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PRODUCTION OF METAL HYDRIDES

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Fig. 1.

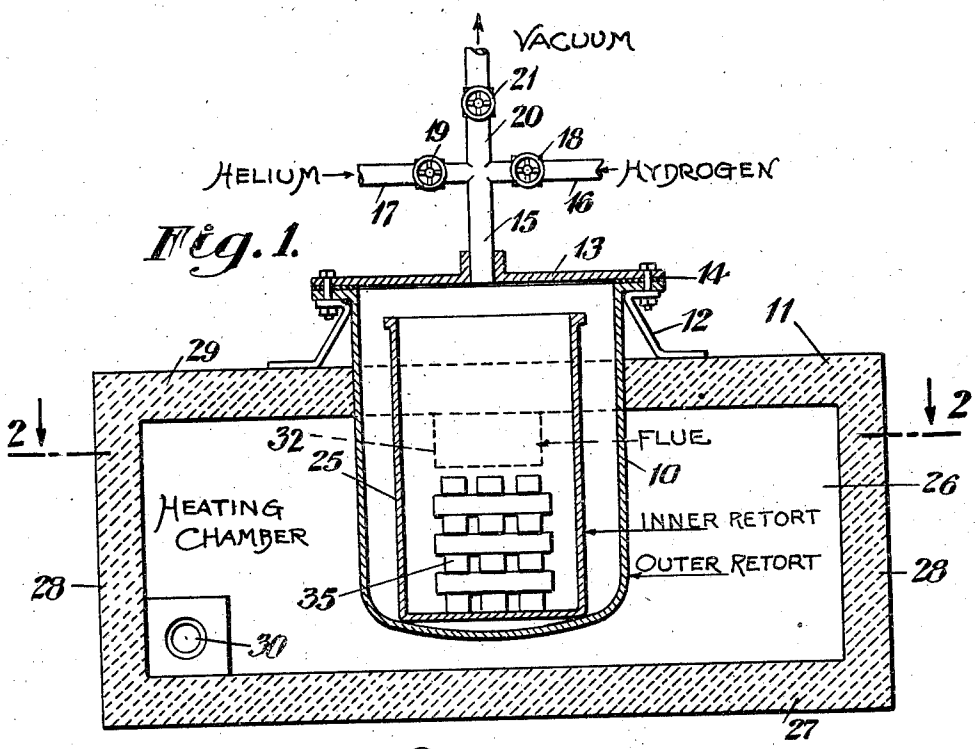
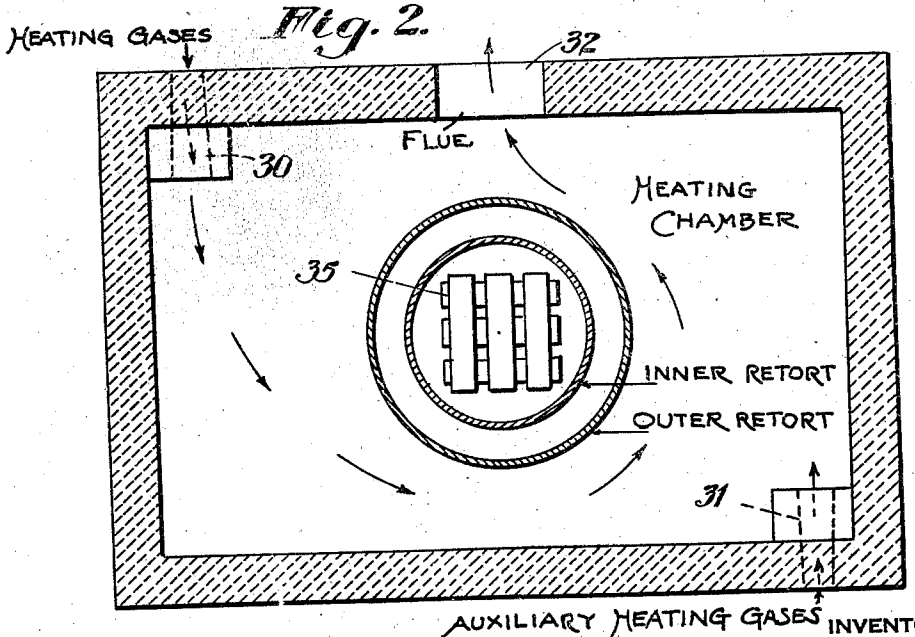


Fig. 2.



