

1

3,444,058

**ELECTRODEPOSITION OF REFRACTORY METALS**

Geoffrey W. Mellors, Strongsville, and Seymour Senderoff,  
Fairview Park, Ohio, assignors to Union Carbide Corporation, a corporation of New York  
No Drawing. Continuation-in-part of application Ser. No. 609,683, Jan. 16, 1967. This application Apr. 8, 1968, Ser. No. 724,677  
Int. Cl. C22d 3/20, 3/14  
U.S. Cl. 204—71 19 Claims

**ABSTRACT OF THE DISCLOSURE**

Zirconium, tantalum, columbium, chromium, hafnium, tungsten, molybdenum, vanadium and alloys thereof can be electrodeposited as dense, structurally coherent plates from a solution of the refractory metal fluoride in a molten alkali-fluoride eutectic mixture, having no appreciable concentrations of chlorides, bromides and oxides. The process obeys Faraday's law and provides a coating essentially unalloyed with the substrate material. A soluble anode comprising the metal to be deposited is used. The metal to be deposited must first be present in the melt prior to producing the deposit as an ion in a sufficiently low valence state wherein said metal ion will not attack the deposited metal.

This application is a continuation-in-part of U.S. patent application Ser. No. 609,683, filed Jan. 16, 1967, now abandoned. Ser. No. 609,683 is a continuation-in-part of U.S. patent application Ser. No. 302,755, filed July 19, 1963, now abandoned. Ser. No. 302,755 is a continuation-in-part of U.S. patent applications Ser. No. 234,394, filed Oct. 31, 1962; Ser. No. 234,396, filed Oct. 31, 1962; and Ser. No. 267,879, filed Feb. 18, 1963, all of which are abandoned. Ser. No. 267,879 is a continuation-in-part of Ser. No. 63,471, filed Oct. 19, 1960; Ser. No. 70,955, filed Nov. 22, 1960; and Ser. No. 136,285, filed Sept. 5, 1961, all of which are now abandoned.

This invention relates to the electrodeposition of metals. In one aspect, this invention relates to the electrodeposition of dense, fine grain, structurally coherent plates of zirconium, hafnium, vanadium, columbium, tantalum, chromium, molybdenum, tungsten and alloys thereof. In a further aspect, this invention relates to an electrodeposition process which obeys Faraday's law and provides a coating essentially unalloyed with the substrate material.

Heretofore, 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. The prior art has often referred to these layers of compacted powders or dendritic growth as "films," as in U.S. Patent No. 1,933,319 to Driggs et al., and such layers do appear to be dense and coherent to the naked eye. However, modern methods of analysis and modern techniques in photomicrography have shown these deposits to be compacted powders, dendritic growths, or diffusion coatings not dense, fine grain, structurally coherent plates. Obviously, loosely compacted powders of these metals are unsuitable as durable refractory articles and mill

2

shapes, especially when subjected to high temperatures and corrosive fluids.

Many reports in the prior art, such as U.S. Patent No. 1,933,319 cited above, have disclosed the electrodeposition of zirconium, columbium, and tantalum from a mixed halide or chloride bath. However, it has been found that these metals cannot be electrodeposited from such baths to form dense, fine grain, structurally coherent plates. As aptly stated in *Electrochemistry of Fused Salts*, 1961 treatise by Delimarski and Markov: "The electrolysis of melts involving the deposition of solid metals has not been used commercially to any large extent due to the impossibility of depositing the metal in compact form. Usually, a powdery, and more seldom, a dendritic deposit is formed, preventing any further processing of the metal. Although a thin layer of deposited metal which is in immediate contact with the cathode usually turns out to be dense, this is obviously due to the formation of a surface alloy and other causes."

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.

One of the present inventors is a coinventor of a process for electrodepositing structurally coherent plates of molybdenum, as described in U.S. Patent No. 2,715,093, issued Aug. 9, 1955. However, this process has very poor throwing power and, as a result, cannot be used to successfully coat the interiors of articles or to coat irregular articles with uniform coatings without complex and costly conforming anode arrangements.

It is, therefore, the main object of the present invention to provide a process for electrodepositing dense, fine grain, structurally coherent deposits of zirconium, hafnium, vanadium, columbium, tantalum, chromium, molybdenum, tungsten and alloys thereof.

It is still another object of this invention that these deposits shall contain no appreciable amounts of the substrate material as is the case in diffusion coatings.

It is still another object to form the deposits at a rate determined by Faraday's law rather than by the rate of diffusion into the substrate.

It is still another object to form the deposits in an electrolyte in which they are not attacked.

It is another object of the invention to provide a process for producing such deposits which are relatively soft.

It is still another object of the invention to provide such a process which will produce thick deposits of pure metal.

It is a further object of the invention to provide such a process which has good throwing power.

It is a still further object of the invention to provide such a process in which the electrolytic bath does not contain oxygenated compounds.

Other aims and advantages of the invention will be apparent from the following description and appended claims.

In accordance with the present invention, there is provided a process for producing dense structurally coherent deposits of a metal selected from the group consisting of zirconium, hafnium, vanadium, columbium, tantalum,

chromium, molybdenum, and tungsten comprising 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 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 valence state of the ion of the metal to be deposited, the temperature of the melt, and the electrolyzing current density being adjusted to produce a dense, structurally coherent deposit of the metal on the base material.

It has been unexpectedly found that all the aforementioned shortcomings and disadvantages of the prior art processes can be overcome by electrodepositing the named metals from the all-fluoride bath described above. This process not only produces dense, fine grain, structurally coherent and ductile deposits with good throwing power, but also can be used to electrowin the metals, i.e., extract the melts from molten salts by electrolysis.

The dense fine, grain, structurally coherent deposits of zirconium, tantalum, and columbium produced by this process are in sharp contrast to the compacted powders or dendrites deposited by prior processes.

The inventive process not only produces dense structurally coherent deposits, but produces plates essentially unalloyed with the substrate, except possibly for a very thin diffusion layer produced thermally at the interface between the substrate and coating. This is in contradistinction to the diffusion coating in which a continuous gradient in composition occurs such that the content of the substrate material in the coating is high near the interface and decreases continuously as the surface is approached.

