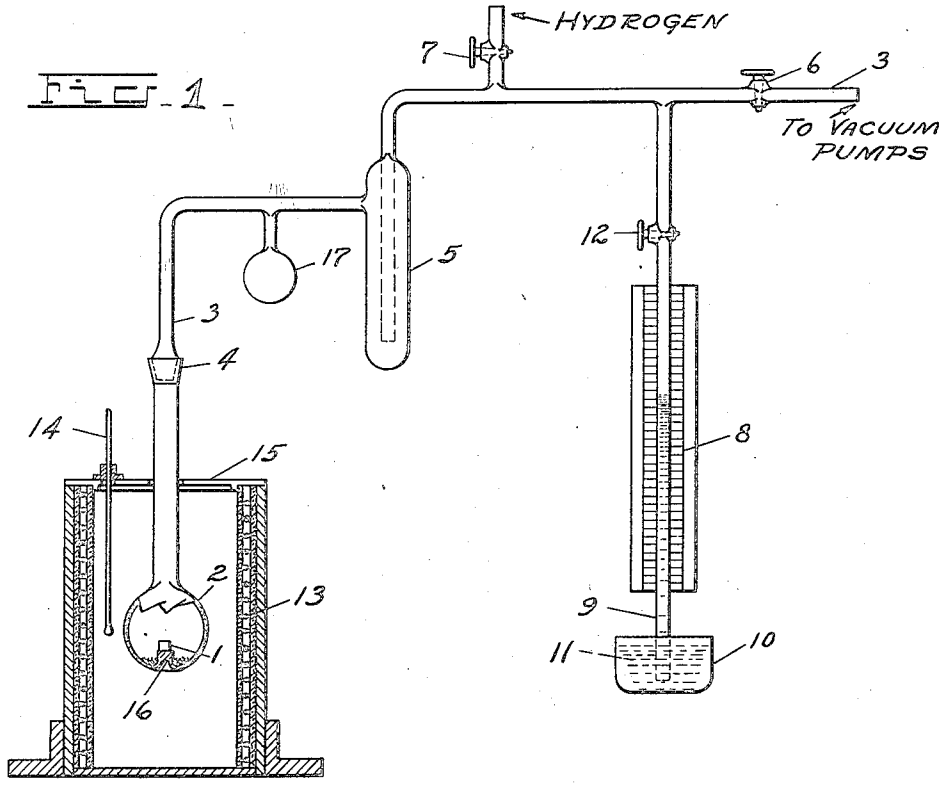
Dec. 8, 1931. F. H. DRIGGS 1,835,024

PREPARATION OF METAL HYDRIDES

Filed Nov. 25, 1929

Fig. 1.



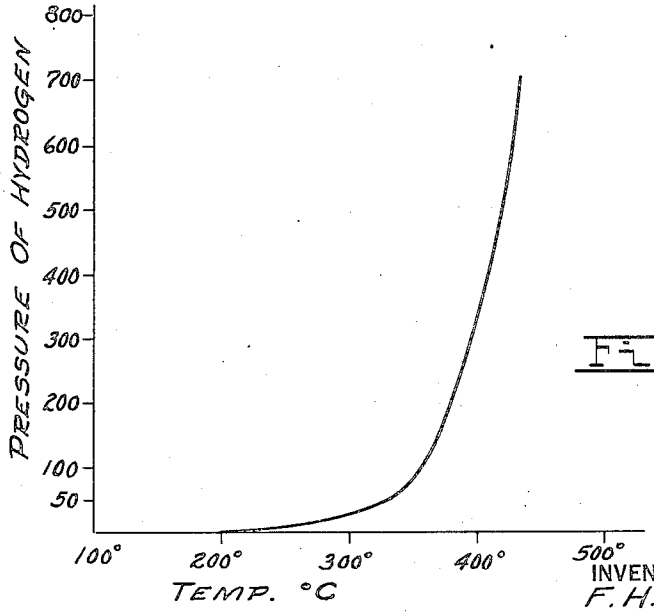


Fig. 2.

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UNITED STATES PATENT OFFICE

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PREPARATION OF METAL HYDRIDES

Application filed November 25, 1929. Serial No. 409,443.

This invention relates to the preparation of metal hydride compounds and more particularly to the preparation of metal hydrides from substantially pure coherent metal bodies, and specifically relates to a method of preparing uranium, thorium, zirconium and the like rare metal hydrides from relatively pure coherent bodies of the same.

In my copending application Serial No. 409,442 filed November 25, 1929, entitled "Preparation metal hydrides," which is assigned to the same assignee as the present invention I have disclosed a method of preparing metal hydrides from metal powders, particularly the rare refractory metal powders, which form compounds with atmospheric gases which are irreducible by hydrogen.

