

Description

Field of the Invention

The present invention relates to improved amorphous metal alloy compositions and structures capable of reversible hydrogen storage. These compositions are capable of efficiently cyclically storing and releasing relatively large quantities of hydrogen without becoming embrittled, inactivated or corroded.

Background of the Invention

Shortages of fossil fuel materials in the recent past has spurred much speculation regarding the feasibility of economies based on other energy sources. One such scenario is a hydrogen-fueled economy. Hydrogen has the highest energy density per unit weight of any chemical. Many projections have been made for an economy based on this element, but the technology is not yet in place to effect such a dramatic change in the world economy. Hydrogen is, however, a technically attractive source of fuel and energy storage. It is essentially non-polluting, the major by-product of combustion being H_2O , and can be made from readily available and abundant raw materials.

While it is well known that hydrogen can be stored as a compressed gas or cryogenically as a liquid, other less energy-intensive and more convenient means are required for widespread utilization of hydrogen as a source of stored energy. It is known that some metals and metal alloys are capable of storing hydrogen reversibly within their lattice. This characteristic may be exploited by exposing the metal or metal alloy to a large pressure of hydrogen, impregnating the metal or metal alloy with hydrogen and later recovering the stored hydrogen by subjecting the impregnated metal or alloy to a change in temperature or pressure.

This characteristic of reversible hydrogen storage for some alloys is also being applied in an electrochemical environment. A metal or metal alloy suitable as a hydrogen storage material may be cathodically biased relative to a suitable counter electrode and charged with hydrogen by the reduction of a proton from solution. Metal alloy systems that have been studied for electrochemical hydrogen storage include $LaNi_5$ -based, $TiMn$ -based, $FeTi$ -based and Mg -based alloys. Although some of these crystalline materials store appreciable quantities of hydrogen, these same crystalline materials are susceptible to phase separation, hydrogen embrittlement and surface oxidation when used in charge/discharge cycles for hydrogen storage. Phase separation occurs in crystalline alloys that are subjected to hydrogen cycling, wherein the alloy components separate and migrate throughout the alloy. In $LaNi_5$ -type alloys, La migrates to the surface of the alloy, where it may rapidly become oxidized.

Hydrogen embrittlement occurs in crystalline alloys as hydrogen is absorbed and desorbed. Hydrogen storage proceeds from the surface of the alloy to its interior, with hydrogen atoms breaking into the

interstitial site of metal matrix atoms and then expanding the lattice. As a result internal stresses may produce flaws and cracks, seriously weakening and embrittling the metal or metal alloy. Surface oxidation may occur if the hydrogen storage material is exposed to oxidative conditions in the presence of an oxidant such as CO_2 , H_2O , KOH , air or oxygen. Surface oxidation interferes with the penetration of hydrogen, reducing the amount of hydrogen absorbed and the rate of absorption. Additionally, these crystalline materials generally cannot withstand corrosive environments, which environments may exist when the materials are utilized in an electrochemical reaction.

Recently, amorphous metal alloy materials have been reported as having the ability to store hydrogen reversibly. Amorphous metal alloy materials have become of interest due to their unique combinations of mechanical, chemical and electrical properties. Amorphous metal materials have compositionally variable properties including high hardness and strength, flexibility, soft magnetic and ferroelectric properties, very high resistance to corrosion and wear, unusual alloy compositions, and high resistance to radiation damage. The unique combinations of properties possessed by amorphous metal alloy materials may be attributed to the disordered atomic structure of amorphous materials that insures that the material is chemically homogeneous and free from the extended defects that are known to limit the performance of crystalline materials.

Amorphous metal alloy systems of $TiCu$ and $ZrCu$ were investigated and contrasted with the absorption properties of the corresponding crystalline intermetallic compounds by Maeland, et al., "Hydrides of Metallic Glass Alloys," *Journal of the Less-Common Metals*; 74, pp. 279-285, 1980. Amorphous metal alloy compositions, under similar conditions of temperature and pressure were capable of absorbing larger amounts of hydrogen than their crystalline counterparts. Maeland, et al. restricted their studies to the gaseous absorption of hydrogen in a hydrogen atmosphere. Novel amorphous metal compositions for reversible hydrogen storage are disclosed in Applicants' co-pending European application, (EP-A 0 197 675 (86301872.7) corresponding to USSN 717,429 herein by reference. This disclosure teaches reversible hydrogen storage materials comprising an amorphous metal alloy of the formula:



wherein A is at least one metal selected from the group consisting of Ag, Au, Hg, Pd and Pt;

M is at least one metal selected from the group consisting of Pb, Ru, Cu, Cr, Mo, Si, W, Ni, Al, Sn, Co, Fe, Zn, Cd, Ga and Mn; and

M' is at least one metal selected from the group consisting of Ca, Mg, Ti, Y, Zr, Hf, Nb, V, Ta and the rare earths; and

wherein a ranges from about 0.005 to about 0.80;

b ranges from about 0.05 to about 0.70; and

c ranges from about 0.08 to about 0.95.

Preferably, the ranges of a, b and c are from about 0.01 to about 0.75; about 0.1 to about 0.5; and from about 0.2 to about 0.85, respectively. Most

preferably, the ranges of a, b and c are from about 0.02 to about 0.7; about 0.2 to about 0.4; and from about 0.3 to about 0.8, respectively.

These amorphous compositions are not affected by phase separation or hydrogen embrittlement. Further, the above amorphous compositions have the ability to store from about 0.35 to more than about 1.1 hydrogen atoms per molecule of alloy and do not exhibit any significant signs of surface passivation or corrosion after repeated hydrogen charge/discharge cycles. However, the A component of these compositions is a necessary component of these amorphous alloys. While the properties of these alloys are ideal for reversible hydrogen storage, their component costs may be prohibitive for widespread applications, especially the A component cost.

