Patented Aug. 7, 1945

2,381,291

UNITED STATES PATENT OFFICE

2,381,291

PROCESS FOR PRODUCING BERYLLIUM

Bengt R. F. Kjellgren, University Heights, Ohio, assignor to The Brush Beryllium Company, Cleveland, Ohio, a corporation of Ohio

No Drawing. Application September 18, 1941, Serial No. 411,403

14 Claims. (Cl. 75—84)

This invention relates to a process for obtaining metallic beryllium from fluoridic beryllium materials by reducing the latter with magnesium at elevated temperatures. It relates especially to an improved process of the type described in which a portion of the fluoridic beryllium material is left unreduced so that its beryllium fluoride content may act to flux the magnesium fluoride which is formed as one product of the reduction reaction. By so conducting the reduction, a fluid slag of magnesium fluoride and beryllium fluoride is formed. The metallic beryllium liberated by the reduction may be readily separated from this slag and in addition, the slag may subsequently be disintegrated easily and its beryllium fluoride content recovered and recycled.

The basic reaction involved in the process is given by the equation:

$$BeF_2+Mg=Be+MgF_2$$

It of course has long been known that magnesium reduces beryllium halides with the formation of metallic beryllium and the corresponding halide of magnesium. In attempting to utilize the reaction, prior workers have encountered numerous difficulties not only in controlling the reaction and in separating the particles of reduced beryllium from the magnesium fluoride, but also in melting and coalescing the particles of reduced metal into a body of dense beryllium. Various workers have found that under some conditions the reaction proceeds so rapidly as to become violent and dangerous, and results in a loss of the beryllium salt through vaporization, and a loss of the metallic magnesium by burning. In attempting to reduce the speed of the reaction, some workers have diluted the beryllium salt with other salts of an inert nature. Other workers have attempted to reduce the rate of reaction by alloying the magnesium with another metal capable of dissolving the metallic beryllium which is reduced, thereby producing a beryllium alloy as one of the end products. The few workers who have attempted to use the reaction without such expedients have been relatively unsuccessful in providing a commercial process. One worker of very recent date has stated categorically that it is impossible to use the reaction commercially. The present invention, however, contravenes this latter statement and provides a process in which the reaction is fully controllable and in which it is possible to produce metallic beryllium of very high purity while utilizing the metallic magnesium with an efficiency of 90% or better. According to this invention, the reaction is kept under control by starting with solid magnesium and solid fluoridic salts, and by completing the reduction at relatively low temperatures (around 900° C.), and in all events at temperatures below the melting point of metallic beryllium. By these measures, the heat generated by the reduction is absorbed, as fast as it is liberated, partly in melting the reacting components and partly in heating the reacting mass. In this way, the heat of the reaction is prevented from heating any of the components to such a high temperature as to cause the rapid rates of reaction which are largely responsible for the violence and uncontrollability of prior art processes. The invention will be understood more fully from the following objects and the accompanying detailed description.

It is an object of the invention to provide an efficient process for reducing fluoridic beryllium salts by means of magnesium.

It is another object to provide a process wherein a considerable quantity of the fluoridic salt remains in the form of unreduced beryllium fluoride after substantially all of the magnesium has been consumed.

It is another object to provide a process in which a part of the fluoridic salt introduced into the reaction vessel remains unreduced and is effective in fluxing the magnesium fluoride which is produced by the reaction, thereby forming a slag which is fluid at the temperatures involved in the process and which may, when solidified, be leached to selectively dissolve and recover the beryllium-containing materials thereof.

It is another object to provide an efficient process of the type described in which recoveries are maintained at a high level by recycling the valuable components of all waste products.

It is another object to provide an improved process for reduced fluoridic beryllium salts by means of magnesium at elevated temperatures without resorting to vacuum or inert atmospheres.

It is another object to produce metallic beryllium from beryllium fluoride at elevated temperatures without losing appreciable amounts of beryllium fluoride by vaporization and without losing appreciable amounts of metallic beryllium by oxidation.

