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[54] ELECTROLYTIC PREPARATION OF LANTHANIDE AND ACTINIDE HEXABORIDES USING A MOLTEN, CRYOLITE-BASE ELECTROLYTE

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[58] **Field of Search** 204/1.5, 86

[56] **References Cited**

OTHER PUBLICATIONS

Cueilleron et al., Chem. Abs., Vol. 67, 74972y, (1967).

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[57] **ABSTRACT**

Lanthanide and actinide hexaborides are electrolytically synthesized using a molten salt electrolyte containing a major portion of cryolite and minor portions of an alkali borate and a source compound to supply the lanthanide or actinide metal. Minor amounts of an alkali hydroxide or carbonate added to the electrolyte tend to improve product recovery and purity. The synthesis may be accomplished in a cell open to the atmosphere to produce highly pure lanthanide and actinide hexaborides.

12 Claims, No Drawings

ELECTROLYTIC PREPARATION OF LANTHANIDE AND ACTINIDE HEXABORIDES USING A MOLTEN, CRYOLITE-BASE ELECTROLYTE

BACKGROUND OF THE INVENTION

Lanthanide and actinide hexaborides generally display high melting points, extreme hardness, and interesting electrical properties. Lanthanum hexaboride, for example, is reported to possess the highest electronic emissivity of any known substance. As a group, these hexaborides are useful as base constituents for high temperature materials and in applications utilizing their thermionic emission properties as in thermionic power generation.

Known methods of preparing lanthanide and actinide hexaborides include the following: (1) Direct combination of the metal with boron; (2) carbon reduction of mixtures of metal oxide and boron anhydrides; (3) reduction of metal oxide with boron carbide; (4) reduction of metal oxide with boron; and (5) fused salt electrolysis. Of these techniques, reduction of metal oxides with boron carbide is known to be practiced commercially but the process requires highly pure boron carbide and metal oxides. The product is often contaminated with boron and metal carbides.

Preparation of lanthanide and actinide hexaborides using known techniques are reported to codeposit boron as a by-product (Samsonov et al., *Boron and Its Compounds and Alloys*, Publishing House of the Academy of Sciences Ukrainian SSR Kiev, 1960, pp. 447–497). This results in borides containing less than stoichiometric quantities of metal. Codeposited boron cannot be removed by conventional solvent leaching. Many investigators such as Andrieux (L. Ann. Chim. Phys., 12, 42, 1929) preferred electrolytes containing a lanthanide oxide, alkaline earth oxide, alkaline earth fluoride, and boric oxide. A shortcoming of these electrolyte systems was the difficulty in obtaining a single-phase product.

SUMMARY OF THE INVENTION

We prepared lanthanide and actinide hexaborides by passing a dc current through a molten electrolyte composed of alkali aluminum fluoride and alkali borate. Dissolved in the bath is an oxide, fluoride or chloride of a lanthanide or actinide metal. Minor amounts of an alkali hydroxide or carbonate added to the bath tends to improve recovery and product purity. Coarse, crystalline hexaboride product is deposited on the cathode. A protective atmosphere is unneccessary. Electrolysis temperatures may vary from about 900° to about 1,100°C and the process may be carried out in a batch, semicontinuous or continuous fashion.

Hence, it is an object of our invention to produce lanthanide and actinide hexaborides.

It is a specific object of our invention to synthesize lanthanide and actinide hexaboride using a cryolite-borate electrolyte 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 lanthanide or actinide compound to form a metal boride deposit on the cathode. The metal boride, which may be a lanthanide hexaboride, an actinide hexaboride, or mixtures of lanthanide and/or actinide hexaborides, 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 may be accomplished by leaching in hot, diluted sulfuric acid.

Constituents of the electrolyte preferably are of technical grade and, of course, are in the anhydrous form. Use of technical grade salt 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 an alkali aluminum fluoride such as cryolite together with minor amounts of an alkali borate and a lanthanide or actinide compound. Additions of minor amounts of alkali hydroxides or carbonates to the electrolyte tend to increase product recovery and purity. The alkali borate preferably is a sodium borate and may be a metaborate, orthoborate, diborate, tetraborate, pentaborate, or mixtures thereof. Naturally occurring borate compounds such as borax may also be used. The lanthanide or actinide compound may be in the form of a chloride, fluoride, oxide, or mixtures thereof. Since a substantial degree of refining occurs during the electrodeposition, impure lanthanide or actinide oxide concentrates may advantageously be used in our process.

