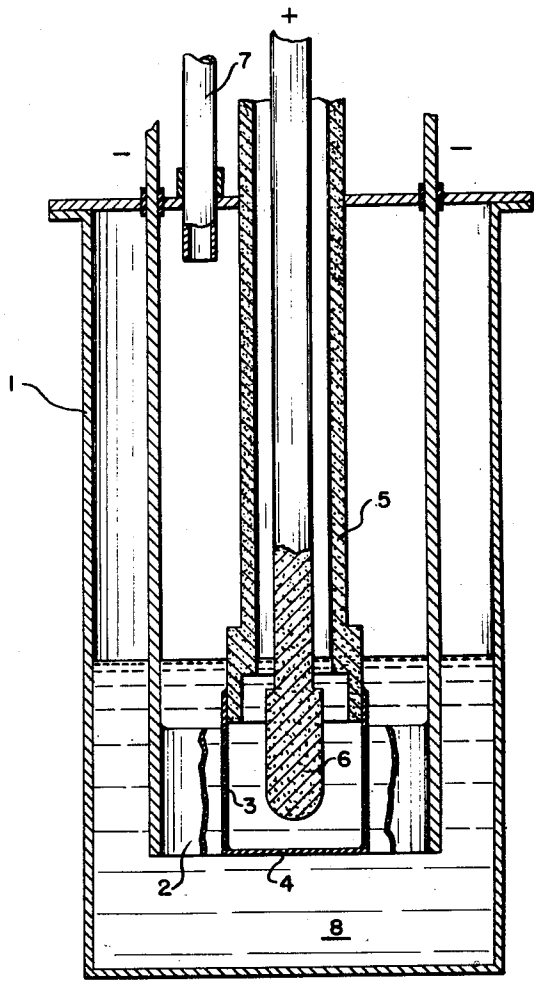
April 23, 1957 W. W. KITTELBERGER 2,789,943

PRODUCTION OF TITANIUM

Filed May 5, 1955



INVENTOR
William W. Kittelberger
BY
Pennie, Edmonds, Morton, Barrows & Taylor
ATTORNEYS

United States Patent Office 2,789,943 Patented Apr. 23, 1957

2,789,943

PRODUCTION OF TITANIUM

William W. Kittelberger, Palmerton, Pa., assignor to The New Jersey Zinc Company, New York, N. Y., a corporation of New Jersey

Application May 5, 1955, Serial No. 506,371

4 Claims. (Cl. 204—64)

This invention relates to the electrolytic production of metallic titanium.

In the production of metallic titanium by electrolytic decomposition of a titanium compound contained in a fused salt bath, it is generally necessary or at least helpful to interpose a porous barrier in the fused salt bath between the anode and the cathode and thus divide the cell bath into anolyte and catholyte portions. Such a barrier is advantageously used in the fused bath electrolysis of titanium chloride, of titanium fluorides such as the alkali metal-titanium double fluorides, and of titanium monoxide. The purposes served by the porous barrier in these representative processes include either the maintenance of a high concentration of electrolytically reducible titanium salt in the vicinity of the cathode, the prevention of lower valence titanium salts being oxidized at the anode, or the prevention of cathodically deposited titanium being attacked by a gas such as chlorine or carbon monoxide evolved at the anode, or a combination of these purposes.

The importance of a physical barrier in the electrolytic production of metallic titanium has prompted a thorough exploration of the use of a wide variety of materials capable of being used as such a barrier. Many of the substances tried for this purpose have been found to be either too porous or too impermeable. On the other hand, many other substances such as aluminum oxide, which can be made into porous barriers of desirable porosity, have been found to deteriorate rapidly during cell operation due to chemical or electrochemical changes which appear to take place within the barrier itself.

I have now discovered that a superlative physical barrier for use in the fused bath electrodeposition of metallic titanium consists of a porous mass of metallic titanium produced in situ in the bath. Such a barrier is established and maintained pursuant to my invention by positioning a perforate metallic structure in the fused salt bath between the anode and cathode so as to separate the bath into anolyte and catholyte portions and by interconnecting this perforate structure in the electrical circuit including the anode and cathode so that the perforate structure is electronegative with respect to the anode. The current flowing between the anode and the perforate structure is then controlled so as to deposit metallic titanium preferentially on the perforate structure, and this electrodepostion of metallic titanium on the perforate structure is continued until the titanium deposit thereon is such as to provide the sufficiently low degree of permeability required to serve as the porous barrier during subsequent deposition of the metallic titanium on the cathode. Thereafter, the current flowing between the anode, the titanium-bearing perforate structure and the cathode is so controlled as to effect deposition of metallic titanium substantially exclusively on the cathode while nevertheless substantially maintaining the porous metallic titanium deposit on the perforate structure.

