

[54] **ELECTROLYTIC PREPARATION OF
ZIRCONIUM AND HAFNIUM DIBORIDES
USING A MOLTEN, CRYOLITE-BASE
ELECTROLYTE**

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[58] Field of Search **204/71**

[56] **References Cited**
UNITED STATES PATENTS

2,936,268 5/1960 Stern et al. **204/71 X**

3,024,176 3/1962 Cook **204/71 X**

FOREIGN PATENTS OR APPLICATIONS

861,743 2/1961 Great Britain **204/71**

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[57] **ABSTRACT**

Zirconium and hafnium diborides are electrolytically synthesized using a molten salt electrolyte containing a major portion of cryolite and minor portions of a sodium alkali, a sodium borate and a source compound to supply the zirconium or hafnium. The synthesis may be accomplished in a cell open to the atmosphere to produce highly pure zirconium and hafnium diborides uncontaminated with their respective oxides.

10 Claims, No Drawings

ELECTROLYTIC PREPARATION OF ZIRCONIUM AND HAFNIUM DIBORIDES USING A MOLTEN, CRYOLITE-BASE ELECTROLYTE

BACKGROUND OF THE INVENTION

Zirconium and hafnium diborides display high melting points, extreme hardness and high electrical conductivity. They show a general chemical inertness toward non-oxidizing acids and many liquid metals and are stable in air to comparatively high temperatures. These borides may be used as abrasives, as electrodes in a variety of electrochemical reactions, as mold materials for liquid metals, as alloy components and as high temperature electrical conductors.

Zirconium diboride has been produced by the following methods: (1) Direct combination of zirconium and boron; (2) metallothermic reduction of mixtures of ZrO_2 and B_2O_3 ; (3) carbon reduction of mixtures of ZrO_2 and B_2O_3 ; (4) reduction of ZrO_2 with boron; (5) reduction of ZrO_2 with boron carbide; (6) precipitation from the gaseous phase; and (7) molten salt electrolysis.

This last method is illustrated by the work of Mellors and Senderoff reported in the J. Electrochem. Soc., V. 113, pp. 60-66. They produced electrolytic, crystalline ZrB_2 plates from an electrolyte containing potassium fluozirconate, potassium fluoborate, lithium fluoride and potassium fluoride. Zirconium boride powders were produced using the systems $NaCl - KCl - ZrCl_4 - KBF_4$ or $NaCl - KCl - ZrF_4 - KBF_4$. Attempts to produce zirconium boride from a $NaCl - KCl - ZrCl_4 - B_2O_3$ melt resulted eventually in the production of zirconium diboride heavily contaminated with zirconium oxide. Another technique for the production of zirconium diboride is illustrated by the Sindeband patent, U. S. Pat. No. 2,741,587. Sindeband used an electrolyte containing B_2O_3 , CaO , CaF_2 and ZrO_2 , but required a metal oxide barrier or diaphragm between the anode and cathode areas to avoid contamination of the boride particles with oxides.

SUMMARY OF THE INVENTION

We have found that zirconium and hafnium diborides of high purity may be produced by a molten salt electrolysis process using technical grade reagents and feed materials. The electrolyte comprises cryolite in major portion, a sodium alkali, a sodium borate and an oxygen-containing zirconium or hafnium compound. A protective atmosphere is unnecessary. Electrolysis temperatures vary from about 900° to about $1,100^\circ C$ and the process may be carried out in a batch, semi-continuous or continuous fashion.

Hence, it is an object of our invention to produce metal borides.

It is a further object of our invention to produce zirconium and hafnium diborides electrolytically.

Another object of our invention is utilize sodium compounds as an electrolyte to synthesize metal borides in a cell open to the air.

DETAILED DESCRIPTION OF THE INVENTION

Our process comprises in its broadest sense the passing of a direct current through a molten salt mixture containing a zirconium or hafnium compound to form a metal boride deposit on the cathode. The metal boride (either zirconium diboride, hafnium diboride, or mixtures of the two) is deposited on the cathode as

clusters of dendritic crystals. Recovery of the metal boride product is accomplished by removing the cathode from the electrolyte and physically dislodging the adhering crystals. Separating of the metal boride crystals from adhering electrolyte may be easily accomplished by water leaching.