While diffusion alloys with the substrate are frequently valuable as corrosion-resistant or hard-facing coatings, they differ from true electroplated coatings in the following ways:

(1) The composition of the diffusion alloy varies through the thickness of the coating; that of the electroplated coating is constant.

(2) The rate of deposition of the diffusion alloy is determined by and is limited by the diffusion rates of the metals in the solid substrate. Since the compositions of the two ends of the diffusion couple are constant, the concentration gradient (and thus the driving force) must decrease with increasing thickness of the diffusion layer and result in an ever-decreasing and ultimately vanishing rate. The rate of deposition of the true electroplated coating is determined by the current, is limited by the diffusion rate of ions in the liquid electrolyte, and is independent of the substrate or rates of solid-state diffusion. While there is in principle no thickness limitation, slowly increasing roughness, with increasing thickness, imposes a practical limit.

(3) The rate of deposition of a diffusion alloy decreases with increasing thickness, and falls to zero when the concentration of substrate metal in the surface of the alloy becomes too low. The function of the current is merely to maintain some metal or metal salt at the surface of the substrate to maximize the concentration gradient driving the diffusion process. Excess material that does not diffuse into the substrate may redissolve in the electrolyte or may be deposited in the form of a poorly attached dendritic deposit overlying the diffusion layer.

The inventive process not only produces dense, structurally coherent deposits, but also has extremely good throwing power. As a result, this process can be used to deposit uniform metal plates on either the exterior or interior of irregularly shaped articles.

The inventive process also produces relatively soft or ductile deposits without the use of supplemental anneal-

ing or heat treatments. This is especially significant in the case of chromium. For example, whereas known processes for electrodepositing chromium often produce deposits having hardnesses of 300 to 900 DPH, the present process deposits chromium having a hardness as low as 145 DPH.

It is important that the electrolytic melt employed in the present invention contain only fluorides and that the metal ion to be reduced be in the appropriate valence state. If other anions, such as chlorides, bromides, or oxides are present as more than minor impurities, or if the valence state is too high, the metal deposit will be in the form of a powder or dendrites. Also, when the valence states are too high, low cathode current efficiency and attack on cathodes also occurs.

Interdependent factors which must be adjusted in the inventive 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. Although numerous examples of each of these factors are described in detail hereinafter, it will be understood that the operating limits for each of these factors always depend somewhat on the particular values 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 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 that 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 of 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 hexafluorovandate (III), potassium heptafluorocolumbate (V), potassium heptafluorotantalate (V), potassium hexafluorochromate (III), and potassium hexafluoromolybdate (III). When the valence of the metal in the easily available compound is higher than that required for deposition, it must first be reduced to the appropriate valence state externally or in situ before electrodepositing the metal. 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 essentially 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.

As indicated previously, the valence state of the metal ion to be reduced is a prime consideration in the process. Two of the metals, zirconium and hafnium, are deposited from what is believed to be their highest stable valence states, i.e., +4. Tantalum is deposited from the 5+ state. This has until recently been considered its highest stable valence state. However, it has been found that electrolysis with a graphite anode of pure fluoride solutions containing  $[T_aF_7]^{-2}$  such as those described here, raises the tantalum to a stable valence state approaching 6+ [J. Electrochem. Soc., 112, 642 (1965), G. W. Melors & S. Senderoff]. The other metals are deposited from deposited from valence states below their well known highest stable state. The required valence states are 3+ for vanadium, chromium and molybdenum, 4+ for columbium and 4.5+ for tungsten. In the case of the six metals which are deposited from valence states below their highest stable valence, 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 prior to plating.

The electrodeposition step should be carried out in an inert, nonoxidizing atmosphere such as argon, neon, helium, or the like, or under vacuum condition. 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.<sup>2</sup>, preferably 25 to 30 ma./cm.<sup>2</sup>, 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.<sup>2</sup>, preferably 40 ma./cm.<sup>2</sup>, and a temperature of 700 to 850° C., preferably 800° C.; columbium at 5 to 100 ma./cm.<sup>2</sup>, preferably 50 ma./cm.<sup>2</sup>, and 675 to 850° C., preferably 770° C.; hafnium at 20 ma./cm.<sup>2</sup> and 600° C.; vanadium at 40 ma./cm.<sup>2</sup> and 770° C.; chromium at 25 to 60 ma./cm.<sup>2</sup> and 800 to 840° C.; molybdenum at 2 to 200 ma./cm.<sup>2</sup>, preferably 10 to 100 ma./cm.<sup>2</sup>, and a temperature of 600 to 900° C., preferably 700 to 850° C.; and tungsten at 3 to 200 ma./cm.<sup>2</sup>, preferably 10 to 100 ma./cm.<sup>2</sup>, 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 which can be determined by the teachings of the present invention.

A wide variety of electrically conductive materials and alloys are available for use as the base material (cathode) in the inventive process. The only limitations on the base material 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, and the refractory metals themselves. This is not true of diffusion coating processes. The base material not only determines the rate of deposition in diffusion coating, but where the rate of diffusion is too low (as in refractory metal substrates), their use is precluded (A. R. Stetson, Material In Design Engineering 57, 81 (March 1963)). 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), a liquid or gaseous soluble anode may be used. Any of the subject metals, regardless of the valence state from which they are deposited, may be electrowon by using a gaseous hydrogen anode with a porous inert collector such as graphite 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 applications because it does not require the handling of active metals, and the anodic product (hydrogen fluoride) bubbles out of the melt. The

use of an undepolarized insoluble anode such as graphite prevents us from obtaining dense coherent deposits.

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 the inventive process are dense, fine grain, structurally coherent plates, as opposed to the layers of compacted powders or dendritic growths produced heretofore. Metal deposits produced by this invention 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 nonmetallic impurities. There seems to be no limit to the thickness of the deposits which can be produced by this process other than slow progressive roughening and dense coherent plates of more than 0.5 inch thickness have been obtained. This is in contrast to the fundamental thickness limitation on diffusion coatings. 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 process of the present invention 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 inventive 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 inventive process may be used not only to deposit the pure metals, but also to deposit various alloys of the subject metals, as well as alloys or compounds of the refractory metals with other elements. 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, it has been possible to prepare dense, structurally coherent deposits of alloys of two or more of the aforementioned refractory metals on the same substrate. Tungsten-molybdenum and

tantalum-chromium alloys have been prepared by the process of this invention. Additionally, alloys or compounds of the refractory metals with other elements can also be prepared. Coatings composed of zirconium diboride, as well as vanadium silicide, and tungsten-nickel alloys have been successfully deposited in accordance with this process.