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PRODUCTION OF METAL HYDRIDES

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14 Claims. (Cl. 23—204)

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This invention relates to the production of metal hydrides and has for its object certain improvements in the method of producing metal hydrides.

Metal hydrides are formed by bringing hydrogen gas into contact with a hydride-forming metal at its temperature of reaction. The reaction is an exothermic one, resulting in an evolution of considerable heat. While external heat is used to start the reaction, the exothermic or internal heat is usually more than enough to support the reaction thereafter. The exothermic heat generated is usually so great that special precautions must be taken to dissipate it to avoid overheating of the metal or the metal hydride. Overheating is objectionable when it fuses the metal to be hydrided, or if it dissociates the metal hydride that has been formed, or if it results in a temperature so high that the metal hydride cannot be formed.

It is customary to place the metal to be hydrided in a heated retort which is closed and evacuated to remove air. Hydrogen gas is then fed into the retort; the retort is externally heated until the metal reaches its temperature of reaction; and the conversion of the metal to its hydride then begins. The exothermic heat resulting from the reaction tends promptly to elevate the temperature still further and the application of external heat to the retort is, therefore, discontinued. To render the retort gastight, it is customary to dispose a gasket between the top of the retort and its cover. The hydrogen initially fed into the retort is consumed very rapidly and a partial vacuum tends to be established within the retort. If the gasket or any part of the retort is not perfectly tight, air is drawn into the retort with the result that partially hydrided metal is oxidized. If the air continues to seep into the retort, the oxidation proceeds until the temperature is so high that hydrogen previously consumed by the metal, to form metal hydride, is evolved from the partially hydrided metal with the resultant formation of a dangerously explosive mixture in the retort.

If the metal to be hydrided is placed in the retort in the form of ingots, for example, overheating by the exothermic heat may not only fuse the ingots together but may fuse them into a single mass. This result is highly disadvantageous for several reasons. In the first place, the metal tends to fuse against the retort wall, which is usually steel, and therefore takes on impurities from the retort. Second, it is usually desired to have the ingot of metal converted into

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an ingot of metal hydride of substantially the same size and shape. Fusion of the ingots makes this result impossible. Third, fusion of the ingots into a single mass results in a hard and compact cake which is removed from the retort with considerable difficulty. Fourth, fusion of the ingots into a single mass makes it practically impossible for the hydrogen completely to permeate the mass and the efficiency of the hydriding action is, therefore, impaired.

The problem of overheating is met in the production generally of metal hydrides. It is a particularly serious problem, however, when converting the more highly reactive metals to their hydrides. This is especially true of the alkaline earth metals, such as calcium, barium and strontium.

As a result of my investigation, I have discovered that the disadvantages just enumerated may be substantially overcome. The hydriding reaction itself may be conducted in such a way as to avoid objectionable overheating. In other words, the amount of exothermic heat generated by the reaction may be so carefully controlled that it no longer becomes necessary to take special precautions to dissipate the excess exothermic heat as rapidly as it is generated.

In the production of metal hydrides by reacting hydrogen gas with a hydride-forming metal confined in a heated reaction zone in accordance with the invention, the rate of formation of the metal hydride is slowed down by diluting the hydrogen with an inert gas. The inert gas is used in amount sufficient to inhibit objectionable overheating of the metal by the exothermic heat of the reaction.

Since the hydride-forming metal is confined in a reaction zone, in a closed retort, dilution of the hydrogen with an inert gas is made to result in a lower concentration of hydrogen than would be the case if the hydrogen were not diluted. In other words, whereas the reaction zone would normally be filled solely with hydrogen at a given pressure, it is now filled with an inert gas admixed with a relatively small amount of hydrogen at the same pressure. That relatively small amount of hydrogen is all the hydrogen available for reaction with the hydride-forming metal until a further amount is fed to the reaction zone. By limiting the amount of hydrogen thus fed to the reaction zone, the rate of formation of the metal hydride may be regulated; and by regulating the rate of formation of the metal hydride, the rate of generation of exothermic heat may be regulated. Therefore, by diluting

the hydrogen in the reaction zone, overheating of the metal or metal hydride may be avoided. With little experience an operative can soon hit upon a suitable dilution to prevent a rise in temperature sufficient to fuse the metal to be hydrided, or to dissociate the metal hydride formed, or to prevent the formation of metal hydride, while at the same time maintaining the reaction zone at a temperature at which the desired hydriding action takes place.

