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Electrolytic Preparation of Titanium and Zirconium Diborides From Their Oxides and Mineral Concentrates

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8053

Electrolytic Preparation of Titanium and Zirconium Diborides From Their Oxides and Mineral Concentrates

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ELECTROLYTIC PREPARATION OF TITANIUM AND ZIRCONIUM DIBORIDES FROM THEIR OXIDES AND MINERAL CONCENTRATES

by

J. M. Gomes,[1] K. Uchida,[2] and M. M. Wong[3]

ABSTRACT

The Bureau of Mines investigated electrolytic techniques for preparing diborides of the group IV B metals. TiB_2, ZrB_2, and HfB_2 were electrodeposited from their respective oxides dissolved in borate-chloride-cryolite electrolytes. Titanium diboride was also electrodeposited from rutile (TiO_2) dissolved in a $Na_2B_4O_7$-Na_2CO_3-Na_3AlF_6-NaCl electrolyte at 1,050° C; 14 kW-hr were required to produce 1 pound of TiB_2. Major impurities in the TiB_2 produced in a 10-deposition cycle experiment, in weight-percent, were Al, 0.2; Cr, 0.3; Fe, 0.1; V, 0.3; C, 1.4; and O, 1.0. Zirconium diboride was electrodeposited from zircon ($ZrSiO_4$) dissolved in a $Na_2B_4O_7$-NaOH-Na_3AlF_6-NaCl-NaF electrolyte at 1,050° C. The ZrB_2 produced in a 10-deposition cycle experiment contained the following impurities in weight-percent; Fe, 0.1; Si, 0.5; C, 0.3; and O, 0.6. Energy required to produce 1 pound of ZrB_2 was 9.3 kW-hr.

INTRODUCTION

In previous investigations, the Federal Bureau of Mines had studied electrowinning metals and carbides directly from mineral concentrates. Tungsten was electrowon from scheelite, tungsten and tungsten carbide from wolframite, and dimolybdenum carbide (Mo_2C) from molybdenite (5-6, 11).[4] Investigations on the electrolytic preparation of binary compounds from oxide feed materials include tungsten carbide (WC) from sodium tungstate, MoS_2 and WS_2 from their trioxides, and metal phosphides from their oxides and silicates (3, 7-8, 10). This investigation was made to recover titanium and zirconium as diborides from their oxides and mineral concentrates. Because of the chemical resistance and electrical conductance of the titanium and zirconium diborides, the electrolytic products may be of value in industrial applications.

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[3]Supervisory chemical engineer.

[4]Underlined numbers in parentheses refer to items listed at the end of this report.

Early investigations to electrodeposit TiB_2 and ZrB_2 are reviewed by Powell and Schwartzkopf (14, 16). Andrieux reported preparing TiB_2 and Zr_3B_4 from their oxides in $CaO-CaF_2-B_2O_3$, $MgO-MgF_2-B_2O_3$, and $Li_2O-LiF-B_2O_3$ electrolytes (1). Investigation of these electrolytes by the Bureau resulted in poor yields and impure deposits. Anthony and Welch electrodeposited ZrB_2 from ZrO_2 and B_2O_3 dissolved in an equimolar mixture of K_2ZrF_6 and KBF_4 at 600° C (2). Mellors and Senderoff reported the electrocoating of ZrB_2 using a ZrB_2 anode in an alkali-fluoride electrolyte containing ZrF_4 and B_2O_3 (13). Schlain reported electrodeposition of TiB_2 coatings using a titanium anode in a titanate-borate electrolyte (15). Cotter investigated preparation of ZrB_2 directly from zircon by reduction with carbon and B_2O_3 as well as with carbon and boron carbide (4). Commercially, titanium and zirconium diborides are prepared by carbothermic reduction of metal oxide-boron mixtures.

MATERIALS, EQUIPMENT, AND PROCEDURES

The analysis of the technical-grade oxide and mineral concentrate feed materials is shown in table 1. Technical-grade reagents were used in the electrolytes.

