

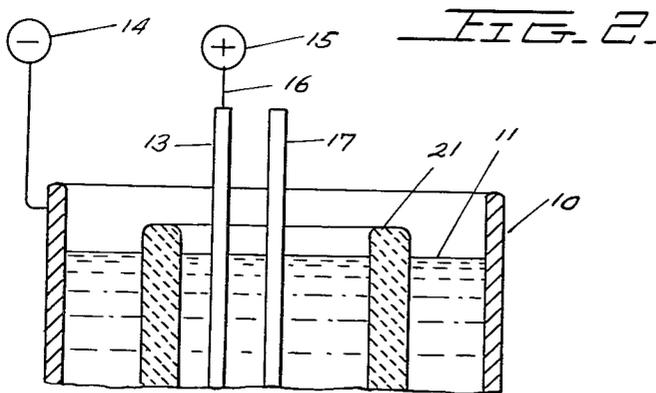
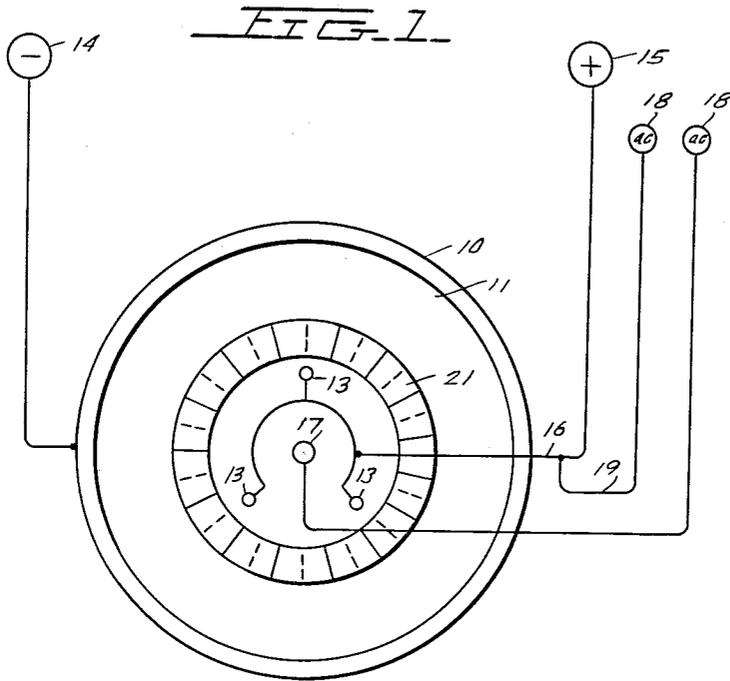
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PRODUCTION OF METAL BORIDES BY FUSED SALT ELECTROLYSIS

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PRODUCTION OF METAL BORIDES BY FUSED SALT ELECTROLYSIS

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This invention relates to the production of metal borides by fused salt electrolysis, and equipment for effectively carrying on such electrolysis.

In the past critical difficulties have been encountered in producing metal borides by fused salt electrolysis in the manner suggested in the literature. When producing metal borides by fused salt electrolysis, the bath must contain a sufficient amount of the metal compound, such as the metal oxide, in order to form on a practically efficient basis, the desired metal boride. However, this has heretofore been practically impossible because various obscure reactions occurring within the fused salt bath during the progress of the electrolysis results in the production of defective borides, limit the yield, and render the process inefficient.

According to one phase of the invention, the critical difficulties resulting in the production of defective borides are overcome by carrying on the fused salt electrolysis in such manner as to suppress and substantially prevent the presence of an excess of the metal compound—such as the metal oxide constituent of the bath—in the form of finely dispersed particles while maintaining at all times dissolved within the fused salt bath the proper concentration of the metal compound required for efficiently carrying on the boride forming electrolysis process.

In accordance with the invention, the metal compound, such as the metal oxide, is maintained within the bath at the proper concentration required for efficient production of the borides, while preventing the presence of finely dispersed oxide particles within the bath by placing in the bath the metal oxide in the form of relatively large solid pieces or structures, so that it may dissolve in the fused salt bath as it is being used up as the electrolysis proceeds.

