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METHOD OF PRODUCING METALLIC BERYLLIUM AND ALLOYS OF BERYLLIUM

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1

This invention relates to metallurgy and more particularly to a metallurgical process for producing metallic beryllium, beryllium-base alloys and light metal alloys containing beryllium.

One object of the invention is to provide an economically practical method of producing substantially pure metallic beryllium, and of producing beryllium-base alloys and light metal alloys of beryllium.

Another object is to provide an economically practical method of producing aluminum alloys containing beryllium.

A further object is to provide an economically practical method of producing aluminum-beryllium "master" alloys.

Other objects will be apparent as the invention is more fully hereinafter disclosed.

Heretofore in the art, the reduction of the halide compounds of beryllium and other metals by magnesium has heretofore been proposed. (See: Kroll 1,359,813 (1920) and 1,740,857 (1929); Gadeau 2,069,705 (1937); Donahue 2,072,067 (1937); Cooper 2,076,067 (1937); Merlub-Sobel 2,135,983 (1938); Adamoli 2,193,363/4 (1940); and Willimore, et al., 2,383,281 (1945).) The major difficulty involved in such a general reduction reaction, however, is that the reducing agent (Mg) is of such low specific gravity that on melting it rises to the surface of the halide fusion limiting the reduction reaction to the contacting surfaces of the molten halide fusion and molten reducing agent.

Another difficulty is that when the temperature of the reduction is permitted to exceed the boiling point of the magnesium, the reduction reaction tends to reverse itself with the beryllium reducing the magnesium halide.

A further difficulty is that when halide compounds of metals having boiling points below that of the temperature of reduction are present in the fusion mixture, these halide compounds also are at least in part reduced.

Another great difficulty is that the high chemical activity of beryllium and magnesium as well as the high chemical activity of those associated metals likely to be reduced by magnesium under the reducing conditions involved, has heretofore generally necessitated the practice of this reduction reaction in a container closed to the atmosphere or in the presence of an inert atmosphere to

2

avoid oxide and nitride contamination in the reduced metal.

These several difficulties and others not enumerated have occasioned the development of the various processes noted in the above patents. I have discovered, however, that by reducing beryllium fluoride with magnesium at a temperature intermediate the melting and boiling points of magnesium while in fusion dilution with an alkaline earth metal fluoride forming with the magnesium fluoride reaction product a fluoride mixture having a melting point below the boiling point of the magnesium, thereafter agglomerating the beryllium metal powder product of the reduction reaction into a semi-sintered porous mass by extended quiescent heating at elevated temperatures approximating but below the boiling point of magnesium and segregating the porous mass from the major part of the fluoride fusion before heating the sintered mass to temperatures approximating the melting point of beryllium, the major part of the difficulties hereinabove set forth are avoided and that beryllium metal of a high degree of purity can be obtained.

I have further discovered that by the practice of this general reduction method in modified form, various desired beryllium-base alloys and light metal alloys of beryllium may also be obtained.

In the practice of the present invention various alternative procedures may be followed without essential departure from the invention as one skilled in the art will perceive from the disclosure of the specific embodiments hereinafter made.

As one specific embodiment of the present invention, but not as a limitation of the same, the invention will first be described as it has been adapted to the production of substantially pure beryllium metal in solid, coherent form.

In this adaptation substantially pure anhydrous beryllium fluoride, prepared by any of the well known methods, is mixed with high grade substantially pure calcium fluoride in approximately equal molar weights. Such a mixture of beryllium and calcium fluoride has a melting point approximating 700° C.

A known weight of this mixture is charged into an open graphite crucible and the crucible and its contents is heated to a temperature approximating 800° C. Preferably the heating of the crucible is accomplished by means of induced electric cur-

rents or by heat radiated from incandesced electrical resistance heating elements.

When a clear liquid fusion of the fluoride mixture is obtained at about 800° C., magnesium metal in massive form, such as ingots or pigs, is charged into the open crucible, in an amount relative to the beryllium fluoride content to provide an excess of magnesium over that theoretically required for reduction in accordance with the following equation:

$$BeF_2 \cdot CaF_2 + Mg = Be + MgF_2 \cdot CaF_2$$

The amount of such excess magnesium may vary widely without essential departure from the present invention, inasmuch as any excess magnesium remaining may subsequently be readily distilled from the beryllium at temperatures approximating and above the melting point of beryllium. Ordinarily, and for the purposes of assuring substantially complete reduction of the BeF_2 content of the fluoride fusion and to provide adequate excess magnesium to protect the beryllium from oxidation during melting, I have found that 5 to 10% excess magnesium is sufficient.

