

UNITED STATES PATENT OFFICE

2,173,290

PROCESS FOR OBTAINING BERYLLIUM
FLUORIDE FREE FROM OXIDECarlo Adamoli, Milan, Italy, assignor to Perosa
Corporation, Wilmington, Del., a corporation of
DelawareNo Drawing. Application June 18, 1937, Serial
No. 148,957. In Italy July 15, 1936

5 Claims. (Cl. 23—88)

The present invention concerns a process for the preparation of beryllium fluoride, this latter being produced in a state of great purity with regard to beryllium oxide.

5 It is known that the beryllium fluoride obtained by any of the processes known until now, based upon the action of liquid or gaseous hydrofluoric acid upon a hydrate, carbonate or oxide of beryllium, exhibits the form of a complex compound of beryllium oxide and fluoride, which even under the best conditions of preparation has a composition of approximately $2 \text{ BeO} \cdot 5 \text{ BeF}_2$. Likewise it is this compound which is employed to prepare beryllium in processes comprising electrolysis of the molten salt either alone or mixed with other fluorides.

10 However by reason of the presence of beryllium oxide in the fluoride in question, such as is obtained by the usual means, even when aiming at obtaining metallic beryllium by a thermal method, it has been preferred to abandon the use of beryllium oxyfluoride and to employ complex fluoberyllates; these latter, however, give rise to a number of difficulties such that the yield of beryllium is extremely small. Likewise with the object of obtaining alloys with a low beryllium content by producing electrolytic deposits of beryllium, the employment of ammonium fluoberyllate has been proposed but it has been observed that this latter compound gives rise to a large evolution of gaseous hydrofluoric acid for a very small yield of beryllium in the electrolysis bath.

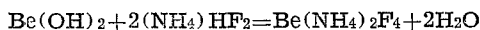
15 Up to now it has only been with the object of scientific research, and only with the small quantities necessary for this object that it has been attempted to prepare beryllium fluoride free from oxide. For this purpose there has been employed either the reaction of dry gaseous hydrofluoric acid upon the beryllium oxyfluoride at a bright red temperature in platinum apparatus, or prolonged heating of ammonium fluoberyllate with the exclusion of air or in a current of CO_2 . Much beryllium fluoride was lost by sublimation, these losses taking place to a substantial degree at the temperature indicated by the experimenters, but this disadvantage was not important for the methods of preparation in question, limited to scientific research.

20 The present invention has for subject a new process of manufacture avoiding the disadvantages of the former processes, to obtain industrially beryllium fluoride practically free from oxide, the said process permitting this manufac-

ture to be effected on an industrial scale with a practically complete yield.

The process consists essentially in causing ammonium acid fluoride in a pure dry state to react at elevated temperature upon dry beryllium hydrate—for example in admixture with the latter—the ammonium acid fluoride being in proportion approaching or practically attaining the quantity corresponding stoichiometrically to that of the beryllium hydrate treated.

This reaction is effected according to the equation:



The operation is carried out at a temperature preferably lower than 500°C . to prevent the sublimation of the beryllium fluoride obtained.

For example, a mixture of beryllium hydrate and ammonium acid fluoride may be caused to react in a metallic receptacle maintained in a suitable furnace heated to 450 – 500°C .

In the case when the water vapour cannot be liberated freely in sufficient quantity, its removal is facilitated by the passage into the reaction mass of a current of inert gas.

At the bottom of the reaction receptacle there is provided in general for this purpose a feed tube through which a current of carbon dioxide or another suitable inert gas is passed. By the presence of this gas the evolution of water is permitted in the form of vapour in quantity corresponding to the reaction formulated above.

With the object of regenerating cyclically the ammonium fluoride employed, there is preferably used a receptacle formed by a swan neck cap the end of which is introduced into a large cold chamber. The neutral ammonium fluoride which is obtained by the splitting (which takes place naturally at the temperature of the operation) of the double fluoride of ammonium and beryllium formed during the above reaction condenses in this cold chamber; consequently by treating this neutral fluoride by hydrofluoric acid for example practically the whole of the ammonium and a part of the fluorine employed may be regenerated and sent back into the cycle in the form of ammonium acid fluoride and thus this latter may be re-utilised for a further operation.

The process according to the invention permits there to be obtained with an excellent yield approaching or reaching practically 100%, beryllium fluoride practically free from oxide which lends itself particularly well to the preparation of metallic beryllium in the alloyed or unalloyed state, in particular by decomposition of the said

beryllium fluoride by means of a decomposing agent, metal or metalloid, capable of liberating the beryllium therefrom.

