JOURNAL OF MATERIALS SCIENCE **39** (2004) 6987 – 6991

Hydriding kinetics of the $La_{1.5}Ni_{0.5}Mg_{17}$–H system prepared by mechanical alloying

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In the study of reaction kinetics between hydrogen and hydriding alloys, what is the most important is to obtain intrinsic kinetic data. The hydriding kinetics of 0.5 g $La_{1.5}Ni_{0.5}Mg_{17}$ sample in the two-phase (α-β) region was investigated as a function of temperature and pressure in the ranges 553–573 K and 0.256–0.992 MPa H_2 respectively. Mathematical analyses of the time-dependent hydrogen absorption curves indicate agreement with Jander diffusion model, $[1-(1-\xi)^{1/3}]^2 = k(T, P)t$, which suggests that the rate-controlling step for hydrogen absorption is three-dimensional diffusion. An apparent activation energy for such diffusion process of 83 ± 1 kJ/mol H_2 has been obtained from the absorption data.

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1. Introduction

Many metal-hydrogen systems have been investigated as hydrogen storage materials, owing to a series of special characteristics of hydrogen storage in metals, such as large hydrogen storage capacity, light mass, low environmental impact, low cost and high natural abundance, magnesium-based alloys are regarded as one of the most attractive candidate for the future hydrogen storage materials. However, because of its high dehydriding temperature (at least 623–673 K) and relatively poor hydriding/dehydriding (H/D) kinetics [1], there exits some obstacle to use magnesium in hydrogen storage. Various attempts have been made to overcome these difficulties, for example, many elements such as V, Ti, Ni, Fe, Mn, Cu, Ag, Al [2–5] have been selected as additives to the magnesium. The surface properties of the alloys were modified by many methods including F-treated [6] and water treating [7]. Many Mg-based composite materials were prepared to enhance activity of magnesium with respect to hydrogen [8–10]. A lot of novel techniques [11–14], e.g., mechanical alloying (MA), melt-spinning and sputtering, have been developed to produce amorphous and nanocrystalline materials. In particular, the mechanical alloying method that processes under a hydrogen environment has reached some special advantages, such as improving the hydriding reaction due to the formation of a continuous active surfaces [15, 16], and preventing Mg from oxidizing under hydrogen environment. Besides, this method can avoid some special precautions coming from the very high Mg vapor pressure at the temperature of the melting point of other elements (Ni, La *et al.*).

However, H/D kinetics are so sensitive to material preparation, gas purity, system design etc, the intrinsic reaction rates of hydrogen absorption and desorption in the Mg-based alloys have still been unclear due to experimental difficulties including measuring method, experimental isothermal and isobaric conditions etc. So many various results were obtained [17, 18] and different interpretation was reported [19–21]. Most kinetics analyses that have identified an intrinsic process as rate limiting are criticized as being invalid because (i) the rate theory used has been inappropriate and (ii) heat flow has not been adequately taken into account.

In present paper $La_{1.5}Ni_{0.5}Mg_{17}$ alloy was investigated to understand deeply the question of the slowest step in the formation of $La_{1.5}Ni_{0.5}Mg_{17}$–H hydride by means of a volumetric method as a function of the sample temperature and hydrogen pressure.

2. Experimental details

The procedure of preparing $La_{1.5}Ni_{0.5}Mg_{17}$ by mechanical alloying was described in detail elsewhere [22]. The kinetic rate of the hydrogen absorption reaction of $La_{1.5}Ni_{0.5}Mg_{17}$ was measured using a specially developed reactor (as shown schematically in Fig. 1) during the temperature changed between 553 and 573 K and the pressure from 0.256 to 0.992 MPa. The reactor enabled both isothermal measurements and unimpeded hydrogen flow rate. 0.5 g $La_{1.5}Ni_{0.5}Mg_{17}$ powder was used to reduce the generation of the reaction heat in order to obtain isothermal or near isothermal conditions, a pair of thermocouple with 0.85 mm diameter was used to measure the temperature accurately.