TABLE 1. - Analysis of feed materials

Material	Major MO_2, pct	Spectrographic analysis, pct													
		Al	Ca	Cb	Cr	Fe	Hf	Mg	Mn	Pb	Si	Sn	Ti	V	Zr
TiO_2..	[1]99.0	0.05	0.4	0.005	0.02	0.003	([2])	0.3	0.003	([2])	0.01	([2])	([3])	0.01	0.02
ZrO_2..	[1]99.0	.05	.35	.01	.05	.015	0.2	.003	.003	([2])	.1	([2])	0.12	([2])	([3])
HfO_2..	[1]95.0	.01	.35	([2])	.02	1.0	([3])	.06	.05	0.5	.03	([2])	.1	[1].05	2.0
Rutile	[1]97.0	.10	.5	.1	.3	.4	([2])	.02	.03	.003	.2	0.1	([3])	.2	.1
Zircon sand.	54.5	1.0	.05	([2])	.03	.07	.6	.04	.02	.01	[4]18	([2])	.6	([2])	([3])

[1]Calculated by difference.
[2]Not detected.
[3]Major.
[4]By chemical analysis.

The electrolytic cell was a 3-inch-ID by 7-inch-deep graphite crucible that served as anode and electrolyte container. The cathode was a 1-inch-diameter graphite or metal rod centrally positioned in the cell. The cell was contained in a silicon carbide cylindrical chamber and capped with a transite lid. The unit was externally heated in a Globar[5] furnace and operated in the atmosphere. During electrolysis, the chamber contained mostly carbon oxide anode gases.

Operating conditions were temperatures of 900° to 1,100° C, initial cathode current densities of 30 to 200 amp/dm^2, and cell potentials of 1.0 to 5.0 volts. The procedure for a multicycle experiment consisted of the following steps: (1) Melting the electrolyte and holding it at the operating temperature; (2) installing the cathode and conducting electrolysis; (3) removing the cathode and deposit from the cell after electrolyzing for a predetermined period; (4) scraping the deposit off the hot cathode; (5) adding feed material and makeup electrolyte to replace dragout; and (6) reinstalling the cathode in the bath and resuming electrolysis after allowing 15 minutes for the cell to stabilize at operating temperature. This procedure was used for experiments of 2 to 10 deposition cycles.

The diboride deposits were first leached in a cold 5-wt-pct sulfuric acid solution to remove the dragout electrolyte and then in a hot 2-wt-pct NaOH solution. The

[5]Reference to specific names is made for identification only and does not imply endorsement by the Bureau of Mines.

leached products were water-washed, dried on a steam bath, and weighed and sampled. Free carbon was removed by treating the diborides in tetrabromoethane ($C_2H_2Br_4$) with a specific gravity of 2.96. The free carbon was collected in the float fraction and the diborides in the sink fraction. Selected electrolytic products were sieved and given other cleaning and separation treatments as noted. The product and electrolyte samples were analyzed by instrumental and wet chemical methods as specified.

EXPERIMENTAL RESULTS

Deposition of TiB_2, ZrB_2, and HfB_2 From Their Oxides

Titanium, zirconium, and hafnium diborides were electrodeposited from their respective oxides using the conditions shown in table 2. Two deposition cycles of 1 hour each were performed. An addition of metal oxide and makeup electrolyte was made prior to the second deposition cycle. Cryolite (Na_3AlF_6)-containing electrolytes were selected for study because the solubilities of TiO_2 and ZrO_2 in cryolite at 1,000° C were reported to be 5 and 14 wt-pct, respectively (9, 12). The addition of 72 mole-pct NaCl in the TiO_2-containing electrolyte was necessary to prevent the codeposition of Ti_2O_3 and a mixture of TiC and TiO.

Hexagonal diborides were deposited in granular clusters of interlocking plates, and were dark metallic gray in color. The TiB_2 and ZrB_2 had air pyctometer densities of 4.38 and 6.02, respectively, compared with the theoretical densities of 4.52 and 6.09. The VHN's (50-gram load)[6] of the TiB_2 and ZrB_2 crystals were 2,980 and 1,770, respectively, compared with values reported in the literature of 3,400 for TiB_2 and 2,200 for ZrB_2 (16).

[6]Vickers hardness number was calculated from value obtained using a Reichert Microhardness Tester.

