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METHOD OF ADDING REFRACTORY METAL HALIDES TO MOLTEN SALT ELECTROLYTES

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ABSTRACT OF THE DISCLOSURE

An integrated solid mass, e.g., a globule, of a tetrachloride of zirconium or hafnium, or a pentachloride of niobium, molybdenum or tantalum is plunged into a molten salt electrolyte composition in order to introduce this metal compound into the salt bath for the purpose of electrodepositing the particular refractory metal of said metal compound.

This invention to be employed in the technical field relating to the electrodeposition (e.g., electrowinning, electrorefining, electroplating) of refractory metals such as zirconium, hafnium, molybdenum, niobium and tantalum. More particularly, it relates to the manner of adding those metals to a fused salt bath for such purposes as electrowinning and electrorefining.

In view of their value in the field of atomic energy wherein hafnium is employed as a control element in reactors while zirconium is employed as a structural reactor material, there is considerable interest in producing these materials in substantially pure elemental form. The principal way in which pure zirconium and hafnium metal have heretofore been commercially produced involves chemical reduction of the tetrachloride of the metal (Kroll process described in U.S. Pat. 2,205,854) followed by formation and subsequent thermal decomposition of the tetraiodide (Van Arkel et al., Preparation of Pure Titanium, Zirconium, Hafnium and Thorium Metals, Z. Anorg. v. Algem. Chem., 148, 345 (1925)). Such methods are not adaptable to continuous processing and require the intermediate production of the metal in impure form, and are therefore costly.

Some work has also been done on electrowinning these metals by adding hafnium or zirconium tetrachloride as a vapor to a molten salt electrolyte (e.g., U.S. Pat. No. 2,936,269). In such a process, the particulate starting material required to produce the vapor feed readily picks up moisture which eventually contaminates the vapor whereby undesirable oxygen begins to deposit with the metal at the cathode of the electrolytic cell. This oxygen build-up problem renders the process undesirable with regard to continuously electrowinning hafnium or zirconium.

There has also been some work done on electrorefining impure hafnium or zirconium (U.S. Bureau of Mines, Report of Investigations No. 6818; U.S. Pat. No. 2,937,-979). However, this latter work, like the previously mentioned commercial tetrahalide decomposition process depends upon impure metal as a starting material in one of the steps of the process.

We have now developed a novel way of adding hafnium or zirconium to a molten salt for electrolytic purposes such as electrowinning and electrorefining. Basically, the process comprises introducing those metals as an integrated solid mass of zirconium tetrachloride or hafnium tetrachloride into a molten salt of alkali and/or alkaline earth metal halide suitable for the purpose of electrodepositing the respective metal. Despite the fact that these two tetrahalides sublime at about 300° C., they can be essentially dissolved in solid form in such a molten salt at

a temperature as high as 500° C. higher than the sublimation point, without marked loss of the volatile tetrachloride. In the same manner, $MoCl_5$, $NbCl_5$ or $TaCl_5$ can be added to such a molten salt despite the fact that these compounds vaporize at less than 300° C.

The preferred way to obtain the solid tetrachloride or pentachloride is to vaporize the impure form of the tetrachloride or pentachloride and to condense the resultant vapors as a high density globule which, by nature, does not readily pick up moisture during handling. With regard to zirconium and hafnium tetrachloride, this is accomplished by vacuum sublimation. The globule can then be easily plunged into molten electrolyte suitable for the purposes electrowinning. As such, an electrolytic process employing such a globule as feed material can be continuously operated without concern for oxygen contamination (through moisture pickup).

Therefore, the problem of requiring production of impure metal as an intermediate or starting material in the production of hafnium or zirconium is solved by the present invention. Furthermore, the problem of oxygen contamination when electrolytically producing these metals is essentially eliminated.

It is therefore an object of the present invention to more readily add a refractory metal such as zirconium, hafnium, molybdenum, niobium or tantalum to a molten salt suitable for the purpose of electrodepositing such a metal. Another object is to employ hafnium or zirconium tetrachloride in the form of an integrated solid mass as the feed material in a fused bath electrowinning process. A still further object is to employ solid, dense globules of hafnium or zirconium tetrachloride, formed by vacuum subliming impure tetrachloride, as the starting material in an electrowinning process. Other objects and advantages will be obvious from the following more detailed description of the invention.

In the practice of the invention, the refractory metal chloride is first obtained in integrated, coherent solid mass form capable of withstanding the rigors of transportation into the molten salt. With regard to hafnium and zirconium, this can be done by vacuum subliming an impure powder form of the tetrachloride and condensing the resultant vapors to a solid globule. Such a globule is high in density and low in surface area whereby it will not react rapidly with moisture in the atmosphere. As such the globule will remain comparatively free of oxygen, which is very desirable with regard to electrowinning operations. Purified pentachloride of molybdenum, niobium or tantalum could be formed in a like manner by melting the powders of these compounds, then vaporizing the melt and condensing the resultant vapor.