Thus it is seen that the potential continues to exist for significant new technological advances in the application of amorphous metal alloys to the development of hydrogen as a fuel and a source of stored energy, especially in the area of electrochemical reversible hydrogen storage. What is needed in this area are economical amorphous metal alloy compositions having the ability to reversibly store hydrogen in significant quantities. Such amorphous metal alloys should not suffer significantly from phase separation or hydrogen-caused embrittlement, nor be susceptible to surface oxidation or corrosion.

It is therefore one object of the present invention to provide economical and improved amorphous metal alloy compositions and structures capable of reversibly storing hydrogen.

It is an additional object of the present invention to provide economical amorphous metal alloy compositions and structures capable of reversibly storing hydrogen in a cyclical fashion without becoming embrittled or suffering from a phase separation.

It is yet another object of the present invention to provide economical amorphous metal alloy compositions and structures capable of reversibly storing hydrogen in a cyclical manner that are not impaired by surface oxidation or corrosion.

These and other objects of the present invention will become obvious to one skilled in the art in the following description of the invention and in the appended claims.

Summary of the Invention

The present invention is directed toward a reversible hydrogen storage material comprising an amorphous metal alloy of the formula:



wherein A is at least one metal selected from the group consisting of Ag, Au, Hg, Pd and Pt;

M is at least one metal selected from the group consisting of Pb, Ru, Cu, Cr, Mo, Si, W, Ni, Al, Sn, Co, Fe, Zn, Cd, Ga and Mn; and

M' is at least one metal selected from the group consisting of Ca, Mg, Ti, Y, Zr, Hf, Nb, V, Ta and the rare earths; and

wherein a ranges from greater than zero to about 0.80;

b ranges from zero to about 0.70; and c ranges from about 0.08 to about 0.95; the material characterized in that a substantial portion of the A component of the alloy is disposed on the surface of the material.

The invention further relates to a reversible hydrogen storage structure having an active hydrogen adsorption surface layer and a bulk hydrogen storage material, the active surface layer comprising an amorphous metal alloy of the formula: $A_aM_bM'_c$

wherein A is at least one metal selected from the group consisting of Ag, Au, Hg, Pd and Pt;

M is at least one metal selected from the group consisting of Pb, Ru, Cu, Cr, Mo, Si, W, Ni, Al, Sn, Co, Fe, Zn, Cd, Ga and Mn; and

M' is at least one metal selected from the group consisting of Ca, Mg, Ti, Y, Zr, Hf, Nb, V, Ta and the rare earths, and

wherein a ranges from about 0.005 to about 0.80;

b ranges from zero to about 0.70; and

c ranges from about 0.08 to about 0.95; and

the bulk storage material comprising a reversible hydrogen storage material.

Preferably, in the formula $A_aM_bM'_c$ A is Pd, Pt or combinations thereof, and M is an element selected from the group consisting of Mn, Ru, Fe, Cu, Ni, Cr, Mo, Al, W and combinations thereof. Most preferably, M is an element selected from the group consisting of Mn, Cu, Ni, Fe, Mo, Cr, W and combinations thereof, and M' is titanium, magnesium, tantalum or a combination thereof. By combinations is meant mixtures and/or alloys of the above-listed elements.

Preferably, the ranges of a, b and c when the A component is concentrated on the surface of the material are from greater than zero to about 0.5; from about 0.1 to about 0.5; and from about 0.2 to about 0.85, respectively. Most preferably, the ranges of a, b and c are from about 0.001 to about 0.2; from about 0.2 to about 0.4; and from about 0.3 to about 0.8, respectively.

Detailed Description of the Invention

The compositions and structures described herein are characterized by utilizing graded or layered hydrogen storage compositions that include an active surface for absorbing and desorbing hydrogen and a bulk interior for hydrogen storage.

The amorphous metal alloys discussed herein are substantially amorphous. By "substantially" is meant that the amorphous metal alloys are at least fifty percent amorphous, as indicated by X-ray diffraction analysis. Preferably, the metal alloy is at least eighty percent amorphous, and most preferably about one hundred percent amorphous, as indicated by X-ray diffraction analysis. The use of the phrase "amorphous metal alloy" refers to amorphous metal-containing alloys that may also comprise non-metallic elements.

Hydrogen storage, especially electrochemical hydrogen storage, involves two phenomena; surface electrochemistry and bulk interstitial hydrogen stor-

age. An active hydrogen absorption surface also acts as an interface between the absorbed hydrogen and the bulk stored hydrogen atoms, and the electrochemical potential of the active surface establishes a portion of the potential difference through which electrons are accelerated during charge and discharge.

As an interface, the active surface must effectively supply the bulk with atomic hydrogen during charging and keep this hydrogen in the material until discharge. A metallic surface, wherein the charge transfer reaction ($H^+ + e^- = H$) is very rapid yet the recombination reaction ($2H_{(bulk)} \rightarrow H_{2(gas)}$) is slow, is ideal for an active hydrogen absorbing surface. This combination of properties increases the amount of hydrogen that is transferred as atomic hydrogen to the bulk and reduces the amount of gaseous hydrogen lost in solution. As taught by P. K. Subramanyan, "Electrochemical Aspects of Hydrogen in Metals", in Comprehensive Treatise of Electrochemistry, Plenum Press, N.Y. 1981, the following metals have faster charge transfer kinetics than recombination kinetics: Ti, Nb, Mo, Ta, W, Cu, Al, Au, Bi, Rh, Ir, Pt, Pd and Ag.