It is another object to reduce ammonium beryllium fluoride directly with magnesium so that the ammonium fluoride component may be utilized to provide protection against oxidation of the magnesium and beryllium.

Another object is to provide a process of the type described in which silicon compounds, occurring as impurities in the reacting components, are prevented to a large extent from being reduced into the metallic beryllium.

Other objects will appear from the following description.

In accordance with the invention, a fluoridic beryllium salt such as beryllium fluoride, ammonium beryllium fluoride, mixtures of these two compounds together, or mixtures of either or both of the compounds with magnesium fluoride,

is caused to react with a lesser quantity of metallic magnesium than is needed to reduce all the beryllium fluoride of the fluoridic salt. The reaction is preferably carried out at temperatures above the melting point of magnesium and below the melting point of beryllium. By reacting the materials in the unbalanced proportions stated, only a part of the fluoridic beryllium salt is reduced by the magnesium, and the remainder is available for use in fluxing the magnesium fluoride which is formed as a product of the reaction. Thus, for example, a quantity of beryllium fluoride, mixed or not with magnesium fluoride, is caused to react with less magnesium than is needed to reduce all of the beryllium fluoride to metallic beryllium. When the reaction begins, there may be no magnesium fluoride present, but as the reaction proceeds, magnesium fluoride is produced as the metallic magnesium is consumed. The magnesium fluoride so formed in situ combines with the unreduced beryllium fluoride to form a slag. When the reaction is complete, the slag has suitable density, fluidity (viscosity) and chemical stability. The composition of the slag changes, of course, as the reaction progresses toward completion, the beryllium fluoride content decreasing gradually with a concurrent increase in the magnesium fluoride content. Those skilled in the art will appreciate, however, that it is possible to proportion the reacting materials at the start of the reaction so that when the reaction is finished, the beryllium fluoride and magnesium fluoride contents will be in the correct ratio to form a slag of the desired composition. The slag which is desired is one which is fluid at temperatures appreciably below the melting point of beryllium and which is relatively stable at temperatures at least slightly above the melting point of beryllium. The compositions of such slags are discussed below. After the reduction has been completed, and a slag of the desired composition has been formed, the whole reaction mass of slag and reduced beryllium may be heated to above the melting point of beryllium, whereupon the reduced particles of metallic beryllium coalesce into a pool of molten beryllium which floats in the molten slag. A thin film of slag covers the molten pool and protects it. After the pool has ben formed, the whole reaction mass may be cooled to below the melting point of beryllium whereupon the pool of beryllium solidifies to form a dense cake of metal which may be removed bodily from the still liquid slag. After the solid cake of beryllium has been removed, the slag may be treated either by cooling it to its freezing point or by pouring it while molten into a quenching medium.

Since the slag produced by the process consists predominantly of water-soluble beryllium fluoride and water-insoluble magnesium fluoride, it is amenable to a selective leaching treatment with water or suitable aqueous solvents. By such treatment it is possible to dissolve the beryllium fluoride (and any beryllium oxide and remnants of metallic beryllium which may also be present) without dissolving appreciable amounts of the magnesium fluoride. The undissolved magnesium fluoride may be discarded, or it may be treated in any suitable manner to convert it to useful materials while the beryllium fluoride, and other materials which have been separated from it, may be recovered as fluorides by suitable processing. The fluorides so recovered may be recycled for reduction with or without further additions of fresh beryllium fluoride. As will be explained more fully hereafter, ammonium beryllium fluoride may be treated in an analogous manner. When this compound salt is used, the process may be conducted so as to recover not only the beryllium content of the slag, but also to recover the ammonium fluoride which is formed.

From the foregoing brief description of the invention, it will be understood that a greater than stoichiometric quantity of the fluoridic beryllium compound is caused to react with metallic magnesium, and that the excess salt which is not reduced by the magnesium is available for use in fluxing the magnesium fluoride produced in the reaction. It should be recognized, however, that the excess fluoridic compound is employed in the process not only to act as a flux, but also to drive the reaction in the desired direction; that is, to drive the reaction toward the formation of metallic beryllium in accordance with the law of mass action. Moreover, the fluoridic compound serves as a temporary protective covering over the metallic magnesium while the above-mentioned slag of beryllium fluoride and magnesium fluoride is being formed. This latter feature will be more clearly understood from the following examples.

