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PAPER A
CHEMISTRY

This paper comprises:

* Letter from the applicant   2007/A(Ch)/e/1-8

* Document 1   2007/A(Ch)/e/9

LETTER FROM THE APPLICANT

H. Too Ltd.

We are a small company, working in the field of new forms of energy. We perform research into many forms of energy including wind energy, solar energy, and fuel cells. Recently, a number of articles have appeared in the media identifying hydrogen as the energy source of the future. Even though we believe this to be slightly exaggerated, hydrogen nevertheless is a promising source of energy. However, before hydrogen can be used on a large scale, there are many challenges to face.

Hydrogen can be used directly in combustion or it can be converted to electricity in a fuel cell. Hydrogen is a highly flammable gas making it difficult to store safely. Hydrogen can be stored as a liquid under high pressure. However, the use of such high pressures does not make this a very suitable method for the consumer market, for example in cars. Another solution is to produce the hydrogen when it is needed. Such systems have been demonstrated to work well. However, these systems are quite sensitive to failure. In any case, these systems also need some hydrogen to be stored for starting up the system and as a backup. Safe storage of hydrogen is therefore an important hurdle to overcome before it can be used on a large scale.

Hydrogen can also be stored in solid materials. The most promising materials are certain types of alloys. As you will surely know, alloys are metallic compounds or metallic mixtures that contain at least two components, at least one of these components being a metal. Many different alloys have been studied in the art. However, none of the prior art alloys have hydrogen storage properties sufficient for practical application. The following problems are often encountered in the hydrogen storage materials of the prior art.

The state of the art alloys are difficult to activate. High temperatures are normally needed to start absorption. Furthermore, the absorption-desorption velocities are normally low. The absorption-desorption velocities are the velocities at which the alloy takes up hydrogen (i.e. absorbs) and gives up hydrogen (i.e. desorbs). Another problem is that these alloys have a relatively small hydrogen storage capacity. These alloys normally absorb between 1 and 2 weight % of hydrogen. In order to store large amounts of hydrogen, a large mass of alloy is needed. Another problem that is often encountered is hysteresis, i.e. there is a difference between the absorption curve and the desorption curve. This means that, for these materials, not all of the hydrogen that was absorbed during the absorption step is released during desorption.

Another problem lies in the fact that the absorption curve is often quite steep. The absorption curve shows how the amount of hydrogen absorbed per unit amount of alloy is influenced by the hydrogen pressure; a steep absorption curve means that one has to increase the hydrogen pressure considerably in order to absorb additional hydrogen in the alloy. It is desirable to have a curve that is as flat as possible for as long as possible. This means that the pressure does not have to increase much to absorb more hydrogen. The flat part of the curve is usually referred to as the plateau region, including also the curve when not perfectly horizontal.

The ideal hydrogen absorption material is therefore one that is easily activated, has a large hydrogen storage capacity, a hydrogen absorption-desorption curve with a wide plateau region of exceptional flatness, a small hysteresis, and a large hydrogen absorption-desorption velocity. The most important of these is the large hydrogen storage capacity.

We have been doing extensive research into solid materials that are capable of storing hydrogen. We believe we have now come up with a material that overcomes most of the problems known in the storage of hydrogen.

Our research has focused on certain alloys of the AB_2-type. These are alloys which represented by the formula $Ti_aZr_{(1-a)}M_2$ (here, Ti and Zr form the A component of the AB_2–type alloy). These alloys have been often described in the prior art (see document D1 which we enclose for your convenience). As you will see from this document, the metal M (i.e. the B-component in the AB_2-type alloy in the formula mentioned above) is at least one of the elements selected from the group consisting of Mn, Cr, V, Fe, Co and Mo. However, the alloys described in D1 also show the same general problems as described above. (Oh, by the way, I forgot to mention that the index "a" in the formula depicted above can have values of from zero to 1; if the index "a" is zero, the alloy does not contain any Ti; if it is 1, then the alloy does not contain any Zr; if the index "a" is between zero and 1, the alloy contains both Ti and Zr).

