Hydriding/dehydriging Properties of Advanced Hydrogen Storage Mg/MWNTs Composites*

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Abstract: The composite Mg-wMWNTs (w = 5%, 20%) was made by catalytic reacting ball-milling under the hydrogen atmosphere. The absorption/desorption kinetics for the composite Mg/MWNTs were examined by taking the apparatus for hydrogen adsorption/desorption. It was found that under 2.0 MPa hydrogen pressure, the maximum hydrogen storage capacities of the two composites(w = 5%, 20%) were very low and similar at 298, 373, 473 and 553 K, the maximum hydrogen storage capacities of the Mg-5%(w) MWNTs were respectively 5.34%, 5.89% and 6.08%; however, only 2.11%, 2.68% and 2.75% for the Mg-20%(w) MWNTs. Compared with the other hydrogen storage composite materials, the Mg-5%(w) MWNTs not only keeps the maximum hydrogen storage capacities better but also has good hydrogen absorption/desorption rates.

Key words: Mg/MWNTs composite; catalytic reacting ball milling; hydriding/dehydriging property
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1 Introdution

Magnesium is an attractive and most promising material for hydrogen storage applications because of its high hydrogen capacity (w = 7.6%), light weight, low cost, no pollution, rich natural resource and suitable scale production. However, because of its high temperature of operation (~673 K) and slow hydriding-dehydriding kinetics, practical application using pure magnesium has been limited. A lot of effort has been devoted to improve the Mg properties by various methods. Ball milling has proved to be an effective means for preparing nanostructured composites[1,2]. In this paper, we hope to obtain a better hydrogen resource material for proton exchange membrane fuel cells (PEMFC) by catalytic reaction ball-milling of magnesium, MWNTs (multi-walled nanotubes), suitable additives zirconium (improving the hydrogen absorbing kinetics[3]) and nickel (as a binder). The hydriding-dehydriding properties were investigated.

2 Experiment

Magnesium (w = 99.4%; 200 mesh), MWNTs (about 100 nm in diameter), zirconium (w = 99.6%; 200 mesh) and nickel (w = 99.6%; 100 mesh) were weighed by a weight-ratio to make up (2.85 Mg + 0.15 MWNTs) + 0.5Zr + 3Ni and (2.40Mg + 0.60MWNTs) + 0.5Zr + 3Ni, which were then fully ground and mixed in the agate bowl and afterwards were placed in sealed stainless steel vial with steel balls (6 ~ 12 mm in diameter), respectively. The ball-to-power weight ratio was 20:1. After many-times operations of vacuuming and injecting hydrogen, the preparation for the Mg/MWNTs composites were carried out by mechanical milling using a ball miller (GN-2 type) under a high-purity hydrogen atmosphere (0.1 MPa), the energetic impingement between steel balls and between steel balls and vial wall would lead that the temperature be go up inside the vial. To prevent overheating in the vial, the ball milling should be stopped 10 min every 20 min operation.

Then, the sample prepared by catalytic reacting ball milling was placed in the stainless steel sample room of the apparatus for hydriding/dehydriding measurement. The hydrogen source is 99.99% high-purity hydrogen. The hydriding-dehydriding properties of the composite were measured at several temperatures and under different hydrogen pressures using the iso-voluminal pressure-metric method.

3 Results and discussion

3.1 Maximum hydrogen storage capacities

It was found that, under 2.0 MPa hydrogen

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pressures, the hydrogen storage capacities of the materials were both very low and similar at 298 K; with the temperature increasing, the maximum hydrogen storage capacities were obviously changed; when at 373 K, 473 K and 553 K, the maximum hydrogen storage capacities of Mg-5% (w) MWNTs were 5.34%, 5.89% and 6.08% but those of Mg-20% (w) MWNTs were only 2.11%, 2.68% and 2.75%. Therefore, on a definite condition, the MWNTs in composites should be in a proper ratio, excessive MWNTs could lower the hydrogen storage properties of composites.