Example 1

Assuming that it is desired to reduce beryllium fluoride by means of the invention to produce about 1.3 pounds of metallic beryllium, the reduction would be carried out as follows: Approximately 4 pounds of magnesium, preferably in the form of small beads, nodules, sticks or lumps, is provided along with about 11 pounds of solid beryllium fluoride which has been crushed or otherwise brought to a divided condition. Preferably the beryllium fluoride should all pass through a ½" screen. The foregoing quantities of divided magnesium and divided beryllium fluoride should be separated into a number of equal portions or charges. For example, five charges could be prepared, each containing .8 of a pound of magnesium and 2.2 pounds of beryllium fluoride. A graphite crucible heated by any suitable means, such as by induction heating or by means of a gas flame, or otherwise, is brought to a temperature sufficient to melt beryllium fluoride (about 800° C.). One of said five charges is then introduced, the divided magnesium thereof being placed in the bottom of the crucible and being covered with the divided beryllium fluoride of the charge. When the magnesium and the beryllium fluoride of this first charge have begun to melt, the magnesium of the second charge is introduced on top of the beryllium fluoride layer of the first. When this latter portion of magnesium has begun to melt, it is covered in turn with the beryllium fluoride of the second charge. The procedure is repeated in the same manner until all five charges have thus been added in alternate layers. The crucible may then be covered loosely with any suitable cover and its temperature raised slowly toward the melting point of beryllium. The rate of heating should be such that the melting point will be reached in about 45 minutes. A short time (usually 15 to 30 minutes) after the last charge has been introduced, the cover may be removed from the crucible and the contents inspected. Stirring may then reveal some unmelted lumps. If so, these should be broken up somewhat. Heating may then be continued until all of the materials of the charge have been melted and have become fluid. It will

be understood, of course, that during this interval of time, the magnesium will have been in reaction with the beryllium fluoride to form magnesium fluoride and metallic beryllium. The metallic beryllium is, of course, in the solid state at the temperature indicated, but is in the form of fine particles dispersed through the melt. The magnesium fluoride combines with the unreduced beryllium fluoride to form a slag which becomes progressively richer in magnesium fluoride. With magnesium and beryllium fluoride proportioned as stated above, the final slag would contain about 25 to 30% of beryllium fluoride, balance substantially all magnesium fluoride. Such a slag melts around 900° C., but does not become sufficiently fluid until its temperature has been raised to about 1100° C. After the operator has determined that all of the charge has been melted, he may raise the temperature more or less rapidly to just slightly above the melting point of berryllium. The slag then becomes fluid and the particles of beryllium rise to the surface and float in the slag without breaking through the surface skin of the latter. By the time the contents of the crucible have reached the melting point of beryllium, the particles of beryllium will have coalesced into a visible mass which finally melts to form a pool of molten beryllium. As soon as that occurs, the heating may be discontinued. Within a few minutes thereafter, the whole contents will have cooled down to below the melting point of beryllium, and the pool of beryllium will soon solidify to form a cake of solid beryllium which remains floating just under the surface of the slag. When the operator has determined that the beryllium cake has solidified completely, he may pick it out of the crucible. The slag may then be poured out of the crucible into either a granulating trough filled with a quenching medium, or into any suitable container to harden. The crucible may then be scraped clean and is ready for use in treating a further batch. When the slag is to be granulated, it is preferably poured into water which has been acidified with hydrofluoric acid or ammonium bifluoride. When it is quenched and granulated in such a solution, it disintegrates rapidly, the beryllium fluoride and any beryllium oxide or metallic beryllium going into solution and the magnesium fluoride remaining undissolved. After all of it has disintegrated and its beryllium content has been dissolved, the undissolved magnesium fluoride may be filtered out and the filtrate may be clarified in a suitable manner. An analysis of the clarified solution shows that it contains practically all of the unreduced beryllium fluoride which remained in the slag, in addition to practically all of the beryllium oxide and metallic beryllium of the slag. The solution is next processed so as to recover its beryllium content in the form of a solid fluoridic salt of beryllium, usually beryllium fluoride. The beryllium fluoride so recovered may then be recycled through the reduction process, or it may be mixed with fresh beryllium fluoride before being recycled. Examination of the magnesium fluoride residue from the filter has shown that it contains practically no metallic beryllium and is entirely free from beryllium fluoride and oxide. It accordingly may be discarded as a waste product, if desired.