The method disclosed therein sets forth a degasification of the metal powder step preliminary to the formation of the hydride compound. The degasification of the metal powder by the method disclosed therein is a slow and tedious process and on any commercial scale materially increases the costs of manufacture. Moreover with the more highly reactive metals, such as uranium and thorium, it is exceedingly difficult to perform the step without deleterious contamination of the metal with the residual gases in the evacuated system.

It is one of the objects of this invention to improve the method of preparing metal hydrides.

It is another object to provide a method of preparing metal hydrides directly from presintered, substantially pure gas free coherent metal bodies.

It is another object of this invention to provide a method of forming metal hydrides from sintered coherent masses of rare refractory metals.

In accordance with the objects of the present invention I have found that a solid mass of coherent metal may be entirely converted over to hydride by forming upon the metal surface metal hydride compounds, effecting thermal decomposition of these compounds with consequent corrosion of the metal surface, again forming surface hydride compounds and repeating the thermal decomposition and forming of fresh hydride until the entire coherent metal body has been converted over to the hydride. In the practice of the present invention I substantially follow the practice of my copending application above identified, in that the metal surface is first exposed to the action of hydrogen at an elevated temperature, the hydrogen pressure being maintained above the equilibrium pressure of the metal hydride compound at the temperature employed, promoting thereby the formation of surface metal hydride compounds.

The temperature of the metal body is then materially increased, or the hydrogen pressure is reduced below the equilibrium pressure, or both factors are varied so as to effect a decomposition of the metal hydride to metal powder, which crumbles or falls away from the coherent metal mass thereby exposing fresh metal surfaces of the mass. The freshly exposed metal surface is again subjected to the action of the hydrogen, preferably at a lower combining temperature, the hydrogen pressures being meanwhile adjusted to be in excess to the equilibrium pressure of the metal hydride compound at that temperature. This operation is repeated as many times as is required to effect the entire conversion of the coherent metal mass to metal hydride compounds, all as will be more fully hereinafter disclosed.

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

Fig. 1 is a schematic diagram of the apparatus employed in the practice of the present invention, and

Fig. 2 is a graphical representation of the

equilibrium pressure-temperature curve of hydrogen metal hydrides by which the practice of the present invention is facilitated.

In Fig. 1 is shown a coherent body of metal 1, enclosed upon a pedestal or reentrant portion 16 in container 2 which is connected in any suitable manner, such as by ground joint 4, to an exhaust system 3 connected in any suitable manner to mechanical exhaust apparatus (not shown) such as mercury diffusion pumps, molecular pumps, oil immersion pumps and the like apparatus capable of giving a high vacuo in container 2 of the order of 1.0 micron pressure which is equivalent to a pressure of about .001 m. m. mercury. Means are provided for preventing the dispersion of oil, mercury or other deleterious vapors from the mechanical exhaust means to the container 2, such as trap 5, which may be surrounded by a suitable liquid air container, not shown.

Means comprising a stop cock 6 are also provided for closing off the exhaust apparatus and means comprising a stop cock 7 are provided for introducing hydrogen gas under pressure to the evacuated container from a reservoir, not shown but indicated. Pressure reading means 8 are provided for determining the pressure of the hydrogen in the system 3 which 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, and means comprising stop cock 12 are provided for shutting off this pressure reading means 8 when so desired.

Heating means comprising a wire wound resistance furnace or oven 13 provided with temperature measuring means 14 are provided to heat the metal body 1 to the desired temperature. A two-piece top 15 for enclosing the container 2 within the furnace 13 is also provided.

In accordance with the present invention the coherent body of metal 1 may be comprised of one of the rare refractory metals uranium, thorium, zirconium, titanium, hafnium and the like, and preferably has been prepared from substantially pure metal powder prepared in accordance with the invention set forth in U. S. Patent 1,704,257 issued March 5, 1929 to J. W. Marden et al., or by any one of 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 copending applications are all assigned to the same assignee as the present invention.

The substantially pure rare refractory metal powder is then compacted and heat-treated to a coherent body in a continuously maintained high vacuo, in accordance with the process 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.

Briefly the sintering process contemplates the heat-treating of the metal body in vacuo in two stages; first, at a relatively low temperature to effect the removal of adsorbed and absorbed gases from the compacted metal powder at a temperature substantially below the combining temperature of the metal powder for the gases, and secondly at a higher temperature approximating the fusion point of the compacted metal powder to effect the coalescing and sintering of the degasified metal powder into a coherent metal body, the said two heat treatments being applied thereto in consecutive order without intervening exposure of the meal to deleterious gaseous absorption.

By this method of sintering the metal powders of the more highly reactive rare refractory metals into a coherent metal body a metal mass is obtained which is substantially free of deleterious impurities of oxides, nitrides, hydrides and the like compounds.