Alternatively, purified zirconium tetrachloride can be formed by condensing the vapors from a molten $ZrCl_4$-NaCl eutectic (Journal of Metals, 1955; vol. 7, No. 10, pp. 1118–1120). Solidified hafnium tetrachloride can be obtained in a like manner (U.S. Bureau of Mines Report of Investigations No. 5734, 1961). If there is no concern for the purity of the integrated solid mass, a coherent mass of any of these refractory metals could be prepared by powder metallurgy techniques.

Solid tetrachloride of Hf or Zr, or pentachloride of Mo, Nb or Ta, once obtained, is plunged into a requisite molten salt at a temperature of about 500°–900° C., preferably 600–700° C., in an inert environment. Broadly, those molten salts heretofore employed, for electrolytic purposes, in combination with these refractory metal tetrachlorides or pentachlorides can be employed in the practice of the present invention. More specifically, halides (e.g., chloride, fluoride, bromide and iodide) of alkali metals (e.g., Na, K, Rb, Cs, Li) and alkaline earth metals (e.g., Ca, Ba, Mg, Sr), and combinations thereof are capable of dissolving the solid refractory metal chlorides.

With particular regard to electrowinning hafnium, I have discovered that molten salts of LiCl-RbCl, KCl, LiCl-CsCl, LiCl-KCl or NaCl-KCl readily dissolve a mass of hafnium tetrachloride, while molten salts of NaCl-KF, NaCl-NaF or NaCl-LiCl-KF are particularly effective for dissolving solid $ZrCl_4$. As will be apparent to those skilled in the art, the optimum ratios of molten salt constituents can be routinely determined for each particular set of operating conditions.

The following example illustrates the effectiveness of the process of the present invention.

EXAMPLE A

1000 grams of hafnium tetrachloride powder obtained by chlorinating HfC were placed at the bottom of a glass flask. Quartz wool held between two nickel wire screens was positioned above the powder. A lid containing a gas inlet, a gas outlet, and a hollow air-cooled pipe protruding therethrough, which pipe was closed at one end, was bolted to the top of the flask so that the closed, air-cooled end of the pipe extended downward into the flask in close proximity to the quartz wool. The flask was then evacuated and heated to 250° C.–350° C. in a furnace. The vacuum-sublimed hafnium tetrachloride powder condensed as a dense ball on the air-cooled end of the pipe. The ball weighed 800 grams, and had a density of about 3 gm./cc. The oxides were left on the bottom of the flask. The pipe with the condensed tetrachloride was then placed into the cell air lock of an electrolytic cell having a graphite anode and nickel cathode, and containing approximately 15 kg. of molten salt electrolyte surrounded by an inert environment. The air lock was then evacuated and backfilled with inert gas. The condensed tetrachloride having an oxygen content of 800 p.p.m. was then plunged into the electrolyte. This same test was repeated with different electrolytes. All the tests were conducted at initial anode and cathode current densities of 216 amp/ft.^{2}. Chlorine gas given off at the anode during electrolysis was vented through either a silica or graphite tube to prevent cell corrosion. The average cathode current efficiency was 94%, and each test was operated for 10 amp/hrs. The resultant deposits at the cathode were leached with dilute HCl, washed, filtered, dried at room temperature and screened into fractions ranging from +20 to −100 mesh. The finer fractions, representing less than 5 weight percent of the electrodeposit, contained the most oxygen, and were discarded. The coarser fractions (+60 mesh) were analyzed, and the results were as follows:

TABLE 1

Impurities [1] present in cathode deposit, p.p.m.	Electrolyte			
	A [2]	B [3]	C [4]	D [5]
Aluminum	<10	<10	90	16
Chromium	<10	<10	<10	26
Hydrogen	60	13	70	<10
Iron	25	26	29	210
Manganese	90	<25	333	246
Nickel	150	60	118	<20
Nitrogen	<10	10	13	15
Oxygen	415	150	380	440
Silicon	32	31	44	<15

[1] The following impurities were below spectrographic determination limits: Co, Pb, Mg, Ti, V.
[2] Electrolyte was at 700° C. and consisted of LiCl-KCl-$HfCl_4$ (LiCl/KCl 1:1 mole ratio; 5% Hf^{++++}).
[3] 700° C., LiCl-RbCl-$HfCl_4$ (LiCl/RbCl 1:1 mole ratio; 5% Hf^{++++}).
[4] 700° C., LiCl-CsCl-$HfCl_4$ (LiCl/CsCl 1:1 mole ratio; 5% Hf^{++++}).
[5] 800° C., KCl-$HfCl_4$ (5% Hf^{++++}).

