

[54] **ELECTROLYTIC PREPARATION OF
TITANIUM AND ZIRCONIUM DIBORIDES
USING A MOLTEN, SODIUM SALT
ELECTROLYTE**

[75] **Inventors:** John M. Gomes, Reno, Nev.; Kenji
Uchida, Ibaragi, Japan

[73] **Assignee:** The United States of America as
represented by the Secretary of the
Interior, Washington, D.C.

[22] **Filed:** Dec. 18, 1972

[21] **Appl. No.:** 316,217

[52] **U.S. Cl.** 204/71

[51] **Int. Cl.** C22d 3/20

[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

Primary Examiner—Howard S. Williams

Assistant Examiner—D. R. Valentine

Attorney—Frank A. Lukasik et al.

[57] **ABSTRACT**

Titanium and zirconium diborides are electrolytically synthesized using a molten sodium salt electrolyte containing cryolite, a sodium alkali, a sodium borate, a sodium halide and a source compound to supply the titanium or zirconium. Substantial refining occurs during the synthesis allowing the use of rutile concentrates as a source of titanium and zircon concentrates as a source of zirconium. The synthesis may be accomplished in a cell open to the atmosphere to produce substantially pure titanium and zirconium diborides.

10 Claims, No Drawings

ELECTROLYTIC PREPARATION OF TITANIUM AND ZIRCONIUM DIBORIDES USING A MOLTEN, SODIUM SALT ELECTROLYTE

BACKGROUND OF THE INVENTION

Titanium and zirconium diborides are characterized by extreme hardness, high melting point, excellent electrical conductivity, general chemical inertness and a high corrosion resistance to molten glasses, salts, and metals. The compounds find use as abrasives, electrodes for high temperature or corrosive-environment electrolytic processes and many other applications wherein their distinctive properties can be used to advantage.

These borides have been prepared in a variety of ways including: (1) direct union of the elements; (2) reduction of the oxide with boron; (3) carbothermic reduction of metal oxide-boron oxide mixtures with free carbon or metal carbides; (4) reduction of metal oxide-boron oxide mixtures using hydrogen or metallic reducing agents such as aluminum, zinc or alkali metals, and (5) molten salt electrolysis. Known electrolytic methods are exemplified by the Sindeband patent (U. S. Pat. No. 2,741,587) and by the Stern et al patent (U. S. Pat. No. 2,936,268). Sindeband used an electrolyte containing B_2O_3 , CaO , CaF_2 and either TiO_2 or 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. Stern et al prepared titanium diboride in a cell having perforated anode compartments containing a mixture of boron carbide and titanium carbide. Their electrolyte contained KCl , $NaCl$, K_2TiF_6 and KBF_4 . An argon atmosphere was maintained over the cell which was operated at about 720° to $730^\circ C$. They also prepared zirconium diboride in an analogous fashion.

In our copending, commonly assigned patent application, Ser. No. 316,216, we disclose and claim the preparation of zirconium and hafnium diborides from their oxides in an electrolytic bath containing a major portion of cryolite. Using that system, we found that titanium diboride could not be prepared from its oxide. We further found that zircon (zirconium silicate) which we attempted to use as a source of zirconium, was also inoperative in that process.

SUMMARY OF THE INVENTION

We have found that high quality titanium diboride may be prepared from rutile concentrates using an electrolytic salt bath of special composition. The bath comprises a mixture of cryolite, a sodium alkali, a sodium borate, sodium halide and either rutile concentrates or zircon concentrates. A protective atmosphere is unnecessary. Electrolysis temperatures may vary from about $900^\circ C$ to about $1100^\circ C$ 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 titanium and zirconium diborides.

It is a further object of our invention to utilize sodium compounds as an electrolyte to synthesize metal borides without the necessity of a protective atmosphere.

Another object of our invention is to utilize mineral concentrates as source materials for titanium and zirconium in the production of their respective diborides.

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 titanium or zirconium compound to form a metal boride deposit on the cathode. The metal boride (either titanium diboride, zirconium 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. Separation of the metal boride crystals from adhering electrolyte is accomplished by leaching in a dilute acid, such as cold 5 percent sulfuric acid. A second leaching in a dilute base, such as 2 percent sodium hydroxide, increases the purity of the product.

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 mixture of cryolite (Na_3AlF_6), a sodium borate, a sodium alkali, a sodium halide and a source of either titanium or zirconium or both. 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 sodium chloride or mixtures of sodium chloride and sodium fluoride. A mixture of sodium chloride and fluoride is strongly preferred when using zircon as a source of zirconium since the fluoride tends to enhance the solubility of silicates. When rutile is used as the source of titanium, it is preferred to use sodium chloride alone since, in this case, little if any benefit is derived from use of the more expensive sodium fluoride.

