(12) UK Patent Application (19) GB (11) 2 164 637 A

(43) Application published **26 Mar 1986**

(21) Application No **8521478**

(22) Date of filing **29 Aug 1985**

(30) Priority data

(31) **653068** (32) **21 Sep 1984** (33) **US**

(51) INT CL^4
C01B 3/02 3/04 3/56 6/00 6/02 6/04 6/24

(52) Domestic classification
C1A E4G1 E4G2 G13 G20 G22 G34 G37 G42 G48 PB5
U1S 1197 1841 2047 2049 2078 2081 2082 C1A

(56) Documents cited
None

(58) Field of search
C1A

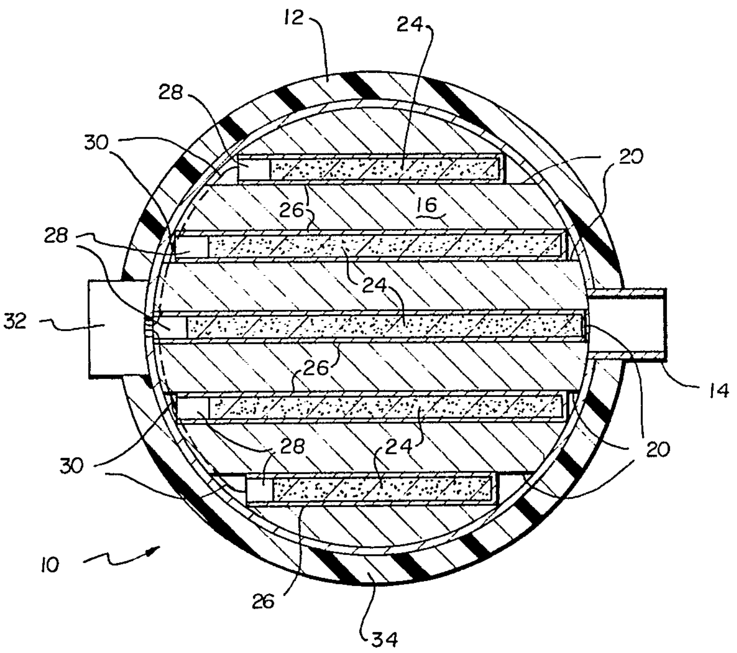
(71) Applicant
General Electric Company (USA-New York),
1 River Road, Schenectady 12305, United States of
America

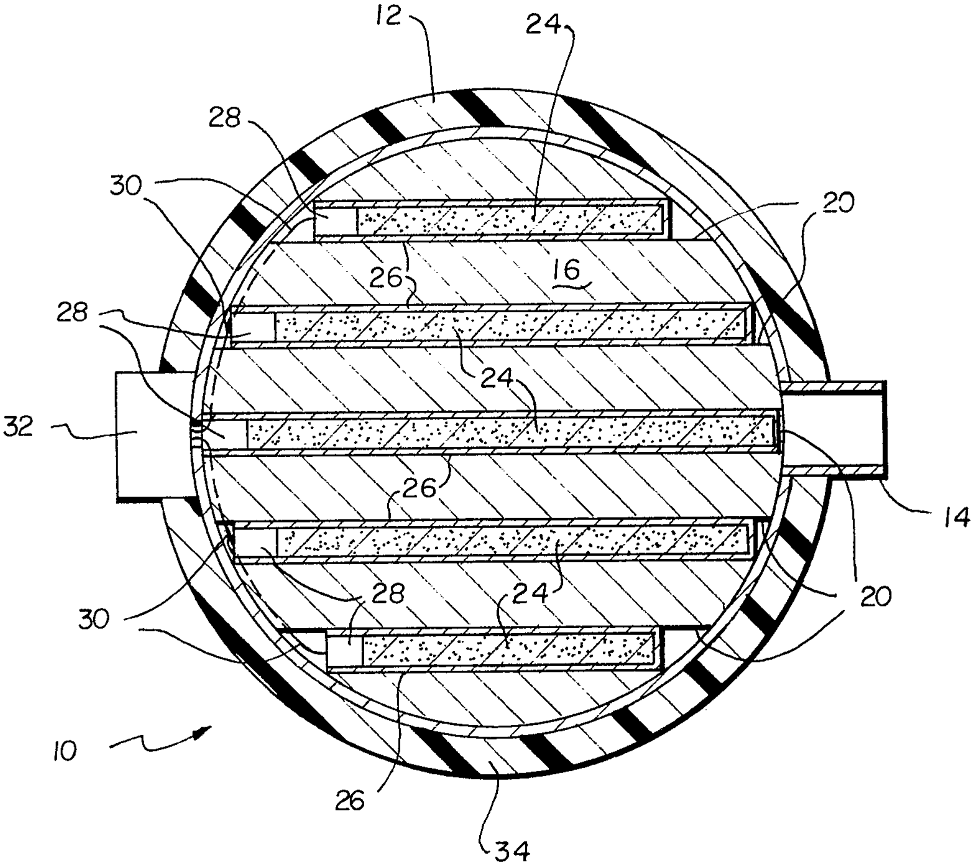
(72) Inventors
Alwin Gustav Steinmayer Jr,
Daniel Paul Ross

