Dec. 5, 1933. L. BURGESS 1,937,509

METHOD OF MAKING BERYLLIUM AND LIGHT ALLOYS THEREOF

Filed Jan. 16, 1932

Fig. 1

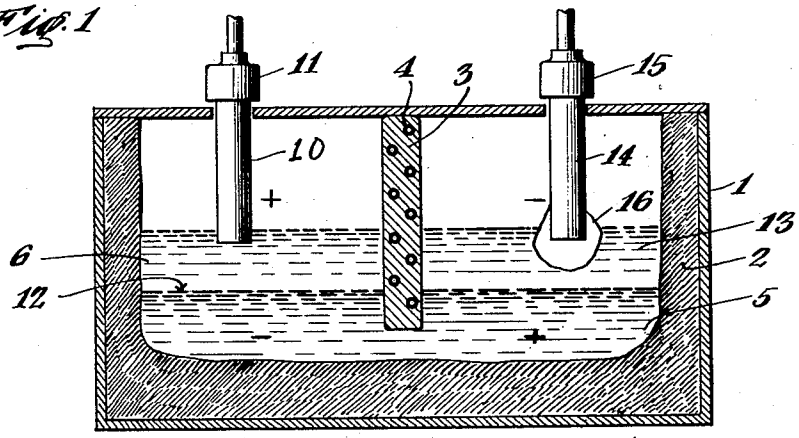


Fig. 2

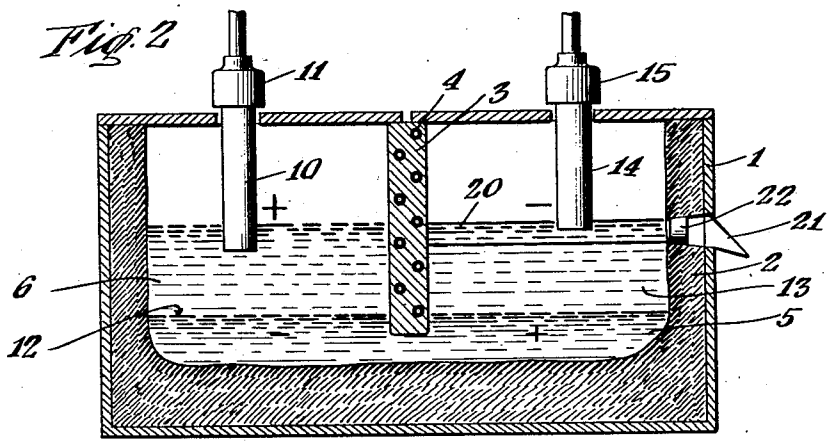
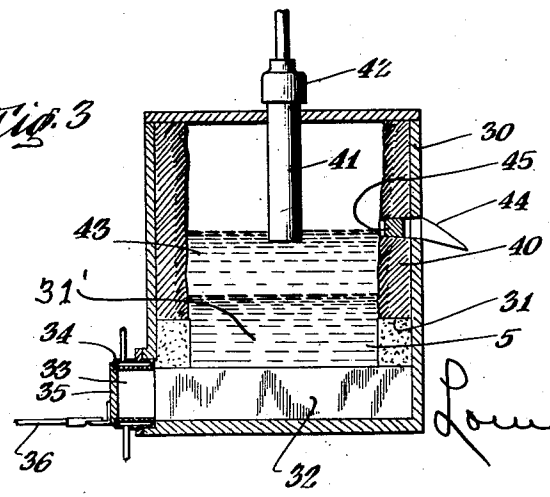


Fig. 3



Louis Burgess
INVENTOR

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METHOD OF MAKING BERYLLIUM AND LIGHT ALLOYS THEREOF

Louis Burgess, New York, N. Y.

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9 Claims. (Cl. 204—19)

The invention will be fully understood from the following description read in conjunction with the drawing, in which,

Fig. 1 is a vertical section through apparatus in which my invention may be carried into effect.

