

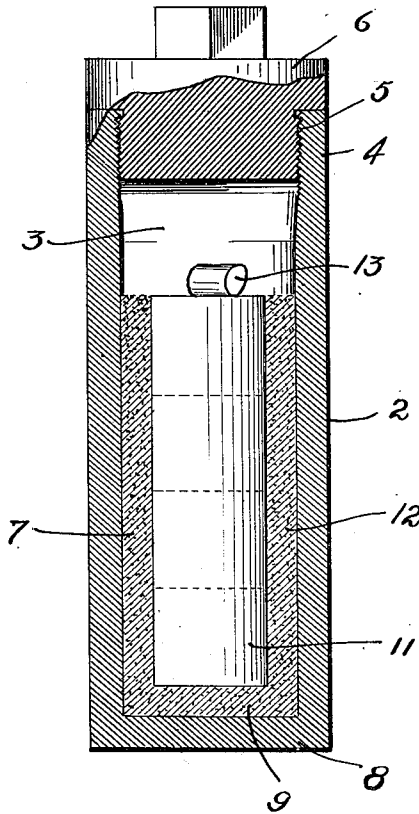
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METHOD OF PREPARING REFRACTORY METALS

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METHOD OF PREPARING REFRACTORY METALS.

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This invention relates to methods of obtaining metals from their compounds and more particularly from the difficultly reducible oxides of the rare refractory metals such as uranium, thorium, and the like.

An object of the present invention is the provision of a process for the production of metals in a high state of purity.

A further object of the invention is the provision of a process which may be controlled to obtain metal powders, particularly the rare refractory metal powders, in varying degrees of fineness.

A further object of the invention is to provide a bomb in which chemical and metallurgical operations may be practiced without the introduction of impurities from the bomb into the products produced therein.

A further object of the invention is to provide a process for protecting the products of the reaction from becoming contaminated by impurities introduced by the container in which the process is practiced.

A still further object is to provide a method of lining a bomb in an expeditious and simple manner.

Other objects of the invention will be apparent from a reading of the following specification.

It has been proposed to obtain the powders of metals, the oxides of which cannot be reduced to metal by means of hydrogen, for example the oxides of uranium, zirconium, thorium, vanadium, tantalum, chromium, titanium, etc. or any other similarly difficultly reducible oxide, by the well known metallurgical processes, one of which involved the reduction of the oxides by means of calcium as a reducing agent. Attempts have also been made to reduce the oxides of certain of the metals mentioned by the alkali metals, but without success. The calcium method is open to objection because of the relative expensiveness of that metal and the impurities contained in the commercial material, also because the heat of reaction is high which causes coarseness of the powders through the agglomerations of the particles thereof.

In order to render effective the alkali metal reduction a further proposal has been made to employ an alkali metal as the reducing agent, together with a fluxing agent such as an alkaline earth halide or an alkali metal halide of a metal other than the alkali metal

employed as the reducing agent. This method has been very successful, although open to several objections when it is the desire to obtain a very pure powder possessing a certain coarseness.

In practicing the methods referred to above, it has been customary to insert the mixed ingredients in an iron bomb, and after sealing the latter, the reaction is started by heating the bomb. The iron, in some manner, finds its way into the metal produced, so that when the powder is sintered to reduce it to the coherent state, it forms, it is believed, with the iron, a low-melting point alloy which forms beads and runs out from the mass leaving cracks in the material and also causing a great deal of trouble in the furnace.

Attempts have been made to prevent the introduction of the iron impurity by lining the bomb with nickel, copper, chromium, etc., but in each case, metallic impurities were introduced which were most undesirable in preparing pure metals.

To illustrate the effect on the physical properties of a metal by the introduction of a small amount of an impurity, reference need only be made to the effect of carbon or any metallic impurity in pure iron. For example, a small amount of silicon or carbon, when introduced into iron, causes the latter to become hard and brittle. The same effect will probably be produced if instead of iron, say uranium or thorium, were used. From our experience with the rare refractory metals and their preparation, we are convinced that when iron is present as an impurity, it is very difficult to obtain the metal with which it is combined in a solid coherent condition owing to the beading previously referred to.

Therefore, in order to provide a process which may be practiced to obtain the rare refractory metal powders in a very pure state and of a predetermined degree of fineness, the following method has been devised.