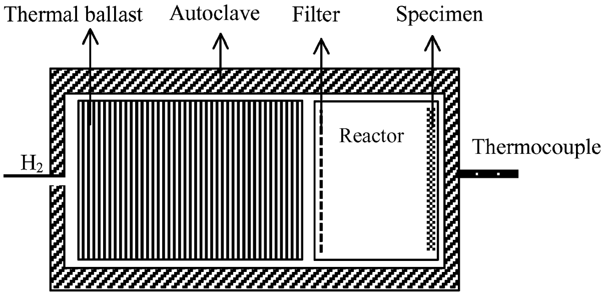

Figure 1 Reactor for kinetic measurements on powder metal hydrides.

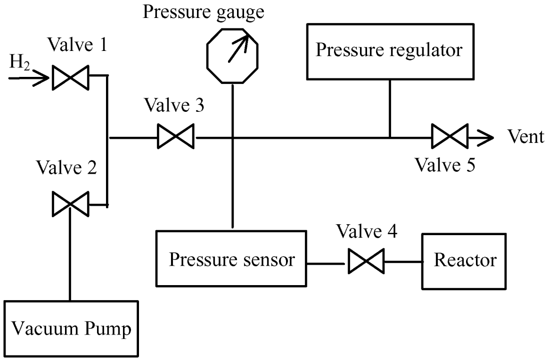

Figure 2 The schematic diagram hydride kinetics apparatus.

The experimental apparatus used to perform kinetics measurement is shown schematically in Fig. 2. It consisted of a stainless steel manifold with ports for adding hydrogen, venting and evacuating system. A designed constant temperature electric furnace was used to keep the sample at constant temperature within ±2 K. In order to measure the kinetics of hydrogen absorption accurately, the sample was evacuated to 0.0133 MPa for 1 h to remove any gas in the system. Then valves 2 and 4 were closed, and the rated hydrogen was introduced to the system suddenly. With the help of a manually operated needle valve 3 the rated hydrogen with a purity of 99.999% was introduced into the reactor. A step-wise method was adopted to measure the kinetics as shown in Fig. 3. The hydriding reaction proceeds linearly from P_i to P_e or from H_i to H_f. Changes $H-H_\mathrm{f}$ in hydride composition were easily converted in pressure terms using pressure composition isothermal data which had previously been correlated with an analytical expression. Those experimental runs were performed by adjusting the pressure levels to a value higher than the previous equilibrium pressure, staring from the α and going to the β phase across the α-β two phase region. Due to the properties of the plateau is of importance for hydride, much attentions was put on the α-β phase region in this study.

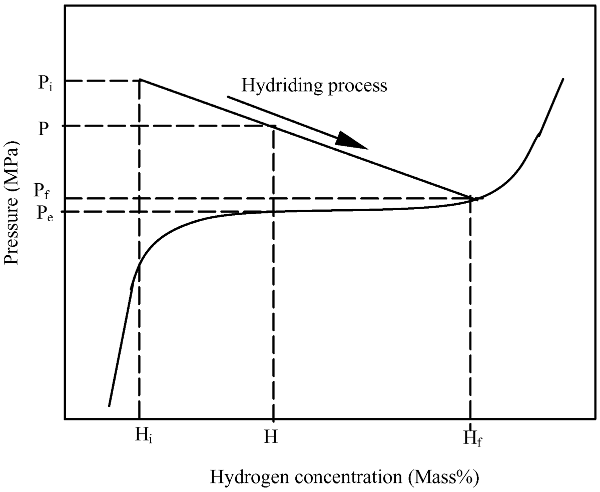

Figure 3 A schematic diagram showing the experimental procedure for determining isothermal hydriding reaction kinetics.

