

[Article ID] 1003- 6326(2002) 02- 0227- 06

Hydrogen storage properties of nanocomposite Mg-Ni-MnO₂ made by mechanical milling^①

WANG Er-de(王尔德), YU Zhen-xing(于振兴), LIU Zhi-yan(刘祖岩)

(School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China)

[Abstract] The hydrogen storage properties of the nanocomposite Mg₉₅Ni₃(MnO₂)₂ (mass fraction, %) were studied. The temperature changes in hydriding/dehydriding process were investigated. The nanocomposite was fabricated by ball milling process of mixed elemental Mg, Ni and oxide manganese MnO₂ under hydrogen pressure (approximately 0.6 MPa). The hydrogen absorption and desorption properties of the samples milled for various times were investigated. A remarkable enhancement of hydrogen absorption kinetics and low operational desorption temperature have been found after the sample milled for over 57 h. For example, this nanocomposite can absorb hydrogen more than 6.0% (mass fraction) in 60 s at 200 °C under 2.0 MPa, and desorption capacity also exceeds 6.0% (mass fraction) in 400 s at 310 °C under 0.1 MPa. The storage properties of samples milled for various times were studied and the kinetics of the samples were analyzed.

[Key words] mechanical milling; nanocomposite Mg-Ni-MnO₂; hydrogen storage materials

[CLC number] TG 139

[Document code] A

1 INTRODUCTION

Metal hydrogen storage materials is very important function materials, during the last 30 years, hydrogen storage materials have been widely investigated in the world. Mg and Mg-based alloys are considered to be most promising hydrogen storage materials because they possess high hydrogen storage capacity and low-cost compared with other metal storage systems. But there remain a number of problems to be solved with these systems, the first is very poor hydrogen absorption and desorption kinetics, the second is too high temperature of dehydrogenation for most applications.

Recently, many investigators have studied Mg-based composites, because these composites have relatively high capacity, favorable thermodynamics and remarkable kinetics in hydriding/dehydriding process. The composites may be divided into two types, one is Mg-simple substance, for example, Mg-M (M = Fe, Ni, V, Pd etc)^[1, 2]. Another type is Mg-compound or Mg-intermetallic compound, for example, Mg-Mg₂Ni^[3], Mg-LaNi₅^[4~8], Mg-FeTi^[9~11], Mg-ZrNiCr, Mg-MnO₂, TiO₂, NiO^[12~15], these nanocomposite are very hopeful in application especially in the hydrogen-oxygen fuel cell. In this paper, we report the hydrogen storage properties of the ball-milled nanocomposite Mg-Ni-MnO₂, and temperature changes in hydriding and dehydriding process, and catalytic effect of MnO₂ in the nanocomposite.

2 EXPERIMENTAL

The nanocomposite was prepared from mixture

of three powders of Mg, Ni and MnO₂. Magnesium (Mg) powder (> 99%), nickel (Ni) powder (> 99.5%) and manganese dioxide (MnO₂) were provided by manufacturer of Shanghai Chemical Reagent Company. The powder's average size was 20 μm as reported by the manufacturer. The three kinds of powders were mixed in stainless vial in mass ratio to 95: 3: 2 of Mg: Ni: MnO₂. The milling was carried out with a QM-1SP4 planetary ball-milling machine made in Nanyang University and balls of stainless steel with a ball to powder mass ratio of 10: 1. The ball's diameter is 20 mm and 10 mm respectively. The grinding was under hydrogen atmosphere (about 0.5 MPa). Because the samples absorb hydrogen in the ball milling process, hydrogen pressure can't keep constant. The hydrogen of the vials must be recharged to 0.5 MPa at intervals. Small amount of powder was taken for analysis and experiment of desorption and absorption hydrogen. All handling was in glove box under argon.

The hydriding/dehydriding cyclic experiments were carried out using the self-made apparatus whose schematic diagram and the reactor is shown in Fig. 1.

X-ray diffraction was performed on a Rigaku apparatus with Cu K_α radiation. The SEM images were obtained on a Hitachi S-570.

