

1

2,870,073

PREPARATION OF THE REFRACTORY METALS BY FUSED SALT ELECTROLYSIS

Menahem Merlub-Sobel and Milton J. Arnoff, Cleveland, and Jack L. Sorkin, Cleveland Heights, Ohio, assignors, by mesne assignments, to Horizons Titanium Corporation, Princeton, N. J., a corporation of New Jersey

No. Drawing. Application November 8, 1955
Serial No. 545,775

12 Claims. (Cl. 204—64)

This invention relates to the preparation of the rare and refractory metals of the fourth, fifth and sixth groups of the periodic table, having an atomic number between 23 and 74, that is, the metals vanadium, chromium, zirconium, columbium, molybdenum, hafnium, tantalum and tungsten. More particularly it relates to the preparation of fused salt compositions adapted to be electrolyzed to produce these elements in the form of a cathode deposit and to the electrolysis of such fused salt compositions.

Numerous processes have been suggested for the preparation of the refractory metals. One type of process which was exhaustively investigated is described in U. S. Patents 1,815,054 and 1,835,025 issued to Driggs and others. The processes therein described and claimed comprised electrolytically depositing a desired refractory metal from a fusion of an alkali metal halide and a double halide compound of an alkali metal and the rare refractory metal. As taught in these patents, the double halide was preferably a fluoride. The processes were disclosed as being applicable to such metals as tantalum, tungsten, manganese, zirconium, thorium and to members of the same groups as these metals.

Instead of employing a fused bath in which the desired metal is present as a double fluoride, we have found that a much simpler and more economical procedure may be effected through the electrolysis of anhydrous chlorides of the metals in question in a fused salt bath composed essentially of at least one alkali metal halide or alkaline earth metal halide. In accordance with our invention, an oxygen-free, anhydrous, chloride-containing bath may be prepared from such common and relatively inexpensive raw materials as oxygen-containing compounds of the metals. By oxygen-containing compounds we intend to include those compounds which, on heating to temperatures no higher than about 1000° C., and particularly when dispersed in a fused salt, form the oxide of the metal in nascent, or reactive form. Among such compounds may be mentioned the hydroxides and hydrated oxides, nitrates, nitrites, oxalates, acetates, carbonates, basic carbonates and other basic salts such as basic chlorides or nitrates, and hydrates which decompose to form the reactive oxide by hydrolysis. It is the fundamental concept of our invention that the oxide of the metal to be converted to the chloride shall be available to the chlorination reaction in nascent or reactive form, it being long known that time-aged or highly-ignited metal oxides are relatively refractory to chlorination. In our invention, not only is the oxide in freshly-prepared reactive form, but it is also highly dispersed in the fused alkali salt, thereby affording excellent physical conditions for conversion to chloride.

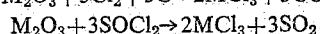
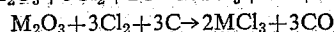
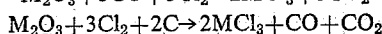
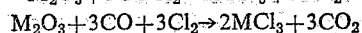
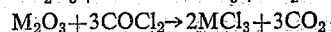
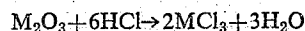
Briefly, in accordance with our process, such oxygen containing compounds are added, either singly or in combination with one another, to a molten pool comprised of at least one alkali metal halide and preferably at least one alkali metal chloride. When the addition is made, a dispersion or possibly a partial solution of the rare and refractory metal oxide is formed in the fused bath while at the same time, any water present flashes off at the

2

elevated temperature of the bath. We have found that when this solution or dispersion is contacted with a suitable chlorinating agent, a reaction occurs in which the desired metal chloride forms in an anhydrous condition in the fused salt bath. In the past when the desired metal chloride has been independently formed and then added to a fused bath, during the interval between formation and addition, the chloride was highly susceptible to hydrolysis and hence picked up a considerable amount of moisture. By our process this interval is eliminated completely and a virtually oxygen-free bath of the chloride is produced.

