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수소저장용 금속수소화물(Mm ($La_{0.6-0.8}$) $Ni_{4.0}Co_{0.6}Mn_{0.2}Al_{0.2}$)의 전열촉진

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Heat transfer enhancement of metal hydride (Mm ($La_{0.6-0.8}$) $Ni_{4.0}Co_{0.6}Mn_{0.2}Al_{0.2}$) for hydrogen storage

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Abstract The effective thermal conductivities of Mm ($La_{0.6}-_{0.8}$) $Ni_{4.0}Co_{0.6}Mn_{0.2}Al_{0.2}$ (TL-492) with hydrogen and helium have been examined. Experiment results show that pressure has great influence on effective thermal conductivity in low pressure range (below 0.5 MPa). And that influence decreases rapidly with increase of gas pressure. The reason is at low pressure, the mean free path of gas becomes greater than effective thickness of gas film which is important to the heat transfer mechanism in this research. And, carbon fibers have been used to try to enhance the poor thermal conductivity of TL-492. Three types of carbon fibers and three mass fractions have been examined and compared. Naturally, the highest effective thermal conductivity has been reached with carbon fiber which has highest thermal conductivity, and highest mass fraction. This method has acquired 4.33 times higher thermal conductivity than pure metal hydrides with quite low quantity of additives, only 0.99 wt% of carbon fiber. This is a good result comparing to other method which can reach higher effective thermal conductivity but needs much higher mass fraction of additives too.

Key words carbon fiber, effective thermal conductivity, metal hydride

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Nomenclature

C.F:carbon fiber
c_p:specific heat at constant pressure, J/kg K
k:effective thermal conductivity, W/m K
T:temperature, K
t:time, s
ρ:density, g/cm³

subscripts

in:in out:out

1. Introduction

There is no doubt that hydrogen will become one of the major energy storage and transfer medium in near future because its contamination-free characteristics during production and combustion. The industrial believes fuel cell and other facilities can use hydrogen as stationary and mobile power sources.

Based on previous researches, some common properties of metal hydrides have discovered. To make metal hydrides work efficiently with hydrogen during hydriding and dehydirding procedure, how to handle the heat which generates or absorbs is an important and inevitable problem. Kim et al.[1] concluded that hydrides have a poor thermal conductivity in the range of 0.1 to 1.0 W/m K, which is too low to transfer heat efficiently. Therefore finding a way to enhance the effective thermal conductivity of metal hydrides is necessary before utilizing metal hydrides with practical applications. A popular method is adding additives which have high thermal conductivity into the metal hydride and form a mixture. Kim et al.[2] used a new technique which is called recompressed expanded graphite technique (REGT) and found the effective thermal conductive could be enhanced to 3-6 W/m K. An improved similar technology by Sánchez, Klein and Groll[3] claimed a higher thermal conductivity, 19 W/m K. However before any effort to enhance, it is in necessary to measure the thermal conductivity of pure metal hydrides first.

2. Experimental Methods

Figure 1shows the experiment test section to examine the effective thermal conductivity. Hydrogen is supplied to the system by compressed high pressure gas (purity >99.99999 %). The test section is a O.D., 19.01 mm(3/4inch) copper tube which has a thermocouple in the center and another thermocouple on the surface. A pair of cross-like frame holders, which have a hole in the center, are used to make sure the head of thermocouple is in the center of the tube. A 0.2 mm diameter thermocouple has been attached to the surface of the tube so the temperature difference between the surface and the center can be measured.

Figure 2 shows the experiment system which has constant temperature bath and a reservoir to suppress the pressure change during experiment. When a test starts, the test section (a O.D., 19.01 mm copper tube) will be put into a constant temperature water bath, while the temperature difference between the center and the surface of the tube will be recorded. The temperature difference between the outer wall and the center of the tube will cause a heat flow will essential change the central temperature of the tube. This changing history of the surface and center temperature will be compared with the calculated temperature by giving a certain value to the thermal conductivity. By finding the smallest difference between the measured and calculated center temperature, the appropriate value of thermal conductivity can be estimated.