3. Results and discussion

The reaction fraction ξ is defined as the ratio of the temporal number of hydrogen moles absorbed to the total number of hydrogen moles absorbed. The hydriding reaction rate of $La_{1.5}Ni_{0.5}Mg_{17}$ is a function of temperature T and hydrogen pressure P_{H_2}. These functional relationships can be experimental investigated and compared with theoretical rate equations, to obtain the rate-limiting step of the hydriding reaction. The hydriding reaction can be expressed as serial reaction of several simple reaction steps that are as follows: (i) surface chemisorption; (ii) diffusion of hydrogen atoms through the β phase; (iii) the interfacial chemical reaction ($\alpha \rightarrow \beta$).

3.1. The effect of temperature on the hydriding reaction rate

In order to determine the temperature correction factor, the hydrogen absorption kinetics at different temperatures was measured for a given pressure. Fig. 4 shows hydrogen absorption curves of the two-phase (α-β) region in $La_{1.5}Ni_{0.5}Mg_{17}$ from 553 to 573 K. Compared these curves, it is known intuitively that the higher temperature the system is, the faster the hydriding reaction rate is. It took 300 s for the transformed fraction to reach 0.88 and 0.98 in the two-phase (α-β) region for 553 and 573 K, respectively. It was found that the capacity of hydrogen absorption of $La_{1.5}Ni_{0.5}Mg_{17}$ prepared by MA method can reach to 4.55–7.01 mass%H under 3 MPa hydrogen pressure and the desorption 4.40–6.90 mass%H in 600 s under 0.0133 MPa above 423 K.

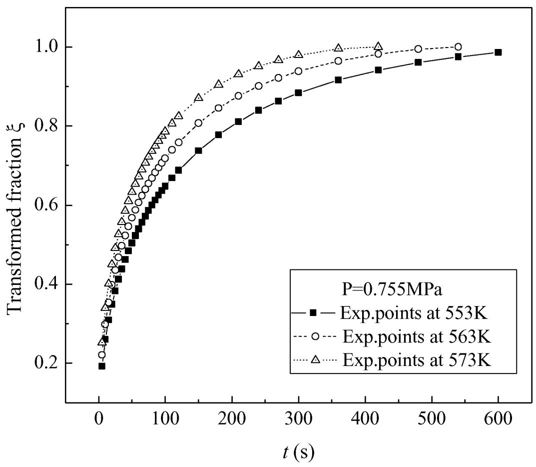

Figure 4 Hydrogen absorption curves in the two-phase (α-β) region of $La_{1.5}Ni_{0.5}Mg_{17}$ at different temperatures.

Compared to the results of Mg-Ni-RE (RE = Ce, Nd, Y, La or La-rich mischmetal) [23–26] alloys reported recently, it took 83 min for $Mg_{86}Ni_{10}Nd_4$ to absorb 4.45 mass%H at 573 K under 3 MPa after 9 cycles for activation and 40 min to desorb the same amount hydrogen. Above 423 K, their alloy can absorb 3.5–4.5 mass%H within 1 ks. In 110 min the hydrogen absorption capacity of $Mg_{75}Ni_{20}Mm_5$ alloy reaches to 3.98 mass%H, which was better than $Mg_{76}Ni_{19}Y_5$ and $Mg_{78}Ni_{18}Y_4$ alloys. $La_{2-x}Ca_xMg_{17}$ ($x = 0.2, 0.4, 1.4, 1.6, 1.8$) series alloys show better hydriding property, $La_{0.6}Ca_{1.4}Mg_{17}$ the best among this alloy series, can absorb 4.8 mass%H at 598 K and under 1 MPa H_2. Although the kinetics of alloys reported in literatures were improved in a certain extent compared to the binary Mg-Ni and Mg-La alloys (e.g., La_2Mg_{17} took 2.5 h to absorb and 3 h to desorb 4.9 mass%H), their hydrogen capacities decreased dramatically and these can't desorb more hydrogen at low temperature. From these results mentioned above, $La_{1.5}Ni_{0.5}Mg_{17}$ alloy manufactured by MA is one of the best candidates of the lightweight hydrogen storage materials.