The process of the invention is illustrated by the following non-limiting example.

In this example 25 kgs. of dry beryllium hydrate were taken and mixed with 68 kgs. of ammonium acid fluoride. This admixture was effected by pouring firstly into the receptacle half the quantity of ammonium fluoride necessary (the total quantity corresponding practically stoichiometrically to the quantity of beryllium hydrate to be treated) then all the hydrate and finally the other half of the ammonium fluoride. The temperature rose spontaneously and the admixture was completed during this elevation of temperature.

This admixture was effected in a cylindrical metallic receptacle constituted in the example in question by a metal intended to be alloyed finally in a further operation with the beryllium. This receptacle had a capacity of 85-90 litres and a diameter of 35-40 cm.

The reaction cylinder was introduced into a suitable furnace with an adjustable electrical resistance so as to enable a temperature of 400° C. to be reached in the interior of the mass in a period of from 3 to 3½ hours.

With the quantities indicated there was obtained in the cylinder as reaction product, beryllium fluoride in a quantity of about 27 kgs. practically free from beryllium oxide and from oxyfluoride; as impurities this beryllium fluoride only contained some fluoride of the metal of the receptacle used.

The neutral ammonium fluoride sublimed and passed out of the cylinder upon which for this purpose a tubular cap was placed which was maintained hot but had a swan neck entering a large cold chamber.

In this cold chamber at the end of the operation the condensed vapours of neutral ammonium fluoride were collected, then this ammonium fluoride was saturated with the necessary hydrofluoric acid with the object of re-utilising it in the form of acid ammonium fluoride for the treatment of a new charge of beryllium hydrate in the apparatus.

I claim:

1. Process for obtaining beryllium fluoride practically free from oxide, which comprises the steps of causing to react at elevated temperature but low enough to prevent sublimation of beryllium fluoride, pure dry ammonium acid fluoride upon substantially dry beryllium hydroxide in a quantity corresponding substantially stoichiometrically to the quantity of beryllium hydroxide, so as to form double fluoride of ammonium and beryllium and to split the same in situ into beryllium fluoride in the solid state and neutral ammonium fluoride in the form of vapour, a current

of an inert gas being caused to pass into the mass during the reaction.

2. Process for obtaining beryllium fluoride practically free from oxide, which comprises the steps of causing to react at elevated temperature but low enough to prevent sublimation of beryllium fluoride, pure dry ammonium acid fluoride in admixture with substantially dry beryllium hydroxide in a quantity corresponding substantially stoichiometrically to the quantity of beryllium hydroxide, so as to form double fluoride of ammonium and beryllium and to split the same in situ into beryllium fluoride in the solid state and neutral ammonium fluoride in the form of vapour, a current of an inert gas being caused to pass into the mass during the reaction.

3. Process for obtaining beryllium fluoride practically free from oxide, which comprises the steps of causing to react at elevated temperature but below 500° C. pure dry ammonium acid fluoride upon substantially dry beryllium hydroxide in a quantity corresponding substantially stoichiometrically to the quantity of beryllium hydroxide, so as to form double fluoride of ammonium and beryllium and to split the same in situ into beryllium fluoride in the solid state and neutral ammonium fluoride in the form of vapour, a current of an inert gas being caused to pass into the mass during the reaction.

4. Process for obtaining beryllium fluoride practically free from oxide, which comprises the steps of causing to react at elevated temperature but low enough to prevent sublimation of beryllium fluoride, pure dry ammonium acid fluoride upon substantially dry beryllium hydroxide in a quantity corresponding substantially stoichiometrically to the quantity of beryllium hydroxide, so as to form double fluoride of ammonium and beryllium and to split the same in situ into beryllium fluoride in the solid state and neutral ammonium fluoride in the form of vapour, a current of carbon dioxide being caused to pass into the mass during the reaction.

5. Process for obtaining beryllium fluoride practically free from oxide, which comprises the steps of causing to react at elevated temperature but low enough to prevent sublimation of beryllium fluoride, pure dry ammonium acid fluoride upon substantially dry beryllium hydroxide in a quantity corresponding substantially stoichiometrically to the quantity of beryllium hydroxide, so as to form double fluoride of ammonium and beryllium and to split the same in situ into beryllium fluoride in the solid state and neutral ammonium fluoride in the form of vapour, a current of an inert gas being caused to pass into the mass during the reaction, condensing the ammonium fluoride and regenerating therewith the ammonium acid fluoride.

CARLO ADAMOLI.