

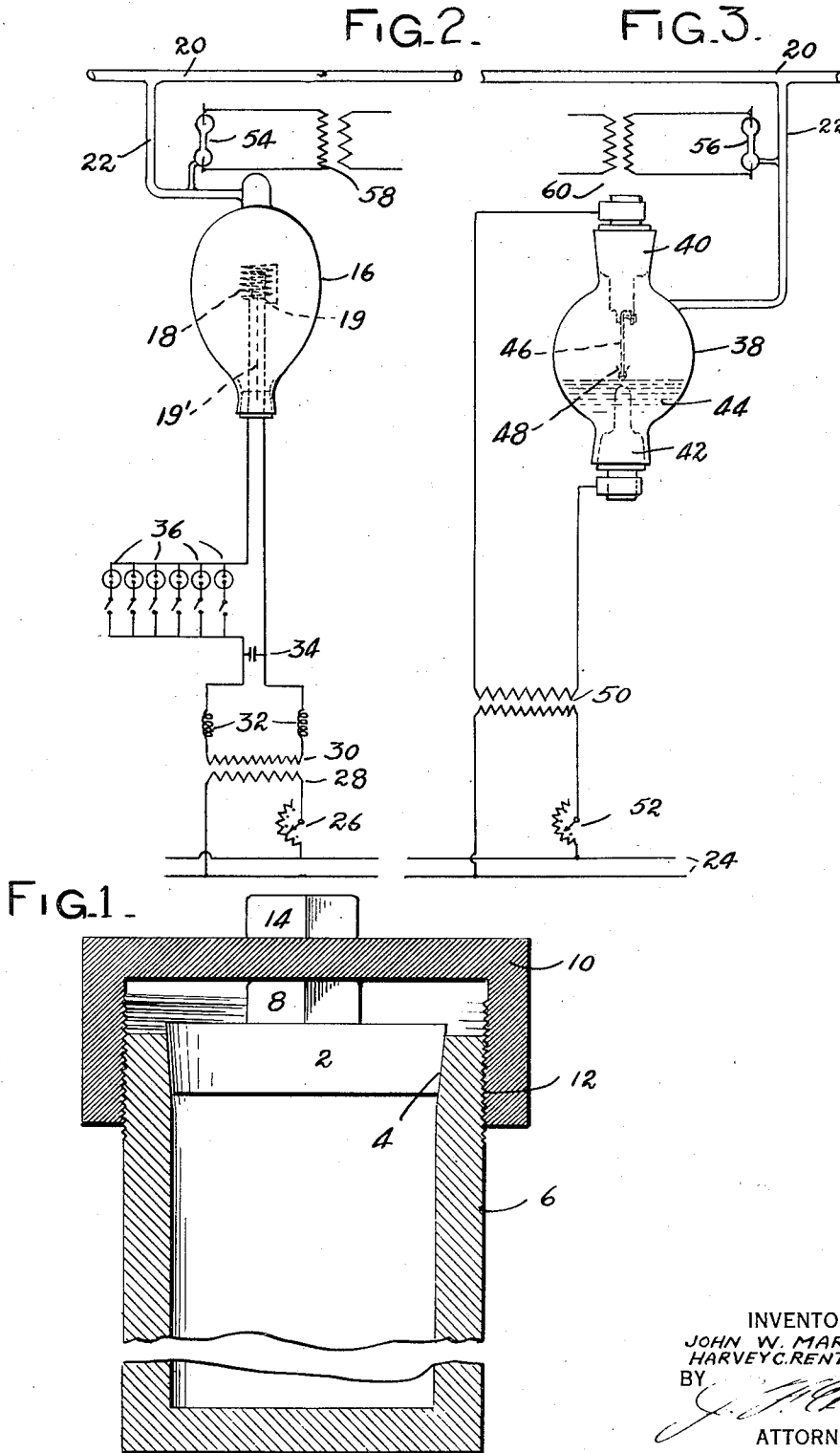
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DUCTILE THORIUM AND METHOD OF MAKING THE SAME

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DUCTILE THORIUM AND METHOD OF MAKING THE SAME

Application filed June 5, 1924. Serial No. 717,940.

This application is a continuation of our prior applications referred to more fully hereinafter.

This invention relates to the production of the more refractory metals such as uranium, thorium, zirconium, titanium, vanadium, chromium, and certain of the rare earth metals, that is, such metals having oxides not completely reducible by hydrogen. More particularly the invention pertains to the production of such metals in a substantially pure, coherent, homogeneous and ductile form.

An object of the invention is to provide a method for the production of such metals or alloys thereof with one another or with other metals in the powder form and in such a manner that their particle size and freedom from deleterious substances affecting their malleability and ductility may be readily and effectively controlled.

It is another object to provide a process for the production of such metals or alloys thereof with one another or with other metals in a coherent and homogeneous form.

It is also an object to provide a process of preparing the metals of the character described in coherent form and substantially free from substances deleteriously affecting their workability or ductility.

It is a further object to provide a commercial process for the production of the more refractory metals, such as those mentioned, in a coherent, homogeneous and ductile form.

It is a still further object to produce coherent, homogeneous, ductile thorium, and the like, that may be readily worked into wire, sheet, disc or other desirable form.

It is yet another object to provide an improved apparatus for carrying out the invention.

Additional objects will become apparent upon reading the description, claims and drawings, in which

Fig. 1 is a view in vertical section of a bomb in which a part of our process is carried out; and

Figs. 2 and 3 are diagrammatic views of

the furnaces for heat-treating the metals and the control circuits therefor.

A number of methods have been proposed heretofore for the production of the metals above mentioned but to our knowledge, no one has succeeded in producing such metals in a homogeneous, coherent and ductile state. Many of these metals are extremely active when in the finely divided state and readily combine with oxygen, nitrogen, and other elements and for that reason, their conversion into the fused or solid, coherent metallic state is attended with the greatest difficulty. The powders of such metals coated with an oxide, for example, cannot be formed into a workable homogeneous body for the reason the oxide prevents the metals from coalescing.