Usually, the reaction mechanism can be analyzed by comparing the observed hydriding rate curves with the rate equations derived from different processes, such as nucleation and growth process, auto-catalytic reactions, phase-boundary-controlled reactions and so on. Some rate equations proposed in the literature [27–30] have been used to treat the experimental data, but the fittings were very unsatisfactory.

In order to more clearly study the mechanism of the hydriding process, experimental data were analyzed according to 41 kinetic equations summarized by Lin [31] one by one, then the form of function that best fits the data together with the temperature and pressure are used to determine the rate-limiting step for the reaction. The hydrogen absorption curves in the two-phase (α-β) region from 553 to 573 K under 0.755 MPa H_2 can be fitted with good accuracy by Jander diffusion model in Fig. 5, which is the rate expression $[1 - (1 - \xi)^{1/3}]^2 = k(T, P)t$, where α is reaction fraction at time t, $k(T, P)$ is the rate constant which depends on temperature and pressure. This kind of rate expression suggests that the rate-controlling step for hydrogen absorption is three-dimensional diffusion.

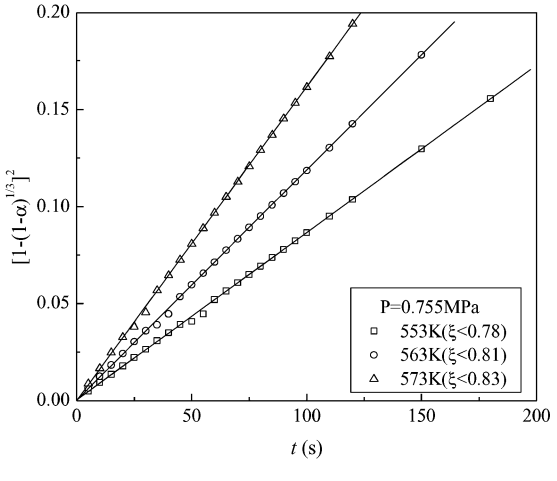

Figure 5 Plots of $[1 - (1 - \xi)^{1/3}]^2$ vs. time for hydriding reaction of the two-phase (α-β) region of $La_{1.5}Ni_{0.5}Mg_{17}$ at different temperatures.

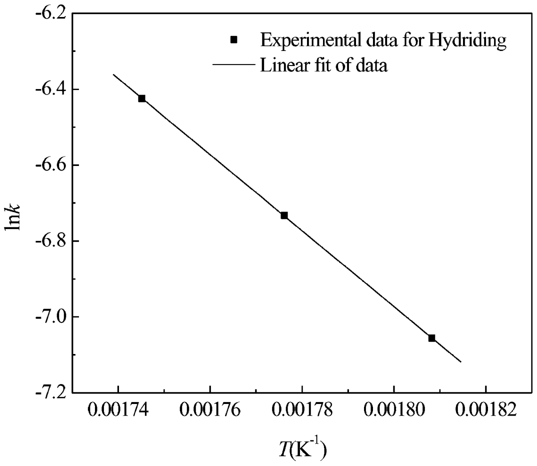

Figure 6 Arrhenius plot of hydriding reaction rate in the two-phase (α-β) region of $La_{1.5}Ni_{0.5}Mg_{17}$.

