United States Patent Office 3,030,284 Patented Apr. 17, 1962

3,030,284

ELECTROLYTIC PRODUCTION OF ELEMENTAL BORON

David R. Stern, Fullerton, Calif., assignor to American Potash & Chemical Corporation, a corporation of Delaware

No Drawing. Filed Nov. 3, 1960, Ser. No. 66,902
4 Claims. (Cl. 204—60)

This is a continuation-in-part of application Serial No. 800,089, filed March 18, 1959, in turn a continuation-in-part of application Serial No. 574,605, filed March 29, 1956, both now abandoned.

This invention relates to the production of highly purified elemental boron by electrolysis, and more particularly to a process of the foregoing type which may be carried out more or less continuously for extended time periods.

Boron can be produced chemically by the reduction of boron oxide (B_2O_3) with magnesium and other reducing metals. However, the efficiency on the utilization of the reducing metal, the formation of borides, the high temperature of reaction, and the difficulty of controlling the reaction conditions has resulted in a process giving low yields and a costly product, which always contains appreciable quantities of suboxides.

Production of boron by electrolysis of various borates and other compounds has been proposed heretofore by various investigators. Some of these have involved the utilization of relatively expensive boron-containing materials, while others required temperatures on the order of 1100° to 1200° C. In any case, the resulting boron secured from the borates usually contained insoluble contaminates which lowered the quality of the product. However, instead of pointing the way to successful production of low-cost boron, these prior art processes have been misleading in that the investigators have stated that the occurrence of suboxides in the product has represented a barrier to the preparation of a high purity elemental boron.

It is therefore an object of this invention to provide for the production of a purified elemental boron by a process which enables high yields and which may be carried out commercially on a more or less continuous basis.

Other objects and advantages of this invention, if not specifically set forth, will become apparent during the course of the description which follows.

It has now been found that elemental boron of a relatively high purity may be formed by the direct electrolytic conversion of B_2O_3 to elemental boron by carbon reduction, the chemistry, in short or summary form, being represented by the following:

$$2B_2O_3+3C \rightarrow 4B+3CO_2$$

Generally, it has been found that the process for producing boron comprising electrolyzing a fused bath by passing a current between a consumable carbon anode and an inert cathode may be carried out in a continuous fashion where the bath consists essentially of a mixture of boric oxide, an alkali metal oxide of the formula M_2O, where M is an alkali metal, the boric oxide being present in a weight concentration of at least 3% in excess of the percentage of boric oxide in the borate of the alkali metal corresponding to the alkali metal oxide having said formula M_2O and up to a total B_2O_3 content in the bath of about 95%, the mole ratio of B_2O_3 to M_2O being greater than two to one by such excess of B_2O_3. It has also been found that the process may be carried out with unusual efficiency where a small amount of an alkali metal fluoride viscosity depressant is present in the bath.

More particularly, the process is carried out by electrolyzing a fused bath containing boric oxide as its major component and a small amount of an alkali metal oxide,

e.g., sodium, potassium or lithium oxide. The proportion of boric oxide to alkali metal oxide should be such that the boric oxide is present in a concentration from at least 3% in excess of that required for an alkali metal borate of the formula $M_2O \cdot 2B_2O_3$, where M is an alkali metal, up to a total B_2O_3 content of about 95%. Thus, the minimum boric oxide content for a given alkali metal borate will be about 3% greater than the value given in the table below, the excess B_2O_3 being derived by the addition thereof to the alkali metal borate. For example, with sodium borate, the B_2O_3 content of the bath is from about 73% to about 95% on the total weight of alkali metal oxide-boric oxide mixture. The upper limit with regard to boric oxide is set by the high temperature required to electrolyze the mixture and the difficulty in providing a suitable container for the mixture, which is extremely corrosive at such high temperatures. This upper limit is usually from about 90% to about 95% boric oxide. Operation at the higher concentrations is preferred since the higher the boric oxide content, the greater is the purity of the product. The following table gives the boric oxide content of each suitable alkali metal borate.

TABLE I

Alkali borate:	Percent B_2O_3 content of alkali borate
Lithium borate	82.3
Sodium borate	69.2
Potassium borate	59.6
Rubidium borate	42.8
Cesium borate	33.0

The chemistry of the process appears to be as follows:

$$6Na_2O \rightarrow 12Na+3O_2 \quad (1)$$
$$2B_2O_3+12Na \rightarrow 4B+6Na_2O \quad (2)$$
$$3C+3O_2 \rightarrow 3CO_2 \quad (3)$$
$$\overline{2B_2O_3+3C \rightarrow 4B+3CO_2} \quad \text{net result}$$

As noted above, it is desired to provide a certain amount of an alkali metal fluoride in the bath which serves as a viscosity depressant and increases current efficiency. At no time during the course of the process should the alkali metal fluoride represent in excess of 10 weight percent of the total contents of the reaction vessel.