3 RESULTS AND DISCUSSION

3.1 Mechanical milling process

X-ray diffraction spectra as a function of milling time for the Mg-Ni-MnO₂ samples is shown in Fig. 2. It can be seen clearly that the intensity of the diffraction peaks of magnesium decrease rapidly as well as

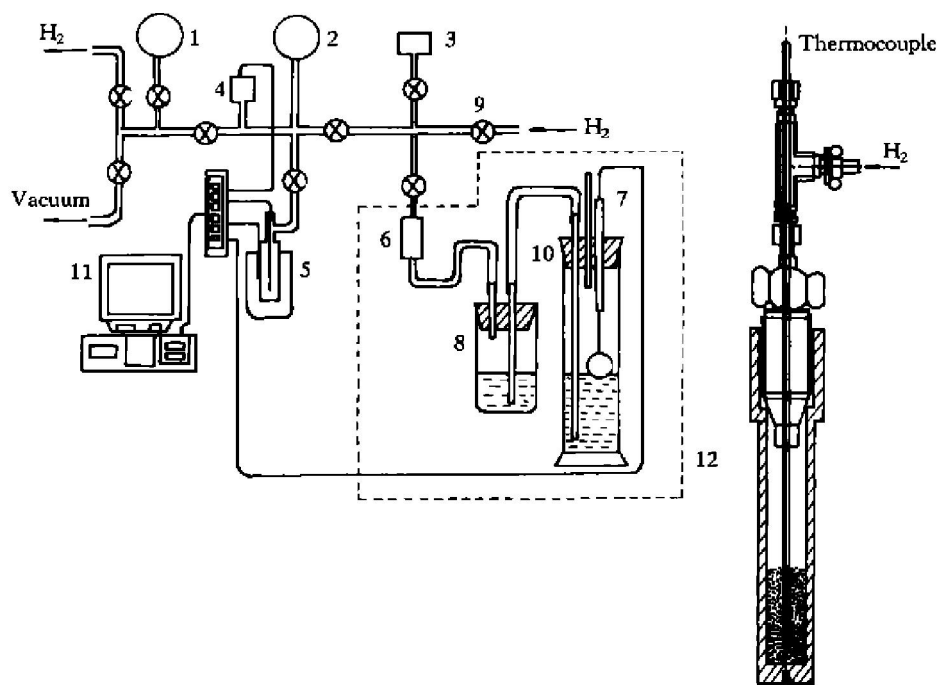


Fig. 1 Schematic diagram of hydriding/dehydriding apparatus

1—Vacuum meter; 2—Pressure meter; 3—Hydrogen storage container; 4—Pressure meter;
5—Reactor and heater; 6—Bellows sealed valves; 7—Displacement sensor; 8—Equilibrium container;
9—Valve; 10—Liquid level cylinder; 11—Computer digital record system; 12—Reactor and thermocouple

width of the peaks increase with increasing milling time. At the same time, the intensity and the width of the peaks of MgH_2 increase rapidly. From Fig. 2, we also observed that, after 82 h of milling, the characteristic diffraction peaks of Mg exist no longer. The diffraction peaks of MgH_2 became very broad, which proved that the crystalline size of MgH_2 diminished into the nanocrystalline range. From the width broadening of Mg peaks, it is considered that the crystalline of MgH_2 partly became amorphous.

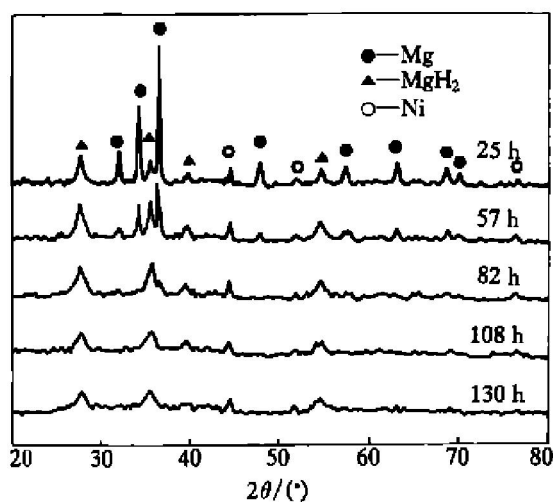


Fig. 2 X-ray diffraction patterns of $\text{Mg-1N}+2\text{MnO}_2$ samples milled for various times

Fig. 3 shows the microstructures of the sample milled for various times. we observed that when ball milling time is 25 h (Fig. 3(a)), the difference of diameter of powders is significant, but this difference

decreases as milling time increasing. When milling time is over 57 h, the average powder size is about $1.0 \mu\text{m}$. Even milling time reached 130 h, the average diameter almost doesn't change.