The activation energy of hydriding reaction was obtained using the Arrhenius law, $k = A\exp^{-(E/RT)}$, where E is the activation energy, k is the rate constant, which is obtained from the slope of the straight line in Fig. 5 for each temperature, R is gas constant and T is reaction temperature. A plot of ln k versus $1/T$ gives a straight line as shown in Fig. 6. The apparent activation energy calculated for the hydriding reaction is 83 ± 1 kJ/molH_2, which is much less than that (112.8 kJ/molH_2) of ball milled MgH_2 [27]. The difference in activation energies for hydrogen absorption between $La_{1.5}Ni_{0.5}Mg_{17}$ and MgH_2 systems may be contributed to the addiction of La and Ni to magnesium and different fabricating method. It is well known that the smaller the activation energy, the larger the rate constant and the faster the reaction rate. Compared to the kinetic properties of $La_{1.5}Ni_{0.5}Mg_{17}$ and MgH_2, the hydriding reaction rate for the former is faster than that for the latter, which is consistent with our experimental study.

3.2. The effect of pressure on the hydriding reaction rate

The reacted fractions of $La_{1.5}Ni_{0.5}Mg_{17}$ alloy were measured as a function of reaction time under the pressure range of 0.256 to 0.992 MPa at 553 K, as shown in Fig. 7. These results show behaviors are qualitatively analogous to the ones already reported for Mg-based alloys [32]. It is apparent seen that the higher the hydrogen pressure, the faster the hydriding reaction rates are, but, if a sufficiently long period of time is considered, hydriding degrees are very closely achieved.

The pressure dependence of the hydriding kinetics has been discussed in various analytical models and used to determine the reaction rate-limiting steps [33, 34]. Various pressure dependence functions have been applied to experimental data on different reasoning and the rate equation $[1 - (1 - \xi)^{1/3}]^2 = k(T, P)t$ proposed by Jander can fit well the pressure experimental data as shown in Fig. 8, which suggests that the rate-limiting step is three-dimensional diffusion. Provided that the pressure-dependent term can be

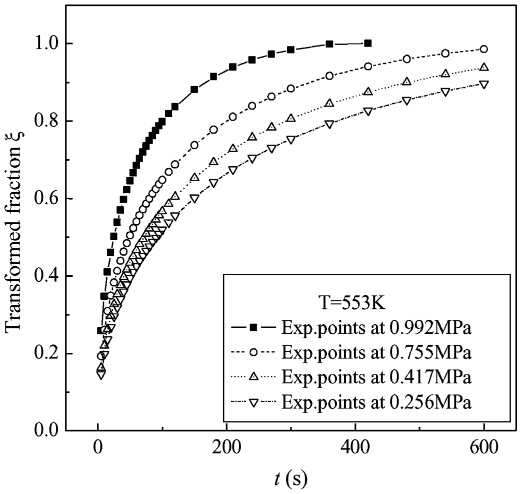

Figure 7 Hydrogen absorption curves in the two-phase (α-β) region of $La_{1.5}Ni_{0.5}Mg_{17}$ at different pressures.

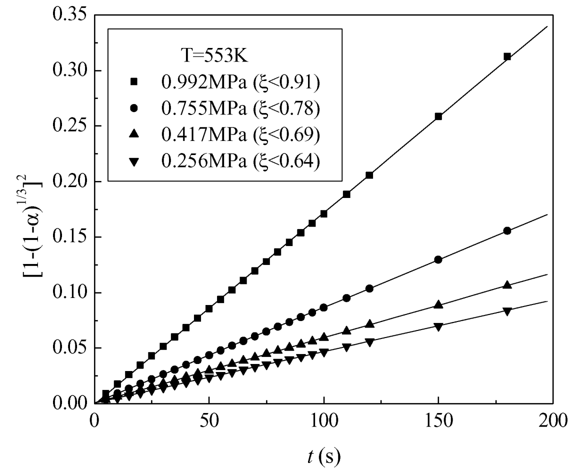

Figure 8 Plots of $[1-(1-\xi)^{1/3}]^2$ vs. time for hydriding reaction of the two-phase (α-β) region of $La_{1.5}Ni_{0.5}Mg_{17}$ at different pressures.

