United States Patent Office 2,899,369 Patented Aug. 11, 1959

2,899,369

SPECIAL ELECTROLYTIC PROCESSING

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No Drawing. Application July 24, 1957
Serial No. 673,773

14 Claims. (Cl. 204—64)

This invention relates to a process for the production of pure and ductile columbium (niobium) and tantalum by the fusion electrolysis of their respective oxygen compounds and oxides.

Tantalum and columbium have not been producible electrolytically in satisfactory pure ductile form. The product has been in powdered condition and so permeated with contaminants as to be of limited practical utility requiring additional expensive processing to refine it.

The primary object of this invention is to provide a process wherein the oxide of columbium or of tantalum may be converted into metal of high purity and ductility directly by fusion electrolysis. It is a further object to provide a process wherein the metal produced is in the form of discrete metal crystals, devoid of powder and readily separable from the electrolyte by simple washing, and wherein the metal crystals are substantially free of oxygen, oxides, carbon, carbides, nitrogen, nitrides, hydrogen, hydrides, silicides, borides, and the like. This electrolysis thus provides a metallic product which can easily and simply be consolidated by inexpensive methods.

Tantalum and columbium have been produced by fusion electrolysis of the respective alkali fluorotantalate (K_2TaF_7) or columbate (K_2CbF_7 or oxycolumbate K_2NbOF_7) dissolved in an alkali halide with or without the addition of the respective pentoxide, Ta_2O_5 or Cb_2O_5. (Driggs et al.: Ind. Eng. Chem. 23, No. 6, pp. 634–637 (1931); Balke: ibid., 27, 1166 (1935); U.S. Patent 1,815,054). The metal obtained in such processes is freed from its adherent electrolyte with great difficulty. The compounds involved in the adherent electrolyte are not dissolved by common solvents and the metal is recovered by ore dressing methods including crushing, grinding, tabling, flotation and the like. As a result the metal is obtained as a finely powdered material still contaminated with undesirable oxygen compounds, carbides, nitrides, hydrides and the like which limit the utility of these metals. Columbium and tantalum have also been produced by sodium reduction of the alkali fluoro-complex halide salts K_2CbF_7 or K_2TaF_7; by calcium reduction of the oxides in the presence of a flux and/or booster; and by hydrogen reduction of the pentachloride, $CbCl_5$ or $TaCl_5$. These methods have produced a purer material but the cost of production is high due to the cost of preparation of the reactants and the cost of product separation.

In the present processing these objectionable complications are avoided and other advantageous objects have been attained by electrolyzing a fused bath consisting of at least one alkaline earth metal halide and to which had been added a portion of at least one alkaline earth metal oxide and adding to this electrolyte at least one oxide of the respective refractory metal and depositing said refractory metal as a pure crystalline and ductile metal on an inert cathode and liberating oxygen at an insoluble anode. In this process of this invention the deposited metal is easily freed from its adhering electrolyte by water washings as the residual component salts are soluble in water or acidulated water.

The process of the invention may be better understood by a consideration of the examples given below.

EXAMPLE I (TANTALUM)

Unless noted to the contrary, in all of the processing the various compounds used were the purest available and underwent further preliminary purification by fusion under an HCl gas blanket, bubbling dry HCl through the chloride melts and electrolyzing to remove moisture and other contaminating impurities. Purified dry argon atmospheres were used in dehydration of the oxides, and during the course of electrolysis. External heating was used to start the electrolysis in each case.

Fused 100 parts of NaCl in a nickel lined cell. The purified melt was transparent and water-white. About ½ parts of Ta_2O_5 were added to the melt and stirred with a solid nickel stirring rod. Visual examination disclosed that little, if any, of the pure dry Ta_2O_5 was dissolved by the melt. On electrolysis using the nickel liner as a cathode and a ⅝-inch diameter graphite rod as an anode immersed centrally in the electrolyte, no collectible tantalum could be found. There was added to the electrolyte pure dried CaO, and no marked improvement in tantalum oxide solubility was noticed. Again on electrolysis of the mix, only sodium metal was deposited and no collectible tantalum metal was found. The steps were repeated with various alkali and/or alkaline earth halide solvents and the results are summarized in the table below. The duration of each run was 1 to 5 hours. Ratios are in w./o., weight in percentage.

