

Feb. 27, 1968

J. E. PERRY

3,371,020

PROCESS FOR THE ELECTRODEPOSITION OF METALS

Filed Dec. 14, 1964

2 Sheets-Sheet 1

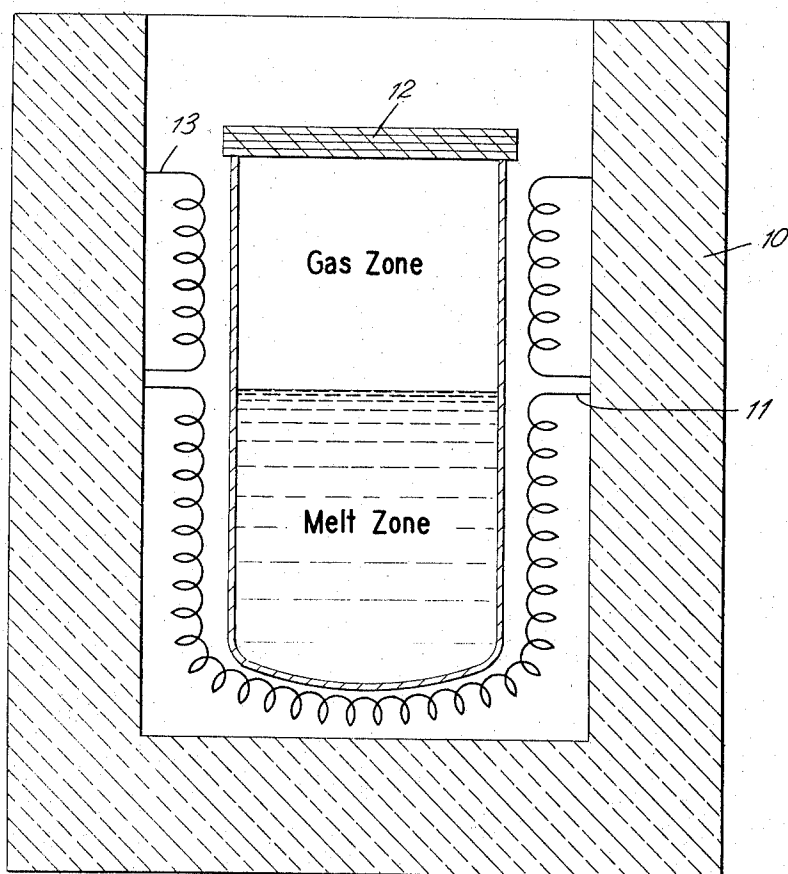


Fig. 1.