Example 2

If it is desired to produce metallic beryllium by reduction of ammonium beryllium fluoride, this latter material may be treated in either one of two ways:

(*a*) The ammonium beryllium fluoride may be heated in any suitable manner and in any suitable container to a temperature of about 950° C., at which temperature it will have been decomposed thermally into ammonium fluoride and beryllium fluoride in accordance with the following equation

$$2NH_4F \cdot BeF_2 \rightarrow 2NH_4F + BeF_2$$

The ammonium fluoride is liberated in the form of vapor and hence is readily expelled from the container and may be recovered by condensing it outside of the container. The beryllium fluoride remains in the container in the molten state, and after it has been heated for a sufficient period of time to drive off all ammonium fluoride, it may be poured out of the container into molds, or onto a surface which causes the molten material to break up into relatively small lumps. In any event, after the beryllium fluoride has been solidified outside of the container, it is subsequently crushed and treated in accordance with the process outlined in Example 1 above.

(*b*) The ammonium beryllium fluoride may be reduced directly by thermal reaction with magnesium. The process by which this may be accomplished is similar to the process of Example 1 in that ammonium beryllium fluoride in a divided form is introduced into the reduction crucible in layers which alternate with the sticks, lumps or beads of metallic magnesium. The proportions, of course, are somewhat different; for example, if it is desired to produce 1.3 pounds of metallic beryllium, 4 pounds of metallic magnesium would be provided together with about 28.5 pounds of ammonium beryllium fluoride. Such proportions yield a final slag which contains between 20% and 30% of beryllium fluoride. It will be recognized, of course, that after the reduction mixture has been placed in the crucible in the manner outlined in Example 1, the ammonium beryllium fluoride will undergo thermal decomposition, liberating vapors of ammonium fluoride and forming molten beryllium fluoride. Thus the same ultimate reaction is involved in reducing ammonium beryllium fluoride as in reducing beryllium fluoride since it is the beryllium fluoride component of the former which reacts with the magnesium to form metallic beryllium. The slag which is formed is effective in protecting the contents, just as in the process of Example 1, but it will also be appreciated that the ammonium fluoride vapors liberated in situ also are helpful in excluding air from the crucible and thereby in reducing oxidation of the metallic magnesium and reduced beryllium. The vapors, of course, may be recovered by condensation or otherwise outside of the crucible and may be recycled. Recycling is desirable as a means of recovering the rather large amounts of beryllium fluoride vapors which are generally contained in the ammonium fluoride vapors.

Example 3

When beryllium oxide is the material at hand from which it is desired to recover metallic beryllium, it may be converted into either ammonium beryllium fluoride or beryllium fluoride and then reduced in accordance with the processes of the foregoing examples. Thus beryllium oxide may be dissolved in an acid solution of ammonium fluoride, ammonium bifluoride, or mixtures of either of these materials with hydrofluoric acid. It is preferable to employ the latter mixtures of ammonium salts rather than hydrofluoric acid alone, so as to form the double am-

monium beryllium fluoride rather than beryllium fluoride since the double salt may be selectively crystallized from the solution. The crystallized double salt is anhydrous and may be obtained in a fairly pure state. Such salt is suitable for direct reaction with magnesium in accordance with Example 2 (*b*), or it may be decomposed thermally to give beryllium fluoride as outlined in Example 2 (*a*).