The powder size is one of key factors for kinetics in hydriding and dehydriding process. In general, small powders will possess bigger specific surface and more active sites for hydrogen decomposition and recombination, less length of hydrogen diffusion, higher surface energy that is helpful to hydrogen absorption and desorption. Big differences of powder diameters of the composite grains also result in negative influences on kinetics behavior of hydriding and dehydriding process.

3.2 Hydrogen storage properties

The nanocomposite $\text{Mg-3N}+2\text{MnO}_2$ possesses excellent kinetic properties even at moderate temperature. At the same time, since the ball milling process is under hydrogen pressure, the sample has already absorbed hydrogen in the milling process, and take places in situ activation, so that the composite can directly use in hydriding and dehydriding cycle and needn't any activation.

Fig. 4 shows absorption curves of the $\text{Mg-3N}+2\text{MnO}_2$ samples milled for various times at 473 K and under 2.0 MPa of hydrogen pressure (when hydriding process finished, the hydrogen pressure only about 1.2 MPa). It is clearly seen that the samples milled for 82 h display best kinetics in the hydriding process, it can absorb 6.2% (mass fraction) hydrogen in 50 s, the hydriding velocity is very amazing.

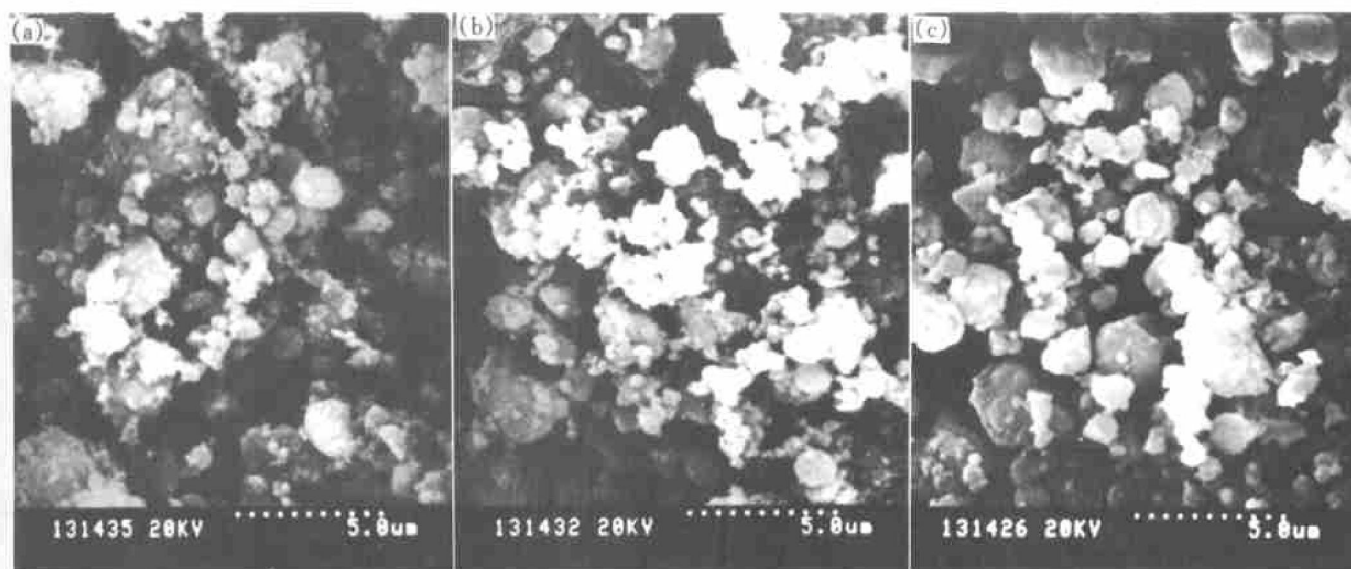


Fig. 3 SEM microstructures of samples milled for various times
(a) -25 h; (b) -57 h; (c) -108 h

