ISSN : 0974 - 7486 Volume 10 Issue 12

Materials Science
An Indian Journal
Review

MSAIJ, 10(12), 2014 [505-507]

An overview on hydrogen storage alloys

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ABSTRACT

Hydrogen storage alloy is one type of new high-performance material. The paper mainly introduces four types of hydrogen storage alloys such as rare earth (AB series) alloys, zirconium (AB type) alloys, metal hydride hydrogen storage materials and metal borohydride hydrogen storage material. According to the full utility of hydrogen storage alloys, their good economic and social benefits are obtained.

KEYWORDS

Overview;
Hydrogen;
Alloys.

INTRODUCTION

With the decrease of available mineral oil resources, storing and utilizing hydrogen becomes more and more important. This latter is expected to result in economic and social benefits[1].

Chinese economic and social development has been limited due to the shortage of natural resources. The output of Chinese crude oil production has been varied between 1.8×10^8 and 2.5×10^8 t per year. Since the Chinese crude oil reservation is about 32.7×10^8 tons, the known crude oil resources are expected to cover the Chinese demands only for 16 years. Since 52% of the processed crude oil comes from overseas, the Chinese government introduced various policies to increase the energy production efficiencies[3] and to decrease taxes for those companies which turn efforts to use renewable energy resources such as wind, water, hydrogen, etc.

Nowadays the efficiency of hydrogen utilization is very low in China, because most of these resources are fired and discharged into the environment, therefore researchers and engineers turn a lot of effort in the development of this area, focusing on increasing the efficiency of hydrogen storage with maximal economic benefits.

It is an urgent demand to storage hydrogen in a more rational way as simple fuel, involving new metal alloys, which could result in improving hydrogen storage. These new metal alloys could improve the energy efficiency. In this paper, four metal alloys are reviewed, rare earth (AB series) alloys, zirconium (AB type) alloys, metal hydride hydrogen storage materials and metal borohydride hydrogen storage material.

DISCUSSION

Rare earth (AB series) alloys[1]

Rare earth hydrogen storage based on alloy materials have the following characters, such as fast speed hydrogen storage reaction, high hydrogen content, small hysteresis effect and reaction heat effect, low and flat plateau pressure, and easy activation. So it can achieve rapid and safe storage of hydrogen. However, the materials have some disadvantage, like poor antitoxic performance and high cost, etc. Therefore, the application

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is limited. In order to improve Hydrogen storage alloy performance and reduce costs, polyhydric mixed rare earth hydrogen storage alloy, also known as La-Ni-Al alloy, is developed by replacing La of LaNi with mixed rare earth (Mm) or replacing Ni with other metal in whole or part. The composition of La-Ni-Al alloy is $LaNi_{5-x}Mx$ (M = Fe, Co, Mn, Al, etc., $_x$=0.1- 4) or Mm $Ni_{5-x}Mx$ (M= Fe, Co, Mn, A1, etc., $_x$=0.1- 4).

La-Ni-Al alloy has some advantage such as fast reaction speed, easy activation, high selectivity, small thermal effects, and high hydrogen content. Among of them, $LaNi_{5-x}Alx$ gets the most attention because after replacing part of Ni with Al, plateau pressure and enthalpy has been significantly distinct, the stability of LaNi has been increased; in addition, Al atomic volume is greater than Ni atomic volume so that LaNi5 lattice parameters and the size of the gap have been different, as well, hydrogen absorption characteristics, such as adsorption capacity, adsorption equilibrium pressure and adsorption rate, etc., have changed.

TABLE 1 shows that with X ($_X$ = 0.25, 0.50, 0.75, 1.00) increasing, the adsorption capacity of hydrides is reduced from 137.2ml/g to 97.8ml/g. The equilibrium pressure at room temperature goes down from 8.0×10^4 Pa to 9.0×10^2 Pa. The adsorption rate reduces accordingly. The standard enthalpy is decreased from -16.7kJ/mol to -28.7kJ/mol. And the standard entropy Δs becomes less from -68.5kJ/mol•K to -78.3kJ/mol•K. Therefore, the adsorption capacity of La-Ni-Al hydrogen storage based materials is decreased with Al content increasing.

TABLE 1 : La -Ni-A1 hydrogen storage based alloy chemical composition and its adsorption capacity for hydrogen

Alloy chemical formula	Hydride chemical formula	Adsorption capacity/mL•g^{-1}
LaNiAl	$LaNi_4AlH_{3.5}$	97.8
$LaNi_{4.25}Al_{0.75}$	$LaNi_{4.25}Al_{0.75}H_{4.2}$	115.1
$LaNi_{4.50}Al_{0.50}$	$LaNi_{4.50}Al_{0.50}H_{4.7}$	126.4
$LaNi_{4.75}Al_{0.25}$	$LaNi_{4.75}Al_{0.25}H_{5.2}$	137.2

Zirconium (AB type) alloys[1]

Zirconium alloy has the following characters at room temperature under a hydrogen pressure between 0.1 - 0.2 MPa. They are large amount of hydrogen absorption capacity, easy activation, fast kinetics, and small thermal effects (2 to 3 times less than LaNi and other materials). The general formula of zirconium alloys is $ZrMn_{1-x}Fe_{1-y}$. As well, there are three mainly compositions. They are $ZrMn_{1-22}Fe_{1-11}$, $ZrMn_{1-53}Fe_{1-27}$ and $ZrMn_{1-11}Fe_{1-22}$. They have rich phase structure, such as C14, C15 and C36-type laves phase and multiple BCC (solid solution). As high theoretical electrochemical capacity (800 mA/g) of the material, the Ovonics company in United States developed MH / Ni battery with a capacity of 420 mA/g, which is known for its negative polarity, so it's also called "second generation MH / Ni battery electrode materials."