3.2 Hydriding/dehydriding kinetics

Hydrogen absorption (desorption) kinetics curves for Mg-5% (w) MWNTs at different temperatures (298 K, 373 K, 473 K and 553 K) under 2.0 MPa hydrogen pressures (in vacuum) are shown in Fig. 1. We observe from Fig. 1 that at above temperatures, each 80% of maximum hydrogen storage capacity can be finished in 20, 15, 2 and 1 min, respectively. The hydrogen absorption rates were exhibited as this order: 298 K < 373 K < 473 K < 553 K. At 373 K, 553K under 2.0 MPa hydrogen pressures, it finished 80% maximum hydrogen storage capacity within 15 min and 1 min, respectively, whereas Mg_{nano}/Graphite[4] absorbed 80% maximum hydrogen storage capacity within 90 min at 573 K. From the Fig. 1, the hydrogen desorption rates were observed as the same order: 298 K < 373 K < 473 K < 553 K. At 473 K in vacuum, it desorbs 3.62% within 30 min whereas $MgH_2/(Cr_2O_3)_{0.002}$ takes up as much hydrogen 3.44% within 90 min[5]. Therefore, contrast to other composites, good results for both absorption and desorption of hydrogen can be achieved for the Mg-5% (w) MWNTs. High-energy ball milling is known to reduce the crystallite size and to create numerous defects in the milled material (leading to the creation of numerous fresh Mg surfaces). However, because of the limitation of the vacuum degree of the ball-milled vial, the fact that nanocrystalline Mg does not show any major improvement of its activation characteristics compared to microcrystalline Mg indicates that a new oxide or hydroxide layer (that prevents the diffusion of hydrogen) is formed. The activation of the composite Mg-5% (w) MWNTs was improved for two reasons: one could be due to the catalytic reacting ball-milling under the hydrogen atmosphere, the other may be the absorption of carbon layers at freshly exposed Mg surfaces and the reaction with oxygen species of highly active carbon radicals formed as a result of C—C bond breaking during the milling operation[5]. Then the impermeable surface oxide/hydroxide layer is not re-formed and that the composite is readily accessible to hydrogen.

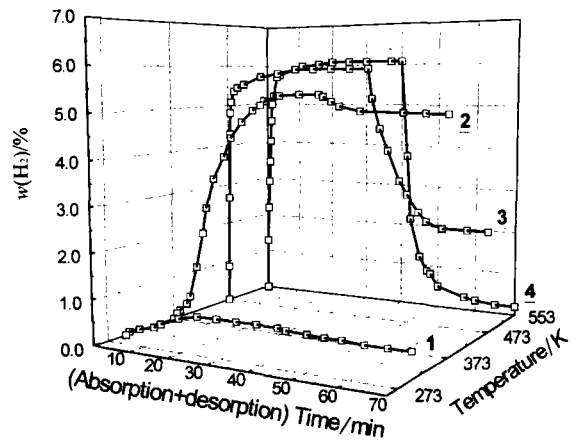

Fig. 1 Hydrogen absorption (desorption) kinetics for Mg-5% (w) MWNTs at different temperatures under 2.0 MPa hydrogen pressure (in vacuum)
1: 298 K, 2: 373 K, 3: 473 K, 4: 553 K

The hydrogen absorption kinetics curves for Mg-20% (w) MWNTs at different temperatures (298 K, 373 K, 473 K and 553 K) under 2.0 MPa hydrogen pressure are shown in Fig. 2. On the above temperatures, we observe that each 80% of maximum hydrogen storage capacity can be finished in 20, 15, 5 and 5 min, respectively. Its hydrogen absorption rates are nearly same at 473 K and 573 K, a little slow at 373 K, the slowest at 298 K. Compared to the Fig 1, the hydrogen absorption rates of Mg-20% (w) MWNTs were almost not changed at 298 K and 373 K; however, its hydrogen absorption rates lowered and slowed at 473 K and 553 K. There may be the follow reasons: with the MWNTs increasing in composite Mg-20% (w) MWNTs, the shapes of MWNTs were not identical after ball-milling, some seriously destroyed, some still complete. During ball milling there are much carbon layers at freshly Mg surfaces, which prevent to form the oxide or hydroxide layer on the material surface. Because the temperature increasing inside the vial is no evitable in practical operation, the carbon on magnesium surface is easy to covalently bond with hydrogen to form hydrocarbons e.g. CH_4, C_2H_4, C_3H_8 (which were desorbed or decomposed in the range of 300 ~ 800 K[6]), then the hydrocarbons could also affect the hydrogen diffusion on Mg surfaces. It is apparently the leading function in composite Mg-20% (w) MWNTs. Therefore, when the temperature is 473 K and 553 K, the hydrogen absorption kinetics of the Mg-20% (w) MWNTs changed, its activation became worse and its hydrogen absorption rates slowed; compared with Mg-5% (w) MWNTs, the maximum hydrogen storage capacities of composite Mg – 20% MWNTs were obviously lowered.