From the foregoing examples it will be recognized that the process is one which may be operated with very high over-all efficiencies since the beryllium content of the slag may be fully recovered, and since the beryllium content of other intermediate products may also be recovered. Thus the slag may be leached until it is completely free of beryllium either as beryllium fluoride, as beryllium oxide, or as metallic beryllium. Accordingly the magnesium fluoride which is discarded carries little if any beryllium and introduces no beryllium loss to the process. In the same manner the fumes which are produced either during the thermal decomposition of ammonium beryllium fluoride as in Example 2 (*a*), or the fumes produced during the reduction of beryllium fluoride in accordance with Examples 1, 2 (*b*), or 3 may also be recovered so that no loss of beryllium as beryllium fluoride or otherwise is occasioned. In consequence of these features of the process I have found that the cyclic process may be operated so that the metal recovered as metallic beryllium accounts for at least 90% of the theoretical amount recoverable. Furthermore, the efficiency of the process as a whole, from the standpoint of beryllium recovered from the system in comparison with the beryllium introduced, is at least 90%, and under most conditions may be well in excess of 95%.

As indicated previously, the process is characterized by using a portion of the reducible fluoridic beryllium salt as a flux to form a slag with the magnesium fluoride. The slag which is formed should, of course, be rather fluid at temperatures around 1200° C. and preferably should have a relatively low viscosity at the melting point of beryllium. Likewise, the slag should have a density which is materially greater than the density of solid beryllium since greater densities aid in improving the gravitational separation and subsequent coalescence of the solid beryllium particles into a mass which ultimately forms the molten pool of beryllium. In this respect also, it will be recognized that the viscosity of the slag is an important factor since even if a slag had a much greater density than that of metallic beryllium, the viscosity might be such that the particles of metallic beryllium would be prevented from rising to the surface and coalescing.

It has been indicated above that it is preferable to separate the reduced beryllium from the slag by coalescing and melting the particles of solid beryllium to form a molten pool which may subsequently be solidified and removed from the still liquid slag. Since this type of separation is simple and very effective, it will be recognized that when it is used, the slag which is formed should preferably be relatively stable at the melting point of beryllium. It has been found that slags containing between about 20% and 50% of beryllium fluoride have suitable fluidity, viscosity and density and also are moderately stable chemically. To produce such slags, the process is carried out by using an excess of beryllium fluoride over stoichiometric proportions which is between about .45 mol and 1.33 mols per mol of magnesium consumed; stated in another way, the reagents are proportioned so that between about 1.45 and 2.33 mols of beryllium fluoride are used per mol of magnesium. While all slags of this range of compositions fume to some extent, slags containing around 20% to 35% beryllium fluoride fume appreciably less than those containing larger amounts of beryllium fluoride. It therefore is preferable to operate the process so that slags of the lower beryllium fluoride content are formed as final slags. As indicated, however, this is not a strict necessity, and slags containing as much as 50% beryllium fluoride may be utilized without detriment to the over-all efficiency of the process if provision is made for recovering the greater quantities of fumes which are produced.

In addition to the advantages which are apparent from the foregoing description, the process has a further advantage in its effect on the small amount of silicon which usually occurs as an impurity in the reducible beryllium compounds. Operation of the process described herein has shown that even though the ammonium beryllium fluoride or beryllium fluoride is contaminated with silicon, the metallic beryllium obtained from the process is remarkably free from silicon. This is explained by the observation that silicon forms a volatile fluoride, and that this fluoride is expelled at least in part when the beryllium compounds are heated. Thus, when ammonium beryllium fluoride is decomposed thermally as in Example 2 (*a*), the fumes of ammonium fluoride are accompanied with fumes of silicon fluoride. The high temperature treatments involved in the process help to eliminate the silicon before it has an opportunity to find its way into the metallic beryllium.

