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Hydrogen absorption of slurry system composed of different MgNi alloy and benzene ①

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Abstract: The hydrogen absorption amount and kinetics of the slurry formed by suspending the MgNi alloy powder in liquid benzene were studied. It is discovered that hydrogen is absorbed by both the solid phase(alloy) and liquid phase(C_6H_6) and the hydrogen absorption rate varies with the temperature and the content of the Mg-Ni in the slurry. Most hydrogen absorption curves of the slurry fall into two regions, in which the mechanism of hydriding reaction in the slurry system is different. In the former region, the hydriding of the alloy proceeds with hydrogen diffusing through C_6H_6. The part in the second region is the outcome of the hydrogenation of C_6H_6. At 548 K and under the hydrogen pressure of 4.5 MPa the saturation capacity for the slurry of 80% C_6H_6 (mass fraction) + 20% MgNi(mass fraction) is 5.9% (mass fraction) hydrogen, which is 97% of the theoretic capacity of the slurry system. The hydride of the alloy MgNi, which is only the hydride of Mg_2Ni phase, Mg_2NiH_4, is an efficient catalyst for the hydrogenation of C_6H_6 into C_6H_{12}($C_6H_6 + 3H_2 \rightarrow C_6H_{12}$) in the slurry system.

Key words: MgNi alloy; slurry; benzene; cyclohexane; metal hydride
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1 INTRODUCTION

Magnesium is known to have very high hydrogen storage capacity(mass fraction 7.6%), but its hydrogen absorption/desorption kinetics is bad and its reaction temperature is high. Magnesium absorbs hydrogen at 573 - 673 K and desorbs hydrogen at atmospheric pressure only above 673 K. In recent years many attempts were made to improve the hydrogen absorption/desorption kinetics of Mg-based hydrogen storage materials[1-4]. AO et al[5] reported that the hydriding/dehydriding kinetics of the magnesium was improved after being treated with some organic compounds such as Aetrahydrofuran(THF). As Mg_2Ni is a well known magnesium-based hydrogen storage material, with a hydrogen storage capacity of 3.6% and a absorption/desorption temperature lower than the pure magnesium. It occurs to us that Mg_2Ni which reacts reversibly with hydrogen may be used as a catalyst to hydrogenate some hydrocarbons such as benzene and toluene. A few reacting products were formed in the hydrogenation of C_6H_6. With cyclohexane and cyclohexene being the main products from a literature review, we learned that cyclohexene was first detected in the low temperature and low pressure hydrogenation of C_6H_6 in 1957[6]. At 318 K and under the low pressure of 3 669 Pa(917 Pa benzene and 2 752 Pa hydrogen) when nickel in the form of a film was used as the catalyst, the amount of cyclohexene formed was very small with the selectivity around 19%. Traditionally the hydrogenation of C_6H_6 is only performed in gaseous state with Pt and Ni as the primary catalyst. The hydrogenation of C_6H_6 in liquid state has not even been extensively studied. Reilly et al[6,7] first proposed the concept of the metal hydride slurry. By suspending metal hydride particles in the chemical-inert solvents(e.g. *n*-octane, *n*-undecane, silicon oil and so on)[8,9], some serious problems, such as the deformation or rupture of the vessels due to the particle fragmentation and the poor heat transfer ability of gas-solid systems, can be easily occurred in a well-stirred slurry system. However, in one of our early studies the hydrogen absorption properties of the slurry of $MlNi_5$ alloy suspended in benzene were investigated[10,11]. It was discovered that the La-rich mischmetal nickel hydrogen storage alloy $MlNi_5$ had good hydrogen absorption behavior when being suspended in C_6H_6, and the hydrogen absorption thermodynamics of the $MlNi_5$ alloy in the slurry system was similar to that of $MlNi_5$ in the gas-solid system; at the same time, the $MlNi_5$ alloy was also found to be a good catalyst for the hydrogenation of C_6H_6. On account of the results of our precious experiments, a study on the hydrogen absorption properties of a slurry system composed of MgNi alloy and benzene was initiated. Mg-based alloy MgNi was chosen

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as Mg_2Ni and it has a higher hydrogen storage capacity than $MlNi_5$ has. An extra amount of nickel was added to Mg_2Ni in expectation of the catalytic function of Ni. Both the hydrogen absorption of the alloy in the C_6H_6 and the hydrogenation of benzene were investigated.

