	23
NaCl	36
$MgCl_2$	29
$CaCl_2$	15

The composition of this mixture can be modified only to such an extent that the modified mixture has a freezing point of less than 600° C. This limitation is temperature results from the necessity to avoid the unfavorable formation of sediment at the bottom of the electrolytic cell during operation.

When gradually cooled, a bath having the above composition provides a primary crystal precipitation at about 440° C. A change in the amount of magnesium chloride contained in the bath from 29 parts to 20 parts causes the primary crystal precipitation to take place at approximately 480° C. With the magnesium chloride and sodium chloride at 34 parts and 41 parts respectively and with 9 parts of lithium chloride and 6 parts of potassium chloride added to the bath, the primary crystal precipitation temperature is about 420° C.

It has been found that an electrolytic bath mixture consisting of barium chloride, magnesium chloride, sodium chloride and calcium chloride, having a freezing point of less than 600° C. retains, relatively stably, divalent titanium chloride or ions thereof at the operating temperature for electrodeposition described below and has sufficient fluidity to permit adequate supply of the desired metal component(s) to the cathode. An electrolytic bath having the above composition may be supplemented with compound(s) of alkali elements or alkaline earth elements such as, for example, potassium chloride or lithium chloride, alone or in combined form, so as to provide for enhanced improved property of the polarization thereof. Since the electrodeposition method of this invention is different in mechanism from those disclosed in the aforementioned patents, the additive components of the electrolytic bath are naturally different from those employed in the foregoing patents and suit the particular properties of the polarization of this electrodeposition mechanism.

The "polarization" in this method is only required to perform the function of "cathode coating" and need not possess other properties as are required in the conventional methods. Accordingly, this invention does not require the use of special components for adjustment of the properties of the bath and the polarization, as for example, cesium chloride. Where components other than the aforementioned four are desired for adjustment of the property of the polarization, potassium chloride is preferred. Especially, good results are obtained by the addition of a mixture containing a three-component system consisting of potassium chloride, magnesium chloride and sodium chloride and having a freezing point of less than 600° C.

The electrodeposition can be performed with direct electrolyzing current as will be apparent from Examples 1 and 2 described below but it is preferred to employ an intermittent current so as to ensure the effect of the "cathode coating" and to abundantly supply the cathode surface with compounds and ions of the desired metal.

The electrodeposition does not require the thermochemical polishing action with titanium trichloride as in prior art methods so that when intermittent current is used the number of intermissions per unit time can be much less than in conventional methods. When using intermittent current, the ratio of the duration of the electrodepositing current, capable of electrodepositing metallic magnesium as well as the desired metal, to the length of the period in which the electrodepositing current is discontinued, is usually broadly in the range of several tens to one to one to ten. The purpose of discontinuing the electrodepositing current is to secure a sufficient supply of the desired metal component(s) to the electrode surface and accordingly it is preferred to minimize the length of the period in which the current is discontinued, provided this purpose is well carried out. The period of discontinuation is dependent upon several electrolyzing conditions namely, the electrolytic bath composition, the duty cycle of the intermittent current, the waveform of the electrodepositing current, the amount of the electrodepositing current, the electrolytic bath temperature, convection and agitation of the electrolytic bath, vibration of the electrode, etc. According to experimental results, it is preferred that the ratio of the duration of the electrodepositing current to the duration of discontinuation of the current be in the range of 20 to 1 to 1 to 10.

When using intermittent electrodepositing current depolarization can be completely achieved by cutting off the electrodepositing current. Accordingly, it is possible to form the polarization with as high an intensity as possible by applying the eelctrodepositing current and to cut off the current immediately as the polarization becomes excessive. Thus, a polarization which completely performs the function of the "cathode coating" can be obtained. On the other hand, it has been found that substantially complete depolarization makes it necessary to suppress the corrosive action of the electrolytic bath of the electrodeposited metal. Unless this corrosive action is suppressed, and aside from a decrease in current efficiency resulting from re-dissolution of the electrodeposited metal into the bath, the electrodeposit is corroded over its entire surface and forms thereon projections and depressions so large that their crystal surfaces can be clearly seen. Accordingly, it is impossible to continue electrodeposition with the electrodepositing surface being maintained as smooth as possible in order to avoid this, calcium chloride is used as one of the electrolytic bath components. Calcium chloride suppresses the corrosive action of the bath to the electrodeposited metal.

In the aforementioned patents it was suggested that calcium chloride be added to the bromide bath in view of its electrodeposition characteristic but that calcium fluoride or calcium oxide be added to the chloride bath instead of calcium chloride. However, it has been found that the use of calcium chloride as one of the electrolytic bath components in the method of this invention markedly suppresses the corrosive action of the electrolytic bath to the electrodeposited metal. This is because of the mechanism of this invention and because of the phase diagrams of the components. And, there is no deterioration of the function of the electrolytic bath as a solvent of the desired metal component(s) and in formation of the "cathode coating."