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 of 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 of 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 lithium, 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 ( $\text{BF}_3$ ) into a melt containing potassium fluoride; the boron trifluoride and the potassium fluoride then react within the melt to form potassium fluoroborate ( $\text{KBF}_4$ ), so that the boron trifluoride is actually present in the melt as a fluoroborate. Alternatively, the melt may be formed directly from  $\text{KBF}_4$  as a starting material, such as by mixing together appropriate proportions of  $\text{KBF}_4$ ,  $\text{NaBF}_4$ , and  $\text{K}_2\text{ZrF}_6$  in an appropriate mixture of alkali fluorides. Of course, the boron trifluoride could also be added by other suitable chemically equivalent starting materials.

The electrodeposition 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.<sup>2</sup>, preferably 150 to 200 ma./cm.<sup>2</sup>. The anode used in the deposition of zirconium diboride preferably contains a major amount of zirconium.

The preparation of other alloy deposits can be prepared as indicated in the examples.

The following examples are illustrative:

#### EXAMPLE I

An electrolytic system was provided with a zirconium anode, a graphite cathode in the shape of a flat plate, and an electrolytic melt consisting of 10 weight percent zirconium tetrafluoride and 90 weight percent of the eutectic composition of LiF, NaF, and KF. This electrolytic system was electrolyzed at a melt temperature of 750° C. and a cathode current density of 30 ma./cm.<sup>2</sup>. In a short time, the cathode was completely covered with a dense, structurally coherent metal plate 0.020 inch thick. The metal plate was identified as zirconium by X-ray spectrum and had a density of 6.4 grams/cm.<sup>3</sup>, which is the theoretical density of zirconium. The metal plate was also mechanically deformable without breaking and contained no impurities in quantities larger than traces as determined spectroscopically.

#### EXAMPLE II

Zirconium was plated at 725° C. from a bath consisting of a base melt of 67.5 weight percent KF and 32.5 weight percent LiF and containing 10 weight percent zirconium tetrafluoride. All other process conditions and the resultant plate were as described in Example I.

#### EXAMPLE III

Zirconium was plated from a bath consisting of a base melt of 67.5 weight percent KF and 32.5 weight percent NaF and containing 10 weight percent zirconium tetrafluoride. All other process conditions and the resultant plate were as described in Example I.

## EXAMPLE IV

A columbium sheet containing approximately 1 to 2 percent tantalum was electrorefined by making it the anode and electrolyzing it in a bath consisting of 10 weight percent columbium fluoride added as potassium heptafluocolumbate and the eutectic composition of LiF, NaF, and KF. The pentavalent columbium was reduced electrolytically to the tetravalent state before commencing the run. The electrolysis was then carried out at a melt temperature of 810° C. and a cathode current density of 40 ma./cm.<sup>2</sup>. The resulting plate deposited on the cathode had a density of 8.4 grams/cm. (the theoretical density of columbium), was structurally coherent, and contained no tantalum or other impurities in quantities larger than traces as determined spectroscopically.

## EXAMPLE V

Columbium was plated from a bath consisting of a base melt of the eutectic composition of LiF, NaF, and KF and containing 30 weight percent columbium fluoride, the columbium having been reduced electrolytically to the tetravalent state. The electrolysis was carried out at a melt temperature of 770° C. and a cathode current density of 50 ma./cm.<sup>2</sup> with a columbium anode, and the resultant plate was as described in Example IV.

## EXAMPLE VI

Additional columbium plates were obtained from baths consisting of a base melt of the eutectic composition of LiF, NaF, and KF and containing 5 to 15 weight percent columbium fluoride, the Cb having been reduced electrolytically to the tetravalent state. The electrolysis was carried out at 810° C. and 80 ma./cm.<sup>2</sup> and at 800° C. and 40 ma./cm.<sup>2</sup> with an anode of columbium rondels in a nickel basket. In all cases, the resultant plates were as in Example IV. The columbium was identified by its characteristic X-ray spectrum and also by emission spectroscopy, the latter demonstrating impurities to be negligible. Sound structure was shown by metallographic examination.

## EXAMPLE VII

Tantalum was plated from a bath consisting of the eutectic composition of LiF, NaF, and KF and containing 30 weight percent tantalum pentafluoride. The electrolysis was carried out at a melt temperature of 800° C. and a cathode current density of 80 ma./cm.<sup>2</sup> with a tantalum anode. The resulting plate on the cathode was identified as tantalum and has a density of 16.6 grams/cm.<sup>3</sup> (the theoretical density of tantalum), a hardness of 95 DPH, was structurally coherent, and contained no impurities.

## EXAMPLE VIII

Additional tantalum plates were obtained from baths consisting of a base melt of the eutectic composition of LiF, NaF, and KF and containing 5 to 15 weight percent tantalum pentafluoride. The electrolysis was carried out at 800° C. and 60 ma./cm.<sup>2</sup> with an anode of tantalum rondels in a nickel basket. In each case, the resultant plate was as in Example VII.

## EXAMPLE IX

An electrolytic system was provided with a graphite anode, a copper cathode in the shape of a flat sheet, and an electrolytic melt consisting of 90 weight percent base melt of the eutectic composition of LiF, NaF, and KF and 10 weight percent TaF<sub>5</sub>. This electrolytic system was electrolyzed at a melt temperature of 770° C., a cathode current density of 70 ma./cm.<sup>2</sup>, and an applied voltage of 4 volts. The electrolysis was continued for 5 hours, at which time the cathode was completely covered with a dense, structurally coherent tantalum plate 0.009 inch thick. The tantalum plate had a density of 16.6 grams/cm.<sup>3</sup> (the theoretical density of tantalum) and a hardness of 139

DPH, was mechanically deformable without breaking, and contained no impurities in quantities larger than traces as determined spectroscopically.