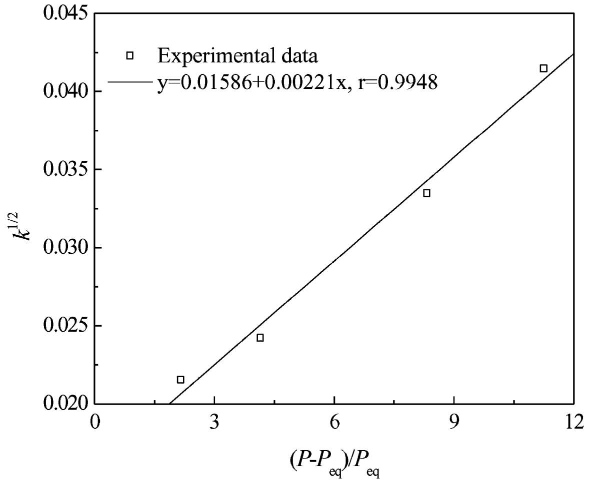

Figure 9 Square root rate constant k versus driving force $(P-P_{\mathrm{eq}})/P_{\mathrm{eq}}$ for diffusion-controlled absorption.

expressed by Jander model, the plots at 553 K show straight lines. This means that a pressure-dependent term ($[1-(1-\xi)^{1/3}]^2 = k(T, P)t$) has a liner relationship with time.

After data analysis, the dependence of the rate constant on absorption pressures was extracted. It was found that the square root of the rate constant varies linearly with the driving force $(P-P_{\mathrm{eq}})/P_{\mathrm{eq}}$, as shown Fig. 9, where P is the pressure prevailing in the system's free volume, including the reactor, volumetric reservoir and ducts. P_{eq} is the absorption equilibrium pressure.

4. Conclusion

Hydrogen absorption kinetics was investigated in $La_{1.5}Ni_{0.5}Mg_{17}$ alloy in the temperature range from 553 to 573 K and the pressure range from 0.256 to 0.992 MPa H_2. The obtained kinetic curves were fitted using various rate equations derived from different kinetic reaction process. It was found that the hydriding kinetics in the two-phase (α-β) region was well in agreement with Jander rate equation, $[1-(1-\xi)^{1/3}]^2 = kt$, which suggests that the three-dimensional diffusion dominates the hydriding process. The apparent activation energy for such diffusion process of 83 ± 1 kJ/molH_2 has been obtained from the absorption data. The square root of the rate constant shows a linear dependence on driving force $(P-P_{\mathrm{eq}})/P_{\mathrm{eq}}$.

