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M. M. WONG

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ELECTROWINNING OF BERYLLIUM

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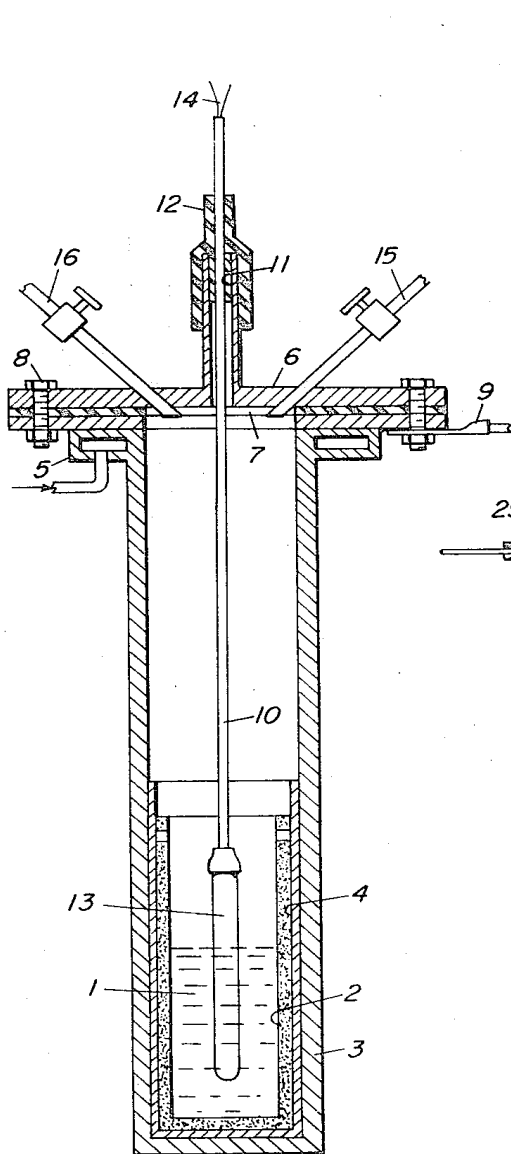