2 EXPERIMENTAL

The purity of raw materials, Mg and Ni, was 99.9%. The purity of the hydrogen used in the experiment was 99.99%. In this experiment the analytic pure benzene was used without any further purification. The MgNi alloy was prepared by arc-melting a mixture of equal mole proportion(1∶1) of Mg and Ni under a high purity argon atmosphere. The XRD spectra of the alloy were obtained on a Philip X'Pert-MPD type X-ray diffractometer with CuK_α radiation. The cast alloy ingot was crushed to particles of 74 μm and then loaded into the reactor for experimentation. The hydrogen absorption properties of the alloy powder were measured with an automatic Sieverts apparatus. The experiments for the hydrogen absorption of the slurry were carried out in a stainless steel reactor. The absorption kinetics of the slurry systems was measured with the volumetric method. For investigating the difference in hydrogenation ability between the alloy and its hydride, alloy or its hydride was tested separately in liquid into benzene in the form of liquid suspension. The hydrogen absorption curves for both cases were plotted. Slurries with different proportions of alloy in benzene(10%, 20% and 50%) were tested. Gas chromatographic examination on the liquid in the slurry was made after the liquid was hydrogenated.

3 RESULTS AND DISCUSSION

Fig. 1 shows the X-ray spectrum of MgNi alloy. Two intermetallic phases, Mg_2Ni and $MgNi_2$ are observed, among which Mg_2Ni is a hydrogen storage alloy and hence responsible for its own hydriding and breaking up the bonds of hydrogen molecules and thereby activating the hydrogen for hydrogenation of C_6H_6. With the intention of getting some free Ni on the surface of alloy, a surplus amount of Ni was added to the B-side of the Mg_2Ni alloy to form a non-stoichiometric composition of $Mg_{50}Ni_{50}$ as mentioned above. However, as shown in the same figure, no free Ni was observed, but only $MgNi_2$ was detected together with Mg_2Ni. As $MgNi_2$ is not a hydrogen storage alloy, the hydrogen storage capacity of MgNi was found lower than that of Mg_2Ni due to the dummy weight of $MgNi_2$.

Fig. 2 shows the hydrogen absorption kinetics curves of MgNi alloy. It can be seen that as the temperature is elevated, both the hydriding speed and the storage capacity increase. Even at the lowest temperature, 453 K, in this study the tested hydriding rate of Mg-Ni is still satisfactory. The hydrogen storage capacity finally arrives at 1.2% (mass fraction) at 453 K and reaches 1.7% (mass fraction) at 523 K. Compared with the single phase Mg_2Ni compound, the absorption kinetics of the diphase MgNi alloy composed of Mg_2Ni+ $MgNi_2$ is higher. That is possibly due to the increase of the interface and the presence of more tunnels between the two phases for hydrogen diffusion.

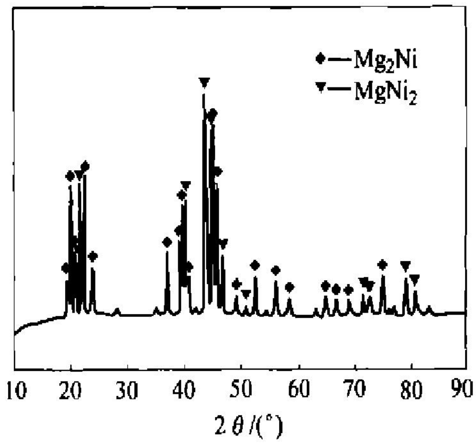

Fig. 1 XRD spectrum of MgNi alloy

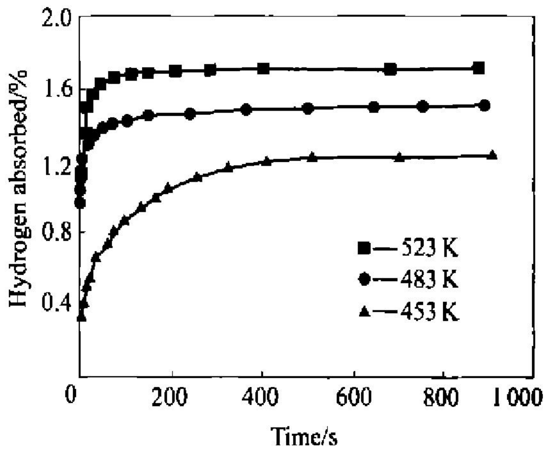

Fig. 2 Hydrogen absorption curves of MgNi alloy at various temperatures under hydrogen pressure of 3.5 MPa