Attempts to repeat this in the same electrolyte failed due to very low cathode current efficiency, approaching zero in some cases. Substitution of a tantalum anode for the graphite anode resulted in attack of the tantalum by the electrolyte so that the valence of the dissolved Ta was reduced to 5+. Subsequent electroplating at the same current density and temperature using the tantalum anode gave deposits with high cathode current efficiency.

## EXAMPLE X

Additional tantalum plates were produced under conditions identical to those described in Example IX, using a tantalum anode, but with different current densities, times, and temperatures, as shown in the following table:

TABLE I

CCD ma./cm. <sup>2</sup>	Time, hrs.:min.	Temp., °C.	Percent efficiency
25	4:15	780	90
80	1:00	780	30
50	1:00	780	45
20	4:00	725	71
100	1:00	772	100
50	2:40	772	91
150	1:15	725	100
100	1:15	725	85
50	2:15	725	77
50	4:45	730	50
50	2:55	730	82
70	5:00	770	91
50	6:15	770	60

In each case, the metal plate had a density of about 16.6 grams/cm.<sup>3</sup> (the theoretical density of tantalum), was structurally coherent and mechanically deformable without breaking, and contained no impurities in quantities larger than traces as determined spectroscopically.

## EXAMPLE XI

An electrolytic system was provided with an alloy anode consisting of 15 atom percent sodium and 85 atom percent lead, a copper cathode in the form of a flat sheet, and an electrolytic melt consisting of 90 weight percent base melt of the eutectic composition of LiF, NaF, and KF and 10 weight percent TaF<sub>5</sub>. This electrolytic system was electrolyzed for about 5 hours at a melt temperature of 770° C., a cathode current density of 50 ma./cm.<sup>2</sup>, and an applied voltage of 0.2 volt. The system was then replenished by the addition of K<sub>2</sub>TaF<sub>7</sub> to the electrolyte and the addition of Na to the anode, after which the electrolysis was continued until depletion occurred again. The final metal deposit on the cathode was 0.008 inch thick, was structurally coherent, and had a density of 16.6 grams/cm.<sup>3</sup>, which is the theoretical density of tantalum. The metal deposit also was mechanically deformable without breaking and contained no impurities in quantities larger than traces as determined spectroscopically.

## EXAMPLE XII

The process described in Example XI was repeated using an alloy anode of 5 mole percent sodium and 95 mole percent lead. The operating conditions and the final deposit were the same as described in Example XI except that more frequent replenishment was required to obtain satisfactory deposits.

## EXAMPLE XIII

The process of Example XI was repeated using an alloy of 15 mole percent calcium and 85 mole percent lead as the anode. The operating conditions and the resulting tantalum deposit were the same as described in Example XI.

## EXAMPLE XIV

An electrolytic system was provided with an alloy anode consisting of 30 mole percent sodium and 70 mole percent lead, a copper cathode in the form of a flat sheet,

## 11

and an electrolytic melt consisting of 90 weight percent of a base melt of the eutectic composition of LiF, NaF, and KF and 10 weight percent  $\text{CbF}_5$ . The columbium was reduced to the tetravalent state by electrolysis. Then this electrolytic system was electrolyzed at a melt temperature of  $770^\circ\text{C}$ ., a cathode current density of 50 ma./cm.<sup>2</sup>, and an applied voltage of 0.05 volt. The electrolysis was continued for 16 hours, which was sufficient to produce a 0.032-inch thick plate of columbium on the cathode. The metal plate had a density of 8.4 grams/cm.<sup>3</sup> (the theoretical density of columbium), was structurally coherent and mechanically deformable without breaking and contained no impurities in quantities larger than traces as determined spectroscopically.

## EXAMPLE XV

The process of Example XIV was repeated using an alloy of 40 mole percent calcium and 60 mole percent lead as the anode. The operating conditions and the resulting columbium deposit were the same as described in Example XIV.

## EXAMPLE XVI

An electrolytic system was provided with an anode consisting of hydrogen gas bubbled into the melt through a porous graphite current collector, a copper cathode in the form of a flat sheet, and an electrolytic melt consisting of 85 weight percent base melt of the eutectic composition of LiF, NaF, and KF and 15 weight percent  $\text{TaF}_5$ . This electrolytic system was electrolyzed at a melt temperature of  $775^\circ\text{C}$ ., a cathode current density of 30 to 50 ma./cm.<sup>2</sup>, and an applied voltage of 0.1 to 0.2 volt. Efficiencies of 96%, 82% and 100% were obtained on three separate trials. In each case, the resulting tantalum deposit on the cathode had a density of 16.6 grams/cm.<sup>3</sup> (the theoretical density of tantalum), was structurally coherent and mechanically deformable without breaking, and contained no impurities in quantities larger than traces as determined spectroscopically.

## EXAMPLE XVII

The process of Example XVI was repeated using 20 weight percent  $\text{TaF}_5$  in the melt, a cathode current density of 50 ma./cm.<sup>2</sup> and a melt temperature of  $770^\circ\text{C}$ . Efficiencies of 75%, 50%, and 66% were obtained on three separate trials. Other operating conditions and the resulting metal deposit were the same as described in Example XVI.

## EXAMPLE XVIII

An electrolytic system was provided with a zirconium anode, a graphite cathode, and an electrolytic melt consisting of 80 weight percent of the eutectic composition of LiF and KF, 10 weight percent  $\text{KBF}_4$ , and 10 weight percent  $\text{ZrF}_4$ . This electrolytic system was electrolyzed at a melt temperature of  $800^\circ\text{C}$ . and a cathode current density of 100 to 200 ma./cm.<sup>2</sup>. Dense, structurally coherent plates of zirconium diboride were plated on the cathode to a thickness of 0.035 inch. The plate was identified as zirconium diboride by X-ray diffraction and chemical analysis. The plate contained no impurities in quantities larger than traces as determined spectroscopically.