The role of the bulk material is to store as many hydrogen atoms as possible reversibly, so as to keep the surface coverage of absorbed hydrogen constant. Though some pure metals with slightly negative heats of formation for the hydride, such as Pd or Ni, will store small amounts of hydrogen reversibly; significantly more hydrogen can be stored in a suitable metallic alloy. In general, alloying components are chosen such that a balance is reached between materials with positive and negative hydride heats of formation. In this way, hydrogen may sit in interstitial sites in the metallic alloy lattice. The balance of alloying components is important since this determines the depth of the potential well in which hydrogen is situated, and thus controls the kinetics of hydrogen diffusion from one interstitial site to the next.

A second consideration in choosing a bulk hydrogen storage alloy composition is that of mechanical stability. Many metallic alloys that store substantial amounts of hydrogen become tremendously embrittled as hydrogen is incorporated into their lattice.

This lack of mechanical integrity may not be critical in some applications, such as when the hydrogen storage material is in the form of a pressed powder. However, if the hydrogen storage material must have mechanical integrity, as when the active hydrogen storing alloy is applied as a coating or as a free standing film, an alloy must be chosen where this embrittlement does not occur.

In one embodiment of this invention, the amorphous metal alloy compositions taught in copending European application EP-A 0 197 675 discussed above, are graded such that a substantial portion of the A component of the composition is disposed on the surface of the amorphous metal alloy composition. By "substantial" is meant that at least fifty percent of the A component is disposed on the surface of the amorphous composition. Preferably, at least seventy-five percent of the A component is disposed on the surface of the amorphous composi-

tion, and most preferably about one hundred percent of the A component is disposed on the surface. The phrase "on the surface" refers to disposing the A component on or near the surfaces of the alloy structure that will come in contact with hydrogen available for absorption into the alloy. Thus, "on the surface" embodies any location in the alloy structure wherein the A component may actively adsorb and/or desorb hydrogen into and/or out of the alloy. In this way, the A component in the composition functions as a highly effective interface material, having fast charge transfer kinetics and permitting relatively few recombination reactions to occur. The interior portion of the amorphous metal alloy composition comprises predominantly M and M' elements of the alloy which are highly effective hydrogen storage materials. By concentrating the A component on the surface of the amorphous metal alloy composition, the A component is most effectively utilized for hydrogen storage. Preferably, the A component is Pd, Pt or a combination thereof. In accordance with the present invention, it is now possible to obtain efficient reversible hydrogen storage compositions having the hydrogen storage ability of the previously taught $a_a M_b M'_c$ compositions in EP-A 0 197 675 and their attendant mechanical stability and resistivity to oxidation and corrosion while at the same time utilizing much smaller quantities of the more expensive A component. This improvement significantly reduces the material costs of such compositions and so increases the feasibility of their use and the potential applications for such materials to store hydrogen.

A second embodiment of the present invention comprises an active surface layer having an amorphous metal alloy composition of the formula $A_a M_b M'_c$

wherein A is at least one metal selected from the group consisting of Ag, Au, Hg, Pd and Pt;

M is at least one metal selected from the group consisting of Pb, Ru, Cu, Cr, Mo, Si, W, Ni, Al, Sn, Co, Fe, Zn, Cd, Ga and Mn; and

M' is at least one metal selected from the group consisting of Ca, Mg, Ti, Y, Zr, Hf, Nb, V, Ta and the rare earths; and

wherein a ranges from about 0.005 to about 0.80;

b ranges from zero to about 0.70; and

c ranges from about 0.08 to about 0.95.

This layer is in intimate contact with a second material that is a reversible bulk hydrogen storage material.

In this embodiment, the ranges of a, b and c are preferably from about 0.01 to about 0.75, from about 0.1 to about 0.5, and from about 0.2 to about 0.85, respectively. Most preferably, the ranges of a, b and c are from about 0.2 to about 0.7, from about 0.2 to about 0.4 and from about 0.3 to about 0.8, respectively.

The bulk storage material may comprise any recognized hydrogen storage material such as those amorphous metal alloys that are utilized in the active layer, other amorphous metal alloys known to reversibly store hydrogen, and crystalline materials known to reversibly store hydrogen. The material

used as this bulk hydrogen storage material need not include an A component in its composition. The bulk storage layer may comprise materials that are highly efficient hydrogen storage materials, but that do not withstand surface passivation or corrosion, as the active surface layer shields the bulk hydrogen storage material from detrimental environmental conditions such as oxidative and corrosive conditions. The bulk storage material, if it need not be mechanically stable, may also comprise materials that are susceptible to phase separation and hydrogen embrittlement, as these characteristics will not significantly effect the bulk hydrogen storage efficiency of the cell.

The compositions and structures of the present invention may exist as powders or solids. It is within the scope of the present invention to include powder materials wherein the intended composition and structure comprises individual amorphous hydrogen storage particles having a composition as described herein above by the formula $A_aM_bM'_c$ and wherein the A component of the composition is concentrated on the surface of each particle. It is also within the scope of the present invention to include a powder material comprising a core of reversible hydrogen storage material coated with the amorphous hydrogen storage materials of the formula $A_aM_bM'_c$ that are described herein as well-suited for the active surface layer.

Alternatively, a structure in accordance with this invention may comprise 'packed particles of a bulk hydrogen storage material covered with an active layer or coating of the amorphous hydrogen storage materials described herein.

Also within the scope of this invention is a solid structure having an amorphous metal alloy composition of the formula $A_aM_bM'_c$ wherein the A component of the composition is concentrated on the active surface of the structure, and structures having a core of any reversible hydrogen storage material that is then coated on its exposed active surfaces with the amorphous hydrogen storage compositions described herein. Hydrogen storage structures are also envisioned wherein the $A_aM_bM'_c$ amorphous metal alloy compositions described herein are deposited onto a substrate. The amorphous metal alloy composition may have an A component concentration on its active surface and/or may have another reversible hydrogen storage material disposed between the amorphous metal alloy composition and the substrate.