INVENTOR
JOHN E. PERRY
BY *William R. Moran*
ATTORNEY

Feb. 27, 1968

J. E. PERRY

3,371,020

PROCESS FOR THE ELECTRODEPOSITION OF METALS

Filed Dec. 14, 1964

2 Sheets-Sheet 2

TEMPERATURE PROFILE IN
ELECTRODEPOSITION CELL

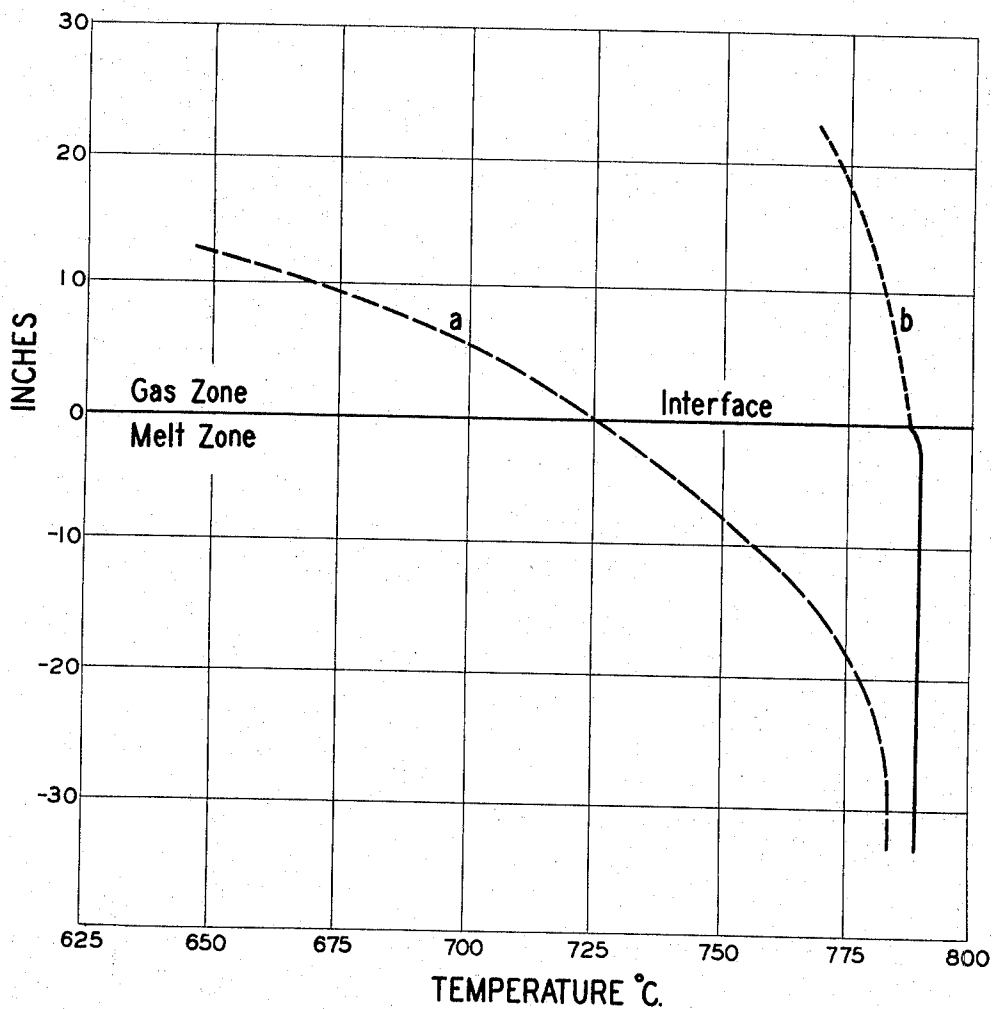


Fig. 2.

INVENTOR
JOHN E. PERRY
BY *William R. Moran*
ATTORNEY

1

3,371,020

PROCESS FOR THE ELECTRODEPOSITION OF METALS

John E. Perry, Bay Village, Ohio, assignor to Union Carbide Corporation, a corporation of New York
Filed Dec. 14, 1964, Ser. No. 418,118
5 Claims. (Cl. 204—39)

This invention relates to an improved process for the electrodeposition of metals, particularly refractory metals, and the alloys and compounds thereof. In one aspect, this invention relates to an improved process capable of yielding dense, fine grain, structurally coherent plates of refractory metals, alloys and compounds of metals of the group: zirconium, hafnium, vanadium, columbium, tantalum, chromium, molybdenum and tungsten. In a further aspect, this invention relates to an improved process useful in the electroplating and electroforming of refractory metals, alloys and the like wherein undesirable roughness and irregularities in the surface of the plated deposit are largely eliminated.

Over the past several decades the electrodeposition of metals has assumed a prominent position in science and industry so that today, a sizable portion of the yearly output of metals is consumed in electrodeposited coatings. A variety of processes are known and currently in use for the electrodeposition of metals on a variety of substrates. In particular a number of processes have been proposed for the electrodeposition of zirconium, columbium, tantalum, chromium, molybdenum, tungsten, and hafnium. However, in the case of zirconium, columbium, and tantalum, none of these previously proposed processes has produced dense, fine grain, structurally coherent plates of the metals. In fact, most of the processes in the prior art are concerned with obtaining these metals in particulate form for use in fusing, rolling and machining processes. These processes usually deposit the metal in the form of a compacted coarse powder or dendritic growth which must be scraped off the substrate on which it is deposited.

Processes are known for the electrodeposition of structurally coherent plates of chromium and tungsten. However, in the case of chromium the metal has always been deposited from an aqueous system and the resulting deposit is always hard or brittle and is frequently cracked. As a result, the chromium must be annealed at high temperatures in order to soften it. In the case of tungsten, known methods for depositing coherent plates require the presence of an oxygenated compound, such as a tungstate. As a result, the tungsten deposited by these processes is not ductile. Moreover, such processes are extremely slow and cannot be carried out other than in the temperature range where tungsten is rendered brittle by carbon.

More recently, a novel process has been discovered which overcomes the aforesaid shortcomings and disadvantages of the prior art for electrodeposition of refractory metals. This process comprises electrolyzing an electrolytic system comprising an electrically conductive base material as a cathode, an anode, and an electrolytic melt having no appreciable concentration of chlorides, bromides, and oxides and consisting essentially of a base melt of at least one fluoride selected from the group consisting of the fluorides of potassium, rubidium, and cesium and at least one fluoride of other elements higher in the

2

electromotive series than the metal to be deposited, and at least one fluoride of the metal to be deposited, the proportions of the fluorides in the melt, the temperature of the melt, usually in the range of from about 575° to about 900° C., and electrolyzing current density being adjusted to produce a dense, structurally coherent deposit of the metal on the base material. This process not only produces dense, fine grain, structurally coherent deposits with good throwing power, but also can be used to electro-win the metals, i.e., extract the metals from molten salts by electrolysis. The dense, fine grain, structurally coherent deposits of metals produced by this process are in sharp contrast to the compacted powders or dendrites deposited by prior processes.