## EXAMPLE XIX

An electrolytic system was provided with a vanadium anode, a copper cathode, and an electrolytic melt consisting of 90 weight percent base melt of the eutectic composition of the fluorides of lithium, sodium, and potassium and 10 weight percent potassium hexafluovanadate ( $\text{K}_3\text{VF}_6$ ) based on  $\text{VF}_3$  content. This electrolytic system was electrolyzed at a melt temperature of  $770^\circ\text{C}$ . and a cathode current density of 40 ma./cm.<sup>2</sup>. In a short time, the cathode was completely covered with a dense, structurally coherent metal plate. The metal plate was identified as vanadium by X-ray diffraction and had a density of 5.96 gm./cm.<sup>3</sup>, which is the theoretical density of

## 12

vanadium. The metal plate also had a hardness of 184 DPH using a 100-gram load, was mechanically deformable without breaking, and contained no impurities in quantities larger than traces as determined spectroscopically.

## EXAMPLE XX

The process described in Example XIX was repeated using  $\text{VF}_3$  in place of the  $\text{K}_3\text{VF}_6$ . The operating conditions and the final deposit were the same as described in Example XIX.

## EXAMPLE XXI

An electrolytic system was provided with a chromium anode, a copper cathode, and an electrolytic melt consisting of 92 weight per cent base melt of the eutectic composition of the fluorides of lithium, sodium, and potassium and 8 weight percent anhydrous  $\text{CrF}_3$ . This electrolytic system was electrolyzed at a melt temperature of  $800^\circ\text{C}$ . and cathode current densities of 25 to 60 ma./cm.<sup>2</sup>. In a short time, the cathode was completely covered with a dense structurally coherent metal plate. The metal plate was identified as chromium by X-ray diffraction and had a density of 7.1 gm./cm.<sup>3</sup>, which is the theoretical density of chromium. The metal plate also had a hardness of 154 DPH, was mechanically deformable without breaking, and contained no impurities in quantities larger than traces as determined spectroscopically. The efficiency was close to 100 percent based on the reduction of trivalent chromium, and analysis of the melt indicated a mean valence of chromium of 2.9 to 3. A photomicrograph of a cross section of the metal plate showed clean, sound metal.

## EXAMPLE XXII

The process described in Example XXI was repeated at a melt temperature of  $840^\circ\text{C}$ . and a cathode current density of 24 ma./cm.<sup>2</sup>. All other operating conditions and the final deposit were the same as described in Example XXI.

## EXAMPLE XXIII

An electrolytic system was provided with a molybdenum anode, a copper cathode, and an electrolytic melt consisting of 90 weight percent base melt of the eutectic composition of the fluorides of lithium, sodium, and potassium, and 10 weight percent potassium hexafluomolybdate ( $\text{K}_3\text{MoF}_6$ ) based on  $\text{MoF}_3$  content. This electrolytic system was electrolyzed at a melt temperature of  $700^\circ\text{C}$ . and a cathode current density of 30 ma./cm.<sup>2</sup>. In a short time, the cathode was completely covered with a dense, structurally coherent metal plate. The metal plate was identified as molybdenum by X-ray spectrum and had a density of 10.2 gm./cm.<sup>3</sup>, which is the theoretical density of molybdenum. The metal plate also had a hardness of 305 DPH using a 500-gram load and contained no impurities in quantities larger than traces as determined spectroscopically.

## EXAMPLE XXIV

The process of Example XXIII was repeated using 12 weight percent  $\text{MoF}_3$  in place of the  $\text{K}_3\text{MoF}_6$  and at a cathode current density of 20 ma./cm.<sup>2</sup>. All other operating conditions and the final deposit were the same as described in Example XXIII.

## EXAMPLE XXV

The process of Example XXIII was repeated with the  $\text{K}_3\text{MoF}_6$  being replaced with gaseous  $\text{MoF}_6$  which was passed into the melt and reacted under the melt surface with molybdenum metal, thus reducing the  $\text{MoF}_6$  to a reduced soluble species of molybdenum fluoride. The molybdenum was further reduced electrolytically to the trivalent state. Analysis of the resultant melt showed a molybdenum mean valence of 3.16 and a metal content calculated as  $\text{MoF}_3$  of 10 weight percent. All other operating conditions

and the final deposit were the same as described in Example XXIII.

#### EXAMPLE XXVI

An electrolytic system was provided with a tungsten anode, a tungsten cathode, and a base melt consisting of the eutectic composition of the fluorides of sodium, potassium, and lithium. Prior to inserting the cathode and anode into the melt, the melt was heated to 750° C. and tungsten metal and gaseous  $WF_6$  were introduced into the melt in order to synthesize the soluble reduced tungsten compound in the melt in situ. The gaseous  $WF_6$  was introduced through a graphite tube bubbler. After the reduced tungsten compound had been formed, the cathode and anode were placed in the melt, and the tungsten was reduced further electrolytically to a mean valence of 4.5. The system was then electrolyzed at a melt temperature of 750° C. and a cathode current density of 20 to 30 ma./cm.<sup>2</sup>. The anode dissolved to form tungsten with a mean valence of 4.5 with a current efficiency of about 100 percent. The cathode current efficiency was also close to 100 percent based on W with a mean valence of 4.5 as the species reduced to metal. The melt contained 4.2 weight percent total tungsten and a mean valence of 4.51. A short time after the electrolysis was started, the cathode was completely covered with a dense, structurally coherent metal plate. The metal plate was identified as tungsten by X-ray spectrum and had a density of 19.3 gm./cm.<sup>3</sup>, which is the theoretical density of tungsten. The metal plate also had a hardness of 360 DPH using a 100-gram load, and contained no impurities in quantities larger than traces as determined spectroscopically.

#### EXAMPLE XXVII

The process of Example XXVI was repeated with the electrolytic melt contained in a graphite crucible which served as the cathode. A smooth, nonporous tungsten liner about 30 mils thick was deposited on the inner walls of the graphite crucible. The properties of this liner were about the same as those of the deposit described in Example XXVI.