The chlorination reaction may be effected with a wide variety of chlorinating agents including anhydrous hydrogen chloride, phosgene, thionyl chloride, mixtures of chlorine with carbon monoxide and mixtures of chlorine with carbon. The chlorinating agent may be introduced into the fused salt melt in any suitable fashion. We have chlorinated with finely divided bubbles, passed into the melt through an inert perforated inlet tube. With appropriate starting materials the chlorination proceeds quantitatively and, depending on the chlorinating agent selected, either water vapor or various oxides of carbon or sulfur are eliminated from the bath as they form.

The chlorination reactions may be represented by the following equations, in which M_2O_3 may be any suitable oxygen containing compound of the refractory metal which is readily decomposed to yield an oxide of the desired metal:



As shown in the foregoing reactions any water vapor and carbon oxides formed as a result of the reaction are readily eliminated from the melt. Accordingly, the fused mass may be electrolyzed directly in the vessel in which the reaction was effected. We prefer, however, to operate the reactor continuously. Accordingly, we withdraw portions of the reaction composition and charge the molten material into an electrolytic cell constructed of a suitably inert material, wherein the molten material is electrolyzed employing a carbon or graphite anode in a manner well known in the art. Chlorine is evolved at the anode and the desired refractory metal is deposited at the cathode. To enable the reactor to run continuously additional amounts of refractory metal compound are added periodically to the fused bath in the reactor and the alkali metal chloride content of the bath in the reactor is replenished from time to time.

The following examples will serve to further illustrate the practice of our invention.

Example I

A mixture of sodium chloride and potassium chloride was fused in a covered graphite crucible at a temperature between 700° and 725° C. The chlorides were proportioned to form a eutectic composition. After the salts were melted a sparger through which hydrogen chloride gas was flowing was inserted into the bath. Forty parts by weight of chromium nitrate $Cr(NO_3)_3 \cdot 9H_2O$ were added to the bath slowly over a period of ten minutes. Due to the rapid release of water vapor and fumes containing oxides of nitrogen, the additions were small in size and were made gradually. About twenty minutes after the final increment of nitrate had been added, the bath had become a transparent red color. The flow of hydrogen chloride was continued for an additional ten

3

minutes, during which time the bath appearance did not change. The sparger was removed and a sample of the bath was withdrawn for analysis. After cooling, the salt was deep violet in color. The test sample was treated with water. Instead of the insolubility characteristic of the chromic oxide resulting from thermal decomposition of the nitrate, the sample dissolved readily to yield a solution which, when analytically tested, showed that the chromium was present as water soluble trivalent chromic ion, undoubtedly as chromic chloride or as a sodium chromium chloride complex.

Example II

The experiment of Example I was repeated, adding a tantalum salt instead of the chromium salt. The tantalum salt added was the hydrated pentoxide produced by acidification of an aqueous solution of potassium hexatantalate. The alkali metal hexatantalates, per se, may be added to the fused salt melt in an entirely similar fashion. The tantalum chloride evolved from the fused melt as rapidly as it formed and was recovered and separated from other gaseous products leaving the cell, by passing it into a large body of molten alkali metal chlorides, wherein it dissolved or formed complexes. From such a bath the metal could be readily recovered by electrolysis.

Example III

Into a fused salt bath prepared by melting sodium chloride in a graphite crucible, there was introduced a stream of chlorine gas. The gas was bubbled into the melt by means of a perforated graphite inlet tube. After the flow of chlorine was initiated, pellets of basic zirconium carbonate and lampblack carbon, intimately admixed in the proportions of 10 parts of basic zirconium carbonate containing about 23.4% ZrO_2 by weight to 1 part by weight of lampblack were gradually fed into the molten bath. The melt was heated to about 800° C. and maintained at this temperature during the chlorination. A sample of the salt bath was taken after completion of chlorination and analyzed for zirconium. It was found that the fused melt contained 2.5% zirconium corresponding to 6.4% $ZrCl_4$ by weight.