Table I

Solvent composition	Temp. in degrees C.	CaO addition to melt	Ta_2O_5 solubility	Observations and results
NaCl	800 to 850	Ta_2O_5 solubility not improved	Nil	No collectible Ta product.
Equimolar NaCl—KCl	750 to 800	do	do	Do.
67.5 KF, 32.5 NaF	do	do	do	Do.
61.1 KCl, 38.9 KF	750 to 850	do	do	Do.
80 LiCl, 20 LiF	650 to 725	do	do	Do.
60 $CaCl_2$, 40 LiCl	725 to 750	Some solubility	Cloudy	Not practical. Ta deposited.
66.8 $CaCl_2$, 33.2 NaCl	750 to 800	do	do	No collectible Ta product.
63 $CaCl_2$, 25 $BaCl_2$, 12 $SrCl_2$	800 to 900	Marked improvement 9 w./o	3 w./o	Ta crystals deposited.
$CaCl_2$	850 to 1,200	None added	3 w./o	Ta found in cell.
$CaCl_2$, CaO	750 to 1,200	CaO—.1 to 20%	10 w./o	Ta crystal deposited.

The cathode current densities were varied from about 0.1 amps./in.^{2} to about 100 amps/in.^{2}. The anode current density was also varied from about 0.1 amp./in.^{2} to about 10 amps./in.^{2}. The presence of any alkali halogen compound in the melt thus apparently prevents the deposition of tantalum in a recoverable state. Usually only the alkali metal deposits. It was also noted if NaCl, for example, were added to an electrolyte like the example cited above containing $CaCl_2$—CaO—Ta_2O_5 successfully depositing tantalum, then after such addi-

tion, the production of collectible tantalum was curtailed or stopped.

A modified procedure is as follows:

EXAMPLE II (TANTALUM)

Using similar equipment to that described in Example I, fused 10 parts of K_2TaF_7. Due to the high vapor pressure of this material, was unable to melt a sufficient quantity to test electrolytically. Added 70 parts of prepurified KCl to the cell and fused the mass together at 750–850° C. Final composition was 85.7 w./o. KCl—14.3 w./o. K_2TaF_7. Using a 1-inch diameter graphite anode and the nickel liner as a cathode electrolyzed the bath. In the presence of an inert gas, the bath polarizes and cannot be operated at any reasonable current density that would permit operating the bath practically on D.C. electrolysis alone. Although it was possible to deposit tantalum from this bath, it is impossible to strip the melt of tantalum salts. The residual salts are difficult to separate from the tantalum by chemical means and in using mechanical methods the metal is downgraded. Also it is noted that the metal is not deposited in the form of growth crystals, but appears to be the result of secondary chemical reduction. If the bath is exposed to air, the polarization tends to disappear and a higher current density may be carried. The polarization can be completely overcome by adding Ta_2O_5 to the melt.

Another test was made using a 50–50 molar eutectic of KCl—NaCl as a solvent with about 28 w./o. K_2TaF_7. Above about 850° C., the bath fumes and smokes excessively. Ran the electrolysis at about 750° C. Again could not strip the bath of tantalum values or maintain a decent continued current flow. The metal gave the appearance of having formed through a process of secondary chemical reductions.

In a cleaned nickel lined cell, fused 64.8 w./o. KCl—25.9 w./o. KF—9.3 w./o. K_2TaF_7 and maintained the temperature of the bath at 750–800° C.; on electrolysis tantalum was deposited, but the bath polarized and could not be electrolyzed for any reasonable length of time. Added Ta_2O_5 to the melt making about a 10 w./o. solution. The melt was clear and transparent. On electrolysis, tantalum could be seen depositing on the cathode wall. Again, it was impossible to strip the bath of tantalum values and the metal could be separated from the electrolyte only with difficulty.

The results of this series of runs are summarized in Table II below. The cathode current densities were varied from a 0.1 amp./in.^{2} to about 10 amps./in.^{2} and the anode current densities were kept below about 5 amps./in.^{2}. In order to overcome polarization effects, the voltage was progressively lowered until it was impractical to electrodeposit.