#### EXAMPLE XXVIII

Tungsten deposits were produced under the same conditions as in Example XXVI but using a melt temperature of 600° C. and a cathode current density of 75 ma./cm.<sup>2</sup>. Additional deposits were produced from a melt containing 5 weight percent tungsten, a melt temperature of 750° C., and cathode current densities of 10 to 100 ma./cm.<sup>2</sup>. In each case, a dense, structurally coherent deposit of tungsten was formed on the cathode. In one case, an electroformed tungsten crucible having a wall thickness of 40 mils was made on a copper mandrel used as the cathode.

#### EXAMPLE XXIX

An electrolytic system was provided with a hafnium anode, a copper cathode, and an electrolytic melt consisting of 92 weight percent of a base melt of the eutectic composition of the fluorides of lithium, sodium and potassium and 8 weight percent hafnium tetrafluoride ( $HfF_4$ ). This electrolytic system was electrolyzed at a melt temperature of 600° C. and a cathode current density of 20 ma./cm.<sup>2</sup>. In a short time, the cathode was completely covered with a dense, structurally coherent metal plate. The metal plate was identified as hafnium by X-ray diffraction and had a density of 13.3 gm./cm.<sup>3</sup>, which is the theoretical density of hafnium. The metal plate contained no impurities in quantities larger than traces as determined spectroscopically.

#### EXAMPLE XXX

Columbium was plated from a bath consisting of a base melt of 69 weight percent KF and 31 weight percent LiF and containing 30 weight percent  $CbF_5$ . After the columbium was reduced electrolytically to the tetravalent state, electrolysis was carried out at a temperature of 770° C. and cathode current density of 50 ma./cm.<sup>2</sup> with a co-

lumbium anode. The resulting plate was structurally coherent with a density of 8.4 grams/cm.<sup>3</sup>, was mechanically deformable without breaking, and contained no impurities.

#### EXAMPLE XXXI

Gaseous tungsten hexafluoride ( $WF_6$ ) was introduced into a base melt consisting of the eutectic composition of the fluorides of sodium, potassium, and lithium, and containing tungsten metal. The gaseous  $WF_6$  was introduced through a graphite tube bubbler. After the reduced soluble tungsten compound had been formed, a tungsten cathode and tungsten anode were placed in the melt and the system was electrolyzed to further reduce the tungsten to a mean valence of 4.5. The plating conditions, including the mean valence of the tungsten metal in the bath, are given in the following table:

TABLE II

Temp., ° C.	Wt. percent W	Mean valence	C.C.D., ma./cm. <sup>2</sup>
750	10.0	4.42	20, 30, 50, 100
750	4.0	4.48	30
750	4.0	4.48	10
750	10.0	4.39	100
650	10.0	4.14	40
600	10.0	4.52	75
525	10.0	4.52	100
750	3.6	3.84	30
750	3.6	3.84	30
750	4.1	4.15	100
750	4.1	4.15	100
750	4.1	4.15	40
600	32.8	4.85	20
600	32.8	4.85	120
750	2.64	4.43	6.9
650	1.03	4.16	30
850	14.2	4.18	50

In each case, the deposited metal plate had a density of 19.3 gm./cm.<sup>3</sup> (the theoretical density of tungsten), was structurally coherent, and contained no impurities in quantities larger than traces.

#### EXAMPLE XXXII

Gaseous molybdenum hexafluoride ( $MoF_6$ ) was introduced into a base melt consisting of the eutectic composition of the fluorides of sodium, potassium, and lithium and containing molybdenum metal. The gaseous  $MoF_6$  was introduced through a graphite tube bubbler and reacted with the molybdenum metal, thus reducing the  $MoF_6$  to a soluble species of molybdenum fluoride. A molybdenum anode and cathode were inserted and the molybdenum in the electrolyte was further reduced electrolytically to the trivalent state. The system was then electrolyzed under the conditions given in the following table:

TABLE III

Temp., ° C	Wt. percent Mo	C.C.D., ma./cm. <sup>2</sup>
675	6	5
700	2	33
700	2	80
800	2	10
800	2	100
850	2	10
600	2	20
800	15	10
800	15	100
850	15	40

In each case, the mean valence of the molybdenum in the melt was approximately 3. Each of the deposited metal plates had a density of 10.2 gm./cm.<sup>3</sup> (the theoretical density of molybdenum), was structurally coherent, and contained no impurities in quantities larger than traces.

#### EXAMPLE XXXIII

An electrolytic system was provided with a tungsten anode and tungsten cathode and an electrolytic melt comprising the eutectic mixture of NaF, KF and LiF in which were present 2.09 weight percent tungsten and 2.01 weight percent molybdenum at the valences of 4.5 and 3.0 respectively. Reduction to the proper valence states was effected in a manner similar to that employed in the previous examples. Thereafter the system was electrolyzed at 780° C. and 20 ma./cm.<sup>2</sup> 25.6 AH of electricity were

passed. A structurally coherent deposit containing 92.04 percent tungsten and 7.96 percent molybdenum was produced on the cathode.

Electrolysis of a similar melt containing 1 weight percent tungsten and 2.4 weight percent molybdenum at 30 ma./cm.<sup>2</sup> produced a structurally coherent deposit containing approximately 86 percent tungsten and 14 percent molybdenum.

#### EXAMPLE XXXIV

An electrolytic system was provided with a vanadium anode and nickel cathode and an electrolytic melt comprising the eutectic mixture of NaF, KF and LiF in which were present 4.1 weight percent of vanadium and 0.34 weight percent silicon at the valences of +3 and +4 respectively. The system was electrolyzed at 775° C. and 20 ma./cm.<sup>2</sup> for a period of 16 hours. A structurally coherent deposit containing 73.56 percent vanadium and 24.12 percent silicon was produced on the cathode.

#### EXAMPLE XXXV

An electrolytic system was provided with a tantalum anode and copper cathode and an electrolytic melt comprising the eutectic mixture of NaF, LiF and KF in which were present 7.4 weight percent tantalum and 0.3 weight percent chromium at the valences of +5 and +3 respectively. The system was electrolyzed at 775° C. and 25 ma./cm.<sup>2</sup> to provide on the cathode a dense, structurally coherent deposit containing 99 percent tantalum and 1 percent chromium. The deposit had a DPH of 160.4.