However, it has been found that in an electrodeposition process wherein a metal is deposited from an electrolytic system comprising an electrolytic melt, marked temperature differences exist within the bath itself. These temperature differences generate thermal currents which cause any small particles present in the bath to be constantly in motion rather than settle out at the bottom. As a result, some of the particles in the fused salt bath become attached to the cathode and subsequent deposits of metal cause imperfections, bumps, and roughness on the deposited metal surface.

It has been observed that the particles in fused salt baths that become attached to the cathode and cause the imperfections and irregularities in the electrodeposit have been found to be finely divided metals or metal compounds. These particles are heavier than the bath and under quiescent conditions usually settle out at the bottom. However, the thermal currents generated as a result of unequal heating and/or unequal heat losses keep any particulate matter in a circulating condition in the electrolyte.

In aqueous electroplating processes, the baths are quite commonly cleaned of particles by filtration techniques. However, the use of a filtering operation in fused salt baths is extremely difficult and cumbersome requiring pumps and filters capable of withstanding continuous high temperature operation to remove particles as small as a few microns in size. This problem is more pronounced in the electrodeposition of refractory metals, wherein marked temperature differences within the bath are frequently encountered.

Accordingly, one or more of the following objects will be achieved by the practice of the instant invention. It is an object of this invention to provide a novel process wherein the aforementioned disadvantages are largely eliminated. It is an object of this invention to provide a novel, improved process for the electrodeposition of metals. A further object of this invention is to provide an improved process for the electrodeposition of metals from an electrolytic system onto a cathode base material wherein roughness and irregularities in the plated deposit are largely eliminated. Another object is to provide an improved process for the electrodeposition of refractory metals, alloys and compounds thereof at temperatures as high as 600° C. and higher. These and other objects will readily become apparent to those skilled in the art in the light of the teachings herein set forth.

In its broad aspect, the present invention relates to an improved process for the electrodeposition of metals, particularly refractory metals and alloys and compounds thereof, wherein the electrodeposit has fewer irregularities

and less roughness than those deposited by currently practiced techniques. The improvement comprises heating the zone above and around the gas-electrolyte interface to a temperature at least up to about the liquidus temperature of the electrolyte whereby any circulation due to thermal currents generated by temperature differences within the bath is minimized.

In the drawings, FIGURE 1 depicts a cell for fused salt electrodeposition surrounded by thermal insulation 10 and equipped with electrolyte resistance heaters 11 and heat shields 12. The zone above and around the gas-electrolyte interface is heated by gas zone resistance heaters 13 in accordance with the teachings of this invention. FIGURE 2 depicts temperature profiles taken on a typical cell which was provided with means for applying heat to the upper walls of the cell sufficient to equalize or at least compensate for heat loss from the melt surface. This was accomplished by the use of additional heaters and heat shields around the gas zone of the cell. Profile *a* represents the temperatures obtained when the gas zone was not heated and is typical of the temperature variations experienced in fused salt electrodeposition cells. Profile *b* represents the temperatures experienced in a fused salt electrodeposition cell when the gas zone was heated in accordance with improved process of the present invention to provide a substantially constant temperature throughout the melt zone.

In fused salt baths wherein heat is applied to the sides of the cell, any heat loss is predominantly from the top surface of the melt. In fact, it has been shown that the heat loss from the surface of a fused salt bath is 100 or more times the heat loss from the insulated sides. For instance, the rate of heat loss at an electrolysis temperature of 775° to 800° C. has been found to be 8.0 kilowatts per square foot of bath surface. In smaller salt baths, i.e., those having diameter of about 6-8 inches, temperature measurements as a function of depth of electrolyte have shown no variation in temperature except in the top six inches of the bath. However, in large baths, e.g., those having a diameter of 36 inches, the temperature difference has been appreciable in the top 20 inches of the bath. The temperature equilibrium in these fused salt baths is efficiently maintained by thermal agitation at an energy level equal to 8 kilowatts per square foot of bath surface area.

As hereinbefore indicated, it has been found that the objectives of this invention are achieved when the zone surrounding the gas-melt interface is heated to a temperature sufficient to substantially reduce or eliminate circulation within the melt due to thermal currents generated by temperature differences. In general, the zone is heated to at least about the liquidus temperature of the electrolytic melt. The liquidus temperature of the melt can be defined as that temperature at which the first solid material forms as the melt is slowly cooled. The liquidus temperature will, of course, be dependent upon the particular composition of the electrolytic melt and hence, will vary for different metals, alloys, or compounds thereof.

