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2,813,069

POROUS ANODE

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This invention relates to the electrolytic deposition of certain transition metals and, more particularly, to the electrolytic deposition of titanium, zirconium, hafnium, vanadium, tantalum and niobium.

In the copending application of two of us, Merle E. Sibert and John T. Burwell, Serial No. 358,194, filed May 28, 1953, there is described and claimed the electrolytic deposition of the aforementioned transition metals by electrolyzing, as the anode of a cell, a substantially 100% density carbide of the transition metal in a fused halide bath under a cell voltage below that at which any bath component, including a halide of the transition metal, decomposes with evolution of a significant amount of free halogen. In the course of this electrolysis of the transition metal carbide, the metal component of the carbide is anodically dissolved in the bath and is transported through the bath for deposition at the cathode under conditions which are virtually the same as those prevailing at conventional aqueous electroplating operations. As the carbide anode becomes depleted in its metal component, and this depletion begins at the surface of the anode structure and develops inwardly, there remains behind a coherent carbonaceous structure substantially free of the metal. However, because of the dense and non-porous structure of the anode material used in the practice of invention of the aforementioned application, the coherent carbonaceous structure developed at the surface of the anode as a result of decomposition of the carbide has a correspondingly dense and non-porous structure and therefore tends to isolate the inner residual mass of metal carbide in the anode from the fused salt electrolyte. As a result, it has been found that only about 20% of the metal constituent of such a dense anode material can be anodically dissolved and deposited at the cathode before the resistance of the anode to further anodic dissolution becomes so high as to require a cell voltage which causes the unwanted and undesirable decomposition of some of the bath components. Consequently, after a minor amount of the metal carbide of the anode structure has been consumed by electrolysis, the aforementioned dense carbide anodes have had to be disintegrated and reprocessed into fresh anode structures.

We have now found that it is possible to produce the aforementioned transition metal carbide anodes having only about one-half the density of the aforementioned carbide anode structures, and we have further found that these relatively low density carbide anodes are amenable to over 90% utilization in continuous electrolytic operation at cell voltages below that at which a significant amount of any fused salt bath component is electrolytically decomposed. Accordingly, our present invention resides in the use of a transition metal carbide anode having an apparent density of approximately 50% of the carbide itself in an electrolytic operation such as that described in the aforementioned Sibert and Burwell application Serial No. 358,194 and in the Sibert and Burwell application Serial No. 383,401, filed September 30, 1953, in both of which the anode is electrolyzed in a fused

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halide bath under a cell voltage below that at which any bath component decomposes with the evolution of a significant amount of free halogen.

We have found that the aforementioned transition metal carbide anodes having a relatively low apparent density may be obtained by substantially the same procedure as that described in the aforementioned application with the exception of particular control over the nature of the carbonaceous component of the carbide and over the sintering conditions under which this anode structure is formed.

Our invention will be more fully understood from the following discussion of the preparation of a low-density high-porosity titanium carbide anode, and the electrolytic decomposition of this titanium carbide anode in a fused salt diluent bath with the resultant deposition of metallic titanium at the cathode of the electrolytic cell. It must be understood, however, that this discussion is directed to titanium carbide merely in the interest of simplicity and that what is said here with regard to titanium applies generally to each of the other transition metals, zirconium, hafnium, vanadium, tantalum and niobium.

The essential chemical characteristic of the titanium carbide which may be used as the titaniferous anode material in practicing our invention, in addition to its being substantially free of impurities other than uncombined carbon, is that it contains no oxygen in the form of incompletely reduced titanium oxides or in any other form. When produced in the presence of carbon monoxide or carbon dioxide, titanium carbide, which is formed by a high temperature reaction between titanium oxide and carbon, tends to retain in the residual carbide product enough oxygen to disqualify it for use in the practice of the invention. Thus, the mere presence of a stoichiometric excess of carbon during reduction of a titanium oxide at a temperature below that at which fusion occurs is not by itself sufficient to produce such oxygen-free carbide and must be supplemented by carrying out the reduction under vacuum conditions so as to remove from the reaction zone any carbon dioxide or carbon monoxide, or both, as rapidly as formed. Therefore, the titanium carbide which is useful in practicing our invention will generally, but not necessarily, contain a small amount, usually about 0.5 to 2% by weight, of free carbon. This free carbon, it will be understood, is a deliberate and extraneous contaminant when it is present in the titanium carbide anode material.

