ELSEVIER

Journal of Alloys and Compounds 356–357 (2003) 409–412

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Hydrogen absorption properties of a slurry system composed of a magnesium alloy powder and C_6H_6

Changpin Chen*, Guanming Cai, Lixin Chen, Yue An, Guohua Xu, Qidong Wang

Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, PR China

Received 1 June 2002; received in revised form 30 October 2002; accepted 15 January 2003

Abstract

The hydrogen absorption properties of slurries composed of $La_{1.8}Ca_{0.2}Mg_{17-x}Ni_x$ alloy powder suspended in liquid C_6H_6 were investigated. It is found that the $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ in benzene liquid has similar hydrogen absorption properties as that of the hydrogen-alloy (gas–solid) reaction and the alloy has a strong catalytic effect on hydrogenation reaction of C_6H_6. The amount of hydrogen absorbed and the hydriding kinetics are related to the temperature, the solid/liquid weight ratio and the surface catalytic activity of the alloy. When the temperature of the slurry is ~473 K, it acquires a good hydriding rate. The hydrogen absorption capacity of the slurry system composed of 50 wt.% $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ alloy and 50 wt.% C_6H_6 reaches 5.5 wt.% of hydrogen at 483 K and 4.5 MPa in 240 min. Results of XRD, XPS and SEM analysis on the crystal structure, surface structure and configuration of the alloy correlated with its catalytic activity are reported and discussed.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Slurry; Magnesium alloy; Benzene cyclohexane conversion; Hydrogen absorption properties

1. Introduction

The hydrogen absorption/desorption kinetics and thermodynamics of the AB_5 type alloys suspended in organic solvents by mechanical stirring have been investigated and reported by Reilly et al. [1,2] and Chen et al. [3,4]. In those experiments, the hydrogen was absorbed only by the hydrogen storage alloy and the liquid media were just used to disperse the alloy powder and to transport the hydrogen to the surface of the powder. Many engineering problems encountered in application of the hydrogen storage alloys for hydrogen storage were solved or avoided by using the slurry system. But the hydrogen absorption capacity on the basis of weight density of the slurry system decreased greatly owing to the extra weight of the liquid used.

The potential of hydrogenating some aromatic hydrocarbons to saturated cyclic products is considered in this study. In general Raney Ni is the most frequently employed catalyst for hydrogenation, but hydrogen storage alloys are proposed here instead. In the solid–liquid phase hydrogenation of an organic compound with a metal hydride, the alloy participates in the hydrogen absorption/desorption reaction during hydriding/dehydriding reaction and functions as a catalyst to activate the hydrogenation of the liquid organic medium. It is also known from some previous studies that the hydride of La–Ni based alloy shows very good catalytic activity for the hydrogenation of *p*-benzoquinone [5]. In this study an Mg-based alloy instead of the La–Ni-based alloys was adopted on account of its higher hydrogen storage capacity.

The aim of this work was to investigate the hydrogen absorption properties of slurries composed of $La_{1.8}Ca_{0.2}Mg_{17-x}Ni_x$ alloy powder and liquid C_6H_6. In this paper, the surface composition and the structure of the Mg-based alloys were analyzed. The relationship between the surface structure of the alloys and the hydriding characteristics of the slurries was also studied.

2. Experimental

As-cast $La_{1.8}Ca_{0.2}Mg_{17-x}Ni_x$ ($x=1$, 3) alloys used in this study were prepared by induction melting the component metallic elements with purity all above 99.9% under high purity argon. Ingots thus obtained were crushed

---

*Corresponding author. Tel.: +86-571-8795-1152; fax: +86-571-8795-1152.

E-mail address: chencp@mail.hz.zj.cn (C. Chen).

0925-8388/03/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0925-8388(03)00225-1

into powder below 300 mesh in air. The hydrogen absorption experiments of the slurry systems were carried out in a stainless steel reactor with a stirrer. The amount of hydrogen absorbed by the slurry was determined by a volumetric method.

The phase structure of samples was determined by X-ray diffraction (XRD) with a Philips X'Pert-MPD type X-ray diffractometer with Cu Kα radiation. The XPS analysis was performed on a PHI-550 ESCA-SAM spectrometer at 10^{-7} Pa using Al Kα radiation, and Ar^+ sputtering at 2.0 kV for 10 and 70 min, respectively. The surface morphology was examined by scanning electron microscopy on a Philips AMRAY electron microscope. The hydrogenation products of benzene were analyzed with a Fison Mega 2 Series MFC 800 chromatograph equipped with a DB-624 capillary column.