The forming of metal hydrides from a coherent metal body of the rare refractory metals uranium, thorium, zirconium, hafnium and the like, is highly desirable in that the amount of deleterious impurities introduced into the resulting hydride is relatively extremely low. This is believed to be due to the fact that the two stage vacuum heat treating step to coherent form, as by the above identified copending application Serial No. 717,940, more completely eliminates the deleterious adsorbed and absorbed gases of the metal powder prior to sintering than is obtained by the practice of the relatively lower degasification heating stage of the above identified copending application filed herewith.

Another advantage is in the relatively short period of time required to effect degasification or removal of the surface gases of a coherent metal body prior to the preparation of the metal hybride.

In the practice of the present invention and as a specific embodiment thereof I will disclose the method I employ in the forming of uranium hydride from a coherent body of uranium.

The uranium metal body 1 prepared and sintered as above disclosed in accordance with the inventions of the above identified patent and copending applications, is placed in a container 2 which is preferably comprised of glass upon a pedestal or reentrant portion 16 thereof in the manner shown, and the container 2 connected to the evacuating system 3 by means of the tapered stopper 4, and the entire system evacuated with stop cocks 7 and 12 closed. When a relatively

high vacuo has been obtained by mechanical exhaust means, trap 5 is surrounded by a suitable liquid air container to prevent the back dispersion of deleterious vapors or gases. Container 2 and metal body 1 is then thoroughly "baked" and freed of surface gases by bringing the temperature of the enclosing furnace or oven up to temperatures just below the softening temperature of the container 2. The uranium metal body may also be heated to incandescence if desired by high frequency induction means.

When a pressure of about 1.0 micron (.001 m. m. mercury) has been obtained in the system the evacuating system is closed by means of stop cock 6, the uranium metal button allowed to cool to about room temperature and the system then filled with pure dry hydrogen from the hydrogen reservoir (not shown but indicated) by opening stop cock 7, and the pressure of the gas adjusted to about 150 m. m. as determined by means of the pressure reading device 8.

The temperature of the uranium metal body is then brought up to about 225° C. at which temperature, reaction of the uranium with the hydrogen atmosphere takes place and proceeds as long as the hydrogen pressure exceeds a pressure of about 3 m. m. of mercury, as is shown in Fig. 2 and more fully set forth in copending application filed herewith. The absorption or reaction of the uranium with the hydrogen proceeds rapidly until the surface is completely coated and then the rate of combination slows up and eventually the further formation of metal hydride is substantially prevented.

By the next step of my invention I raise the temperature of the metal body to about 350 to 400° C. at which temperature the equilibrium pressure for hydrogen and uranium hydride is between about 80 and 320 m. m. mercury and effect thereby a decomposition or dissociation of the uranium hydride compound formed in the first step, the metal powder product of the decomposition falls away from the surface of the coherent mass and collects in the bottom of the container 2 in the manner shown. I then reduce the temperature of the container 2 to about 225° C again, form more hydride upon the uranium metal body and repeat the decomposition of the hydride by again increasing the temperature to 350° to 400° C. This is repeated as many times as is required to entirely convert the uranium body over to the hydride compound which is eventually collected as a loose powder in the bottom of the container 2.

From the weight of the uranium metal body 1 the approximate amount of hydrogen required to effect entire conversion may be readily calculated, and the capacity of the system 3 adjusted by means of suitable reservoirs 17 to hold the same, and suitable precautions must be taken so that the system will safely carry the higher pressures of gases required by this method.

An alternative method would be to evacuate the hydrogen from the system when reaction between the uranium metal surface and the hydrogen has ceased, or to reduce the pressure below the equilibrium pressure at the initial combining temperature of 225° C. effecting thereby the dissociation of the uranium hydride compound, or a still higher temperature in combination with the reduced pressures may be employed to obtain substantially the same effect as is obtained in the first illustration of the practice of my invention.

While I have disclosed herein the specific method I employ in producing uranium hydride from a coherent uranium metal body it is apparent that there may be many modifications made therein in both the process and apparatus without substantially departing from the nature of the invention, and that the invention is adaptable to be employed in the manufacture of other metal hydrides than uranium, and that such modifications, departures and applications thereof are anticipated as may fall within the scope of the following claims.

What is claimed is:

1. The method of converting coherent metal bodies into metal hydride compounds which comprises converting the surface of the metal body to hydride, effecting thermal decomposition of said hydride, and repeating the process until entire conversion of the metal body has been effected.

2. The method of converting coherent metal bodies into metal hydride compounds which comprises repeatedly heating the metal body in hydrogen to a temperature at which the metal body reacts with the hydrogen to form metal hydride compounds at the surface maintaining the hydrogen at pressures substantially above the dissociation pressure of the formed metal hydride, intermediate each heating decomposing the surface hydride compounds.