As may be seen from the above, the alkali metal fluoride does not enter into the reaction. It is also possible and it is within the scope of the claims hereinafter to substitute for a portion or all of the alkali metal fluoride a small amount of an alkali metal fluoborate, e.g., a quantity such that the alkali metal fluoride which forms therefrom never exceeds 10% of the total weight of the bath; an excess of MF, where M is an alkali metal, over the 10% level will cause the reaction to terminate.

The process of the invention may be carried out continuously for long periods of time, the only shut-down required being when the cathode and/or anode need replacement. As will be noted in the examples set forth below, this permits continuous operations without necessity for discarding the Na_2O-containing bath. If it necessary only that additional B_2O_3 be added to maintain the level thereof above the minimum suggested earlier.

To practice the invention, a fused mixture of the desired proportions is charged into a crucible constructed of a suitable material, e.g., metal or graphite, which is protected by an external metal shell. The fused salts may be initially brought to operating temperature by external heating, induction heating, or resistance heating of the salts. An operating temperature of from 800° to 1000° C. is preferred, the lower limit, of course, being the melting point of the mixture. After the operating temperature is reached, the fused mixture is electrolyzed by the application of an electric current of suitable voltage

and current density between steel cathodes and graphite anodes. The passage of current is sufficient to maintain the electrolyte at the desired temperature. At the beginning of electrolysis, the voltage demand is low and steadily rises for a constant current input due to increased resistance resulting from the deposit obtained on the cathode.

A layer of protective ferro-boron can be applied separately or in situ to the steel cathode to increase its useful life. The cathode can be removed and replaced occasionally and thus a substantially continuous electrolytic process is possible. A particular advantage of this process is that the deposit on the cathode is easily removed; when the cathode is placed in water it completely disintegrates without any necessity for grinding. Since any electrolyte adhering to the deposit is water-soluble, no leaching problem is presented.

In the recovery of boron, I have not found evidence of any appreciable quantity of any boron suboxides; in the system sodium oxide-boric oxide, the major impurity in the product is sodium. When potassium oxide is used in place of sodium, there is a negligible metallic contamination. When boron of a particularly high purity is desired, the electrolyzed material containing sodium is readily treated to yield a high purity product. The purification is effected by heating the boron to an elevated temperature of about 1000° C. or higher to volatilize the sodium, preferably under reduced pressure, or at atmospheric pressure under an inert gas sweep. The recovered sodium is in elemental form. The apparatus employed for the boron purification can consist of a tantalum crucible inserted in a suitable housing to maintain an inert atmosphere and heated by induction heating.

Examples are set forth below for illustrative purposes, but they are not to be interpreted as imposing limitations on the scope of the invention other than as set forth in the appended claims.

EXAMPLES 1 AND 2

A cell body consisting of a cylindrically shaped cell, 24 inches in diameter by 26 inches high, made from mild steel sheet, was fitted with five graphite support pedestals which were placed within the cell and the cell filled with a layer of insulating powder up to the level of the support. A graphite crucible 20 inches O.D. by 17 inches I.D., 18 inches high and 15 inches deep, was set on the supports and centered within the cell body by a permanent seated guide pin. Additional insulating powder was tamped between the graphite crucible and shell wall to the level of the crucible top. Several layers of insulating bricks were then placed over the packing. The cell head was next bolted onto the body. The head consisted of a steel plate having eight 1⅞ inch diameter electrode ports. Four anode electrode ports were spaced equidistant on a 10 inch circle and four heating electrode ports equally spaced on a 14 inch circle. The original head was provided with a cathode removal chamber, 4 inches in diameter by 8 inches high of steel plate and welded to the cell head. The cooling chamber was provided with a ⅛-inch standard pipe nipple which served as an inert gas inlet, a flanged opening, and a matching chamber cover. During the second phase of the investigation a second cell cover was used without the cathode cooling chamber and in which both the anode and A.C. electrode ports were on the same hole circle (10 inch).

Neoprene gaskets were used between the cell head and shell and also at the closure of the cathode cooling top. The electrode ports were furnished with transite bushings which served as electrical insulators. The electrode connectors were fabricated of 2-inch copper rod stock with a ¾–10 N.C. copper stud on the electrode end and ½–13 N.C. stud at the wire end. The connectors were wrapped with ¼-inch copper tubing for water cooling. Quick-disconnect fittings were placed on the tube lines which in turn were connected to hard rubber hoses. This arrangement enabled a change of electrodes when required with a minimum of down time.

Several grades of graphite were used as crucible material. These included National Carbon Company grade CS graphite and also grade code 82 graphite. Insulating bricks fabricated from National Carbon Company grade 20 porous carbon were used in several of the earlier runs. The bricks oxidized quite readily; thereafter, magnesia insulating bricks grade K–20 were used and proved quite adequate. Insulation powders used in the cell consisted of Ajax-Electrothermic Corporation Norblack, carbon black, and also Permanente Periclase, a granular form of silimenite refractory.