When pure magnesium and fluoridic beryllium salts are used, the process is capable of producing metallic beryllium of exceptionally high purity. In such cases, the principal impurity found in it is magnesium. The composition of the slag is such, however, that the magnesium content is seldom over a few tenths of one per cent. Accordingly, the beryllium is generally better than 99% pure. As pointed out previously, the excess beryllium fluoride in the slag helps to drive the reduction toward completion, thus causing the magnesium to be almost entirely consumed, and preventing the presence of appreciable amounts of magnesium in the beryllium. In this respect the slag is also effective for use in a subsequent purification step. When the slag is used to remove the last few tenths of a per cent of magnesium from the beryllium, its beryllium fluoride content should be greater than that of the slag which was formed when the beryllium was produced. Thus, if the slag which was produced by the reduction process contained about 25% beryllium fluoride, purification should be effected with a fresh slag whose beryllium fluoride content is between 35% and 50%, and is preferably at the latter value. A fresh slag having the same beryllium fluoride content as that of the slag produced in the reduction process is relatively ineffective in removing magnesium, since the magnesium exists apparently as a result of an equilibrium. This equilibrium needs to be shifted in order to remove the magnesium from the beryllium. This shift can be accomplished by increasing the beryllium fluoride concentration of the slag. By purifying the beryllium under such conditions, its purity may be increased to well over 99.5%.

The slag is also useful in treating particles of beryllium, such as turnings, chips, powders, small lumps, etc., since by floating these particles beneath the surface of the molten slag while heating them to the melting point of beryllium, they can be coalesced into a pool of molten compact beryllium in the same manner as described above.

Having now disclosed the invention, what is claimed is:

1. A process for producing beryllium by thermal reduction of a fluoridic beryllium salt selected from the group consisting of beryllium fluoride, ammonium beryllium fluoride and mixtures of these salts with each other, said process comprising the steps of: reacting to completion a greater than stoichiometric quantity of said fluoridic beryllium salt with metallic magnesium at temperatures above the melting point of magnesium and below the melting point of metallic beryllium to induce the formation of magnesium fluoride and solid metallic beryllium, the excess of said fluoridic salt over stoichiometric proportions being between about .45 and 1.33 mols per mol of magnesium consumed in the reaction and thereby being sufficient to form with the magnesium fluoride produced by the reduction a slag which is fluid at temperatures around the melting point of beryllium; thereafter heating the reaction mass to above the melting point of beryllium to coalesce the reduced beryllium into a pool of molten metal; and separating the coalesced beryllium from the beryllium fluoride-magnesium fluoride slag which remains.

2. A process for producing beryllium by thermal reduction of a fluoridic beryllium salt selected from the group consisting of beryllium fluoride, ammonium beryllium fluoride and mixtures of these salts with each other, said process comprising the steps of: reacting to completion a greater than stoichiometric quantity of said fluoridic beryllium salt with metallic magnesium at temperatures above the melting point of beryllium fluoride and below the melting point of metallic beryllium to induce the formation of magnesium fluoride and solid metallic beryllium, the excess of said fluoridic salt over stoichiometric proportions being between about .45 and 1.33 mols per mol of magnesium consumed in the reaction and thereby being sufficient to form with the magnesium fluoride produced by the reduction a slag which is fluid at temperatures around the melting point of beryllium; thereafter heating the reaction mass to above the melting point of beryllium to coalesce the reduced beryllium into a pool of molten metal; separating the coalesced beryllium from the beryllium fluoride-magnesium fluoride slag which remains; leaching the soluble beryllium-containing components of said slag from the remaining insoluble magnesium-containing components thereof; and recycling the beryllium-containing components so recovered from the slag.

3. A process for producing metallic beryllium from beryllium oxide, said process comprising the steps of: converting the beryllium oxide to ammonium beryllium fluoride; decomposing the ammonium beryllium fluoride thermally to produce beryllium fluoride and vaporous ammonium fluoride; condensing the vaporous ammonium fluoride and recycling it for reaction with additional beryllium oxide to form additional ammonium beryllium fluoride; reacting to completion a greater than stoichiometric quantity of the beryllium fluoride with metallic magnesium at temperatures which induce the formation of magnesium fluoride and solid metallic beryllium, the excess of said beryllium fluoride over stoichiometric proportions being between .45 and 1.33 mols per mol of magnesium consumed in the reaction and thereby being sufficient to form with the magnesium fluoride produced by the reduction a slag which is fluid at temperatures around the melting point of beryllium; increasing the temperature of the reaction mixture to melt the beryllium so reduced and to cause it to coalesce; solidifying the coalesced beryllium while the latter remains within the said slag; separating the solidified beryllium from the molten magnesium fluoride-beryllium fluoride slag which remains; solidifying said slag; leaching said slag to dissolve substantially all of its soluble beryllium-containing components without dissolving appreciable amounts of its insoluble magnesium-containing components; converting the soluble beryllium-containing components of the resulting leach liquor into ammonium beryllium fluoride; and recycling the latter.