In adding the magnesium to the molten fluoride fusion I have found it preferable to hold the magnesium down under the surface of the fluoride fusion until it melts and rises to the surface of the fusion. To accelerate the rate of reaction I have also found it desirable to stir the molten fusion and molten metal in such manner as to interfere with the normal tendency of the beryllium metal to segregate in the upper portion of the fluoride fusion below the molten magnesium, thus blocking the continuance of the reduction reaction to completion.

The rate of reaction, with stirring as preferred, is relatively rapid even in large reacting amounts, but is relatively quiet due to the dilution of the BeF_2 by the alkaline earth metal fluoride present. The amount of heat evolution in the reduction is such as to raise the temperature of the fusion to about 1000° C., which is above the melting point of the $MgF_2 \cdot CaF_2$ mixture resulting from the reduction reaction.

At the conclusion of the reduction reaction, stirring of the bath is terminated and the fusion is maintained quiescent at a temperature approximating but substantially below 1100° C., (the B. P. of magnesium) for an extended time interval to permit the beryllium metal powder suspended throughout the fusion to agglomerate together in the upper portion of the fusion into a semi-sintered porous metallic mass.

The semi-sintered porous metallic mass is then separated from the major portion of the molten fluoride compounds, preferably by draining or decanting the liquid fluoride fusion therefrom as completely as possible, and the said mass is then heated to a temperature approximating 1300° C. to melt the beryllium. The residual fluoride fusion in the porous mass protects the beryllium metal powder from oxidation at temperatures below the boiling point of magnesium and the magnesium vapors arising above about 1100° C. protect the beryllium metal powder from oxidation until it is molten. Extended heating of the molten beryllium while in contact with the residual fluoride fusion present should be avoided to reduce the beryllium losses, incident to a reversal of the reduction reaction, to a low order.

I have found it preferable to heat the porous metal mass relatively quickly to the melting point of the beryllium, and after fusion to cool the

crucible and its contents relatively quickly to a temperature below the solidification temperature of the molten beryllium metal, and to separate the solidified metal from the fluoride fusion before heating the beryllium for any extended time interval at temperatures above 1300° C. to distill therefrom the residual magnesium present therein.

To remove the residual magnesium from the solidified molten beryllium I have found it sufficient to melt the beryllium in one end of an elongated chamber or container open to the atmosphere through a small opening in the opposite end, which end is air-cooled to a temperature below the boiling point of magnesium. In such a chamber or container the magnesium vapors evolved from the molten beryllium metal at the heated end are condensed at the cooler end but the magnesium vapors intermediate the ends provide a protective reducing atmosphere over the molten beryllium metal preventing the air from contacting therewith.

By the practice of this method of heating, solid coherent beryllium metal of a high degree of purity may be readily obtained, the precise degree of purity being dependent upon the purity of the fluoride compounds and magnesium employed and upon the amount of contaminating impurities extracted from the graphite crucibles employed. Beryllium metal having a purity as high as 99.8% is usually obtained without much difficulty. Various economies may be effected in the process without essential departure therefrom, as one skilled in the art will perceive.

As a second specific embodiment of the present invention, the practice of the invention in the preparation of aluminum-beryllium alloys will be described. In the formation of light metal alloys of beryllium a plurality of different alloys may be produced by the practice of this invention.

At the present time considerable amounts of beryllium are desired in the form of aluminum-beryllium or aluminum-beryllium-magnesium alloys of relatively high beryllium content for addition to aluminum and aluminum-magnesium alloys to form relatively low beryllium content aluminum or aluminum-magnesium final alloys. These high beryllium content aluminum or aluminum-magnesium alloys are known in the art as "master" alloys, or "hardener" alloys.

The adaptation of the present invention to the production of the so-called "master" alloys of aluminum-beryllium or aluminum-magnesium-beryllium containing from 5 to 25% beryllium will be described. In this adaptation substantially the same practice is followed as hereinabove disclosed during the reduction reaction except that where an alloy of aluminum and beryllium substantially free of magnesium is desired, the amount of magnesium added to the fluoride fusion is substantially less than that empirically required to ensure the substantial conversion of all of the beryllium fluoride to magnesium fluoride during the reduction reaction. Where aluminum-magnesium-beryllium alloys are desired the amount of the magnesium employed is increased to provide an excess approximating that desired in the final alloy.

Following the practice of the reduction reaction above disclosed, aluminum, preferably in small pieces, is gradually added to the fusion in the total amount required to form the desired percent aluminum-beryllium alloy, and the temperature of the bath is maintained high enough to prevent solidification of the alloy until substantially all of the beryllium has been dissolved

by the aluminum. This temperature usually is below the boiling point of magnesium.