The use of the calcium fluoride or calcium oxide as a corrosion-preventing agent of the chloride electrolytic bath introduces into the chloride bath, fluorine or oxygen which are negative elements different from those contained in the bath. This is attended with several disadvantages in manufacturing on a large industrial scale. However, the use of the calcium chloride as one of the electrolytic bath components permits the suppression of the corrosive action of the electrolytic bath as desired by sutiable selection of the electrolysis temperature and without industrial disadvantages. Further, the addition of calcium chloride to the electrolytic bath permits suppression of migration of the titanium compounds or ions in the bath without spoiling other favorable properties of the bath.. It has been found that calcium chloride is indispensable to this method in order that large quantities of titanium dichloride dissolved in the electrolytic bath at temperatures above 500° C. may be retained therein for a relatively long period of time at a temperature below 500° C., and also in the adjustment of the amount of the titanium component(s) in the bath by heating.

The temperature of the electrolytic bath near the electrode to be electrodeposited with titanium or its alloys

is preferably as low as possible in order to suppress the corrosive action of the bath on the electrodeposited metal. The lower limit of the bath temperature in the vicinity of the electrode is about 400° C.; it has been experimentally determined that this temperature limit satisfies the requirement that metallic magnesium once electrodeposited on the electrode is returned into the electrolytic bath. The upper limit of the electrolytic bath temperature near the electrode is 600° C. Above this temperature thermal decomposition and consequent loss of the desired metal compound(s) occur and the salutary function of hte "cathode coating" is not effected. The temperature of the electrolytic bath in the vicinity of the electrode which is suitable for continuous use in the electrolytic operation is in the range of 400° C. to 580° C. The bath temperature, at that location, most suitable for relatively easy and stable electrodeposition of the desired metal or its alloy with high quality and in a desired form, is from 400° C. to 520° C.

When the electrolytic bath deteriorates after use at a temperature less than 500° C. for an extended period of time, the deterioration can be reversed by heating the bath to a temperature of more than 500° C. If metallic titanium is contained in the electrolytic bath titanium trichloride rapidly reacts with it, converting the latter into titanium dichloride.

The electrolytic bath of this invention has a unique property. When it is maintained at a temperature less htan 500° C. for an extended period, titanium dichloride is gradually converted into titanium trichloride. Consequently, it is of great importance to use the electrolytic bath under conditions which prevent the excessive increase of titanium trichloride in the bath near the electrode to be electrodeposited. If the electrolytic operation is carried out with titanium dichloride in the bath near the electrode in an amount in excess of 8 mol percent relative to the total amount of the five bath components e.g. barium chloride, magnesium chloride, sodium chloride, calcium chloride and titanium dichloride, the desired electrodeposition is achieved with ease. It is advisable to select the electrolytic bath composition so that when the bath has been heated up to a temperature above 500° C. titanium dichloride is dissolved to as great an extent as possible but titanium trichloride is not as much dissolved. Even if used continuously for many hours, the electrolytic bath can be substantially completely prevented from deterioration by consistently maintaining a portion of the bath at a temperature above 500° C. preferably above 520° C., and the bath near the electrode at a desired electrolytic temperature. The bath should then be intermixed by convection or forced circulation. Where metallic titanium is present in that portion of the electrolytic bath held at the high temperature, even if a great amount of halide gas or titanium trichloride is generated by electrolysis in the bath or even if a higher valent titanium chloride such as trivalent or tetravalent titanium chloride is supplied to the bath as a raw material source of the desired metal, the titanium compound(s) existing in the bath are always maintained in a condition suitable for electrolysis and stable electrolyzing operation can be continued for an extended period of time.

Where crude or scrap metal or alloy is used as a raw material source of an electrodeposit for the purpose of electrorefining or electrolytic recovery, etc. of the desired metal or alloy, it is advisable to locate the raw material in that portion of the electrolytic bath which is held at the high temperature. This results in good dissolution of the raw material into the electrolytic bath and removal of the anode effect which hinders the electrolysis.

It appears that when the electrolytic bath is heated up to a temperature exceeding 500° C., complex salts are partially produced in the bath. However, even if these complex salts are formed in the bath, it is still necessary to maintain the amount of titanium trichloride at less than one-half of that of the titanium dichloride. If the solubility of the titanium dichloride in the low-temperature bath is lower than that in the high-temperature bath, a decrease in the bath temperature causes titanium dichloride to be precipitated in a colloidal form and to be suspended in the bath but this is not detrimental to the electrodeposition. Even if electrolysis is carried out in a bath in which solid barium chloride or magnesium chloride is suspended, no solid particles of these chlorides are likely to be contained in the electrodeposit.

The electrolyzing current employed must be capable of electrodeposition of the desired metal and electrodeposition of metallic magnesium on the electrode surface for the purpose of the formation and maintenance of a special "polarization" or polarized region which inhibits the growth of the electrodeposit on the projections of the surface and promotes the growth of the electrodeposit at the depressions.

Consequently, the electrolyzing current must be of such a voltage as will electrodeposit the desired metal and a positive element other than the desired metal i.e., at the minimum, magnesium on the electrode. There is no limitation on the waveform on the electrolyzing current. When the electrodepositing current is intermittent, it is immaterial whether the electrodepositing current is alternated with an electric current of relatively lowered voltage, or of reversed polarity, or with a period wherein no current is passed through the electrode. Where it is desired to further smooth the surface of the product, it is preferred to alternate the electrodepositing current with a reverse current. The reverse current can be supplied from an outside power source or can be supplied with the electromotive force of a battery established between the electrode for the electrodeposition and the opposing electrode.