4. A process for producing metallic beryllium from beryllium oxide, said process comprising the steps of: converting the beryllium oxide to ammonium beryllium fluoride; reacting said ammonium beryllium fluoride with metallic magnesium, in the proportions of between about 1.45 and 2.33 mols of beryllium fluoride per mol of magnesium, at temperatures below the melting point of metallic beryllium and for a period of time sufficient to cause all the magnesium to be consumed, thereby to induce the decomposition of said ammonium beryllium fluoride into beryllium fluoride and vaporous ammonium fluoride, and to form magnesium fluoride and solid beryllium; meanwhile condensing the vaporous ammonium fluoride as it is liberated and recycling it for reaction with additional beryllium oxide to form additional ammonium beryllium fluoride; heating the reaction mixture to above the melting point of beryllium to coalesce the reduced beryllium into a pool of molten metal; separating the coalesced beryllium from the beryllium fluoride-magnesium fluoride slag which remains; selectively extracting the beryllium content of said slag from the magnesium fluoride content thereof; converting the beryllium content so extracted into ammonium beryllium fluoride; and recycling the latter.

5. The process as claimed in claim 4 wherein said beryllium oxide is converted to ammonium beryllium fluoride by reacting the oxide with an aqueous solution of a material selected from the group consisting of ammonium bifluoride and mixtures of ammonium fluoride with hydrofluoric acid.

6. The process as claimed in claim 4 wherein said selective extraction is effected by leaching the solidified beryllium fluoride-magnesium fluoride slag with an aqueous solution of a material selected from the group consisting of ammonium bifluoride and mixtures of ammonium fluoride with hydrofluoric acid.

7. A process for producing beryllium by thermal reduction, said process comprising the steps of: introducing into a crucible solid magnesium together with more beryllium fluoride than is required to react with all the magnesium, said excess over the required amount being between .45 and 1.33 mols of beryllium fluoride per mol of magnesium; heating the whole to about 900° C. and holding this temperature until substantially all the metallic magnesium has been consumed in producing magnesium fluoride and metallic

beryllium; thereafter raising the temperature of the whole to above the melting point of beryllium to first liquify the slag which is formed between the said magnesium fluoride and said excess beryllium fluoride and then to cause the metallic beryllium to coalesce into a pool of molten metal; then cooling the whole to solidify the coalesced beryllium without solidifying the said slag; removing the solidified beryllium from said slag; solidifying said slag; leaching said solidified slag to selectively extract the soluble beryllium content thereof without extracting appreciable amounts of its insoluble magnesium fluoride content; and recycling the beryllium content so extracted.

8. A process for producing beryllium by thermal reduction, said process comprising the steps of: introducing metallic magnesium and fluoridic salts of beryllium of the group consisting of beryllium fluoride and ammonium beryllium fluoride into a crucible in the proportions of between about 1.45 and 2.33 mols of beryllium fluoride per mol of magnesium; heating said materials to about 900° C. and holding this temperature until substantially all of said metallic magnesium has been consumed in forming metallic beryllium and a slag consisting predominantly of beryllium fluoride and magnesium fluoride; raising the temperature of the reaction mass to above the melting point of beryllium to first liquify the slag which is formed between said magnesium fluoride and the unconsumed beryllium fluoride and then to cause the metallic beryllium to coalesce into a pool of molten metal; and removing the coalesced beryllium from the said slag.