It has been suggested to prepare the powders of the metals of the character specified by the reduction of their oxides by means of calcium under suitable conditions, but no particular attempt was made to control the purity or size of particles of the metal produced, nor was it possible to cause the metallic powders prepared by the calcium reduction process, to coalesce or fuse into coherent, homogeneous and ductile metallic bodies. As early as 1904, Huppertz (Chemisches Centralblatt (1904) vol. 1, page 1383) published a method for the production of the refractory metal powders, such as of titanium and the like, by action of calcium vapor on titanium oxide or other oxides when heated in an electric furnace. A more extensive investigation on the calcium method of reduction of refractory oxides was published by Burger in 1907. (Dissertation at Basel, 1907.) See also Gmelin Kraut Handbuch der Anorganische Chemie. Vol. III, part 1, page 1207. Kuzel and Wedekind (Br. Patent 23,215 Oct. 11, 1909; U. S. Patent 1,088,909, March 3, 1914) have patented this method for the production of many of the metal powders listed above using calcium metal for effecting the reduction. These methods, however, are not satisfactory for preparing metallic powders from which coherent, homogeneous,

ductile metallic bodies may be produced because of contamination, etc.

A method of converting tungsten powder to the coherent metallic state is well known but such method is dependent upon a special process for obtaining the metal powder and also upon a complicated and long drawn out series of mechanical operations before it is had in satisfactory ductile form. This method of preparing ductile tungsten is wholly unsatisfactory for the production of the metals heretofore specified, because of their greater chemical activity and also because their oxides are not reducible by hydrogen.

The present invention, therefore, provides a process for the production of the metals of the character above noted in coherent, homogeneous and ductile form in a practical manner, from stable compounds which are available on the market in relatively large quantities.

In practicing the invention we begin with a compound of the metal, purify it, if necessary, reduce the same and subsequently treat the metal thus secured by heat and by other means to obtain a coherent, homogeneous, ductile metal product.

In an application by John W. Marden et al., Serial No. 618,544, filed February 12, 1923, entitled Method of preparing refractory metals and assigned to the assignee of the present application, a process for the reduction of refractory metal compounds to obtain the metallic powder has been described, and in practicing the present invention, we have found it desirable to follow the calcium-chloride reduction process set forth therein with certain advantageous modifications and variations which will be described more fully hereinafter. This process may be termed the first step in our process. For what we may term the second step of our process; namely, sintering and treating to the coherent and homogeneous metal form, we prefer to follow, with certain advantageous modifications, the process substantially as set forth in our application, Serial No. 432,325, filed December 21, 1920, entitled Sintering and fusing of metal powders into coherent metals and assigned to the assignee of the present application, the present application being a continuation-in-part thereof and we may utilize, for practicing such heat-treatment, the furnace described in the patent to Harvey C. Rentschler, No. 1,480,301, issued January 8, 1924, entitled Furnaces and assigned to the assignee of the present application. We may employ for some purposes the furnace described in our copending application, Serial No. 488,230, filed July 28, 1921, entitled "Furnaces" and also assigned to the assignee of the present ap-

plication. A third step may be referred to as fabricating the metal.

We have found that by a combination of the processes set forth in the copending applications, noted supra, when practiced in accordance with the modifications herein-after set forth, we are able to obtain a refractory metal of the character previously referred to in homogeneous, coherent and ductile form which, to our knowledge has not been done heretofore. In other words, we reduce compounds of the metals to obtain metallic powders free from deleterious substances affecting the malleability of the metals, thereafter heat-treating the metal particles to cause them to coalesce into a coherent, homogeneous, ductile mass and thereafter fabricate such metal into useful forms, such as wire, sheet, plate and the like.

More specifically our present invention contemplates the reduction of compounds of the metals under consideration to obtain the metallic powders thereof free from contamination. This reduction is effected in a bomb by employing a suitable flux such as calcium chloride and a reducing agent such as calcium by the process hereinafter fully described. The purity of the metallic oxide employed is a special feature of the invention as will be appreciated later. Upon obtaining the pure powder of a given metal it is subjected to a sintering and heat-treatment under non-oxidizing conditions during or between said heat-treatments. As a result of these treatments a bar or slug of the metal is produced which may be fabricated or worked into any desired form, the resultant product possessing ductility, malleability, etc. These several steps for the sake of clearance are taken up and described in detail below.

However, in order to obtain the metals in a homogeneous, coherent, and ductile state, it is necessary that the chemical materials utilized in effecting the preparation of the metallic powders be prepared with special care, and for this purpose we provide special methods for the production of such materials free from deleterious substances that adversely affect the workability of the resultant metals. Therefore, before proceeding with the detailed description of the main process contemplated herein, we will first set forth the preparation of the chemical materials of the desired purity together with a description of the bomb in which the chemical reduction of the metallic oxides is effected.

Preparation of calcium chloride

We prefer to employ as a fluxing agent a halide of an alkaline earth metal such as calcium chloride, but other suitable metal halides may be employed for this purpose.

The calcium chloride should be in a very pure condition and care should be exercised to see that any chemical impurities which it may contain are removed. Generally we have found that certain grades of calcium chloride available on the market are sufficiently clean so that they need only be heated to about 450° C. to thoroughly dry them. The drying of the calcium chloride may be performed in any suitable form of heater which will not introduce impurities and which is capable of control so that the temperature for drying may be maintained at about 450° C. for a sufficient period of time. The calcium chloride after drying, may be pulverized to pass a 40 or 60 mesh sieve and maintained in the dry condition until used. It should be stated here, that the rate of reaction may be effectively controlled by increasing or decreasing the amount of calcium chloride or other fluxing material and the amount of alkaline earth metal reducing agent. By thus controlling the rate of reaction and varying the temperature of the bomb, the size of the metal particles may be satisfactorily governed, as will more particularly appear hereinafter.

The calcium chloride is added principally for the following purposes: first, to act as a flux to form a more or less fluid medium in which the reaction takes place; second, to take up the calcium oxide which is one of the products of reaction with the formation of oxy-compounds, to remove it from the zone of reaction and to allow the reaction to go to completion; third, to permit the thorium metal, which is heavy, to settle to the bottom and thus afford an effectual seal against oxidizing influences, and; fourth, dependent upon its proportion, to increase or decrease the reaction rate.

Preparation of the calcium

We find it desirable in practicing our process to employ a reducing agent, such as calcium, which is free from deleterious substances.