Constituents of the electrolyte preferably are of technical grade and of course are in the anhydrous form. Use of technical grade salts offers considerable economic advantage in carrying out our process while the use of more highly pure electrolyte components contributes little if any improvement to the process.

The electrolyte constituents comprise a major portion of cryolite (Na_3AlF_6) together with minor amounts of a sodium borate, a sodium alkali and an oxygen-containing compound of zirconium or hafnium. The sodium borate may comprise a metaborate, orthoborate, diborate, tetraborate, pentaborate or mixtures thereof. Naturally occurring borate compounds, such as borax, may also be used. The sodium alkali may be either sodium hydroxide or sodium carbonate and preferably comprises a mixture of the two. Zirconia (ZrO_2), hafnia (HfO_2) or the sodium salts of either zirconium or hafnium oxyacids, such as sodium zirconate (Na_2ZrO_3), are used as the boride metal source.

The electrolyte composition may vary over a wide range so long as all of the listed constituents are present and so long as the ratio of zirconium or hafnium or their sum to boron is maintained within certain limits. Only the metal diboride is deposited if the atomic ratio Zr, Hf/B is maintained within the range 1:4 to 5:2. The following table illustrates a range of electrolyte compositions which have been found to be suited for use in our process:

TABLE I

Component	Range, mole pct.	Range, wt pct
ZrO_2	5-16	5-13
Na_2CO_3	5-16	4-11
Na_3AlF_6	50-60	68-72
$Na_2B_2O_4$	5-20	5-15
NaOH	10-12	3-5

Operating temperatures may range from about 900° to $1,100^\circ C$ but the highest yields were obtained in the temperature range of 950° to $1050^\circ C$. This last range is preferred. Current density can vary widely; from about 10 to about 225 a/dm². Cell potential is dependent to some extent upon cell geometry but typically ranges from about 1.3 to 6.0 volts.

The electrolytic cell may conveniently comprise a graphite crucible serving the double function of container and anode. A graphite or refractory metal rod or plate, preferably centrally positioned, may serve as the cathode. Graphite is suitable for use in all portions of the electrolytic cell in contact with the electrolyte since the electrolyte does not contain potassium. Not only are potassium salts more expensive than the corresponding sodium salts, but potassium ions intercalate with graphite resulting in physical damage or even failure of cell components. Other refractories, such as silicon nitride, may also be used in the fabrication of electrolytic cells suitable for use in our process. Since the process does not require a protective atmosphere, any convenient heating means, including oil or gas fired furnaces, may be used to maintain the required electrolysis temperatures. A particularly preferred heating means consists of an electric resistance pot furnace.

When operating our process in a batch manner, the bath ingredients are mixed and fused. After fusion, which effectively dehydrates any salts in the hydrated or partially hydrated form, the bath is stabilized at operating temperature. The cathode member is inserted into the bath and electrolysis is begun. Electrolysis is continued for a period of time sufficient to build up an adhering mass of boride crystals on the cathode after which the cathode is removed from the bath. Excess electrolyte is shaken from the cathode deposit and the deposit is then physically removed from the cathode as by scraping. Remaining electrolyte is leached from the crystal mass using water or preferably a dilute acid. Cold, sulfuric acid of about 5 percent concentration is appropriate for use as a leaching agent. The process may be operated on a semi-continuous or continuous basis by adding electrolyte components to the bath as they become depleted and by periodically changing cathodes thus removing the boride product from the electrolytic cell.

The following examples represent specific embodiments of our process and more fully illustrate our invention.

EXAMPLE 1

An electrolytic cell was constructed which consisted of a graphite crucible functioning both as a container and an anode and a graphite rod which functioned as a cathode. The anode crucible was 3 inches in internal diameter and seven inches in height while the cathode was one inch in diameter. The cathode was placed centrally within the anode crucible leaving a one-inch space between the cathode and sidewalls and 1½ inches from the cell bottom. Heating means for the cell consisted of an electric resistance furnace and the cell was open to the air.