FIG. 1

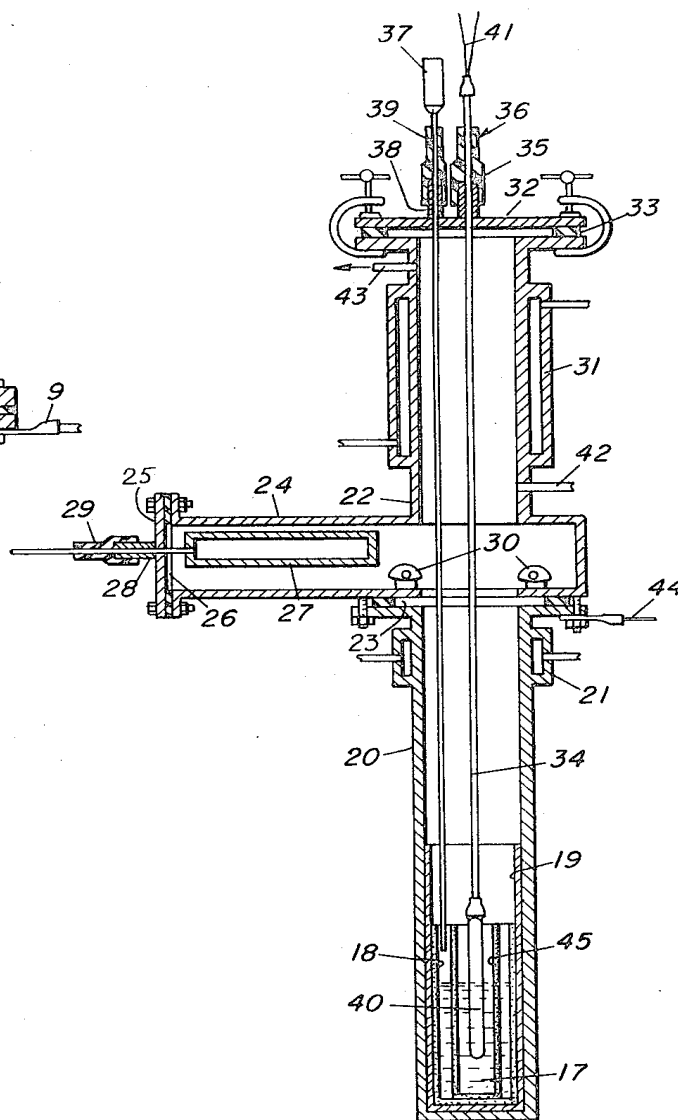


FIG. 2

INVENTOR  
MORTON M. WONG

BY *Ernest S. Cohen*  
*William S. Brown*  
ATTORNEYS

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## ELECTROWINNING OF BERYLLIUM

Morton M. Wong, Reno, Nev., assignor to the United States of America as represented by the Secretary of the Interior

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11 Claims

### ABSTRACT OF THE DISCLOSURE

A method of electrowinning beryllium from a fused salt electrolyte containing beryllium fluoride comprising electrolyzing at a temperature below the melting point of the beryllium, followed by heating a mixture of the fused salt and beryllium metal to a temperature above the melting point of beryllium to coalesce the beryllium. The beryllium metal finds utility in a variety of applications where high melting temperature, light weight, high strength, good thermal conductivity, low thermal neutron absorption cross section, and high scattering cross section are required, e.g., in space vehicles and nuclear reactors.

FIG. 1 shows the apparatus used in carrying out the process of the invention as a batch process.

FIG. 2 shows the apparatus used in carrying out the process of the invention as a semicontinuous process.

Electrowinning of beryllium from a fused salt electrolyte is known and is disclosed, e.g., in U.S. Pat. No. 1,427,919. However, prior art processes have had a number of serious disadvantages, such as low efficiency, emission of toxic gases, codeposition of other metals, etc. It has now been found, in accordance with the invention, that these disadvantages may be largely overcome by means of a two step process in which the beryllium is first electro-deposited from a fused salt bath and, subsequently, a mixture of the deposited beryllium metal and the fused salt both is heated to a temperature above the melting point of the beryllium metal in order to coalesce the metal. This enables ready separation of the metal from the fused bath. The process of the invention has been found particularly applicable where beryllium fluoride, or a mixture of beryllium fluoride and beryllium oxide, is to be used in the electrolyte. Use of these compounds as feed is highly desirable since they are easy and economical to prepare and handle.

To permit satisfactory electrodeposition and coalescence of beryllium metal the electrolyte must possess reasonable electrical conductance, dissolve enough BeO and BeF<sub>2</sub> to meet the electrolysis demand, not volatilize the component salts appreciably at the electrolysis temperature, and not react rapidly with beryllium metal at the coalescence temperature. It has been found that the presence of beryllium fluoride (BeF<sub>2</sub>) in the electrolyte is essential to economical production of good quality beryllium metal. Furthermore, the use of certain fluorides in the electrolyte may have deleterious effects in the electrolytic process. For example, MgF<sub>2</sub> and CaF<sub>2</sub> tend to result in deposits that contain alkaline earth-beryllium intermetallic compounds. Electrolytes containing NaF or KF yield beryllium metal, but heating at the higher temperature to coalesce the beryllium in an open crucible results in fuming and burning of the alkali metals, with disappearance of the beryllium metal.

Electrolysis of a fused bath consisting of BeO, BeF<sub>2</sub> and LiF, with or without BaF<sub>2</sub>, has been found to give particularly good results and this combination of salts is, therefore, the preferred electrolyte composition. This electrolyte composition also permits continuous addition of BeO to the fused bath as the source of beryllium metal.

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The electrolytic process may be carried out by means of either a batch process or a semicontinuous process. The batch process is conventional and consists of electrolysis of a fused salt bath in any suitable container such as a graphite crucible, which also serves as the anode. The cathode may consist of any inert, conductive metal, such as nickel, iron, molybdenum or tungsten. The temperature at which the electrolysis is conducted may range from about 500° to 900° C., with about 700 to 750° C. being the preferred range. Too low a temperature reduces electrolyte conductance and the solubility of BeO while too high a temperature increases volatilization of BeF<sub>2</sub> and corrosion of cell components. The current and voltage employed for the deposition will range from about 4 to 20 amperes and 2.5 and 5.0 volts, respectively. The electrolysis is conducted in an inert atmosphere such as helium, argon, and the cell gases CO<sub>2</sub> and CO. Optimum values of these variables will depend on the composition of the electrolyte, the particular electrolytic apparatus employed, desired deposition rate of the beryllium, etc., and is best determined experimentally.