The calcium used for our process may be made from calcium chloride, such as the above stated, by the electrolytic process, and for our purpose, we have used calcium which has shown on analysis not more than .02 or .03 of 1% iron and proportionately low impurities of other sorts. If the calcium chloride used in the production of calcium has been carefully prepared, the resultant product will be proportionately purer. In practice, we have found it best to discard the first piece of calcium made from a fresh electrolytic bath, since iron and other impurities appear to concentrate therein. The calcium thus prepared is maintained in an inert environment until ready for use. When ready for use, the surface coatings of oxide and calcium chloride are removed

and the calcium is rapidly cut up into particles of such size as would pass a 5 or 10 mesh sieve. To prevent oxidation and rapid deterioration in the atmosphere, the calcium cuttings are immediately mixed with the metal oxide and the fluxing agent and loaded into the bomb.

Preparation of the metallic oxide

As hereinbefore mentioned, we prefer to produce thorium metal powder from thorium oxide and for that purpose, the latter should be prepared with special care. Thorium nitrate may be ignited in such a manner, that thorium oxide produced therefrom is coarse and heavy, that all nitrate is destroyed, and that no impurities are introduced. Great care must also be taken to ignite the thorium nitrate at such a temperature, that the thorium oxide when formed will not be heated to too high temperatures for this will prevent the most satisfactory reduction. In explanation at this point, it may be stated that results seem to indicate that thorium oxide heated to certain temperatures will be more readily reducible, than if it be heated to higher temperatures, which makes it quite difficult to reduce. In order to get pure thorium oxide and to avoid the introduction of any impurities, such as silica, we may ignite the thorium nitrate very gently in a porcelain dish of the wide type in an electric furnace, but not over the open gas flame where there is a possibility of introducing carbon or other impurities.

The first gentle ignition of the nitrate to about 400° to 500° C., causes the thorium nitrate to puff up and form a voluminous mass which afterwards sinks down, gradually becoming more compact. If the heating be continued in the porcelain dish to too high a temperature, the thorium seems to absorb or take up a small amount of silica which is most undesirable and for this reason, after the puffing is over, the mass substantially settled and the nitrate practically destroyed, the powder is placed in relatively small portions in platinum crucibles and the ignition continued to about 800° or 850° C. in the electric furnace to destroy any sulphates which occur in the commercial thorium nitrate. The oxide thus prepared becomes quite compact and heavy after it has been so heated for a couple of hours and, after it has been pulverized to pass a 200 mesh sieve, is suitable for our purpose.

For the purpose of completely describing our invention to best advantage, we shall illustrate it as applied to the production of coherent, homogeneous and ductile thorium as an example, and will explain the operations in connection with its specific preparation, although it should be borne in mind that our process is susceptible of applica-

tion to many metals, including those hereinbefore mentioned, with perhaps slight modifications coming well within the broad phases of our invention. Therefore, we do not wish to be considered as limiting our invention in reciting specific metals or details.

The bomb

Before proceeding with the detailed description of our process, we will first describe the special bomb in which we prefer to practice the chemical reaction, reference being had to Fig. 1 of the accompanying drawings for the purpose.

The bomb construction differs from that set forth in application, Serial No. 618,544 referred to, in that a plug 2 having a taper 4, i. e., a taper of slight angularity, is adapted to fit within a similarly tapered opening in the cylindrical bomb 6 and may be forced therein to a tight fit by means of a projection 8 adapted to be compressively engaged by a screw cap 10 which is secured to the bomb by means of screw threads 12. The cap 10 is also provided with a projection 14, similar to the projection 8 so that each may be engaged by a wrench or other tool for turning them. After a charge has been inserted into the bomb, the plug 2 is put in place and may be gently turned to insure intimate contact between its tapered sides and the tapered seat formed in the bomb wall. The cap 10 is then screwed down upon the bomb until it engages the projection 8 with the desired degree of compression. In opening the bomb, this process is reversed, the projection 8 providing means to grip the plug 2 for its removal.

The taper 4 may be of any desired angle but since a long taper makes the plug difficult of removal and a short taper does not provide the wedging action necessary to secure a tight joint, we prefer a compromise between the two as shown. The plug and its tapered seat 4 should both be carefully ground to provide a tight fit for it is necessary that a hermetic seal be maintained. The bomb may warp to a slight extent after it is first used, in which case the stopper or plug should be reground and reseated. We have found through experiment that the stopper rarely needs further working after it has been reground once or twice.

The bomb may be made of iron or steel or of any other metal or composition that will withstand the temperatures and pressure incident to the reaction within and that will not contaminate the product. The threads of the cap of the bomb may be painted with a paste made of fluffy magnesium oxide and water which serves two purposes; to fill the joint to maintain it airtight and to keep the iron threads from sticking after high temperature treatment.

As it is of prime importance that the metal produced in the bomb be wholly uncontaminated, we have found it preferable to make one run in the bomb before it is used for the production of the best powder. This may be because the iron of the bomb contains small amounts of carbon, silica and other impurities which are impossible to remove in any way, other than to soak them up during the heat-treatment of the metal powders which it is desired to make.

It is extremely necessary for successful results, that the bomb be cleaned thoroughly of rust and other deleterious substances which may affect the purity of the product. For rust and the usual impurities which collect within the bomb, we have found that hydrochloric acid and water in equal proportions with perhaps a small amount of acetic acid is quite effective for the purpose. Formic acid or almost any other organic acid may be used in place of the acetic acid.

Before a run is made and after the stopper has been ground into place, the acid mixture is poured into the bomb up to the edge of the ground joint, care being exercised to avoid wetting the ground joint with the acid. If the rough layer of oxide is thin, a few minutes will suffice to give a clean white iron surface, whereupon the acid is quickly poured out and the bomb thoroughly washed with water to remove as much of the acid as is possible. The drying may be completed by rinsing with alcohol, etc., wiping out with a clean dry cloth and finished by blowing clean air over the surface.

As hereinbefore stated, the bomb may be provided with an insulating lining (not shown) of calcium oxide, as disclosed in application, Serial No. 618,544 previously referred to, an oxide of other alkaline earth metals, magnesium, alumina, or any material that will not deleteriously affect the product, or it may be lined with a metal such as platinum, tungsten and the like, if desired. In some instances, such as that selected for description herein, the lining is unnecessary, but if a lining be used it may be of the thickness set forth in application, Serial No. 618,544. However, the thickness may be varied over wide ranges.