When the aforementioned electrodepositing current is intermittent, its duty cycle need not be regular. It is also possible to use an electrodepositing current which intermits at shorter time intervals in the longer duration of the current itself as in the Example 5 described later. The current capable of electrodepositing magnesium on the electrode together with the desired metal is a current having a voltage higher than that corresponding to the difference between a decomposition voltage of magnesium chloride and a voltage necessary for halogenation of the desired metal or its compound occurring at the anode. In addition, when a titanium compound of low valency exists in the electrolytic bath near the anode, high valent titanium compound(s) are formed by halogenation on the anode.

Accordingly, it is preferred to divide the electrolytic bath into two parts by a diaphragm of aluminum or the like. Into each part is inserted respectively, the electrode for electrodeposition and the other electrode. This prevents the low valent compound of the desired metal in the bath from undergoing halogenation by electrolysis when the desired metal is made from its compound, except when the desired metal is supplied to the bath in a metallic form as a raw material for electrolysis for the purpose of electroforming, electroplating, electrorefining or electrolytic recovery, of the metal from scrap metal. No difference in electrodeposits has been observed when using soluble and insoluble anodes.

It is necessary to prevent the crude compound in the electrolytic bath from oxidizing as is encountered with other methods employing titanium chloride as a raw material. One method to prevent oxidation is to blanket the surface of the electrolytic bath with an inert gas such as argon, helium or nitrogen and thereby exclude air from the bath.

In the drawing:

The figure shows a sectional view of an electrolytic cell suitable for carrying out the method of this invention.

The figure shows an electrolytic cell and a furance suitable for carrying out the electrolysis while keeping the up-

per part of the electrolytic bath at a relatively low temperature and keep the bottom of the bath at a relatively high temperature. Reference numeral **1** designates a furnace; reference numerals **2**, **3**, **4**, **5** and **6** designate heating units; and reference numerals **7**, **8** and **9** designate heat-insulating plates for defining the several heating areas of the heating units. Reference numeral **10** refers generally to an electrolytic vessel made of soft steel, numeral **11** to a jacket for water-cooling, numeral **12** to an inlet tube for cooling water, numeral **13** to a discharge pipe for cooling water, and reference numeral **14** to graphite powder packed as a buffer in the space between an electrolytic cell **15** made of quartz glass and the electrolytic vessel **10**. Reference numeral **16** designates an electrolytic bath, numeral **17** an electrode for electrodeposition (cathode), numeral **18** a counter electrode (anode), numeral **19** an opening for the electrode **17** and numeral **20** an opening for the anode **18**. Reference numeral **21** identifies a chamber for the electrode **17** in which air is replaced with an inert gas after the electrode has once been inserted and sealed so as to prevent the electrolytic bath **16** from contacting air when the electrode is changed. Reference numeral **22** designates a cut-off for cutting off the chamber **21** from the electrolytic vessel **10**, numeral **23** an inlet for an inert gas, numerals **24** and **25** exhaust ports and numeral **26** a tube made of quartz glass through which the inert gas for agitating the electrolytic bath is blown.

In carrying out the electrodeposition, the upper part, i.e., the neighborhood of the electrode for electrodeposition **17**, can be maintained at a relatively low temperature suitable for electrodeposition and the bottom of the electrolytic bath can be maintained at a temperature above 500° C. This temperature difference is accomplished by lowering the voltage of the upper heatingg units and raising that of the lower heating units so as to adjust the heating values of heating units **2**, **3**, **4**, **5** and **6**.

The invention will be further described by the following examples which illustrate the electrodeposition of titanium, iron-titanium alloy and aluminum-titanium alloy.

The following electrodepositions were performed in the electrolytic furnace and in the electrolytic vessel illustrated in the figure. The dimensions of electrolytic cell **15** made of quartz glass were 75 mm. in inner diameter and 500 mm. in depth. The molar ratios of titanium dichloride and titanium trichloride in the following electrolytic bath compositions indicate the amounts present in the bath in the vicinity of the electrode for electrodeposition when the bath temperature was adjusted to electrolyzing conditions after metallic titanium and titanium trichloride were added to the bath and the bath temperature was raised to 560° C.

EXAMPLE 1

(1) Bath temperature:

Depth of the bath: about 300 mm.
520° C. to 560° C. at the bottom part of the bath.
463° C. to 465° C. in the vicinity of electrode **17** for electrodeposition.

(2) Bath composition (in the vicinity of electrode **17** for electrodeposition):

In molar ratio:	Parts
$BaCl_2$	13.87
$MgCl_2$	19.85
NaCl	38.13
$CaCl_2$	9.28
KCl	3.46
$TiCl_2$	13.40
$TiCl_3$	2.01

(3) Electrodes:

Electrode for electrodeposition: Molybdenum plate, 10 mm. wide and 0.2 mm. thick. Length of the immersed part, 25 mm.