The physical characteristic of the titanium carbide anode material required for the practice of our invention is that the small crystals of titanium carbide forming the anode be firmly sintered into a rigid, relatively strong mass having a porous structure and an apparent density approximately one-half that of the titanium carbide itself. It is important that the adjoining crystals of titanium carbide in the anode be firmly sintered together while at the same time the essential porous structure of the titanium carbide mass is preserved. Thus, because of the porosity of the carbide anode material, relatively free movement of electrolyte and dissolved titanium metal is permitted throughout the carbide mass, and, because of the firmly sintered nature of the anode material, more than 90% of the titanium component of the titanium carbide anode material may be electrolytically removed therefrom without significant destruction of the residual carbide-carbon structure. The electrolytic decomposition of such a porous titanium carbide anode under the conditions set forth herein results in the transference of the titanium component of the carbide anode to the cell cathode while leaving the carbon component of the carbide as a black, solid, self-coherent mass in the physical shape of the original anode.

A titanium carbide anode having the aforementioned

chemical and physical characteristics can be readily produced from raw materials either directly in a single operation or less directly in an operation involving first the production of titanium carbide and then the formation of an anode from this carbide material. Irrespective of the method employed to form the titanium carbide anode material, however, the raw materials that must be used are purified titanium dioxide (or other oxide of titanium) having a particle size of about 20 microns or smaller and purified carbon in the form of graphite having a particle size of 44 microns or less (i. e. minus 325 mesh Tyler Standard). These purified and finely divided raw materials comprising a mixture of stoichiometric proportions of the titanium oxide and graphite, together with about 1% to 2% excess graphite to insure a minimum of oxygen in the final product, are brought into intimate contact with one another by means of a ball mill or other grinding device. The resulting mixture of titanium oxide and graphite is then treated in either of the following alternative procedures to manufacture a carbide anode material suitable for the practice of our invention.

In the more direct procedure for the manufacture of the anode material, the mixture of titanium oxide and graphite is mixed with about 2% of a binder such as methyl cellulose and with sufficient water to form a plastic moldable mass. The plastic mixture is then extruded, pressed or otherwise formed into the rectangular slabs, cylindrical rods, coarse lumps or other shapes required of the anode. The formed anodes are dried and then are heated in a controlled atmosphere furnace to convert the raw materials into the desired titanium carbide anode material. Care must be taken to remove the carbon monoxide evolved during the conversion of titanium oxide to titanium carbide from the zone of the reaction substantially as rapidly as it is formed in order to prevent the inclusion of oxygen in the final carbide anode material. Moreover, the temperature should be closely controlled to insure firm sintering of the crystals of titanium carbide formed by the reaction while at the same time avoiding such drastic sintering or fusion of these crystals which would destroy the essential porosity of the anode material. The atmosphere of the furnace is evacuated until the pressure therein is reduced to about 20 microns of mercury, and the temperature of the furnace is raised to within the range of about 2100° to 2200° C. and is maintained within this range throughout the reaction period while continuing active vacuum pumping. This sintering operation, it will be noted, is carried out in the complete absence of any sintering aid, such as the alkali and alkaline earth metal halides, which are used in practicing the method of the aforementioned Sibert and Burwell application, Serial No. 358,194 to produce a high density carbide with this relatively low sintering temperature range. After the conversion of the raw materials to the desired porous titanium carbide anode is complete (as indicated by the cessation of evolution of carbon monoxide from the anode) the furnace is allowed to cool while maintaining the vacuum. After reaching room temperature, the vacuum is broken and the resulting sintered anode material is removed from the furnace.