(74) Agent and/or Address for Service
Brookes & Martin, High Holborn House, 52-54 High
Holborn, London WC1V 6SE

(54) Metallic hydride hydrogen storage for balloon inflation

(57) A low weight, small total volume, high volumetric capacity hydrogen storage system, as for the high altitude inflation of balloons launched from rockets, comprises a solid unitary matrix of an endothermically decomposable metallic hydride, such as magnesium hydride, enclosed within a spherical containment shell. The matrix has a plurality of uniformly distributed holes therein into each of which is inserted a high specific energy chemical heat source which reacts to provide exothermic energy to decompose the hydride. The chemical heat sources, which preferably comprise intermetallics, are disposed within ceramic tubes received in the holes along with an electrically operated reaction initiator for the chemical heat source. An electrical actuator is disposed on the exterior of the containment shell for actuating the reaction initiators.




12
24
28
30
20
16
26
28
30
20
24
32
26
14
26
30
28
24
20
10
26
34

SPECIFICATION

Metallic hydride hydrogen storage for balloon inflation

Background of the invention

This invention relates generally to hydrogen generation methods and systems, and more particularly to methods and systems applicable to the high altitude inflation of thin film balloons launched from rockets.

Systems for inflating thin film balloons launched from rockets at high altitudes of the order of 70,000-100,000 feet for example, must satisfy a number of rather stringent requirements. Because of space and weight limitations in the rocket, it is desirable that the inflation systems have high volumetric capacity with a small total volume and that they be low in weight. They must be capable of being safely stored for long periods of time, and must be capable of rapidly releasing inflation gas so as to afford a balloon filled time of the order of only a few minutes. Moreover, because of the high altitude at which inflation occurs the fragile nature of the thin films from which balloons are constructed, it is necessary to ensure that the system does not create water vapor, which could form film-cutting ice at high altitude temperatures, or chemicals which would attack the thin films or form unwanted thermal coatings.

Hydrogen is preferred over helium as an inflation gas for such applications, since it provides the greatest specific lift of any of the other possible gases which may be employed for inflation (7% better than helium, for example). One pound of hydrogen displaces about thirteen pounds of air, while one pound of helium displaces only seven pounds of air. However, there are problems, principally related to safety, associated with hydrogen gas inflation systems. Hydrogen may be stored in either a gaseous or a liquid form or generated in a chemical system. A major disadvantage of gas storage systems is the need for very high pressures and for very heavy containment vessels to meet the high pressure requirements. There are obvious safety problems inherent in the use of high pressure containers. Cryogenic liquid storage systems eliminate the need for high pressure storage, but have limited shelf life because of heat leakage. Moreover, cryogenic systems have safety problems related to exposure to supercooled materials and the possibility of hydrogen venting due to damage or defects in the system installation.

Chemical systems for generating hydrogen are known which employ compounds, such as hydrides, that liberate hydrogen through chemical reaction or thermal decomposition. Such systems avoid many of the safety problems associated with compressed gas and cryogenic storage systems, and have been proposed for inflating balloon systems and the like employed as site markers. Known systems of this type, however, do not satisfy the small total volume, low weight, and rapid gas generation requirements of inflation systems for the high altitude inflation of large payload-carrying balloons launched from rockets. It is desirable to provide hydride-based hydrogen generation systems and methods for use as inflation systems for such purposes, and it is to this end that the present invention is directed.

Summary of the Invention

The invention affords a hydrogen generation system and method which are particularly well adapted for the high altitude inflation of balloons and the like. The invention is based upon the use of thermally decomposable metallic hydrides as a medium for safely storing hydrogen gas, and the use of chemical reactants which are inert, safe, and have a long life as a source of rapidly released heat for decomposing the metallic hydrides to dissociate hydrogen therefrom.