TABLE 2. - Deposition of TiB_2, ZrB_2, and HfB_2 from their oxides at 1,000° C

Deposition cycle	Volts	Amp	Cathode current density, amp/dm²	Deposit weight, grams	Analysis of products, wt-pct[1]										
					Chemical		Interstitial		Spectrographic						
					Metal	Boron	C	O	Al	Ca	Fe	Hf	Si	Ti	Zr
ELECTROLYTE COMPOSITION, MOLE-PCT: 3 TiO_2, 3 Na_2CO_3, 9 Na_3AlF_6, 72 NaCl, 13 $Na_2B_4O_7$															
First.....	5.0	100	150	23	68.2	30.7	0.70	0.18	0.2	0.01	0.4	ND	0.02	(2)	ND
Second....	5.0	100	150	21	-	-	.69	.72	.2	.01	.4	ND	.02	(2)	ND
ELECTROLYTE COMPOSITION, MOLE-PCT: 7 ZrO_2, 12 $Na_2B_4O_7$, 20 NaOH, 60 Na_3AlF_6															
First.....	4.9	100	60	30	80.0	19.3	0.33	0.36	0.01	0.02	0.04	0.01	.4	0.4	(2)
Second....	4.8	100	60	28	-	-	.40	.51	.02	.08	.02	.02	.03	.03	(2)
ELECTROLYTE COMPOSITION, MOLE-PCT: 12 HfO_2, 10 $Na_2B_4O_7$, 22 NaOH, 56 Na_3AlF_6															
First.....	2.0	20	30	16	86.5	10.4	0.11	0.14	0.01	0.03	0.4	(2)	0.01	0.6	2.2
Second....	2.1	20	30	19	-	-	.09	.23	.01	.03	.4	(2)	.01	.1	.7

ND Not detected.

[1]Product treated in $C_2H_2Br_4$ to remove free carbon.

[2]Major.

Deposition of TiB_2 From Rutile

The electrodeposition of TiB_2 from rutile concentrates (97 wt-pct TiO_2) was investigated with the same electrolyte system used for TiO_2 described earlier. The titanium-boron ratio in the electrolyte was investigated to study its effect on the codeposition of Ti_2O_3. Results showed that TiB_2 was the only major product obtained with electrolytes initially having a titanium-boron atomic ratio of 1:20 to 1:12. Increasing the ratio to 1:8 or 1:4 resulted in deposits containing major quantities of Ti_2O_3. Besides graphite cathodes, tungsten, iron, and titanium cathodes were investigated as a means of decreasing carbon contamination in the deposits. Carbon content of 0.2 to 2.0 wt-pct was obtained using the titanium cathode. Tungsten and iron cathodes were not satisfactory because the deposits were contaminated with excessive quantities of the respective metals. Studies of cathode current density showed that operating at current densities in excess of 200 amp/dm^2 resulted in decreased yield and increased carbon contamination of the diboride product. The yield decreased from 0.14 g/amp-hr at 200 amp/dm^2 to 0.10 g/amp-hr at 300 amp/dm^2, and the carbon content of the deposits increased to 5.0 wt-pct at current densities in excess of 300 amp/dm^2.

The effects of prolonged electrodeposition from the same electrolyte on purity, yield, and recovery of product were studied in 10 cycles. The original electrolyte contained, in mole-pct: rutile (TiO_2), 4.5; Na_2CO_3, 4.5; Na_3AlF_6, 9; $Na_2B_4O_7$, 18; and NaCl, 64. Operating conditions were ten 1-hour deposition cycles at 140 amperes, cell potential of 4.2 to 5.0 volts, cathode current density of 200 amp/dm^2, and temperature of 1,025° C. An electrolyte addition of 30 grams rutile, 20 grams Na_3AlF_6, 20 grams $Na_2B_4O_7$, 20 grams B_2O_3, and 40 grams NaCl was made prior to each succeeding deposition. The anode was the 3-inch-ID graphite crucible, and the cathode was a 1.0-inch-diameter titanium rod. Operating results and a material balance are shown in table 3 and the analysis of the TiB_2 products in table 4. An electron microscope photograph of the TiB_2 crystals (fig. 1) shows the interlocking platelike structure of the individual clusters.