The results in Table 1 show that hafnium with a low oxygen content is readily produced by the process of the present invention.

The following example illustrates the solubility of solid hafnium or zirconium tetrachloride in a molten halide electrolyte.

EXAMPLE B

Test 1.—Two globules or balls (943 total grams) of condensed hafnium tetrachloride were plunged into molten LiCl-RbCl-$HfCl_4$ (10 kg.) heated to 500° C., and having a hafnium concentration of 1% and a LiCl/RbCl mole ratio of 1:1. When analyzed 2 hours later, the hafnium concentration was 4.8 percent.

Test 2.—A ball (50 grams) of condensed hafnium tetrachloride was plunged into molten KCl (1 kg.) heated to 800° C. When analyzed 20 minutes later the hafnium concentration was 2.7 percent. A second ball (50 grams) was plunged into the electrolyte and 15 minutes later the hafnium concentration was found to be 5.3 percent. A third ball (50 grams) was then plunged into the electrolyte and 25 minutes later the hafnium concentration was found to be 8.2 percent.

Test 3.—A ball (48 grams) of condensed zirconium tetrachloride was plunged into molten NaCl-KF (1500 grams) heated to 830° C. and having a NaCl/KF mole ratio of 6:1. When analyzed 15 minutes later, the zirconium concentration was 1.2 percent. A second ball (48.5 grams) was then plunged into the electrolyte, and 15 minutes later the zirconium concentration was found to be 2.5 percent.

These tests show that despite the relatively low sublimation point of hafnium and zirconium tetrachloride (both about 300° C.), these materials as integrated solid masses can be rapidly dissolved in molten halide electrolytes without rapid loss of sublimed material.

As previously urged, one advantage of the present invention over the prior art is that the process can be operated continuously. Further, in comparison to electrorefining of hafnium as set out in the U.S. Bureau of Mines Report of Investigations No. 6818, the present invention eliminates the need of a plurality of furnace controls, and requires only comparatively inexpensive apparatus to perform the operation. Still further, due to the solid compact nature of the refractory metal chloride feed material, handling and operational time is greatly reduced.

What is claimed is:

1. In a fused bath electrodeposition of a metal selected from the group consisting of hafnium, zirconium, molybdenum, niobium and tantalum, wherein a chloride of said metal is added to a molten salt electrolyte composition, said chloride being tetrachloride as to hafnium and zirconium, and pentachloride as to molybdenum, niobium and tantalum, the improvement comprising adding said chloride to said molten salt as an integrated, coherent solid mass, wherein said mass is prepared by vaporizing said chloride of said metal and condensing resultant vapors to form said mass.

2. The process of claim 1 wherein said electrodeposition consists of electrowinning said metal, wherein said metal is hafnium or zirconium, and wherein said vaporizing step comprises vacuum subliming hafnium or zirconium tetrachloride powder at a temperature of about 250° C.–350° C.

3. The process of claim 2 wherein said metal is hafnium, and wherein said molten salt is selected from the group consisting of LiCl-RbCl, KCl, LiCl-CsCl, LiCl-KCl, and NaCl-KCl.

4. The process of claim 2 wherein said metal is zirconium, and wherein said molten salt is selected from the group consisting of NaCl-KF, NaCl-NaF, and NaCl-LiCl-KF.

5. In a fused bath electrodeposition of a metal selected from the group consisting of hafnium, zirconium, molybdenum, niobium and tantalum, wherein said metal is added to a molten salt electrolyte composition selected from the group consisting of halides of alkali metals, halides of alkaline earth metals, and mixtures thereof, said step of adding said metal comprising feeding directly into said molten salt a chloride of said metal, said chloride being an integrated, coherent solid mass, said chloride being tetrachloride as to hafnium and zirconium, and pentachloride as to molybdenum, niobium and tantalum; wherein said

mass is prepared by vaporizing said chloride of said metal, and condensing resultant vapors to form said mass.

6. The process of claim 5 wherein said electrodeposition consists of electrowinning said metal, wherein said metal is hafnium or zirconium, and wherein said vaporizing step comprises vacuum subliming hafnium or zirconium tetrachloride powder at a temperature of about 250° C.–350° C.

7. The process of claim 6 wherein said metal is hafnium, and wherein said molten salt is selected from the group consisting of LiCl-RbCl, KCl, LiCl-CsCl, LiCl-KCl, and NaCl-KCl.

8. The process of claim 6 wherein said metal is zirconium, and wherein said molten salt is selected from the group consisting of NaCl-KF, NaCl-NaF, and NaCl-LiCl-KF.

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