



An overview of advanced materials for hydrogen storage

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Abstract: In a future sustainable energy system based on renewable energy, environmentally harmless energy carriers like hydrogen, will be of crucial importance. One of the major impediments for the transition to a hydrogen based energy system is the lack of satisfactory hydrogen storage alternatives. In the last years, the possible to store hydrogen in various materials was extensively studied.

This paper is a preliminary study with the focus on advanced nanostructured materials such as solids of large surface area based on carbon structures, metals and different types of metal alloys, other intermetallic compounds, etc. as possibilities for hydrogen storage. The newest materials used for hydrogen storage are light metal alloys. We have so far focused in this review almost exclusively on experimental studies. Also there are presented the most important characteristics of these materials such as mechanical strength, porosity and affinity to hydrogen, and also the recent developments in the search for innovative materials with high hydrogen-storage capacity and our contribution in this field.

Keywords: Metallic alloys, Nanomaterials, Hydrogen storage materials, Carbon structures

1. INTRODUCTION

The current interest in hydrogen is primarily due to environmental concerns of the harmful emissions from the fossil fuels used presently. Also, a demand for more efficient power sources has increased the interest in different kinds of new technologies, such as fuel cells using hydrogen or hydrocarbons as fuel [1].

While hydrogen has many obvious advantages, there remains a problem with storage and transportation. Pressurised hydrogen gas takes a great deal of volume compared with, for example, gasoline with equal energy content - about 30 times bigger volume at 100 atm gas pressure. Condensed hydrogen is about ten times denser, but is much too expensive to produce and maintain [2]. There are also obvious safety concerns with the use of pressurised or liquified hydrogen in vehicles. The results obtained and presented by many studies show that three kinds of materials are competitive for to be use in hydrogen storage processes. These are materials based on carbon structures, metals and metal alloys. We will refer especially at these kinds of materials.

2. MATERIALS BASED ON CARBON STRUCTURES

The best performance in hydrogen storage was achieved with materials based on carbon structures of highest effective porosity. The two forms of carbon that is the most known to us

are diamond and graphite. In diamond each atom is fully co-ordinated symmetrically in space in all three dimensions. Graphite on the other hand, is build up of a two dimensional hexagonal sheet of carbon atoms, with long distance between each sheet. Figure 1 shows the structure of graphite diamond,fullerenes and of single-wall carbon nanotube.

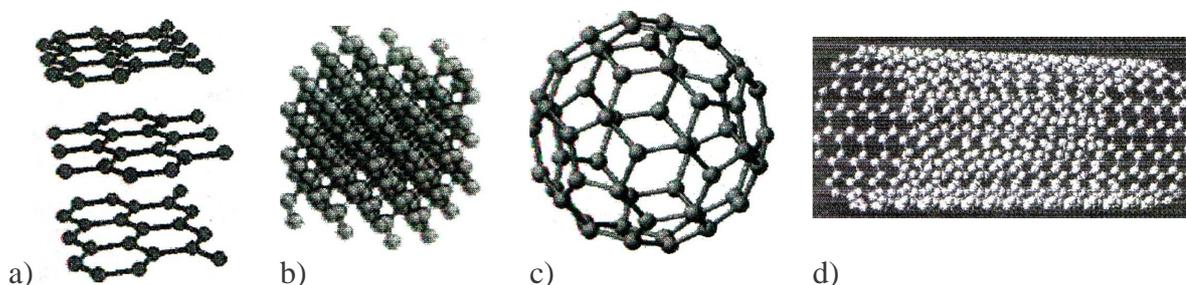


Figure1. Structure of: graphite(a); diamond(b); fullerenes(c); and of single-wall carbon nanotube(d)

However, there are also other forms of carbon structures such as fullerenes and nanotubes, that are the newest advanced carbon structures, with special properties. Fullerenes are single or multiple layers of graphite wrapped together into very stable ball (figure 1c) or tube molecules-single wall carbon nanotubes(SWCT) ,figure 1d, respectively. These are a new class of carbon aromatic compounds with unusual structural, chemical and physical properties which, in turn, will lead to novel and unexpected applications, such as hydrogen storage.