The semicontinuous process is similar to that of the batch process, except that the cell is maintained continuously at the operating temperature, BeO is replenished continuously or after each electrodeposition and make-up electrolyte is added periodically. This embodiment of the process of the invention is more described in Example 5 below.

Following completion of the electrodeposition step the mixture of beryllium metal and fused salt bath is heated, preferably rapidly, to a temperature above the melting point of the metal to cause it to coalesce. The heating may be carried out in any conventional apparatus capable of supplying the required heat, without adversely affecting the beryllium-salt mixture, as by contamination. Suitable apparatus include induction furnaces, electric resistance furnaces, etc. The heating is conducted at a temperature in the range of about 1280 to 1450° C., preferably about 1300° C. As stated above, this heating step results in coalescing of the beryllium metal. The resulting consolidated metal is much less liable to oxidation by air or water, or to chemical attack by acids, than is the finely-divided metal formed by the electrodeposition. Furthermore, it is readily separated from the fused salt by conventional means, e.g., by pouring through a screen of suitable mesh size after the metal-salt mixture is cooled to a temperature well below the melting point of beryllium but well above the melting point of the bath, for example 900° C.

Following recovery of the beryllium metal from the fused salt mixture the metal is preferably further purified by leaching in a solution of an acid, such as nitric acid, to remove any salt that adheres to the metal.

The following examples will serve to more particularly describe the process of the invention.

### EXAMPLES 1-4

In these examples the process was carried out in the apparatus shown in FIG. 1.

The electrolyte 1 was contained in a graphite crucible 2 (7 cm. inside diameter), which was protected against the diffusion of electrolyte to the mild steel pot 3 (10 cm. inside diameter and 50 cm. in length) by a nickel liner 4. The flange of the pot was equipped with a water-cooling gland 5, and the pot was sealed to a lid 6 with a neoprene gasket 7 and bolts 8. An anode lead 9 was connected to the pot, and a tubular cathode lead 10 was introduced through the lid, electrically insulated with a Teflon bushing 11 and sealed by a rubber sleeve 12. A closed-end nickel or iron tube 13 (1.3 cm. in diameter) was used as the cathode, and a thermocouple 14 was placed inside the lead and cathode to measure the elec-

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trolyte temperature when desired. Connections were provided in the lid for inert gas and water aspirator 15 and oil bubbler 16. The electrolytic cell was heated in an electric furnace.

After the salts making up the electrolyte were mixed and placed in the graphite crucibles the cell was evacuated and back-filled with helium.

When the electrolyte was heated to a temperature in the range of 700° to 750° C., electrolysis was conducted with a small stream of helium sweeping through the cell. After a deposition cycle was completed, the oil bubbler, through which the effluent gas passed, was closed off and the cell was maintained under helium atmosphere. The cathode was lifted from the electrolyte and the cell was allowed to cool.

After the cell was cooled, the graphite crucible and its contents were placed in an induction furnace to quick coalesce the beryllium metal into beads by heating at approximately 1,300° C. for 4 minutes. If metal adhered to the cathode after electrolysis, the deposit was stripped from the cathode and returned to the metal-salt mixture in the crucible before the coalescence operation.

The induction furnace contained a graphite liner packed with zirconia in mica sheets and cemented in place with a mixture of fireclay and  $\text{Al}_2\text{O}_3$ . The furnace was heated by water-cooling induction coils which were connected to a high frequency power source (6 kw. high-frequency converter) and mounted in an insulating frame.

After the beryllium metal was coalesced the metal and salt were cooled. The metal beads were separated from the salt, and the bulk of the salt, which still contained usable beryllium values, could be recycled. The metal beads were leached in water until most of the adhered salt was dissolved, and then the leaching solution was discarded. The metal beads were again leached in dilute nitric acid solution until it was free of salt, and the metal was then washed in water and dried.