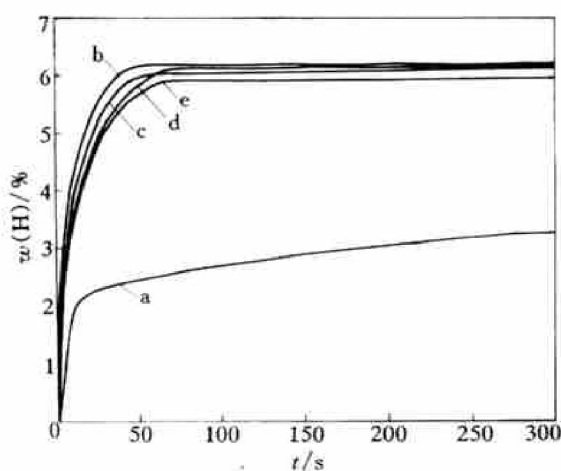


Fig. 4 Desorption curves of samples milled for various times

(a) -25 h; (b) -57 h; (c) -82 h; (d) -108 h; (e) -130 h

This fast hydriding process is due to ‘ignition process’. The ignition phenomena is shown in Fig. 5, it is observed that the temperature of sample quickly rises up to 415 °C in 5 s. In fact, the ‘ignition’ is not new concept, but it is a very important phenomena, it deserved especially attention. Magnesium reacts with hydrogen will release heat, the enthalpy of formation of MgH_2 is 74.3 kJ/mol^[2]. The large amount of heat will be produced from fast hydriding process, and it can’t transfer to environment in time, therefore there must take place ‘ignition’. Under same reaction condition, the hydriding/dehydriding kinetics was evaluated by ignition temperature. In general, if the sample possess well kinetics, it must take place ignition phenomena, and temperature will rise up to a higher level. Fig. 6 shows the absorption and temperature curves of sample milled for 25 h at 200 °C under 2.0 MPa. We observed that the sample has slow kinetics and the ignition temperature only reaches

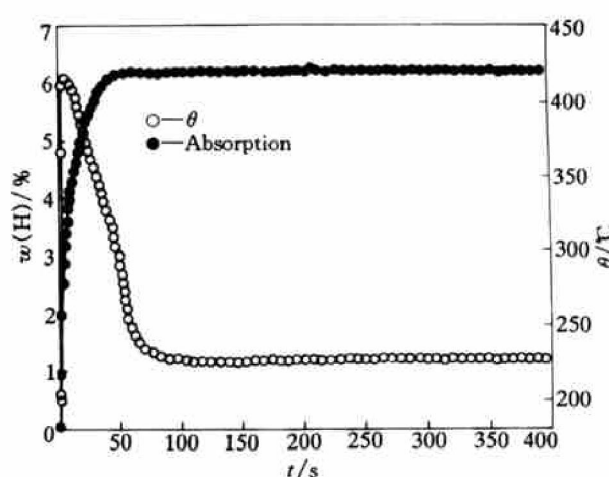


Fig. 5 Absorption ($w(H)$) and temperature of nanocomposite Mg-Ni-MnO_2 milled for 82 h at 200 °C under 2.0 MPa

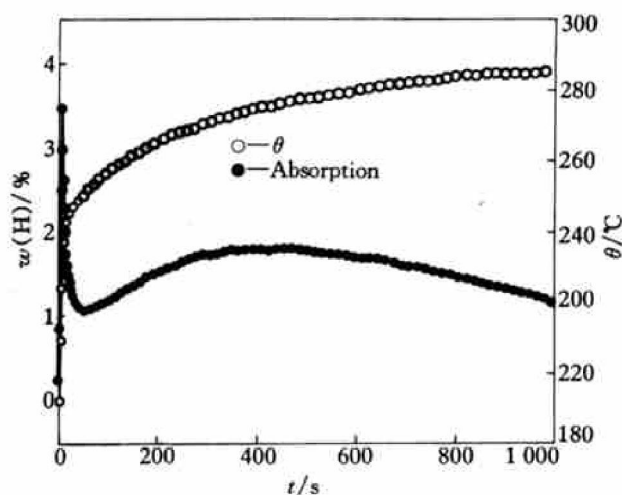


Fig. 6 Absorption and temperature of nanocomposite Mg-Ni-MnO_2 milled for 25 h at 200 °C under 2.0 MPa

280 °C, this shows that the kinetics of the sample is poor. In the short ball milling process, powder size is big and wasn't completely activated, and the Mg phase grain didn't tightly contact with Ni and MnO_2 grains.