A 1,000-g electrolyte charge was prepared having the following composition:

TABLE 2

Component	Weight-percent	Mole-percent
ZrO ₂	9	11
Na ₂ CO ₃	8	11
Na ₂ B ₂ O ₄	10	17
NaOH	3	11
Na ₃ AlF ₆	70	52

An electrolysis was then performed for 1 hour at a temperature of 1,000±10°C. Current was 40 amps corresponding to a cathode current density of 60 a/dm² and the cell potential was 4.5 V. At the end of the electrolysis period, the cathode was removed from the bath and the crystal mass clinging to the cathode was scraped off. Total weight of the cathode deposit was 54 g of which 12.4 g consisted of zirconium diboride and the remainder was adhering electrolyte. Yield of zirconium diboride thus was 0.31 g/amp-hr.

Separation of electrolyte from boride product was accomplished by leaching in cold, 5 percent sulfuric acid. The ZrB₂ was then washed with water, dried, weighed and analyzed. Vicker's microhardness, determined with a 50-g load, was found to be 1,770. Size distribution of zirconium diboride crystals in weight percent was found to be: -65 + 100 mesh, 2.0; -100 + 200 mesh, 38.1; -200 + 325 mesh, 48.5; -325 mesh, 11.4.

The product analyzed 80 percent Zr as determined by activation analysis. Vacuum fusion and combustion analyses indicated the carbon content to be 0.80 percent and the oxygen content to be 0.4 percent. A spec-

trographic analysis of the ZrB₂ product was also performed with the following results:

TABLE 3

Spectrographic analysis, wt pct

Al	0.01	Ni	0.002
Ca	0.02	Si	0.01
Cu	0.002	Ti	0.60
Fe	0.40	Hf	0.01
Mn	0.03	V	0.002
Mg	0.01		

EXAMPLE 2

The electrolytic cell of Example 1 was used to electrolytically synthesize and deposit hafnium diboride. A 1000-g electrolyte charge was prepared having the following composition:

TABLE 4

Component	Weight-percent	Mole-percent
HfO ₂	13.0	12
Na ₂ CO ₃	9.0	12
Na ₂ B ₂ O ₄	8.0	8
NaOH	3.0	12
Na ₃ AlF ₆	67.0	56

An electrolysis was then performed for one hour at a temperature of 1,000 ± 10°C. Current was 40 amps which corresponds to a cathode current density of 60 a/dm² and the cell potential was 4.2 v. At the end of the electrolysis, the cathode was removed and the hafnium diboride deposit was treated as in Example 1. Total weight of the cathode deposit was 54 g of which 20 g was HfB₂. Yield of HfB₂ was 0.50 g/amp-hr.

Vacuum fusion and combustion analyses indicated the carbon content of the hafnium diboride product to be 0.11 percent and the oxygen content to be 0.14 percent. Spectrographic analysis gave the following results:

TABLE 5

Spectrographic analysis, weight-percent

Al	0.01	Ni	0.008
Ca	0.30	Si	0.01
Cu	0.005	Ti	0.10
Fe	0.40	V	0.005
Mg	0.01	Zr	0.70
Mn	0.06		

EXAMPLE 3

The electrolytic cell of Example 1 was used in an attempt to electrolytically synthesize and deposit titanium diboride. An electrolyte charge was prepared having the following composition:

TABLE 6

Component	Weight-percent	Mile-percent
TiO ₂	8	14
Na ₂ CO ₃	11	14
Na ₂ B ₂ O ₄	9	11
NaOH	3	11
Na ₃ AlF ₆	69	50

An electrolysis was then performed for 1.5 hours at a temperature of 1,000±10°C. Current was 30 amps which corresponds to a cathode current density of 45 amp/dm² and the cell potential was 2.4 to 3.0 volts. At the end of the electrolysis, the cathode was removed and the deposit was treated as in Example 1. After removing adhering electrolyte, there was recovered a cathode deposit weighing 5.0 grams.

The cathode deposit was dark purplish in color and consisted of hexagonal prismatic crystals. An X-ray

diffraction analysis was performed in an attempt to identify the product. The analysis revealed a weak pattern corresponding to carbon, a medium-pattern corresponding to Ti_2O_3 and a strong pattern which remained unidentified. Titanium diboride was absent.