## EXAMPLE 1

The electrolyte was composed of 135 g.  $\text{BaF}_2$ , 169 g.  $\text{LiF}$ , and 196 g.  $\text{BeF}_2$  with 30 g.  $\text{BeO}$  also added. Electrolysis was performed at an average temperature of 740° C. and applied voltage of 4.8 volts. The average current was 15 amperes; cathode current density, 784 amp/sq. ft., and anode current density, 84 amp/sq. ft. The metal product, coalesced and leached, had the following analysis, expressed in parts per million: O, 190; C, 600; Al, 1,050; Ba, 600; Ca, 130; Cu, 150; Fe, 820; Mg, 38; Mn, 80; Ni, 1,850; and Si, 400. The Be content was 99.2 percent.

## EXAMPLE 2

The electrolyte was composed of 135 g.  $\text{BaF}_2$ , 169 g.  $\text{LiF}$ , and 196 g.  $\text{BeF}_2$  with no addition of  $\text{BeO}$ . Electrolysis was conducted at 735° C. and 4.8 volts. The average current was 9.5 amperes; cathode current density, 50 amp/sq. ft., and anode current density, 54 amp/sq. ft. The metal product, coalesced and leached, had the following analysis, in parts per million: O, 320; Al, 1,250; Ca, 64; Cr, 210; Cu, 10-100; Fe, 1,000-10,000; Mg, 33; Mn, 440; Ni, 500-5,000; and Si, 100-1,000.

## EXAMPLE 3

The electrolyte was composed of 196 g.  $\text{LiF}$  and 354 g.  $\text{BeF}_2$  with 30 g.  $\text{BeO}$  added. Electrolysis was performed at 720° C. and 4.7 volts. The average current was 13 amperes; cathode current density, 721 amp/sq. ft., and anode current density, 75 amp/sq. ft. The metal product, coalesced and leached, had the following analysis, in parts per million: O, 480; N, 60; C, 300; Al, 1,500; Ca, 105; Cu, 44; Fe, 640; Mg, 52; Mn, 125; Ni, 2,400; Si, 370; and Ti, 235. The Be content was 99.3 percent.

## EXAMPLE 4

The electrolyte was composed of 196 g.  $\text{LiF}$  and 354 g.  $\text{BeF}_2$  with no addition of  $\text{BeO}$ . Electrolysis was performed at 718° C. and 4.7 volts. The average current was 19

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amperes; cathode current density, 984 amp/sq. ft., and anode current density 105 amp/sq. ft. The metal product, coalesced and leached, had the following analysis, in parts per million: O, 220; C, 400; Al, 1,400; Ca, 105; Cr, 250; Cu, 78; Fe, 100-1,000; Mg, 43; Mn, 66; Ni, 100-1,000; Si, 720; Ti, 1,000, and V, 310.

## EXAMPLE 5

In this example the process was carried out in the apparatus shown in FIG. 2. This apparatus was similar to that of Examples 1-4, except for modifications to enable replenishment of  $\text{BeO}$  and make-up electrolyte and periodic removal of electrodeposited metal. The electrolyte 17 was contained in graphite crucible 18 with nickel liner 19 in steel pot 20. The flange of the pot was equipped with water-cooling gland 21 and the pot was sealed to water-cooled air lock 22 by means of neoprene gasket 23. The function of air lock 22 was to allow removal of deposits without exposing the cell to the atmosphere. The air lock consisted of a slide gate housing 24 which was sealed to lid 25 with neoprene gasket 26. Slide gate 27 was introduced through lid 25 via a nipple 28 and rubber sleeve 29. Locking cams 30 were provided for the purpose of raising the slide gate 27 to seal the pot 20 or lowering the slide gate 27 to open the pot. The air lock was cooled by means of water-cooling gland 31 and sealed by means of lid 32 and neoprene gasket 33.

Cathode lead 34 was introduced through lid 32 via Teflon bushing 35 and rubber sleeve 36. Feed tube 37 was introduced through nipple 38 and rubber sleeve 39. A closed-end iron tube 40 served as the cathode and thermocouple 41 was placed inside the cathode lead and the cathode. Connections 42 and 43 were provided for inlet and outlet, respectively, of inert gas and anode lead 44 was connected to pot 20.