Composition of the electrolyte may vary over a fairly wide range. The following table illustrates a range of electrolyte compositions which have been found to be suited for use in our process:

Table 1

Component	Range, Mole Pct.
Lanthanide or Actinide Compound	2 – 20
Alkali Aluminum Fluoride	50 – 85
Alkali Borate	10 – 25
Alkali Hydroxide or Carbonate	0 – 30

Operating temperatures may range from about 900° to 1,100°C, but best results are obtained in the temperature range of 950° to 1,050°C. This last range is preferred. Current density can vary widely; from about 15 to 150 amps per square decimeter. Depending somewhat upon cell geometry, the cell potential is generally in the range of 2.0 to 5.0 volts.

The electrolytic cell may conveniently comprise a conductive crucible serving the double function of container and anode. A conductive 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 when potassium is absent from the electrolyte composition. Potassium ions intercalate with graphite resulting in physical damage or even failure of graphitic cell components. For this reason, as well as for reasons of economy, we prefer sodium as the alkali metal component of our electrolyte. 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 acids. Hot sulfuric acid diluted about 1:1 with water is a preferred leaching agent. After leaching, free carbon can be removed by water elutriation or by heavy media separation. The process may be operated on a semicontinuous 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 serve to 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 served as a cathode. The anode crucible was three inches in internal diameter and seven inches in height, while the cathode was 1 inch in diameter. The cathode was centrally placed within the anode crucible leaving a 1-inch space between the cathode and sidewalls and 1½ inches from the bottom. Heating means for the cell consisted of an electric resistance furnace and the cell was open to the air.

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

Table 2

Component	Weight-Percent	Mole-Percent
CeO_2	7	8
$Na_2B_2O_4$	14	22
Na_3AlF_6	79	70

An electrolysis was then performed for three one-hour cycles at a temperature of 1,000° ± 10°C. The current was 60 amps at a cell potential of 4.4 volts. After each one-hour electrolysis cycle, the cathode was withdrawn and the deposit scraped off. The cathode was then replaced in the electrolyte and the electrolysis was continued. Cathode deposits were cooled and then leached in hot 1:1 sulfuric acid to remove the adhering electrolyte. Free carbon was removed from the hexaboride product by a float-sink separation in methylene iodide and the product was then washed in ether, dried, and sampled.

Total weight of the three cathode deposits was 250g of which 36 grams was cerium hexaboride and 214 grams was adhering electrolyte. Yield of cerium hexaboride was 0.2g/amp-hr. Vacuum fusion and combustion analysis of the product indicated the carbon content to be 0.72% and the oxygen content to be 0.52%. A spectrographic analysis of the CeB_6 product showed the following contaminating metals in weight percent: Al, 0.5; Ba, 0.05; Ca, 0.10; Cu, 0.01; Fe, 0.35; Mg 0.01; Mn, 0.14; Si, 0.20, and Ti, 0.01.

EXAMPLE 2

The elctrolytic cell of Example 1 was used to synthesize and deposit lanthanide hexaborides using an impure lanthanide oxide feed material of the following composition:

Table 3

Analysis of Impure Lanthanide Oxides Feed Material

	Weight-Percent		Weight-Percent
Ce	42.3	Ca	0.3
La	23.9	Ba	4.7
Nd	9.8	C	.6
Pr	3.2	Fe	.7
Sm	.6	S	.1
Gd	.1	Si	1.0
Y	.2	F	2.0

A 1000g electrolyte charge was prepared having the following composition:

Table 4

Component	Weight-Percent	Mole-Percent
Lanthanide Oxide (Ln_2O_3)	7	5
$Na_2B_2O_4$	15	20
Na_3AlF_6	70	60
Na_2CO_3	8	15

An electrolysis, consisting of three one-hour cycles, was then performed at a temperature of 1000° ± 10°C. During the first cycle, cell potential was 3.0 volts and current was 30 amperes; cell potential was 4.0 volts and current was 55 amperes during the second cycle, and cell potential was 5.0 volts and current was 100 amperes during the third hour. The procedure used for recovering the cathode deposits was the same as in Example 1. Results were as follows:

Table 5

		Product	Adhering Electrolyte
Weight of deposit cycle	1	6.0	25
	2	11.5	53
	3	17.1	118
Totals		34.6	296
Yield of LnB_6 per amp hr - 0.2			

Vacuum fusion and cumbustion analyses were performed on the products of cycles 2 and 3. The hexaboride product of cycle 2 showed 0.34% carbon and 0.61% oxygen, while the product of cycle 3 showed 0.48% carbon and 0.35% oxygen.