According to another phase of the invention, the efficiency with which the desired metal borides are produced, is greatly increased by providing out of the metal compound—such as the metal oxide which must be present as an essential ingredient of the fused salt bath—a porous barrier separating the anode region of the bath from the cathode region within which the desired metal boride formed by electrolysis is deposited.

In accordance with the invention, a porous solid body or bodies of the metal compound, such as metal oxide, are placed therein in the form of a beaker-like structure, or in the form of porous solid lumps or blocks—arrayed or otherwise positioned within the bath so as to provide a porous barrier separating the anode region from the cathode region of the bath, which usually has the form of an electrically conducting vessel of refractory material such as carbon, holding therein the fused molten salt bath.

The foregoing and other objects of the invention will be best understood from the following description of exemplifications of the invention, reference being had to the accompanying drawings wherein:

Fig. 1 is a diagrammatic top view of one form of

equipment for producing metal borides by fused salt electrolysis in accordance with the invention; and

Fig. 2 is a vertical cross-section of the equipment of Fig. 1.

The present invention is applicable to the production by fused salt electrolysis of various metal borides including the borides of titanium, tantalum, columbium, zirconium, hafnium, vanadium and chromium. By way of example, there will now be described the process of producing zirconium boride by fused salt electrolysis in accordance with the invention, a generally similar process being suitable and highly effective for producing the other metal borides.

A fused salt bath which has been found very effective in practice for producing refractory metal borides in accordance with the invention is one containing calcium oxide CaO, calcium fluoride CaF₂, the oxide of the desired metal, and boron oxide B₂O₃. Instead of calcium oxide, other alkali metal or alkaline earth metal oxides or mixtures thereof may be used. Instead of calcium fluoride, the other alkali or alkaline earth halides, such as alkali or alkaline earth fluorides or chlorides, or mixtures thereof, may be used. Instead of the metal oxide, other metal compounds which will be held dissolved in the fused salt bath may be used, such as potassium zirconium fluoride instead of zirconium oxide. Instead of boric anhydride B₂O₃, a borate may be used, making the addition of calcium oxide totally, or partly unnecessary.

When producing zirconium boride or other refractory borides by fused salt electrolysis, difficulties are encountered due to disturbing side reactions which result in the production of defective borides, limit the yield, and lower the overall efficiency, unless the process is carried on under certain critical conditions.

The formation of the desired metal borides by electrolysis in the fused salt bath consumes the metal oxide ingredients of the bath. In order to maintain the efficiency of the electrolysis process, provision must be made for continuous replacement of the metal oxides consumed in formation of the metal borides. However, it was found that if any excess undissolved metal oxide is present in the form of finely dispersed particles within the fused salt bath, the oxide particles serve as nuclei for the deposition of the metal boride. Metal boride particles formed around oxide nuclei are of inferior quality and will not yield cemented metal boride bodies of the desired physical characteristics.

According to the invention, the fused salt bath is maintained substantially free of fine metal oxide particles and the required excess of metal oxide for the bath is provided as follows: The metal oxide concentration of the fused salt bath is kept down to amounts which are readily dissolved in the fused salt bath, and the required excess is supplied by placing in the bath solid oxide bodies, such as lumps or pieces which cannot be kept in suspension within the fused salt bath, and cannot serve as nuclei for the formation of metal boride within the bath.

This arrangement avoids the critical difficulties encountered with prior art processes. In addition, it greatly increases the efficiency of the electrolysis process, and results in the formation of metal boride particles of greater purity, and which are substantially free from particles having metal oxide nuclei. In practice the electrolysis is carried on as long as the rate of yield is maintained at the desired rate, and is stopped after the rate of yield starts decreasing.

According to another phase of the invention disclosed herein, other critical difficulties are overcome by keeping the anode and cathode products produced by the electrolysis separated from each other within the fused salt bath. To this end, the metal oxide of the desired boride, such as zirconium oxide, is prepared in the form of a

porous crucible structure or enclosure surrounding the anode region within the fused salt bath and keeping it separated from the cathode region wherein the metal boride produced by electrolysis accumulates. The barrier enclosure may be conveniently formed by piling up shaped blocks resembling building blocks, to form a porous barrier extending across the fused salt bath, and separating the anode region from the cathode region, or regions thereof.