In practicing our invention we employ as the reducing agent an alkaline earth metal, preferably calcium, and employ as the fluxing agent a halide of the same alkaline earth metal employed as the reducing agent, although the halides of other metals of the alkali or alkaline earth group of metals may be employed. A mixture of the metallic oxide, the alkaline earth metal and the alkaline earth metal halide is formed, the reducing

metal being in about 50% excess of the theoretical quantity required. This mixture is heated in a suitable vessel, preferably a bomb, which is evacuated or provided with any other suitable inert environment from which nitrogen and oxygen are absent.

In the accompanying drawing is illustrated a vertical sectional view, partly in elevation, of a bomb provided with an insulating lining of calcium oxide, within which the charge is placed. The bomb comprises a hollow iron cylinder 2 having a chamber 3 within the same. The bomb may be about 10 inches in height and 4 inches in diameter with a wall thickness of approximately a half inch. The upper end 4 of the bomb is provided with an internal tapered thread 5 into which fits a tapered threaded plug 6 to the threads of which a sealing compound may be applied just previous to the insertion of the plug into the bomb. The inner walls of the chamber 3 in the bomb are preferably provided with an insulating layer 7 of calcium oxide or other satisfactory material which may preferably be applied in a manner more fully described hereinafter.

In placing the mixture into the bomb, we observe the following precautions in order to prevent the introduction of impurities from the bomb. The bottom 8 of the bomb is covered with a layer 9 of pure, specially prepared highly ignited lime which contains no iron, silicon, or insoluble impurities. By insoluble impurities we mean insoluble in dilute acetic acid. After the bottom of the bomb has been covered about a quarter inch deep by thoroughly packing with a clean iron plunger, the mixture of calcium chloride, finely cut calcium, and the rare refractory metal oxide is pressed into cakes 11 somewhat smaller than the inside of the bomb. A cake is placed centrally on the lined bottom of the bomb and lime powder 12 is run in around the cake and packed down with a clean copper or iron ring. Usually, three or four cakes are pressed and put in, one at a time, the lime being packed around each one of them, after its introduction within the bomb, so that the final formation comprises an insulating layer of the lime interposed between the mixture and the walls of the bomb. A piece 13 of calcium is placed upon the uppermost cake to combine with the residual air remaining in the bomb or materials within the same. The bomb is then sealed by inserting the plug 6 after having previously applied a sealing mixture of magnesium oxide and linseed oil thereto. The bomb may be evacuated or provided with an inert environment, although we do not find this necessary as the lump of calcium removes the residual air. The reaction is then started by the external application of heat.

After the reaction is complete and the bomb permitted to cool, the contents thereof may be removed by means of a star drill which is

small enough so that it does not touch the sides of the bomb at any time and which has a stop on the handle so that the drill cannot come closer than $\frac{1}{8}$ " of the bottom. In that way practically all of the charge is removed, but no iron is knocked loose from the bomb mechanically and practically no corrosion can take place or iron be introduced since there is no contact between the specimen and the metal of the bomb.

We may also, if the bomb and the contents are kept cool, disintegrate the charge with water, which process avoids the necessity of cutting loose the charge with a drill. In practicing this method of removal, considerable care should be exercised to have the bomb and contents cool, otherwise the rare metal powder, particularly in the case of uranium, will interact with the hot water and thus destroy the former's purity.

The contents of the bomb upon removal may be treated in any well known manner to remove the undesirable products of the reaction. For example, such purification may consist of washing with dilute acid, water, etc. so that only the pure metal powder remains.

We believe that by practicing the foregoing method more nearly ideal conditions prevail for the production of pure metal powders for the following reasons: First, the alkaline earth metal halide may, with certain refractory oxides, serve as a flux so that the oxide is converted to the chloride, partially at least, where it is readily reduced. Second, the powder which is formed usually settles to the bottom of the fused mass so that the fluid calcium chloride would very effectually seal it away if any leakage in the bomb occurred after the reduction of the metal. Third, the calcium chloride serves as a medium so that the calcium and the oxide come very intimately into contact. The reduction, therefore, by this method, is very complete. Fourth, the alkaline earth metal halide or flux material slows up the reduction and thus provides a means for the regulation of the coarseness of the powder by the excess of the fluxing agent, so that when the temperature of reduction and the excess of reducing agent are once determined, a practically 100% yield of the metal powder may be obtained without losing any large amount of it, which would necessarily have to be screened away on account of it being too coarse to press. By following the method outlined, we have found that the temperature and amount of flux material may be regulated within certain limits so that successive preparations of the powder give uniform results.

In applicants' copending application, Serial No. 504,154, filed September 29, 1921, assigned to the present assignee, reference is made to the use of potassium chlorate for this purpose.