Fig. 3 shows the hydriding kinetics curves of the slurry with 10% MgNi. Compared with the hydrogen absorption curves for solid alloy particles, every hydriding curve of the slurry can be divided into two parts. The first part denotes the absorption of hydrogen in the first 90 min by the slurry system up to the hydrogen storage capacity of 0.5% (mass fraction). In this period of time, both the solid phase alloy and liquid phase benzene in the slurry were absorbing hydrogen, but the speed for both was very

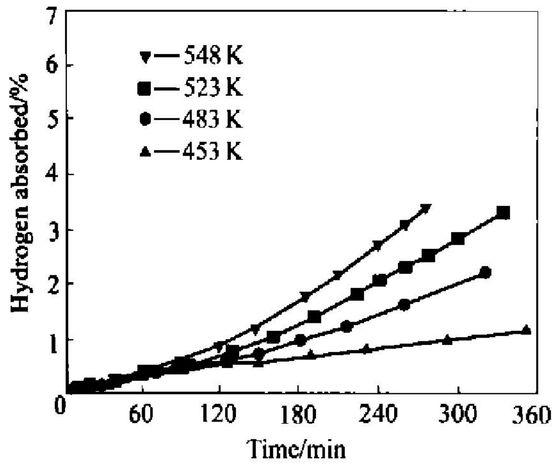

Fig. 3 Hydriding kinetics of slurry system with 10% Mg_2Ni at various temperatures under hydrogen pressure of 4. 5 MPa

slow. After 90 min the reaction changed into the second stage, in which the rate of hydrogenation of the benzene accelerated. It can be seen from the curves that the hydriding rate increased significantly and was controlled by the temperature of the slurry. At 453 K, the rate of hydrogen absorption was still low and was nearly a constant. As the temperature increased to 483 K the hydrogen absorption rate increased noticeably. The temperature range in which the slurry started to absorb hydrogen rather quickly was very close to that found in our previous investigations for the slurry composed of the AB_5 type alloy and benzene[10, 11]. Fig. 3 suggests also that the hydrogenation of benzene does not take place noticeably until a definite amount of MgNi has transformed to a hydride(Mg_2NiH_4) on absorbing hydrogen or that the hydrogenation process of benzene is only catalyzed by the hydride Mg_2NiH_4 in the slurry; as the catalysis of hydrided MgNi proceeds, the rate of hydrogenation of benzene increases rapidly. Fig. 4 shows the hydrogen absorption curves of the slurry with 20% MgNi at various temperatures under the hydrogen pressure of 4. 5 MPa. The absorption rate of this slurry is evidently much higher compared with that of the slurry with 10% MgNi. The absorption rate curves are also composed of two parts as shown in Fig. 4, but the difference in the hydrogenation rates in the two parts is much smaller than that of the curves for the slurry with 10% MgNi. The increase in the amount of hydrogen absorbed in the first part of the curve is from the increase of the amount of alloy, which transforms into hydride in the slurry. The increase of hydrogenation rate with the increase of temperature is the same as that for the slurry with 10% MgNi. At 548 K under 4. 5 MPa, after 260 min, the hydrogen storage capacity reached 5. 9% (mass fraction), which is 97% of the theoretic capacity of this slurry. When the hydrogenation reaction stopped, a small amount of the organic compound in the slurry was taken out and analyzed. The results show, that the content of the cyclohexane is above 99%, which means that nearly all benzene has been transformed into cyclohexane.

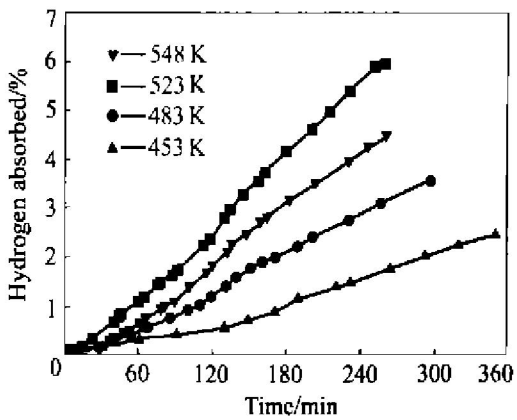

Fig. 4 Hydrogen absorption curves of slurry with 20% MgNi at different temperatures under hydrogen pressure of 4. 5 MPa