Counter electrode: Carbon rod, 8 mm. in diameter. Length of the immersed part, 150 mm. Distance between electrodes, 40 mm.

(4) Electrolyzing current: Direct current.

Cell voltage: 1.5 volts.
Current value: 1.5 amp.

(5) Agitation: With argon gas bubbles, 50 cc. blown into the electrolytic bath per minute.

Vibration of electrode for electrodeposition:
Direction of vibration: 45° relative to the plane surface of the electrode.
Amplitude: 1.5 mm.
Frequency: 50 times per second.

(6) Duration of electrolysis: 30 minutes.
(7) State of electrodeposition:

Plane portion: flat surface but slightly undulating.
Side portion: swollen out of the form of a bank, tip of lower end corner of the electrode projected in an earthworm form and several pits formed in the round surface of the projection.

EXAMPLE 2

(1) Bath temperature: The same as in Example 1.
(2) Bath composition: (in the vicinity of electrode **17** for electrodeposition):

In molar ratio:	Parts
$BaCl_2$	19.34
$MgCl_2$	23.80
NaCl	30.28
$CaCl_2$	12.62
$TiCl_2$	12.53
$TiCl_3$	1.43

(3) Electrodes: The same as in Example 1.
(4) Electrolyzing current: Direct current.

Cell voltage: 1.6 volts.
Current value: 1.5 amp.

(5) Agitation: With argon gas bubbles, 50 cc. blown into the electrolytic bath per minute.

Vibration of electrode for electrodeposition: the same vibration as in Example 1 was effected intermittently.
Period: 1.2 sec.
Vibration time: 0.9 sec.
Standstill time: 0.3 sec.

(6) Duration of electrolysis: The same as in Example 1.
(7) State of electrodeposition:

Plane portion: A little rough crystals but good flat surface.
Side portion: Swollen out in the form of a bank, several pits formed.

EXAMPLE 3

(1) Bath temperature:

Depth of the bath: about 300 mm.
520° C. to 560° C. at the bottom part of the bath.
441° C. to 43° C. in the vicinity of the electrode for electrodeposition.
(2) Bath composition (in the vicinity of the electrode for electrodeposition):

In molar ratio:

	Parts
$BaCl_2$	18.11
$MgCl_2$	20.50
NaCl	34.08
$CaCl_2$	11.55
KCl	3.48
$TiCl_2$	11.25
$TiCl_3$	1.03

(3) Electrodes:
Electrode for electrodeposition: Molybdenum plate, 10 mm. wide and 0.2 mm. thick. Length of the immersed part, 25 mm.
Counter electrode: Titanium rod, 6 mm. in diameter. Length of the immersed part, 70 mm. Distance between electrodes, 40 mm.
(4) Electrolyzing current: Intermittent direct current.

Cell voltage: 3.5 volts.
Current value: 3 amps.
Period: 1.2 sec.
Conduction time: 0.3 sec.
Cut-off time: 0.9 sec.

(5) Agitation: With argon gas bubbles, 70 cc. blown into electrolytic bath per minute.

Vibration of electrode for electrodeposition:
Direction of vibration: 45° relative to the plane surface of the electrode.
Amplitude: 1.5 mm.
Frequency: 50 times per second.

(6) Duration of electrolysis: 30 minutes.
(7) State of electrodeposition:

Plane portion: Glossy and good flat surface composed of very fine crystals.
Side portion: Swollen out like a bank consisting of hemispherically round lumps. Lower end grown like a skirt extending in parallel with the electrode plane surface and with a glossy surface having hemispherically round lumps.

EXAMPLE 4

(1) Bath temperature:

Depth of the bath: about 300 mm.
520° C. to 560° C. at the bottom part of the bath.
450° C. to 453° C. in the vicinity of the electrode for electrodeposition.

(2) Bath composition (in the vicinity of the electrode for electrodeposition):
In molar ratio:

	Parts
$BaCl_2$	10.49
$MgCl_2$	19.49
NaCl	24.26
$CaCl_2$	23.09
KCl	10.80
$TiCl_2$	10.76
$TiCl_3$	1.11

(3) Electrodes: The same as in Example 3.
(4) Electrolyzing current: The following currents superimposed on each other.

Right direction current (depositing): Intermittent direct current.
Power source voltage: 11.3 volts.
Current value: 4 amp.
Period: 1.2 sec.
Conduction time: 0.3 sec.
Cut-off time: 0.9 sec.

Reverse direction current (corroding): Intermittent direct current.
Power source voltage: 2.7 volts.
Current value: 0.75 amp.
Period: 1.2 sec.
Conduction time: 0.4 sec.
Cut-off time: 0.8 sec.

These two currents were superimposed so that conduction of the reverse direction current might be initiated 0.2 second after completion of the conduction of the right direction current.
(5) Agitation: The same as in Example 3.
(6) Duration of electrolysis: The same as in Example 3.
(7) State of electrodeposition:
Plane portion: Good glossy flat surface.
Side portion: Swollen out like a bank. Lower end grown like a short skirt extending a little in parallel with the electrode plane surface and the surface of the extending portion difficult to be distinguished from the electrodeposit on the plane surface of the electrode.