To enable those skilled in the art to practice our invention, we will describe, in detail, one method of applying the principle involved, and, for this purpose, will select uranium oxide as an example of a difficultly reducible oxide, calcium as the alkaline earth metal or reducing agent, and calcium chloride as the alkaline earth halide or fluxing agent.

10 An intimate mixture is prepared in any suitable manner of 92 parts by weight of uranium oxide (UO_2), or under slightly differing conditions equivalent quantities of the other oxides of uranium, a large excess (120 parts by weight) of calcium prepared from purified calcium chloride, and a suitable quantity or about 200 parts by weight of purified calcium chloride. The calcium chloride purchased as chemically pure and labelled "calcined" contains water, and in practicing our process we prefer to carefully dry the same at about $450^\circ C.$ or at a higher temperature, so that it contains only a few tenths of one percent of moisture. If the commercial "calcined" calcium chloride is used, then it is necessary to employ an excess of calcium to combine with the oxygen. It is desirable to have very pure materials, since a small amount of iron for example, appears to cause beading due to the formation of low-melting point alloys, etc. Silicon also makes the metal hard and brittle.

35 The mixture is pressed into cakes somewhat smaller than the bomb into which they are placed. A lining of pure calcium oxide is placed around the cakes in the manner heretofore described, after which the bomb is sealed. The bomb may then be evacuated or provided with an inert environment, or in lieu of this treatment a lump of calcium may be placed on top of the charge, prior to sealing of the bomb, to combine with any residual air remaining within the same. External heat is applied to raise the temperature of the bomb to a bright red heat or about $900^\circ C.$ to $1000^\circ C.$ and this temperature is maintained from two to three hours. The temperature limit to which the bomb is heated depends upon the actual proportion of calcium and calcium chloride used and upon the duration of heating. Definite instructions concerning this matter are not given for the reason the proportions and duration of heating must be varied with different grade oxides, which are used. For example, uranium oxide having the chemical formula UO_2 takes a different temperature, excess of reagents and time of heating than is required for the oxide having the formula U_3O_8 .

65 After the completion of the reaction, the products are allowed to cool and are then removed from the container by means of a drill or the charge is simply disintegrated with water as above indicated. The mass is

treated in any desired manner well known to one skilled in the art to eliminate all but the uranium powder.

The following procedure has been followed in treating the products of the reaction to remove all but the rare refractory metal powder. The mass is allowed to disintegrate in water, the latter being constantly stirred so as to bring about a more intimate contact with the mass. After settling, the supernatant liquor is decanted, and the residue washed with fresh water. The washing treatment is repeated several times after which dilute acetic acid is added to the residue to remove matter soluble therein. The residue is then washed with water and the residue again acidified as before. The acid and water washing treatments are repeated about four times after which the residue is put through a suction filter and washed with distilled water. The distilled water washing in the filter is followed by washing with alcohol. The powder is partially dried by suction and it is then quickly put through a 200 mesh screen a little at a time. If the powder is exposed to the air for a short time, it frequently spontaneously ignites and is burned to oxide so that this must be done quickly. The powder is preserved by being placed in pure alcohol. Before forming the powder into a slug for treatment in accordance with the metallurgical process described in the application of John W. Marden and H. C. Rentschler, Serial No. 432,325, filed December 21, 1920, and assigned to the Westinghouse Lamp Company, it is given the acid-wash treatment described in the application of John W. Marden, Serial No. 583,376, filed August 21, 1922, and assigned to the Westinghouse Lamp Company.

The powder thus produced readily passes the 200 mesh sieve and can be pressed into hard solid cakes having much the appearance of molybdenum under the same conditions. It might be stated that when the powder is too fine it can be filtered only with difficulty and when pressed squeezes out at the sides of the press. When the powder is too fine, it is extremely difficult to degasify in the furnace since the large volume of gas causes cracks to be produced even when extreme care is exercised. It is usually necessary to press and handle pure uranium powder wet with alcohol in order to avoid spontaneous combustion in the air. Also a powder which is too fine shrinks to a large extent in the furnace, yielding misshapen slugs or buttons. When a powder is too coarse it does not hold its shape after pressing, but crumbles and can be handled only with difficulty.

Many other methods may be followed in lining the bomb. For instance, the lining material may be pressed around a core, which latter may be withdrawn, or it may be wetted and painted in. Obviously other materials

may be employed as the lining material, for example, strontium oxide. However, it should be remembered that the material employed or the method followed in lining the bomb with the same should be such as to avoid the introduction of impurities.