Fig. 2 is a vertical section of apparatus in which a further embodiment of my invention may be carried into effect.

Fig. 3 is a cross-section through a further form of apparatus in which another embodiment of the invention may be carried out.

Referring specifically to Fig. 1, the apparatus comprises the casing or shell 1 which may be of iron or steel and which contains the lining or layer 2 which operates as electrical and thermal insulation between the fluid contents of the apparatus and the shell. The lining 2 may either be built up of preformed blocks of suitable refractory material, or may be formed in situ by filling the shell 1 with fluid electrolyte and permitting the same to solidify in part adjacent the shell 1 thereby forming the lining 2. 3 designates a bridge wall which may also be formed of suitable refractory material, but is preferably formed in situ through freezing electrolyte about the pipes 4 which are connected in series so that a suitable cooling fluid may be circulated through the same. The layer 5 may, generally speaking, be composed of an alloy of beryllium with heavier metals which are less electropositive than beryllium. A number of binary and ternary alloys of this sort may be formed which will operate in the process. The alloying metals should be substantially heavier than beryllium, less electropositive than beryllium in relationship to the electrolyte employed, and the alloy formed should be freely fluid at the temperature of electrolysis. The alloy must exist as a single homogeneous liquid phase. While silver may be employed, I prefer to form the layer 5 of an alloy consisting predominantly of beryllium and copper, or of beryllium and copper containing a few percent of silicon, which latter agent will operate within certain ranges of concentration to depress the freezing point and impart greater fluidity. Alternatively, or in addition to the silicon, there may be added a few percent of other metals less electropositive than beryllium which have a low melting point and are normally liquid at the temperature of electrolysis. In any event, the alloy so formed should have a specific gravity in excess of 3 at the temperature of electrolysis. The layer 6 indicates generally a suitable electrolyte containing an electrolyzable beryllium compound, and in which electrolyte the beryllium compound has a lower voltage of dissociation than the other constituents present, unless of course the process is operated to simultaneously produce an alloy of other elements than beryllium. Preferably, however, the beryllium compound present in the electrolyte is the most easily dissociable compound upon electrolysis. Within the limits of temperature at which the alloy consisting of beryllium and copper is fluid, the electrolyte must consist essentially of fluorides. It may consist predominantly of another fluoride or fluorides of higher dissociation potential than beryllium fluoride, containing in solution a few percent of beryllium fluoride and/or beryllium oxide. Preferably, however, the electrolyte 6 contains a substantial proportion of beryllium fluoride, and to impart the maximum fluidity and conductivity at least one fluoride with an element more electropositive than beryllium and which therefore forms a fluoride of higher dissociation potential should be present. The fluorides of the alkali metal and alkaline earth metals conform to this description. In this case, a few percent of beryllium oxide may be present dissolved in the fluoride electrolyte. 10 indicates an anode which may be of any suitable type, but preferably consists of a rod of carbon or graphitized carbon carried by the holder 11. It will of course be understood that a number of such rods are employed in parallel sufficient to carry the requisite amperage into the apparatus. In carrying out the operation, current is applied to the anode 10 whereby the electrolyte 6 is electrolyzed in series with the alloy layer 5 as cathode, thereby dissociating the beryllium compound in solution in the electrolyte 6 and liberating beryllium at the surface 12 of the alloy 5. The alloys will undergo considerable flow during electrolysis due principally to the electrical field to which it is subjected, and the beryllium liberated at the surface 12 will therefore be incorporated with the main body of the alloy. In order to produce the elemental beryllium, either per se or in the form of a light alloy of beryllium, the alloy layer 5 is electrolyzed as anode through a suitable electrolyte in series with a suitable cathode. This may, generally speaking, be done either simultaneously with or in succession to the steps hereinbefore described.