TABLE 3. - Results of repetitive deposition of TiB_2 from rutile

Results:	
TiB_2 product before heavy liquid separation, grams	216
TiB_2 product after heavy liquid separation, do	205
Titanium in feed recovered as TiB_2, pct	78.0
Deposition, grams TiB_2/amp-hr	0.147
Energy required, kW-hr/lb TiB_2	14.0
Dragout electrolyte, grams	756
Ratio, dragout/TiB_2	3.7
Materials balance:	
Input, grams:	
Rutile	310
Electrolyte (original)	1,073
Electrolyte (makeup)	900
Total	2,283
Output, grams:	
TiB_2 product	216
Dragout electrolyte	756
Oxygen in anode gases[1]	249
Final electrolyte	980
Total	2,201
Materials accounted for, pct	.96
Loss (dusting, fuming, moisture), pct	.4

[1]Calculated on the basis of decomposition of TiO_2 and B_2O_3 to form TiB_2 product.

TABLE 4. - Analysis of TiB_2 products electrodeposited from rutile

Cycle	Deposit weight, grams	Interstitial analysis, pct		Spectrographic analysis, pct								
		C	O	Al	Cb	Cr	Fe	Mg	Mn	Si	V	Zr
1...	21	2.3	1.0	0.1	0.07	0.2	0.1	0.006	0.01	0.01	0.3	ND
2...	23	3.4	1.3	.1	.07	.2	.1	.006	.02	.02	.2	0.04
3[1]..	24	-	-	-	-	-	-	-	-	-	-	-
4...	18	3.0	1.0	.1	.07	.2	.1	.01	.02	.02	.2	.02
5[1]..	23	-	-	-	-	-	-	-	-	-	-	-
6...	19	5.0	1.1	.1	.07	.2	.1	.005	.02	.02	.3	.02
7[1]..	17	-	-	-	-	-	-	-	-	-	-	-
8...	21	6.7	1.2	.1	.07	.2	.1	.005	.01	.01	.3	.005
9[1]..	25	-	-	-	-	-	-	-	-	-	-	-
10...	25	6.8	1.0	.1	.07	.2	.1	.005	.01	.01	.2	.02

ND Not detected.

[1]Product not analyzed.