EXAMPLE 5

(1) Bath temperature: The same as Example 4.
(2) Bath composition: The same as Example 4.
(3) Electrodes: The same as Example 4.
(4) Electrolyzing current: Intermittent direct curent.

Power source voltage: 12.5 volts.
Current value: 4.5 amp.
Period: 0.03 sec.
Conduction time: 0.02 sec.
Cut-off time: 0.01 sec.
This current was further intermitted.
Period: 1.2 sec.
Conduction time: 0.3 sec.
Cut-off time: 0.9 sec.

(5) Agitation: With argongas bubbles, 70 cc. blown into the electrolytic bath per minute.

Vibration of electrode for electrodeposition: The same vibration as in Example 1 was effected intermittently.
Vibration time: 0.9 sec.
Standstill time: 0.3 sec.

Vibration of the electrode was rendered to correspond to cut-off of the intermittent current and standstill of the electrode to conduction of the intermittent current.
(6) Duraion of electrolysis: 45 minutes.
(7) State of electrodeposition:

Plane portion: Good flat surface composed of fine crystals.
Side portion: Swollen out like a bank consisting of hemispherically round lumps. Lower end grown like a short skirt extending in parallel with the plane surface of the electrode.

EXAMPLE 6

(1) Bath temperature: The same as in Example 3.
(2) Bath composition: The same as in Example 3.
(3) Electrodes: The same as in Example 3.
(4) Electrolyzing current: Intermittent direct current.

Cell voltage: 6.6 volts.
Current value: 4.5 amp.
Conduction time: 0.0067 sec.
Cut-off time: 0.0033 sec.

This current was further intermitted.

Period: 1.2 sec.
Conduction time: 0.3 sec.
Cut-off time: 0.9 sec.

(5) Agitation: The same as in Example 5.
(6) Duration of electrolysis: The same as in Example 3.
(7) State of electrodeposition:

Plane portion: Flat surface composed of very fine crystals.
Side portion: Swollen out like a bank consisting of hemispherically round lumps, pits formed at some places.

EXAMPLE 7

The electrolyzing conditions were the same as in Example 6 except the electrolyzing current; the state of electrodeposition was substantially the same as in Example 6. The electrolyzing current was a ripple current produced by full-wave rectification of an alternating current of a peak value voltage of 4.2 volts, a current value

of 3 amp, and a frequency of 50 c./sec. and the ripple current was intermitted as follows:

Period: 1.2 sec.
Conduction time: 0.3 sec.
Cut-off time: 0.9 sec.

EXAMPLE 8

(1) Bath temperature:

Depth of the bath: about 300 mm.
520° C. to 560° C. at the bottom part of the bath.
440° C. to 443° C. in the vicinity of the electrode for electrodeposition.

(2) Bath composition: The same as in Example 4.
(3) Electrodes: The same as in Example 4.
(4) Electrolyzing current: The following currents superimposed on each other were intermittently applied as follows.

Period: 1.2 sec.
Conduction time: 0.3 sec.
Cut-off time: 0.9 sec.

Right direction current: Intermittent direct current.

Power source voltage: 15.3 volts.
Current value: 5 amp.
Period: 0.03 sec.
Conduction time: 0.02 sec.
Cut-off time: 0.01 sec.

Reverse direction current: Intermittent direct current.

Power source voltage: 2.6 volts.
Current value: 0.7 amp.
Period: 0.03 sec.
Conduction time: 0.008 sec.
Cut-off time: 0.022 sec.

These two currents were superimposed on each other so that conduction of the reverse direction current might be initiated 0.001 second after completion of the conduction of the right direction current.

(5) Agitation: The same as in Example 5.
(6) Duration of electrolysis: The same as in Example 4.
(7) State of electrodeposition:

Plane portion: Glossy and good flat surface.
Side portion: Swollen out like a bank and glossy.

The following will describe examples of this invention empolying an electrodepositing current of higher current density.

EXAMPLE 9

(1) Bath temperature:

Depth of the bath: about 300 mm.
520° C. to 560° C. at the bottom part of the bath.
438° C. to 440° C. in the vicinity of the electrode for electrodeposition.

(2) Bath composition (near the electrode for electrodeposition):

In molar ration:	Parts
$BaCl_2$	11.64
$MgCl_2$	26.74
NaCl	33.94
$CaCl_2$	9.17
KCl	7.41
$TiCl_2$	9.53
$TiCl_3$	1.58

(3) Electrodes:

Electrode for electrodeposition: Molybdenum plate, 10 mm. wide and 0.2 mm. thick. Length of the immersed part 25 mm.
Counter electrode: Carbon plate, 20 mm. wide and 8 mm. thick. Length of the immersed part 200 mm.
Distance between electrodes 30 mm.

(4) Electrolyzing current: Intermittent direct current:

Cell voltage: 6.6 volts
Current value: 7.5 amp.
Period: 1.2 sec.
Conduction time: 0.3 sec.
Cut-off time: 0.9 sec.