In the apparatus illustrated in Figs. 1 and 2, the second stage electrolysis with the copper beryllium alloy as anode is carried simultaneously with the first stage electrolysis hereinbefore de-

scribed. In this case, the fluid electrolyte 13 floats upon a part of the alloy layer 5. The cathode 14 may be of any suitable type and preferably consists of a rod of carbon or graphitized carbon carried by a suitable holder 15. It will of course be understood that while one rod is diagrammatically shown for purposes of illustration, a number of such rods will be employed in parallel, depending upon the total amperage to be carried through the electrolyte. When making pure beryllium unalloyed with other metals, the material will plate out in solid phase as a body 16 of metal adhering to the lower end of the cathode 14. Owing to the fact that the boiling or sublimation temperature of beryllium is very close to the melting point, the beryllium is plated out on to the cathode 14 in solid form. The temperature of electrolysis may range from a temperature in the electrolyte approaching the melting point of beryllium down to the lowest temperature at which the alloy layer 5 and the electrolyte will be freely fluid. When operating with an alloy layer 5 consisting almost entirely of copper and beryllium, temperatures of from 950 to 1250° are preferred. A temperature of from 1100 to 1200° is prefered. In this case the alloy layer 5 preferably contains from 4 to 12% by weight of beryllium. The addition of other metals to the alloy layer 5 which depress the freezing point will materially extend the range of temperatures within which the operation may be efficiently carried out, and will also render it possible to operate with higher percentages of beryllium. Where the alloy layer 5 consists entirely of copper and beryllium, the melting point starts to rise sharply as the beryllium content is increased above 10%. The applied voltage will be sufficient to carry the necessary amperage through the furnace, and the two factors of amperage and voltage will be so correlated as to maintain the desired predetermined temperature. The electrolyte layer 6 and 13 may vary from a few up to several inches in thickness. The amperage will be, generally speaking, in the neighborhood of 1000 amperes per square foot. It is always possible by increasing the thickness of the electrolyte to increase the specific resistance of the cell and correspondingly increase the temperature of operation. Diminishing the thickness of the electrolyte layers will have the converse effect.

In the modified apparatus shown in Fig. 2, corresponding parts have been identified by corresponding numerals. The apparatus shown in Fig. 2 is, however, designed to eliminate the necessity for removing solid beryllium from the extremity of the cathode 14 and to permit the material to be handled in liquid phase. In this case the rod 14 contacts with a layer 20 of light metal or alloy floating upon the electrolyte 13. This may for example be a layer of beryllium aluminum alloy, or may alternatively at the start of the operation be a layer of pure aluminum. In either event, the electrolyte must be so compounded as to float the layer 20 which is in this case the true cathode throughout the entire range of concentrations. In general, the layer 20 will become lighter during electrolysis owing to increase in its beryllium content, and the electrolyte should be compounded to support the layer 20 in its condition of maximum density. In this case, particular attention must be paid to the composition of the electrolyte, and fluorides of the alkali metal and/or alkaline earth metals must be present in sufficient amounts to make the electrolyte more dense than the layer 20 throughout the entire operation. This may be effected by the use of barium fluoride and potassium fluoride in amounts sufficient to impart the requisite density. An electrolyte in roughly the following proportions is recommended:

	Percent
Beryllium fluoride	20–25
Barium fluoride	35–40
Potassium fluoride	35–40

With the apparatus shown in Fig. 2, the operation is continued until the layer 20 has attained the desired concentration of beryllium. The concentration of beryllium in the layer 20 must not be permitted to reach such a point as to cause solidification or thickening of the same. The danger point may, however, be readily determined by comparing the temperature of electrolysis with tables showing the melting points of beryllium aluminum alloys. When the predetermined concentration of beryllium has been reached in the layer 20, it may be tapped from the cell into any suitable receiving vessel through the tapping duct 21 which is normally closed by means of the plug 22. When this has been done, the layer 20 is replenished either with pure aluminum, or an alloy of beryllium and aluminum containing less than the desired beryllium content and operations resumed.