Alternatively, a titanium carbide powder may be prepared from the mixture of titanium oxide and graphite, and this powder may then be formed into the desired low density carbide anode material. In this alternative procedure, the mixture of titanium oxide and graphite is placed in a controlled atmosphere furnace and the air within the furnace is evacuated by means of a high speed vacuum pump until the pressure therein is reduced to about 20 microns. The mix is thereupon heated to a temperature within the range of about 1500° to 2000° C. for about 2 hours while continuing active vacuum pumping in order to remove the evolved carbon monoxide from the zone of reaction. On completion of the reaction the furnace is cooled, the vacuum is broken, and

the carbide material is removed. The resulting titanium carbide material is then crushed to minus 40 mesh (Tyler Standard) and is mixed with about 2% of a binder such as methyl cellulose and with sufficient water to form a plastic mass. The plastic carbide mass is formed into the desired anode shape, is dried to remove excess water, and then is fired in a controlled atmosphere furnace to sinter the carbide and form the desired porous anode material. The firing should be conducted under a vacuum of about 20 microns in order to avoid the occlusion of oxygen (from carbon oxides) in the titanium carbide product, and the temperature at which the firing is conducted should be closely controlled so that the carbide mass is firmly sintered without drastic sintering or fusion in order to preserve the porosity and low density of the anode material. The temperature of the furnace should therefore be maintained within the range of about 2100° to 2200° C. throughout the firing period and in the absence of any mineralizer or other sintering aid such as is used in forming a high density carbide pursuant to the method described in the aforementioned Sibert and Burwell application. On completion of the sintering operation, the furnace is cooled, the vacuum is broken, and the carbide anode material is removed for use in the electrolytic process.

As hereinbefore noted, the titanium carbide anode material produced according to either of the foregoing procedures is a rigid, self-supporting material having an apparent density of approximately 50% that of the titanium carbide of which it is formed. That is, the apparent density of the anode material is approximately 2.2 gm./cc. as compared to the actual density of titanium carbide, which is about 4.25 gm./cc. The low density and porous structure of the anode material is due to the use of highly purified and finely divided raw materials, the graphitic form of the carbon constituent of the anode, and the close control of the sintering temperatures employed. An average analysis of a titanium carbide anode produced in accordance with our procedure shows less than .02% oxygen, less than .02% nitrogen, less than .005% hydrogen, and substantially theoretical amounts of titanium and carbon.

The high purity carbide anode material is electrolytically decomposed in a fused salt diluent bath composed of a mixture of alkali metal halides and a halide of the transition metal, the bath composition and the electrolytic condition being those described in the first mentioned Sibert and Burwell application. The cell voltage, as noted hereinbefore, is maintained below about 3 volts in order to prevent the electrolytic decomposition of any of the fused salt components of the bath. The anodic decomposition of the carbide anode results in the dissolution in the fused salt bath of the transition metal component of the carbide anode. This transition metal is transferred through the bath and is deposited on the cathode in the form of firmly adhering crystals. The cathode, which may be formed from a metal such as iron that is unaffected by the fused salt bath, is periodically removed from the bath and a new cathode is substituted therefor. The electrolysis may be continued without interruption, except for the substitution of fresh cathodes, until at least 90% of the transition metal component of the carbide anode material has been anodically dissolved in the fused salt bath and (except for mechanical losses) has been deposited at the cathode.

The fused salt baths which may be used in the practice of our invention may vary considerably in composition. For example, the fused salt bath may be composed, in addition to the transition metal halide, of one or a mixture of the chlorides, bromides, iodides and fluorides of alkali metals such as sodium and potassium. The titanium (or other transition metal) halide may be a chloride, bromide, iodide or fluoride and may be a simple halide or a complex halide such as a double fluoride of titanium

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and an alkali metal (also known as an alkali metal fluotitanate). The titanium halide should be present in the bath in the amount of at least about 5% by weight and generally up to about 25% by weight. The presence of fluorine in the bath in the form of such an alkali metal-titanium double fluoride, or of a simple alkali metal fluoride, promotes the formation of larger particles of cathodically deposited titanium than that which is obtained by any one or a mixture of the other halides. Except for this special effect of an added fluoride, the specific composition of the bath appears to have no effect upon the quality of the titanium metal deposited. Illustrative bath compositions which are useful in the practice of our invention are set forth in the following table, the numerical values under each salt heading representing the parts by weight or percentage of each component in the bath:

K_2TiF_6	NaCl	KCl	NaBr	KBr	NaI	KI
5	95	--	--	--	--	--
10	90	--	--	--	--	--
10	45	45	--	--	--	--
5	30	20	20	15	10	--
10	20	--	30	--	30	10