The perforate structure on which the porous titanium deposit is built up pursuant to my invention must be electrically conductive. I have found it to be particularly satisfactory for this purpose to use a metallic structure composed of nickel, corrosion-resistant nickel-base alloys, stainless steels, molybdenum, or the like. Of these metals, nickel and the nickel-base alloys are presently preferred because there is no significant tendency for these metals to become attacked by or dissolved in the fused salt bath when the metal structure is initially immersed in the bath. In the case of perforate structures composed of a metal such as stainless steel or the like, it is advisable to connect the structure in the cell circuit before the material is inserted into the bath so that its negative potential is at least equal to the solution potential of the metal in the bath.

The perforate structure may be of any appropriate form on which a porous deposit of metallic titanium can be formed. Thus, the structure may be plate-like and rendered perforate by drilling or by otherwise forming a multiplicity of small closely spaced openings therein. However, I have found it to be particularly satisfactory to use a grid or screen-like structure. The mesh size of the screen appears not to be critical provided that the openings in the screen are sufficiently small to permit the building up thereover of a coherent but porous adherent deposit of metallic titanium which can be maintained on the screen during prolonged cell operation.

The deposition of metallic titanium on the perforate structure is initiated by positioning this structure in the bath between the anode and cathode and by interconnecting the perforate structure in the electrical circuit including the anode and cathode so that the perforate structure is electronegative with respect to the anode. The voltage between the anode and the perforate structure required for this purpose will, of course, depend upon the composition of the bath and particularly upon the decomposable titanium compound contained in the bath. In each specific instance the voltage impressed between the anode and the perforate structure should be sufficient to effect electrodeposition of metallic titanium on the perforate structure, although it is permissible that some metallic titanium be simultaneously deposited on the cathode.

Inasmuch as subsequent normal cell operation pursuant to the invention requires the maintenance of the metallic titanium deposit on the perforate structure during deposition of titanium on the cathode, both the perforate structure and the cathode should be electrically interconnected so that it is possible at all times to control distribution of current flowing between these two electronegative cell elements and the anode. Thus, both the perforate structure and the cathode are connected to the negative side of the cell voltage source and a variable resistance is interposed in series with either the perforate structure or the cathode in order to control the distribution of the cell current between these two electronegative cell components.

When the perforate structure is initially immersed in the cell bath, the current distribution betwen this perforate structure and the cathode should be adjusted so that the primary or even exclusive deposit of metallic titanium takes place on the perforate structure. This current distribution is maintained until the deposit of titanium formed on the perforate structure is sufficiently dense to provide a porous physical barrier which will establish the desired separation of the bath into anolyte and catholyte portions. The amount of metal that must be deposited per unit area to achieve the desired lowering of permeability is dependent on conditions such as the permeability of the original perforate structure, the permeability of the deposit, the concentration of lower titanium chlorides in the catholyte during subsequent operation, and also on

particular operating conditions such as pressure fluctuations in the compartments, temperature of operation, viscosity of the bath, and possibly other conditions.

In the case of a halide bath containing lower titanium chlorides and with use of titanium tetrachloride as the titaniferous source of material, the evolution of a significant amount of titanium tetrachloride at the anode along with the chlorine normally evolved there is an indication that the barrier is not sufficiently impervious to the flow of electrolyte. Such evolution of titanium tetrachloride at the anode is evidence of diffusion or migration into the anolyte of either titanium dichloride or titanium trichloride from the catholyte, with subsequent oxidation in the anolyte to titanium tetrachloride.

After the requisite density of the titanium deposit has been attained on the perforate structure, the current distribution between this structure and the cathode is altered so as thereafter to deposit titanium preferentially on the cathode. However, care should be taken that there is sufficient current flow to the perforate structure to maintain a potential at least equal to the solution potential of the metallic titanium thereon and yet insufficient to excessively increase the mass of the titanium deposit on the perforate structure. The actual current flow required for this purpose will of course depend largely upon the cell geometry, but the physical condition which it must maintain, to wit, the desired density of the titanium deposit on the perforate structure, can be readily ascertained as described hereinbefore.