These compositions and structures can be prepared by any of the standard techniques for fabricating such materials. With respect to fabricating amorphous metal alloys, physical and chemical methods such as electron beam deposition, ion implantation, chemical reduction, thermal decomposition, ion cluster deposition, ion plating, liquid quenching, solid state diffusion, RF and DC sputtering may be utilized to form the compositions herein. One or more methods may be combined advantageously to produce the composite structures taught herein. The A component of a composition may be concentrated on the surface of an amorphous metal alloy by first

producing the desired metal alloy composition absent the A component, then depositing the A component onto the surface of the formed composition, and annealing this structure to form the desired amorphous metal alloy.

An example of this method which can be utilized to produce an extremely low, and uniformly dispersed, concentration of the A component on the surface of the amorphous metal alloy composition is to immerse a film or powder comprising the desired alloy composition absent the A component in an environment where the A component is dilutely present and can be deposited onto the film or powder, such as a solution containing an A-bearing compound therein. Once the A component or A-bearing compound has settled onto the alloy film or powder, then the film or powder may be heat treated to form the desired amorphous metal alloy composition, the heat treating occurring at a temperature below the crystallization temperature of the amorphous metal alloy.

To insure the desired hydrogen storage properties of the amorphous metal alloy material disclosed herein, it is intended that these materials be exposed to an environment wherein the temperature of the alloy does not reach or exceed its crystallization temperature.

The presence of other elements as impurities in the compositions taught herein is not expected to seriously impair the ability of these compositions to reversibly store hydrogen. Thus, trace impurities such as O, N, C, S, Se, Te, B, P, Ge, Sb, As and Ar are not expected to be seriously detrimental to the preparation and performance of these compositions.

The following examples demonstrate the hydrogen storage ability of the compositions and structures described in the present invention. It is to be understood that these examples are utilized for illustrative purposes only, and are not intended in any way, to be limitative of the present invention.

EXAMPLES

Example 1

This example demonstrates the formation of a graded structure in accordance with the invention wherein the A component of the desired amorphous metal alloy is concentrated on the surface of the alloy by first depositing the M and M' components of the composition onto a substrate, then depositing the A component thereon, and finally annealing the structure to form the desired amorphous metal alloy composition.

A layer, about 4,000 Angstroms thick, of $Ni_{40}Ti_{60}$ was sputtered onto a titanium substrate in a vacuum. Thereafter, without breaking the vacuum, about 1,500 Angstroms of palladium was evaporated onto the $Ni_{40}Ti_{60}$ layer. This structure was then heat treated at about 300°C for about 12 hours. The resulting structure comprised a bulk hydrogen storage layer of $Ni_{40}Ti_{60}$, an amorphous graded composition of Pd-Ni-Ti, with a palladium concentration graded from zero to about 0.80, and excess crystalline Pd.

This structure was utilized as an electrode in an electrolytic cell opposite a nickel hydroxide counter electrode. The electrolyte in the cell was potassium hydroxide. The hydrogen electrode was cyclically charged at about 1 mA until the cell voltage stabilized, and then discharged at about 0.1 mA. The electrode was charged and discharged about 20 times, after which the efficiency of the hydrogen electrode was calculated in terms of a charge density measured as a charge-per-weight (mA-hr/gm) and a charge-per-volume (mA-hr/cm³). The electrode was seen to have a charge density of about 217 mA-hr/gm and about 1697 mA-hr/cm³.

Example 2

This example demonstrates the formation of a reversible hydrogen storage structure having an active hydrogen absorption surface disposed on a bulk hydrogen storage material. The active hydrogen storage layer is of the form A_aM'_c.

A layer, about 6,000 Angstroms thick, of an amorphous alloy having an approximate composition Fe₄₀Ti₆₀ was sputtered on a titanium substrate in a vacuum. While maintaining the vacuum, a layer of about 790 Angstroms thick of an amorphous alloy, Pd₄₀Ti₆₀, was sputtered onto the Fe₄₀Ti₆₀ layer.

This structure was then used as a hydrogen storage electrode in a cell having an electrolyte of 2N H₃PO₄ and a counter electrode of graphite. The hydrogen storage electrode had an active surface area of about 1.5 cm². The hydrogen electrode was cyclically charged at about 1 mA until the cell voltage stabilized, and then discharged at about 0.1 mA. The efficiency of the hydrogen electrode was calculated in terms of a charge density and found to be about 143 mA-hr/gm on a charge-per-weight basis and about 875 mA-hr/cm³ on a charge-per-volume basis.

Example 3

This example demonstrates a process for obtaining a composition in accordance with the above teaching wherein the amount of the A component is extremely low.

A splat-cooled foil of amorphous Ni₆₄Hf₃₆, about 40 microns thick, was etched in a 1 percent aqueous hydrogen fluoride solution for about 1 minute and then dipped into a dilute palladium chloride-containing solution for ten seconds. The palladium chloride-containing solution comprised about 40 ml of concentrated HCl and 1 gm of palladium chloride per liter of water. A small amount of palladium settled on the Ni₆₄Hf₃₆ foil during this dipping process. The foil was then heat treated in a vacuum at about 275°C for about 48 hours. The resultant material was found to be an amorphous material having an approximate composition of Pd_{0.001}Ni₆₄Hf₃₆.

This composition was used as a hydrogen storage electrode in an electrolytic cell, the hydrogen storage electrode having an active surface area of about 1.5 cm². The electrolytic cell also employed a nickel hydroxide counter electrode and an electrolyte of potassium hydroxide. After about 60

charge/discharge cycles, the efficiency of the hydrogen electrode was calculated in terms of a charge density and found to be about 54 mA-hr/gm on a charge-per-weight basis and about 645 mA-hr/cm³ on a charge-per-volume basis.