In practice, sufficient heat is applied to the upper walls of the cell to heat the gas zone and equalize or compensate for the heat loss from the melt surface. By heating the zone above and around the gas-melt interface, the temperature of the salt bath is maintained at the given operating temperature and the temperature differential between the surface and other points below the surface is greatly minimized. Since the heat loss from the fused salt bath is by way of radiation and conduction to the upper walls of the bath, the additional heat greatly reduces or eliminates the heat losses from the bath surface. Hence, thermal currents generated by temperature differences are for all practical purposes eliminated, and particulate matter is allowed to settle to the bottom of the cell.

In one embodiment, particularly the plating of refractory metals, the zone above and around the gas-melt in-

terface is heated to a temperature such that the difference between the lower and upper portions of the electrolytic melt is less than about 10° C., and more preferably less than about 2° C. In a particularly preferred embodiment, the zone is heated to a temperature at which the gas zone and electrolytic melt are substantially in thermal equilibrium.

In general, the method by which the heating of the zone surrounding the gas-melt interface is effected is not necessarily critical and a variety of means can be employed. For example, in addition to the resistance heaters surrounding the melt zone of the electrodeposition cell, electrical resistance heaters can be arranged around the periphery of the gas zone and gas-melt interface if desired. Heat shields are also usually employed at the top of the gas zone to further reduce heat loss and maintain substantially a thermal equilibrium at the gas-melt interface.

As previously indicated, the improved process of this invention is applicable to any electrodeposition procedure wherein the temperature differences within the bath are of sufficient magnitude to cause thermal pumping, i.e., circulation of the electrolyte. However, the process is particularly applicable to the electrodeposition of refractory metals by a recently discovered technique wherein roughness and imperfections in the electrodeposited plate were encountered. This recently discovered technique represents a marked technological advance in the production of highly corrosion resistant equipment for both industrial and military needs.

The process utilizes an electrolytic melt which contains only fluorides. If other anions, such as chlorides, bromides or oxides are present as more than minor impurities, the metal deposit will be in the form of a powder or dendrites. Interdependent factors which must be adjusted in the process to produce a dense coherent deposit are the proportions of the various fluorides in the electrolytic melt, the electrolyzing current density, and the melt temperature. It has been noted that each of these factors always depend somewhat on the particular metal of the other interdependent factors and on the particular metal being deposited. However, these limits can be readily determined for any given electrolytic system by simply adjusting one or more of the variables and observing the nature of the resulting deposit.

The electrolytic melt consists of at least one fluoride of the metal to be deposited and the base melt, i.e., the melt without any fluorides of the metal to be deposited. The base melt is at least one fluoride selected from the fluorides of potassium, rubidium, and cesium and at least one fluoride of other elements higher in the electromotive series than the metal to be deposited. The exact composition of the base melt required to produce dense coherent deposits depends not only on the particular temperature and current density employed, but also on the particular metal being deposited. In the case of zirconium, columbium, tantalum, tungsten, and molybdenum, the base melt should contain between about 10 and about 90 weight percent, preferably between about 30 and about 75 weight percent, of at least one fluoride selected from the group consisting of the fluorides of potassium, rubidium, and cesium. The balance of the base melt for these metals consists of at least one fluoride of other elements higher in the electromotive series than the metal to be deposited. One preferred base melt which can be used to deposit any of the subject metals is the eutectic composition of the fluorides of lithium, sodium, and potassium, which consists of 29.25 weight percent, LiF, 11.70 weight percent NaF, and 59.05 weight percent KF and has a melting point of about 454° C. Other suitable base melts for the various metals are described below in the specific examples.

The concentration of the fluoride of the metal to be deposited in the electrolytic melt depends on the particular base melt, temperature, and current density employed and

5

on the particular metal being deposited. When zirconium, columbium, or tantalum is deposited by the present process the fluoride of the metal to be deposited should be dissolved in the base melt in a concentration between about 5 and about 30 weight percent, preferably between about 5 and about 15 weight percent, based on the simple metal fluoride, and the concentration should be maintained within the range throughout the electrolyzing process. When tungsten is deposited, the melt should contain between about 1 and about 33 weight percent, preferably between 3 and 10 weight percent, tungsten metal. When molybdenum is deposited, the melt should contain between about 1 and about 20 weight percent, preferably between 3 and 10 weight percent, molybdenum metal. In the case of vanadium, chromium, or hafnium deposited from a base melt of the eutectic composition of the fluorides of lithium, sodium, and potassium, suitable concentrations of metal fluoride are 8 weight percent for chromium and hafnium, and 10 weight percent for vanadium, all based on the simple metal fluoride.