Auxiliary equipment included a panel board with voltmeter and ammeters for both the A.C. and D.C. circuits, a Hoskins pyrometer with a chromel-alumel thermocouple for temperature measurements, and a Fischer and Porter purge meter to control the flow of argon gas.

D.C. power was supplied to the cell by a 70–420 ampere arc-welder. The A.C. heating electrodes were energized with power from a movable core transformer welder with a 420 ampere welding capacity. The transformer was limited to 70 amperes on the primary circuit and therefore limited the 100 percent duty loading to about 300 amperes. A second A.C. welder transformer was installed into the heating circuit during the latter stages of the study as a booster power supply. The booster transformer had a capacity of 7 kva.

The cathode consisted of a 13-inch piece of mild steel rod, 1¼-inch in diameter with a 9/32-inch hole drilled to 1 inch of the bottom, to accompany a thermocouple. The cathode rod was threaded or welded to a 27-inch length of thick-walled Shelby tubing, ¾-inch diameter by 9/32-inch inside diameter. The Shelby tube shank was threaded with ¾–10 N.C. at the top and connected to a copper bar. The negative D.C. lead, number 14 copper wire, was bolted to this bar. The cathode was immersed into the melt anywhere from 4–10 inches, depending upon the current density desired. For succeeding runs the cathodes were cleansed, buffed and reused. Wherever operating temperatures exceeded 950° C., a bright-silvery coating of ferro-boron formed on the rod. The coating did not appear to change the electrical characteristics of the cathode; therefore, no attempt was made to remove it from the rod prior to succeeding electrolyses.

Several grades of carbon were used as anode electrodes. These included the following:

National Carbon Company—Grade AGX graphite
National Carbon Company—Grade AGR graphite
National Carbon Company—Grade GA carbon

The usual anode electrodes measured 1¼-inch diameter by 24 inches long and were drilled and tapped on one end with ¾–10 N.C. female thread to accompany the water-cooled copper electrode connector.

The results of two different runs are presented in Tables II and III. Table II gives operating conditions while Table III gives the process raw material consumption on the basis of pounds of material required per pound of boron product.

As may be seen in Table II, this process may be carried out for an extremely long period of time and during that time substantial quantities of B_2O_3 are consumed with very little, if any, Na_2O being consumed. In the first run, as can be seen in Table II and at the middle of Table III which summarizes the information obtained regarding pounds of B_2O_3 and Na_2O and carbon consumed per pound of product obtained, it will be seen that 0.82 pound of Na_2O per pound of boron product or a total of 6.03 pounds of Na_2O were consumed. This Na_2O consumption was due to "drag-out," or the physical removal of Na_2O from the bath at the time that it was necessary to replace the carbon electrodes and to remove the boron product. In this run, work was done with a

relatively viscous system with a result that the Na_2O clung to the anodes and cathodes and a certain quantity thereof was removed when the electrodes were taken from the bath. Since the quantity of Na_2O present at the outset, however, was so small, as contrasted with the quantity of B_2O_3 present, it will be understood that the removal of a certain quantity of Na_2O in this fashion is to be expected where a viscous system is used.

addition of either alkali metal fluoride or alkali metal fluoborate. In this event, the melt is somewhat more viscous and the current efficiency reduced somewhat. In each of the examples which follow, the process was carried out briefly without the addition of a viscosity depressant. In each instance, an electrolyte of the indicated composition was heated to the indicated temperature and subjected to electrolysis under the voltage and current

TABLE II

Material Balance Data

Examples 1 and 2—Electrolytic System	Total Ampere-Hours	Days Continuous Operation	Product		Raw Materials (Lbs.)						
			Wt. (Lbs.)	Aver. Percent B	Fed			Consumed			
					B_2O_3	Na_2O	NaF	B_2O_3	Na_2O	NaF	Carbon
90 wt. percent B_2O_3—10 wt. percent Na_2O	44,947	58	7.35	87	195.04	24.45	--------	26.24	6.03	--------	13.16
90 wt. percent B_2O_3—5 wt. percent Na_2O—5 wt. percent NaF	212,663	78	26.1	88	534.81	24.42	74.77	131.79	--------	50.14	30.8

TABLE III

Process Raw Materials Consumption

System	Lbs./Lb. of Product			D.C. Energy—Kw.—Hours Per Pound	NaF
	B_2O_3	Na_2O	Carbon		
Theoretical	2.80	0	0.72	3.96	0
90 Wt. percent B_2O_3—10 Wt. percent Na_2O	3.57	0.82	1.79	251.0	0
90 Wt. percent B_2O_3—5 Wt. percent Na_2O—5 Wt. percent NaF	3.05	0	1.18	165.0	1.15

