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METHOD FOR THE MANUFACTURE OF BERYLLIUM AND ALLOYS

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8 Claims. (Cl. 204—19)

This invention relates to a method for the convenient and economical manufacture of beryllium. It is useful in the production of elementary beryllium and may effectively be employed as part of a process for the production or continuous production of alloys of beryllium.

The earliest methods for the isolation of beryllium were thermal in nature, the alkali metals being used to reduce beryllium halides, such as the chloride or the double alkali beryllium fluoride. Later, electrolytic efforts hinged around the decomposition of the alkali beryllium fluorides, such as Na_2BeF_4 ; in more recent times, electrolytic operations have centered about double fluoride mixtures higher in beryllium content, such as $\text{NaF} \cdot 2\text{BeF}_2$, and about the anhydrous BeCl_2 . The last mentioned has one great advantage over all other materials hitherto suggested as initial material for electrolytic operations: It permits of continuous operation, since there is nothing to build up in the electrolytic bath; full decomposition of the added substance, BeCl_2 , occurs, and the bath returns to its original state, ready for further additions of the electrolyzable substance.

However, anhydrous BeCl_2 is quite difficult and costly of manufacture, requiring the heating of normal beryllium compounds in the simultaneous presence of chlorinating and reducing agents; this has made its use on a commercial scale quite expensive, though technically it is admirable in most respects.

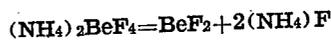
As for the fluorine compounds of beryllium, when combined with alkali fluorides in molecular compounds they have been far easier and less expensive to manufacture, but they suffer from the fact that continuous operation is impossible. Addition of Na_2BeF_4 to an electrolysis bath, for example, results in the release of Be at the cathode and half of the total added fluorine at the anode, but there is meanwhile a continuous building up of NaF in the bath. Sooner or later, the increasing amount of NaF in the bath makes continued operation impossible.

Moreover, Na_2BeF_4 is too low in beryllium content to yield well-operating electrolytic baths; such baths are too easily subject to "anode effect", particularly when in association with any excess NaF over that present in the Na_2BeF_4 itself.

Pure BeF_2 , while theoretically far more desirable than any double fluoride—since, like BeCl_2 , it would leave nothing in the bath after electrolysis of the beryllium content—has hitherto been practically unknown as a chemical entity, because of

great difficulties in its isolation. Evaporation of an aqueous solution containing only BeF_2 leaves nothing but a gummy basic mixture (frequently termed the oxyfluoride); even repeated evaporation with excess HF merely changes the ratio of basicity; fluorine content.

Aside from direct union of beryllium and fluorine, and reaction of dry HF on beryllium metal, there has hitherto been known only one procedure for making pure BeF_2 —thermal decomposition of the double ammonium beryllium fluoride, in accordance with the reaction:



Experience with the double ammonium beryllium fluoride as a source of beryllium fluoride in electrolyses has hitherto been quite discouraging and devoid of hopefulness. And, because of the previous failure, under the conditions tried, of this double ammonium beryllium fluoride as a source of electrolyzable material, it has been assumed that no convenient method exists for utilizing BeF_2 as electrolytic material.

Contrary to all such past beliefs, I have found that the double ammonium beryllium fluoride, properly used, offers an almost ideal source of electrolyzable beryllium. In the past, the additions, for the most part, of ammonium beryllium fluoride have been to baths predominant in alkali earth fluorides, with high operating temperatures—specifically, at or above the melting point of beryllium (1280°C). Under the conditions of such high temperature operation, various factors appear as interference, among them reaction between the liberated ammonia ($\text{NH}_4\text{F} = \text{NH}_3 + \text{HF}$) and the metallic beryllium.

I have found that, in electrolytic operations held below the melting point of beryllium and preferably below 1000°C . (with the metal consequently appearing as flakes or spangles instead of as a molten regulus) the direct addition of ammonium beryllium fluoride does not cause such undesired reactions. I find that, by adding this compound to a bath preferably of sodium or other alkali fluoride, decomposition of the double compound takes place; and, as a result, there is formed in the bath a mutually soluble mixture of the alkali fluoride and beryllium fluoride, which can be varied in the matter of ratio of components, as desired. In this way, the proportion of BeF_2 in the bath can be raised sufficiently above the point where anode effect objectionably sets in so that this unhappy factor does not present itself at all in normal operation. The ammonium

beryllium fluoride should be slowly added to the fused bath to avoid objectionable agitation.

5 Instead of using a single alkali fluoride as the preliminary operating fusion bath, I can use
 10 equally well, mixtures of the alkali fluorides, as well as mixtures of these with alkaline earth
 15 fluorides. Indeed, any single fluoride or mixture of fluorides more electropositive than beryllium will do for the purpose. The only requirement is
 20 that the fusion bath be freely fluid and electrolyzable at a temperature below the melting point of beryllium. For reasons of convenience and comfort of operation, I prefer to operate with the
 25 alkali fluorides, which permit electrolysis to proceed smoothly in the 600° C.-800° C. range.

This invention works particularly well in conjunction with the electrolytic process divulged in application of J. B. Arnold and myself, Serial No. 732,435, filed June 26, 1934, for the manufacture
 20 of alloys of beryllium with heavier metals, such as copper, wherein massive metal cathodes are employed. In such use, higher temperatures are usually needed say from 900° C. to 1000° C. in the
 25 case of copper. When used with massive copper cathodes, for example, the inventions of application Serial No. 732,435 and of this application, yield a continuous flow of liquid copper-beryllium alloy of about 2% to about 6% beryllium content.

30 Having described my invention, I claim:—

1. In the electrolytic production of beryllium, the steps of adding ammonium beryllium fluoride to a fusion of the fluorides of one or more metals more electropositive than beryllium, and of electrolyzing at a temperature below the melting point
 35 of beryllium.

2. The process of obtaining elementary beryllium which includes the steps of adding ammonium beryllium fluoride to a fusion of the fluorides of one or more metals more electropositive than beryllium, and subjecting the mixed
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fusion to electrolysis at a temperature below the melting point of beryllium.

3. In the electrolytic production of beryllium, the steps of adding ammonium beryllium fluoride to a bath of a fluoride of one or more metals more electropositive than beryllium, and of electrolyzing at a temperature below the melting point of beryllium. 5

4. In the electrolytic production of beryllium, the steps of adding ammonium beryllium fluoride to a bath of a fluoride of one or more metals more electropositive than beryllium, and of electrolyzing at a temperature below the melting point of beryllium, and preferably below 1000° C. 10

5. The process of forming fused mixtures of beryllium fluoride and the fluorides of one or more metals more electropositive than beryllium which includes the steps of slowly or gradually adding ammonium beryllium fluoride to a fusion of the other fluoride or fluorides and of holding
 20 the temperature below the melting point of beryllium.

6. The process of forming fused mixtures of beryllium fluoride and the fluorides of one or more alkali metals which includes the steps of
 25 slowly or gradually adding ammonium beryllium fluoride to a fusion of the alkali fluoride or fluorides, and of holding the temperature below the melting point of beryllium.

7. The process of forming fused mixtures of beryllium fluoride and sodium fluoride which includes the steps of slowly or gradually adding ammonium beryllium fluoride to a fusion of sodium fluoride and of holding the temperature
 30 below the melting point of beryllium.

8. In the electrolytic production of beryllium, the steps of adding ammonium beryllium fluoride to a fusion of the fluorides of one or more alkali metals, and of electrolyzing at a temperature below the melting point of beryllium. 35

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