A crucible 10, of graphite for instance, serves as a vessel holding therein a fused salt bath 11, the graphite vessel 10 serving also as the cathode. The graphite vessel 10 is embedded in suitable heat insulating material and mounted within a suitable support structure, not shown, in accordance with the accepted practice in fused salt bath electrolysis. Within the interior of the cathode vessel 10 are shown immersed three anodes 13, which may have the form of graphite rods. Electric current for the electrolysis is supplied by a direct current source having positive and negative terminals indicated by (-) sign 14, and (+) sign 15, respectively. The negative direct current terminal 14 is shown connected to the graphite crucible 10, serving as the cathode. The three graphite anodes 13 are connected through a common lead 16 to the positive direct current terminal 15.

In operation, the fused salt bath 11 is heated by passing an alternating electric current between an additional electrode 17 connected to the terminal 18 of a source of heating current and one of the other electrodes, such as the anode electrodes 13 which are shown connected to a lead 19 to the other terminal 18 of the heating current, lead 19 forming a branch of the anode lead 16 connected to the positive direct current terminal 15. The heating circuit electrode 17 may likewise be a graphite electrode, and an alternating current source is shown used as a source of heating current connected to the two heating current terminals 18 which are labelled by the legend (ac).

By way of example, the following fused salt bath composition was found to give a good yield when used for producing zirconium boride:

	Mol
B ₂ O ₃ -----	1
CaO -----	1
CaF ₂ -----	1
ZrO ₂ -----	1/6

Good results are obtained with the several ingredients supplied, either in the technically pure grade or in the commercially pure grade. In originally preparing the bath, the properly proportioned ingredients are kept ready mixed in powder form. The additional supply of the metal oxide which is used up as the electrolysis proceeds, is provided in the form of lumps or pieces positioned within the bath, so that they may dissolve therein and keep the bath at the desired concentration.

In accordance with a phase of the invention disclosed herein, the additional lumps of the metal oxide, are positioned in the bath so that they form a porous barrier structure 21 enclosing the sides and the bottom region of the anodes 13 and separating the bath region adjacent the cathode 10 to prevent reactions between anode products and the metal borides which are formed by the electrolysis and accumulate at the cathode. In an equipment having a plurality of individual anodes 13 immersed in the bath, each of the anodes 13 may be surrounded with its individual porous barrier enclosure separating the region adjacent each anode from the other portions of the bath extending toward the cathode 10. Good results are obtained by providing a single porous continuous vessel-like barrier enclosure 21 separating the region within which the array of anode electrodes 13 is positioned from the cathode region of the bath. The barrier structure 21 may be made in the form of a porous

integral hollow structure of the metal oxide, such as zirconium oxide, which has sufficient porosity as to permit the electrolysis process to proceed between the anodes 13 and the cathode 10. With a barrier arrangement of the invention of the type described above, the efficiency and yield in the production of the desired borides was increased 50%. The vessel-like barrier structure of zirconium oxide or the other desired metal oxides may be formed out of the metal oxide particles by the conventional, known ceramic processes used in making vessels or beakers of aluminum oxide or other refractory metal oxides.

As indicated in the drawing, the shield or barrier structure 21 is made of segmental porous blocks, piled and assembled into a hollow porous barrier vessel enclosure surrounding the region of the bath within which the anodes 13 are positioned, and separating it from the cathode region of the bath, extending along the inner surface of the crucible 10 serving as a cathode.

The metal oxide blocks serving as the barrier vessel 21 may be constructed in a manner analogous to toy building blocks with interlocking male and female portions so that when assembled they will remain assembled as a porous barrier 21.

In initially starting the operation of such fused salt electrolysis bath, the properly proportioned ingredients are mixed in powder form and placed within the graphite vessel 10 serving as the cathode. The barrier wall vessel 21 of the metal oxide blocks is positioned within the vessel before placing therein the powdered bath ingredients. Alternatively, a layer of the metal oxide blocks is first deposited on the bottom wall of the vessel 10 before placing thereover the metal oxide barrier wall 21, whereupon the vessel 10 is filled with the mixed powdered ingredients.