The following specific example is illustrative of the practice of my invention. The operation was carried out in apparatus such as that shown in the accompanying drawing in which the single figure is a sectional elevation of an electrolytic cell. The cell was made up from a covered cylindrical container 1 composed of a corrosion-resistant nickel-base iron-containing alloy within which there was concentrically supported a deposition cathode in the form of a circular band 2 of the same alloy. Concentrically mounted within the deposition cathode band was a cup-shaped diaphragm the side walls 3 of which were composed of nickel wire cloth that had been calendered to lower its permeability, the bottom 4 of the diaphragm cup consisting of an impervious nickel sheet. The upper edge of the diaphragm cup was connected to a cylindrical graphite tube 5 which served as an exit duct for chlorine evolved from a graphite anode 6 concentrically positioned within the diaphragm cup. Titanium tetrachloride was supplied to the cell atmosphere exteriorly of the graphite chlorine duct through an inlet 7. The cell bath 8 consisted of a eutectic mixture composed of 55 mol percent lithium chloride, 40 mol percent of potassium chloride and 5 mol percent of sodium chloride, and was of sufficient volume to extend slightly above the upper edge of the diaphragm cup. The bath was maintained at a temperature of about 550° C. by means of electric resistance units surrounding the cylindrical cell container, and the anode, the cathode, the screen diaphragm and the cell container were electrically connected so that the cell current could be controllably divided between the cathode and the diaphragm during cell operation.

The cell operation comprised four successive stages. During the first stage, wherein the desired density of the titanium deposit was developed on the screen diaphragm, the cell current was distributed so that 20 amperes passed to the screen diaphragm and 60 amperes were passed to a cathode for a period of 4 hours while titanium tetrachloride was delivered to the cell atmosphere above the catholyte (that portion of the bath exterior of the screen diaphragm) at a rate corresponding to the total current used for reduction of the titanium tetrachloride to titanium metal. This rate was 1.0254 cc. of liquid titanium tetrachloride per ampere-hour. During the second stage of the operation, the same distributed cell currents were maintained but the titanium tetrachloride was added at the rate of 1.794 cc. per ampere-hour for a period of 4 hours so as to establish a lower chloride concentration equivalent to approximately 2.75% titanium dichloride in the catholyte.

At the conclusion of the second stage of the operation, the cell current was divided between the diaphragm and the cathode in the amounts of 15 and 45 amperes, respectively, for a period of 19 hours. Throughout this third period, titanium tetrachloride was added at the initial rate of 1.0254 cc. per ampere-hour. At the end of this period, the addition of titanium tetrachloride was discontinued and a fourth or stripping stage was carried out while maintaining the screen diaphragm and cathode currents at the same levels (15 and 45 amperes, respectively). At the end of the stripping stage, the screen diaphragm-graphite anode assembly and the cathode were raised from the molten salt bath in several steps to allow time for molten salt to drain back into the molten salt bath. After this drainage had been completed and the cell had been cooled until the titanium metal deposit on the cathode was at a temperature within the range of 200°–250° C., the cathode and screen diaphragm were removed from the cell.

After leaching entrained salt from these two titanium metal deposits, it was found that 94.8% of the crystalline titanium metal deposit obtained from the cathode had a particle size coarser than 44 microns. An ingot prepared from this portion of the deposit had a Rockwell A hardness of 35. Of the metal deposited on the screen diaphragm, about 85% was coarser than about 44 microns. Based upon the total cell current and total titanium tetrachloride fed to the cell, an over-all current efficiency of 88.3% was determined.

It will be appreciated, accordingly, that my novel method of forming and maintaining a porous physical barrier for use in the electrolytic production of metallic titanium contributes materially to the longevity of sustained operation. Once formed, the barrier appears to function satisfactorily for such an extended period of cell operation that a number of cathodes can be used successively without significant interruption of the operation. The life of the barrier presently appears to be limited only by the ability of an operator to maintain the porous titanium deposit on the perforate structure. Although an excessively massive deposit can sometimes be restored to the desired degree of porosity, a sloughing off of a portion of the deposit such as to expose a significant portion of the perforate structure necessitates interruption of the operation to the extent necessary to re-establish a coherent porous titanium deposit on the perforate structure. It is also significant to note that the placement of the perforate structure within the cell is governed by the well-established criteria for the placement of any conventional diaphragm or barrier in an electrolytic cell. Once positioned, the perforate structure is transformed in situ pursuant to the invention and is thus free of the hazards of mishandling and mechanical damage heretofore experienced in the installation of a pre-formed barrier.