3. The method of forming metal hydride compounds from coherent metal bodies which comprises repeatedly heating the metal body in hydrogen to a temperature at which the hydride compound is formed, the pressure of the hydrogen being maintained substantially above the equilibrium pressure of the metal hydride compound at that temperature, effecting intermediate each heating decomposition of the surface metal hydride compounds by thermal decomposition at higher temperatures at gas pressures below the equilibrium pressure at the higher temperature of heating.

4. The method of forming metal hydride compounds from coherent metal bodies which comprises repeatedly heating the

metal body in hydrogen to a temperature at which the hydride compound is formed, maintaining the pressure of the hydrogen above the equilibrium pressure of the metal hydride compound formed, effecting intermediate each heating a decomposition of the surface metal hydride compounds by a reduction in the hydrogen gas pressures substantially below the dissociation pressure of the metal hydride compound at the temperature to which it is heated.

5. The method of forming uranium hydride from coherent uranium metal which comprises repeatedly heating the uranium metal in an atmosphere of hydrogen to a temperature at which uranium hydride may be formed, maintaining during the heating a hydrogen pressure substantially greater than the dissociation pressure of the uranium hydride, intermediate each of the heatings decomposing the uranium hydride formed.

6. The method of forming uranium hydride from coherent uranium metal which comprises repeatedly heating the uranium metal in an atmosphere of hydrogen to a temperature at which uranium hydride may be formed, maintaining during the heating a hydrogen pressure substantially greater than the dissociation pressure of the uranium hydride, effecting intermediate each of the heatings a thermal decomposition of the uranium hydride.

7. The method of forming uranium hydride from coherent uranium metal which comprises repeatedly heating the uranium metal in an atmosphere of hydrogen to a temperature at which uranium hydride may be formed, maintaining during the heating a hydrogen pressure substantially greater than the dissociation pressure of the uranium hydride, effecting intermediate each of the heatings a decomposition of the uranium hydride by substantially reducing the hydrogen gas pressure below the dissociation pressure of the metal hydride at the temperature to which it is heated.

8. The method of forming uranium hydride from a coherent metal body which comprises alternately heating the metal in a hydrogen atmosphere to temperatures approximating 225° C. and 350° C. maintaining a gas pressure at the first mentioned temperature substantially in excess of 3.0 m. m. mercury and at the last mentioned temperature substantially below about 80 m. m. mercury pressure.

9. The method of preparing metal hydride compounds which comprises enclosing a coherent body of the metal in a container, evacuating the container, degasifying the metal body and container, introducing an atmosphere of hydrogen in the container, heating the metal body to a temperature at which surface formation of metal hydrides is promoted maintaining at this temperature a pressure of hydrogen in excess of the dissociation pressure of the metal hydride being formed, further heating the metal body to more elevated temperatures in gas pressure substantially below the dissociation pressure of the metal hydride at the higher temperature, reducing the temperature of the metal body to the lower temperature, and repeating the steps until the entire metal body has been converted to hydride.

10. The method of preparing uranium metal hydride which comprises enclosing a coherent mass of uranium in a container, evacuating the container, degasifying the metal and container, introducing an atmosphere of hydrogen into the container, and then repeatedly heating the metal body to temperatures at which the metal reacts with the hydrogen atmosphere maintaining a gas pressure substantially in excess to the decomposition pressure of the uranium hydride compound at that temperature, and intermediate each of said heating operations decomposing the metal hydride formed.

11. The method of preparing uranium metal hydride which comprises enclosing a coherent mass of uranium in a container, evacuating the container, degasifying the metal and container, introducing an atmosphere of hydrogen into the container, and then repeatedly heating the metal body to temperatures at which the metal reacts with the hydrogen atmosphere maintaining a gas pressure substantially in excess to the decomposition pressure of the uranium hydride compound at that temperature and intermediate each of said heating operations effecting thermal decomposition of the metal hydride formed.

12. The method of preparing uranium metal hydride which comprises enclosing a coherent mass of uranium in a container, evacuating the container, degasifying the metal and container, introducing an atmosphere of hydrogen into the container, and then repeatedly heating the metal body to temperatures at which the metal reacts with the hydrogen atmosphere maintaining a gas pressure substantially in excess to the decomposition pressure of the uranium hydride compound at that temperature and intermediate each of said heating operations effecting dissociation of the metal hydride formed by heating the hydride compound under gas pressure substantially below the equilibrium pressure thereof.

13. The method of preparing uranium metal hydride which comprises enclosing a coherent body of uranium in a container, evacuating the container, degasifying the metal body and container, introducing a hydrogen atmosphere in the container, and then repeatedly heating the uranium first at a temperature of about 225° C. in a hydrogen gas pressure materially in excess of about 3.0

m. m. mercury and then to a temperature of about 350° in a hydrogen gas pressure materially less than about 80 m. m. of mercury until the mass of uranium metal has been entirely converted to hydride.

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

FRANK H. DRIGGS.