The results were not satisfactory. All the material produced in these types of electrolysis was not of the highest purity and had to undergo further refining before an acceptable ductile material was produced. A definite contributor to impurities was the association of insoluble electrolyte with the metal. The metal appeared to have been the result of secondary chemical reduction. The probable mechanism may be:

$$K^+ + Cl^- \xrightarrow{\text{electrolysis}} K^\circ + \tfrac{1}{2}Cl_2 \quad (1)$$

$$5K^\circ + K_2TaF_7 = 7KF + Ta \quad (2)$$

in oxide free electrolytes. In electrolytes containing the oxide in melt:

Electrolysis:

$$K^+ + Cl^- + C(\text{anode}) + \text{oxygen} = K^\circ + CO(\text{gas}) \quad (3)$$

EXAMPLE III (TANTALUM)

In the same type of apparatus used above fused 100 parts of $CaCl_2$ under an HCl atmosphere. Bubbled dry HCl gas through the melt to decompose oxides, carbonates, and to purge the melt of residual moisture. Electrolyzed the bath to remove metallic impurities and finally to deposit some calcium metal within the cell. Passed dry argon gas through cell during and after electrolysis. Carefully added about 1 part of pre-purified and anhydrous Ta_2O_5 to the melt. Observed that little, if any, Ta_2O_5 was accepted and dissolved by the melt. However, electrolyzed the melt and continued to add Ta_2O_5 to the bath in small amounts and continuously during electrolysis. The temperature was maintained between 850–1050° C. After passing about 75 ampere-hours through the cell, removed the 1-inch diameter graphite anode and allowed the salts to freeze under the protective inert atmosphere. The salts were leached from the metal by cold water and the metal vacuum dried without heat. The metal was silver gray in color and composed of small particles. It was apparent that the metal had been formed predominantly as a result of secondary chemical reduction.

Repeated the steps as above but this time added 5 parts of prepurified CaO to the $CaCl_2$—Ta_2O_5 mix. Almost instantly the insoluble oxide was taken up and accepted by the melt. The solution was clear and transparent. The temperature varied between 985° C. and 1050° C. Added bit by bit of Ta_2O_5 to the melt during the run but kept the concentration by weight less than 10%. Restarted electrolysis using the nickel liner as a cathode and a 1-inch diameter graphite rod as an anode. Passed about 200 ampere-hours through the cell and noted that there was no polarization, and according to the back E.M.F. tantalum appeared to be deposited predominantly by primary electrolysis. After the tantalum component of the cell had been stripped (as seen by the jump

Table II (Tantalum)

Electrolyte composition	Temp. in degrees C.	Characteristics of run	Observations and results
KF—K_2TaF_7	800–850	Intense polarization in inert gas. Nickel cathode. Graphite anode. Salts difficult to remove from deposit.	Melt is volatile and smokes. Metal is dark gray in color. Efficiency is very low. Metal is fine and appears to be the result of secondary chemical reduction.
KCl—NaCl, K_2TaF_7	750	Nickel cathode. Graphite anode. Polarized in inert gas. Cannot run continually.	Metal is brighter in color than run above. However, it was extremely difficult to separate the insoluble salts from the metal powder. The metal was powdery and seemed to have resulted from secondary chemical reduction. Current efficiency below 50%.
KCl—KF, K_2TaF_7—Ta_2O_5	750–800	Nickel cathode. Graphite anode. Polarized at an A.C.D. 5 amps./in^2. Can run in inert gas or in air.	Bath fumes at higher temperature. Metal is less bright than run above. The bulk of the metal is fine and mossy. No large silvery crystals. Cannot strip bath of tantalum values. Could not separate metal from electrolyte with ease. Current efficiency higher than above.

in back E.M.F.), the anode was withdrawn and the cell contents were allowed to freeze. The salts were dissolved in HCl acidified water and the metal dried under vacuum without heat. The metal was found to be composed of silvery bright crystals well-formed and massive. There were no discolored salts of off color, i.e. gray-black, metal. The metal was screened and 84.7% was retained on a 60-mesh screen.