The array of graphite electrodes 13 and 17, mounted on a suitable insulating support, are positioned in the anode region of the bath surrounded by the metal oxide barrier vessel 21 before this region is filled with the powder body of the mixed bath ingredients.

After the furnace electrode vessel 10 is filled with the mixed bath ingredients in the manner described above, a molten pool of bath ingredients is produced in the region between the heating electrodes 13 and 17 of opposite polarity as by heating it with a torch applied thereto. Once the molten pool of bath ingredients is formed, further heat energy is supplied by heating current flowing between the electrodes 13 and 17 from the heating terminals 18 of opposite polarity which may be supplied, for instance, through the secondary side of an alternating current supply transformer. After the contents of the entire vessel 10—except the metal oxide lumps of the porous barrier 21—have been molten, the fused salt bath is ready for starting the electrolysis process by closing the direct current circuit. The amount of heating current supplied during the electrolysis is adjusted so as to maintain the bath temperature at a desired level, which has been found to be between 1000° C. and 1200° C. As the level of the molten bath drops, additional bath ingredients may be added from the previously prepared properly proportioned mixture of powder ingredients, the lumps or blocks of the metal oxide maintaining the desired metal oxide concentration within the bath.

It is also possible to prepare first a salt mixture which does not contain the oxide of the boride-forming metal: This mixture is introduced into the furnace, heated with a torch until a molten pool is formed and then kept in the liquid state by the heating current. At this stage, the oxide of the boride-forming metal is introduced by adding a salt mixture containing a proportion of this oxide which is large enough to attain the proportion desired in the final bath. By way of example, in the production of zirconium boride, two mixtures, A

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and B are prepared. The compositions correspond to the following proportions:

Mixture A

	Mol
B ₂ O ₃ -----	2
CaO -----	1
CaF ₂ -----	1

Mixture B

	Mol
B ₂ O ₃ -----	2
CaO -----	1
CaF ₂ -----	1
ZrO ₂ -----	½

About 3 parts (by weight) of Mixture A are introduced into the furnace. After this mixture is melted, by applying first the torch and then the heating current, 1 part of Mixture B is added to the bath.

The formation of boride consumes the oxide of this metal. Efficient electrolysis requires continuous replacement of the oxide consumed. According to the invention, the desired excess of the metal oxide is provided in solid form and placed in the bath so that it will be dissolved by the bath at a rate corresponding to the oxide consumption. Excess undissolved oxide in the form of finely dispersed particles was found to serve as nuclei for the deposition of boride. Boride depositions on oxide nuclei must be avoided, since boride particles thus formed contain oxide cores and are of inferior quality. This difficulty was overcome by keeping the oxide concentration of the original composition down to amounts which are readily dissolved, and by providing the required excess of solid oxide in the form of lumps or pieces which are not kept in suspension and cannot serve as nuclei. It was also found that cathode and anode regions of the bath must be separated by porous barriers in order to prevent interaction of cathode and anode products which interaction manifests itself in continuous decrease of overall current efficiency with increased time of the run. Since the oxides of the boride-forming metals are available in porous form, the separators can be fabricated of these materials. Thus, beaker-shaped porous barriers enveloping the anodes of the bath can take the place of the added lumps and provide the supply of metal oxide required for replacement of dissolved oxide consumed by the electrolytic reaction.

By arranging the metal oxide pieces immersed in the molten bath in the form of a barrier separating the cathode region of the bath from the anode region, disturbing side reactions between anode products and cathode products are suppressed. In particular, such barrier prevents metal borides which accumulate at the cathode from being carried to the anode region, and their decomposition.

In carrying on the electrolysis, it is good practice to have a ready prepared mixture of the bath ingredients so that, as the level of the bath drops, it is replenished by adding thereto suitable quantities of the available mixture of its ingredients.

The desired metal borides may be produced at a satisfactory efficiency with a procedure and equipment of the type described above by electrolysis carried on with a cathode current density in the range between about 7 to 12 amp./sq. in. (amperes per square inch). In practice, the process has been carried on effectively for a long period of time with a cathode current density of about 10 amp./sq. in.