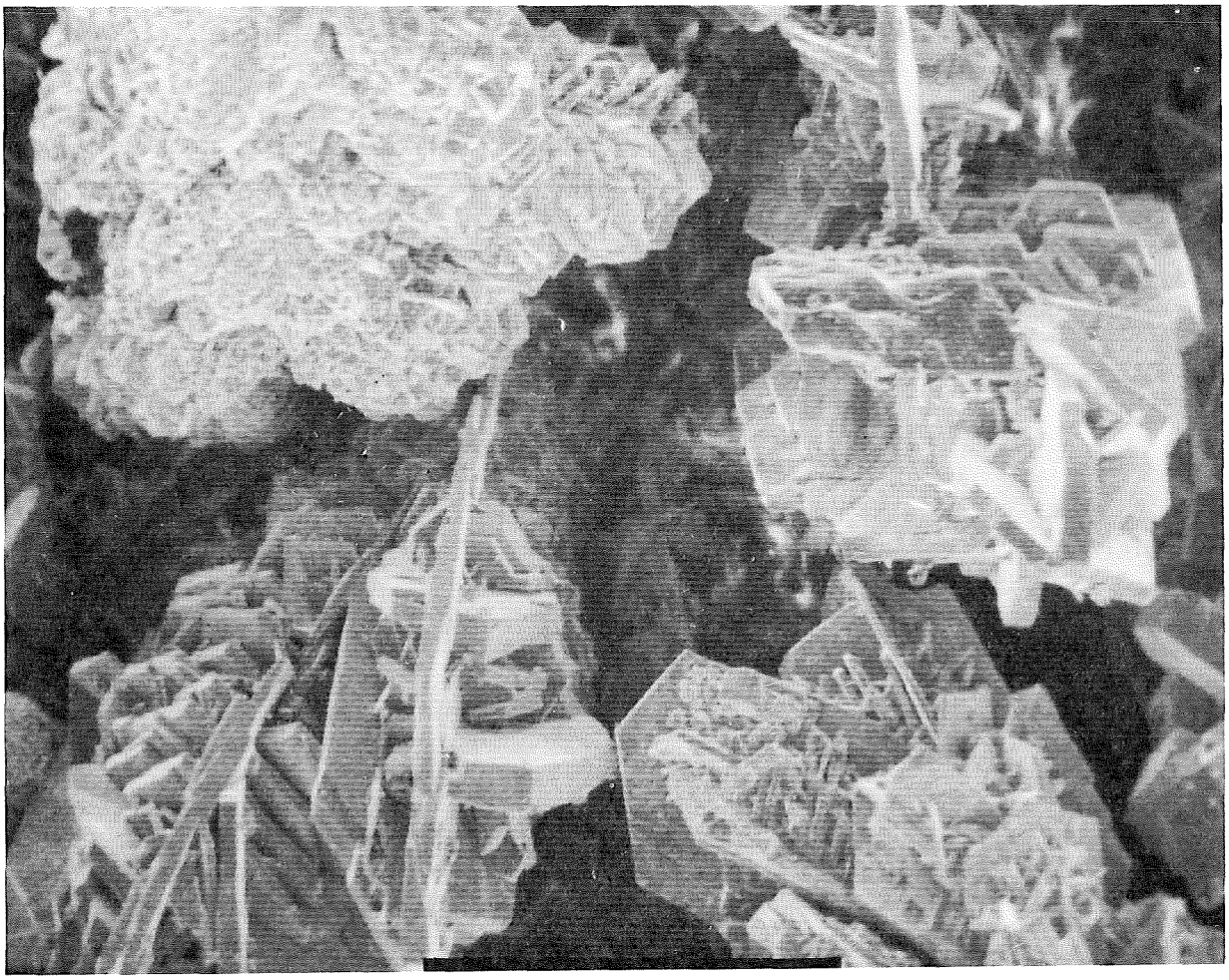

FIGURE 1. - TiB_2 crystals electrodeposited from rutile. Bar scale = 100 micrometers.

Seventy-eight percent of the titanium in the rutile was recovered as TiB_2, and 14 kW-hr were required to produce 1 pound of TiB_2. Analysis of the acid leach products showed that the free carbon content increased with successive deposition cycles.

The sieve size distribution of a composite of the 10 deposits is shown in table 5. The carbon and oxygen contents of the sized fractions after treatment in tetrabromoethane are shown also. TiB_2 was the only titanium compound detected by X-ray diffraction in the products. The approximate 1-wt-pct oxygen content indicates the products could contain approximately 3.0 wt-pct Ti_2O_3. Spectrographic analysis showed the composite to contain the following metallic impurities, in weight-percent: Al, 0.2; Cb, 0.07; Cr, 0.3; Fe, 0.1; Mg, 0.004; Mn, 0.01; Si, 0.01; V, 0.3; and Zr, 0.02.

TABLE 5. - Size distribution and interstitial analysis of TiB_2 composite[1]

Sieve size, mesh	Distribution, wt-pct	Interstitial analysis, wt-pct	
		C	O
+35.....	13.0	1.4	0.9
-35+65.....	15.4	1.2	1.1
-65+100....	24.0	1.3	.9
-100+200...	27.5	1.8	1.0
-200+325...	14.8	1.5	.9
-325.....	5.3	1.5	1.3

[1]Treated in tetrabromoethane to remove free carbon.

Deposition of ZrB_2 From Zircon

The major difference between electrowinning ZrB_2 from zircon ($ZrSiO_4$) and zirconia (ZrO_2) is the effect of 1 mole of SiO_2 per mole of ZrO_2 in zircon. The buildup of SiO_2 in the electrolyte with successive additions of zircon results in an increase in viscosity of the electrolyte and the contamination of products by silicon. The $Na_2B_4O_7$-Na_3AlF_6-NaOH electrolyte system used for electrowinning ZrB_2 from ZrO_2 was investigated using zircon feed. The yield per ampere-hour of electrolysis was less than 0.1 gram, and the products contained 1.0 to 3.0 wt-pct silicon and over 2.0 wt-pct carbon. Adding at least 30 mole-pct of NaCl to the electrolyte resulted in increasing the yield to 0.3 g/amp-hr. The addition of 10 mole-pct NaF to the electrolyte resulted in decreasing the silicon content of the ZrB_2 product to less than 0.1 wt-pct and decreasing viscosity of the electrolyte. An electrolyte containing $Na_2B_4O_7$, Na_3AlF_6, NaOH, NaCl, and NaF was used for the subsequent experiments.