EXAMPLE IV (COLUMBIAN)

Repeated the steps of Example III with columbium oxide except that a $BaCl_2$—$SrCl_2$ eutectic was used instead of the $CaCl_2$. The purified bath was crystal clear and water-white. To 100 parts of the solvent at 1050–1200° C. added ½ part of purified and anhydrous Cb_2O_5. After stirring obtained a cloudy solution indicating rejection of the Cb_2O_5. On initial electrolysis, it was apparent that something other than Cb was depositing. Thereupon added prepurified and anhydrous BaO and SrO to the melt. Immediately the bath cleared and the Cb_2O_5 was accepted and dissolved therein. Added more BaO and SrO until the ratio by weight of the solvents was: 64 $SrCl_2$:36 $BaCl_2$:10 SrO:10 BaO. The concentration of Cb_2O_5 was kept below 3 w./o. Inserted a molybdenum cathode and a graphite anode and electrolyzed the melt. The initial cathode current density was about 28.7 amps./inch^2. During the course of electrolysis, purified and anhydrous Cb_2O_5 was continuously dusted into the catholyte as such a rate so as not to exceed the rate of consumption of the solute or the 3% by weight Cb_2O_5. At the end of the 5 hour run, no further Cb_2O_5 was added to the bath and the electrolysis was continued until the bath was seen to be stripped of columbium values. The salts were separated from the cathode and the cathode deposit by cold water, followed by a dilute HCl treatment, water wash, hot KOH rinse and water rinse. The metal was dried without heat and examined. The metal was found to be free of salts and was bright gray in color. The crystals were not as bright nor as large as those obtained using a $CaCl_2$—CaO bath. The consolidated metal was very ductile.

EXAMPLE V (COLUMBIUM)

Repeated the steps of Example III except that the purified $CaCl_2$—CaO bath was maintained with less than 4 w./o. Cb_2O_5 solution. The temperature was 1100–1200° C. The initial cathode current density (a tantalum cathode) was 44.6 amps./in.^{2} and the anode current density was not greater than 8.2 amps./in.^{2}. The metal was easily separated from the adherent salts by water elutriation. The metal was found to be silvery bright and in the form of large well-formed crystals. No powdery metal was found.

The runs using the successful alkaline earth chloride-oxide mixtures were repeated, wherein the composition of the electrolyte was varied over the following ranges:

	Percent
$CaCl_2$	0–99
$BaCl_2$	0–77
$SrCl_2$	0–92
CaO	0.1–20
SrO	0.1–12
BaO	0.1– 8

The ratio of $CaCl_2$:CaO was varied from 5:1 to 100:1. The preferred solvent is a 95$CaCl_2$—5CaO electrolyte. The concentration of Ta_2O_5 and Cb_2O_5 was also varied widely from a few tenths of a percent to a super-saturated solution. The preferred concentration of refractory metal oxide solute lies below about 5 w./o. and depends on the cathode current density and the temperature.

The higher the current density, the higher the solute concentration should be. The cathode current density can be varied widely, but the best-formed metal is produced between 10 and 50 amps./in.^{2} (initial). At the lower current densities, a solute concentration of about 3 w./o. is preferred. The anode current density is kept below about 10 amps./in.^{2} and preferably below about 5 amps./in.^{2}. The temperature may be varied over wide limits from 700 to over 1250° C. However, the purest and most ductile metal is formed at about 900–1100° C. and 950–1050° C. is preferred.

Without commitment to any theory it appears that in the absence of the alkaline metal oxide (as CaO, for instance) there is a small molecular solubility of the refractory metal oxides (Cb and Ta oxides) in the halide melt. As a result, there are few, if any, Cb or Ta ions of any kind available for decomposition and deposition. Consequently, a powdery material results which is highly susceptible to contamination. In the presence of the alkaline earth metal oxide, on the other hand, there is a large increase in the solubilities of these Cb and Ta oxides and a change in the ionic nature of the solute so that now there are Cb and Ta ions of some sort available and these metals then seem to be the result of a primary electrolytic deposition. This results in the formation of crystals that grow in size with time. The character of the deposition is completely changed. The efficiency of deposition rises sharply from about 50% or less without CaO to about 90% or more with the CaO. The metal made in this way is very ductile with a hardness below 100 Brinell, and usually between 40 and 60 Brinell. The purity varies with the purity of the oxide feed. With a highly purified feed, a very pure metal was obtained whose combined Cb—Ta content was in excess of 99.9%. The analytical methods for oxygen, nitrogen, hydrogen and carbon in these metals are not fully reliable. It was found that the more ductile metal is made using the preferred $CaCl_2$—CaO electrolyte, keeping the concentration of the Ta or Cb oxide below 3 w./o., in a cell using a basket type cathode and a compartmentalized cell, with an inert gas atmosphere.