During the operation, fluorine generated in the first stage of electrolysis at the lower extremity of the anode 10 will pass out of the apparatus without contact with the beryllium or aluminum alloy undergoing formation. This eliminates complications due to the presence of fluorine and beryllium in the same space as it occurs in the ordinary and prior art method of generating beryllium. The elimination of the fluorine at the lower end of the anode 10, moreover, renders it possible to float the cathode layer 20 on the electrolyte 13. While the operation may be carried out without replenishment of the beryllium compound in the electrolyte 6, it is preferably carried out with the intermittent or continuous replenishment of the beryllium compound in the same so as to maintain a substantial uniform composition of the electrolyte 6 throughout the operation. The electrolyte 13 does not normally undergo substantial change, inasmuch as beryllium passes into the same from the alloy 5 in amounts equal to that liberated at the cathode 14. The composition of the alloy layer 5 will not undergo substantial change in operation as the amount of beryllium abstracted from this layer is substantially balanced by that introduced.

The operation may be effectively carried out in the relatively simple apparatus shown in Fig. 3. This comprises the shell 30 which carries the carbon lining 31 adjacent the interior lower portion of the shell. This may consist of a carbon lining tamped into position and suitably bonded, or may alternatively consist of preformed carbon blocks laid and cemented in position. The block type has been illustrated in the figure. Electrical contact with the carbon lining or pit may be made in any suitable manner. In the form illustrated, the block 32 adjacent the floor of the shell 30 is formed with a machined cylindrical butt 33 which fits snugly into the annular water cooled sleeve 34. This is sealed to the shell 30 and carries the end closure 35 to which the bus-bar 36 is connected. The upper part of the shell carries a thermally and electrically insulating lining 40, preferably formed in situ by

freezing electrolyte on the walls of the shell. The electrode 41 which may consist of carbon or graphitized carbon is carried by the holder 42 and several such electrodes are employed in parallel to carry the requisite amperage. The pit 31' carries the alloy 5 hereinbefore described, and the electrolyte 43 is provided floating upon the surface of the fluid alloy 5. In operating this apparatus, electrolysis is carried out for a period with the electrode 41 as anode and the alloy 5 as cathode. During this period, the concentration of beryllium in the layer 5 is continuously increasing. Before the concentration of beryllium in the layer 5 reaches such a point as to cause undue loss of fluidity or freezing, the operation is reversed, making the layer 5 anode and the electrode 41 cathode, so that the beryllium is plated out on the lower end of the electrode 41. As the layer 5 becomes impoverished in beryllium, the operation is discontinued and the beryllium removed from the lower end of the electrode 41. The electrolyte does not change in composition during the second stage of operation and is preferably held constant by suitable replenishments during the first stage.

In the preferred method of operating this apparatus, the electrolyte is compounded as hereinbefore described to support a cathode layer of aluminum or of beryllium aluminum alloy consisting principally of aluminum. In this case, electrolysis is started with the electrode 41 as anode and the alloy layer 5 as cathode and carried out preferably with suitable replenishments of the dissociated beryllium compound until the layer 5 has become enriched in beryllium content. The operation is then temporarily discontinued. The electrode 41 is raised slightly and a layer of molten aluminum or aluminum beryllium alloy is gently introduced; so that it floats on the surface of the electrolyte 43. The electrode 41 is then adjusted to contact with the fluid metal introduced, which latter then becomes the true cathode. Electrolysis is then continued with the alloy layer 5 as anode and the introduced light metal as cathode until the alloy 5 has become impoverished in beryllium, whereupon the light metal which has now become correspondingly enriched in beryllium is tapped into a suitable receiving vessel through the duct 44 which is normally closed by the plug 45.

The foregoing description is for purposes of illustration, and it is therefore my intention that the invention be limited only by the appended claims or their equivalents in which I have endeavored to claim broadly all inherent novelty.