(5) Agitation: With argon gas bubbles, 70 cc. blown into the electrolytic bath per minute.

Vibration of eelctrode for electrodeposition: Intermittent vibration.
Direction of vibration: 45° relative to the plane surface of the electrode.
Amplitude: 5 mm.
Frequency: 50 times per second.
Vibration time: 0.9 sec.
Standstill time: 0.3 sec.
Vibration of the electrode was made to correspond to discontinuation of the intermittent current and static electrode to conduction of the intermittent current.

(6) Duration of electrolysis: 60 minutes.
(7) State of electrode:

Plane portion: Glossy good flat surface.
Side portion: Difficult to be distinguished from the plane portion. A little thicker than the plane portion.

EXAMPLE 10

(1) Bath temperature:

Depth of the bath: about 300 mm.
520° C. to 560° C. at the bottom portion of the bath.
440° C. to 443° C. in the vicinity of the electrode for electrodeposition.

(2) Bath composition in the vicinity of the electrode for electrodeposition:

In molar ratio:	Parts
$BaCl_2$	8.07
$MgCl_2$	23.71
NaCl	26.89
$CaCl_2$	12.77
KCl	14.72
$TiCl_2$	13.66
$TiCl_3$	0.17

(3) Electrodes: The same as in Example 9.
(4) Electrolyzing current: Intermittent direct current.

Cell voltage: 8.1 volts.
Current value: 12 amp.
Period: 2.4 sec.
Conduction time: 0.6 sec.
Cut-off time: 1.8 sec.

(5) Agitation: With argon gas bubbles, 70 cc. blown into the electrolytic bath per minute.

Vibration of electrode for electrodeposition:
Direction of vibration: 45° relative to the plane surface of the electrode.
Amplitude: 5 mm.
Frequency: 50 times per second.
Vibration time: 1.8 sec.

(5) Standstill time: 0.6 sec. Vibration of the electrode was made to correspond to discontinuation of the intermittent current and static electrode to conduction of the intermittent current.
(6) Duration of electrolysis: 30 minutes
(7) State of electrodeposition:

Plane portion: A little glossy good surface.
Side portion: The same condition as the plane portion but a little thicker than the latter.

EXAMPLE 11

(1) Bath temperature: The same as in Example 10.

(2) Bath composition in the vicinity of the electrode for electrodeposition:

In molar ratio:	Parts
$BaCl_2$	10.00
$MgCl_2$	34.74
NaCl	23.58
$CaCl_2$	12.30
KCl	7.81
$TiCl_2$	10.77
$TiCl_3$	0.81

(3) Electrodes: The same as in Example 10.

(4) Electrolyzing current: Continuous application of current produced by half-wave rectification of alternating current having a frequency of 50 cycles per second.

Cell voltage, maximum value (peak value): 3.2 volts.
Current value: 6.25 amp.

(5) Agitation: The same as in Example 10. Vibration of the electrode was effected irrespective of the electrolyzing current.

(6) Duration of electrolysis. The same as in Example 10.

(7) State of electrodeposition:

Plane portion: Flat surface composed of fine crystals.
Side portion: Swollen out like a bank consisting of hemispherically round glossy lumps.

The electrolytic baths used in the foregoing examples do not contain cesium chloride. Cesium chloride may be added to the baths but in any event the amount of titanium trichloride in the electrolytic bath in the vicinity of the electrode for electrodeposition should be controlled at less than one-half that of titanium dichloride. Spectrum analysis showed that the electrodeposited products contained a very small amount of magnesium. However, the amount of magnesium contained in the electrodeposits is less than that in first-class sponge titanium on the market manufactured by the Kroll process and including magnesium in 400 p.p.m.

Examples 12 and 13 which follow are directed to the electrodeposition of titanium-iron alloy and titanium-aluminum alloy respectively.

EXAMPLE 12

The electrolyzing conditions were the same as in Example 3 except for the bath composition.

(2) Bath composition in the vicinity of the electrode for electrodeposition:

In molar ratio:	Parts
$BaCl_2$	18.10
$MgCl_2$	20.51
NaCl	34.08
$CaCl_2$	11.55
KCL	3.47
$TiCl_2$	10.92
$TiCl_3$	1.00
$FeCl_2$	0.37

(7) State of electrodeposition: Substantially the same in shape as in Example 3. Chemical analysis showed titanium 94.7 and iron 5.1 in weight percent.

EXAMPLE 13

(1) Bath temperature:

Depth of the bath: about 300 mm.
520° C. to 560° C. at the bottom of the bath.
458° C. to 460° C. in the vicinity of the electrode for electrodeposition.

(2) Bath composition in the vicinity of the electrode for electrodeposition:

In molar ratio:	Parts
$BaCl_2$	11.16
$MgCl_2$	23.29
NaCl	20.83
$CaCl_2$	14.68
KCl	16.83
$TiCl_2$	11.20
$TiCl_3$	0.80
$AlCl_3$	1.20

(3) Electrodes:

Electrode for electrodeposition: Titanium plate, 10 mm. wide and 0.3 mm. thick. Length of the immersed part 25 mm.
Counter electrode: Carbon plate, 20 mm. wide and 8 mm. thick. Length of the immersed part 200 mm.
Distance between electrodes 30 mm.