If so desired, when calcium and calcium chloride are used as reducing agents, it is possible to completely remove the undesirable products of the reaction and the excess of reducing agents by means of pure alcohol and a solution of an acid in alcohol such as hydrogen chloride, thus avoiding the use of water and contamination due thereto.

In practicing our process we emphasize the importance of employing pure materials in order to obtain the pure refractory metal powders. Therefore, such precautionary measures may be taken, as practice may dictate, of eliminating, as far as is practically possible, from the materials, such as the oxides, the calcium, the calcium chloride, the calcium oxide, and other reagents, any impurities, such as iron, free carbon, carbides, etc., which may be present therein and which may operate detrimentally in reducing the refractory metal powder to the homogeneous coherent condition by heat treatment in the vacuum furnace described in the copending application of Harvey C. Rentschler, Serial Number 430,118 filed December 13, 1920, and assigned to the Westinghouse Lamp Company.

Modifications of the process described above may occur to those skilled in the art, but such as fall within the scope of the appended claims are contemplated by us as forming part of our invention.

What is claimed is:

1. The method of producing rare refractory metals such as uranium, thorium and the like from their difficultly reducible oxides which comprises heating to a reacting temperature such oxides, an alkaline earth metal and an alkaline earth halide.

2. The method of producing rare refractory metals such as uranium, thorium and the like from their difficultly reducible oxides which comprises heating to a reacting temperature such oxides, an alkaline earth metal and an alkaline earth halide, the base of which is the same as the alkaline earth metal employed.

3. The method of producing uranium powder which comprises heating to a reacting temperature an oxide of uranium, an alkaline earth metal and an alkaline earth halide.

4. The method of producing uranium powder which comprises heating to a reacting temperature an oxide of uranium, an alkaline earth metal and an alkaline earth halide, the base of which is the same as the alkaline earth metal employed.

5. The method of producing uranium powder

which comprises heating to a reacting temperature uranium oxide, calcium chloride and calcium.

6. The method which comprises forming a mixture of uranium oxide, and alkaline earth halide and an alkaline metal, enclosing said mixture in a bomb, excluding oxygen and nitrogen from said bomb, raising the mixture to reaction temperature, permitting the bomb to cool, and then treating the reaction products to eliminate all except the uranium.

7. The method of producing uranium powder of any degree of fineness which comprises forming a mixture of any uranium oxide such as UO_2 , an alkaline earth halide and an alkaline earth metal, the proportions of the last named ingredient being in about 50% excess of the theoretical quantity required, placing the mixture in a bomb, excluding oxygen and nitrogen from said bomb, heating the bomb to a red heat for about two hours, permitting the bomb to cool and treating the reaction products to eliminate all but the uranium powder.

8. The method of producing uranium powder of any degree of fineness which comprises heating to a reacting temperature an oxide of uranium, calcium and calcium chloride in predetermined excess proportions and applying heat for a predetermined period depending upon the fineness of powder desired and the particular oxide of uranium used.

9. The method of reducing difficultly reducible oxides of refractory metals which comprises heating the oxide of a refractory metal in the presence of a halide to convert the oxide to a halide and simultaneously reducing the halide thus formed.

10. The method of reducing the difficultly reducible oxides of refractory metals which comprises heating to a reacting temperature, an oxide of a refractory metal and an alkaline earth halide to convert the oxide to a refractory metal halide and simultaneously converting the halide to metal by means of calcium.

11. The method of reducing the difficultly reducible oxides of refractory metals which comprises heating to a reacting temperature, an oxide of a refractory metal and calcium chloride to convert the oxide to refractory metal chloride, rendering ineffective such products of the reaction which prevent the reduction from going to completion and simultaneously reducing the refractory metal halide thus formed by heating the same in the presence of calcium.

12. The method of reducing the difficultly reducible oxides of refractory metals which comprises heating to a reacting temperature, an oxide of the refractory metal, a converting agent capable of converting the oxide to a halide and also capable of removing reaction products which retard further conver-

sion, and a reducing agent capable of reducing said refractory metal halide which is formed during the reaction.

- 5 13. The step in the production of pure rare refractory metal powders by reduction of the oxides in a bomb which consists in insulating the charge from the walls of the bomb by interposing a layer of calcium oxide between the charge and the walls of the bomb.
- 10 14. The step in the production of pure

uranium powder by reduction of an oxide thereof in a bomb, which consists in surrounding the charge with an insulating layer of calcium oxide.

In testimony whereof, we have hereunto subscribed our names this 10th day of February, 1923. 15

JOHN WESLEY MARDEN.
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