In the foregoing description we have been concerned with the preparation of the chemical materials employed in practicing our main process for the production of the metals under consideration. This process divides itself into three steps or stages which will now be described.

Preparation of the metallic powder

The ingredients for filling the bomb having been made ready as hereinbefore specifically pointed out, we find it preferable to use one part of the metal oxide with one

part of calcium chloride and three quarters of a part of calcium metal in the case of thorium oxide. These proportions are by weight and may be varied for thorium metal preparation and may differ over considerable ranges in the preparation of different metals. It is customary to weigh the thorium oxide into a closed bottle, to weigh out the calcium chloride separately and to finally weigh out the calcium. The dry pulverized calcium chloride is mixed with the coarse and heavy thorium oxide, and the pure metallic calcium cuttings, with the exception of a small portion added and the mixture agitated to thoroughly intermix the particles of the ingredients. We prefer to do the mixing within a stoppered bottle by thoroughly shaking it, since calcium chloride and calcium readily absorb moisture and oxygen from the atmosphere when not under seal.

While the mixture thus made be compacted into cakes and placed within the lined bomb as set forth in said application, Serial No. 618,544, we prefer to quickly pour it from the mixing container into an unlined bomb, press it down gently, place the remaining portion of calcium cuttings on top of the charge, insert the wedge-shaped stopper in place and turn it gently to properly seat it.

The screw cap is then placed upon the bomb and turned down until the desired degree of compression of the stopper has been attained. While we may prefer to slightly compact or compress the charge within the bomb, it is generally unnecessary to do so if an excess of calcium be used to clean-up the air.

The bomb is now placed in an electric furnace, a pyrometer inserted for temperature readings, the temperature increased to about 950°C ., and maintained constant for such period of time as may be necessary to allow the bomb to obtain the same temperature throughout, as that of the furnace.

Upon the completion of the heating, the bomb is lifted out of the furnace while bright red hot and allowed to stand in the air for a few minutes to cool, whereupon it may be rapidly cooled in any suitable manner such as by cold running water.

It has been found by experience that the bomb should be thoroughly cooled before opening it. A bomb originally containing about one quarter of a pound of metal oxide may require about an hour of this treatment for thorough cooling and no attempt should be made to open the bomb until it is quite cold to the hand, because of the chemical activity of both thorium and calcium when slightly warm or hot. The screw cap may be removed in any suitable manner and the top around the tapered plug thoroughly cleaned. The charge, which consists of a

compact mass of calcium chloride, calcium oxide, thorium and excess calcium, may be removed from the bomb in any suitable manner as by chiseling.

Before cutting out the charge, filtered water is prepared for its disintegration and for this purpose, we prepare about 80 liters per pound of thorium oxide used for the first washing and disintegration. This great volume of water is necessary in order to maintain the mixture cool to prevent thorium oxidation.

The fine material, as it is cut from the charge within the bomb, is added in small portions at a time into a vessel containing the filtered or distilled water while continuously and vigorously stirring it to prevent the particles from settling in one place and heating.

When the charge has been cut out by the chisel, drills or other means, as far as it is practical to do so, the bomb itself may be set in a dish of cold running water and while kept cool, filtered water run within to disintegrate the remaining material clinging to the sides and bottom of the bomb. The material so obtained may be poured into the large bulk of the solution.

After gas has ceased to be evolved, stirring is discontinued, the insoluble material permitted to settle, and the liquid poured or siphoned off. A second portion of distilled water in the ratio specified above is added and the mixture again stirred for five or ten minutes, whereupon the residue is allowed to remain and the supernatant liquid again poured away. This should be done several times until the liquid above the insoluble material has become clear or is slightly dark, due to the suspension of a small amount of extremely finely divided thorium. This may be safely poured away since the amount of thorium lost is small and it is desirable to remove any exceedingly fine thorium powder.

After the final washing with water, two or more liters of filtered water per quarter pound of thorium oxide may be added to the residue and the mixture stirred with considerable violence while from 250 to 300 cc. of concentrated nitric acid is slowly added. This will give a solution of about 1 part HNO_3 to 8 parts H_2O . It will be noticed that a copious evolution of gas takes place, but if the process has been carefully followed, only a slight indication of the presence of carbides in the calcium or thorium oxide by the evolution of acetylene will be observed. Five minutes of intensive washing with the acid may be given and thereafter it is diluted with about 20 liters of filtered water and after being permitted to settle, the acidulated liquid is poured away. This acid washing may be repeated about three times depending upon the continued

evolution of gases. If, for example, any odor of hydrogen sulphide remains upon a third acid washing, the acid treatment should be repeated at least twice more.

5 Upon the completion of the acid washing, the charge is washed two or more times with 20 liter portions of filtered water to remove the acid, the metal powder is filtered upon a Buchner funnel, washed with alcohol and 10 ether and sucked as dry as possible with an aspirator. The powder while still somewhat wet, is placed upon a 60 mesh sieve and as it dries, is brushed through into a tube or the like so that it may be connected 15 to a vacuum pump to remove the remaining alcohol, ether and any moisture remaining and to obtain it in as clean and as dry a condition as possible.

The powders produced consist of bright 20 particles with clean surfaces as seen under the microscope but upon exposure to the atmosphere their surfaces become dimmed over or dull with an oxide coating. The powders thus prepared show by actual 25 chemical analysis to be substantially free from oxide or other deleterious substances which would prevent the subsequent heat-treatment hereinafter specified from converting the powder into a coherent, homogeneous and ductile body or mass. 30

Sintering and heat-treatment

15 The metal powder whether produced by the process outlined above or by any other process which will produce a pure powder susceptible of being pressed into slugs or buttons of the desired shape and sintered into a ductile or malleable body, is now 0 ready for the sintering and treating process.