We have now found that by adding small amounts of certain non-metallic elements to the alloy, we can solve most of the problems of the hydrogen storage alloys. Especially, the problems of hysteresis are almost eliminated. We made extensive tests using all non-metallic elements to find out which non-metallic elements are suitable for our purposes. The result of these tests was that only those non-metallic elements mentioned in the present examples have a positive effect on the alloy. The addition of any other non-metallic element in the alloys has a negative effect on the performance of the alloys and is to be avoided. The non-metallic elements mentioned in the present examples must, however, be present in the alloy in a total concentration of at least 0.01 atomic percent in order to achieve any measurable effect. This means that the traces of non-metallic elements usually present as impurities in the metals from which the alloys are to be formed or in the respective alloys of the state of the art will have no positive effect.

The "total concentration" of these non-metallic elements is the sum of the individual concentrations of these elements. If one atomic percent of sulphur and 1 atomic percent of selenium are employed, the total concentration of these non-metallic elements is 2 atomic percent.

By adding these non-metallic elements up to a certain concentration, the flatness width of the plateau region are increased.

The addition of the non-metallic element(s) can be achieved in several ways. The alloy can be made from the metallic and non-metallic elements by melting. Each of the non-metallic elements is preferably added as a chemical compound containing only the element and one of the metals present in the alloy. For example, sulphur could be added as titanium sulphide. The non-metallic element(s) mentioned above must not be present in a total concentration of more than 5 atomic percent. Otherwise the non-metallic elements (or their chemical compounds formed by reaction with a metal) do not dissolve completely in the alloy so that the alloy is useless. An addition of such a low concentration of these non-metallic element(s) does not affect the metallic character so that the product is still an alloy. For our purposes, these non-metallic elements preferably are present in a total concentration of up to 2 atomic percent. Two atomic percent of the non-metallic elements means that 2 % of the atoms of the alloy are non-metallic atoms. Above this concentration, the effective hydrogen transfer capacity becomes less. Also, the alloys become more brittle at higher concentrations of non-metallic elements. This is probably due to slight distortions in the crystal lattice. Best results are obtained with total concentrations of 0.5 to 1 atomic % of these non-metallic elements. When preparing the alloy it is essential that the components of the alloy are melted in a protective atmosphere furnace. The components may, for example be melted in an arc melting furnace under an argon atmosphere.

It is believed that the above-mentioned positive effect is not only attained for the AB_2 alloys mentioned above. On the contrary, recent experiments performed in our laboratories show that the effect (i.e. a high effective hydrogen transfer capacity) can be attained for all AB_2–type alloys with Ti and/or Zr as the A-component. It is in our interest that you try to obtain as broad protection as possible for our invention.

A special problem of AB_2-type alloys with Ti and/or Zr as the A-component and containing the non-metallic element(s) mentioned above is that the crystal lattices of the hydrogen storage body will undergo expansion and shrinkage through absorption and desorption of hydrogen (To our surprise we have found that this problem does not occur in AB_2-type alloys with Ti and/or Zr as the A-component that do not contain the non-metallic element(s) present in our alloys). Such volume changes can be within the range of 10 to 25%. During multiple cycles of absorption and desorption, fine cracks form in the alloy. As such, these alloys are unusable, because their structure changes too much during use.

In order to solve this additional problem, we have performed some more experiments. We have now found that, when an extremely fine powder (i.e. one having an average particle diameter of less than 100 nm; 1 nm = 10^{-9} m) is used as the hydrogen storage body, cracks in the alloy are reduced. In fact, it would appear that the smaller the individual particles, the less alloy cracking occurs. We have found that particles having an average particle diameter of less than 50 nm show good stability of the particles. Particles having an average particle diameter of less than 20 nm are particularly good. These particles also have an improved hydrogen absorption due to their high surface area per gram of material. We have also tested alloys, that do not contain the non-metallic element. Surprisingly, for these alloys no improvement in hydrogen absorption properties was observed when they were converted into extremely fine powders.

Any method of making ultra small particles can be used, as long as the methods provide good reproducibility. A very good method of making these particles is by vaporisation-deposition. In this technique, the hydrogen storage material is vaporised and small particles are deposited from the vapour phase onto a surface from which they can be removed and collected.

In order to make the hydrogen storage material of our invention, you have first to make the alloy with the non-metallic element. From this alloy one can then make the small particles.