3. Results and discussion

3.1. Hydriding properties of slurry composed of benzene and $La_{1.8}Ca_{0.2}Mg_{17-x}Ni_x$ (x=1, 3) alloys

Fig. 1 shows that the hydrogen absorption rate curves of the slurries composed of benzene and $La_{1.8}Ca_{0.2}Mg_{16}Ni$ alloy with two different weight ratios at 483 K and under 4.5-MPa hydrogen pressure. Both the alloy and benzene react with hydrogen throughout the entire process. During the first 30 min, hydrogen is absorbed mostly by the alloy with rather high hydriding rate. Afterwards the hydrogen is used for the hydrogenation of benzene at a reaction rate noticeably lower than the rate of hydriding of the alloy. From the same figure, it can be seen that the hydrogenation rate of benzene increases as the $La_{1.8}Ca_{0.2}Mg_{16}Ni$ content in the slurry system increases. The hydrides of La–Ni alloys have been used by Lunin et al. [5] as catalysts for the hydrogenation of benzene and *p*-benzoquinone and the activity of La–Ni hydrides has been studied. According to them the intermetallic compounds LaNi, $LaNi_3$ and $LaNi_5$ have no catalytic effect on the hydrogenation of *p*-benzoquinone, but the hydrides of these intermetallic compounds showed some activity for hydrogenation. In the study of the hydrogenation of *p*-benzoquinone, they realized that during hydrogenation of liquid organic compounds with the hydrides of intermetallic compounds, the hydrogenation process involved not only the reaction of the liquid with the hydrogen, activated by the surface of the metal catalyst, but also the reaction with the hydrogen dissociated from the hydride phase. In the present experiment, the hydride $La_{1.8}Ca_{0.2}Mg_{16}NiH_x$ shows very good catalytic activity for benzene hydrogenation. This result confirms the conclusions from Lunin et al. [5] that metal hydrides have good catalytic activity for the hydrogenation of aromatic hydrocarbons to saturated cyclic products. The reaction products were analyzed by gas chromatography to obtain the conversion and the selectivity of benzene to cyclohexane. In the present reaction condition the conversion rate is 98% and the selectivity is 100%.

Fig. 2 shows the hydrogenation rate curves of the slurries composed of benzene and different amounts of $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ at 483 K and under 4.5-MPa hydrogen pressure. For this slurry system similarly, both $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ alloy and benzene react with hydrogen. The hydrogenation properties of the slurry composed of benzene and $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ are similar to those of the slurry composed of benzene and $La_{1.8}Ca_{0.2}Mg_{16}Ni$. In the beginning, the hydriding of $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ is the main reaction, but subsequently the hydrogenation of benzene becomes the chief reaction. Fig. 2 indicates that the hydrogenation rate of the benzene increases as the content of the alloy in the slurry increases. Only the rate of hydrogenation of $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ is faster at any stage than the corresponding rate for $La_{1.8}Ca_{0.2}Mg_{16}Ni$. The hydrogen absorption capacity of the slurry system com-

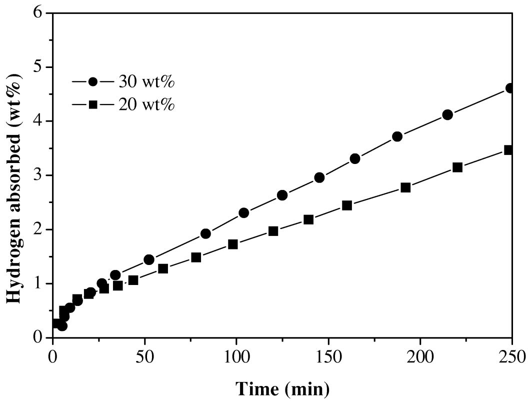

Fig. 1. Hydrogenation rate curves of the slurry composed of $La_{1.8}Ca_{0.2}Mg_{16}Ni$ and benzene at 483 K and under a hydrogen pressure of 4.5 MPa.