As above, we shall consider thorium for illustrative purposes and will describe the process specifically applicable to that metal, 5 although it will be understood that with slight modifications, according to the peculiarities of the material, it may be applied to the production of other metals. The button or slug having been formed by suitable 3 pressure and without the addition of any binding material, is placed within the furnace for sintering and heat-treatment. This furnace may be either of the type described in our aforesaid copending application, Serial No. 488,230, or that described in Patent 5 No. 1,480,301. In either case, the highest vacuum or a completely inert atmosphere must be obtained and maintained from the beginning to the completion of the heat-treating process. 10

In Figs. 2 and 3 of the drawings, we have shown two types of furnaces, together with the circuits for their operation.

Referring to Fig. 2 of the drawings, a vitreous envelope 16, containing an induction

coil 18 hermetically sealed therein, may be connected to an exhaust line 20 by means of connection 22. Connections from an electrical source 24 comprise an adjustable rheostat or a variable inductance 26, a step-up 70 transformer comprising primary and secondary windings 28 and 30, respectively, air choke coils 32 to eliminate high frequency surges from harming the transformer, a condenser 34 and a battery of mercury spark 75 gaps 36 arranged in parallel so that one or more may be used as desired. The charge to be treated may be placed within the coil 18 and supported in position upon or within a crucible 19 or disk of thoria or other 80 desirable high melting point material which may be supported by a wire 19'. This briefly describes the furnace together with the circuit arrangement, partly described and claimed in said Patent 1,480,301. 85

As shown in Fig. 3, the furnace described and claimed in said application, Serial No. 488,230, comprises a vitreous envelope 38 within which electrodes 40 and 42 are hermetically sealed, the electrode 42 making 90 contact with a pool of mercury 44 which serves to maintain continuous contact with the metal slug 46 through the clip 48 secured to the lower end of the slug, the upper end of which is clamped to the electrode 40. 95 The circuit for this furnace comprises a step-down transformer 50 and a variable resistance or reactance 52 for the primary thereof.

For the purpose of observing the degree 100 of vacuum attained or existing within the furnaces 16 or 38, we prefer to use spectrum tubes, designated 54 and 56 for the induction furnace 16 and the contact furnace 38, respectively. These tubes are of the ordinary 105 discharge type having electrodes about four inches apart with a capillary tube of about one-eighth inch inside bore connecting the bulbous portions. These tubes are operated by having about 3000 volts from small 110 transformers 58 and 60, connected to a suitable source not shown, impressed between the electrodes. The use and value of these spectrum tubes for determining the degree of vacuum within the furnaces will be clearer 115 as the description proceeds.

The spectrum tubes may be replaced or used in conjunction with McLeod gauges (not shown) but we prefer to use the former. Instead of using either the spectrum tube 120 or gauge for the induction furnace, a discharge between turns of the high frequency coil or to the leading-in wires may serve as an indication that gases are being evolved too rapidly or, if the discharge does not take 125 place, it may be considered as an indication that the gases are being liberated in a satisfactory and not too rapid manner.

In preparing metal for its manufacture into sheet or the like form, we may prefer 130

to use the furnace 16 and for such purpose, the slug or button is mounted within a crucible or upon a plate of thoria 19 or other suitable material that is positioned substantially centrally within the high frequency coil. In this case, of course, the heating is done by high frequency induction, while the vacuum pumps are operating to remove any gases given off by the metal during treatment.

The heating schedule is carried out slowly at first, in order to cause the evolution of gases from the wall of the furnace and from within the button or slug and thereafter the heating current is gradually raised at such a rate that the gases and vapors are expelled from the metal under treatment without fracturing the specimen or causing chemical reaction of the gases therewith. A suitable vacuum is maintained to avoid objectionable arcing between the turns of the high frequency coil of the furnace.

Upon heating the mass, gas may be evolved from the metal under treatment, in this case from the thorium, and the presence of an objectionable quantity may be indicated by the character of discharge taking place in the spectrum tube. The absence of any discharge may be taken as an indication that the gases are not being too rapidly liberated and will not deleteriously affect the metal undergoing treatment.

Should it appear from the spectrum tube or from other sources that the gases are being given off too rapidly, it is advisable to diminish the current through the primary until the evolution is reduced to a satisfactory rate. No prediction can be made as to what rate of evolution of gas should be maintained, since many variable factors come under consideration in this connection and the best that can be said is that experience and experimentation must be relied on in each separate instance.

Upon continued treatment, the metallic mass becomes sintered along the edge first, becomes a better conductor and causes further sintering progressively to the interior, until all the powder becomes coherent and homogeneous. The degree of heating determines the uniformity of the sintered metal and generally the longer and hotter the slug or button is heated, the more dense and coherent it becomes. The temperature of the thorium being treated should be increased until it is raised to near its melting point and maintained thereat until such time as all particles thereof sinter together or coalesce into a homogeneous coherent form.

We have also discovered that thorium metal may be melted in or on thoria or other suitable containers or supports and that the fused metal may be used for extensive cold working. The purity of the

product is indicated by the definiteness of its melting point.

In cases where it is desired to manufacture a long slug of metal from which wire, sheet, plate or the like may be fabricated, we prefer to employ the furnace described and illustrated in our copending application, Serial No. 488,230, previously referred to, and hereinafter termed the contact furnace.

Bars of thorium, for example, in the coherent, ductile state, may be prepared as follows. The pure metal powder is formed into compact slugs by subjecting the powder to pressure within a separable mold. The quantity of powder required for each molding operation is carefully weighed, such quantity being determined by such factors as size and shape of the compressed slug. The weighted powder is placed within the mold in such a manner, as to obtain a uniform distribution within the same and is then subjected to a pressure transversely to the longitudinal axis of the mold or the slug, of such a degree as to compact the powder so that the slug which is formed thereby may be readily handled and clamped within the contact furnace.

In removing the slugs from the mold, care should be exercised to see that they are not cracked and we have found that cracking may be avoided by first withdrawing the end sections of the mold, thus permitting the compressed powder to expand along the longitudinal axis of the slug.

It was found unnecessary to previously sinter these slugs or bars in an atmosphere of hydrogen, as is the case with tungsten and molybdenum, because the pressed slugs are very rigid and may be easily handled without danger of fracture.

One end of the slug is then secured to the upper clamp within the furnace, a lower clamp being fastened to the lower end of the slug, the length of the clamp being such as to maintain contact with the mercury electrode in the bottom of the furnace during the heat-treatment of the slug.

