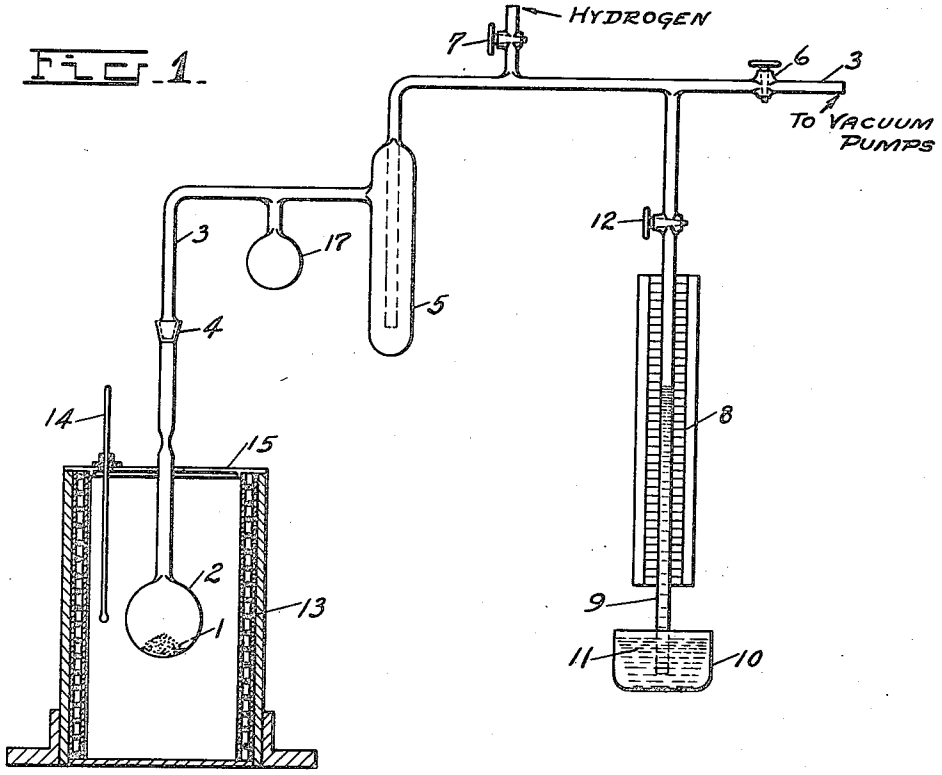
Aug. 4, 1931. F. H. DRIGGS 1,816,830

PREPARATION OF METAL HYDRIDES

Filed Nov. 25, 1929

Fig. 1.



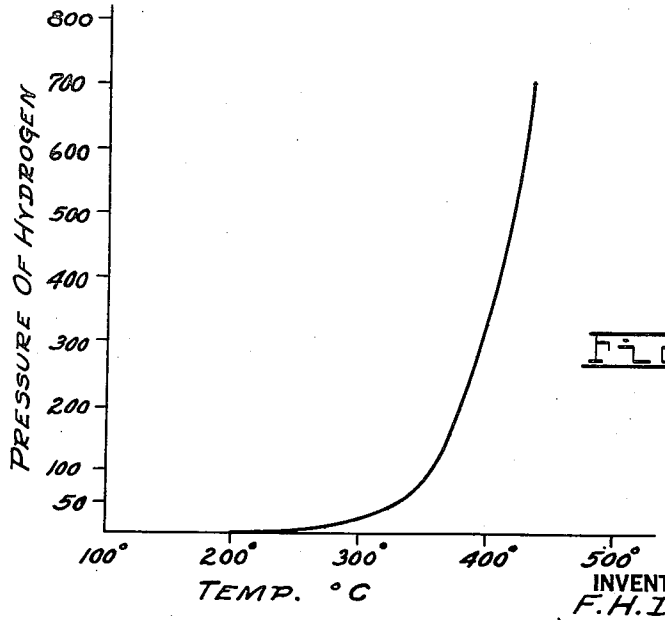


Fig. 2.

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UNITED STATES PATENT OFFICE

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PREPARATION OF METAL HYDRIDES

Application filed November 25, 1929. Serial No. 409,442.

This invention relates to a method of preparing metal hydrides and in particular the hydrides of highly reactive rare refractory metals.

