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(54) HYDROGEN-STORAGE MATERIAL

(71) We, PHILIPS ELECTRONIC AND ASSOCIATED INDUSTRIES LIMITED, of Abacus House, 33 Gutter Lane, London, EC2V 8AH, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The invention relates to a hydrogen-storage material containing titanium and iron in a mutual ratio in gram-atoms between 4:1 and 0.67:1, to a hydride of such a hydrogen-storage material, to a method for storing and giving off hydrogen whilst using such materials and their hydrides and to apparatus for storing and subsequently releasing hydrogen gas.

15 It is known that materials consisting of iron and titanium in the form of compounds and alloys are suitable for storing hydrogen by forming hydrides under pressure at ambient temperature. By decreasing the pressure above the hydrogen-containing material and/or heating the hydrogen-containing material, hydrogen is released from the hydrogen-containing material. United States Patent Specification 3,516,263 and United States Patent Specification 3,508,414 discloses a material which contains 35—75 weight% Ti, the remainder being Fe. It appears in practice that an elaborate treatment of the material is necessary after preparation before the material can quickly absorb and release hydrogen at ambient temperatures.

35 This "activation treatment" may, for example, consist in heating the material to a temperature of 400°C or higher in vacuo

whilst continuously pumping, followed by cooling to room temperature and admitting hydrogen at a pressure of approximately 35 atmospheres whereafter the hydrogen is released again from the material by vacuum-pumping and heating; this procedure must be repeated a number of times to obtain such a degree of activation that at approximately 20°C the material can reversibly absorb and release hydrogen at a sufficient speed at room temperature depending only upon the pressure of hydrogen above the material.

The invention provides a hydrogen-storage material consisting of a total of from 95 to 70 atom% of iron and titanium, and a total of from 5 to 30 atom% of one or more of the metals chromium, zirconium, manganese and vanadium, wherein the atomic ratio of iron to titanium in the material is between 1:0.67 and 1:4.

Apparatus for storing and subsequently releasing hydrogen gas may comprise a reservoir having an obturable opening and containing a hydrogen-storage material according to the invention.

A method of absorbing, storing and releasing hydrogen using a hydrogen-storage material according to the invention may comprise the steps of subjecting an activated hydrogen-storage material according to the invention to an external hydrogen pressure which exceeds the equilibrium pressure (as hereinafter defined) of the hydrogen-storage material at the working temperature so as to form a hydride of the hydrogen-storage material, wherein subsequently during storage of the hydrogen, the hydride of the hydrogen-absorbing material

remains exposed to a hydrogen pressure exceeding the equilibrium pressure at the storage temperature, and wherein hydrogen is released from the hydride of the hydrogen-storage material by reducing the hydrogen gas pressure to which the hydride is subjected to a value which is less than the equilibrium pressure at the release temperature, or by heating the hydride of the hydrogen-storage material.

The "equilibrium pressure" at a given temperature is the pressure at which a partly hydrogenated hydrogen-storage material can be caused, with the aid of a small pressure variation, to absorb or release in a reversible process considerable volumes of hydrogen.

The presence of chromium, zirconium, manganese or vanadium in the hydrogen-storage material results, in many cases, in that a same quantity of hydrogen is absorbed at a lower hydrogen pressure than with materials which consist only of titanium and iron, whilst the total capacity of absorption in ml of hydrogen per gram of material is, in general, of the same order of magnitude as with materials which consist only of titanium and iron. This has the advantage that the reservoirs may be simpler in construction, as they need only be able to withstand relatively lower pressures. Furthermore, there is a greater freedom of choice of hydrogen-storage materials so that it is possible, for a given application, to utilize a material having the most favourable properties as regards hydrogen absorption. For energy storage by means of hydrogen absorption in which one wants to use a maximum hydrogen-pressure of 2 atmospheres at approximately 20°C in a simple apparatus, a hydrogen-storage material which contains, besides Ti and Fe in an atomic ratio of between 2.5:1 and 1.1:1, Mn is a quantity of 5 to 30 atom% based on the total number of atoms in the material appeared particularly suitable: an example of such a material is $\text{TiFe}_{0.8}\text{Mn}_{0.2}$.

The hydrogen-storage materials according to the invention are prepared by fusing the constituent metals in the proper ratio by means of arc melting in a non-oxidizing atmosphere, for example a neutral or reducing

atmosphere or in vacuo, and cooling the casting down to room temperature. If desired the casting may then be pulverized. Activation can now be carried out in a simple manner at approximately 20°C by exposing the material to hydrogen at a pressure of 30 to 40 atmospheres. Usually the material reaches its maximum storage capacity after only one cycle of loading with hydrogen and a subsequent release of hydrogen.

Some embodiments of the invention will now be described with reference to the following Examples and to the single Figure of the accompanying drawing, which is a sectional elevation of a hydrogen-storage apparatus.

Examples.

By fusing the relevant elements in the required quantities, castings were produced having compositions defined by the following formulae.