The metal borides which are produced adjacent the surface of the cathode vessel 10 accumulate at its bottom, and they may be withdrawn therefrom through a suitable gate passage lined with carbon. In order to protect the molten metal borides from freezing into a solid block of great hardness and difficult to break, they are discharged into circulating water so as to

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quench and break up the discharged boride body into a conglomerate of frozen particles and lumps.

To remove the contents of a furnace vessel 10, which is not provided with a gate, the current is shut off, and its entire contents are poured into circulating water, thereby quenching and breaking them up into a conglomerate of frozen lumps and particles.

Other metal borides, including borides of titanium, tantalum, columbium, chromium, vanadium and hafnium, may be formed in a similar way by electrolysis in a fused salt bath carried on in accordance with the principles of the invention for producing the desired high purity borides.

In order to separate the metal boride particles from the impurities, the boride agglomerate with its impurities, is subjected to comminution treatments whereby it is broken down and comminuted into particles having an average particle size of about -100 mesh, thereby loosening the metal boride particles from the metal oxide particles, and other substances, and making it possible to subject the mass of powder particles to an initial separation treatment.

To this end, particles and lumps of the quenched agglomerate are dried and crushed to a uniform particle size, such as -20 mesh, which permits their further comminution to -100 mesh by ball-milling. The comminuted mass of loose particles having an average particle size of about -100 mesh is then subjected to a gravity separation treatment, as by a shaking table which separates the particles having the same density as the boride particles from particles of lower density.

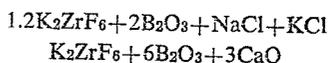
The resulting mass of loose particles, having about the same density as the refractory boride particles, is then leached with hydrochloric acid solution in concentration of 1:1.5, and then washed with water to remove all traces of acid, yielding a mass of particles containing zirconium boride and zirconium oxide, the other impurities having been dissolved by the hydrochloric acid.

The tailings from the shaking table may contain boron oxide, calcium oxide, calcium fluoride, zirconium oxide, and also about 1% or less of zirconium boride. The tailings may be re-used for preparing a mixture for the fused salt bath with proper adjustment for the composition of the tailings. The middlings from the shaking table are re-passed thereover to obtain a further separation between the yield of particles having the same density as the metal boride and tailings of lower density.

The purified and clean loose powder mass of an average particle size of -100 mesh and about the same density as the metal boride particles, and containing substantially only metal boride particles and metal oxide particles, is then subjected to a flotation treatment which separates the metal boride particles from the metal oxide particles, yielding, after washing and drying, a body of loose refractory metal boride particles about 98 to 99% pure.

The zirconium boride powder of 98% to 99% purity is then ball-milled to size under a cover of purified mineral oil in an atmosphere of purified argon to reduce the powder particles to an average size of about 2 microns, or in general of the order of 1 to 3 microns. If the ball-milling to size is carried on in a steel ball mill, the ball-milled powder particles are subjected to a leaching treatment with very dilute sulphuric acid in a concentration of 1 to 30 for dissolving the iron contents, whereupon the powder is washed with water, followed by washing with alcohol, and drying.

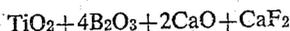
By way of example, the following compositions of a fused salt bath are suitable for producing zirconium boride by electrolysis in accordance with the principles of the invention:



In general, the same procedure is followed in producing by electrolysis in a fused salt bath other refractory metal

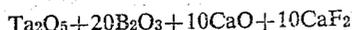
boride powders, including the borides of titanium, tantalum, hafnium, chromium, columbium and vanadium, in a form suitable for use in refractory cemented metal boride compositions, by substituting the oxide of the desired other metal for zirconium oxide.

By way of example, titanium boride of desirable characteristics may be produced by electrolysis carried on in accordance with the principles of the invention with a fused salt bath of the following composition:

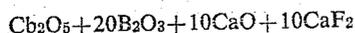


The titanium oxide of the bath may be replaced by potassium titanium fluoride K_2TiF_6 .