I claim:

1. Process of making beryllium, which comprises maintaining a fluid alloy of beryllium and a metal or metals relatively more dense than beryllium and less electropositive than beryllium in relation to fluorine, maintaining floating on at least a part of the said alloy a fluid electrolyte containing a metallic fluoride or fluorides of higher dissociation potential than beryllium fluoride, and containing a compound selected from the group consisting of beryllium fluoride and beryllium oxide, electrolyzing said electrolyte in series with said alloy as cathode and with a suitable anode, thereby dissociating said beryllium compound, liberating beryllium at said cathode and adding to the beryllium in said fluid alloy, maintaining floating on at least a part of said fluid alloy an electrolyte, containing a metallic fluoride or fluorides of higher dissociation potential than beryllium fluoride and containing a compound selected from the group consisting of beryllium oxide and beryllium fluoride, and electrolyzing said last mentioned electrolyte in series with said fluid alloy as anode and in series with a suitable cathode, thereby depositing beryllium at the said last mentioned cathode.

2. Process of making beryllium, which comprises maintaining a fluid alloy consisting predominantly of beryllium and copper, maintaining floating on at least a part of said fluid alloy a fluid electrolyte containing a metallic fluoride or fluorides of higher dissociation potential than beryllium fluoride and containing a compound selected from the group consisting of beryllium fluoride and beryllium oxide, electrolyzing said electrolyte in series with said alloy as cathode and in series with a suitable anode, thereby dissociating said beryllium compound, liberating beryllium at the said cathode and adding to the beryllium in said fluid alloy, maintaining floating on at least a part of the said fluid alloy an electrolyte containing a metallic fluoride or fluorides of higher dissociation potention than beryllium fluoride and containing a compound selected from the group consisting of beryllium fluoride and beryllium oxide, and electrolyzing said last mentioned electrolyte in series with said beryllium copper alloy as anode and in series with a suitable cathode.

3. Process of making beryllium, which comprises maintaining a fluid alloy of beryllium and a metal or metals more dense than beryllium and less electropositive than beryllium in relation to fluorine, maintaining floating on at least a part of said alloy a fluid electrolyte containing a fluoride or fluorides selected from the alkali metal and alkaline earth metal fluorides and containing a compound selected from the group consisting of beryllium fluoride and beryllium oxide, electrolyzing the said electrolyte in series with said alloy as cathode and with a suitable anode, thereby dissociating said beryllium compound, liberating beryllium at the said cathode, and adding to the beryllium in said fluid alloy, maintaining floating on at least a part of the said fluid alloy an electrolyte containing a fluoride or fluorides selected from the alkali metal and alkaline earth metal fluorides, and electrolyzing said last mentioned electrolyte in series with said fluid alloy as anode and in series with a suitable cathode, thereby depositing free beryllium at the said cathode.

4. Process of making beryllium, which comprises maintaining a fluid alloy of beryllium and a metal or metals relatively more dense than beryllium and less electropositive than beryllium in relation to fluorine, maintaining floating on a part of said alloy a fluid electrolyte containing a metallic fluoride or fluorides of higher dissociation potential than beryllium fluoride and containing a compound selected from the group consisting of beryllium fluoride and beryllium oxide, electrolyzing said electrolyte in series with said alloy as cathode and with a suitable anode, thereby dissociating the said beryllium compound, liberating beryllium at the said cathode and adding to the beryllium in said fluid alloy, maintaining floating on a part of the said fluid alloy a second fluid electrolyte containing a metallic fluoride or fluorides of higher dissociation potential than beryllium fluoride and containing a compound selected from the group consisting of beryllium fluoride and beryllium oxide, electrolyzing said second electrolyte in series with said fluid alloy as anode and with a suitable cathode,

thereby depositing beryllium at the said last mentioned cathode.