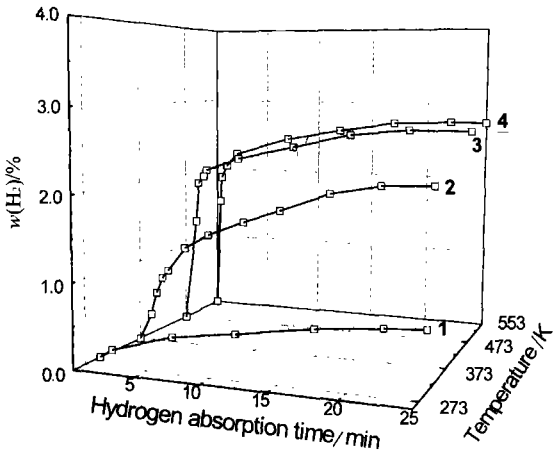

Fig.2 Hydrogen absorption kinetics for Mg-20%(w)MWNTs at different temperatures under 2.0 MPa hydrogen pressure
1:298 K, 2:373 K, 3:473 K, 4:553 K

4 Conclusions

The results of the present study are summarized as follows:

(1) Under 2.0 MPa hydrogen pressures, the hydrogen storage capacities of the materials were both very low and similar at 298 K; with the temperature increasing, the maximum hydrogen storage capacities were obviously changed; when at 373 K, 473 K and 553 K, the maximum hydrogen storage capacities of Mg-5%(w) MWNTs were 5.34%, 5.89% and 6.08% but those of Mg-20% MWNTs were only 2.11%, 2.68% and 2.75%.

(2) Under certain temperature and pressure, compared with the other hydrogen storage composite materials, the Mg-5%(w)MWNTs not only keeps the maximum hydrogen storage capacities better but also has good hydrogen absorption/desorption rates.

(3) When the temperature is 473 K and 553 K, the hydrogen absorption kinetics of the Mg-20%(w)MWNTs changed, its activation became worse and its hydrogen absorption rates slowed.

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References:

[1] Imamura H, Tabata S, Shigetomi N, et al. *J Alloys Compd*, 2002, 330-332: 579-583.
[2] Bouaricha S, Dodelet J P, Guay D, et al. *J Alloys Compd*, 2000, 307: 226-233.
[3] Zaluska A, Zaluski L, Strom-Olsen J O. *J Alloys Compd*, 1999, 288: 217-225.
[4] Oelerich W, Klassen T, Bormann R. *Materials Transactions*, 2001, 42(8): 1588-1592.
[5] Bouaricha S, Dodelet J P, Guay D, et al. *J Alloys Compd*, 2001, 325: 245-251.
[6] Zuttel A, Nutzenadel C, Sudan P, et al. *J Alloys Compd*, 2002, 330-332: 676-682.

新型储氢复合材料 Mg/MWNTs 的氢化性能

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摘 要: 采用催化反应球磨方法, 研制成复合材料 Mg-MWNTs(w=5%, 20%)。利用储放氢实验装置, 测试了 Mg/MWNTs 吸放氢动力学性能。研究发现, 复合材料 Mg-MWNTs(w=5%, 20%)在 298 K 和 2.0 MPa 氢压时最大储氢量都很低; 在 373 K、473 K 和 553 K 温度时, Mg-5%(w)MWNTs 的最大储氢量分别为5.34%、5.89% 和 6.08%; 而 Mg-20%(w) MWNTs 只有 2.11%、2.68% 和 2.75%。与其它储氢复合材料相比, 复合材料 Mg-5%(w)MWNTs 在保持较好的最大储氢量基础上, 具有很好的吸放氢动力学性能。

关键词: 复合材料 Mg/MWNTs; 催化反应球磨; 吸放氢动力学性能
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