Fig. 7 shows ignition temperature of the sample milled for various times. We noticed that when ball milling time exceeds over 82 h, for example, the samples milled for 108 h and 130 h, they didn't show better kinetics as expected, the ignition temperature is lower than that of the sample milled for 82 h. This may be caused by oxygenation in long time ball milling process and operation.

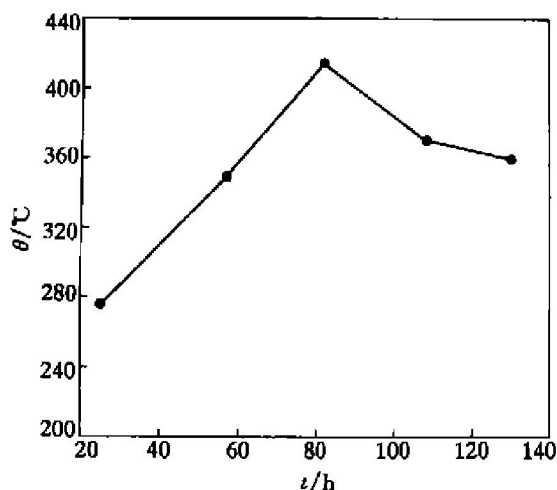


Fig. 7 Ignition temperature vs ball milling time of nanocomposite Mg-Ni-MnO₂

Fig. 8 shows desorption curves of the nanocomposite Mg-Ni-MnO₂ milled for various times, the sample milled for 82 h displayed remarkable dehydriding kinetics, it can desorb 6.2% (mass fraction) hydrogen in 400 s at 310 °C under 0.1 MPa. For the samples milled for 130 h (e) and 25 h (a) desorption velocity of the sample is slow. We experimented desorption of the sample milled for 82 h at various temperature of wall of reactor, the temperature is from 320 °C to 355 °C. the experiment results are shown in Fig. 9. It is clearly seen that the changes of desorption temperature of sample in reactor is very little, although the wall temperature of the reactor is from 320 °C to 355 °C. The desorption curve and temperature curve are shown in Fig. 10 and Fig. 11, respectively. It is observed that the temperature of dehydrogenation is changing in whole dehydriding process, and the temperature of sample is not equal to temperature of the wall of the reactor, especially in the initial stages. In dehydriding process, dehydriding velocity is not only related to hydrogen storage material self, but also related to heat transfer velocity. These show that heat transfer rate is a key fact in desorption process, it controls progress of desorption process. Fig. 12 shows the PCT curve of the Mg-Ni-MnO₂ at 300 °C. From Fig. 12, we observed

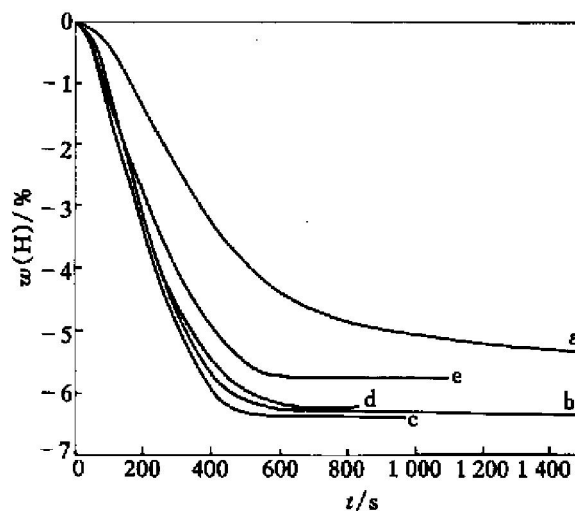


Fig. 8 Desorption curves of sample milled for various times at 310 °C under 0.1 MPa
(a) —25 h; (b) —57 h; (c) —82 h; (d) —108 h; (e) —130 h