The hydriding curves of the slurry with different contents of MgNi are shown in Fig. 5. In the hydriding curve of the slurry with 50% MgNi the slope of the curve is nearly a constant value and the slopes of the two parts of the curve do not show much difference as compared with the slopes of the curves for slurry systems with lower alloy contents. As the hydrogen storage capacity of MgNi alloy is much smaller than that of benzene, the saturation hydrogen capacity of the slurry decreases as the alloy content in the slurry is increased. The saturation hydrogen capacity(4. 2%, mass fraction) of the slurry with 50% MgNi is smaller than that(5. 9%, mass fraction) of the slurry with 20% MgNi. From Fig. 5, it can be seen that the absorption rate increases as the content of alloy increases. According to a study of Reilly et al[12] the hydrogen absorption rate of the alloy in the slurry composed of alloy and n-undecane or silicon oil is controlled by the mass transfer process of hydrogen in the liquid, which is determined by the temperature of the slurry, the hydrogen pressure and the amount of suspended alloy particles. As the content of the alloy increases, the rate of hydrogen transferred through the liquid is reduced or the rate of hydrogen of the alloy is reduced. However, in the present experiment, the hydriding(or hydrogen absorbing) materials in the slurry are not only the hydrogen storage alloy but also benzene(C_6H_6). As the content of the alloy in the slurry increases, the amount of catalyst (metal hydride) and the contact efficiency of C_6H_6 with the metal hydride increase, which are both propitious to the increase of the hydrogenation rate of benzene. So the in-

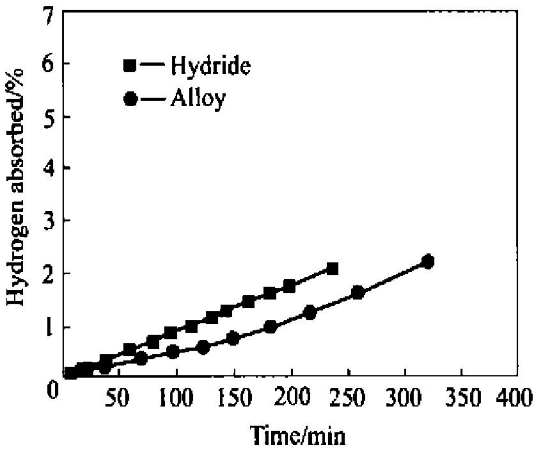

Fig. 5 Hydrogen absorption curves of slurry with different alloy contents at 483 K under 4.5 MPa

crease of the whole hydriding rate of the slurry system, which depends mainly on the increase of the hydrogenation rate of benzene, increases as the content of the alloy increases.

The hydrogen absorption kinetics of the slurry composed of C_6H_6 and the MgNi alloy versus the slurry composed of C_6H_6 and metal hydride Mg_2NiH_4 was also compared. Fig. 6 shows the two hydriding curves of the 10% MgNi+ C_6H_6 slurry and the 10% $MgNiH_x$ (metal hydride) + C_6H_6 slurry respectively. From Fig. 6 it can be seen that the hydriding curve of the slurry with 10% $MgNiH_x$ (metal hydride) is a straight line without any bent or change in curvature, which means the hydriding rate of benzene when catalyzed by the metal hydride is nearly a constant. But the hydriding curve of the slurry composed of MgNi alloy and benzene falls into two distinct regions. The first region shows that the amount of hydrogen absorbed by the slurry is the amount of hydrogen used in hydriding the alloy; the second region is the rate of absorbed hydrogen determined almost entirely by the rate of hydrogen reacted with benzene catalyzed by the metal hydride ($MgNiH_x$) formed in the first part of reaction. As in MgNi prepared by us only the portion of Mg_2Ni phase is hydrided into Mg_2NiH_x and acts henceforth as the catalyst, and the role played by $MgNi_2$ in the reaction is get to be studied.

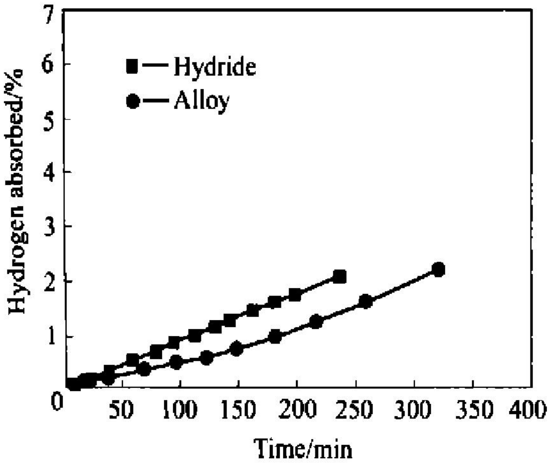

Fig. 6 Hydrogen absorption curves of slurry with 90% benzene at 483 K under 4.5 MPa

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