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2,820,748

PROCESS FOR ELECTROWINNING ZIRCONIUM AND HAFNIUM

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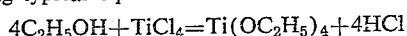
8 Claims. (Cl. 204—59)

This invention relates to a new and improved process for the obtaining of titanium and/or its congeners by electrolytic means.

This application is a continuation-in-part of my co-pending application for a Process For Electrowinning Titanium or Its Congeners, Serial No. 330,917, filed January 12, 1953.

Attempts to electrowin the metals of the fourth group of the periodic table of the elements and specifically to recover pure, titanium, zirconium or hafnium from aqueous solutions or from melts containing their compounds have resulted either in the deposition of very thin films or in the formation of a metal so dispersed within the melt that its recovery therefrom was very difficult.

Work also has been done toward plating out the metals of the fourth group from non-aqueous solutions of their halogen compounds. In those experiments the metals were used mainly in the form of their quadrivalent salts, for example, the readily available titanium or zirconium tetrachlorides, but because of the great chemical activity of such compounds the organic solvents employed, which were mostly of an alcohol or glycol type, probably reversibly reacted with those salts in accordance with the following typical equation:



and so, perhaps because of the linkage of titanium to oxygen in the resulting titanium ethylate, an oxygen free titanium could not be recovered from an alcoholic solution of that compound.

In order to overcome any such harmful chemical activity, of the tetrahalides of the metals of the fourth group of the periodic table of the elements, it occurred to me to study the use of certain double halogen or addition compounds of the above cited group of elements and as a result of that study and its extensions I made the discovery that the metals of the fourth group of the periodic table; when in solution, as their double halogen salts, in substantially non-aqueous solvents and while under oxidizing conditions, could be recovered therefrom in a commercially pure form when the conditions were so adjusted that the discharge potentials of the cations in the solvent were appreciably different.

The present invention thus covers the electrowinning of titanium and its congeners by the employment of a non-aqueous electrolyte, liquid at usual temperatures, which contains halogen salts of the metals of the fourth group, for example, titanium tetrachloride, associated with halogen salts of other metals and under oxidizing conditions.

The double halogen compounds of the fourth group of metals, in which the metal apparently has the coordination number 6 since it actuates 4 main valences and 2 minor valences, are represented by the salts, for example, of hexachlorotitanic acid.

That acid and its potassium and ammonium salts, as well as the sodium salt of the corresponding zirconium compound, are described in the literature and their prep-

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aration, for example, by salting out with hydrochloric acid or by reaction of the constituents, with and without pressure, is well known. I have also prepared those titanium compounds by reacting either hydrogen chloride or ammonium chloride or potassium chloride, in an essentially non-aqueous solvent (i. e. one that contains no more H₂O than is present in the commercial product) with titanium tetrachloride, either in concentrated form or diluted with, for example, carbon tetrachloride, in the cold. By that same general procedure I have interacted other metallic salts, in approximately the stoichiometrical amounts, with titanium tetrachloride or zirconium tetrachloride. Of the other metallic salts with which I have experimented I will mention here only the chlorides of iron, copper, nickel, mercury, lithium, cadmium and lead but by following the above outlined technique the complexes of the metals of the fourth group of the periodic table may be formed either alone or intermixed with one another or with the salts of other elements in various proportions and at various concentrations.

As usable solvents, for such metallo-complexes or addition compounds of hexavalent titanium or its congeners and in which an electrolysis may be carried out under oxidizing conditions, I mention here the ternary compounds: ethylene glycol, propylene glycol, glycerine, methanol, butanol, ethanol, propanol, ethyl ether, glycolic acid and/or other essentially anhydrous liquids fluid at room temperature which will conduct the electric current under the conditions of this invention.

In the process of the present invention the metal of the fourth group of the periodic system, when present as a complex of hexavalent titanium, or its congeners, with a chloride of another metal and while in a substantially anhydrous solvent, appears to go directly from its high valence state down to that of the metal. In order to maintain that state of high valence an oxidizing agent, i. e. one that increases the positive valence of an element, is employed.

In theory any oxidizing agent; either gaseous, liquid or solid or combinations thereof, might be used to accomplish the above aim. In practice, however, it is found that not all oxidizing agents are equally advantageous because in certain cases some may be too active and others too sluggish. Of the oxidizing agents tested in connection with this invention and in most cases with good results there may be mentioned gaseous or atmospheric oxygen or chlorine which latter may be generated in situ or added to the electrolyte. Of the solid oxidants, ammonium persulfate, calcium hypochlorite, the normally insoluble higher oxides of lead or manganese or in special cases such compounds of copper or of iron as contain available oxygen may be cited. Barium peroxide also may be used but in that event the electrolyte should contain some free acid such as gaseous HCl or even HNO₃ in order to keep the pH of the solution on the acid side. Of the liquid oxidants one may use strong hydrogen peroxide or a concentrated solution of sodium hypochlorite or even nitric acid provided that they do not react in a deleterious manner with the electrolyte.