We strongly prefer to utilize rutile concentrates as a source material for titanium in our process and zircon concentrates as a source material for zirconium. We have found that substantial refining occurs during the synthesis and metal diborides produced from the mineral concentrates are of high quality and purity by commercial standards. Economic savings thus are considerable. For example, a pound of contained zirconium in technical grade ZrO_2 costs about three times as much as a pound of contained zirconium in the form of zircon concentrates. A similar situation exists between rutile concentrates and titanium dioxide. Zirconium and titanium oxides or the sodium salt of either zirconium or titanium oxyacids, such as sodium zirconate or sodium titanate, may also be utilized in our process. Use of more highly pure source materials to supply zirconium or titanium generally results in a somewhat more pure metal boride product. This increase in product purity is small and usually does not offset the large increased expense of the more highly pure source compounds.

The electrolyte composition may vary over a fairly wide range so long as all of the listed constituents are present and so long as the ratio of titanium or zirconium or their sum, to boron, is maintained within certain limits. Generally speaking, the atomic ratio of boron to either titanium or zirconium must be maintained at a value substantially greater than 1 to achieve satisfactory results. We prefer to maintain the ratio of B:Ti above about 12 and most preferably in the range

of about 12 to 20. When this ratio drops much below 12, there results the codeposition of titanium oxides, particularly Ti_2O_3 . This codeposition is observable at a ratio of 8 and becomes quite pronounced at a ratio of 4. It is possible to operate at ratios above 20 but yield and purity suffers. When synthesizing zirconium diboride, we prefer to use a B:Zr atomic ratio greater than 6 and most preferably in the range of 6 to 12. This preferred range is based primarily upon purity and yield of the desired diboride product. Here also, it is possible to extend these ranges but at a sacrifice of purity and yield. Exemplary electrolyte compositions for production of titanium and zirconium diborides are set out in the following table. It is emphasized that these compositions are not fixed and may vary considerably so long as boron to metal atomic ratios are maintained in the proper range and so long as all constituents are present. All values are in weight percent.

Table 1

Constituent	To produce:	
	TiB ₂	ZrB ₂
TiO ₂	3	—
ZrSiO ₄	—	12
Na ₂ CO ₃	4	—
NaOH	—	4
Na ₃ AlF ₆	20	40
Na ₂ B ₄ O ₇	28	20
NaCl	45	20
NaF	—	4

These exemplary compositions represent an atomic ratio of boron to titanium of about 15 and a boron to zirconium ratio of about 6.

Operating temperatures may range from about 900° to 1,100°C but the highest purity products were obtained in the temperature range of 1,000° to 1,050°C. This last range is preferred. Current density can vary widely; from about 10 to about 250 amp/dm². Cell potential is dependent to some extent upon cell geometry but typically ranges from 3 to 6 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 a dilute acid. Cold, sulfuric acid of about 5 percent concentration is appropriate for use as a leaching agent. A second leach using a dilute base, such as 2 percent sodium hydroxide, further increases product purity. 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 7 inches in height while the cathode was 1 inch in diameter. The cathode was placed centrally within the anode crucible leaving a 1-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.

An electrolyte charge for the preparation of titanium diboride and having the composition set out in Table 1 was fused within the crucible. The source material for titanium was industrial grade TiO₂. This titanium dioxide was relatively pure, showing by spectrographic analysis about 100 ppm silicon and 1,200 ppm zirconium. Spectrographic analysis of the cryolite used in the electrolyte showed the major impurities to be calcium, iron, magnesium and silicon.

An electrolysis was then performed for one hour at a temperature of 1,000°C. Current was 100 amps corresponding to a cathode current density of 150 amp/dm² and the cell potential was 5.0 volts. 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. Titanium diboride was separated from adhering electrolyte by a first leach in cold 5 percent sulfuric acid followed by a second leach in 2 percent sodium hydroxide solution. Weight of the recovered titanium diboride was 23 grams for a yield of 0.2 g/amp-hr.

Spectrographic analysis of the titanium diboride product showed less than 100 ppm aluminum; 2,000 ppm calcium, 300 ppm copper; 7,000 ppm iron; 30 ppm manganese and 100 ppm silicon. Vacuum fusion and combustion analyses showed a carbon content of 7,000 ppm; oxygen 1,800 ppm; and nitrogen 10 ppm.

EXAMPLE 2

The electrolytic cell of Example 1 was used to synthesize and deposit titanium diboride using rutile concentrates as a source of titanium. The electrolyte contained 4 percent rutile, 5 percent sodium carbonate, 19 percent cryolite, 36 percent sodium chloride and 36 percent sodium tetraborate. All percentages listed are by weight. Spectrographic analysis of the rutile showed 100 ppm aluminum; 3,000 ppm chromium; 4,000 ppm iron; 200 ppm magnesium; 300 ppm manganese; 1,000 ppm niobium; 1,000 ppm tin; 2,000 ppm silicon; 2,000

ppm vanadium; 100 ppm tungsten; 1,000 ppm zirconium and smaller amounts of copper and nickel.