After the furnace has been carefully sealed, a very high vacuum is produced within the furnace and thereafter a low current is passed through the slug. This current is gradually raised at such a rate, that a good vacuum may be maintained throughout the heat-treatment. The spectrum tube may be employed to indicate the degree of vacuum. At first, the slug is not as good a conductor of the current owing to the presence of gases therein and during the early stages, it may be found necessary to utilize a higher voltage in order to pass the low current. After substantially all the gases have been removed, the current may be increased to approximately 85% of the current required to fuse the bar and this current maintained for approximately 12

to 15 minutes until the bar is in a thoroughly sintered condition. With a $\frac{1}{8}$ " square bar and $3\frac{1}{2}$ " in length, it was found that at about 21 amp. of current in the primary of the transformer 50, having a ratio of about 20 to 1, that the bars would melt off. After determining this temperature, the value of the heating current was determined to be from 20 to 90 amp. in the primary of the transformer. If the bar is of larger size, for example $\frac{1}{4}$ " in diameter, the heating current is approximately 550 amp.

In treating the bar, care should be exercised in maintaining control of the treating current, for the reason that during the degasifying of the bar, some times the resistance of the bar may suddenly decrease, which obviously produces a rush of current through the bar which results in the fusion of the metal.

After the bar has been thoroughly treated to sinter or weld the particles of metal into a coherent mass, the current may be turned off. The bar should be permitted to cool within the furnace and should not be removed therefrom until it is quite cool, otherwise it will be subject to oxidation.

From bars prepared in accordance with the preceding processes, we have fabricated very fine thorium wire which is quite ductile when cold.

It is not necessary to start with the powder of the metal for the process may be practiced by employing compounds decomposable at high temperatures. For instance, thorium hydride may be readily decomposed by high temperature treatment in a vacuum.

Although the invention as herein described relates to the production of a homogeneous, coherent metal, it may be well adapted to the production of alloys containing several metals, as will be readily perceived. In preparing such alloys, we may utilize a mixture of metal powders of two or more of the more refractory or rare metals and sinter the mixture in either of the furnaces in accordance with the process described supra; or we may mix a rare metal powder with one or more of the more common metal powders and sinter or fuse the same to form an alloy.

We may also produce alloys from the compounds of rare or other metals as from hydrides, or the like.

55 *Fabrication*

The metal formed in accordance with our process is very pliable or ductile at room temperatures and may be rolled, swaged, drawn or otherwise worked in the cold state and may even be drawn into very fine wire, although it may be rendered more readily workable and less liable to form cracks or splinters by occasionally heat-treating at low temperatures, for substantially low tem-

peratures, during mechanical working. We have formed the metal by cold-working into wire electrodes and other useful shapes and articles, admirably adaptable for a wide variety of purposes.

A few specific instances of preparation into useful articles will be described. In making disc-targets for X-ray tubes, we have pressed the metal powder into cakes or buttons about $\frac{1}{4}$ " thick and about an inch and a half in diameter, and have followed the process hereinbefore set forth for the high frequency induction furnace, treating the button for several minutes at a temperature just below the melting point of the metal and rolling, when cold, to the thickness desired. We have made thorium discs for this purpose with a heat-treatment of seven minutes after the gases were removed. After thorough cooling, we cross-rolled the button with flat rolls to a thickness of $\frac{1}{16}$ inch. The edges were trimmed off to make a round disc which was used very effectively in an X-ray tube.

In manufacturing thorium wire, we treated the slugs as has been previously described and in the best vacuum attainable and thereafter cut the bars into 1 inch lengths for convenience. They were then trimmed down to $\frac{1}{16}$ inch round rods and placed inside $\frac{3}{8}$ inch (outside diameter) iron tubes so that the thorium rod tightly fitted within them. Cold rolled steel was not as satisfactory for our purpose as very soft and pure Norway iron (such as that used in welding).

Norway iron of this character can be rolled and drawn without splitting and does not develop cracks on long continued working as does cold-rolled steel. We were able to roll down the composite bars to about 30 mils diameter with grooved rolls and thereafter draw the wire down to about 7 mils with dies. This yielded pure and ductile thorium wire of about 1 to 3 mils diameter after the iron was removed with a warm, 1 to 8 or 1 to 6, nitric acid solution. The wire thus formed is of uniform diameter, strong and is readily adapted for filaments for lamps and other purposes.

These fabrications have indicated the very great ductility of thorium metal as it was susceptible of extensive cold working. It has been shown upon chemical analysis and by microphotographs, that the thorium metal we have obtained is substantially pure. It has also been found that the melting point of thorium is about 2100° K., its density or specific gravity 11.3, its specific resistance 18 to 20×10^{-6} ohm cms. at room temperature and its temperature co-efficient of resistance to be .0021. It has also been found that it has a hardness of 72, Brinnell scale, after cold-working and that while it is harder than very soft copper and softer than cast iron, its ductility resembles that

of copper or gold. The metal is relatively non-volatile up to its melting point.

Although we have described a preferred method of producing the more refractory metals in the ductile form, it will be readily perceived from the various modifications described, and thereby be understood, that the invention is of broad scope and we do not wish to be limited other than by the spirit of the invention and the scope of the appended claims.

In some of the appended claims we have used the term "more refractory metals" by which we mean such metals as uranium, thorium, zirconium, titanium, vanadium, chromium, and certain of the rare metal earths; that is, such metals having oxides not reducible by hydrogen.

What is claimed is:

1. The method of forming coherent, rare refractory metals, the oxides of which are not completely reducible by hydrogen, from a decomposable compound, thereof, which comprises heating such a decomposable compound to the decomposition temperature, removing the products of the decomposition except the metal and continuing the heat treatment above the decomposition temperature until all of the metal is in a coherent, homogeneous form, said operations being conducted under non-oxidizing conditions and without exposure of the metal between said heat treatments to oxidizing conditions.

2. The method of forming coherent, rare refractory metals, the oxides of which are not completely reducible by hydrogen, from a decomposable compound thereof, which comprises heating such a decomposable compound to the decomposition temperature, removing the products of the decomposition except the metal and continuing the heat treatment above the decomposition temperature until all of the metal is in a coherent, homogeneous form, said operations being conducted in an inert environment and without exposure of the metal between said heat treatments to oxidizing conditions.