A sufficient amount of inert gas is fed into the reaction zone to keep it under positive pressure as the reaction goes to completion. Due to the presence of the inert gas, which does not react with the hydride-forming metal, the consumption of the limited amount of hydrogen in the reaction zone by the hydriding reaction does not cause a partial vacuum to be established within the retort. The pressure of the inert gas in the retort is sufficiently high so that when the limited amount of hydrogen in the reaction zone is consumed to produce metal hydride, the drop in pressure is not sufficient to create a vacuum; in other words, the pressure within the retort does not fall below atmospheric pressure outside of the retort. If, therefore, the retort should develop a leak, air will not seep into the retort.

In a presently preferred practice of the invention, a suitable amount of inert gas is introduced into the retort, and hydrogen gas is then fed automatically into the retort at a predetermined pressure until the reaction has gone to completion. That is, when the pressure within the retort drops below a given level, hydrogen is automatically fed into the retort to restore the pressure. The amount of inert gas in the retort and the amount of hydrogen progressively fed into the retort may be so correlated that the concentration of hydrogen in the retort does not rise to a point at which the rate of formation of the metal hydride results in an excessive generation of heat. This control may in fact be used to maintain the reaction zone at an optimum temperature for the desired conversion.

These and other advantages of the invention will be better understood by referring to the accompanying drawing, taken in conjunction with the following description, in which:

Fig. 1 is a diagrammatic representation, in cross-section, of an apparatus that may be employed in the practice of the invention; and

Fig. 2 is a cross-section on the line 2—2 of Fig. 1.

The apparatus shown comprises an outer retort 10 supported within a heating furnace 11, the retort being held in position by means of two or more supports 12 resting on the top of the heating furnace. The retort is made preferably of heat-resistant steel. It is fitted with a removable cover 13, a gasket 14 being disposed between the cover and a bent over circumferential portion of the upper end of the outer retort. The removable cover has attached thereto a lower vertical pipe 15 with lateral branch pipes 16 and 17 fitted with pressure control valves 18 and 19, respectively. Branch 16 is connectable with a source of hydrogen and branch 17 with a source of inert gas, such as helium or argon. An upper vertical branch pipe 20, provided with a valve 21, connects with the lower vertical pipe 15 and is connectable with a source of vacuum. A removable inner retort 25 fits within the outer retort.

The heating furnace 11 consists essentially of a rectangular chamber 26 having a refractory bottom 27, side and end refractory walls 28, and

a refractory top 29 having an opening of a size not much larger than, and adapted to receive, the outer retort. An expanding opening 30 is provided at or near a lower corner of one of the side walls of the chamber for the introduction of heating gases into the chamber. A similar opening 31 is preferably provided at or near an opposite corner as a spare or auxiliary means for introducing heating or cooling gases into the chamber. When not in use, opening 31 is suitably closed. A flue opening 32 extends through the same wall as opening 30, preferably at a higher level, so that heating gases passed into the chamber through opening 30 tend to pass almost completely around the outer retort before leaving the chamber through flue opening 32.

The apparatus may be used as follows: A charge of calcium ingots 35, for example, is placed in the bottom of inner retort 25, in a reaction zone. A plurality of the ingots is advantageously stacked on top of one another, as shown, so as to expose as much surface as possible, the ends and sides of the ingots preferably not being in contact with the wall of the inner retort. The inner retort is then placed in outer retort 10 and removable cover 13 is placed on outer retort 10 and locked thereon to provide a sealed joint. Vertical branch 20 is then connected to a source of vacuum. With valve 21 of the vertical branch open, and valves 18 and 19 in lateral branches 16 and 17 closed, the outer and inner retorts are placed under vacuum to remove objectionable air.

Heating gases are passed through opening 30 into heating chamber 26 where they circulate almost completely around the retort and then pass through flue opening 32 to the outside atmosphere. As the lower portion of outer retort 10 is heated, the lower portion of inner retort 25 is also heated. The evacuation of the inner and outer retorts is preferably continued during this initial heating operation because it aids in the removal of objectionable air. On completion of the evacuation step, valve 21 is closed.