1. $\text{TiFe}_{0.9}\text{Cr}_{0.1}$
2. $\text{TiFe}_{0.8}\text{Cr}_{0.2}$
3. $\text{TiFe}_{0.7}\text{Cr}_{0.3}$
4. $\text{TiFe}_{0.9}\text{Zr}_{0.1}$
5. $\text{TiFe}_{0.8}\text{Zr}_{0.2}$
6. $\text{TiFe}_{0.8}\text{Mn}_{0.2}$
7. $\text{TiFe}_{0.4}\text{Mn}_{0.6}$
8. $\text{TiFe}_{0.8}\text{V}_{0.2}$
9. $\text{TiFe}_{0.8}\text{V}_{0.2}$
10. $\text{Ti}_{0.9}\text{FeZr}_{0.1}$
11. $\text{TiFe}_{0.8}\text{Zr}_{0.2}\text{Fe}$

The materials having compositions defined by the formulae 1 to 11 were activated by exposing them at a temperature of 20°C to hydrogen at a pressure of 30 atmospheres until no further hydrogen was absorbed, whereafter hydrogen was removed from the materials and the quantity of absorbed hydrogen released was measured. After this activation treatment, an equilibrium was obtained in all cases within a few minutes on exposure to a hydrogen atmosphere. The following table specifies for the above-mentioned compounds the activation time and the absorption capacity in ml of hydrogen at 760 mm of mercury per gram of material at 20°C.

TABLE

Example	Composition	Activation time (1)	Absorption capacity (2) in ml/gr.
1	TiFe _{0.9} Cr _{0.1}	+	225
2	TiFe _{0.8} Cr _{0.2}	++	223
3	TiFe _{0.7} Cr _{0.3}	+++	229
4	TiFe _{0.9} Zr _{0.1}	+++	241
5	TiFe _{0.8} Zr _{0.2}	++++	270
6	TiFe _{0.8} Mn _{0.2}	++	190
7	TiFe _{0.4} Mn _{0.6}	+++	230
8	TiFe _{0.9} V _{0.1}	++	242
9	TiFe _{0.8} V _{0.2}	++++	273
10	Ti _{0.9} FeZr _{0.1}	+++	242
11	Ti _{0.8} FeZr _{0.2}	+++	217
A	TiFe	---	230
(1) - more than 24 hours + within 10 hours ++ within 5 hours +++ within 60 minutes ++++ within 5 minutes			(2) at a hydrogen pressure of 30 atm/20°C.

An apparatus for storing hydrogen whilst using the hydrogen-storage materials according to the invention comprises in its simplest form a reservoir 1 for a hydrogen-storage material 2, provided with a pressure gauge 5, a supply and discharge pipe 6 provided with a controllable shut-off valve 4 and a heating device 3. Charging the material 2 with hydrogen is effected after the reservoir 1 has been evacuated, by admitting hydrogen into the reservoir 1 until the pressure in the reservoir 1 rises to above the equilibrium pressure of the hydrogen-storage material 2; the hydrogen can be released from the hydrogenated hydrogen-storage material 2 by reducing the hydrogen pressure above the material 2 to below the equilibrium pressure or by increasing the temperature of the hydrogenated hydrogen-storage material 2 to above ambient temperature. An advantage of the hydrogen-storage materials according to the invention is, in this connection, that the equilibrium pressure at a given temperature is in general

lower than the equilibrium pressure of materials consisting only of titanium and iron so that the reservoirs need not be constructed so as to be able to withstand relatively high pressures and the reservoirs need not be exposed to high temperatures when activating the material.

WHAT WE CLAIM IS:—

1. A hydrogen-storage material consisting of a total of from 95 to 70 atom% of iron and titanium, and a total of from 5 to 30 atom% of one or more of the metals chromium, zirconium, manganese and vanadium, wherein the atomic ratio of iron to titanium in the material is between 1:0.67 and 1:4.

2. A hydrogen-storage material as claimed in Claim 1, consisting of iron, titanium and manganese, wherein the atomic ratio of iron to titanium is between 1:1.1 and 1:2.5.

3. A hydrogen-storage material substantially as herein described with reference to any of Examples 1 to 11.

4. Apparatus for storing and subsequently releasing hydrogen gas, comprising a reservoir having an obturable opening and containing a hydrogen-storage material as claimed in any preceding Claim. 25
5. A hydride of a hydrogen-storage material as claimed in any of Claims 1 to 3.
6. A method of absorbing, storing and subsequently releasing hydrogen using a hydrogen-storage material as claimed in any of Claims 1 to 3, the method comprising the steps of subjecting the activated hydrogen-storage material to an external hydrogen pressure which exceeds the equilibrium pressure (as hereinbefore defined) of the hydrogen-storage material at the working temperature so as to form a hydride of the hydrogen-storage material, wherein subsequently during storage of the hydrogen, the hydride of the hydrogen-absorbing material remains exposed to a hydrogen pressure exceeding the equilibrium pressure at the storage temperature, and 30
7. A method of preparing material and activating a hydrogen-storage material as claimed in any of Claims 1 to 3, the method comprising the steps of fusing the constituent elements together by arc melting in a non-oxidizing atmosphere or in vacuo, and exposing the resultant material to a pressure of from 30 to 40 hydrogen atmospheres at the ambient temperature. 35
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