3. The method of forming coherent, rare refractory metals, the oxides of which are not completely reducible by hydrogen, from a decomposable compound thereof, which comprises heating such a decomposable compound to the decomposition temperature, removing the products of the decomposition except the metal and continuing the heat treatment above the decomposition temperature until all of the metal is in a coherent, homogeneous form, said operations being conducted in a high vacuum and without exposure of the metal between said heat treatments to oxidizing conditions.

4. The method of forming coherent, homogeneous thorium which comprises heating thorium hydride until the same is dissociated, removing the hydrogen and heat-

ing the thorium until it is in a coherent, homogeneous state, said operations being conducted in an inert environment and without exposure of the metal between said heat treatments to oxidizing conditions.

5. The method of forming coherent, homogeneous thorium which comprises heating thorium hydride until the same is dissociated, removing the hydrogen and heating the thorium until it is in a coherent, homogeneous state, said operations being conducted in a high vacuum and without exposure of the metal between said heat treatments to oxidizing conditions.

6. The method of forming coherent, homogeneous thorium from a dissociable compound thereof which comprises heating a dissociable compound of thorium until the same is dissociated into thorium and gaseous products, removing the gaseous products and heating the thorium until it is in a coherent, homogeneous state, said operations being conducted under non-oxidizing conditions and without exposure of the thorium between said heat treatments to oxidizing conditions.

7. The method of forming coherent, homogeneous rare refractory metals, the oxides of which are not completely reducible by hydrogen, from powders thereof which comprises heating the powder of such a metal at such a temperature and rate that the gases are liberated without combining with the metal or disintegrating the same, and continuing the heat treatment at a more elevated temperature until the metal is in a coherent, homogeneous state, said heat treatments being conducted under non-oxidizing conditions and without exposure of the metal between said heat treatments to oxidizing conditions.

8. The method of forming coherent, homogeneous rare refractory metals, the oxides of which are not completely reducible by hydrogen, from powders thereof which comprises heating the powder of such a metal at such a temperature and rate that the gases are liberated without combining with the metal or disintegrating the same, and continuing the heat treatment at a more elevated temperature until the metal is in a coherent, homogeneous state, said heat treatments being conducted in an inert environment and without exposure of the metal between said heat treatments to oxidizing conditions.

9. The method of forming coherent, homogeneous rare refractory metals, the oxides of which are not completely reducible by hydrogen, from powders thereof which comprises heating the powder of such a metal at such a temperature and rate that the gases are liberated without combining with the metal or disintegrating the same, and continuing the heat treatment at a more ele-

vated temperature until the metal is in a coherent, homogeneous state, said heat treatments being conducted in a high vacuum and without exposure of the metal between said heat treatments to oxidizing conditions.

10. The method of forming coherent, homogeneous thorium from a powder thereof which comprises heating thorium powder at such a temperature and rate that all absorbed and adsorbed gases are substantially liberated, removing the liberated gases and continuing the heat treatment at a more elevated temperature until the particles coalesce to form a coherent, homogeneous body, said heat treatments being conducted under non-oxidizing conditions and without exposure of the thorium between the heat treatments to oxidizing conditions.

11. The method of forming coherent, homogeneous thorium from a powder thereof which comprises heating thorium powder at such a temperature and rate that all absorbed and adsorbed gases are substantially liberated, removing the liberated gases and continuing the heat treatment at a more elevated temperature until the particles coalesce to form a coherent, homogeneous body, said heat treatments being conducted in an inert environment and without exposure of the thorium between the heat treatments to oxidizing conditions.

12. The method of forming coherent, homogeneous thorium from a powder thereof which comprises heating thorium powder at such a temperature and rate that all absorbed and adsorbed gases are substantially liberated, removing the liberated gases and continuing the heat treatment at a more elevated temperature until the particles coalesce to form a coherent, homogeneous body, said heat treatments being conducted in a high vacuum and without exposure of the thorium between the heat treatments to oxidizing conditions.

13. The method of forming coherent, homogeneous thorium which comprises slowly heating the thorium in the powder state to a temperature at which the particles coalesce, the rate of heat treatment being such that the thorium is denuded of absorbed and adsorbed gases prior to its reaching a temperature at which a combination of the gases and metal would take place, said heat treatment being conducted without exposure of the metal to oxidizing conditions.

14. The method of forming a coherent, rare refractory metal alloy, the oxides of the constituent metals of which are not completely reducible by hydrogen, which comprises slowly heating a mixture of such metals in the powder state to a temperature at which the particles thereof coalesce, the rate of heat treatment being such that the material is denuded of adsorbed and ab-

sorbed gases prior to its reaching a temperature at which a combination of the gases and metals would take place, said heat treatment being conducted without exposure of the metals to oxidizing conditions.

15. The method of forming coherent, homogeneous rare refractory metals, the oxides of which are not completely reducible by hydrogen, which comprises compressing such a metal in the powder state into a compact mass, preheating the compacted mass at such a temperature and rate to liberate the adsorbed and absorbed gases without contaminating the metal, removing the liberated gases and continuing the heat treatment at such a temperature as to cause the particles to coalesce and form a coherent, homogeneous body, said heat treatments being conducted in an inert environment and without exposure of the metal between the heat treatments to oxidizing conditions.

16. The method of forming coherent, homogeneous rare refractory metals, the oxides of which are not completely reducible by hydrogen, which comprises compressing such a metal in the powder state into a compact mass, preheating the compacted mass at such a temperature and rate to liberate the adsorbed and absorbed gases without contaminating the metal, removing the liberated gases and continuing the heat treatment at such a temperature as to cause the particles to coalesce and form a coherent, homogeneous body, said heat treatments being conducted in a high vacuum and without exposure of the metal between the heat treatments to oxidizing conditions.

17. The method of forming coherent, homogeneous thorium which comprises agglomerating thorium powder to form a compact mass, heating the mass at such a temperature and rate as to liberate the gases therefrom without contaminating the metals and further heat treating the metal at a higher temperature until the particles coalesce to form a coherent, homogeneous body, said heat treatments being conducted in an inert environment and without exposure of the metal between the heat treatments to oxidizing conditions.