The fused salt was then electrolyzed by inserting an anode and a cathode through openings provided in the cover of the crucible. The electrolysis, carried out at 750° C. under an atmosphere of argon at a current density of about 100 amperes/square decimeter, and a cell voltage of about 2.3 volts produced a deposit of zirconium metal on the steel cathode.

While the foregoing examples illustrate a preferred manner of adding the transition metal oxygen containing compound to a molten salt bath, it is advantageous in many instances to melt the oxygen containing compound and the carrier salt at the same time and then to chlorinate the resulting mixture. Accordingly, it is not our intention to limit the following claims to any particular manner of forming the fused reaction bath, provided that the metal oxygen compound is present therein in reactive form.

The transition metal chlorides produced in accordance with our invention may be separated from the fused salt melt by any suitable technique, such as extraction by an organic solvent, or, as we prefer, they may be further processed to obtain the metal itself, e. g., by electrolysis of the fused bath or by reduction with a powerful reducing agent such as an alkali or alkaline earth metal (e. g. sodium).

We claim:

1. The process of preparing an anhydrous chloride of a metal of the group consisting of vanadium, niobium, tantalum, zirconium, hafnium, chromium, molybdenum and tungsten, which comprises: preparing a fused salt melt consisting of at least one alkali metal halide, adding to the melt a compound of said metal selected from the

4

oxygen containing compounds of said metal which decompose to yield an oxide of said metal in said melt, and chlorinating said freshly formed metal oxide contained in the resulting melt by admitting an externally produced chlorinating agent into the melt wherein it converts the freshly formed oxide into an anhydrous chloride of the metal.

2. The process of preparing an anhydrous chloride of a metal of the group consisting of vanadium, niobium, tantalum, zirconium, hafnium, chromium, molybdenum and tungsten, which comprises: preparing a fused salt melt consisting of at least one, adding to the alkali metal halide melt a compound of said metal selected from the oxygen containing compounds of said metal which decompose to yield an oxide of said metal in said melt and chlorinating the freshly formed metal oxide contained in the resulting melt by admitting an externally produced chlorinating agent of the group consisting of chlorine, phosgene, thionyl chloride, hydrogen chloride, mixtures of carbon monoxide and chlorine and mixtures of carbon and chlorine into the melt wherein it converts the freshly formed oxide into an anhydrous chloride of the metal.

3. The process of preparing an anhydrous chloride of a metal of the group consisting of vanadium, niobium, tantalum, zirconium, hafnium, chromium, molybdenum and tungsten, which comprises: preparing a fused melt of sodium chloride, adding to the molten sodium chloride a compound of said metal selected from the oxygen containing compounds of said metal which decompose to yield an oxide of said metal and chlorinating the freshly formed metal oxide contained in the salt melt by admitting a chlorinating agent into the melt wherein it converts the freshly formed oxide into an anhydrous chloride of the metal.

4. The process of preparing an anhydrous chloride of a metal of the group consisting of vanadium, niobium, tantalum, zirconium, hafnium, chromium, molybdenum and tungsten, which comprises: preparing a fused salt melt consisting of an alkali metal halide, adding to the melt a compound of said metal selected from the oxygen containing compounds of said metal which decompose to yield an oxide of said metal in said melt, chlorinating the freshly formed metal oxide contained in the salt melt by admitting an externally produced chlorinating agent thereto and recovering the resulting anhydrous chloride of said metal in solution in a fused alkali metal halide.

5. The process of preparing an anhydrous chloride of zirconium, which comprises: preparing a fused salt melt consisting of alkali metal halide, adding to the alkali metal halide a compound of zirconium selected from the oxygen containing compounds of zirconium which decompose to yield zirconium oxide in said melt, and chlorinating the freshly formed zirconium oxide contained in the melt by admitting an externally produced chlorinating agent thereto, whereby an anhydrous chloride of zirconium is produced.

6. The process of preparing an anhydrous chloride of chromium, which comprises: preparing a fused salt melt consisting of alkali metal halide, adding to the alkali metal halide a compound of chromium selected from the oxygen containing compounds of chromium which decompose to yield chromium oxide in said melt and chlorinating the freshly formed chromium oxide contained in the melt by admitting an externally produced chlorinating agent thereto, whereby an anhydrous chloride of chromium is produced.