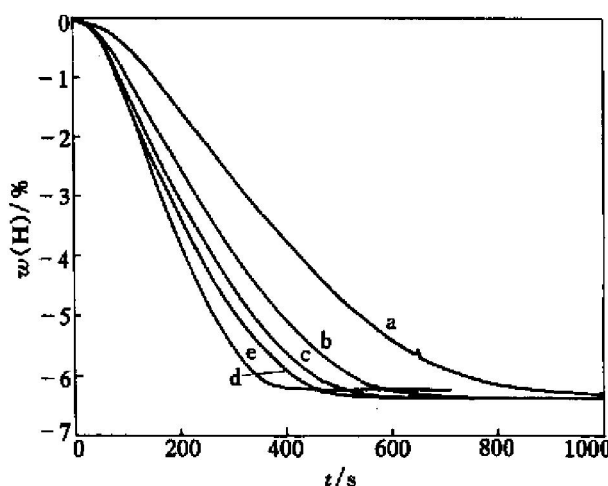


Fig. 9 Desorption curves of Mg-Ni-MnO₂ milled for 82 h at various wall temperatures of reactor
(a) —320 °C; (b) —330 °C; (c) —340 °C;
(d) —350 °C; (e) —355 °C

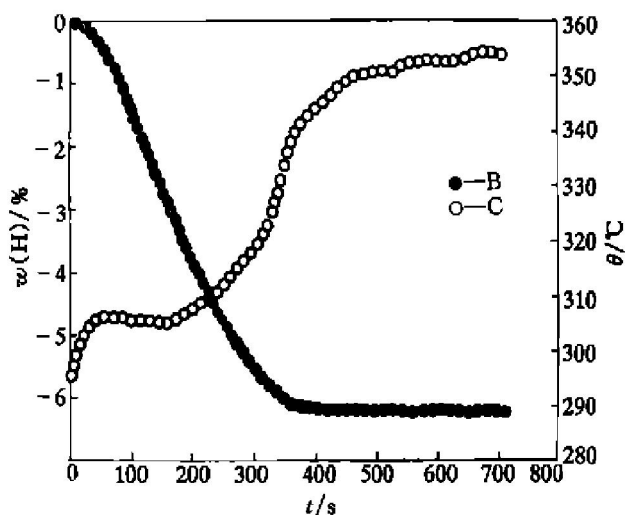


Fig. 10 Desorption and temperature of Mg-Ni-MnO₂ milled for 82 h when wall temperature of reactor being 350 °C

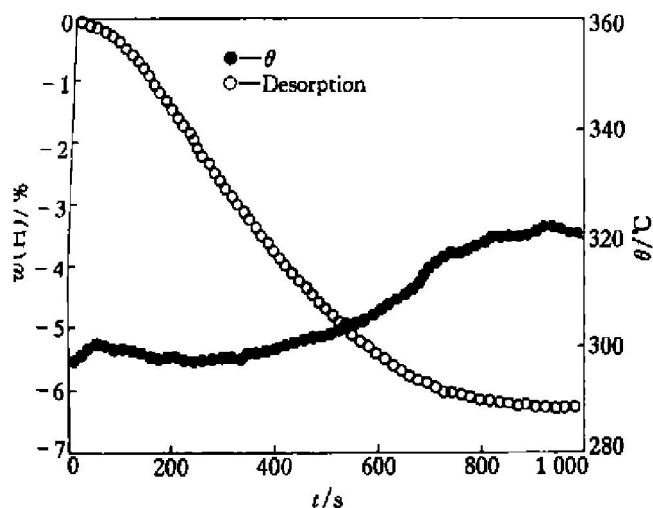


Fig. 11 Desorption and temperature curves of Mg-Ni-MnO₂ milled for 82 h when wall temperature of reactor being 320 °C