Investigations were made to determine the effect of varying the zirconium-boron ratio in the electrolyte on the oxygen and carbon content of the diborides. Products containing 2.1 to 2.4 wt-pct carbon and 0.3 to 0.5 wt-pct oxygen were obtained from electrolytes having a zirconium-boron atomic ratio of 1:10 and 1:6. Increasing the ratio to 1:4 resulted in decreasing the yield from 0.35 to 0.10 g/amp-hr. Decreasing the ratio to 1:12 and 1:24 resulted in increasing the carbon content to 3.0 and 5.5 wt-pct, respectively. Investigations of using metal cathodes and varying current densities showed results similar to those obtained in the corresponding studies for TiB_2 deposition from rutile. Carbon contents as low as 0.3 wt-pct were obtained with the metal cathodes. Zirconium was the best because both the iron and tungsten cathodes contaminated the products with the respective metals in excess of 1.0 wt-pct. Increasing the current density over 200 amp/dm^2 resulted in increasing the carbon content of the deposits from about 1.0 wt-pct to 3.0 wt-pct at 300 amp/dm^2.

The effect of repetitive deposition of ZrB_2 from the same electrolyte was studied in a 10-cycle experiment. The anode was a 3-inch-ID graphite crucible, and the cathode was a 1-inch-diameter zirconium rod. The 1,227-gram electrolyte originally contained the following constituents, in mole-percent: zircon, 7; $Na_2B_4O_7$, 11; NaOH, 11; Na_3AlF_6, 22; NaF, 13; and NaCl, 36. The operating temperature was 1,050° C, the current was 120 amperes, the cathode current density was 180 amp/dm^2, the cell potential ranged from 3.8 to

5.0 volts, and each deposition cycle was conducted for 1 hour. An addition of 60 grams zircon, 10 grams B_2O_3, 15 grams $Na_2B_4O_7$, 15 grams Na_3AlF_6, and 20 grams NaCl was made prior to each succeeding deposition cycle except the sixth.

The formation of a viscous liquid phase on the bottom of the cell was observed as electrodeposition cycles continued. The buildup of this phase decreased the diboride recovery by lessening adherence of the ZrB_2 to cathode. After the fifth deposition cycle, the two phases in the electrolyte were decanted into separate vessels. The viscous lower phase weighed 137 grams and the fluid upper phase 815 grams. The analyses of the upper and lower phases after the 5th and 10th cycles are shown in table 6. After discarding the viscous lower phase, an addition of 60 grams $ZrSiO_4$ and 352 grams of new electrolyte constituents was made to the upper phase prior to the sixth cycle, adjusting the electrolyte to the original weight of 1,227 grams. The quantity of dragout electrolyte during the 6th through 10th cycles was 633 grams compared with 448 during the first five cycles. This increase in dragout during the last five cycles probably accounted for the presence of only 55 grams of lower phase after the 10th cycle.

TABLE 6. - Analysis of electrolyte phases

Electrolyte	Weight, grams	Neutron activation analysis, wt-pct							Chemical analysis, wt-pct B
		Al	Cl	F	Na	O	SiO_2	ZrO_2	
Upper phase:									
After 5th cycle.....	815	4	14	25	39	10	6	3	3
After 10th cycle.....	806	4	15	23	33	13	6	3	3
Lower phase:									
After 5th cycle.....	137	5	6	15	20	20	26	20	5
After 10th cycle.....	55	6	6	12	18	20	38	20	5

The operating results and material balance for the 10-cycle experiment are shown in table 7. Over 73 percent of the zirconium in the feed was recovered as ZrB_2, 9.3 kW-hr were consumed per pound of ZrB_2, and the ratio of dragout electrolyte to ZrB_2 was 4.3:1. The energy consumption and dragout ratio were higher compared with the ZrB_2 deposition from ZrO_2, in which the energy consumption was 2.9 kW-hr/lb of ZrB_2 and the dragout-ZrB_2 product ratio was 2.8:1.