All pressure transducers which accuracy is 0.2% have been calibrated by a standard piston pressure meter which accuracy is 0.1%. And all thermocouples have been calibrated by a set of ± 0.1℃ standard thermometers. A constant temperature water bath with ± 1℃ accuracy provided a stable thermal environment. The temperature of water in the water bath is set as 70℃.The gas pressure in the test section will be recorded by the pressure sensor installed at the top of reservoir. About 100 gram metal hydride is in the tube and will be activated or oxidized before experiment if necessary.

At the present study, adding carbon fiber into MH alloy to make a mixture will be tested. Properties of three kinds of carbon fiber which, will be called CF1, CF2 and CF3 at the present research respectively, are listed in Table 1. To add carbon fiber into metal hydrides, first, the authors cut the carbon fibers into 17 mm long pieces, which equals to the inner-diameter of the copper tube. Then these pieces have been distributed evenly in a length of 65 mm to make brushes. For each test, two of these brushes, which have the same number of pieces, have been used to make a 130 mm long carbon fiber brush. The head of the thermal couple will be located in the center of the tube and between the two carbon fiber brushes. Then the metal hydrides powder will be filled into the test section very carefully with knocking the copper tube softly to make sure the solid particles fill into the brushes tightly and uniformly. Four different densities of carbon fiber in the metal hydrides have been examined for each kind of carbon fiber, which are 20, 40, 80 and 120 pieces, in 65 mm. To make it easy to label, they are called as condition 1, 2, 3 and 4 respectively here.

A doubt about these carbon fibers is, after filling the copper tube with metal hydrides powder which is quite heavy; probably the brushes will be damaged so the confidence of the collected data will be compromised. Even the filling metal hydrides powder procedures have been carried out very carefully, this possibility still exists because these carbon fibers are very fragile.

Figure 3 shows the pictures of carbon fiber of CF1 with condition 3 after experiment. As we can see here, the brush remains intact even it has been tested with metal hydrides up to 2 MPa.

3. Results and discussion

1.1 Effective thermal conductivity of pure TL-492

A group of differential equations, from equation(1) to (4), are used to calculate the effective thermal conductivity of metal hydrides. Suissa, Jacob and Hadari[4] have tried to analyze the influence of temperature on the thermal conductivity and found it is only slightly dependent on temperature, about 0.02 W/m K in the range of 100-400 ℃. Bae[5] also claimed the same conclusion at a temperature range from 30 to 80℃. The authors have pre-tested the thermal conductivity of TL-492 at 50, 60 and 70 ℃ and their results agreed with each other very closely. So the formal test only performed at 70℃.The experiment had been conducted with 0-2 MPa helium and hydrogen, and temperature at 70℃.

Figure 4 shows the distribution of control volumes inside the tube, which has 12 cells inside the inner wall surface (in MH bed), and 3 cells in the wall of the tube, along the radial direction. There are three boundary conditions in this calculation model, the central cell, the outside surface cell, and the cells between them. For any cell, the heat balance can be described by the following equations.

These equations are also suitable for the central cell and the outside surface cell by changing boundary condition. Theoretically, the heat generation in equation (4) is 0 in this case because there is no reaction between helium and metal hydrides. However because there will be a heat generation if hydrogen and activated MH alloy reacts, it is difficult to examine the thermal conductivity of activated metal hydrides with hydrogen directly. Therefore, the test of hydrogen and activated metal hydrides will not be conducted. And even the test of hydrogen and metal hydrides before activated should be performed carefully

Table 1. Properties of carbon fiber

	Density, ρ (g/cm^3)	Linear density (g/m)	k (W/mK)
CF1	2.15	270	210
CF2	2.20	270	620
CF3	2.21	365	800