The reversible hydrogen storage ability of the amorphous metal alloy compositions taught herein provide heretofor unattainable hydrogen storage ability, resistance to oxidation, and stability in economically feasible compositions and so represent a substantial advancement to hydrogen storage and its ancillary technologies and applications.

Thus, it is believed that any of the variables disclosed herein can readily be determined and controlled without departing from the spirit of the invention herein disclosed and described. Moreover, the scope of the invention shall include all modifications and variations that fall within the scope of the attached claims.

Although several amorphous metal alloy compositions have been exemplified herein, it will readily be appreciated by those skilled in the art that other amorphous metal alloys falling within the scope of the compositions described herein as well-suited for reversibly stored hydrogen could be substituted therefore.

It is to be understood that the foregoing examples have been provided to enable those skilled in the art to have representative examples by which to evaluate the invention and that these examples should not be construed as any limitation on the scope of this invention. Inasmuch as the composition of the amorphous metal alloys employed in the present invention and their graded and/or layered structure can be varied within the scope of the total specification disclosure, neither the particular A, M or M' components nor the relative amounts of the components in the alloys exemplified herein shall be construed as limitations of the invention.

Claims

1. A reversible hydrogen storage material comprising a at least 50% amorphous metal alloy of the formula:

A_aM_bM'_c

wherein A is at least one metal selected from the group consisting of Ag, Au, Hg, Pd and Pt; M is at least one metal selected from the group consisting of Pb, Ru, Cu, Cr, Mo, Si, W, Ni, Al, Sn, Co, Fe, Zn, Cd, Ga and Mn and M' is at least one metal selected from the group consisting of Ca, Mg, Ti, Y, Zr, Hf, Nb, V, Ta and the rare earths; and

wherein a ranges from greater than zero to about 0.80; b ranges from zero to about 0.70; and c ranges from about 0.08 to about 0.95;

the material characterised in that at least fifty percent of the A component of said alloy is disposed on the surface of said material.

2. The reversible hydrogen storage material in accordance with claim 1 wherein A is Pd, Pt or a combination thereof.

3. The reversible hydrogen storage material in accordance with claim 1 wherein M is at least one

This structure was utilized as an electrode in an electrolytic cell opposite a nickel hydroxide counter electrode. The electrolyte in the cell was potassium hydroxide. The hydrogen electrode was cyclically charged at about 1 mA until the cell voltage stabilized, and then discharged at about 0.1 mA. The electrode was charged and discharged about 20 times, after which the efficiency of the hydrogen electrode was calculated in terms of a charge density measured as a charge-per-weight (mA-hr/gm) and a charge-per-volume (mA-hr/cm³). The electrode was seen to have a charge density of about 217 mA-hr/gm and about 1697 mA-hr/cm³.

Example 2

This example demonstrates the formation of a reversible hydrogen storage structure having an active hydrogen absorption surface disposed on a bulk hydrogen storage material. The active hydrogen storage layer is of the form A_aM'_c.

A layer, about 6,000 Angstroms thick, of an amorphous alloy having an approximate composition Fe₄₀Ti₆₀ was sputtered on a titanium substrate in a vacuum. While maintaining the vacuum, a layer of about 790 Angstroms thick of an amorphous alloy, Pd₄₀Ti₆₀, was sputtered onto the Fe₄₀Ti₆₀ layer.

This structure was then used as a hydrogen storage electrode in a cell having an electrolyte of 2N H₃PO₄ and a counter electrode of graphite. The hydrogen storage electrode had an active surface area of about 1.5 cm². The hydrogen electrode was cyclically charged at about 1 mA until the cell voltage stabilized, and then discharged at about 0.1 mA. The efficiency of the hydrogen electrode was calculated in terms of a charge density and found to be about 143 mA-hr/gm on a charge-per-weight basis and about 875 mA-hr/cm³ on a charge-per-volume basis.

Example 3

This example demonstrates a process for obtaining a composition in accordance with the above teaching wherein the amount of the A component is extremely low.

A sput-cooled foil of amorphous Ni₆₄Hf₃₆, about 40 microns thick, was etched in a 1 percent aqueous hydrogen fluoride solution for about 1 minute and then dipped into a dilute palladium chloride-containing solution for ten seconds. The palladium chloride-containing solution comprised about 40 ml of concentrated HCl and 1 gm of palladium chloride per liter of water. A small amount of palladium settled on the Ni₆₄Hf₃₆ foil during this dipping process. The foil was then heat treated in a vacuum at about 275°C for about 48 hours. The resultant material was found to be an amorphous material having an approximate composition of Pd_{0.001}Ni₆₄Hf₃₆.

This composition was used as a hydrogen storage electrode in an electrolytic cell, the hydrogen storage electrode having an active surface area of about 1.5 cm². The electrolytic cell also employed a nickel hydroxide counter electrode and an electrolyte of potassium hydroxide. After about 60

charge/discharge cycles, the efficiency of the hydrogen electrode was calculated in terms of a charge density and found to be about 54 mA-hr/gm on a charge-per-weight basis and about 645 mA-hr/cm³ on a charge-per-volume basis.

The reversible hydrogen storage ability of the amorphous metal alloy compositions taught herein provide heretofor unattainable hydrogen storage ability, resistance to oxidation, and stability in economically feasible compositions and so represent a substantial advancement to hydrogen storage and its ancillary technologies and applications.

Thus, it is believed that any of the variables disclosed herein can readily be determined and controlled without departing from the spirit of the invention herein disclosed and described. Moreover, the scope of the invention shall include all modifications and variations that fall within the scope of the attached claims.