TABLE 7. - Results of repetitive deposition of ZrB_2 from zircon

Results:	
ZrB_2 product before heavy liquid separation, grams	258
ZrB_2 product after heavy liquid separation, do	253
Zirconium in feed recovered as ZrB_2, pct	73.5
Deposition, grams ZrB_2/amp-hr	0.214
Energy required, kW-hr/lb ZrB_2	9.3
Dragout electrolyte, grams	1,081
Ratio, dragout/ZrB_2	4.2
Materials balance:	
Input, grams:	
Zircon	684
Electrolyte (original)	1,093
Electrolyte (makeup)	832
Total	2,609
Output, grams:	
ZrB_2 product	258
Dragout electrolyte	1,081
Viscous lower phase after 5th cycle	137
Viscous lower phase after 10th cycle	55
Final electrolyte, fluid phase	879
Oxygen in carbon oxide gases from anode[1]	114
Total	2,524
Material accounted for, pct	97
Loss (dusting, fuming, moisture), pct	3.0

[1]Calculated on the basis of decomposition of ZrO_2 and B_2O_3 to form ZrB_2 product.

The ZrB_2 products obtained from electrolysis of zircon are shown in figure 2 and the analysis is given in table 8. The electron microscope photograph shows an interlocking plate structure similar to the TiB_2 particles, with the plates being stubbier and the clusters more compact. The products were impure and contained carbon, silicon, and aluminum as the major impurities. To remove free carbon and low-density particles, the products were composited and sieved, and the sized fractions were retreated in the tetrabromoethane and releached in 5 wt-pct sulfuric acid. The analyses of the reprocessed products are shown in table 9. The carbon, aluminum, calcium, and silicon in the products were noticeably decreased.

The hafnium content of the deposits increased as electrolysis progressed. The 1st through 6th deposits contained 0.02 wt-pct hafnium and the 8th and 10th deposits contained 0.05 and 0.1 wt-pct hafnium, respectively. The zirconium-hafnium ratio in the early deposits was about 4,000:1; in the original ore, it was 67:1. This zirconium-hafnium ratio of 4,000:1 indicates a significant selective deposition of zirconium from hafnium.

TABLE 8. - Analysis of ZrB_2 products electrodeposited from zircon

Cycle	Product weight, grams	Interstitial analysis, pct		Spectrographic analysis, pct						
		C	O	Al	Ca	Fe	Hf	Mn	Si	Ti
1	21	0.4	0.49	0.05	0.05	0.4	0.02	0.06	0.3	0.8
2	25	1.8	.87	.02	.05	.07	.02	.006	.7	.3
3[1]	19	1.2	-	-	-	-	-	-	-	-
4	27	2.4	.70	.3	.05	.07	.02	.004	1.0	.1
5[1]	17	1.6	-	-	-	-	-	-	-	-
6	27	.8	.88	.3	.06	.4	.02	.03	.7	.3
7[1]	24	.7	-	-	-	-	-	-	-	-
8	21	1.0	.47	.3	.08	.06	.05	.006	1.0	.1
9[1]	12	1.4	-	-	-	-	-	-	-	-
10	17	1.8	.97	.5	.08	.04	.1	.004	1.0	.1
5[2]	26	1.2	1.8	.3	.10	.07	.2	.01	2.0	.5
10[2]	22	3.4	4.7	.2	.4	.15	.1	.02	>3.0	1.0

[1]Products not analyzed.
[2]Product in cell.

TABLE 9. - Size distribution and analysis of reprocessed zirconium diboride products

Size fraction, mesh	Distribution, wt-pct	Interstitial analysis, wt-pct		Spectrographic analysis, wt-pct						
		C	O	Al	Ca	Fe	Hf	Mn	Si	Ti
+35	3.8	0.32	0.29	0.04	<0.05	0.1	0.02	0.01	0.5	0.2
-35+60	11.3	.19	.28	.04	<.05	.1	.02	.01	.5	.1
-60+100	27.0	.27	.60	.05	<.05	.1	.03	.01	.5	.1
-100+200	27.2	.27	.72	.05	<.05	.07	.03	.01	.5	.1
-200+325	16.7	.37	.83	.05	<.05	.07	.2	.01	.5	.1
-325	14.0	.29	1.10	.2	<.05	.07	.2	.01	.5	.1