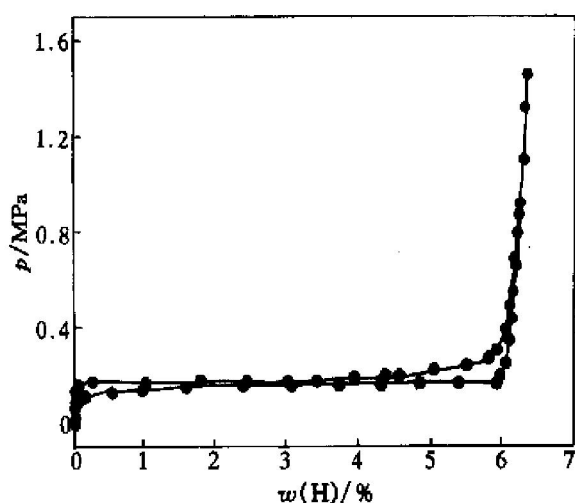


Fig. 12 Pressure-composing isothermal of nanocomposite Mg-3Ni-2MnO₂ milled for 82 h at 300 °C

that plateau pressure reaches 1.919×10^5 Pa at 300 °C and absorption and desorption hysteresis is little.

3.3 Catalytic effect of MnO₂

The nanocomposite has remarkable kinetics in hydriding/dehydriding process and lower desorption temperature, this is partly due to catalytic effect of MnO₂. During the long time ball milling process, MnO₂ grains and Ni grains can tightly contact with Mg grains. We all know that Ni has catalytic effect for hydriding/dehydriding process. In fact, the MnO₂ has more intense chemisorption for hydrogen, It even can decompose directly hydrogen molecular to hydrogen atoms on the surface of MnO₂ grain in the low temperature^[16]. MnO₂ also is a well known reducing reagent in hydrogen reductive process in catalytic chemistry^[16]. From above description, it is known that MnO₂ possesses bidirectional catalytic effect in hydriding and dehydriding process. In absorp-

tion process, hydrogen molecular decomposes easily to hydrogen atom on the surface of MnO₂ grain, this promote hydrogen atom diffuse into Mg matrix. In fact, the catalytic effect MnO₂ is proved even in the ball milling process. In Fig. 13, there are two XRD patterns corresponding to the Mg-3Ni (mass fraction, %) sample (1) and the Mg-Ni-MnO₂ sample (2), respectively, both samples were produced by ball milling for 52 h under hydrogen pressure (approximately 0.5 MPa) under same condition. We can observe clearly the difference of XRD patterns between (1) and (2), In XRD pattern (2), comparing XRD pattern (1), the magnesium peaks disappear more quickly and the intensity and width of MgH₂ peaks increase more quickly. This hydriding process shows that the MnO₂ in the Mg-Ni-MnO₂ sample has intense catalytic effect.

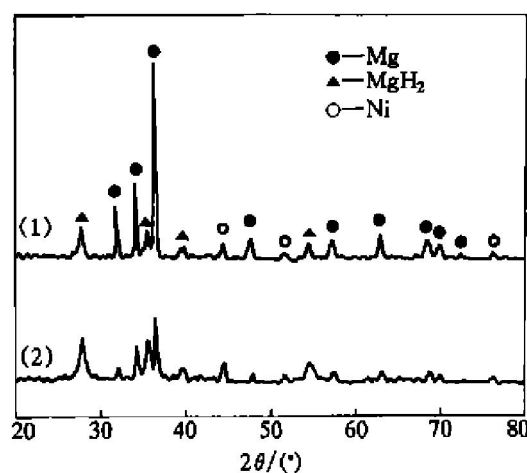


Fig. 13 X-ray patterns of samples milled for 52 h under hydrogen pressure (1) —Mg-3Ni; (2) —Mg-3Ni-2MnO₂(mass fraction, %)

In dehydriding process, the MnO₂ also shows catalytic effect, it can reduce desorption temperature and promote kinetics, the Mg-Ni-MnO₂ sample desorbs hydrogen more quickly and desorption temperature is 20~ 30 °C lower than that of the Mg-Ni sample.

4 CONCLUSION

The nanocomposite possess remarkable kinetics in hydriding/dehydriding process, especially in absorption hydrogen, it displays excellent kinetics. In the fast absorption hydrogen process, the nanocomposite will trigger the 'ignition process', the temperature will reach 415 °C in 5 s, and the hydriding process can finish in 50 s. This indicates that the nanocomposite has promising application as hydrogen storage materials for fuel cell.