Although several amorphous metal alloy compositions have been exemplified herein, it will readily be appreciated by those skilled in the art that other amorphous metal alloys falling within the scope of the compositions described herein as well-suited for reversibly stored hydrogen could be substituted therefore.

It is to be understood that the foregoing examples have been provided to enable those skilled in the art to have representative examples by which to evaluate the invention and that these examples should not be construed as any limitation on the scope of this invention. Inasmuch as the composition of the amorphous metal alloys employed in the present invention and their graded and/or layered structure can be varied within the scope of the total specification disclosure, neither the particular A, M or M' components nor the relative amounts of the components in the alloys exemplified herein shall be construed as limitations of the invention.

Claims

1. A reversible hydrogen storage material comprising a at least 50% amorphous metal alloy of the formula:



wherein A is at least one metal selected from the group consisting of Ag, Au, Hg, Pd and Pt; M is at least one metal selected from the group consisting of Pb, Ru, Cu, Cr, Mo, Si, W, Ni, Al, Sn, Co, Fe, Zn, Cd, Ga and Mn and M' is at least one metal selected from the group consisting of Ca, Mg, Ti, Y, Zr, Hf, Nb, V, Ta and the rare earths; and

wherein a ranges from greater than zero to about 0.80; b ranges from zero to about 0.70; and c ranges from about 0.08 to about 0.95;

the material characterised in that at least fifty percent of the A component of said alloy is disposed on the surface of said material.

2. The reversible hydrogen storage material in accordance with claim 1 wherein A is Pd, Pt or a combination thereof.

3. The reversible hydrogen storage material in accordance with claim 1 wherein M is at least one



metal selected from the group consisting of Mn, Ru, Fe, Cu, Ni, Cr, Mo, Al and W.

4. The reversible hydrogen storage material in accordance with claim 1 wherein M' is titanium, magnesium, tantalum or a combination thereof.

5. The reversible hydrogen storage material in accordance with claim 1 wherein a ranges from greater than zero to about 0.5; b ranges from about 0.1 to about 0.5; and c ranges from about 0.2 to about 0.85.

6. The reversible hydrogen storage material in accordance with claim 1 wherein a ranges from about 0.001 to about 0.2; b ranges from about 0.2 to about 0.4; and c ranges from about 0.3 to about 0.8.

7. The reversible hydrogen storage material in accordance with claim 1 wherein at least seventy-five percent of said A component is disposed on the surface of said material.

8. The reversible hydrogen storage material in accordance with claim 1 wherein about one hundred percent of said A component is disposed on the surface of said material.

9. A reversible hydrogen storage structure having an active hydrogen absorption surface layer and a bulk hydrogen storage material, the active surface layer comprising a at least 50% amorphous metal alloy of the formula:

$A_aM_bM'_c$

wherein A is at least one metal selected from the group consisting of Ag, Au, Hg, Pd and Pt; M is at least one metal selected from the group consisting of Pb, Ru, Cu, Cr, Mo, Si, W, Ni, Al, Sn, Co, Fe, Zn, Cd, Ga and Mn; and M' is at least one metal selected from the group consisting of Ca, Mg, Ti, Y, Zr, Hf, Nb, V, Ta and the rare earths; and wherein a ranges from about 0.005 to about 0.80; b ranges from zero to about 0.70; and c ranges from about 0.08 to about 0.95; and the bulk storage material comprising a reversible hydrogen storage material.

10. The reversible hydrogen storage structure in accordance with claim 9 wherein said bulk storage material comprises an amorphous material capable of reversible hydrogen storage.

11. The reversible hydrogen storage structure in accordance with claim 9 wherein said bulk storage material comprises a crystalline material capable of reversible hydrogen storage.

12. A process for the formation of a reversible hydrogen storage material comprising a at least 50% amorphous metal alloy of the formula:

$A_aM_bM'_c$

wherein A is at least one metal selected from the group consisting of Ag, Au, Hg, Pd and Pt; M is at least one metal selected from the group consisting of Pb, Ru, Cu, Cr, Mo, Si, W, Ni, Al, Sn, Co, Fe, Zn, Cd, Ga and Mn; and M' is at least one metal selected from the group consisting of Ca, Mg, Ti, Y, Zr, Hf, Nb, V, Ta and the rare earths; and wherein a ranges from greater than zero to about 0.80; b ranges from zero to about 0.70; and c ranges from about 0.08 to about 0.95;

and wherein a substantial portion of the A component is disposed on the surface of said material, the process comprising

a) forming said M and M' components into a shape;

b) disposing said shape in an environment wherein said shape is exposed to A-containing compounds and said A-containing compounds and said A-containing compounds are caused to settle onto said shape; and

c) heat treating said shape at a temperature below the crystallization temperature of the amorphous metal alloy so as to form said alloy.

13. The process in accordance with claim 12 wherein said M and M' component shape of step a) is formed on a substrate.

14. The process in accordance with claim 12 wherein said M and M' component shape is a thin film.

15. The process in accordance with claim 12 wherein said M and M' component shape is a powder.

16. The process in accordance with claim 12 wherein said M and M' component shape is amorphous.

17. The process in accordance with claim 12 wherein said environment of step b) comprises a solution containing A-bearing compounds therein.

Revendications

1. Matériau de stockage réversible de l'hydrogène, comprenant au moins 50% d'alliage métallique amorphe de formule:

$A_aM_bM'_c$

dans laquelle A est au moins un métal choisi dans le groupe constitué de Ag, Au, Hg, Pd et Pt, M est au moins un métal choisi dans le groupe constitué de Pb, Ru, Cu, Cr, Mo, Si, W, Ni, Al, Sn, Co, Fe, Zn, Cd, Ga et Mn et M' est au moins un métal choisi dans le groupe constitué de Ca, Mg, Ti, Y, Zr, Hf, Nb, V, Ta et les terres rares et dans laquelle a est compris entre une valeur supérieure à zéro et environ 0,80; b est compris entre environ zéro et environ 0,70; et c est compris entre environ 0,08 et environ 0,95;

ce matériau étant caractérisé en ce qu'au moins cinquante pour cent du composant A dudit alliage sont disposés sur la surface du matériau.