Where a small amount of a fluoborate is present at the outset, such fluoborate reacts with the alkali metal liberated at the cathode whereby to cause the reduction of the alkali metal according to the formula

$$KBF_4+3Na \rightarrow B+KF+3NaF$$

Where only a small amount of the alkali metal fluoborate is present at the outset, its presence may be disregarded once the reaction has proceeded even for a short period of time, since all of it is reduced and no longer affects the reaction. However, the addition thereto of further alkali metal fluoborates so as to maintain its relative level in the melt would result in the continued liberation of the fluoride ion which in turn unites with sodium or potassium to form an alkali metal fluoride which cannot be electrolyzed and which builds up so as to require cessation of the process after only a limited period of time.

This procedure was carried out in the following example, wherein sodium fluoborate was used instead of the sodium fluoride, the sodium fluoborate being converted to sodium fluoride immediately after current flow commenced. The alkali metal fluoborate should preferably be consistent with the alkali metal oxide employed, e.g., sodium fluoborate should be used with sodium oxide, and potassium fluoborate should be used with potassium oxide.

EXAMPLE 3

[Electrolyte 73% B_2O_3–17% Na_2O–10% $NaBF_4$]

Product:

Percent boron	75.9
Percent HNO_3 insol	0.2
Percent Fe	2.4
Percent Na	9.2
Diff	10.9

Electrolysis data:

Current efficiency	91.9%.
Volts	20.5.
Current density	8.14 amps./sq. in.
Temperature	832° C.

It is also possible to carry out the process without the set forth. The product recovered on the cathode had the indicated composition. It will be observed that each of the operations was conducted at a temperature close to and preferably above the boiling point of metallic sodium, 880° C., for higher purity product. For this reason, some release of sodium from the cathode deposit may occur in the electrolytic cell. A massive liberation of sodium is not evident in the cell, however, and any vaporization of sodium occurs smoothly, very little being trapped within the cathode deposit so that there is a minimuum of sodium contamination of the boron.

EXAMPLE 4

[Electrolyte 90% B_2O_3–10% K_2O]

Product:

Percent boron	91.5
Percent HNO_3 insol	1.1
Percent Fe	2.1
Percent K	0.09
Percent O_2	5.2
	99.99

Electrolysis data:

Current efficiency	45.2%.
Volts	31.7.
Current density	7.02 amps./sq. in.
Temperature	1015° C.

EXAMPLE 5

[Electrolyte 90% B_2O_3–10% LiO_2]

Product:

Percent boron	87.3
Percent HNO_3 insol	2.9
Percent Fe	3.4
Percent Li	1.3
Percent O_2	5.1
	100.0

Electrolysis data:

Current efficiency	45.6%.
Volts	9.6.
Current density	7.05 amps./sq. in.
Temperature	916° C.

Obviously, many and various modifications may be made without departing from the spirit and scope of this invention, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A continuous process for producing boron comprising electrolyzing a fused bath by passing a current between a consumable carbon anode and an inert cathode, said bath consisting essentially of a mixture of an alkali metal fluoride representing no more than 10% by weight of the total weight of the said bath, boric oxide and an alkali metal oxide of the formula M_2O, where M is an alkali metal, the boric oxide being present in a weight concentration at least 3% in excess of the percentage of boric oxide in the borate of the alkali metal corresponding to the alkali metal oxide having said formula M_2O and up to a total B_2O_3 content in the bath of about 95%, the mole ratio of B_2O_3 to M_2O being greater than 2 to 1 by such excess of B_2O_3, said alkali metal borate being of the formula $M_2B_4O_7$.

2. The process of claim 1 wherein the alkali metal oxide is Na_2O and wheerin the alkali metal fluoride is NaF.

3. A continuous process for producing boron comprising electrolyzing a fused bath by passing a current between a consumable carbon anode and an inert cathode, said bath consisting essentially of a mixture of boric oxide and an alkali metal oxide of the formula M_2O, where M is an alkali metal, the boric oxide being present in a weight concentration at least 3% in excess of the percentage of boric oxide in the borate of the alkali metal corresponding to the alkali metal oxide having said formula M_2O and up to a total B_2O_3 content in the bath of about 95%, the mole ratio of B_2O_3 to M_2O being greater than 2 to 1 by such excess of B_2O_3, said alkali metal borate being of the formula $M_2B_4O_7$.

4. A process as in claim 3 wherein the alkali metal oxide is sodium oxide and elemental boron is deposited on the cathode and contains sodium as an impurity, and purifying the boron by heating to an elevated temperature to volatilize the sodium.

References Cited in the file of this patent

UNITED STATES PATENTS

2,848,396 Murphy et al. ---------- Aug. 19, 1958

FOREIGN PATENTS

162,655 Great Britain ---------- Apr. 22, 1920