In each of the above examples, the electrolysis was carried out in an inert atmosphere of argon.

The above examples demonstrate the operation of the present invention in a wide variety of operating conditions. However, it will be apparent that the same are susceptible of numerous modifications within the scope of this invention.

What is claimed is:

1. A process for producing dense, structurally coherent deposits of: (I) metals selected from the group consisting of zirconium, hafnium, vanadium, columbium, tantalum, chromium, molybdenum and tungsten; (II) alloys of at least two metals of (I); and (III) alloys and compounds of at least one metal of (I) with other metals which form a structurally coherent deposit with metals of (I), which process comprises:

(A) providing an electrolytic melt having no appreciable concentration of chlorides, bromides, and oxides and consisting essentially of:

(i) a base melt consisting essentially of:

(a) between about 10 and about 90 weight percent of at least one fluoride selected from the group consisting of the fluorides of potassium, rubidium, and cesium and

(b) a balance of at least one fluoride of other elements higher in the electromotive series than metal to be deposited, and

(ii) at least one fluoride of metal to be deposited, said metal to be deposited being present in said base melt prior to producing said structurally coherent deposits as an ion in a valence state suitable for the reduction to said coherent deposit and during production of said coherent deposit in that sufficiently low valence state wherein said metal ion will not attack the deposited metal;

(B) providing in said melt a soluble anode comprising said metal to be deposited and an electrically conductive base material as a cathode;

(C) electrolyzing said melt in an inert atmosphere to form on said base material a deposit containing essentially none of said base material, the deposition of said deposit proceeding at a rate determined by the current passing and independent of said base material.

2. A process for producing dense, structurally coherent

deposits of metals selected from the group consisting of zirconium, hafnium, vanadium, columbium, tantalum, chromium, molybdenum and tungsten, and alloys of at least two of said metals, which process comprises:

(A) providing an electrolytic melt having no appreciable concentration of chlorides, bromides, and oxides and consisting essentially of:

(i) a base melt consisting essentially of:

(a) between about 10 and 90 weight percent of at least one fluoride selected from the group consisting of the fluorides of potassium, rubidium, and cesium and

(b) a balance of at least one fluoride of other elements higher in the electromotive series than metal to be deposited, and

(ii) at least one fluoride of metal to be deposited, said metal to be deposited being present in said base melt prior to producing said structurally coherent deposits as an ion in a valence state suitable for the reduction to said coherent metal deposit and during production of said coherent deposit in that sufficiently low valence state wherein said metal ion will not attack the deposited metal;

(B) providing in said melt a soluble anode comprising said metal to be deposited and an electrically conductive base material as a cathode;

(C) electrolyzing said melt in an inert atmosphere to form on said base material a deposit containing essentially none of said base material, the deposition of said deposit proceeding at a rate determined by the current passing and independent of said base material.

3. The process of claim 2 wherein said base melt contains between about 10 and about 90 weight percent of at least one fluoride of potassium and at least one fluoride of other elements higher in the electromotive series than metal to be deposited.

4. The process of claim 2 wherein the electrolysis is carried out in an argon atmosphere.

5. The process of claim 2 wherein said base melt is the eutectic composition of the fluorides of lithium, sodium, and potassium.

6. The process of claim 2 wherein said base melt is the eutectic composition of the fluorides of sodium and potassium.

7. A process for producing dense structurally coherent deposits of zirconium, which process comprises:

(A) providing an electrolytic melt having no appreciable concentration of chlorides, bromides, and oxides and consisting essentially of:

(i) a base melt consisting essentially of:

(a) 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

(b) a balance of at least one fluoride of other elements higher in the electromotive series than zirconium, and

(ii) between about 5 and about 30 weight percent at least one fluoride of zirconium based on the simple fluoride, said zirconium being present in said base melt during production of said coherent deposit essentially in the tetravalent state wherein said zirconium will not attack said structurally coherent deposit;

(B) providing in said melt a soluble anode comprising zirconium and an electrically conductive base material as a cathode;

(C) electrolyzing said melt in an inert atmosphere to form on said base material a zirconium deposit containing essentially none of said base material, the deposition of said zirconium deposit proceeding at a rate determined by the current passing and independent of said base material.

8. The process of claim 7 wherein the cathode current density is between about 5 and about 40 milliamperes per square centimeter, and the temperature of said electrolytic melt is between about 675 and about 800° C.

9. A process for producing dense structurally coherent deposits of tantalum, while process comprises:

(A) providing an electrolytic melt having no appreciable concentration of chlorides, bromides, and oxides and consisting essentially of:

(i) a base melt consisting essentially of:

(a) 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

(b) a balance of at least one fluoride of other elements higher in the electromotive series than tantalum, and

(ii) between about 5 and about 30 weight percent at least one fluoride of tantalum, based on the simple fluoride, said tantalum being present in said base melt during production of said coherent deposit essentially in the pentavalent state wherein said tantalum will not oxidize said structurally coherent deposit;

(B) providing in said melt a soluble anode comprising tantalum and an electrically conductive base material as a cathode;

(C) electrolyzing said melt in an inert atmosphere to form on said base material a deposit of tantalum containing essentially none of said base material, the deposition of said tantalum proceeding at a rate determined by the current passing and independent of said base material.

10. The process of claim 9 wherein the cathode current density is between about 5 and about 100 milliamperes per square centimeter, and the temperature of said electrolytic melt is between about 700 and about 850° C.

11. A process for producing dense structurally coherent deposits of columbium, which process comprises:

(A) providing an electrolytic melt having no appreciable concentration of chlorides, bromides, and oxides and consisting essentially of:

(i) a base melt consisting essentially of:

(a) 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

(b) a balance of at least one fluoride of other elements higher in the electromotive series than columbium, and

(ii) between about 5 and about 30 weight percent at least one fluoride of columbium, based on the simple fluoride, said columbium being present in said base melt during production of said coherent deposit essentially in the tetravalent state wherein said columbium will not attack said structurally coherent deposit;

(B) providing in said melt a soluble anode comprising columbium and an electrically conductive base material as a cathode;

(C) electrolyzing said melt in an inert atmosphere to form on said base material a columbium deposit containing essentially none of said base material, the deposition of said columbium deposit proceeding at a rate determined by the current passing and independent of said base material.