2. Matériau de stockage réversible de l'hydrogène suivant la revendication 1, dans lequel A est Pd, Pt ou une combinaison de ceux-ci.

3. Matériau de stockage réversible de l'hydrogène suivant la revendication 1, dans lequel M est au moins un métal choisi dans le groupe constitué de Mn, Ru, Fe, Cu, Ni, Cr, Mo, Al, W.

4. Matériau de stockage réversible de l'hydrogène suivant la revendication 1, dans lequel M' est le titane, le magnésium, le tantale ou une combinaison de ceux-ci.

5. Matériau de stockage réversible de l'hydrogène suivant la revendication 1, dans lequel a a une valeur comprise entre une valeur supérieure à zéro et environ 0,5; b vaut d'environ 0,1 à environ 0,5 et c vaut d'environ 0,2 à environ 0,85.

6. Matériau de stockage réversible de l'hydrogène suivant la revendication 1, dans lequel a vaut d'environ 0,001 à environ 0,2; b vaut d'environ



0,2 à environ 0,4; et c vaut d'environ 0,3 à environ 0,8.

7. Matériau de stockage réversible de l'hydrogène suivant la revendication 1, dans lequel au moins soixante-quinze pour-cent du composé A sont disposés sur la surface du matériau.

8. Matériau de stockage réversible de l'hydrogène suivant la revendication 1, dans lequel environ cent pour-cent du composant A sont disposés sur la surface du matériau.

9. Structure de stockage réversible de l'hydrogène, comportant une couche superficielle active d'absorption de l'hydrogène et un matériau de stockage en masse de l'hydrogène, la couche superficielle active comprenant au moins 50% d'alliage métallique amorphe des formule:



dans laquelle A est au moins un métal choisi dans le groupe constitué de Ag, Au, Hg, Pd et Pt; M est au moins un métal choisi dans le groupe constitué de Pb, Ru, Cu, Cr, Mo, Si, W, Ni, Al, Sn, Co, Fe, Zn, Cd, Ga et Mn; et M' est au moins un métal choisi dans le groupe constitué de Ca, Mg, Ti, Y, Zr, Hf, Nb, V, Ta et les terres rares; et dans laquelle a est compris entre zéro et environ 0,80; b est compris entre zéro et environ 0,70; et c est compris entre environ 0,08 et environ 0,95, et le matériau de stockage en volume est constitué d'un matériau de stockage réversible de l'hydrogène.

10. Structure de stockage réversible de l'hydrogène suivant la revendication 9, dans laquelle le matériau de stockage en volume est constitué par un matériau amorphe susceptible d'un stockage réversible de l'hydrogène.

11. Structure de stockage réversible de l'hydrogène suivant la revendication 9, dans laquelle le matériau de stockage en volume est constitué d'un matériau cristallin susceptible d'un stockage réversible de l'hydrogène.

12. Procédé de formation d'un matériau de stockage réversible de l'hydrogène comprenant au moins 50% d'alliage métallique amorphe de formule:



dans laquelle A est au moins un métal choisi dans le groupe constitué de Ag, Au, Hg, Pd et Pt; M est au moins un métal choisi dans le groupe constitué de Pb, Ru, Cu, Cr, Mo, Si, W, Ni, Al, Sn, Co, Fe, Zn, Cd, Ga et Mn; et M' est au moins un métal choisi dans le groupe constitué de Ca, Mg, Ti, Y, Zr, Hf, Nb, V, Ta et les terres rares; et dans laquelle a est compris entre une valeur supérieure à zéro et environ 0,80, b est compris entre zéro et environ 0,70 et c est compris entre environ 0,08 et environ 0,95, et dans lequel une partie notable du composant A est disposée sur la surface du matériau, ce procédé consistant:

a) à mettre en forme les composants M et M'

b) à disposer cette forme dans un environnement dans lequel cette forme structurale est exposée à des composés contenant A et on fait se déposer ces composés contenant A sur cette forme et

c) à soumettre cette forme structurale à un traitement thermique, à une température inférieure à la température de cristallisation de l'alliage métalli-

que amorphe, de manière à former l'alliage.

13. Procédé suivant la revendication 12, selon lequel la forme structurale des composants M et M' de l'étape a) est formée sur un substrat.

14. Procédé suivant la revendication 12, selon lequel les composants M et M' sont sous forme d'un film mince.

15. Procédé suivant la revendication 12, selon lequel les composants M et M' sont sous forme d'une poudre.

16. Procédé suivant la revendication 12, selon lequel les composants M et M' sont sous forme amorphe.

17. Procédé suivant la revendication 12, selon lequel l'environnement de l'étape b) est constitué par une solution contenant des composés portant A.

Patentansprüche

1. Material für reversible Wasserstoffspeicherung umfassend mindestens 50% amorphe Metalllegierung der Formel:



worin A mindestens ein Metall ist, ausgewählt aus der Gruppe bestehend aus Ag, Au, Hg, Pd und Pt; M mindestens ein Metall ist, ausgewählt aus der Gruppe bestehend aus Pb, Ru, Cu, Cr, Mo, Si, W, Ni, Al, Sn, Co, Fe, Zn, Cd, Ga und Mn und M' mindestens ein Metall ist, ausgewählt aus der Gruppe bestehend aus Co, Mg, Ti, Y, Zr, Hf, Nb, V, Ta und den Seltenen Erden; und worin a von größer als 0 bis ungefähr 0,80 geht; b von 0 bis ungefähr 0,70 geht; und c von ungefähr 0,08 bis ungefähr 0,95 geht; das Material dadurch gekennzeichnet ist, daß mindestens 50% der Komponente A der Legierung auf der Oberfläche des Materials niedergeschlagen ist.