Briefly stated, a hydrogen generating system in accordance with the invention comprises a containment shell having disposed therein a solid, unitary, thermally decomposable metallic hydride matrix having a predetermined percentage of voids therein to afford a controlled release of hydrogen gas upon decomposition. The hydride matrix is shaped to conform to the interior configuration of the containment shell and to fill substantially the interior volume of the containment shell. The hydride matrix is further formed with a plurality of uniformly distributed holes therein, each of which receives a chemical heat source for providing exothermic energy required for hydrogen dissociation in the hydride matrix, and reaction initiated means for the heat source. Means for activating the reaction initiating means is disposed in the exterior surface of the containment shell, and the shell is provided with an outlet passage for liberated hydrogen gas.

Preferably, the containment shell has a spherical shape, since this shape affords the greatest storage volume in the smallest space, thereby minimizing the total volume required for the system, and is the best shape in terms of strength for a pressure structure, thereby enabling the containment shell wall thickness and weight to be minimized. The metallic hydride matrix is preferably magnesium hydride, which may be catalyzed by the addition of five to ten percent by weight of nickel. The chemical heat source preferably comprises intermetallics or other exothermic chemical reactants, since they provide the greatest heat with the minimum weight and volume and can be reliably actuated. The heat source may be clad with ceramic, for example, as by enclosure in tubes inserted into the holes in the hydride matrix, to prevent reaction between the released hydrogen and the heat source metals. Preferred heat sources include titanium diboride and mixtures of beryllium and $Mg(ClO_4)_2$.

Brief Description of the Drawing

The sole figure illustrates a cross sectional view of a hydrogen gas generator in accordance with the invention.

Description of the Preferred Embodiments

The invention is particularly well adapted to a hydrogen generation system for inflating balloons launched from high altitude rockets, and will be described in that context. However, as will be appreciated, the invention has greater utility and this is illustrative of merely one application of the invention.

As previosuly indicated, the principal requirements for a hydrogen inflation system for a balloon launched at high altitudes from a rocket include high volumetric capacity and a small total volume, low weight, safety, long storage life, and a rapid release of gas to afford a balloon fill time of the order of two to three minutes, for example. As between volume and weight, volume is generally the most stringent requirement, although both volume and weight are quite important. In addition, it is important that the hydrogen gas generated be free of water vapor and contaminants which could damage the balloon. The hydrogen gas generator of the invention, comprising a thermally decomposable metallic hydride storage medium and a high specific thermal energy chemical source for providing the heat required for hydrogen dissociation, satisfies these requirements admirably and has other important features and advantages which will become apparent from the description which follows.

As shown in the figure, a hydrogen generator 10 in accordance with the invention may comprise a thin-walled containment vessel or shell 12 which is preferably spherical and may be formed of stainless steel, for example. A spherical configuration is preferable since it affords the greatest storage volume in the smallest space, and is the best configuration to employ for a pressure vessel. A tubular, for example, gas outlet 14 is provided in the wall of containment vessel 12 and is adapted for connection to a balloon fill tube (not illustrated). Within the containment vessel 12 is disposed a solid unitary metallic hydride matrix 16 (to be described more fully shortly) comprising a solid spherical ball of metallic hydride dimensioned to fill substantially the interior volume of the containment vessel. To enable the hydride matrix to be disposed within the containment vessel, the containment vessel may be formed in a well-known manner as two hemispherical sections which are assembled together about the hydride matrix. The hydride matrix may be further formed with a plurality of holes 20 herein which may extend completely through the matrix. Within each hole is disposed an electrically-actuated high specific thermal energy heat source 24 (also to be described more fully hereinafter). Heat sources 24 may be clad with a material which inert to hydrogen, such as a ceramic or other suitable material, to prevent reaction between the hydrogen gas liberated from the hydride matrix and the heat source materials, as by enclosing the heat sources within cylindrical ceramic tubes 26 disposed within holes 20. An electrical igniter 28 comprising a conventional electrical squib, for example, may be provided for each heat source and connected by electrical le 30 to an electrical actuator 32 comprising, for example, a battery and a switch (not illustrated). If desired, a layer of thermal insulation 34 may be disposed about the exterior surface of containment vessel 12, although this may be omitted since the heat loss during hydrogen dissociation will be less than about one percent of the heat generated by the heat source.