3. METALS AND METAL ALLOYS FOR HYDROGEN STORAGE

Hydrogen is a highly reactive element and is known to form hydrides and solid solutions with thousands of metals and alloys. Most of the natural elements adsorb hydrogen under proper conditions. Metal hydrides are composed of metal atoms that constitute of a host lattice and hydrogen atoms that are trapped in interstitial sites, such as lattice defects. The trap site can be a vacancy or a line defect. In the case of a line defect, a string of hydrogen atoms may accumulate along the defect. Such a string increases the lattice stress, especially if two adjacent atoms recombine to form molecular hydrogen [3]. Since adsorption of hydrogen increases the size of lattices [3,4], the metal is usually ground to a powder in order to prevent the decrepitation of metal particles.

Normally the hydrides are divided into high temperature hydrides and low temperature hydrides depending on the temperature absorption/desorption. In the low temperature hydrides, the hydrogen normally is bound through covalent bonding and the metal hydride consists of high molecular weight material. In the high temperature hydrides, the hydrogen is normally ionic bound, and the metal hydride consists of low molecular weight material. The hydrogen storage capacities are higher for the high temperature hydrides. The most common examples of hydrogen storing alloys are Fe-Ti hydrides, La-Ni hydrides, Ti-Zr-V series of hydrides, etc.

Hydride systems based on existing metal hydrides cannot store large amounts of hydrogen and the development of new kinds of hydride materials is required.

3.1. Light metal alloys for hydrogen storage

If metal hydrides are to become important energy carriers in mobile vehicles, the mass of the system needs to be reduced from today's devices, such as FeTi. This puts strong

constraints on the chemical elements which can be used. A very promising approach is to use magnesium. The hydride, MgH_2 , can store up to 7.6 % weight percent of hydrogen [5,6].

The automobile industry has set 5-5.6% weight percent as a target for efficient hydrogen storage. But there are three problems with pure Mg: (i) The rate at which hydrogen absorbs and desorbs is too low because diffusion of hydrogen atoms through the hydride is slow. Problem (ii) is that the hydrogen molecules do not readily dissociate at the surface of Mg to generate the hydrogen atoms that diffuse into the metal. Transition metals can catalyse this bond breaking/formation event at the surface, but not main group elements [7]. Problem (iii) is that hydrogen atoms bind too strongly with the Mg atoms, i.e. the enthalpy of formation of the hydride is too large, so that the hydride needs to be heated to very high temperature, around 350°C , in order to release hydrogen gas at high enough pressure (over 1 atm) [5]. A useful metal hydride should release the hydrogen in the temperature range between 50 and 100°C . It is important to distinguish between problems (i) and (ii) although they both have to do with the kinetics of absorption and desorption processes. These problems could be solved efficiently by different means, but problem (iii) remains unsolved. Our studies performed till now were focused on these three problems.

The first problem could be reduced by forming a composite of small Mg crystals agglomerated together as opposed to a large chunk of Mg crystal. The clusters formed by ball milling are micrometer sized such as seen in the scanning electron microscopy (SEM) and the transmission electron micrograph (TEM) images (figure 2). The size of the magnesium grains in this composite is 40-200 nm. Hydrogen absorption and desorption of this material was found to be reasonably fast.