2. Material für reversible Wasserstoffspeicherung nach Anspruch 1, worin A Pd, Pt oder eine Kombination davon ist.

3. Material für reversible Wasserstoffspeicherung nach Anspruch 1, worin M mindestens ein Metall ist, ausgewählt aus der Gruppe bestehend aus Mn, Ru, Fe, Cu, Ni, Cr, Mo, Al und W.

4. Material für reversible Wasserstoffspeicherung nach Anspruch 1, worin M' Titan, Magnesium, Tantal oder eine Kombination davon ist.

5. Material für reversible Wasserstoffspeicherung nach Anspruch 1, worin a von größer als 0 bis ungefähr 0,5 geht; b von ungefähr 0,1 bis ungefähr 0,5 geht; und c von ungefähr 0,2 bis ungefähr 0,85 geht.

6. Material für reversible Wasserstoffspeicherung nach Anspruch 1, worin a von ungefähr 0,001 bis ungefähr 0,2 geht; b von ungefähr 0,2 bis ungefähr 0,4 geht; und c von ungefähr 0,3 bis ungefähr 0,8 geht.

7. Material für reversible Wasserstoffspeicherung nach Anspruch 1, worin mindestens 75% der Komponente A auf der Oberfläche des Materials niedergeschlagen sind.

8. Material für reversible Wasserstoffspeicherung nach Anspruch 1, worin ungefähr 100% der Komponente A auf der Oberfläche des Materials niedergeschlagen sind.



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9. Struktur für reversible Wasserstoffspeicherung mit einer aktiven Oberflächenschicht für Wasserstoffabsorption und einer Hauptmenge des Materials für Wasserstoffspeicherung, wobei die aktive Oberflächenschicht umfaßt eine zu mindestens 50% amorphe Metallegierung der Formel:

$A_a M_b M'_c$

worin A mindestens ein Metall ist, ausgewählt aus der Gruppe bestehend aus Ag, Au, Hg, Pd und Pt; M mindestens ein Metall ist, ausgewählt aus der Gruppe bestehend aus Pb, Ru, Cu, Cr, Mo, Si, W, Ni, Al, Sn, Co, Fe, Zn, Cd, Ga und Mn; und M' mindestens ein Metall ist, ausgewählt aus der Gruppe bestehend aus Ca, Mg, Ti, Y, Zr, Hf, Nb, V, Ta und den Seltenen Erden; und

worin a von ungefähr 0,005 bis ungefähr 0,8 geht; b von 0 bis ungefähr 0,70 geht; und c von ungefähr 0,08 bis ungefähr 0,95 geht; und wobei die Hauptmenge des Speichermaterials ein Material für reversible Wasserstoffspeicherung umfaßt.

10. Struktur für reversible Wasserstoffspeicherung nach Anspruch 9, worin die Hauptmenge des Speichermaterials ein amorphes Material, geeignet für reversible Wasserstoffspeicherung, umfaßt.

11. Struktur für reversible Wasserstoffspeicherung nach Anspruch 9, worin die Hauptmenge des Speichermaterials ein kristallines Material, geeignet für reversible Wasserstoffspeicherung, umfaßt.

12. Verfahren zur Bildung eines Materials für reversible Wasserstoffspeicherung umfassend eine zumindestens 50% amorphe Metallegierung der Formel:

$A_a M_b M'_c$

worin A mindestens ein Metall ist, ausgewählt aus der Gruppe bestehend aus Ag, Au, Hg, Pd und Pt; M mindestens ein Metall ist, ausgewählt aus der Gruppe bestehend aus Pb, Ru, Cu, Cr, Mo, Si, W, Ni, Al, Sn, Co, Fe, Zn, Cd, Ga und Mn; und M' mindestens ein Metall ist, ausgewählt aus der Gruppe bestehend aus Ca, Mg, Ti, Y, Zr, Hf, Nb, V, Ta und den Seltenen Erden; und

worin a von größer als 0 bis ungefähr 0,80 geht; b von 0 bis ungefähr 0,70 geht; c von ungefähr 0,80 bis ungefähr 0,95 geht; und worin ein wesentlicher Anteil der Komponente A auf der Oberfläche des Materials niedergeschlagen ist, wobei das Verfahren umfaßt

a) Formen der Komponenten M und M' in eine Form;

b) Niederschlagen dieser Form in eine Umgebung, worin diese Form der A-haltigen Verbindungen ausgesetzt ist und die A-haltigen Verbindungen veranlaßt werden, sich auf dieser Form abzusetzen; und

c) Wärmebehandlung dieser Form bei einer Temperatur unterhalb der Kristallisationstemperatur der amorphen Metallegierung, so, um die Legierung zu bilden.

13. Verfahren nach Anspruch 12, worin die Form der Komponenten M und M' aus Schritt a) auf einem Substrat gebildet ist.

14. Verfahren nach Anspruch 12, worin die Form der Komponenten M und M ein dünner Film ist.

15. Verfahren nach Anspruch 12, worin die Form der Komponenten M und M' ein Pulver ist.

16. Verfahren nach Anspruch 12, worin die Form der Komponenten M und M' amorph ist.

17. Verfahren nach Anspruch 12, worin die Umgebung von Schritt b) eine Lösung umfaßt, enthaltend darin A-tragende Verbindungen.