Decomposition of a titanium carbide anode during electrolysis proceeds with the deposition of metallic titanium on the cathode and the development of a residual carbon structure or regulus at the anode. When the titanium carbide anode has been formed under optimum temperature conditions, there is a negligible tendency for this carbide-carbon residue to become detached from the anode and enter into the bath. However, it is possible to guard against possible contamination of the titanium deposit with liberated particles of carbon or titanium carbide by interposing an inert mechanical barrier between the anode and the cathode as mentioned hereinbefore. Such a barrier may comprise, for example, a graphite partition pierced with a number of very fine holes with the top of the partition positioned below the surface of the fused salt bath so as to insure the presence of a low resistance electrical path through the bath. In general, however, the provision of a trough-shaped well or the like in the lower portion of the cell structure is sufficient to collect any particles of the carbon residue which become detached from the anode. Such a collector of carbon particles may be provided in conjunction with a mechanical barrier by mounting a graphite cylinder, pierced with a number of fine holes, concentrically about the anode with the upper end of the cylinder positioned below the surface of the fused salt bath and with the lower end of the cylinder either embedded in the cell bottom or in a layer of solid bath composition maintained in the solid state by water cooling of the lower portion of the cell.

The electrolysis is carried out under purified argon in which all oxygen, hydrogen, water vapor, nitrogen, and the like have been eliminated by conventional cleaning techniques well known in the technical arts. When titanium carbide anodes are properly made the electrolytic reaction proceeds quietly as long as a significant amount of titanium carbide remains in the anode structure. Most efficient utilization of the titanium carbide dictates a physical shape such as to provide a relatively large surface area-to-volume ratio. With these conditions properly observed, at least 90% of the titanium content of the titanium carbide immersed in the fused salt bath may be deposited on the cathode without interrupting the electrolysis or raising the cell voltage above about 3 volts.

The cathodically deposited titanium metal is formed as a tightly adhering, densely deposited and well-crystallized metal. The cathode with the deposited titanium metal and adhering fused salt is periodically withdrawn into a separate cell chamber so that it may be cooled out of contact with air, whereupon a fresh cathode is immediately

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inserted in its place. After cooling of the withdrawn cathode is completed, the cathode deposit is knocked off and is disintegrated by treatment with hot water. The disintegrated cathode deposit is washed several times until substantially all of the salt has been removed, after which the powdered metal is dried under vacuum. It may then be compressed and fused either under a vacuum or under a controlled atmosphere of argon or helium to form a massive ingot.

The following examples are illustrative but not limitative to the practice of our invention.

Example I

Titanium carbide anode material was prepared by mixing pure titanium dioxide with an amount of finely divided graphite about 1% in excess of that required to convert all of the titanium dioxide to titanium carbide. The particle size of the titanium dioxide in the mixture was less than 20 microns and the particle size of the graphite was less than 44 microns. The mixture of titanium dioxide and graphite was ground together in a ball mill and then was mixed with about 1% of methyl cellulose binder and with enough water to wet the mixture. The resulting plastic mass was then formed into a rectangular anode shape approximately 3 x 4 x 1 inch. The anode shape was placed in a controlled atmosphere furnace connected to a high speed vacuum pump and the pressure within the furnace was reduced to below about 20 microns. The furnace was heated to a temperature of about 2100° C. and this temperature was maintained for about 2 hours. Continuous active vacuum pumping removed carbon monoxide from the furnace substantially as rapidly as it was evolved from the reaction mass. At the end of the reaction period, the titanium dioxide and graphite had been converted to a sintered mass of fine titanium carbide crystals. The apparent density of the titanium carbide anode material was 2.2 gms./cc., or approximately 50% of the density of titanium carbide itself. The sintered carbide anode weighed 330 grams of which 263 grams comprised the available titanium constituent thereof.