References

1. M. STIOUI, A. GRAYEVSKY, A. RESNIK, D. SHALTIEL and N. KAPLAN, *J. Less-Comm. Metals* **123** (1986) 9.
2. G. LIANG, J. HUOT, S. BOILY, A. VAN NESTE and R. SCHULZ, *J. Alloys Comp.* **282** (1999) 286.
3. Y. TSUSHIO, H. ENOKI and E. AKIBA, *ibid.* **285** (1999) 298.
4. QIAN LI, QIN LIN, LI-JUN JIANG and KUO-CHIH CHOU, *ibid.* **359** (2003) 128.
5. QIAN LI, QIN LIN, KUO-CHIH CHOU and LI-JUN JIANG, *J. Mater. Sci.* **39** (2004) 61.
6. F.-J. LIU and S. SUDA, *J. Alloys Comp.* **232** (1996) 212.
7. M. D. HAMPTON, J. K. LOMNESS and L. A. GIANNUZZI, *Int. J. Hydrogen Energy* **27** (2002) 79.
8. M. ZHU, Y. GAO, X. Z. CHE, Y. Q YANG and C. Y. CHUNG, *J. Alloys Comp.* **330–332** (2002) 708.
9. G. LIANG, J. HUOT, S. BOILY, A. VAN NESTE and R. SCHULZ, *ibid.* **297** (2000) 261.
10. M. KHRUSSANOVA, J.-L. BOBET, M. TERZIEVA, B. CHEVALIER, D. RADEV, P. PESHEV and B. DARRIET, *ibid.* **307** (2000) 283.
11. S. J. JI, J. C. SUN, Z. W. YU, Z. K. HEI and L. YAN, *Int. J. Hydrogen Energy* **24** (1999) 59.
12. F. C. CENNARI, F. J. CASTRO and G. URRETAVIZCAYA, *J. Alloys Comp.* **321** (2001) 46.
13. TAE-WHAN HONG and YOUNG-JIG KIM, *ibid.* **330–332** (2002) 584.
14. KEITA ISOGAI, SHIN-ICHI YAMAURA, HISAMICHI KIMURA and AKIHISA INOUE, *J. JPN Inst. Metals* **65**(6) (2001) 477.
15. S. ORIMO and H. FUJII, *J. Alloys Comp.* **232** (1996) L16.
16. S. ORIMO, H. FUJII and K. IKEDA, *ibid.* **253–254** (1997) 80.
17. J. HUOT, G. LIANG, S. BOILY, A. VAN NESTE and R. SCHULZ, *ibid.* **293–295** (1999) 495.
18. T. AKIYAMA, T. A. TAZAKI, R. TAKAHASHI and J. YAGI, *Intermetallics* **4** (1996) 659.
19. F. VON ZEPPELIN, H. REULE and M. HIRSCHER, *J. Alloys Comp.* **330–332** (2002) 723.
20. J. K. LOMNESSA, M. D. HAMPTON and L. A. GIANNUZZI, *Int. J. Hydrogen Energy* **27** (2002) 915.
21. YUSUKE ASAKUMA, SHINSUKE MIYAUCHI, TSUYOSHI YAMAMOTO, HIDEYUKI AOKI and TAKATOSHI MIURA, *ibid.* **28** (2003) 529.

22. QIAN LI, LI-JUN JIANG, QIN LIN, CHOU KUO-CHIH, FENG ZHAN, QIANG ZHENG and XIU-YING WEI, *J. Rare Earths* **21**(3) (2003) 337.
23. JINGTIAN YIN, TETSUYOSHI YAMADA, OSAMU YOSHINARI and KAZUHIDE TANAKA, *Mater. Trans.* **42**(4) (2001) 712.
24. TONY SPASSOV, VESSELINA RANGELOVA and NIKOLAY NEYKOV, *J. Alloys Comp.* **334** (2002) 219.
25. TONY SPASSOV and UWE KOSTER, *ibid.* **279** (1998) 279.
26. GUAN-MING CAI, CHANG-PIN CHEN, YUN CHEN, LI-XIN CHEN and QI-DONG WANG, *Int. J. Hydrogen Energy* **28** (2003) 509.
27. G. LIANG, J. HUOT, S. BOILY and R. SCHULZ, *J. Alloys Comp.* **305** (2000) 239.
28. W. ZHANG, J. CIMATO and A. J. GOUDY, *ibid.* **201** (1993) 176.
29. M. N. MUNGOLE and R. BALASUBRAMANIAM, *Int. J. Hydrogen Energy* **23** (1998) 349.
30. B. BERNHARDT and K. BOHMHAMMEL, *Thermochimica Acta* **382** (2002) 249.
31. LIN QIN, CHEN NING, YE WEN and LIU RENMING, *J. Univ. Sci. Tech. Beijing* **4** (1997) 34.
32. J. F. FERNANDEZ and C. R. SANCHEZ, *J. Alloys Comp.* **340** (2002) 189.
33. B. VIGEHOLM, J. KJOLLER, B. LARSEN and A. S. PEDERSEN, *J. Less-Common. Metals* **89** (1983) 135.
34. JEA WAN OH, CHUN YONG KIM, KEE SUK NAHM and KYU SUNG SIM, *J. Alloys Comp.* **278** (1998) 270.

Received 1 December 2003
and accepted 12 July 2004