Heretofore in the art it has been customary to prepare the hydrides of metals by heating the metal powder in a stream of freshly purified dry hydrogen, or to incandesce the metal powder in an hermetically sealed container containing an atmosphere of hydrogen. By either of these methods it is not possible to obtain, substantially pure metal hydrides, particularly when the metal powders employed are comprised of rare refractory metal powders. This is due to the fact that the rare refractory metal powders contain surface adsorbed and absorbed gases which combine with the metal powders to form compounds therewith which are irreducible by hydrogen.

One of the objects of this invention is to provide a method for preparing substantially pure metal hydrides.

Another object of this invention is to provide a method of producing metal hydrides from metal powders which are reactive with atmospheric gases to form compounds irreducible by hydrogen.

Another object of this invention is to prepare substantially pure rare refractory metal hydrides.

Other objects will appear as the invention is more fully disclosed.

In accordance with the objects of my invention I have found that metal hydrides, and in particular metal hydrides of the rare refractory metals may be prepared in a high state of purity by incandescing substantially pure metal powder to elevated temperatures in a predetermined pressure of hydrogen.

In the practice of my invention I first prepare a substantially pure rare refractory metal powder, incorporate the powder in an hermetically sealed container, evacuate the container and thoroughly free the metal powder of surface adsorbed and absorbed gases. The degasified metal powder is then incandesced in a substantially pure dry hydrogen atmosphere, maintaining at the temperature of incandescence a hydrogen pressure in the container in excess of the dissociation pressure of the particular metal hydride being formed, at the particular temperature to which the same is being heated.

Before further disclosing the nature of my invention reference should be had to the accompanying drawings wherein,

Fig. 1 is a schematic diagram of the apparatus employed in the preparation of metal hydrides by the present invention, and

Fig. 2 is a graph showing a typical pressure temperature equilibrium curves used in the practice of the present invention.

In preparing metal hydrides in accordance with the present invention the metal powder 1 is placed in a container 2, preferably comprised of glass, which is connected to a suitable exhaust system 3 by any suitable means such as by ground stopper joint 4. To prevent the diffusion of deleterious vaporizable impurities, such as mercury vapor, hydrocarbon vapor, moisture and the like impurities from the exhaust system to the metal powder, there is interposed therebetween a liquid air trap 5.

Means comprising a stop-cock 6 are provided for closing off the exhaust apparatus (not shown but indicated) which may be any suitable type of mechanical exhaust means such as mercury diffusion pumps, molecular pumps, and the like capable of giving a high vacuo in container 2 of the order of 1.0 micron pressure which is equal to about .001 m. m. mercury pressure. Means comprising a stop-cock 7 are also provided for introducing hydrogen gas under pressure from a reservoir not shown but indicated. Pressure reading means 8 are provided for determining the hydrogen pressure in system 3, which means in the present illustration comprises a long glass tube extension 9 of the system 3 dipping into a container 10 which is open to the atmosphere and filled with mercury 11. Means comprising a stop-cock 12 are provided for shutting off this pressure reading means 8 when desired.

Heating means comprising a wire wound resistance furnace or oven 13, provided with temperature measuring means 14, are provided to heat the metal powder 1 to the desired temperatures. A two piece top 15 for

enclosing the container 2 within the furnace 13 is also provided.

As an illustration of the practice of the present invention I will disclose the method I employ in producing uranium hydride from uranium metal powder.

The uranium metal powder or other rare refractory metal powders employed in the preparation of rare metal hydrides may be prepared either by the calcium-calcium chloride reduction method set forth in U. S. Patent 1,704,257 issued March 5, 1929 to J. W. Marden et al, or by the electrolytic methods set forth in my copending applications Serial No. 275,264 filed May 4, 1928, Serial No. 277,096 filed May 11, 1928, Serial No. 309,682 filed October 1, 1928, Serial No. 316,624 filed November 1, 1928, or Serial No. 351,451 filed March 30, 1929, which patent and applications are all assigned to the same assignee as the present invention.

In either the calcium or calcium chloride reduction method or the electrolytic method of producing the metal powders, there is a wet concentration step wherein the metal powders are subjected to a water and acid wash to free of associated impurities. It is then customary to free the metal powder of moisture by repeated washing with alcohol, preferably on a suction filter and then remove the alcohol by washing the metal powder with ether. The ether wet metal powder is then dried, either in the open air or in vacuo and the metal powder is ready for compacting and sintering into coherent form in accordance with the invention set forth in copending application Serial No. 717,940 filed June 5, 1924 by J. W. Marden et al which application is also assigned to the same assignee as the present invention.