18. The method of forming coherent, homogeneous thorium which comprises agglomerating thorium powder to form a compact mass, heating the mass at such a temperature and rate as to liberate the gases therefrom without contaminating the metal and further heat treating the metal at a higher temperature until the particles coalesce to form a coherent, homogeneous body, said heat treatments being conducted in a high vacuum and without exposure of the metal between the heat treatments to oxidizing conditions.

19. The method of producing rare refractory metals, the oxides of which are not

entirely reducible by hydrogen, in ductile form which comprises producing such a metal in powder form in a pure state and free from substances which deleteriously affect its ductility, heating the powder at such a temperature and rate to liberate the adsorbed and absorbed gases, removing the liberated gases and continuing the heat treatment at a more elevated temperature until the particles coalesce and form a ductile body, said heat treatment being conducted in an inert environment and without exposure of the metal between heat treatments to oxidizing conditions.

20. The method of producing rare refractory metals, the oxides of which are not entirely reducible by hydrogen, in ductile form which comprises producing such a metal in powder form in a pure state and free from substances which deleteriously affect its ductility, heating the powder at such a temperature and rate as to liberate the adsorbed and absorbed gases, removing the liberated gases and continuing the heat treatment at a more elevated temperature until the particles coalesce and form a ductile body, said heat treatment being conducted in an inert environment and without exposure of the metal between heat treatments to oxidizing conditions.

21. The method of producing rare refractory metals, the oxides of which are not entirely reducible by hydrogen, in ductile form which comprises producing such a metal in powder form in a pure state and free from substances which deleteriously affect its ductility, compressing the powder to form a compact mass, heating the mass at such a temperature and rate as to liberate the adsorbed and absorbed gases, removing the liberated gases and continuing the heat treatment at a more elevated temperature until the particles coalesce and form a ductile body, said heat treatment being conducted in an inert environment and without exposure of the metal between heat treatments to oxidizing conditions.

22. The method of producing rare refractory metals, the oxides of which are not entirely reducible by hydrogen, in ductile form which comprises producing such a metal in powder form in a pure state and free from substances which deleteriously affect its ductility, compressing the powder to form a compact mass, heating the mass at such a temperature and rate as to liberate the adsorbed and absorbed gases, removing the liberated gases and continuing the heat treatment at a more elevated temperature until the particles coalesce and form a ductile body, said heat treatment being conducted in a high vacuum and without exposure of the metal between heat treatments to oxidizing conditions.

23. The method of producing rare re-

fractory metals, the oxides of which are not completely reducible by hydrogen, in ductile form which comprises reducing a compound of such a metal under such conditions that a pure powder is obtained which is free from substances deleteriously affecting the workability of the metal, compressing the powder to form a compact mass, heating the mass at a temperature and rate at which adsorbed and absorbed gases are liberated without contaminating the metal, removing the gases thus liberated, and heat treating the mass until the particles coalesce to form a ductile body, said heat treatments being performed in an inert environment and without exposure of the metal between the heat treatments to oxidizing conditions.

24. The method of producing rare refractory metals, the oxides of which are not completely reducible by hydrogen, in ductile form which comprises reducing a compound of such a metal under such conditions that a pure powder is obtained which is free from substances deleteriously affecting the workability of the metal, compressing the powder to form a compact mass, heating the mass at a temperature and rate at which adsorbed and absorbed gases are liberated without contaminating the metal, removing the gases thus liberated, and heat treating the mass until the particles coalesce to form a ductile body, said heat treatments being performed in a high vacuum and without exposure of the metal between the heat treatments to oxidizing conditions.

25. The method of producing rare refractory metals, the oxides of which are not completely reducible by hydrogen, in ductile form, which comprises reducing a compound containing the metal under such conditions that substantially all substances deleteriously affecting the workability of the metal are removed and a metal powder obtained which is coarse, compressing the coarse powder to form a compact mass, heat treating the mass at a temperature and rate that adsorbed and absorbed gases are liberated, removing the liberated gases and further heat treating at more elevated temperatures until the particles coalesce to form a ductile body, said heat treatments being performed in an inert environment and without exposure of the metal between the heat treatments to oxidizing conditions.

26. The method of forming thorium in ductile form which comprises reducing a compound containing thorium under such conditions that substantially all substances deleteriously affecting the workability of thorium are removed and a metal powder is obtained which is coarse, compressing the coarse powder to form a compact mass, heat treating the mass at a temperature and rate that adsorbed and adsorbed gases are liber-

ated, removing the liberated gases and further heat treating at more elevated temperatures until the particles coalesce to form a ductile body, said heat treatments being
5 performed in an inert environment and without exposure of the metal between the heat treatments to oxidizing conditions.

27. The method of improving the properties of ductile, rare refractory metals, the
10 oxides of which are not completely reducible by hydrogen, which comprises producing such a metal in the coherent, homogeneous state, free from such substances as deleteriously affect the workability of the metal
15 and then working the metal under non-oxidizing conditions to the desired form by rolling, swaging or drawing.

28. The method of improving the properties of ductile thorium which comprises producing thorium metal in a coherent, homogeneous state and free from such substances
20 as deleteriously affect the workability of the metal, and then working the metal under non-oxidizing conditions to desired form by rolling, swaging, or drawing.

29. The method of improving the properties of ductile, rare refractory metals, the oxides of which are not completely reducible by hydrogen, which comprises reducing a
30 compound containing such a metal to the pure powdered state, sintering the powder in a high vacuum at such a temperature and rate as to obtain a coherent, homogeneous body, and subjecting the product thus obtained to mechanical working by rolling,
35 swaging or drawing, said sintering and working operations being done under such conditions that substantially all deleterious substances affecting the workability of the metal are eliminated.

30. The method of improving the properties of ductile thorium which comprises forming thorium powder of a grain size capable of being agglomerated into a mass
45 which may be handled without crumbling, said powder being free from impurities affecting the mechanical working of the metal, agglomerating the powder into a compact mass, degasifying the mass at temperatures
50 at which the metal does not combine with the gases, further heating the agglomerated mass until it becomes coherent and homogeneous, and mechanically working the coherent body to the desired form by rolling,
55 swaging or drawing.

In testimony whereof, we have hereunto subscribed our names this 4th day of June 1924.

JOHN WESLEY MARDEN.

60 HARVEY CLAYTON RENTSCHLER.