Valve 19 in lateral branch 17 is then opened to admit a suitable amount of inert gas, such as helium or argon, into the retorts. Enough inert gas is introduced to create a positive pressure, for example 10 to 15 pounds per square inch, within the retorts. Helium is the more readily available inert gas at the moment but argon is in some respects more desirable because it is heavier and tends to diffuse less slowly from the retorts. A limited amount of hydrogen gas is then passed into the retorts by opening valve 18 in lateral branch 16. The heating gases are passed into the heating chamber until the inner retort and hence calcium ingots 35 reach a temperature at which the hydriding reaction starts.

$$Ca + H_2 \rightarrow CaH_2$$

As soon as the reaction begins, exothermic heat is generated and the temperature of the charge tends to rise still further. Introduction of the heating gases into the heating chamber is then stopped. Hydrogen gas is preferably fed automatically into the retorts at a predetermined pressure until the reaction has gone to completion. This may be accomplished by a suitable pressure control valve. Valve 18 may, for example, be considered as a pressure control valve in lateral branch 16 or as a conventional pressure control valve connected to the outlet of a tank of hydrogen gas connected to lateral branch 16. When the pressure within the retorts drops below a given level, additional amounts of hydrogen are

automatically fed into the retorts to restore the pressure. The amount of inert gas maintained in the retorts and the amount of hydrogen progressively fed into the retorts may be so correlated that the concentration of hydrogen in the retorts does not rise to a point at which the heat of formation of the calcium hydride results in an excessive rise in temperature. This control may be used to maintain the reaction zone in the inner retort at an optimum temperature for the desired conversion, and thus avoid overheating together with its objectionable results.

While the method of the invention has been illustrated with calcium, it will be clear that the other alkaline earth metals are applicable, such as barium and strontium. The method may also be practiced with the alkali metals, such as sodium, potassium and lithium. It may also be practiced with other hydride-forming metals. The invention is more particularly applicable to the highly reactive hydride-forming metals, especially in their primary form. While not as important, it will also be clear that the invention is applicable to the production of the so-called impure metal hydrides, such as those made by the magnesium process; for example, by reacting an alkaline earth or an alkali metal oxide with magnesium in the presence of hydrogen gas.

By regulating the amounts of inert gas and hydrogen gas, the reaction zone may be readily maintained at a temperature sufficiently high for the desired hydriding reaction to take place and at the same time sufficiently low to prevent undesired fusion of the hydride-forming metal. Under these optimum operating conditions, the ingots of hydride-forming metal are converted into ingots of metal hydride of substantially the same size and shape.

Various other procedures may be employed in the practice of the invention. For example, the pressure in the retort may be raised a few points above atmospheric pressure by injecting a suitable amount of hydrogen or inert gas or both. This prevents the infiltration of air into the retort if the retort, or gaskets, are not quite tight. If inert gas is initially used to raise the pressure in the retort, hydrogen may then be injected to raise the pressure a suitable amount, for example ten to fifteen pounds. The reaction may then be permitted to proceed until the hydrogen is consumed. At that point the reaction stops, until additional hydrogen is admitted. In this way the speed of reaction and therefore the evolution of exothermic heat may be controlled. In other cases it may be desirable to admit a mixture of hydrogen and inert gas to the retort more or less simultaneously. If the procedure is well established, the dilution may be such that the reaction does not proceed too rapidly and the hydrogen is never completely consumed since it is gradually supplied to the retort. The inert gas acts continuously as a diluting medium or a brake.

While the invention is illustrated with the use of helium as the inert gas, it will be clear to those skilled in this art that other inert gases, such as argon, may be employed, either alone or admixed. The monatomic inert gases appear to be particularly useful. It is important only that the gas employed be inert with respect to the ingredients going into the charge and that it function as a diluent and brake to the speed of reaction or conversion.

In the production of sodium hydride, the sodium combines with the hydrogen at a relatively low temperature; and since sodium hydride dissociates very rapidly at temperatures above 400° C., it is important to prevent the generation of excessive exothermic heat as the hydride-forming reaction takes place. This can be done by the suitable use of inert gas. The invention is likewise applicable, for example, in the treatment of lithium containing silicon and lithium containing boron to produce lithium hydride, and of sodium containing boron to produce sodium hydride, although such combinations are not considered true alloys.

It will be clear to those skilled in this art that the invention is applicable generally to the production of metal hydrides and that in the appended claims the hydride-forming metal may be considered initially present as such or in the form of a compound, or an alloy or other combination; but in any event in a form in which the metal itself is or is made available for reaction with the hydrogen to form the desired metal hydride.

This application is a continuation-in-part of my copending applications Serial Nos. 503,793 and 503,794, filed September 25, 1943. In my copending application Serial No. 544,048, filed July 8, 1944, the claims are directed to the method of producing alkaline earth metal hydrides broadly and calcium hydride specifically in accordance with the invention.