In general, metallic hydride storage media are characterized by large volumetric storage capacities when compared to gaseous or liquid hydrogen storage. However, most metallic hydrides hold relatively small percentages of hydrogen per unit weight of hydride. Therefore, the selection of the particular hydride for matrix 16 should be judiciously made to avoid weight penalties which otherwise may be encountered. The following Table 1 gives the hydrogen weight percentage and volumetric storage capacity of several different metallic hydrides in comparison with compressed gas hydrogen storage, employing a composite filament wound (Kevlar filaments for example) pressure vessel having an aluminum liner, which can store hydrogen at pressures of the order of 500 atmospheres (atm.).

TABLE 1

Comparison of hydrogen storage media

Medium	Hydrogen * Weight %	Storage Capacity of H_2 g/ml volume
MgH_2	7.6	0.132
TiH_2	4.0	0.187
VH_2	3.8	0.234
$FetiH_2$	1.9	0.123
$TiFe_{.7}Mn_{.2}H_{1.9}$	1.72	0.09
$LaNi_5H_{6.7}$	1.5	0.126
LH_2	100	0.07
Gaseous H_2 at		
500 atm, 298°K	100	0.04
100 atm, 298°K	100	0.008

* Container or heat source weight not included.

Of the metallic hydrides listed, magnesium hydride (Mgh$_2$) and vanadium hydride (VH_2) are attractive from a minimum weight and volumetric storage capacity point of view. However, the selection of a particular optimum hydride depends not only upon its weight and volume characteristics, but also upon the relationship of its physical parameters and its thermal requirements. The most significant physical properties of a metallic hydride for a lightweight, small external volume, high volumetric storage capacity system are its dissociation pressure as a function of temperature, and its pressure versus composition isotherm. The latter property determines hydrogen dissociation rate as a function of temperature.

The desirable pressure versus temperature characteristics of the hydride are that it have very low pressure at storage temperatures, and only moderate pressures at its hydrogen dissociation temperature. Since balloon inflation involves only a single dissociation reaction, rather than a cyclic operation as is characteristic of other known hydride applications, it is desirable from a safety standpoint to use a hydride with a relatively high dissociation temperature.

Magnesium hydride is the preferred hydride since it has the advantage of minimum weight, very low pressures at storage temperatures, and only modest pressures (of the order of 2 atm., for example) at temperatures of the order of 660°F, where decomposition is quite rapid. At altitudes of the order of 70,000 feet, a pressure of 2 atm. is sufficiently high to give a good gas flow rate into the balloon. Magnesium hydride is also preferable to vanadium hydride, since vanadium hydride decomposes rapidly at a rather low temperature, which could present safety problems.

The use of magnesium hydride for the metallic hydride matrix 16 of hydrogen generator 10 affords a hydrogen storage system having a volume of only about 40% that of compressed gas storage at 500 atm., and only about 70% of that of a liquid hydrogen storage system. At normal ambient storage temperatures, magnesium hydride releases no hydrogen. Even at much higher temperatures, such as in a fire, its hydrogen generation pressure is rather low (of the order of 2 atm. at 660°F). Accordingly, it avoids the inherent safety problems associated with compressed gas storage and allows the use of a rather lightweight containment vessel, such as a 1/32 inch wall stainless steel tank. In addition, magnesium hydride has a rather long shelf life of several years. As noted earier, hydride matrix 16 is preferably a solid unitary body having a predetermined percentage of voids and passageways therein to enable control of the rate at which the dissociated hydrogen is released. The matrix may be formed by repeatedly subjecting a solid sphere of magnesium to heat and hydrogen gas until the magnesium is converted to magnesium hydride and a desired void volume is obtained. Preferably, the void volume is of the order of 20-25%. This construction affords better control over the hydrogen outgassing characteristics of the hydride matrix than is possible if the matrix was granular, for example. Preferably, the magnesium hydride is catalized by the addition of approximately 5-10% by weight of nickel.