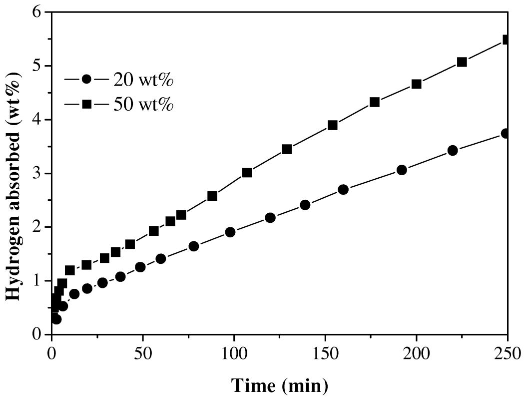

Fig. 2. Hydrogenation rate curves of the slurry composed of $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ and benzene at 483 K and under a hydrogen pressure of 4.5 MPa.

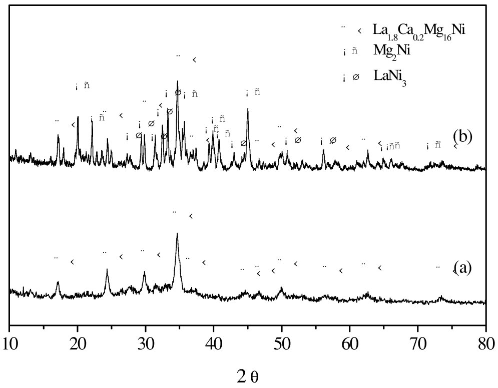

Fig. 3. (a) XRD patterns of the as-cast $La_{1.8}Ca_{0.2}Mg_{16}Ni$ alloy; (b) XRD patterns of the as-cast $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ alloy.

posed of 50 wt.% $La_{1.8}Ca_{0.2}Mg_{16}Ni$ alloy and 50 wt.% C_6H_6 reaches 5.5 wt.% of hydrogen at 483 K and 4.5 MPa in 240 min.

3.2. Crystal structure, surface morphology and structure of the alloys

Fig. 3(a), which is the X-ray diffractogram of the as-cast $La_{1.8}Ca_{0.2}Mg_{16}Ni$ alloy, shows that the alloy $La_{1.8}Ca_{0.2}Mg_{16}Ni$ is a simple phase intermetallic compound. Fig. 3(b), which is the X-ray diffractogram of $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ alloy, indicates that it contains two main phases, $La_2Mg_{16}Ni$ and Mg_2Ni together with a third minor $LaNi_3$ phase.

The morphology of the $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ alloy particles was examined by a scanning electron microscope which showed that the as-cast alloy has a smooth surface.

Fig. 4 gives the XPS spectra for Mg_{2p} and La_{3d} core level of the $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ alloy before and after being sputtered for 10 and 70 min. It can be seen that the samples are oxidized to MgO on the surface. As the sputtering time increases the binding energy of the Mg_{2p} electron decreases. The XPS spectra for La_{3d} show that both oxidized La and metallic La exist on the surface of the alloy.

3.3. Surface composition of the $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ alloys

Fig. 5 is the depth profile of $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ obtained with Ar^+ sputtering. It is shown that the outmost layer in the surface of $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ is a magnesium-rich layer. The content of nickel and calcium is hard to measure by analysis apparatus. The oxygen content is rather high (~30 wt.%) in the entire surface region, which means that for the as-cast alloy, Mg and La have been oxidized to a considerable depth. Even after being sputtered for 70 min, the content of the oxygen in the sample surface was still ~29 at.% and the content of nickel was very low. Lunin et al. [6] in his early investigations considered that intermetallic compounds had very good catalytic activity due to the segregation of the metallic Ni particles and La-oxide to the surface. In our experiment, the content of Ni at the surface is not believed to be the main cause for the hydrogenation activity of benzene. The hydrogen absorption curves of two slurries, which were composed of C_6H_6+Mg_2Ni and C_6H_6+Mg_2NiH_4 hydride, respectively, were studied and compared in our former work [7,8]. The results show that the hydriding rate of the slurry consisting of the metal hydride Mg_2NiH_4 was twice as high as that of the slurry consisting of the Mg_2Ni alloy. Such results seem to indicate that the metal hydride Mg_2NiH_4 has the better catalytic effect for benzene hydrogenation. Soga et al. [9] also found that the catalytic activity of $LaNi_5H_6$ was much higher than that of $LaNi_5$ in a study of ethylene hydrogenation reaction. They concluded that the hydrogen for ethylene hydrogenation process was not provided by H_2 in the system, but by the active H atom from the metal hydride. In the present hydrogenation reaction at 483 K, the hydrides

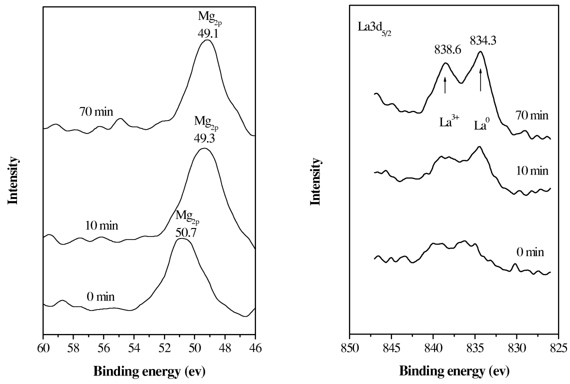

Fig. 4. Mg_{2p} and $La3d_{5/2}$ core level spectra of $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ particles (*t* in min gives the sputtering time).