The sintered carbide anode was placed into a previously prepared fused salt diluent bath. The composition of the fused salt diluent bath comprised 60 parts by weight of reagent grade sodium chloride and 9 parts by weight of pure anhydrous potassium fluotitanate. The fused salt bath, the temperature of which was maintained at about 850° C., had previously been subjected to a purification electrolysis to remove therefrom all traces of oxygen and water. The electrolysis of the titanium carbide anode material was carried out at the aforesaid temperature at a cell voltage of between 2.5 and 3.0 volts. The titanium metal anodically dissolved at the anode was deposited on a cathode formed of a one-inch diameter steel rod. During the course of the electrolysis the steel cathode became heavily coated with a layer of deposited titanium metal necessitating replacement of the cathode with a fresh cathode at frequent intervals. The cathodic deposit of titanium metal on each of the cathodes was removed therefrom under conditions that prevented the contamination of the metallic deposit with atmospheric oxygen.

Of the total of 263 grams of titanium available in the titanium carbide anode, 248 grams of crystallized titanium metal was deposited at the cathode. This amount of titanium deposited at the cathode represented a 94% recovery of the titanium content of the carbide anode. The final weight of the carbide anode was 78 grams, of which 66 grams was graphitic carbon. The average overall current efficiency was approximately 60%. The metallic titanium recovered from the anode was washed to remove adhering salts and the resulting metal crystals were melted under an inert atmosphere to form an ingot weighing 218 grams. The loss of 30 grams in weight of metal deposited at the cathode was due to metal fines washed away and other mechanical losses. The titanium metal had a Brinell hardness of 140–180.

Example II

The operation described in Example 1 was repeated for each of the other transition elements, zirconium, hafnium, vanadium, tantalum and niobium, the only variations being that the carbide of the transition element was substituted for titanium carbide and that the potassium double fluoride of the respective transition element was substituted for the potassium titanium fluoride referred to in Example 1. Electrochemical efficiencies and metal recovery efficiencies were substantially the same for each of these transition elements as they were in the case of titanium.

We claim:

1. In a method of electrolytically depositing a metal of the group consisting of titanium, zirconium, hafnium, vanadium, tantalum and niobium, which comprises the steps of preparing an anhydrous fused salt bath consisting essentially of at least one alkali metal halide and at least about 5% by weight of a halide of said metal, introducing into said bath a carbide of said metal to be electrodeposited, passing an electrolyzing current through the fused bath between said carbide and a cathode in electrical contact with said bath, and recovering the resultant cathodically deposited metal; the improvement which comprises: providing said carbide as a sintered porous rigid mass having a density after sintering of approximately one-half that of the solid metal carbide and having a self-coherent carbon skeleton which remains after removal of metal from the mass during said electrolysis.

2. In a method of electrolytically depositing titanium, which comprises the steps of preparing an anhydrous fused salt bath consisting essentially of at least one alkali metal halide and at least about 5% by weight of a halide of titanium, introducing into said bath a titanium carbide, passing an electrolyzing current through the fused bath between said carbide and a cathode in electrical contact with said bath, and recovering the resultant cathodically deposited titanium; the improvement which comprises: providing said carbide as a sintered porous rigid mass having a density after sintering of approximately one-half

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that of the solid metal carbide and having a self-coherent carbon skeleton which remains after removal of titanium from the mass during said electrolysis.

3. In a method of electrolytically depositing titanium, which comprises the steps of preparing an anhydrous fused salt bath consisting essentially of at least one alkali metal halide and at least about 5% by weight of a halide of titanium, introducing into said bath a titanium carbide, passing an electrolyzing current through the fused bath between said carbide and a cathode in electrical contact with said bath, and recovering the resultant cathodically deposited titanium; the improvement which comprises: providing said carbide as a sintered porous rigid mass having a density after sintering of approximately 2.2 grams/cubic centimeter and having a self-coherent carbon skeleton which remains after removal of the titanium from the mass during said electrolysis.

4. In a method of electrolytically depositing zirconium, which comprises the steps of preparing an anhydrous fused salt bath consisting essentially of at least one alkali metal halide and at least about 5% by weight of a halide of zirconium, introducing into said bath a carbide of said metal to be electrodeposited, passing an electrolyzing current through the fused bath between said carbide and a cathode in electrical contact with said bath, and recovering the resultant cathodically deposited zirconium; the improvement which comprises: providing said carbide as a sintered porous rigid mass having a density after sintering of approximately one-half that of the solid metal carbide and having a self-coherent carbon skeleton which remains after removal of zirconium from the mass during said electrolysis.

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