In order to rapidly dissociate the stored hydrogen in the magnesium hydride matrix, external heat must be applied to raise the temperature of the hydride to its decomposition temperature of approximately 650°F. For each pound of hydrogen released from the matrix, external heat of the order of 16,000 BTU/lb. of hydrogen generated (approximately 1100 BTU/lb. of MgH_2) must be supplied to the matrix. The heat source for providing this external heat desirably has minimum weight and volume, which requires a high specific thermal energy source, and can be reliably actuated. An electrically actuated chemical heat source comprising intermetallics or other thermite-type chemical reactants may be utilized for this purpose. For example, the reaction of beryllium and $Mg(Cl0_4)_2$ releases 7200 BTU/lb. and over 1,000,000 BTU per cubic foot. The volume percentage of these reactants in relation to the total volume of the containment vessel would be of the order of only 13%. Another advantage of using intermetallics as a heat source is that they do not generate gases when they react, which would have to be vented and could produce undesirable contaminants. As previously noted, depending upon the particular reactants employed, it may be necessary to clad the heat source reactants, as by disposing them in a ceramic tube, for example, in order to isolate them from the hydrogen released by the hydride matrix. The following Table 2 gives the characteristics of some other intermetallic reactions which may be employed for the heat source.

TABLE 2

Characteristics of Reacting Intermetallics

Reactants	Experimental* Heat of Reaction BTU/lb	Volumetric Heat of Reaction BTU/cu ft	Ignition Temperature in air °F	Average Reaction Temperature °F
Li, B	2061	158,200	392	4532
Ti, B_2	2205	337,100	1022	5432
Ti, C	1463	228,300	1112	3722
Be, C_2**	3150	417,800	2192	5018

* Inert gas, ** Theoretical

Titanium diboride, for example, is a good choice for a heat source. It has a relatively high heat of reaction and a relatively high ignition temperature of over 1000° F in air, which is desirable for avoiding premature ignition in a hot environment, such as a fire, for example, but has the ability to initiate ignition in a fraction of a second using an electrically heated lamp filament. The weight and volume of a titanium diboride heat source as a percentage of the weight and volume of the magnesium hydride matrix are of the order of 36% and 28%, respectively.

The following Table 3 gives the size and weight of a magnesium hydride/titanium diboride generator capable of producing ten pounds of hydrogen.

TABLE 3

Generator size and weight to produce 10 lbs of hydrogen

	Weights
MgH_2	132 lbs
Titanium Diboride & Clad	75 lbs
Containment Shell	10 lbs
Initiator Battery and Miscellaneous Fittings	8 lbs
Total Weight	225 lbs
	Size
Sphere	18 inches O.D.

The hydrogen stored in the magnesium hydride matrix can be rapidly released within the desired time of approximately two to three minutes provided that the matrix temperature can be maintained at a value of the order of 660°F. For the generator of Table 3, the heat which must be transferred to the matrix and the required delivery time is given in the following Table 4.

TABLE 4

Heat Required to Generate 10 lbs of Hydrogen

Raise Hydrogen Generator Temperature from 60° to 660°F (Estimated Heat Capacity = 0.25 BTU/lb–°F)	33,750 BTU
Endothermic Energy for Dissociation	160,000 BTU
Total Energy	193,750 BTU
Heat Transfer Rate (2 minutes delivery)	5.80×10^6 BTU/hr

As shown in Table 4, to deliver 10 pounds of hydrogen, the heat source must generate a net energy of 193,750 BTU, and deliver this energy at a rate of 5.8×10^6 BTU/hr. To meet this energy delivery requirement, it is desirable that the heat source tubes 24 be uniformly distributed throughout the hydride matrix. The number of tubes, the tube diameter, and the tube spacing may be readily determined to ensure sufficient heat transfer area to meet the energy rate delivery requirements.

In addition, it is necessary to ensure that there is sufficient flow passage area so that the hydrogen generated can be released from the generator. Because of the logarithmic dependence of gas pressure on temperature, the temperature rise within the matrix will be small for large increases in gas pressure, and the effect of pressure build-up on heat transfer will be minimal. To maintain a maximum hydrogen pressure of the order of 5 psia or less, for example, the rate at which hydrogen gas is dissociated from the matrix can be controlled by controlling the matrix void volume in relation to the dimensions of the outlet opening 14 of the containment vessel. It is desirable that the matrix void volume be of the order of 20-25%, since as void volume increases the volume of the generator necessary to deliver the required volume of gas increases and the thermal conductivity of the metallic matrix decreases. A void volume of the order of 20-25% will not reduce the matrix thermal conductivity by any appreciable amount at the dissociation temperature of magnesium hydride.

The use of intermetallics as the heat source for the hydride matrix is a particularly significant and advantageous feature of the invention. Intermetallics are inert, safe and have a relatively long storage life.

Moreover, disposing the intermetallics within ceramic tubes isolates the reaction products and ensures that the hydrogen liberated from the hydride matrix is clean and free from contaminants which could damage the thin film materials from which the balloon is constructed. From a safety standpoint, it is merely necessary to ensure that premature ignition of the heat source does not occur. Accordingly, the electrical actuator 32 should have a low probability of false ignition, which is rather easy to ensure using conventional techniques.