Multiple zirconium hydrogen storage alloy is developed by replacing part of Zr with Ti of zirconium alloy, and part of V, Cr, Mn, etc. with Fe, Co, Ni, etc. These materials can be activated at slightly above the room temperature. In the process of dehydrogenation, almost all of the hydrogen will be emerged at $T \geq 100$ °C. The amount of the hydrogen storage can reach up to 70% of the total within 20 s while $ZrMn_{1-22}Fe_{1-11}$ and $ZrMn_{1-53}Fe_{1-27}$ is absorbing hydrogen. The process of hydrogen absorption can be completed within 60 s. Otherwise, 40 % of the hydrogen can be dehydrogenated within 50 s, and almost all of the hydrogen can be released within 300 - 400 s.

Metal hydride hydrogen storage materials[4]

Metal hydride is a class of complex metal hydrides containing $[A1H_4]$ or $[A1H_6]$ ligand group. It typically includes $NaA1H_4$, $LiAlH_4$, $Mg(AlH_4)_2$, Na_2LiA1H_6, $LiMg(AlH_4)_3$ and so on. There's difference between metal hydride hydrogen absorption and desorption process with intermittent metal hydride. Metal hydride hydrogen absorption and desorption process is achieved by Al-H bond bonding and fracture. It includes a series of decomposition reactions. For example, $NaAlH_4$ has three steps of the hydrogen liberation.

$$3NaAlH_4 \rightarrow Na_3AlH_6 + 2Al + 3H_2 \quad (1)$$

$$Na_3AlH_6 \rightarrow 3NaH + Al + 1.5H_2 \quad (2)$$

$$3NaH \rightarrow 3Na + 1.5H \quad (3)$$

Theoretically, the weight of $NaAlH_4$ storage capacity can reach up to 7.4 wt% under the condition of no catalysts addition and the three-step decomposition reaction occurs at 210°C, 250°C 和 425°C or so respectively. However, Bogdanovi c and Schwichardi first reported that 2 mol% $Ti(OBun)_4$ catalyst (mol%: mole percent) has been mixed with $NaAlH_4$, which can effectively improve the thermodynamic and kinetic properties of the system. Therefore, hydrogen reaction temperature will go down to 100°C and 160°C in the first two steps. In addition, the reaction can be performed reversely. So the metal hydride will act as a high-capacity hydrogen storage material.

Bogdanovic find that hydrogen desorption capacity of $NaAlH_4$ with 2 mol% $ScCl_3$ addition can reach 4.5 wt% - 4.9 wt%, higher than the $TiCl_3$ sample 4.0 wt% addition. Moreover, the hydrogenated time of Sc-doped $NaAlH_4$ is about 30 minutes. It takes only about 20 minutes to absorb 90% of the hydrogen, which is 1/3 time of $TiCl_3$ samples doped. The studies about trichloride of rare earth elements (La, Ce, Pr, Nd, Sm, Er, and Gd) doped in $NaAlH_4$ show that $CeCl_3$ and $PrCl_3$ has better catalytic performance. Hydrogenation / dehydrogenation rate of $CeCl_3$ addition system is similar with the one of $ScCl_3$, but show that it has a better stability of the cycle. The reversible hydrogen storage capacity still remains at 4.0 wt% or more after 29 cycles of hydrogen absorption and desorption.

Metal borohydride hydrogen storage material[4]

Metal borohydride is a class of complex metal hydrides containing $[BH_4]$ ligand group. It typically includes $LiBH_4$, $NaBH_4$, $Mg(BH_4)_2$, $Ca(BH_4)_4$ etc. Their hydrogen contents are all more than 10 wt %. Theoretically, the hydrogen content of $LiBH_4$ is up to 18.5 wt%. However, only 3 hydrogen atoms can be released from the high enthalpy (-177 kJ/mo1) at 680 °C, which is equivalent to 13.8 wt%.

$$LiBH_4 \rightarrow LiH + B + 3/2H_2 \quad (4)$$

Vajo found that the reaction pathway of the liberation of hydrogen of $LiBH_4$ has distinctly changed if milling composed of $LiBH_4$ and MgH_2 (molar ratio 2 : 1).

$$2LiBH_4 + MgH_2 \rightarrow 2LiH + MgB_2 + 4H_2 \quad (5)$$

Thermodynamic enthalpy is decreased by nearly 40 %, about 46 kJ/mol - H_2 due to more stable MgB_2 hydrogen product formation. Therefore, the hydrogen desorption temperature of LiBH has been significantly reduced, and improved its reversibility of hydrogen absorption and desorption.

The results show that $6LiBH_4$-Cal_2 and $2LiBH_4$-Al, both of them, have a good reversibility of hydrogen absorption and desorption. After hydrogen, the composite system of $6LiBH_4$-Cal_2 can absorb about 9.0 Wt % of hydrogen under the condition of 400 °C and 10 MPa. Thus, the stability study of the metal borohydride is one of the effective ways to improve its reversibility of hydrogen absorption and desorption.

CONCLUSION

Hydrogen can be used to produce high value chemical production in China. Hydrogen based on above metal alloys protect the environment and increase the income of a petrochemical plant. The main benefits are as follows: using hydrogen and protecting the local environment, decreasing fossil fuel consumption, and avoiding greenhouse gas emissions, such as SO_2, NO_x, and CO_2, and total suspended particles. Economic developments are initiated and improved using the reviewed new metal alloys.

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