The metal fluoride employed may be simple or complex; but if a complex fluoride is used, its cation must be higher in the electromotive series than the metal to be deposited, and its anion must not contain oxygen. Typical useful metal fluorides are the simple fluorides and double fluorides such as potassium hexafluorozirconate^(IV), potassium hexafluorovanadate^(III), potassium heptafluorocolumbate^(V), potassium heptafluotantalate^(V), potassium hexafluorochromate^(III), and potassium hexafluoromolybdate^(III). Where the solubility of the particular metal fluoride employed is very low, it may be fixed in the melt by reduction with the appropriate metal. For example, in the deposition of tungsten or molybdenum it is preferred to place tungsten or molybdenum metal in the electrolytic bath and then introduce gaseous tungsten hexafluoride or molybdenum hexafluoride, which are insoluble, into the bath through a graphite bubbler. The tungsten or molybdenum metal reduces the insoluble hexafluoride gas to a soluble fluoride, from which the tungsten or molybdenum is electrolytically deposited.

The process deposits four of the subject metals (zirconium, hafnium, tantalum, and chromium) from their highest stable valence states in the particular system under consideration, i.e., 4+ for zirconium and hafnium, 5+ for tantalum and 3+ for chromium. The other metals are deposited from valence states below the highest stable state, i.e., 3+ for vanadium and molybdenum and 4+ for columbium and tungsten. In the case of the four metals which are deposited from reduced valence states, a compound of the metal in the appropriate valence state may be prepared externally and added to the electrolytic melt. Alternatively, the metal ion may be reduced in situ in the melt. In the case of tungsten hexafluoride, the tungsten is preferably reduced to a lower valence state by contacting the gaseous tungsten hexafluoride with tungsten metal in the melt and further reduction accomplished by electrolysis.

The electrodeposition step should be carried out in an inert, nonoxidizing atmosphere such as argon, neon, helium, or the like, or under vacuum conditions. If an inert gas is employed, it may be at a pressure above or below atmospheric pressure, as long as it is substantially inert with respect to the melt and the metal. The container for the melt may be made of any material which has no deleterious effect on the melt or the deposited metal and is not attacked by the melt during operation.

The operating limits for the electrolyzing temperature and current density depend on the particular melt employed and on the metal being deposited. Also, the uppermost limit for the current density generally decreases as the concentration of the plating metal fluoride in the melt decreases. Of course, the temperature of the electrolyte must always be above the melting point of the particular melt employed. For example, zirconium can be deposited at a cathode current density of 5 to 40 ma./cm.²,

6

preferably 25 to 30 ma./cm.², and a temperature of 675 to 800° C., preferably 750° C.; tantalum can be deposited at a cathode current density of 5 to 100 ma./cm.², preferably 40 ma./cm.², and a temperature of 700 to 850° C., preferably 800° C.; columbium at 5 to 100 ma./cm.², preferably 50 ma./cm.², and 675 to 850° C., preferably 770° C.; hafnium at 20 ma./cm.² and 750° C.; vanadium at 40 ma./cm.² and 770° C.; chromium at 25 to 60 ma./cm.² and 800 to 840° C.; molybdenum at 2 to 200 ma./cm.², preferably 10 to 100 ma./cm.², and a temperature of 600 to 900° C., preferably 700 to 850° C.; and tungsten at 3 to 200 ma./cm.², preferably 10 to 100 ma./cm.², and a temperature of 525 to 900° C., preferably 725 to 850° C. It will be understood that these are only illustrative examples of suitable operating conditions for the deposition of dense coherent deposits of the various metals, and that such deposits can be produced at many other conditions.

A wide variety of electrically conductive materials and alloys are available for use as the base material (cathode). The only limitations on the base material for this particular process are that it be not excessively reactive with the melt and that it not melt at or below the operating temperature. For example, satisfactory deposits are obtained on stainless steel, graphite, nickel, and copper. In some cases, it may be desirable to pretreat the base material, as by anodizing. The actual choice of a particular base material and the pretreatment to be given to it in any specific case depend on several factors. Among such factors are the type of metal to be deposited, the geometry of the article to be plated, and the dimensional tolerances required in the plated article. In large-scale operations in which the deposited metal is to be removed from the base material, reusable base materials are preferred.

The source of the metal to be deposited in the subject electrolytic system may be either the anode or the electrolytic melt, and the type of anode used depends on whether the anode or the melt is to be the source of metal. When the anode is the source, any of the subject metals can be deposited by using a soluble anode which must be composed in whole or in part of the metal to be plated. Such anode materials include rods, plates, rondels, chunks, or other discrete particles of the particular metal to be deposited. If a particulate anode material is used, it can be held in place by a suitable mesh retainer, such as nickel. When the anode is the source, the voltage applied across the cathode and anode may be below the breakdown potential of the melt.