A series of three electrolytic cycles were performed using the same electrolyte but adding additional rutile prior to the second and third deposition cycles. Temperature was held constant over the three cycles at $1025^{\circ} \pm 10^{\circ}\text{C}$ but cathode current density was varied from 165 to 240 amp/dm². Average yield of titanium diboride was 0.23 g/amp-hr over the 3 cycles.

Spectrographic analysis of the product fractions showed about 300 ppm aluminum; 2,400 to 3,400 ppm chromium; 700 to 1,400 ppm iron; 700 to 1,200 ppm niobium; 100 to 150 ppm tin and 2,000 to 4,000 ppm vanadium. Other metals, including tungsten, calcium, magnesium, manganese and silicon were either not detected or were present in concentrations of less than 100 ppm. Vacuum fusion and combustion analyses showed a carbon content ranging from 4,900 to 8,200 ppm and an oxygen content ranging from 8,600 to 9,400 ppm.

EXAMPLE 3

The electrolytic cell of Example 1 was used to synthesize and deposit zirconium diboride using zircon concentrates as a source of zirconium. The electrolyte contained 12 percent zircon, 4 percent sodium hydroxide, 40 percent cryolite, 20 percent sodium tetraborate, 20 percent sodium chloride and 4 percent sodium fluoride. All percentages are by weight. Neutron activation analysis of the zircon disclosed 40.5 percent zirconium, 29.3 percent oxygen and 15.5 percent silicon. Spectrographic analysis of the zircon showed 10,000 ppm aluminum; 300 ppm chromium; 700 ppm iron; 600 ppm magnesium and 200 ppm manganese.

A series of three electrolytic cycles were performed using the same electrolyte but adding additional zircon prior to the second and third deposition cycles. Temperature was held constant over the three cycles at $1025^{\circ} \pm 10^{\circ}\text{C}$ but cathode current density was varied from 120 to 240 amp/dm². Average yield of zirconium diboride was 0.23 g/amp-hr over the three cycles but highest yield was obtained at intermediate levels of current density.

Spectrographic analysis of the zirconium diboride product, after treatment in heavy liquids to remove free carbon, showed 100 to 200 ppm aluminum; 50 to 400 ppm chromium; 1,500 to 3,500 ppm iron; 50 to 500 ppm manganese, 100 to 200 ppm silicon, and less than about 20 ppm magnesium. Vacuum fusion and combustion analyses showed the carbon content to range from 4,700 to 5,800 ppm and the oxygen content to vary from 110 to 2,400 ppm.

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. Graphite, metal, or conductive refractory rods can be suspended within the electrolyte to func-

tion 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 titanium and zirconium diborides and mixtures of the two which comprises:

preparing an electrolyte bath by fusing a mixture of ingredients; those ingredients comprising cryolite, a sodium alkali, sodium borate, a sodium halide and a metal compound chosen from the group consisting of titanium and zirconium oxides, rutile concentrates, zircon concentrates, the sodium salts of titanium and zirconium oxyacids and mixtures thereof, the atomic ratio of boron to titanium being greater than about 12 and the ratio of boron to zirconium being greater than about 6;

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 titanium diboride, zirconium diboride, or mixtures thereof.

2. The process of claim 1 wherein the electrolyte temperature is maintained within the range of 900° to 1100° during electrolysis.

3. The process of claim 2 wherein the sodium alkali is chosen from the group consisting of sodium hydroxide, sodium carbonate, sodium oxide 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 sodium halide is chosen from the group consisting of sodium chloride, sodium fluoride and mixtures of the two.

6. The process of claim 5 wherein the electrolyte temperature is maintained within the range of $1,000^{\circ}$ to $1,050^{\circ}\text{C}$ during electrolysis and wherein the cathode current density is maintained within the range of 10 to 250 amp/dm² during the electrolysis.

7. The process of claim 6 wherein the metal compound comprises rutile concentrates and wherein the cathode deposit comprises titanium diboride.

8. The process of claim 7 wherein the atomic ratio of boron to titanium in the electrolyte is in the range of 12 to 20 and wherein the sodium halide is sodium chloride.

9. The process of claim 6 wherein the metal compound comprises zircon concentrates and wherein the cathode deposit comprises zirconium diboride.

10. The process of claim 9 wherein the atomic ratio of boron to zirconium in the electrolyte is in the range of 6 to 12 and wherein the sodium halide is a mixture of sodium chloride and sodium fluoride.

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