Although an inert gas atmosphere is preferred, it is not mandatory as pure and ductile metal has been made using a covered and compartmentalized cell. Also instead of using the respective pentoxide feeds, it is also possible to feed the cell with the lower valent oxides and obtain high purity and ductile metal. One should keep in mind that moisture or water in any form plays havoc with the process of the invention and the cell and should be avoided. Also, the presence of carbonate, sulfates, and the like should be avoided as they contribute to the degeneration of the process and yield metal contaminated with carbon and the like.

The feeding of excess Cb or Ta oxide beyond the solubility limit of the electrolyte should be avoided as it does not help the performance of the process. Similarly, continued starvation of the electrolyte is to be avoided as Ca will codeposit at high cathode current densities and in subsequent treatment hydrogen discharge may render the metal brittle and difficult to work.

Having described in considerable detail a process for the production of pure and ductile columbium and tantalum by fusion electrolysis of their oxides, it is understood that the invention is not limited in scope to many of the specific details described herein but that many modifications may be made without departing from the spirit or scope of the invention.

I claim:

1. A process for the electrolytic production of a pure and ductile metal of the group columbium and tantalum comprising electrolyzing between an anode and a cathode a molten electrolyte comprising a solvent mixture of at least one halide of the group of alkaline earth halides and at least one oxide of the group of alkaline earth oxides, and also containing a substantial amount of at least one oxide of the said group columbium and tantalum, thereby discharging oxygen at said anode and depositing said pure and ductile metal in large crystalline form on said cathode.

2. A process for the electrolytic production of a pure and ductile metal of the group columbium and tantalum as set forth in claim 1, wherein said electrolysis is carried out in a compartmentalized cell under an inert gas atmosphere.

3. A process for the electrolytic production of pure and ductile tantalum by fusion electrolysis of its oxides comprising electrolyzing a substantial amount of at least one tantalum oxide in an electrolyte solvent mixture composed of at least one halide of the group of alkaline earth halides and at least one oxide of the group of alkaline earth oxides, thereby depositing pure and ductile tantalum on a cathode.

4. A process for the electrolytic production of tantalum as set forth in claim 3 wherein said electrolyte solvent comprises chlorides and wherein said tantalum oxide is tantalum pentoxide.

5. A process for the electrolytic production of tantalum as set forth in claim 3 wherein said electrolyte solvent comprises $CaCl_2$ and CaO and contains Ta_2O_5.

6. A process for the electrolytic production of tantalum as set forth in claim 5 wherein the molecular ratio of CaO to Ta_2O_5 in said final electrolyte is greater than 1:1.

7. A process for the electrolytic production of tantalum as set forth in claim 3 wherein said electrolysis is carried out in a compartmentalized cell.

8. A process for the electrolytic production of tantalum as set forth in claim 3 wherein said electrolysis is carried out under an inert gas atmosphere.

9. A process for the electrolytic production of pure and ductile columbium by fusion electrolysis of its oxides comprising electrolyzing a substantial amount of at least one columbium oxide in an electrolyte comprising a solvent mixture of at least one halide of the group of alkaline earth halides and at least one oxide of the group of alkaline earth oxides, thereby depositing pure and ductile columbium on a cathode.

10. A process for the electrolytic production of columbium as set forth in claim 9 wherein said electrolyte solvent comprises chlorides and wherein said columbium oxide is columbium pentoxide.

11. A process for the electrolytic production of columbium as set forth in claim 9 wherein said electrolyte solvent comprises $CaCl_2$ and CaO and contains Cb_2O_5.

12. A process for the electrolytic production of columbium as set forth in claim 11 wherein the molecular ratio of CaO to Cb_2O_5 in said final electrolyte is greater than 1:1.

13. A process for the electrolytic production of columbium as set forth in claim 9 wherein said electrolysis is carried out in a compartmentalized cell.

14. A process for the electrolytic production of columbium as set forth in claim 9 wherein said electrolysis is carried out under an inert gas atmosphere.

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