7. The process of preparing a metal of the group consisting of vanadium, niobium, tantalum, zirconium, hafnium, chromium, molybdenum and tungsten, which comprises: preparing a fused melt consisting of at least one alkali metal halide, adding to the alkali metal halide melt a compound of said metal selected from the oxygen containing compounds of said metal which decompose to yield an oxide of said metal dispersed in said melt, chlori-

5

nating the metal oxide contained in the salt melt by admitting a chlorinating agent thereinto thereby producing an anhydrous chloride of said metal, and recovering the said metal from said chloride.

8. The process of preparing a metal of the group consisting of vanadium, niobium, tantalum, zirconium, hafnium, chromium, molybdenum and tungsten, which comprises: preparing a fused melt consisting of at least one alkali metal halide, adding to the alkali metal halide melt a compound of said metal selected from the oxygen containing compounds of said metal which decompose to yield an oxide of said metal in said melt, chlorinating the metal oxide contained in the salt melt by admitting a chlorinating agent thereinto thereby producing an anhydrous chloride of said metal in solution in said fused salt melt and electrolyzing the fused solution to obtain said metal as a cathode deposit.

9. The process of preparing a metal of the group consisting of vanadium, niobium, tantalum, zirconium, hafnium, chromium, molybdenum and tungsten, which comprises: preparing a fused melt of sodium chloride, adding to the molten sodium chloride a compound of said metal selected from the oxygen containing compounds of said metal which decompose to yield an oxide of said metal in said melt, chlorinating the freshly formed metal oxide contained in the melt by admitting into the melt a chlorinating agent of the group consisting of chloride, phosgene, thionyl chloride, hydrogen chloride, mixtures of carbon monoxide and chlorine and mixtures of carbon and chlorine, thereby producing an anhydrous chloride of said metal in solution in said fused salt melt and electrolyzing said fused solution to obtain said metal as a cathode deposit.

10. The process of preparing a metal of the group consisting of vanadium, niobium, tantalum, zirconium, hafnium, chromium, molybdenum and tungsten, which

6

comprises: preparing a fused melt of sodium chloride, adding to the molten sodium chloride a compound of said metal selected from the oxygen containing compounds of said metal which decompose to yield an oxide of said metal in said melt, chlorinating the metal oxide contained in the melt by admitting a chlorinating agent thereinto, thereby producing an anhydrous chloride of said metal in solution in said fused melt and recovering said metal from said dissolved anhydrous chloride.

11. The process of preparing zirconium which comprises preparing a fused melt consisting of at least one alkali metal chloride, adding a zirconium carbonate to the molten chloride, chlorinating the resulting dispersion of zirconium oxide in the melt by admitting a chlorinating agent thereinto, thereby producing an anhydrous zirconium chloride in solution in said alkali metal chloride and recovering the zirconium therefrom.

12. The process of preparing chromium which comprises preparing a fused melt consisting of at least one alkali metal chloride, adding a nitrate of chromium to the molten chloride, chlorinating the resulting dispersion of chromium oxide in the melt by admitting a chlorinating agent thereinto, thereby producing an anhydrous chloride of chromium in solution in said alkali metal chloride and recovering the chromium therefrom.

References Cited in the file of this patent

UNITED STATES PATENTS

30	2,302,604	Dolbear	Nov. 17, 1942
	2,598,833	Renman	June 3, 1952

FOREIGN PATENTS

35	562,777	Great Britain	Jan. 10, 1944
	635,267	Great Britain	Apr. 5, 1950
	164,283	Australia	Apr. 8, 1954

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,870,073

January 20, 1959

Menahem Merlub-Sobel et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, lines 12 and 13, strike out "alkali metal halide" and insert the same after "one", and before the comma, in line 12, same column.

Signed and sealed this 19th day of May 1959.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON

Commissioner of Patents