The nanocomposite Mg-3Ni-2MnO₂ is made by ball milling process under hydrogen pressure, the composite can completely absorbs hydrogen during mechanically milling process and it needn't any acti-

vation before using for hydriding/dehydriding process. it is found that the nanocomposite milled for 82 h has best kinetics. When ball milling exceeds 82 h, the composite doesn't show better kinetics, this may be caused oxygenation in handling process.

The dehydriding kinetics behavior is related to heat transfer rate of circumstance, and on the whole, temperature of hydriding process keep constant in the initial stage. In some content, it is considered that heat transfer rate is controlling step in hydriding process.

MnO₂ has obvious key effect on hydriding and dehydriding process, it can promote kinetics behavior and reduce temperature of hydriding process.

[REFERENCES]

- [1] Zaluska A, Zaluski L, Ström-Olsen J O. Nanocrystalline magnesium for hydrogen storage [J]. J Alloys Comp, 1999, 288: 217– 225.
- [2] Liang G, Huot J, Boily S, et al. Hydrogen storage properties of the mechanically milled MgH₂-V nanocomposite [J]. J Alloys Comp, 1999, 291: 295– 299.
- [3] Liang G, Huot J, Baily S, et al. Hydrogen storage in mechanically milled Mg-LaNi₅ and MgH₂-LaNi₅ composite [J]. J Alloys Comp, 2000, 297: 261– 265.
- [4] Zaluska A, Zaluski L, Ström-Olsen J O. Synergy of hydrogen sorption in ball-milled hydrides of Mg and Mg₂Ni [J]. J Alloys Comp, 1999, 289: 197– 206.
- [5] Sun Dalin, Enoki H, Bououdina M, et al. Phase components and hydriding properties of the sintered Mg-*x*% LaNi₅ (*x* = 20~ 50, mass fraction) composites [J]. J Alloys Comp, 1999, 282: 252– 257.
- [6] Sai Raman S S, Srivastava O N. Hydrogenation behaviour of the new composite storage aterials Mg-*x*% CFMmNi₅(mass fraction) [J]. J Alloys Comp, 1996, 241: 167– 174.
- [7] Liang G, Boily S, Huot J, et al. Hydrogen absorption properties of a mechanically milled Mg-50% LaNi₅ composite [J]. J Alloys Comp, 1998, 268: 302– 307.
- [8] Terzieva M, Khrussanova M, Peshev P. Hydriding and dehydriding characteristics of Mg-LaNi₅ composite materials prepared by mechanical alloying [J]. J Alloys Comp, 1998, 267: 235– 239.
- [9] GUO X L, WANG E D, Fangshoushi. Hydrogen absorption and desorption characteristics of mechanically milled Mg-35% (mass fraction) FeTi_{1.2} powders [J]. J Alloys Comp, 1995, 223: 111– 114.
- [10] Schlaphbach L, Seiler A, Stucki F. Surface segregation in FeTi and its catalytic effect on the hydrogenation [J]. Mat Res Bull, 1978, 13: 697– 706.
- [11] Dutta K, Mandal P, Ramakrishna K, et al. The synthesis and hydrogenation behavior of some new composite storage materials: Mg-*x*% (mass fraction) FeTi (Mn) and La₂Mg₁₇-*x*% (mass fraction) LaNi₅[J]. Int J of Hydrogen Energy, 1994, 19: 253– 257.
- [12] Jun Yang, Ciureanu M, Roberge R. Hydrogen storage properties of nanocomposite of Mg and Zr-Ni-Cr alloys [J]. Materials Letters, 2000, 43: 243– 239.
- [13] Song M Y, Park H R. Verification of the rate-controlling step in the dehydriding reaction of Mg₂Ni hydride [J]. Journal of Materials Science Letters, 1997, 16: 1774– 1775.
- [14] Wang P, Wang A M, Zhang H F, et al. Hydrogen characteristics of Mg-TiO₂(rutile) composite [J]. J Alloys Comp, 2000, 313: 218– 223.
- [15] WU Yue. Catalytic Chemistry [M], (in Chinese). Beijing: Science Press, 1998. 1179.

(Edited by HUANG Jin-song)