Spectrographic analyses of the products recovered from all three cycles were performed with the following results in weight percent:

Table 6

Cycle	Al	Ba	Ca	Fe	Mg	Mn	Si
1	0.20	0.50	0.50	0.30	0.005	0.06	0.10
2	.20	.50	.50	.30	.005	.04	.03

Table 6-continued

Cycle	Al	Ba	Ca	Fe	Mg	Mn	Si
3	.40	.50	.50	.20	.010	.03	.02

As may be seen from a comparison of the hexaboride product analyses with the analysis of the impure lanthanide oxide feed, a substantial degree of refining takes place during the electrolysis.

EXAMPLE 3

A number of other electrolysis runs were made with a variety of electrolyte compositions and feed materials. These experiments are set out in the following table:

Table 7

Exp.	Product	Electrolyte, Mole-Percent
1	CeB_6	$5CeO_2$, $5CeF_3$, $54Na_3AlF_6$, 12NaOH, $12Na_2CO_3$, $12Na_2B_2O_4$
2	"	$8CeCl_3$, $70Na_3AlF_6$, $22Na_2B_2O_4$
3	"	$8CeF_3$, $70Na_3AlF_6$, $22Na_2B_4O_7$
4	"	$8CeO_2$, $70Na_3AlF_6$, $22Na_2B_2O_4$
5	"	$9CeO_2$, $80KAlF_4$, $11Na_2B_2O_4$
6	"	$15CeF_3$, $65K_3AlF_6$, $20Na_2B_2O_4$
7	"	$9Ce_2O_3$, $78Li_3AlF_6$, $13Na_2B_2O_4$
8	LaB_6	$3La_2O_3$, $55Na_3AlF_6$, 14NaOH, $14Na_2CO_3$, $14Na_2B_2O_4$
9	LaB_6	$6LaF_3$, $70Na_3AlF_6$, 12NaOH, $12Na_2CO_3$, $12Na_2B_2O_4$
10	YB_6	$3Y_2O_3$, $6YF_3$, $55Na_3AlF_6$, 12NaOH, $12Na_2CO_3$, $12Na_2B_2O_4$
11	GdB_6	$6Gd_2O_3$, $70Na_3AlF_6$, $24Na_2B_2O_4$
12	DyB_6	$6Dy_2O_3$, $70Na_3AlF_6$, $24Na_2B_2O_4$
13	ThB_6	$2ThO_2$, $3ThF_4$, $56Na_3AlF_6$, 13NaOH, $13Na_2CO_3$, $13Na_2B_2O_4$
14	LnB_6	$5Ln_2O_3$, $60Na_3AlF_6$, $15Na_2CO_3$, $20Na_2B_2O_4$

In all cases, the hexaboride product was of high quality and the synthesis proceded without complication.

These examples are illustrative of the results obtained by practicing our invention. Many minor modifications of 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. Conductive rods of graphite may be suspended in the electrolyte to function as both anode and cathode and refractory metal rods may be used as cathodes. Multiple anodes or cathodes may be utilized instead of the single electrode system described.

We claim:

1. An electrolytic process for the preparation of lanthanide and actinide hexaborides and mixtures thereof which comprises:

preparing an electrolytic bath by fusing a mixture of ingredients; those ingredients comprising a major portion of an alkali aluminum fluoride and minor portions of an alkali borate and a metal compound selected from the group consisting of lanthanide and actinide oxides, chlorides, fluorides, and mixtures thereof;

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 hexaboride, said hexaboride being a lanthanide hexaboride, an actinide hexaboride, or mixtures thereof.

2. The process of claim **1** wherein the alkali aluminum floride is cryolite.

3. The process of claim **2** wherein the electrolyte temperature is maintained within the range of 900° to 1,100°C during electrolysis.

4. The process of claim **3** wherein the alkali borate is a sodium borate and wherein the electrolyte contains a minor amount of a compound selected from the group consisting of sodium hydroxide, sodium carbonate, and mixtures thereof.

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

6. The process of claim **5** wherein the electrolyte temperature is maintained within the range of 950° to 1050°C during electrolysis.

7. The process of claim **6** wherein the electrolyte contains from about 50 to 85 mole percent cryolite.

8. The process of claim **7** wherein the metal compound is a lanthanide compound.

9. The process of claim **8** wherein the lanthanide compound is an impure mixture of lanthanide oxides.

10. The process of claim **8** wherein the lanthanide compound is selected from the group consisting of lanthanum oxide, lanthanum fluoride, and lanthanum chloride.

11. The process of claim **1** wherein the metal hexaboride containing cathode deposit is leached with acid to remove adhering electrolyte therefrom.

12. The process of claim **11** wherein the acid is hot, sulfuric acid.

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