For the purposes of the present invention it is preferable to employ the ether wet rare metal powder in the practice of my invention for the reason that such metal powders do not have an adsorbed or absorbed surface layer of atmospheric gases to be removed prior to the forming of the rare metal hydride, and the degasification of the metal powder step of the present invention, therefore, resides in the proper and complete evacuation of the ether from the metal powder, at a time just prior to the forming of the metal hydrides, which ether removal may be accomplished at room temperatures.

I may employ, however, the dried metal powders of most of the rare metals in the forming of hydride compounds the exceptions being uranium unless the particle size of the uranium is relatively large, or thorium, when extremely finely subdivided.

Such metal powders are substantially pyrophoric and spontaneously combust when exposed to the atmosphere. In coarser form these two metal powders may be readily employed in the practice of my invention as the heat of formation of surface oxides is insufficient to incandesce the coarser metal particles as in the smaller particle size metal powders.

In either event the metal powder product, ether wet or air dried, is placed in container 2, and thoroughly evacuated by means of mechanical exhaust means, stop cocks 7 and 12 of the system illustrated in Fig. 1 being closed during the electric evacuation process, and following the obtainance of a reasonably high vacuo within the system, trap 5 is enclosed by the usual type liquid air container. The metal powder may be placed in container 2 loosely as indicated in the drawings, or it may be compacted into a button prior to the placing of the same in the container 2.

The metal powder is then gently heated by means of furnace 13 to slightly elevated temperatures for a prolonged interval of time to facilitate the removal of surface adsorbed gases from the container 2 and the metal powder 1, if the ether wet metal powder is not employed care being taken not to heat the metal powders to temperatures at which the metal powder will combine with the residual evolved gases. With uranium this combining temperature is relatively very low and temperatures much in excess of 200° C. to 225° C. should be avoided.

Following thorough degasification of the metal powder the evacuating apparatus is closed off from the system by means of a stop cock 6, the metal powder cooled to below the combining temperature of the metal for hydrogen and the system filled with chemically pure dry hydrogen to a pressure of about 150 m. m. mercury as measured by means of the pressure measuring device 8.

By previously determining the approximate weight of the metal powder 1, an approximation of the amount of hydrogen required for complete conversion of the metal to hydride may be made, and the capacity of the system 3 adjusted or arranged accordingly, such as by providing a suitable gas reservoir 17.

In Fig. 2 of the accompanying drawings I have set forth the specific pressure-temperature equilibrium curve which is to be followed in the manufacture of uranium hydride.

Referring to the curve in Fig. 2 of the drawings, I have found that uranium metal powder when properly degasified in accordance with the above identified procedure will react with hydrogen at temperatures approximating 200 to 225° C., and that the equilibrium pressure of hydrogen to uranium hydride at this temperature is about 3 m. m. of mercury. This means that in order to form uranium hydride at this temperature the hydrogen pressure must be in excess of about 3 m. m. pressure of mercury and that the amount of the excess hydrogen must equal approximately that amount which is necessary

to completely react with the uranium to form the hydride compound UH_4.

If a temperature approximating 300° C. is applied to the uranium metal a pressure of hydrogen in excess of about 20 m. m. mercury must be maintained in order to promote the formation of the hydride compound.

It may be seen from curve 1 in Fig. 2 that the required pressure of hydrogen to promote the forming of the uranium hydride increases rapidly with increase in temperature until at 435° C. a hydrogen pressure in excess of about 700 m. m. mercury is required.

For practical purposes, therefore, the lower temperatures of forming the hydride compound are to be preferred, and the procedure I usually employ is to introduce into the evacuated container 1 and system 3 a hydrogen pressure of about 150 m. m. mercury. I then heat the degasified uranium metal powder 1, which preferably is of a particle size ranging from 50 to 500 mesh, to a temperature of about 225° C. and when the hydrogen pressure has been reduced to about 3 m. m. mercury, increased amounts of hydrogen are introduced, continuing the introduction of the hydrogen as frequently as the pressure reduces to 3 m. m., or until no further decrease in pressure is obtained. In this manner complete conversion of the uranium metal powder to hydride is obtained.