12. The process of claim 11 wherein the cathode current density is between about 5 and about 100 milliamperes per square centimeter, and the temperature of said electrolytic melt is between about 675 and about 850° C.

13. A process for producing dense structurally coherent deposits of tungsten which process comprises:

(A) providing an electrolytic melt having no appreciable concentration of chlorides, bromides, and oxides and consisting essentially of:

(i) a base melt consisting essentially of:

(a) 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

(b) a balance of at least one fluoride of other elements higher in the electromotive series than tungsten, and

(ii) between about 1 and about 33 weight percent of at least one fluoride of tungsten based on the simple fluoride, said tungsten being present in said base melt during production of said coherent deposit essentially at a mean valence of 4.5 wherein said tungsten will not attack said structurally coherent deposit;

(B) providing in said melt a soluble anode comprising tungsten and an electrically conductive base material as a cathode;

(C) electrolyzing said melt in an inert atmosphere to form on said base material a tungsten deposit containing essentially none of the base material, the deposition of said tungsten deposit proceeding at a rate determined by the current passing and independent of said base material.

14. The process of claim 13 wherein the cathode current density is between about 3 and about 200 milliamperes per square centimeter, and the temperature of said electrolytic melt is between about 525 and about 900° C.

15. A process for producing dense structurally coherent deposits of tungsten, which process comprises:

(A) providing an electrolytic melt having no appreciable concentration of chlorides, bromides, and oxides and consisting essentially of tungsten metal in a base melt consisting essentially of between about 10 and about 90 weight percent of at least one fluoride selected from the group consisting of the fluorides of potassium, rubidium, and cesium;

(B) introducing gaseous tungsten hexafluoride into said melt and in contact with said tungsten metal so as to form a soluble reduced ion of tungsten in said melt, which is further reduced electrolytically to a mean valence of 4.5 the concentration of said tungsten in said melt being between about 3 and about 10 weight percent;

(C) disposing a soluble anode comprising tungsten and an electrically conductive base material as a cathode in said melt;

(D) and electrolyzing said melt at a current density of between about 10 and about 100 milliamperes per square centimeter and a temperature of between about 725 and about 850° C.

16. A process for producing dense structurally coherent deposits of molybdenum, which process comprises:

(A) providing an electrolytic melt having no appreciable concentration of chlorides, bromides, and oxides and consisting essentially of:

(i) a base melt consisting essentially of:

(a) 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

(b) a balance of at least one fluoride of other elements higher in the electromotive series than molybdenum, and

(ii) between about 1 and about 20 weight percent of at least one fluoride of molybdenum based on the simple fluoride, said molybdenum being present in said base melt during production of said coherent deposit essentially in the trivalent state wherein said molybdenum will not attack said structurally coherent deposit;

(B) providing in said melt a soluble anode comprising molybdenum and an electrically conductive base material as a cathode;

19

(C) electrolyzing said melt in an inert atmosphere to form on said base material a molybdenum deposit containing essentially none of said base material, the deposition of said molybdenum deposit proceeding at a rate determined by the current passing and independent of said base material.

17. The process of claim 16 wherein the cathode current density is between about 2 and about 200 milliamperes per square centimeter, and the temperature of said electrolytic melt is between about 525 and about 900° C.

18. A process for producing dense structurally coherent deposits of molybdenum, which process comprises:

(A) providing an electrolytic melt having no appreciable concentration of chlorides, bromides, and oxides and consisting essentially of molybdenum metal in a base melt consisting essentially of between about 10 to about 90 weight percent of at least one fluoride selected from the group consisting of the fluorides of potassium, rubidium, and cesium;

(B) introducing gaseous molybdenum hexafluoride into said melt and in contact with said molybdenum metal therein, so as to form a soluble reduced ion of molybdenum in said melt which is further reduced electrolytically so as to form trivalent molybdenum in said melt, the concentration of said trivalent molybdenum in said melt being between about 3 and about 10 weight percent;

(C) disposing a soluble anode comprising molybdenum and an electrically conductive base material as a cathode in said melt;

(D) and electrolyzing said melt at a current density of between about 10 and about 100 milliamperes per square centimeter and temperature of between about 700 and 850° C.

19. A process for producing dense structurally coherent deposits of zirconium diboride, which process comprises:

(A) providing an electrolytic melt having no appreciable concentration of chlorides, bromides, and oxides and consisting essentially of:

- (i) a base melt consisting essentially of:
  - (a) 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

20

(b) a balance of at least one fluoride of other elements higher in the electromotive series than zirconium and boron,

(ii) between about 5 and about 30 weight percent of at least one fluoride of zirconium, based on the simple fluoride, and said zirconium being present in said base melt during production of said coherent deposit solely in the tetravalent state wherein said zirconium will not attack said structurally coherent deposit;

(iii) between about 5 and about 11 weight percent boron trifluoride present in the melt as a fluoborate;

(B) providing in said melt a soluble anode and an electrically conductive base material as a cathode;

(C) electrolyzing said melt in an inert atmosphere to form on said base material a zirconium diboride deposit containing essentially none of said base material, the deposition of said zirconium diboride deposit proceeding at a rate determined by the current passing and independent of said base material.

References Cited

UNITED STATES PATENTS

1,842,254	1/1932	Driggs	204—64	XR
1,927,773	9/1933	Chittum	204—39	
2,786,809	3/1957	Raynes	204—39	
2,820,745	1/1958	Von Bichowsky	204—39	XR
2,920,021	1/1960	Ueltz	204—64	
2,984,605	5/1961	Cooper	204—39	XR
2,985,569	5/1961	Gendvil	204—64	
3,024,174	3/1962	Stetson	204—39	
3,028,324	4/1962	Ransley	204—293	XR
3,124,520	3/1964	Juda	204—86	

FOREIGN PATENTS

791,153	2/1958	Great Britain.
824,316	11/1959	Great Britain.

JOHN H. MACK, *Primary Examiner.*

G. KAPLAN, *Assistant Examiner.*

U.S. Cl. X.R.

204—39, 64