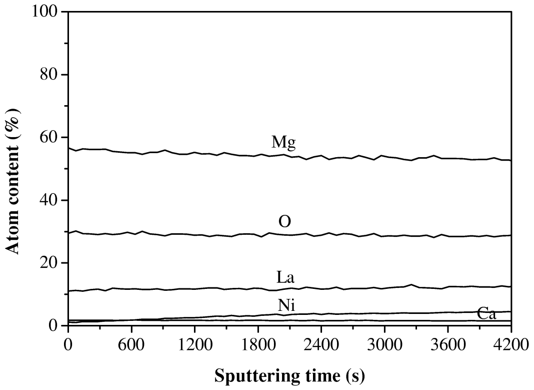

Fig. 5. The AES depth profiles of the $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ alloy after sputtering.

$La_{1.8}Ca_{0.2}Mg_{16}NiH_x$ and $La_{1.8}Ca_{0.2}Mg_{14}Ni_3H_x$ are still able to function as good hydrogenation catalysts. So, in such a system, H atoms from the metal hydride are very active and the metal hydride is the catalytic center of the benzene hydrogenation.

4. Conclusion

For the slurries composed of $La_{1.8}Ca_{0.2}Mg_{17-x}Ni_x$ ($x=$ 1, 3) alloys and benzene, during hydrogenation the alloy absorbed hydrogen first and then the benzene began to be hydrogenated under the catalysis of the metal hydride. The hydrides $La_{1.8}Ca_{0.2}Mg_{16}NiH_x$ and $La_{1.8}Ca_{0.2}Mg_{14}Ni_3H_x$ both show good catalytic activity for benzene hydrogenation. The hydrogenation rate of the benzene increases as the content of the alloy in the slurry increases. The hydrogen absorption capacity of the slurry system composed of benzene and 50 wt.% of $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ reaches 5.5 wt.% of hydrogen at 483 K and 4.5 MPa in 240 min.

The state and surface content of Ni are not believed to be the main factor affecting the rate of the benzene hydrogenation. In the present hydrogenation reaction at 483 K, the hydrides $La_{1.8}Ca_{0.2}Mg_{16}NiH_x$ and $La_{1.8}Ca_{0.2}Mg_{14}Ni_3H_x$ still exist and seems to act as hydrogenation catalysts. H atoms from the metal hydride are very active and the metal hydride acts as the catalytic center of the benzene hydrogenation.

Acknowledgements

This work is supported by the State Key Project for Fundamental Research of China and the National Natural Science Foundation of China.

References

[1] J.J. Reilly, J.R. Johnson, J. Less-Common Met. 104 (1984) 175–190.

[2] J.J. Reilly, J.R. Johnson, T. Gamo, J. Less-Common Met. 131 (1987) 41–49.

[3] G.M. Cai, C.P. Chen, Y. An, G.H. Xu, L.X. Chen, Q.D. Wang, J. Rare Earths 20 (2002) 28–30.

[4] Y. An, C.P. Chen, G.H. Xu, L.X. Chen, Q.D. Wang, J. Rare Earths 20 (2002) 113–115.

[5] V.V. Lunin, N.N. Sychev, V.I. Bogdan, Kinet. Catal. 33 (1992) 447.

[6] V.V. Lunin, O.I. Kryukov, S.O. Kozhinskii et al., Kinet. Catal. 24 (1983) 233.

[7] G.M. Cai, C.P. Chen, Y. An, G.H. Xu, L.X. Chen, Q.D. Wang, Trans. Nonferrous Met. Soc. China 13 (2003) 29.

[8] C. Chen, G. Cai, Y. Chen, Y. An, G. Xu, Q. Wang, J. Alloys Comp. 350 (2003) 275.

[9] K. Soga, H. Imamura, S. Ikeda, J. Phys. Chem. 81 (1977) 1762.