As may be appreciated from the foregoing, the invention affords a particularly simple and highly advantageous hydrogen generator which may be employed as a hydrogen source for inflating a balloon launched from a high altitude rocket. Hydrogen generators in accordance with the invention avoid the disadvantages of compressed gas or liquid hydrogen storage systems, have low weight and high volumetric capacity, and are capable of a high rate of hydrogen generation. Other applications of a hydrogen generator in accordance with the invention include its use in a power source which delivers high peak powers for short time periods and it can be used in conjunction with power conversion devices such as open cycle magnetohydrodynamic generators, fuel cells, and dynamic power conversion machinery operating on a Brayton cycle or Stirling cycle, for example.

While a preferred embodiment of the invention has been shown and described, it will be appreciated by those skilled in the art that changes may be made in the embodiment without departing from the principles and spirit of the invention, the scope of which is defined in the appended claims.

CLAIMS

1. A hydrogen generation system comprising a containment shell having an outlet passage and having disposed therein a solid unitary matrix of an endothermically decomposable metallic hydride having a predetermined percentage of voids therein to afford a controlled release of hydrogen upon decomposition, the hydride matrix being shaped to conform to the interior configuration of the containment shell and being dimensioned to fill substantially the interior volume of the containment shell, and the matrix having a plurality of uniformly distributed holes therein, a chemical heat source disposed within each hole for providing exothermic energy to decompose the hydride, reaction initiating means for each chemical heat source, and means disposed on the exterior of the containment shell for actuating the reaction initiating means.
2. The system of Claim 1, wherein said metallic hydride comprises magnesium hydride.
3. The system of Claim 2, wherein the magnesium hydride is catalyzed by the addition of 5-10% by weight of nickel.
4. The system of Claim 2, wherein said predetermined percentage of voids is of the order of 20-25% of the matrix volume.
5. The system of Claim 1, wherein said chemical heat source comprises one or more intermetallics.
6. The system of Claim 5, wherein said chemical heat source is clad with a material which is inert to hydrogen.
7. The system of Claim 6, wherein the chemical heat sources are disposed within ceramic tubes received in said holes.
8. The system of Claim 1, wherein said chemical heat source comprises titanium diboride.
9. The system of Claim 1, wherein said chemical heat source comprises beryllium and $Mg(ClO_4)_2$.
10. The system of Claim 1, wherein said containment shell is spherical.
11. The system of Claim 1, wherein said reaction initiating means and said actuating means are electrically operated.
12. The system of Claim 1, wherein said system is sized to be disposed within a rocket and is adapted for the high altitude inflation of a balloon launched from said rocket.
13. The system of Claim 1, wherein said containment shell has a thermal insulator on its exterior surface.
14. A method of generating hydrogen comprising disposing within a containment shell having an outlet passage a solid unitary matrix of an endothermically decomposable metallic hydride having a predetermined percentage of voids therein to afford a controlled release of hydrogen upon decomposition and the matrix having a plurality of uniformly distributed holes therein, the matrix being shaped to conform to the interior configuration of the containment shell and being dimensioned to fill substantially the containment shell, providing a high specific energy chemical heat source within each hole, initiating reaction of the chemical heat source to produce heat for thermally decomposing the hydride to liberate hydrogen, and collecting the liberated hydrogen at said outlet.
15. The method of Claim 14, wherein said hydride comprises magnesium hydride.
16. The method of Claim 15 further comprising catalyzing the magnesium hydride by the addition of 5-10% by weight of nickel.
17. The method of Claim 14, wherein said voids comprise 20-25% by volume of the hydride matrix.
18. The method of Claim 14, wherein said chemical heat source comprises one or more intermetallics.
19. The method of Claim 18 further comprising cladding said intermetallics with a material that is inert to hydrogen.
20. The method of claim 19, wherein said material comprises a ceramic.

21. The method of claim 14, wherein said chemical heat source comprises titanium diboride.

22. The method of claim 14, wherein said chemical heat source comprises beryllium and $Mg(ClO_4)_2$.

23. A hydrogen generation system substantially as hereinbefore described with reference to and as illustrated in the drawing.

24. A method of generating hydrogen as claimed in claim 14 and substantially as hereinbefore described.

Printed in the UK for HMSO, D8818935, 2/86, 7102.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.