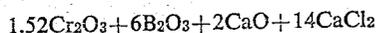
For the production of tantalum boride, a fused salt bath of the following composition will give satisfactory results:



For the production of columbium boride, a fused salt bath of the following composition will give satisfactory results:



For the production of chromium boride, a fused salt bath of the following composition is satisfactory:



The novel principles of the invention will suggest various modifications thereof, and it is accordingly desired that the invention shall not be limited to any of the exemplifications described herein.

I claim:

1. In producing metal boride of a metal selected from the group consisting of zirconium, titanium, tantalum, columbium, chromium, vanadium and hafnium by electrolysis within a fused salt bath, the procedure of providing a fused salt bath consisting of a metal compound of the metal of the desired boride and of additional bath ingredients within which said metal compound will dissolve at elevated temperatures in the range between about 900° to 1300° C. at which the ingredients of said bath remain molten, with said additional bath ingredients comprising a boron oxide and a substance selected from the group consisting of alkali metal oxides, alkaline earth metal oxides, alkali metal salts and alkaline earth metal salts and mixtures thereof; maintaining within said bath a substantially continuous vessel-like porous barrier consisting predominantly of said metal compound, heating the contents of said bath to an elevated temperature within said range, at which said contents remain in molten condition; passing direct current between an anode immersed in one region of said bath separated by said barrier from a remaining region of said bath and a cathode in contact with said remaining region of said bath for effecting therein an electrolysis and forming said metal boride deposited in the region of said cathode whereby, during the electrolysis, the solvent action of said molten bath on said porous barrier automatically maintains the effective concentration of the metal compound within the molten bath down to an amount sufficiently low as to maintain said metal compound substantially fully dissolved in the molten

bath and the formation of dispersed undissolved particles of said metal compound within said molten bath is substantially suppressed.

2. In producing metal boride of a metal selected from the group consisting of zirconium, titanium, tantalum, columbium and chromium, vanadium and hafnium by electrolysis within a fused salt bath, the procedure of providing a fused salt bath consisting of a metal oxide of the metal of the desired boride and of additional bath ingredients within which said metal oxide will dissolve at elevated temperatures in the range between about 900° and 1300° C. at which the ingredients of said bath remain molten, with said additional bath ingredients comprising a boron oxide and a substance selected from the group consisting of alkali metal oxides, alkaline earth metal oxides, alkali metal salts and alkaline earth metal salts and mixtures thereof; maintaining within said bath a substantially continuous vessel-like porous barrier consisting predominantly of said metal oxide, passing electric heating current through the portion of said bath confined in said vessel-like barrier and thereby heating the contents of said bath to an elevated temperature within said range, at which said contents remain in molten condition; passing direct current between an anode immersed in one region of said bath separated by said barrier from a remaining region of said bath and a cathode in contact with said remaining region of said bath for effecting therein an electrolysis and forming said metal boride deposited in the region of said cathode whereby, during the electrolysis, the solvent action of said molten bath on said porous barrier automatically maintains the effective concentration of the metal oxide within the molten bath down to an amount sufficiently low as to maintain said metal oxide substantially fully dissolved in the molten bath and the formation of dispersed undissolved particles of said metal oxide within said molten bath is substantially suppressed.

3. In producing metal borides by the procedure claimed by claim 1, passing direct current between an anode immersed in a region of said bath surrounded by said barrier and a cathode in contact with a region of said bath outside the region surrounded by said barrier.

4. In producing metal borides by the procedure claimed by claim 2, passing direct current between an anode immersed in a region of said bath surrounded by said barrier and a cathode in contact with a region of said bath outside the region surrounded by said barrier.

References Cited in the file of this patent

UNITED STATES PATENTS

732,616	Burgess et al. -----	June 30, 1903
771,646	Von Kugelen et al. -----	Oct. 4, 1904
1,060,839	Hauss -----	May 6, 1913
1,196,699	Keyes et al. -----	Aug. 29, 1916
1,818,173	Suchy et al. -----	Aug. 11, 1931
1,833,425	Jessup -----	Nov. 24, 1931

FOREIGN PATENTS

627,947	Germany -----	Mar. 27, 1936
---------	---------------	---------------