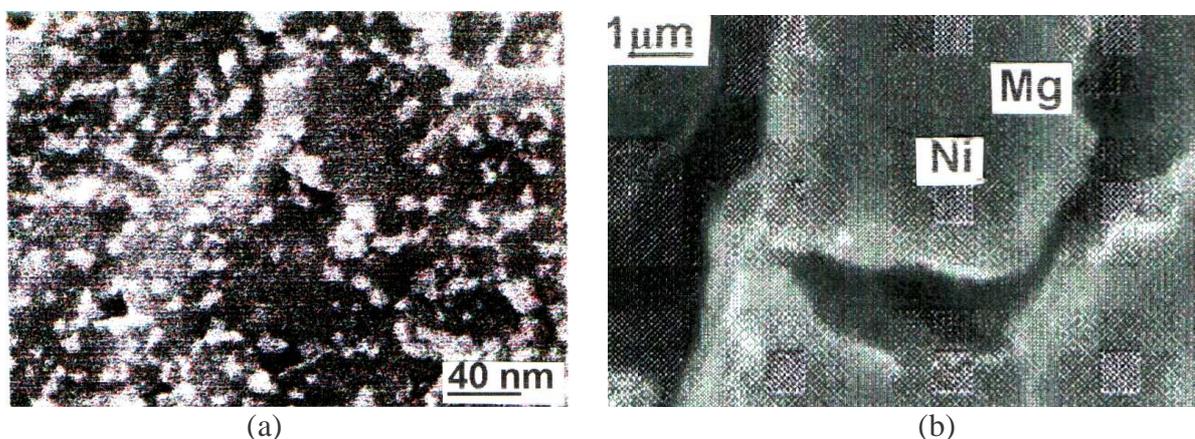


Figure 2. A scanning electron microscopy (SEM) micrograph of a powder of Mg particles which have small Ni clusters attached on the surface in order to catalyse the break up of hydrogen molecules during adsorption (a) and transmission electron microscopy (TEM) micrograph of the powder showing the nanocrystalline structure of the particles (b)

The dark regions represent crystalline domains, while the lighter regions are less dense and likely amorphous. The scanning electron microscopy (SEM), shown in figure 2a, reveals the crystalline structure of the particles. The second problem, the dissociation of hydrogen molecules on the surface, could be solved by adding a small amount of a catalytically active metal on the surface of the Mg clusters, as shown in figure 2b.

The third problem with pure Mg as a hydrogen storage device is the most serious one, thanks to the high enthalpy of formation of the hydride. Some improvement has been shown

to occur by adding Ni to Mg. The desorption temperature of the Mg₂Ni alloy is about 50-60 degrees lower than for pure Mg, but this is still far from low enough. The addition of the heavy transition metal greatly reduces the storage capacity, down to 3.8 % from 7.6% in pure Mg. A better solution would be to add a light metal that has low affinity to hydrogen, for example aluminium or another light main group element that competes with hydrogen for the valence electrons of Mg. This strategy has apparently not been tried and will be pursued in a new proposed project.

3.2. Alanates and other hydrides

Some of the lightest elements in the periodic table, for example lithium, boron, sodium and aluminium, form stable and ionic compounds with hydrogen [8]. The hydrogen content reaches values of up to 18 mass% for LiBH₄. Lithium used in the same way would deliver up to 14 mass% of hydrogen.

Besides the alloys described above, there are several other families of intermetallics having a capability of hydrogen adsorption, none of which has attained commercial interest. These include, for example, A₂B, AB₃, A₂B₇, A₃B, etc. The A elements are usually Ti, Zr, Hf, Th, or a lanthanide (atomic number 57-71). The B elements can be a variety of transition and non-transition metals, such as V, Cr, Mn, and Fe. Some of these have good hydrogen capacities but do not have favorable absorption/desorption characteristics.

4. CONCLUSIONS

The research is focused on solid-state storage using gas on solid adsorption in materials such as high surface area carbon, or absorption in the interstices of a metal hydride. In solid state storage, gas on solids and metal hydrides are the options which are safer technologies and they provide high storage capacity than physical storage systems. Basic concept on mechanisms of solid state storage is essential in order to get more knowledge about high performance storage materials such as storage capacities, rates of charge and discharge, thermal and mechanical effects of available materials, increasing capability of manufacturing of new storage materials, like magnesium based hydrides and high surface area activated carbon. Also, materials systems, such as fullerenes, carbon nanotubes, light metal alloys are very promising new materials they have a good potential in storing hydrogen.

REFERENCES

1. G.Sandrock, K.J.Gross, G.Thomas, J.Alloys Comp. 339,299 (2002);
2. C.M.Jensen, R.Zidan, N.Mariels, A.Hee, C.Hagen, INT.J. Hydrogen Energy, 24,461, (1999);
3. Carter T., Cornish L., Engineering Failure Analysis, Vol. 8, (2001), pp. 113-121;
4. Fischer P., Yvon K., Hydrogen in Intermetallic Compounds I, Ed. Schlapbach, Springer-Verlag, Germany (1988), 75;
5. R. Griessen and T. Riesterer, Hydrogen in Intermetallic Compounds I, ed. By L. Schlapbach, Topics Appl. Phys., Vol 63 (Springer, Berlin, (1988). p. 219;
6. H. Buchener and R. Povel, Int.J. Hydrogen Energy, 7 (1982) p.259;
7. G.Liang, J.Huot, S.Boily, A.Van Neste, R.Schulz, Journal of Alloys and Compounds, 292, (1999), pp 247-252;
8. L.Schlapbach, A.Zuttel, Nature, Vol.414/15 Nov. (2001),pp 353-358;