I claim:

1. In the method of producing metal hydrides by reacting a hydride-forming metal with hydrogen gas at an elevated temperature, the improvement which comprises confining a charge of hydride-forming metal in a reaction zone, admitting hydrogen gas and a substantial amount of inert gas to the reaction zone, heating the hydride-forming metal in the reaction zone in the presence of the hydrogen gas and inert gas to a temperature sufficiently high to start the hydriding reaction, limiting the amount of hydrogen gas initially admitted to the reaction zone to limit the exothermic heat generated by the reaction to an amount insufficient to fuse the heated hydride-forming metal, gradually admitting further amounts of hydrogen gas to the reaction zone to continue the hydriding reaction in the presence of the inert gas, and regulating the rate of formation of the metal hydride and hence the rate of generation of exothermic heat until the hydriding reaction has gone substantially to completion in the presence of the inert gas by regulating the amounts of hydrogen gas thus admitted to the reaction zone to prevent fusion of the heated hydride-forming metal.

2. Method according to claim 1, in which the reaction zone is evacuated to remove air therefrom before the hydrogen and inert gases are admitted.

3. Method according to claim 1, in which the amount of inert gas admitted is sufficient to place and maintain the reaction zone and charge under substantial positive pressure.

4. Method according to claim 1, in which the charge is heated to a temperature sufficiently high to start the hydriding reaction by the application of externally applied heat, discontinuing the application of externally applied heat, and continuing the hydriding reaction solely with the regulated amount of exothermic heat thus generated.

5. Method according to claim 1, in which the hydrogen gas is fed into the reaction zone automatically at a predetermined pressure until the hydriding reaction goes to completion.

6. Method according to claim 1, in which the

reaction zone is evacuated to remove air therefrom before the hydrogen and inert gases are admitted, and admitting the inert gas in amount sufficient to place and maintain the reaction zone and charge under substantial positive pressure.

7. Method according to claim 1, in which the reaction zone is evacuated to remove air therefrom before the hydrogen and inert gas are admitted, admitting the inert gas in amount sufficient to place and maintain the reaction zone and charge under substantial positive pressure, heating the charge to a temperature sufficiently high to start the hydriding reaction by the application of externally applied heat, discontinuing the application of externally applied heat, and continuing the hydriding reaction solely with the regulated amount of exothermic heat thus generated.

8. In the method of producing alkali metal hydrides by reacting an alkali metal with hydrogen gas at an elevated temperature, the improvement which comprises confining a charge of alkali metal in a reaction zone, admitting hydrogen gas and a substantial amount of inert gas to the reaction zone, heating the alkali metal in the reaction zone in the presence of the hydrogen gas and inert gas to a temperature sufficiently high to start the hydriding reaction, limiting the amount of hydrogen gas initially admitted to the reaction zone to limit the exothermic heat generated by the reaction to an amount insufficient to fuse the heated alkali metal, gradually admitting further amounts of hydrogen gas to the reaction zone to continue the hydriding reaction in the presence of the inert gas, and regulating the rate of formation of the alkali metal hydride and hence the rate of generation of exothermic heat until the hydriding reaction has gone substantially to completion in the presence of the inert gas by regulating the amounts of hydrogen gas thus admitted to the reaction zone to prevent fusion of the heated alkali metal.

9. Method according to claim 8, in which the reaction zone is evacuated to remove air therefrom before the hydrogen and inert gases are admitted.

10. Method according to claim 8, in which the amount of inert gas admitted is sufficient to place and maintain the reaction zone and charge under substantial positive pressure.

11. Method according to claim 8, in which the charge is heated to a temperature sufficiently high to start the hydriding reaction by the application of externally applied heat, discontinuing the application of externally applied heat, and continuing the hydriding reaction solely with the regulated amount of exothermic heat thus generated.

12. Method according to claim 8, in which the hydrogen gas is fed into the reaction zone automatically at a predetermined pressure until the hydriding reaction goes to completion.

13. Method according to claim 8, in which the reaction zone is evacuated to remove air therefrom before the hydrogen and inert gases are admitted, and admitting the inert gas in amount sufficient to place and maintain the reaction zone and charge under substantial positive pressure.

14. Method according to claim 8, in which the reaction zone is evacuated to remove air therefrom before the hydrogen and inert gas are admitted, admitting the inert gas in amount sufficient to place and maintain the reaction zone and charge under substantial positive pressure, heating the charge to a temperature sufficiently high to start the hydriding reaction by the application of externally applied heat, discontinuing the application of externally applied heat, and continuing the hydriding reaction solely with the regulated amount of exothermic heat thus generated.

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