5. Process of making beryllium, which comprises maintaining a fluid alloy consisting predominantly of beryllium and copper, maintaining floating on a part of said alloy a first fluid electrolyte containing a metallic fluoride or fluorides of higher dissociation potential than beryllium fluoride and containing a compound selected from the group consisting of beryllium chloride and beryllium oxide, electrolyzing the said electrolyte in series with said alloy as cathode and with a suitable anode, thereby dissociating the said beryllium compound, liberating beryllium at the said cathode and adding to the beryllium in said alloy, maintain floating on a part of the said fluid alloy a second fluid electrolyte containing a metallic fluoride or fluorides of higher dissociation potential than beryllium fluoride and containing a compound selected from the group consisting of beryllium fluoride and beryllium oxide, electrolyzing said second electrolyte in series with said fluid alloy as anode and with a suitable cathode, thereby depositing beryllium at the said last mentioned cathode.

6. Process of making beryllium, which comprises maintaining a fluid alloy of beryllium and a metal or metals more dense than beryllium and less electropositive than beryllium in relation to fluorine, maintaining floating on a part of said alloy a fluid electrolyte containing a fluoride or fluorides selected from the alkali metal and alkaline earth metal fluorides and containing a compound selected from the group consisting of beryllium fluoride and beryllium oxide, electrolyzing the said electrolyte in series with said alloy as cathode and with a suitable anode, thereby dissociating the said beryllium compound, liberating beryllium at the said cathode and adding to the beryllium in said fluid alloy, maintaining floating on a part of the said fluid alloy a second electrolyte containing a fluoride or fluorides selected from the alkali metal and alkaline earth metal fluorides, and electrolyzing said last mentioned electrolyte in series with said fluid alloy as anode and with a suitable cathode, thereby depositing free beryllium at the said cathode.

7. Process of making beryllium, which comprises maintaining a fluid alloy of beryllium and a metal or metals relatively more dense than beryllium and less electropositive than beryllium in relation to fluorine, maintaining floating on said alloy a fluid electrolyte containing a metallic fluoride or fluorides of higher dissociation potential than beryllium fluoride and containing a compound selected from the group consisting of beryllium fluoride and beryllium oxide, electrolyzing said electrolyte in series with said alloy as cathode and with a suitable anode, thereby dissociating said beryllium compound, liberating beryllium at the said cathode and adding to the beryllium in the said alloy, thereafter reversing the electrolysis, and electrolyzing the said electrolyte in series with said alloy as anode and with a suitable cathode, thereby depositing beryllium at the said last mentioned cathode.

8. Process of making beryllium, which comprises maintaining a fluid alloy consisting predominantly of beryllium and copper, maintaining floating on said fluid alloy a fluid electrolyte containing a metallic fluoride or fluorides of higher dissociation potential than beryllium fluoride and containing a compound selected from the group consisting of beryllium fluoride and beryllium oxide, electrolyzing said electrolyte in series with said fluid alloy as cathode and with a suitable anode, thereby dissociating said beryllium compound, liberating beryllium at the said cathode and adding to the beryllium in said fluid alloy, thereafter reversing the electrolysis, and electrolyzing the said electrolyte in series with said fluid alloy as anode and in series with a suitable cathode, thereby depositing free beryllium at the said cathode.

9. Process of making beryllium, which comprises maintaining a fluid alloy of beryllium and a metal or metals more dense than beryllium and less electropositive than beryllium in relation to fluorine, maintaining floating on said alloy a fluid electrolyte containing a fluoride or fluorides selected from the alkali metal and alkaline earth metal fluorides and containing a compound selected from the group consisting of beryllium fluoride and beryllium oxide, electrolyzing the said electrolyte in series with said alloy as cathode and with a suitable anode, thereby dissociating said beryllium compound, liberating beryllium at the said cathode and adding to the beryllium in the said fluid alloy, thereby reversing the electrolysis, and electrolyzing the said electrolyte in series with said fluid alloy as anode and in series with a suitable cathode, thereby depositing free beryllium at the said cathode.

LOUIS BURGESS.