I claim:

1. In the electrolytic production of metallic titanium wherein, as a result of electric current passing between an electrically connected anode and a cathode immersed in a fused salt bath and separated by a porous physical barrier, the titanium component of a titanium compound present in the bath is deposited on the cathode, the improvement which comprises establishing and maintaining the requisite physical barrier by positioning a perforate structure of electrically conductive material in the bath between the anode and cathode so as to separate the bath into anolyte and catholyte portions, interconnecting the perforate structure in the electrical circuit including the anode and cathode so that the perforate structure is electronegative with respect to the anode, controlling the current flowing between the anode and the perforate structure so as to deposit metallic titanium on the per-

forate structure, continuing the electrodeposition of metallic titanium on the perforate structure until the titanium deposit thereon is sufficient to provide the degree of permeability required to serve as the porous barrier during subsequent deposition of metallic titanium on the cathode, and thereafter controlling the current flowing between the anode, the titanium-bearing perforate structure and the cathode so as to effect deposition of metallic titanium on the cathode while substantially maintaining the porous metallic titanium deposit on the perforate structure.

2. In the electrolytic production of metallic titanium wherein, as a result of electric current passing between an electrically connected anode and a cathode immersed in a fused salt bath and separated by a porous physical barrier, the titanium component of a titanium compound present in the bath is deposited on the cathode, the improvement which comprises establishing and maintaining the requisite physical barrier by positioning a metallic perforate structure in the bath between the anode and cathode so as to separate the bath into anolyte and catholyte portions, interconnecting the perforate structure in the electrical circuit including the anode and cathode so that the perforate structure is electronegative with respect to the anode, controlling the current flowing between the anode and the perforate structure so as to deposit metallic titanium on the perforate structure, continuing the electrodeposition of metallic titanium on the perforate structure until the titanium deposit thereon is sufficient to provide the degree of permeability required to serve as the porous barrier during subsequent deposition of metallic titanium on the cathode, and thereafter controlling the current flowing between the anode, the titanium-bearing perforate structure and the cathode so as to effect deposition of metallic titanium on the cathode while substantially maintaining the porous metallic titanium deposit on the perforate structure.

3. In the electrolytic production of metallic titanium wherein, as a result of electric current passing between an electrically connected anode and a cathode immersed in a fused salt bath and separated by a porous physical barrier, the titanium component of a titanium compound present in the bath is deposited on the cathode, the improvement which comprises establishing and maintaining the requisite physical barrier by positioning a metallic screen in the bath between the anode and cathode so as to separate the bath into anolyte and catholyte portions, interconnecting the perforate structure in the electrical circuit including the anode and cathode so that the perforate structure is electronegative with respect to the anode, controlling the current flowing between the anode and the perforate structure so as to deposit metallic titanium on the perforate structure, continuing the electrodeposition of metallic titanium on the perforate structure until the titanium deposit thereon is sufficient to provide the degree of permeability required to serve as the porous barrier during subsequent deposition of metallic titanium on the cathode, and thereafter controlling the current flowing between the anode, the titanium-bearing perforate structure and the cathode so as to effect deposition of metallic titanium on the cathode while substantially maintaining the porous metallic titanium deposit on the perforate structure.

4. In the electrolytic production of metallic titanium from titanium tetrachloride wherein, as a result of electric current passing between an electrically connected anode and a cathode immersed in a fused halide salt bath and separated by a porous physical barrier, the titanium component of a decomposable titanium salt present in the bath is deposited on the cathode, the decomposable titanium salt in the bath comprising titanium trichloride formed by the interaction of titanium dichloride in the bath and externally supplied titanium tetrachloride, the improvement which comprises establishing and maintaining the requisite physical barrier by positioning a perforate structure of electrically conductive material in the bath between the anode and cathode, interconnecting the perforate structure in the electrical circuit including the anode and cathode so that the perforate structure is electronegative with respect to the anode, controlling the current flowing between the anode and the perforate structure so as to deposit metallic titanium on the perforate structure, continuing the electro-deposition of metallic titanium on the perforate structure until the titanium deposit thereon is sufficient to provide the degree of permeability required to serve as the porous barrier during subsequent deposition of metallic titanium on the cathode, and thereafter controlling the current flowing between the anode, the titanium-bearing perforate structure and the cathode so as to effect deposition of metallic titanium on the cathode while substantially maintaining the porous metallic titanium deposit on the perforate structure.

References Cited in the file of this patent

UNITED STATES PATENTS

1,567,791	Duhme	Dec. 29, 1925
1,934,643	Rafton	Nov. 7, 1933
2,319,624	Olsen	May 18, 1943

FOREIGN PATENTS

678,807	Great Britain	Sept. 10, 1952
1,064,892	France	Dec. 30, 1953