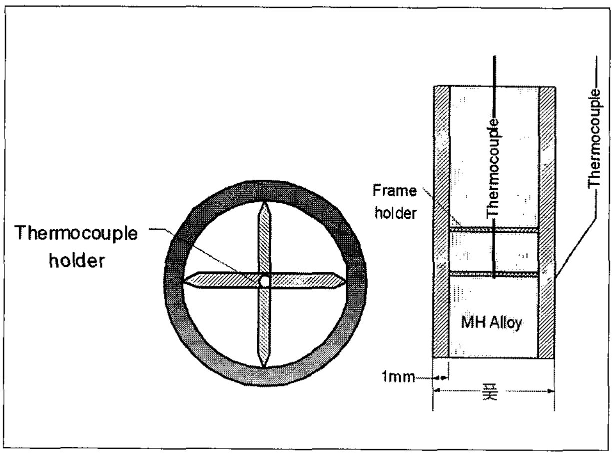

Fig. 1 Description of test section

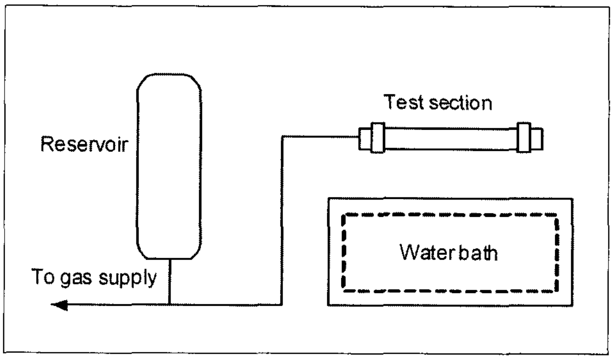

Fig. 2 Scheme of thermal conductivity test system

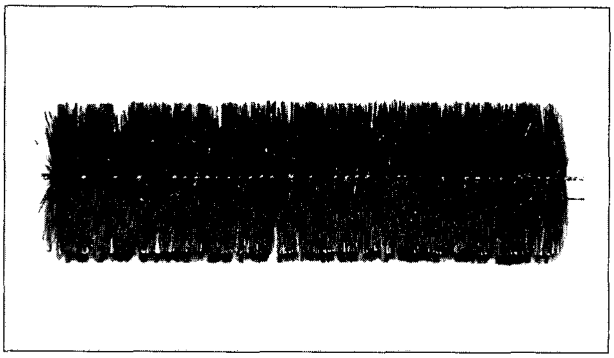

Fig. 3 Picture of carbon fiber brush after examination

because some alloys may be partially activated at low temperature, and cause the recorded data untrustworthy.

For pure TL-492 five groups of experiment data have been collected, and all of these results are shown in Figure 5. By comparing the results, the difference caused by helium and hydrogen can be estimated. Based on the

$$Heat\ input = -k_{in}\frac{T_i^{n+1} - T_{i-1}^{n+1}}{\frac{dR_i+dR_{i-1}}{2}}\left[R_i-\frac{dR_i}{2}\right]d\theta \qquad (1)$$

$$Heat\ output = -k_{out}\frac{T_{i+1}^{n+1} - T_i^{n+1}}{\frac{dR_{i+1}+dR_i}{2}}\left[R_i+\frac{dR_i}{2}\right]d\theta \qquad (2)$$

$$Heat\ absorption = \rho_i c_{p,i} R_i d\theta_i dR_i\ \frac{T_i^{n+1} - T_i}{dT} \qquad (3)$$

$$Heat\ generation = \rho_i c_{p,i} R_i d\theta_i dR_i \qquad (4)$$

experimental result of Bae[5], hydrogen will cause about 1.2 times higher thermal conductivity than helium. But the authors found the result of hydrogen is about 1.29-1.43times higher than helium, with TL-492 before activation. At the same time, the ratio between hydrogen and helium with oxidized metal hydride is 1.17-1.31. The reason of the difference could be the alloy (before activation procedure) reacted with hydrogen during the reaction even it is not activated. The testing temperature is 70℃ which is not high enough to activate the alloy fully but must have made some TL-492 particles have the ability to absorb a little hydrogen. That reaction will cause heat generation and will lead to higher thermal conductivity. This affection has been observed more clearly with $LaNi_5$ because it can be activated with lower temperature.

1.2 Effect of carbon fibers

Carbon fiber has high thermal conductivity and it is inert to hydrogen. Comparing to other methods, like coating the metal hydrides particles or making compacts, adding carbon fiber is much easier to accomplish. All three kinds of carbon fiber have been examined at the present research, and there are four different weight percentages for each kind of carbon fiber, as listed in Table 2.