<u>Examples:</u>

Example 1:

An AB_2–type alloy with Ti and/or Zr as the A-component and Mn, Cr and V as the B-component is made. In order to incorporate sulphur, part of the titanium is added in the form of titanium sulphide (TiS_2). The amount of titanium sulphide is such as to result in 0.5 atomic % sulphur in the alloy. All of the ingredients are melted in an arc melting furnace under an argon atmosphere.

This sulphur-containing alloy is converted to ultra fine particles using vaporisation-deposition. Analysis by transmission electron microscopy (TEM) shows that most of the particles have a particle diameter between 5 and 10 nm. The average particle diameter is 8 nm.

The ultra-fine particles are used in hydrogen absorption experiments. The results of these experiments are shown in table 1.

Examples 2 to 5:

These examples concern the same alloy as described in example 1. The only difference lies in the non-metallic elements used. In these examples, nitrogen, selenium, carbon and boron are used, all in concentrations of 0.5 atomic % as in example 1. The results are also shown in table 1.

Comparative example:

The comparative example concerns the same alloy, but without any addition of non-metallic element.

Table 1: Addition of 0.5 atomic percent of non-metallic element to alloy containing Ti, Mn, Cr and V.

	Element added	Hydrogen uptake (weight percent)	Improvement
Example 1	Sulphur	1.81%	13.1%
Example 2	Nitrogen	1.77%	10.6%
Example 3	Selenium	1.79%	11.9%
Example 4	Carbon	1.76%	10.0%
Example 5	Boron	1.73%	8.1%
Comp. example 1	None	1.60%	None

Example 6:

In this example the concentration of sulphur in the alloy is varied. The same alloy as used in example 1 is used. Sulphur concentrations of 0.1, 0.5, 1.0, 2.0 and 5.0 atomic % are used. The results of these experiments are given in table 2.

**Table 2:** Effect of varying amounts of sulphur in alloys containing Ti, Zr, Mn, Cr and the hydrogen uptake.

Atomic % sulphur	0.1%	0.5%	1.0%	2.0%	5.0%
Improvement	12.2%	13.1%	13.6%	13.5%	11.0%

Example 7:

In this example the effect of the particle diameter is studied. The hydrogen storage material of example 1 is made with different average particle diamters. This is done by varying the conditions in the vaporisation-deposition apparatus. These variations are known to the person skilled in the art. The particle diameter is determined by transmission electron microscopy (TEM). The results of these experiments are given in table 3.

Table 3: Effect of the particle diameter of alloys containing Ti, Zr, Mn, Cr and V and 0.5 atomic % sulphur on the hydrogen uptake.

Particle diameter	1 nm	8 nm	20 nm	50 nm	100 nm
Improvement	13.3%	13.1 %	13.0%	12.1%	9.7%
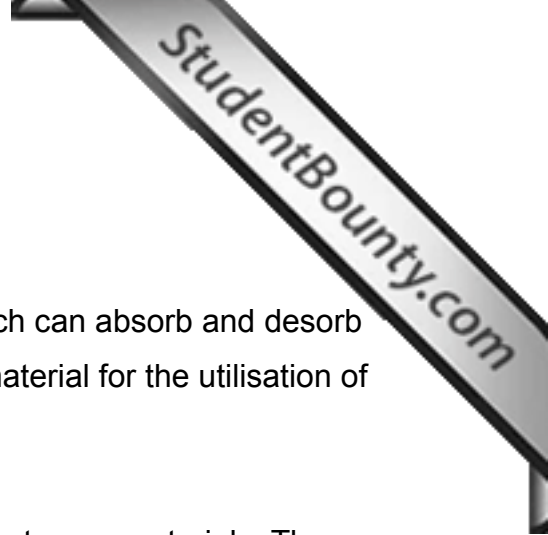
DOCUMENT D1

The present invention relates to a hydrogen storage alloy which can absorb and desorb hydrogen in a reversible manner and serves as an effective material for the utilisation of

5   hydrogen energy.

We have found that certain AB_2-alloys are excellent hydrogen storage materials. These alloys may be represented by the formula

$Ti_aZr_{(1-a)}M_2$, wherein M is at least one of the elements selected from the group consisting

10   of Mn, Cr, V, Fe, Co and Mo, $0 \le a \le 1$.

The alloys can be produced simply by melting its components, e.g. in a protective atmosphere furnace.