9. A process for producing metallic beryllium which comprises the steps of: reacting substantially anhydrous fluoridic salts of beryllium of the group consisting of beryllium fluoride and ammonium beryllium fluoride with metallic magnesium at temperatures above the melting point of magnesium but below the melting point of metallic beryllium, said salt and metallic magnesium being proportioned so that the said salt is in excess of stoichiometric proportions and provides an excess of between about .45 and 1.33 mols of beryllium fluoride per mol of magnesium consumed in the reaction, whereby a slag consisting substantially of beryllium fluoride and magnesium fluoride is formed; maintaining the temperature of the reacting mass as aforesaid until the metallic magnesium has been consumed; thereafter raising the temperature of the reaction mass to slightly above the melting point of metallic beryllium to coalesce the reduced beryllium into a pool of molten metal; separating the coalesced beryllium from the said slag; treating said slag to selectively extract the beryllium content thereof; and recycling the beryllium content so extracted.

10. A process for producing beryllium from beryllium oxide, said process comprising the steps of: reacting beryllium oxide with an aqueous solution containing at least one of the compounds selected from the group consisting of ammonium bifluoride and mixtures of ammonium fluoride with hydrofluoric acid, to form ammonium beryllium fluoride; selectively crystallizing the ammonium beryllium fluoride from said solution; thermally decomposing the crystallized ammonium beryllium fluoride into ammonium fluoride and beryllium fluoride; and reacting the beryllium fluoride obtained from said decomposition with metallic magnesium in the proportions of between about 1.45 and 2.33 mols of beryllium fluoride per mol of magnesium at temperatures above the melting point of magnesium and below the melting point of metallic beryllium, said reaction being continued until substantially all of the magnesium has been consumed; separating the metallic beryllium so liberated from the magnesium fluoride-beryllium fluoride slag which remains; solidifying said slag and leaching it with an aqueous fluoride solution containing at least one compound selected from the group consisting of ammonium bifluoride and mixtures of ammonium fluoride with hydrofluoric acid, to dissolve the beryllium fluoride, beryllium oxide and metallic beryllium thereof without dissolving magnesium fluoride therefrom; and recycling the resulting beryllium content of the leaching solution.

11. A process for producing metallic beryllium, said process comprising the steps of: providing a charge consisting of metallic magnesium and a fluoridic beryllium salt selected from the group consisting of beryllium fluoride, ammonium beryllium fluoride and mixtures of these salts with each other, said charge being proportioned so that the said fluoridic salt provides between about 1.45 and 2.33 mols of beryllium fluoride per mol of magnesium; maintaining a crucible heated to above the melting point of magnesium but below the melting point of metallic beryllium while introducing said charge progressively into said crucible in such manner that a plurality of aliquot parts of the metallic magnesium of said charge are disposed alternately in stacked relation with a corresponding number of aliquot parts of said fluoridic salt with each aliquot of magnesium beneath its corresponding aliquot of fluoridic salt; maintaining the temperature of the reaction mass below the melting point of metallic beryllium until substantially all of the magnesium has been consumed in forming metallic beryllium and magnesium fluoride; thereafter heating the reaction mass to above the melting point of beryllium to coalesce the reduced beryllium into a pool of molten metal, and separating the coalesced beryllium from the slag which remains.

12. The method as claimed in claim 11 which includes the additional steps of selectively separating the beryllium-containing components of said slag from the magnesium-containing components thereof; and recycling the beryllium-containing components so separated.

13. A method for coalescing solid particles of metallic beryllium into a compact body, said method comprising the steps of: providing a molten slag containing beryllium fluoride and magnesium fluoride in the proportions of from about 20% to 50% beryllium fluoride and balance magnesium fluoride; and floating said solid particles in said slag beneath the surface thereof while heating the slag and particles from a temperature above about 1000° C. to a temperature slightly above the melting point of beryllium.

14. A slag for use in protecting and treating metallic beryllium, said slag containing beryllium fluoride and magnesium fluoride in the proportions of from about 20% to 50% beryllium fluoride and balance magnesium fluoride.

BENGT R. F. KJELLGREN.