I may, however, introduce into the evacuated system a sufficient amount of hydrogen to effect entire conversion of the metal powder to hydride, if desired. I have found, however, that with uranium, for example, the reaction between uranium and hydrogen is exothermic and when once initiated at the temperature of 225° C. progresses rapidly by reason of the incandescing of the metal powder particles as a result of the exothermic heat evolved in the reaction. As a consequence it is difficult to control the reaction and it may even become explosively violent. I prefer, therefore, with this metal to limit the quantity of hydrogen within the system 3, and to add increments thereto as the reaction progresses. With other metals this precaution is not strictly an essential.

Other metal hydrides may be prepared by the procedure such as has been herein disclosed for the prepartion of uranium hydride. In particular the rare refractory metal hydrides of thorium, zirconium, titanium, hafnium and the like may be so prepared.

Thorium hydride may be prepared by this method and I have determined that the initial combining temperature of thorium for hydrogen is about 360° C. at which temperature the equilibrium pressure of hydrogen is extremely low, indicating that the thorium hydride compound is quite stable at this temperature. The equilibrium pressure does not rise so rapidly with increased temperature as with uranium hydride and at about 425° C. the equilibrium pressure is only about 20 microns which is about .02 m. m. mercury. Zirconium and titanium metals behave similarly to thorium in the preparation of their hydrides but all may be prepared readily by the present invention. I have found that the degasification of the metal powders prior to the formation of the hydride is highly essential in the preparation of these metal compounds.

It may be seen, therefore, that the present invention is susceptible to adaptation to the manufacture of a number of different metal hydrides, and that there may be many modifications and departures made from the specific embodiment herein set forth without departing essentially from the nature of the invention as set forth in the following claims.

What is claimed is:

1. The method of preparing uranium hydride which comprises heating uranium metal powder in a hydrogen atmosphere to temperatures in excess of about 225° C. maintaining at the temperature of heating a pressure of hydrogen in excess of the dissociation pressure of uranium hydride at that temperature.

2. The method of preparing uranium hydride which comprises heating uranium metal powder to temperatures in excess of about 225° C. and below about 450° C. in an atmosphere of substantially pure hydrogen, maintaining the pressure of said hydrogen at from about 3.0 m. m. of mercury to about 760 m. m. mercury, depending upon the temperature of said heating.

3. The method of preparing uranium hydride which comprises heating uranium metal powder in hydrogen to a temperature about 225° C. maintaining the pressure of said hydrogen at that temperature in excess of about 3.0 m. m. of mercury.

4. The method of preparing metal hydrides from metal powders which comprises enclosing the metal powder in a container, evacuating the container, degasifying the metal powder, introducing an atmosphere of hydrogen into the container and heating the metal powder to elevated temperatures to effect the formation of the metal hydride compound, maintaining the hydrogen pressure in excess of the equilibrium pressure of said metal hydride compound at the temperature of said heating.

5. The method of preparing the hydride compounds of the rare refractory metals which comprises enclosing the metal powder in a container, evacuating the container, degasifying the metal powder, introducing an atmosphere of hydrogen into the container and heating the metal powder to elevated temperatures to effect the formation of the hydride compound maintaining the hydrogen pressure in excess of the equilibrium

pressure of the hydride compound at the temperature of said heating.

6. The method of preparing uranium hydride which comprises enclosing uranium metal powder in a container, evacuating the container, degasifying the metal powder, introducing an atmosphere of hydrogen into the container, and heating the uranium metal powder to elevated temperatures below about 450° C., maintaining at the temperature of heating a hydrogen pressure in excess of the equilibrium pressure of the uranium hydride formed.

7. The method of preparing uranium hydride which comprises enclosing uranium metal powder in a container, evacuating the container, degasifying the metal powder, introducing an atmosphere of hydrogen into the container, and heating the metal powder to about 225° C., maintaining the pressure of hydrogen in the container in excess of about 3.0 m. m. mercury.

8. The method of preparing the hydrides of highly reactive rare refractory metals which comprises forming a substantially pure metal powder, enclosing the metal powder in a container, evacuating the container, degasifying the metal powder by prolonged heat-treatment at relatively low temperatures in the continuously maintained high vacuo, introducing an atmosphere of hydrogen in the evacuated container, and heating the metal powder to elevated temperatures in said hydrogen atmosphere maintaining the pressure of said hydrogen at all times in excess of the equilibrium pressure of the metal hydride compound at the temperature of heating.

In testimony whereof, I have hereunto subscribed my name this 22nd day of November, 1929.

FRANK H. DRIGGS.