(4) Electrolyzing current: Intermittent direct current.

Cell voltage: 6.4 volts.
Current value: 6 amp.
Period: 1.2 sec.
Conduction time: 0.3 sec.
Cut-off time, 0.9 sec.

(5) Agitation: The same as in Example 9.
(6) Duration of electrolysis: 30 minutes.
(7) State of electrodeposition

Plane portion: Very good glossy flat surface.
Side portion: Swollen out like a round bank and glossy.

Spectrum analysis showed that the electrodeposited product contained several percent aluminum. Substantially the same amount of magnesium as in the Examples 1 to 11 was detected. In this case, when the electrode for electrodeposition was a molybdenum plate, the electrodeposit cracked and partially came off. This is probably due to the difference between the coefficients of thermal expansion of the electrodeposit and molybdenum.

In each of the foregoing examples, when the amount of titanium trichloride was about one-half of that of titanium dichloride in the electrolytic bath in the vicinity of the electrode for electrodeposition, as sampled at the electrolyzing temperature and quenched, it was appreciably difficult to grow the electrodeposit in a compact form. Where the amount of trichloride exceeded two-thirds of that of the titanium dichloride, the electrodeposit could not be obtained in a desired form even though experiments were conducted under various conditions.

A molybdenum plate was used as the electrode for electrodeposition in the foregoing examples and the electrodeposit firmly adhered to the electrode surface. When the electrode is a titanium or iron plate, the electrodeposit adheres to the electrode to such an extent as not to be scraped off for the purpose of analyzing its quality.

In each of the foregoing examples, an electrolytic cell made of quartz glass was employed with outer heating. When using a cell made of porous carbon blocks or silica bricks, each of the heating units is inserted in the bath to make the bath have self-lining of the electrolytic cell.

In each of the foregoing examples titanium trichloride and metallic titanium, which are raw materials of the desired metal, are each added to the electrolytic bath in an amount exceeding the solubility of titanium salt and these materials remain as sediment at the bottom of the electrolytic cell. The examples were conducted with titanium dichloride as a raw material being formed by the reaction of titanium with its compound of high valency. It is also possible, of course, to form the desired titanium dichloride by electrolytic reduction of titanium tetrachloride or trichloride supplied to the electrolytic bath.

In the examples the forced circulation of the electrolytic bath between the part of the bath held at a high temperature and the part at a low temperature was performed by

blowing argon gas into the bath. It is also possible to use a propeller made of an anti-corrosive material such as quartz glass, carbon, tantalum, or the like, instead of blowing the gas. This is very convenient because it permits circulation of a desired amount of the bath without dispersion of the bath from its surface.

Although the examples describe, as the polarization adjustment means, the vibration of the electrode for electrodeposition, this is for convenience of indicating the degree of agitation. It will be readily understood that it is possible to rotate the electrode for electrodeposition in the bath or a plate in order to change the direction of flow and cause a violent flow of the bath in one direction in order to repeatedly strike against the electrode for electrodeposition at one place and at suitable intervals so as to achieve the adjustment of the polarization.

For facilitating macroscopic control of the shape of the deposit being electrodeposited at a relatively high current density, it is preferred, in order to adjust the polarization, to subject the electrode surface to a periodic violent bath flow which strikes against the electrode surface at a frequency of less than several hundred times per minute and preferably less than six hundred times per minute. The frequency depends upon the electrolytic bath composition, the electrolyzing temperature, the current density and the state of agitation. Where depolarization is obtained by intermitting an electrodepositing current of a relavtively high current density, without the aid of periodic impingement of the bath upon the electrode surface, it is preferred for macroscopic shaping of the electrodeposit to remove the polarization relatively intensively during a period of discontinuation of the above current at a frequency of less than 600 times per minute and preferably less than 300 times per minute. A short on-off period of this current is effective to cause the crystals of the electrodeposit to be fine but involves much difficulty in macroscopic shaping of the electrodeposit. However, this difficulty can be overcome by employing periodic violent impingement of the bath on the electrode surface at a frequency of less than 600 times per minute for periodic depolarization.

While this specification has described the electrodeposition of an alloy in connection with the electrodeposition of titanium containing iron or aluminum, it will be understood that any metal, which is electrochemically nobler than magnesium and whose chloride is soluble in the electrolytic bath of this invention, can be electrodeposited with the ratio of the metal to the electrodeposit being controlled at will by suitable addition of the metal compound to the bath. In the electrodeposition of the alloy, it is sufficient only to control the amount of trichloride of titanium which is a base metal of the alloy.

It will be apparent that many modifications and variations may be effected without departing from the scope of the novel concepts of this invention.

What is claimed is:

1. A method for the electrodeposition of titanium comprising the steps of: forming a fused salt electrolytic bath containing (1) a mixture of the chloride salts of barium, magnesium, sodium and calcium, said mixture having a freezing point below 600° C., and (2) titanium dichloride; and electrolyzing said bath while maintaining a temperature therein above 400° C. and below 580° C. and while further maintaining the molar ratio of titanium trichloride to titanium dichloride, in the vicinity of the eletcrode to be electrodeposted, at less than 0.5.