When the electrolytic melt is the source of the metal to be deposited (electrowinning), an insoluble, soluble, or gaseous anode may be used, depending on the particular metal to be deposited. An insoluble anode, such as graphite or carbon, may be used in the electrowinning of any of the metals which are deposited from their maximum stable valence states, i.e., zirconium, hafnium, tantalum, and chromium. With the insoluble anode, the applied voltage must be at least as high as the breakdown potential of the melt. Any of the subject metals, regardless of the valence state from which they are deposited, may be electrowon by using a gaseous hydrogen anode or a soluble anode containing an active metal selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, and aluminum. In these cases, the applied voltage need not be as high as the breakdown potential of the melt, but only sufficient to overcome the resistance of the electrolyte and the very small polarization of the electrode. When the active metal anode is used, the melt is gradually diluted by active metal fluoride formed at the anode and by deposition of refractory metal at the cathode; thus, for continuous operation, it is best that the melt be recirculated through an external station where the active metal fluoride is removed and refractory metal fluoride added. The gaseous hydrogen anode is generally preferred for electrowinning applica-

tions because it does not require the handling of active metals, and the anodic product (hydrogen fluoride) bubbles out of the melt. The hydrogen anode is also preferred over the insoluble anode because the anodic product is hydrogen fluoride, which is less corrosive than the fluorine gas which is produced at the insoluble anode. Thus, the hydrogen anode permits the use of less expensive and more readily available construction materials for containers, barriers, baffles, and other cell components.

Since the concentration of the fluoride of the metal to be deposited decreases during electrowinning, the melt must be replenished with the plating metal fluoride so that the concentration of that fluoride in the melt is continuously maintained within the required range. For example, in the electrowinning of zirconium, tantalum, or columbium, the concentration of the plating metal fluoride in the melt should be maintained between about 5 and about 30 weight percent.

The metal deposits produced by this particular process are dense, fine grain, structurally coherent plates, as opposed to the layers of compacted powders or dendritic growths produced heretofore. Metal deposits have a density of at least 98 percent of the theoretical density of the metal deposited, and are generally mechanically deformable without breaking and substantially free of non-metallic impurities. There seems to be no limit on the thickness of the deposits which can be produced by this process, and dense coherent plates of more than 0.5 inch thickness have been obtained. One of the advantages of this process is that it can produce metal foils. As used herein, a metal "foil" is distinguished from a film in that a foil is capable of maintaining a structurally coherent shape without a substrate for support, whereas a film is incapable of maintaining a structurally coherent shape without a substrate for support.

The aforesaid process may be used to electrorefine any of the subject metals. This is achieved by making an anode from compounds or alloys wherein one of these metals is present as one of the major constituents, placing the anode in the aforescribed bath containing a fluoride of the metal, and cathodically depositing the pure metal. This process is also useful for separating the various metals from each other.

The process may also be used to electroplate or electroclad any of the subject metals on a base material of any desired shape. Because of its unusual throwing power, this process is especially useful for depositing metal on intricately shaped base materials or on internal surfaces. When the base material is initially provided with a clean and oxide-free surface, this process produces a metal deposit which is bonded to the substrate by atomic attractive forces. Each initially deposited atom of the coating is in intimate contact with the surface atoms of the substrate. In contrast to this atomic bonding achieved by the present invention, the bonding in roll cladding is attained by mechanical means where on a molecular scale there are only a few isolated points of contact.

Similarly, this process may be used to electroform articles of any desired shape. The manner in which the electroformed article is separated from the base material depends on the nature of the base material, the shape of the formed article, and whether the base material is to be reused. For example, a nickel base can be dissolved in nitric acid or mechanically removed by chipping or drilling. A graphite base is usually removed mechanically by chipping or drilling.

In contrast to most other base materials, a base made of Hastelloy C can be easily removed from the deposited metal by simply pulling the base away from the metal.

The process may be used not only to deposit the pure metals, but also to deposit various alloys or compounds of the subject metals. This may be accomplished by introducing into the melt the respective fluorides of the materials required to make the desired alloys or compounds, or

by employing secondary anodes of the desired materials. For example, dense structurally coherent plates of zirconium diboride can be deposited by electrolyzing a melt consisting of a base melt containing between about 10 and about 90 weight percent at least one fluoride selected from the group consisting of the fluorides of potassium, rubidium, and cesium, and a balance of at least one fluoride of other elements higher in the electromotive series than zirconium, and boron; about 5 to 30 weight percent as a fluoride of zirconium, based on the simple fluoride; and about 5 to 11 weight percent boron trifluoride present in the melt as a fluoroborate.