A perforated graphite crucible 45 was placed between anode and cathode in order to confine  $\text{BeO}$  in the anode area.

Operation of the cell for semicontinuous electrodeposition was similar to that described previously for the batch operation, with the following modifications: The cell was maintained continuously at the operating temperature.  $\text{BeO}$  in the cell was replenished continuously or after each electrodeposition, and make-up electrolyte was added periodically when needed. Electrolyzing conditions favorable to production of adherent deposits were used. After an electrodeposition, the deposit was removed from the pot and sealed in the air lock by closing the slide gate valve.

The deposit was cooled in, and then removed from, the air lock. A number of deposits of metal with entrained salt were combined, mixed with a small quantity of  $\text{LiF}$  in a graphite crucible, and heated in an induction furnace at 1300° C. for 4 minutes to coalesce the beryllium metal. Power to the induction furnace was then turned off. When the metal-salt mixture was cooled to 900° C., the mixture was poured through a 40 x 40 mesh stainless steel screen to separate the metal from the salts. After the metal was cooled to room temperature, it was leached in water and dilute nitric acid solution as described earlier. Following is a specific embodiment:

The initial electrolyte was composed of 300 g.  $\text{BeF}_2$ , 250 g.  $\text{LiF}$  and 30 g.  $\text{BeO}$ . A series of electrodepositions were made with an addition of  $\text{BeO}$  to the bath after each electrodeposition. The electrolyses were performed at 700° C., applied voltage of 2.6 volts, an average current of 3.8 amperes, cathode current density of 167 amp./sq. ft., and anode current density of 42 amp./sq. ft. 83-ampere-hours of electrolyses were performed in 8 electrodeposition cycles. The combined metal recovered, after coalescence and leaching, was 10.3 grams, giving a cathode current efficiency of 74 percent. The metal product had the following analysis, expressed in parts per million: O, 1600; C, 1000; N, 20; Al, 1250; Ca, 1500; Cr, 90; Cu, 10; Fe, 4600; Mg, 100; Mn, 600; Ni, 500; Si, 60. The Be content was 98.8 percent.

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What is claimed is:

1. A method fo electrowinning beryllium comprising the steps of

- (1) Electrolyzing a fused salt bath consisting essentially of beryllium fluoride and a member selected from the group consisting of beryllium oxide, lithium fluoride, barium fluoride, and mixtures thereof, at a temperature below the melting point of beryllium to form a mixture of beryllium metal and fused salts and
- (2) heating this mixture of beryllium metal and fused salts at a temperature from about 1280 to 1450° C. to coalesce the metal.

2. The method of claim 1 in which the fused salt bath consists essentially of a mixture of beryllium oxide, beryllium fluoride and lithium fluoride.

3. The method of claim 1 in which the fused salt bath consists essentially of a mixture of beryllium fluoride, barium fluoride and lithium fluoride.

4. The method of claim 1 in which the fused salt bath consists essentially of a mixture of beryllium fluoride and lithium fluoride.

5. The method of claim 1 in which the fused salt bath consists essentially of a mixture of beryllium oxide, beryllium fluoride, barium fluoride and lithium fluoride.

6. The method of claim 1 in which the electrolysis is conducted at a temperature of from about 500 to 900° C.

7. The method of claim 1 including the additional step of separating the mixture of coalesced beryllium and fused salts by pouring the mixture, while at a temperature below the melting point of the beryllium metal but above

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the melting point of the salt mixture, through a stainless steel screen.

8. The method of claim 7 including the additional step of purifying the beryllium metal from sal contaminants by leaching with an acid solution.

9. The method of claim 8 in which the acid is nitric acid.

10. The method of claim 1 in which the electrolysis step is carried out as a batch process.

11. The method of claim 1 in which the electrolysis step is carried out as a semicontinuous process in which (1) the electrolytic cell is maintained continuously at the operating temperature, (2) beryllium oxide and make-up electrolyte are periodically added, (3) the BeO addition is confined in the anode area by means of a perforated graphite crucible located between the cathode and anode and in electrical contact with the latter.

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CARL D. QUARFORTH, Primary Examiner

R. L. TATE, Assistant Examiner

U.S. Cl. X.R.

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