Figure 6 shows experiment results of CF3 to compare the influence of the weight percentage for each carbon fiber. Obviously, with higher thermal conductivity and higher percentage of carbon fiber, higher effective of thermal conductivity can be reached. The highest

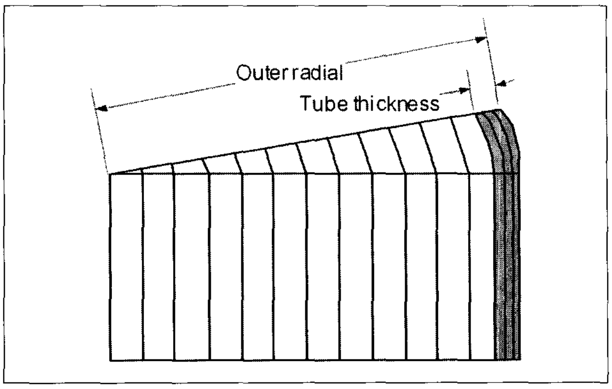

Fig. 4 Control volumes of test section

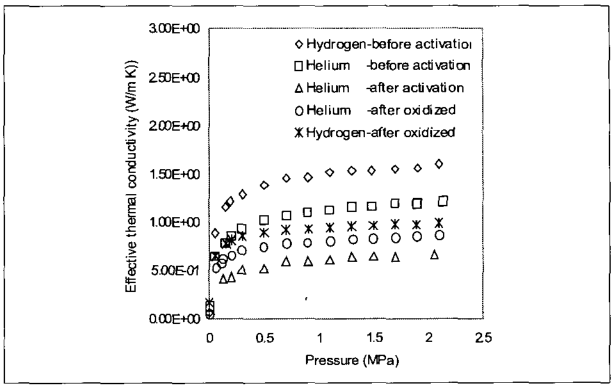

Fig. 5 Effective thermal conductivity with pure TL-492

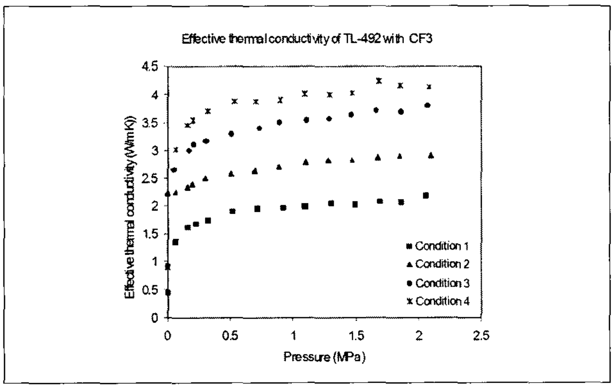

Fig. 6 Influence of carbon fibers

Table 2 Carbon fiber parameters

	k (W/m K)	Weight percentage			
		Con.1	Con.2	Con.3	Con.4
CF1	210	0.21%	0.41%	0.86%	1.32%
CF2	620	0.21%	0.44%	0.89%	1.40%
CF3	800	0.31%	0.60%	1.38%	2.17%

experiment result is 4.2 W/m K, with condition 4 of CF3, in another word, 2.17% weight percentage. This result is not very high comparing to other researchers' results; but it is relatively good because the highest weight percentage is only 2.17%. Sánchez, Klein and Groll[3] acquired effective thermal conductivity of a compact of expanded graphite and metal hydride mixer as 11.2 W/m K with a high weight percentage of 34% graphite. Kim et al.[2] had a result of near 6 W/m K with 23 wt.% graphite in REGT compacts. They all took high ratio of additives which could seriously compromise the hydriding/dehydriding abilities of metal hydrides.

4. Conclusions

Effective thermal conductivities of TL-492 with hydrogen and helium have been tested. Roughly, the effective thermal conductivity of TL-492 with hydrogen is about 1.17-1.31 times higher than helium. And that result agrees with Bae[5] very well.

Three types of carbon fibers have been utilized to enhance the thermal conductivity. For each carbon fiber, four weight percentage ratios have been tested. The highest effective thermal conductivity is 4.2 W/m k with 2.17% weight percentage of CF3. This value is about 4.33 times higher than pure TL-492 with hydrogen.

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