In carrying out an electrolysis of a halogen complex of a metal of the fourth group, while in a solution in one or more of the useful solvents in substantially non-aqueous state, a simple cell may be used. There also may be employed a cell which has partitions or diaphragms and in which the electrolyte either is stationary or is circulated within the separate compartments or else the application of circulation may be utilized in a cell of the simple type.

The cathode in the chosen cell may be of mercury, lead, copper, cadmium, titanium or zirconium or hafnium or of any satisfactory material or alloy, and it may be

fixed or rotatable. For most purposes I prefer to use titanium or zirconium as a cathode and while, for example, mercury has a high hydrogen overvoltage it also has a tendency to form insoluble compounds such as mercurous chloride which can contaminate the deposit and in addition mercury does not appear to wet titanium nor amalgamate therewith.

The anode may be of either a permanent or soluble type. Of the former I mention graphite and of the latter either impure or scrap titanium metal and its alloys or else a non-metallic substance, such as the active form of titanium nitride as mentioned in U. S. Patent No. 1,783,684, may be employed. In some cases and with non-aqueous solvents it may be desirable to carry out the electrolysis at a temperature above that of room provided that the solvent is not appreciably harmed thereby.

Having now, in general, outlined the methods of this invention I will illustrate it by specific examples:

Example 1.—Into a carefully dried 2 liter flask equipped with closure is placed 1 mol of thoroughly dry HgCl_2 (271.5 g.) then there is added 189 g. of water-white TiCl_4 (1 mol) and the mixture completely frozen by keeping it in a Dry Ice freezing bath. Next there is poured into the flask one liter of commercially anhydrous methanol which has been precooled to about -25°C . The external temperature of the flask then is raised very slowly to ca. -20° while its contents are stirred, whereupon the titanium tetrachloride thaws very gradually and the particles of mercuric chloride disappear. The resulting water-white solution then is transferred to a simple electrolysis cell having a titanium cathode at the bottom and a graphite anode above it. During the electrolysis at room temperature sufficient gaseous chlorine is introduced into the electrolyte, in the vicinity of the cathode, to assure there the absence of titanium salts of lower valence. As soon as the electrolysis is started, at, for example, a current density of 75 amps./ft.², spongy titanium deposits on the cathode. The electrolysis is continued while stirring gently until the electrolyte, as regards titanium, is about half exhausted, whereupon the current is interrupted, any flow of Cl_2 shut off and the electrolyte removed and filtered and the filtrate put aside. Then the filter paper and the cathode are washed free of soluble titanium salts, for example, with methanol and/or H_2O . Finally the cathode and contents of the filter paper are dried under high vacuum and subsequently the temperature in the vacuum drying vessel is raised enough to distil off any entrained metallic mercury and/or mercury salts. The resulting sponge of titanium is somewhat pyrophoric and should be kept preferably in an inert atmosphere until ready for compression and/or fusion into a dense form. The half-spent filtered catholyte may be restored to its original condition by pouring it, chilled to about -25°C ., upon the required amounts of the pre-frozen ingredients and in a manner like that described above.

Example 2.—Into a dried 500 ml. Pyrex bottle, with a ground glass graphited stopper, are placed 42.4 g. of powdered anhydrous lithium chloride, then there are added 55 ml. of C. P. TiCl_4 (Ca. 94.6 g.). The two ingredients are mixed by gently rotating the bottle or by adding a few glass marbles and shaking. The resulting slurry is frozen by placing the bottle in Dry Ice. In the meantime 400 ml. of commercially anhydrous ethylene glycol are cooled down to below -22°C ., following which the cold glycol is poured into the Pyrex bottle and onto its thoroughly frozen contents. The frozen cake therein next is thawed so slowly that no noticeable reaction takes place between the melting TiCl_4 and the glycol. After the clear liquid has reached room temperature it is made up to 500 ml. with additional glycol and well mixed. The electrolysis is carried out in a simple cell with an anode of scrap titanium wrapped in glass cloth to prevent fall-out of impurities and with a cathode of pure titanium. The oxidant, introduced a close to the cathode, is care-

fully dried air or air enriched with oxygen. When air alone is used its oxidizing effect appears to be increased by the presence of a small amount of nitric acid (catalyst). The titanium during this electrolysis deposits as a feathery mass on the cathode. The current density there being about the same as used in Example 1. The recovery of the titanium, which may proceed batch-wise or continuously, may take place as in the preceding example.