Suitable base melts for the deposition of zirconium diboride are the eutectic composition of the fluorides of potassium, sodium, and potassium; the eutectic composition of the fluorides of potassium and lithium; and the eutectic composition of the fluorides of potassium and sodium. The boron trifluoride may be provided by bubbling gaseous boron trifluoride (BF_3) into a melt containing potassium fluoride; the boron trifluoride and the potassium fluoride then react within the melt to form potassium fluoroborate (KBF_4), so that the boron trifluoride is actually present in the melt as a fluoroborate. Alternatively, the melt may be formed directly from KBF_4 as a starting material, such as by mixing together appropriate proportions of KBF_4 , NaBF_4 , and K_2ZrF_6 . Of course, the boron trifluoride could also be added by other suitable chemically equivalent starting materials.

The electrodisposition of zirconium diboride is carried out at temperatures of 700 to 900° C., preferably 775 to 875° C., and cathode current densities of 5 to 350 ma./cm.², preferably 150 to 200 ma./cm.². The anode used in the deposition of zirconium diboride preferably contains a major amount of zirconium.

The following examples are illustrative:

Example I

Tantalum was plated onto a copper rod cathode from a bath consisting of the eutectic composition of LiF, NaF, and KF and containing 15 weight percent tantalum fluoride. The electrolysis was carried out at a melt temperature of 775° C. and a cathode current density of 30 ma./cm.². Although the top of the cell was covered by a heat shield and the cell otherwise insulated, no attempt was made to apply additional heat to the gas zone above the melt. Temperature profiles taken on the cell indicated that the difference between the lower and upper portion of the melt was greater than 50° C. The resulting plate on the cathode was identified as tantalum and had a density of 16.6 grams/cm.³ (the theoretical density of tantalum), a hardness of 95 DPH, and was structurally coherent. However, a careful inspection of the plated tantalum surface revealed roughness and irregularities.

The electrodeposition was then repeated under the aforementioned conditions with the exception that additional heaters were placed around the gas zone and gas-melt interface. During the electrolysis, the gas zone was heated to provide a substantially constant temperature throughout the melt zone. Temperature profiles taken on the cell indicated that the temperature in the melt zone varied only by a few degrees and this was confined to the top 1 to 2 inches of melt. The resulting plates were smooth and free of roughness and bumps and superior to those produced by the first process wherein no additional heat was employed.

Example II

Columbium was plated onto a copper rod cathode from a bath consisting of the eutectic composition of LiF, NaF, and KF and containing 10 weight percent tantalum fluoride. The electrolysis was carried out at a melt temperature of 775° C. and a cathode current density of 50 ma./cm.². Although the top of the cell was covered by a heat shield and the cell otherwise insulated, no attempt was made to apply additional heat to the gas zone above

the melt. Temperature profiles taken on the cell indicated that the difference between the lower and upper portion of the melt was greater than 50° C. The resulting plate on the cathode was identified as columbium and was structurally coherent. However, a careful inspection of the plated columbium surface revealed roughness and irregularities.

The electrodeposition was then repeated under the aforementioned conditions with the exception that additional heaters were placed around the gas zone and gas-melt interface. During the electrolysis, the gas zone was heated to provide a substantially constant temperature throughout the melt zone. Temperature profiles taken on the cell indicated that the temperatures in the melt zone varied only by a few degrees and this was confined to the top 1 to 2 inches of melt. The resulting plates were smooth and free of roughness and bumps and superior to those produced by the first process where no additional heat was employed.

Example III

Tungsten was plated onto a copper rod cathode from a bath consisting of the eutectic composition of LiF, NaF, and KF and containing 15 weight percent tantalum fluoride. The electrolysis was carried out at a melt temperature of 775° C. and a cathode current density of 30 ma./cm.². Although the top of the cell was covered by a heat shield and the cell otherwise insulated, no attempt was made to apply additional heat to the gas zone above the melt. Temperature profiles taken on the cell indicated that the difference between the lower and upper portion of the melt was greater than 50° C. The resulting plate on the cathode was identified as tungsten and was structurally coherent. However, a careful inspection of the plated tungsten surface revealed roughness and irregularities.

The electrodeposition was then repeated under the aforementioned conditions with the exception that additional heaters were placed around the gas zone and gas-melt interface. During the electrolysis, the gas zone was heated to provide a substantially constant temperature throughout the melt zone. Temperature profiles taken on the cell indicated that the temperature in the melt zone varied only by a few degrees and this was confined to the top 1 to 2 inches of melt. The resulting plates were smooth and free of roughness and bumps and superior to those produced by the first process wherein no additional heat was employed.