EXAMPLE 4

The electrolytic cell of Example 1 was used in an attempt to electrolytically synthesize and deposit zirconium diboride using zircon concentrates as a source compound for zirconium. An electrolyte charge was prepared having the following composition:

TABLE 7

Component	Weight-percent	Mile-percent
ZrSiO ₄	9	8
Na ₂ CO ₃	9	14
Na ₂ B ₂ O ₄	9	12
NaOH	3	12
Na ₃ AlF ₆	70	54

An electrolysis was then performed for 2 hours at a temperature of $1,025^{\circ}\pm 10^{\circ}\text{C}$. Current was 50 amps which corresponds to a cathode current density of 75 amp/dm² and the cell potential was 2.9 to 3.4 volts. At the end of the electrolysis the cathode was removed from the bath, excess electrolyte shaken off and the crystal mass clinging to the cathode was scraped off. Three successive leachings in 10 percent sulfuric acid were required to remove the adhering electrolyte. Weight of recovered zirconium diboride was 8.0 grams for a yield of 0.08 gram/amp-hr.

Spectrographic analysis of the zirconium diboride product showed (weight percent): aluminum, 0.50; calcium, 0.30; iron, 0.30 and silicon, 0.25. Vacuum fusion and combustion analysis indicated the carbon content to be 1.9 percent and the oxygen content to be 0.79 percent. The cooled, spent electrolyte was examined and found to contain two phases. The upper phase was dense white containing many bubbles and the lower phase was a dense white-black mixture having a vitreous luster.

Preparation of zirconium diboride from zircon was judged to be unsuccessful. The product was impure compared to that obtained from zirconium oxide, the yield per ampere-hour was extremely low, the quantity of electrolyte adhering to the cathode deposit was very large and the electrolyte formed two phases. Formation of two liquid phases in the electrolyte essentially precludes the further use of the electrolyte for additional deposition cycles.

These examples are illustrative of the results obtained by practicing our invention. Many minor modifications in apparatus and procedure will be apparent to those familiar with the art. For example, polarity of the cell may be reversed making the crucible function as the cathode. Suspended graphite or refractory metal

rods can be suspended in the electrolyte bath to function as both anode and cathode. Multiple anodes or cathodes may be utilized instead of the single electrode system described.

We claim:

1. An electrolytic method for the preparation of zirconium and hafnium diborides and mixtures of the two which comprises:

preparing an electrolyte bath by fusing a mixture of ingredients; those ingredients comprising a major portion of cryolite and minor portions of a sodium alkali, a sodium borate and a metal compound chosen from the group consisting of zirconium and hafnium oxides, sodium salts of zirconium and hafnium oxyacids and mixtures thereof, the atomic ratio of zirconium and hafnium to boron being within the range 1:4 to 5:2;

passing a direct current through the electrolyte between an anode and a cathode while maintaining the electrolyte in a molten state, and

recovering as a cathode deposit a crystalline metal diboride, said diboride being zirconium diboride, hafnium diboride, or mixtures thereof.

2. The process of claim 1 wherein the electrolyte temperature is maintained within the range of 900° to $1,100^{\circ}\text{C}$ during electrolysis.

3. The process of claim 2 wherein the sodium alkali is chosen from the group consisting of sodium hydroxide, sodium carbonate and mixtures thereof.

4. The process of claim 3 wherein the sodium borate is chosen from the group consisting of borax, sodium metaborate, sodium orthoborate, sodium diborate, sodium tetraborate, sodium pentaborate and mixtures thereof.

5. The process of claim 4 wherein the electrolyte temperature is maintained within the range of 950° to $1,050^{\circ}\text{C}$ during electrolysis and wherein the cathode current density is maintained within the range of 10 to 225 amps per square decimeter during electrolysis.

6. The process of claim 5 wherein the electrolyte bath contains from about 50 to 60 mole percent cryolite.

7. The process of claim 6 wherein the metal compound is zirconia and wherein the metal diboride is zirconium diboride.

8. The process of claim 6 wherein the metal compound is hafnia and wherein the metal diboride is hafnium diboride.

9. The process of claim 1 wherein the metal diboride containing cathode deposit is leached with an aqueous solvent to remove adhering electrolyte therefrom.

10. The process of claim 9 wherein the aqueous solvent is a dilute acid.

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