Alternatively, the aluminum may be added with the magnesium, separately or in the form of an aluminum-magnesium alloy, with an extended time of heating and with stirring as above described, to obtain substantially complete reduction of the beryllium fluoride content of the fluoride fusion or such a percentage reduction thereof, as may be desired.

This alternative procedure is preferred in the case of forming aluminum-magnesium-beryllium alloys, as in this instance, the reduction reaction may be permitted to proceed for the required time interval to obtain in the aluminum-magnesium alloy the desired beryllium content.

In this modification of the present invention, the beryllium as it is reduced to metal by the magnesium content of the molten aluminum-magnesium alloy enters directly into solution in the molten aluminum, and the recovery of the same from the molten fluoride fusion thereby is greatly simplified, it only being necessary to cool the crucible to the solidification temperature of the resultant aluminum-beryllium alloy to permit its removal from the crucible free of associated fused fluoride salts. Alternatively, the molten beryllium-aluminum alloy may be poured off into one ladle and the molten salt into another, if desired.

As a typical example of the practice of this modification, a fluoride fusion mixture containing about 580 grams BeF_2 and 700 grams of CaF_2, when reduced by 200 grams of magnesium produces on the addition of 700 grams of aluminum, either at the time of the magnesium addition or after the magnesium reduction has been completed, an alloy containing approximately 12% Be, approximately 15% Mg, balance Al.

This alloy is particularly well suited for use as a master alloy in the forming of aluminum-base alloys containing both magnesium and beryllium, particularly where the beryllium content of the resultant final alloy is limited to relatively small or low fractional percentages. Beryllium contents as low as 5% and as high as 20% are readily obtainable in the practice of this invention, in the aluminum and in the aluminum-magnesium base.

One of the major advantages of forming Al.Be master alloys in this manner is that relatively impure magnesium and aluminum may be employed instead of substantially pure metal. This permits the utilization of relatively large amounts of so-called scrap Al or scrap Mg in the practice of the present invention, as most of the alloying constituents present in these scrap metals are normally to be found as constituents in the final Be-containing aluminum alloy.

By the practice of this general method, it is likewise possible to introduce into the master alloy of Al.Be or Al.Mg and Be, as well as into the substantially pure Be prepared in accordance with the present invention, various desired rare, rare earth and heavy metal constituents by incorporating in the halide fusion mixture desired amounts of magnesium-reducible salts of these metals, the molten beryllium, or beryllium-aluminum alloy or an alloy of beryllium aluminum and magnesium functioning to dissolve these desired alloy metals.

In place of magnesium, several other metals may be employed as a reducing agent in the practice of the present invention, such as Ca, Ba, Sr

and Li. Each of these metals lie above beryllium in the halide displacement series and have favorable melting and boiling points. If desired the reducing action of magnesium may be supplemented by one or more of these metals. Due to the difficulty of obtaining these metals in the pure state and of introducing the same into the halide fusion mixture in the substantially pure state, alloys of these metals with either magnesium or aluminum are preferred as reducing agents in the practice of this invention.

In place of calcium fluoride, barium and strontium fluorides may be substituted in part or in whole in the practice of the present invention. Lithium fluoride also may be substituted in part or in whole for the alkaline earth metal fluoride.

Various other modifications and departures will occur to those skilled in the art and all such modifications and departures are contemplated as may fall within the scope of the following claims.

What I claim is:

1. The method of reducing beryllium fluoride with the resulting production of metallic beryllium substantially free of any impurity introduced in the course of said reduction which comprises forming a molten bath consisting essentially of a mixture of beryllium fluoride and calcium fluoride having a melting point between about 650° and 1100° C., adding metallic magnesium to the molten bath within said temperature range in amount sufficient to reduce the beryllium content of the bath to metallic beryllium, maintaining agitation of the bath throughout the reduction reaction with the resulting production of finely divided metallic beryllium suspended in a molten bath composed essentially of magnesium fluoride and calcium fluoride together with any unreduced beryllium fluoride, and subsequently recovering the metallic beryllium from the reaction mass.

2. The method according to claim 1 in which the metallic beryllium is recovered from the reaction mass by segregating the metallic beryllium from the major portion of the molten magnesium fluoride-calcium fluoride bath, and heating the segregated metallic beryllium product to a temperature sufficient to melt and thereby recover the metallic beryllium.

3. The method according to claim 1 in which the metallic beryllium is recovered by dissolving the beryllium formed during the reduction reaction in metallic aluminum, and then separating the resulting molten aluminum-beryllium mixture from the other reaction products.

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