Although the invention has been illustrated by the preceding examples, it is not to be construed as limited to the materials employed therein, but rather, the invention encompasses the generic area as hereinbefore disclosed. Various modifications and embodiments of this invention can be made without departing from the spirit and scope thereof.

What is claimed is:

1. In an electrodeposition process wherein metals, alloys and compounds thereof, are deposited in an electrolytic system on an electrically conductive cathode base material, said electrolytic system comprising (1) a gas zone and (2) an electrolyte zone heated by heating means and having temperature differentials within said electrolyte zone sufficient to cause circulation of said electrolyte, the improvement which comprises heating said gas zone using heating means separate from the heating means of said electrolyte zone to a temperature at least up to about the liquidus temperature of said electrolyte whereby said circulation is minimized.

2. In an electrodeposition process wherein metals, alloys and compounds thereof, are deposited in an electrolytic system on an electrically conductive cathode base material, said electrolytic system comprising (1) an inert gas zone and (2) an electrolytic melt zone heated by heating means and having temperature differentials within said melt sufficient to cause circulation of said melt, the improvement which comprises heating said gas zone using

heating means separate from the heating means of said electrolytic melt at least to a temperature at which said inert gas zone and said electrolytic melt are substantially isothermal, whereby said circulation is minimized.

3. In an electrodeposition process wherein metals, alloys, and compounds of at least one metal selected from the group consisting of zirconium, hafnium, vanadium, columbium, tantalum, chromium, molybdenum and tungsten, are deposited in an electrolytic system on an electrically conductive cathode base material at temperatures of at least about 575° C.; said electrolytic system comprising:

- (1) an inert gas zone;
- (2) an electrolytic melt heated by heating means and having no appreciable concentration of chlorides, bromides and oxides and consisting essentially of
 - (a) a base melt of at least one fluoride selected from the group consisting of the fluorides of potassium, rubidium and cesium and at least one fluoride of other elements higher in the electromotive series than metal to be deposited, and
 - (b) at least one fluoride of metal to be deposited, said electrolytic melt having temperature differentials within said melt sufficient to cause circulation of said melt;

the improvement which comprises heating said gas zone using heating means separate from the heating means of said electrolytic melt at least to a temperature at which said inert gas zone and said electrolytic melt are substantially isothermal, whereby said circulation is minimized.

4. In an electrodeposition process wherein metals, alloys, and compounds of at least one metal selected from the group consisting of zirconium, hafnium, vanadium, columbium, tantalum, chromium, molybdenum and tungsten, are deposited in an electrolytic system on an electrically conductive cathode base material at temperatures of at least about 575° C.; said electrolytic system comprising:

- (1) an inert gas zone;
- (2) an electrolytic melt heated by heating means and having no appreciable concentration of chlorides, bromides and oxides and consisting essentially of
 - (a) a base melt of at least one fluoride selected from the group consisting of the fluorides of potassium, rubidium and cesium and at least one fluoride of other elements higher in the electromotive series than metal to be deposited, and
 - (b) at least one fluoride of metal to be deposited, said electrolytic melt having temperature differentials within said melt sufficient to cause circulation of said melt;

the improvement which comprises heating said gas zone using heating means separate from the heating means of said electrolytic melt at least to a temperature wherein the difference between the lower and upper portions of said electrolytic melt is less than about 10° C., whereby said circulation is minimized.

5. In an electrodeposition process wherein metals, alloys and compounds of at least one metal selected from the group consisting of zirconium, hafnium, vanadium, columbium, tantalum, chromium, molybdenum and tungsten, are deposited in an electrolytic system on an electrically conductive cathode base material at temperatures of at least about 575° C.; said electrolytic system comprising:

- (1) an inert gas zone;
- (2) an electrolytic melt heated by heating means and having no appreciable concentration of chlorides, bromides and oxides and consisting essentially of
 - (a) a base melt of at least one fluoride selected from the group consisting of the fluorides of potassium, rubidium and cesium and at least one fluoride of other elements higher in the electromotive series than metal to be deposited, and

11

(b) at least one fluoride of metal to be deposited,
said electrolytic melt having temperature differ-
entials within said melt sufficient to cause circula-
tion of said melt;

the improvement which comprises heating said gas zone 5
using heating means separate from the heating means
of said electrolytic melt at least to a temperature
wherein the difference between the lower and upper por-
tions of said electrolytic melt is less than about 2° C.,
whereby said circulation is minimized.

10

12

References Cited

UNITED STATES PATENTS

1,984,745	12/1934	Kaizik	204—267	X
2,424,179	7/1947	McNitt	204—245	X

HOWARD S. WILLIAMS, *Primary Examiner*.G. KAPLAN, *Assistant Examiner*.