Example 3.—23.3 g. of sublimed zirconium tetrachloride are added to 10.7 g. of sublimed ammonium chloride. The mixture is cooled to 0°C ., or below, and there is added thereto 500 ml. of absolute ethanol, denatured with about 20% of anhydrous methanol, and prechilled to -10°C . During this addition the temperature of the container is kept close to that figure. When the ingredients are all in solution the resulting electrolyte is transferred to a cell and electrolyzed with the use of a graphite anode and a zirconium cathode. Calcium hypochlorite (about 3.0 g.) being used as a supplementary oxidant at the cathode. The cell is stirred gently by using air which has been saturated at room temperature with methanol. The zirconium is deposited as a thin film or semi-sponge on the cathode.

Example 4.—1.6 g. of hafnium tetrachloride and 0.535 g. of sublimed ammonium chloride are dissolved in 50 ml. of anhydrous methanol under the conditions of Example 3. With, for example, a gold cathode and a graphite anode the hafnium may be seen as a silvery deposit on the gold. All the other procedures, with that exception, parallel those of Example 3.

Now having described my invention what I claim is:

1. Process for the electrolytic production of a metal of the group consisting of zirconium and hafnium which comprises passing an electrolyzing current from an anode through an anhydrous electrolyte which consists essentially of a solution in a solvent from the aliphatic group consisting of ethylene glycol, propylene glycol, glycerine, methanol, ethanol, propanol, ethyl ether and glycolic acid, of a complex of a salt of a metal from the group consisting of zirconium and hafnium complexed with a cation selected from the group consisting of lithium, sodium, potassium, ammonium, copper, mercury and cadmium both salts having a common anion, to a cathode while maintaining the metal being produced at a maximum valence in said electrolyte by the addition of an oxidizing agent selected from the group consisting of oxygen, chlorine, ammonium persulfate, calcium hypochlorite, hydrogen peroxide and nitric acid.

2. Process for the electrolytic production of a metal of the group consisting of zirconium and hafnium which comprises passing an electrolyzing current from an anode through an anhydrous electrolyte consisting of a solution, in a solvent selected from the group consisting of ethylene glycol, propylene glycol, glycerine, methanol, ethanol, propanol, ethyl ether and glycolic acid, of a complex of a salt of a metal from the group consisting of zirconium and hafnium complexed with a cation selected from the group consisting of lithium, sodium, potassium, ammonium, copper, mercury and cadmium both salts having a common anion, to a cathode while maintaining the metal being produced at a maximum valence in said electrolyte by the addition of an oxidizing agent selected from the group consisting of oxygen, chlorine, ammonium persulfate, calcium hypochlorite, hydrogen peroxide and nitric acid.

3. Process for the electrolytic production of a metal of the group consisting of zirconium and hafnium which comprises passing an electrolyzing current from an anode through an anhydrous electrolyte consisting of a solution, in a solvent selected from the group consisting of ethylene glycol, propylene glycol, glycerine, methanol, ethanol, propanol, ethyl ether and glycolic acid, of a complex of a salt of a metal from the group consisting of zirconium and hafnium complexed with a cation selected

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from the group consisting of lithium, sodium, potassium, ammonium, copper, mercury and cadmium both salts having chlorine as a common anion, to a cathode while maintaining the metal, being produced, in said electrolyte at a maximum valence by the addition of an oxidizing agent selected from the group consisting of oxygen, chlorine, ammonium persulfate, calcium hypochlorite, hydrogen peroxide and nitric acid.

4. Process for the electrolytic production of a metal of the group consisting of zirconium and hafnium which comprises passing an electrolyzing current from an anode through an anhydrous electrolyte consisting of a solution, in a solvent selected from the group consisting of ethylene glycol, propylene glycol, glycerine, methanol, ethanol, propanol, ethyl ether and glycollic acid of a complex of a tetrachloride of a metal from the group consisting of zirconium and hafnium with a cation selected from the group consisting of lithium, sodium, potassium, ammonium, copper, mercury and cadmium to a cathode while maintaining the metal, being produced, in said electrolyte at a maximum valence by the addition of an oxidizing agent selected from the group consisting of oxygen, chlorine, ammonium persulfate, calcium hypochlorite, hydrogen peroxide and nitric acid.

5. Process of claim 4 in which the tetrachloride of

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a metal from the group consisting of zirconium and hafnium is zirconium tetrachloride.

6. Process for the electrolytic production of zirconium which comprises passing an electrolyzing current from a graphite anode through an anhydrous electrolyte consisting of a solution in denatured anhydrous ethanol of a complex of zirconium chloride and ammonium chloride to a zirconium cathode while maintaining the zirconium in said electrolyte at a valence of four through the addition of calcium hypochlorite.

7. The process of claim 4 in which the tetrachloride of a metal from the group consisting of zirconium and hafnium is hafnium tetrachloride.

8. Process for the electrolytic production of hafnium which comprises passing an electrolyzing current from a graphite anode through an anhydrous electrolyte consisting of a solution in methanol of a complex of hafnium tetrachloride and ammonium chloride to a cathode while maintaining the hafnium in said electrolyte at a valence of four through the addition of calcium hypochlorite.

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