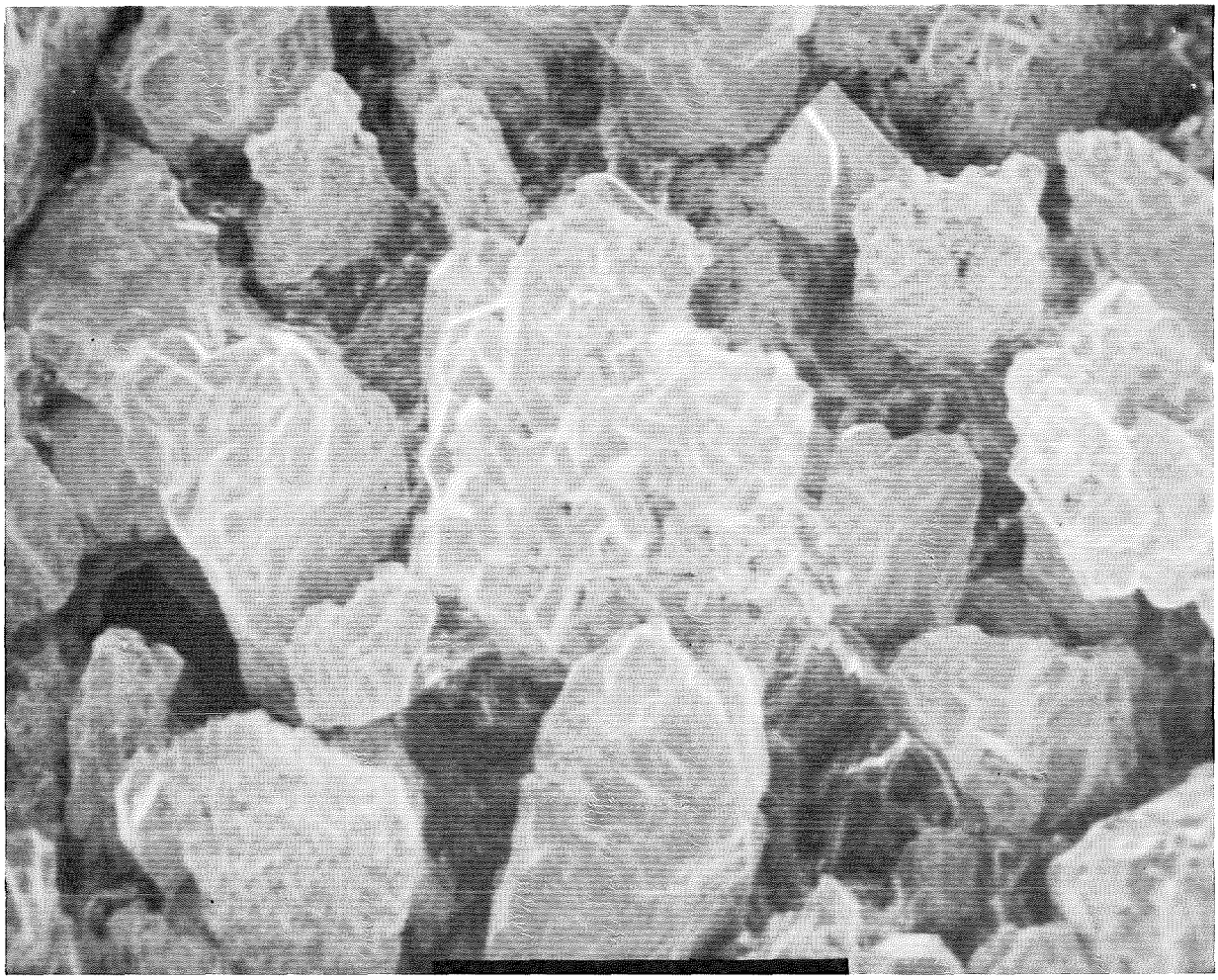

FIGURE 2. - ZrB_2 crystals electrodeposited from zircon. Bar scale = 100 micrometers.

CONCLUSIONS

Titanium, zirconium, and hafnium diborides of approximately 98-percent purity can be electrodeposited from their respective oxides dissolved in borate-cryolite-carbonate electrolytes at 1,050° C. Titanium diboride can be similarly electrodeposited from rutile concentrate. The recovery of titanium as diboride was 78 percent, and 14 kW-hr were required to produce 1 pound of TiB_2. Similarly zirconium diboride can be electrodeposited from zircon sand. The buildup of silica in the electrolyte, however, resulted in the formation of a viscous phase which hindered the cell operation and decreased the recovery of ZrB_2. Over 73 percent of the zirconium fed to the cell was recovered as ZrB_2, and 9.3 kW-hr were required to produce 1 pound of ZrB_2.

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