2. The method of claim **1** wherein the temperature of said bath is intermittently raised above 500° C. in order to maintain the said molar ratio of titanium trichloride to titanium dichloride.

3. The method of claim **1** wherein the temperature of the said bath in the vicinity of the electrode for electrodepostion is maintained below 500° C. and a portion of said bath is maintained at a temperature above 500° C. in order to maintain the said molar ratio of titanium trichloride to titanium dichloride and said bath is intermixed with itself.

4. The method of claim **1** wherein the electrolytic bath also contains potassium chloride and said bath has a freezing point less than 600° C.

5. The method of claim **1** wherein the electrolytic bath also contains a three-component system consisting of potassium chloride, magnesium chloride and sodium chloride and said bath has a freezing point less than 600° C.

6. The method of claim **1** wherein the electrodeposition is carried out while maintaining the bath in the vicinity of the electrode for electrodeposition at a temperature from 400° C. to 520° C.

7. The method of claim **1** wherein titanium is located in said bath for adjustment of the condition thereof.

8. The method of claim **1** wherein the electrolytic bath contains titanium as an anode.

9. The method of claim **1** wherein the anode is carbon.

10. The method of claim **1** wherein the electrodeposition is carried out in an electrolytic bath containing, in the vicinity of the electrode for electrodeposition, divalent titanium compound in an amount at least equal to the solubility of said compound at the electrodepositing temperature.

11. The method of claim **1** wherein the electrode surface is subjected to periodic impingement of the bath at frequency of less than 600 times per minute, said impingement being accompanied by an agitation effect violently acting on the electrode surface.

12. The method of claim **1** wherein an electrodepositing current capable of electrodepositing magnesium with titanium is used having an intermittent component of a frequency of less than 600 times per minute.

13. The method of claim **1** wherein the electrode for electrodeposition is violently moved at a frequency of less than 600 times per minute.

14. The method of claim **13** wherein the electrode for electrodeposition is moved more violently in the discontinuation period of the intermittent component of the electrodepositing current than in the conduction period of the current.

15. The method of claim **1** wherein an electrolyte bath with outer heating is used.

16. The method of claim **1** wherein an electrolytic bath with inner heating is used.

17. A method for the electrodeposition of a titanium alloy consisting of titanium and at least one additional metal comprising the steps of: forming a fused salt electrolytic bath containing (1) a mixture of the chloride salts of barium, magnesium, sodium and calcium, said mixture having a freezing point below 600° C., (2) titanium dichloride, and (3) a source of metal to be alloyed with titanium; and electrolyzing said bath while maintaining a temperature therein above 400° C. and below 580° C. and while further maintaining the molar ratio of titanium trichloride to titanium dichloride, in the vicinity of the electrode to be electrodeposited, at less than 0.5.

18. The method of claim **17** wherein the temperature of said bath is intermittently raised above 500° C. in order to maintain the said molar ratio of titanium trichloride to titanium dichloride.

19. The method of claim **17** wherein a portion of said bath is maintained at a temperature above 500° C. in order to maintain the said molar ratio of titanium trichloride to titanium dichloride and said bath is intermixed with itself.

20. The method of claim **17** wherein the electrolytic bath also contains potassium chloride and said bath has a freezing point less than 600° C.

21. The method of claim **17** wherein the electrolytic bath also contains three-component system consisting of potassium chloride, magnesium chloride and sodium chloride and said bath has a freezing point less than 600° C.

22. The method of claim **17** wherein the electrodeposition is carried out while maintaining the bath in the

vicinity of the electrode for electrodeposition at a temperature from 400° C. to 520° C.

23. The method of claim **17** wherein the source of alloy metal is located in said bath for adjustment of the condition thereof.

24. The method of claim **17** wherein the electrolytic bath contains titanium alloy as an anode.

25. The method of claim **17** wherein the anode is carbon.

26. The method of claim **17** wherein the electrodeposition is carried out in an electrolytic bath containing, in the vicinity of the electrode for electrodeposition, divalent titanium compound in an amount at least equal to the solubility of said compound at the electrodepositing temperature.

27. The method of claim **17** wherein the electrode surface is subjected to periodic impingement of the bath at a frequency of less than 600 times per minute, said impingement being accompanied by an agitation effect violently acting on the electrode surface.

28. The method of claim **17** wherein an electrodepositing current capable of electrodepositing magnesium with titanium alloy is used having an intermittent component of a frequency of less than 600 times per minute.

29. The method of claim **17** wherein the electrode for

electrodeposition is violently moved at a frequency of less than 600 times per minute.

30. The method of claim **17** wherein the electrode for electrodeposition is moved more violently in the discontinuation period of the intermittent component of the electrodepositing current than in the conduction period of the current.

31. The method of claim **17** wherein an electrolytic bath with outer heating is used.

32. The method of claim **17** wherein an electrolytic bath with inner heating is used.

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JOHN H. MACK, Primary Examiner

D. R. VALENTINE, Assistant Examiner

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