한국수소 및 신에너지학회 논문집(2005.3), 제16권 제1호
Trans. of the Korean Hydrogen and New Energy Society (2005.3), Vol. 16, No. 1, pp. 25~30

반응성 기계적 분쇄에 의해 제조한 Mg-10wt.% MnO의 수소 저장 성질

송명엽†*, 권익현*, 권성남*, 박찬기*, 배종수**
*전북대학교 공학연구원 공업기술연구센터 신소재공학부
**한국기계연구원 재료연구부 나노분말재료그룹

Hydrogen Storage Properties of Mg-10wt.%MnO Prepared by Reactive Mechanical Grinding

Myoungyoup Song†*, Ikhyun Kwon*, Sungnam Kwon*, Changi Park*, and Jong Soo Bae**
**Division of Advanced Materials Engineering, Research Center of Industrial Technology, Engineering Research Institute, Chonbuk National University, 664-14 1ga Deogjindong Deogjingu Jeonju, Chonbuk, 561-756, Republic of Korea*
***Nanopowder Materals Group, Materials Technology Department, Korea Institute of Machinery & Materials, 66 Sangnamdong, Changwon, Kyungnam, Republic of Korea*

ABSTRACT

수소 분위기에서 10wt.%MnO와 기계적인 분쇄(반응성 기계적 분쇄)에 의해 Mg의 수소 저장 성질을 향상시켰다. 회전 속도는 250 rpm, 밀링시간은 2 h, 그리고 시료 대 볼 중량비는 1/45이었다. 준비한 Mg-10wt.%MnO 시료는 활성화를 위한 수소화물 형성 분해 싸이클링이 필요없었으며, 첫 번째 싸이클 593K 12 bar H_2에서, 10분 동안에 3.12wt.%, 60분 동안에 3.95wt.%의 수소를 흡수하였다. 또한 Mg-10wt.%MnO는 593K 0.8 bar H_2에서 60분 동안에 2.12wt.%의 수소를 방출하였다. MnO와 Mg의 방응성 분쇄는, 핵생성을 용이케 하고 (Mg 입자의 표면에 결함 형성과 첨가물에 의해), Mg 입자의 표면에 crack을 만들어 Mg의 입자 크기를 줄여 그 결과 수소 원자의 확산 거리를 작게 함으로써 수소 흡수 방출 속도를 증가시킨다. 수소화물 형성 분해 싸이클링은 Mg 입자의 표면에 crack을 만들고 Mg의 입자 크기를 줄여 수소 흡수 방출 속도를 증가시킨다.

주요기술용어 : H_2 sorption properties of Mg (Mg의 수소저장성질), MnO addition (MnO 첨가), Reactive mechanical grinding (반응성 기계적 분쇄), Hydriding and dehydriding rates (수소화물 형성 • 분해 속도), Nucleation (핵생성), Diffusion distance (확산거리).

1. Introduction

Magnesium has many advantages for a hydrogen storage material : large hydrogen storage capacity (7.6wt.%), low cost and abundance in the earth's crust. But its hydriding and dehydriding kinetics are very

---

† Corresponding author : songmy@chonbuk.ac.kr

slow. A lot of work to ameliorate the reaction kinetics of magnesium with hydrogen has been done by alloying certain metals with magnesium[1~4], by mixing metal additives with magnesium, by plating nickel on the surface of magnesium [5].

Song[6] reviewed the kinetic studies of the hydriding and the dehydriding reactions of Mg. Many works do not agree with one another on the rate controlling step(s) for hydriding or dehydriding of magnesium. However, there is no contradiction in the points that the hydriding and dehydriding reactions of Mg are nucleation controlled under certain conditions and progress by a mechanism of nucleation and growth, and that the hydriding rates of Mg are controlled by the diffusion of hydrogen through a growing Mg hydride layer.

The hydriding and dehydriding kinetics of Mg can be improved, therefore, by a treatment such as mechanical alloying[7~10] which can facilitate nucleation by creating many defects on the surface and/or in the interior of Mg, or by the additive acting as active sites for the nucleation, and shorten diffusion distances by reducing the effective particle sizes of Mg.

Bobet et al.[11] reported that mechanical alloying in H_2(Reactive Mechanical Grinding) for a short time(2 h) is an effective way to improve strongly the hydrogen storage properties of both magnesium and Mg+10wt.%Co, Ni or Fe mixtures.

The oxides are brittle, and thus they may be pulverized during mechanical grinding. The added oxides and/or their pulverization during mechanical grinding may help the particles of magnesium become finer.

In this work, we chose MnO as the oxide to add to Mg. Mg-10wt.%MnO alloys were prepared by mechanical grinding under H_2 (reactive mechanical grinding) in a planetary ball mill and their hydrogen storage properties were investigated.

2. Experimental details

Pure Mg powder(particle size 50 μm) was mixed with 10wt.% MnO (Manganese(Ⅱ) oxide, purity 99%, Aldrich) (sample total weight = 8g) in a stainless steel container with hardened steel balls (total weight = 360g) closed in a hermetic way. The average particle size of MnO was smaller than 88 250 μm. All the handlings were performed in a glove box under Ar in order to prevent oxidation. The mill container was then filled with high purity hydrogen gas (≈ 10bar). The disc revolution speed was 250 rpm and the milling time was 2 h. These milling conditions were chosen because Mg-10wt.%Fe_2O_3 prepared before under these conditions exhibited good hydrogen storage properties[12].

The hydriding apparatus has been described

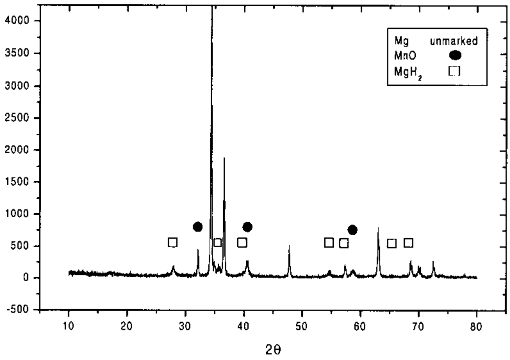

Fig. 1. X ray(CuKα) powder diffraction patterns of Mg 10wt.% MnO as prepared at 250rpm for 2 h with weight ratio of sample to ball 1/45.

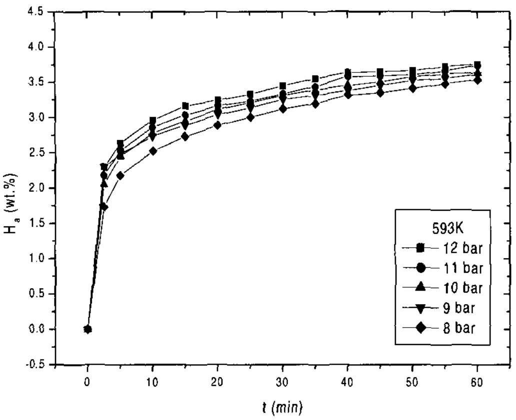

Fig. 2. Microstructure observed by SEM of Mg 10wt.% MnO as prepared at 250 rpm for 2h with weight ratios of sample to ball 1/45.

previously[13]. The absorbed or desorbed hydrogen quantity was measured as a function of time by a volumetric method. X ray diffraction (XRD) analysis was carried out for the as milled powders. The microstructures were observed by SEM (scanning electron microscope).

3. Results and discussions

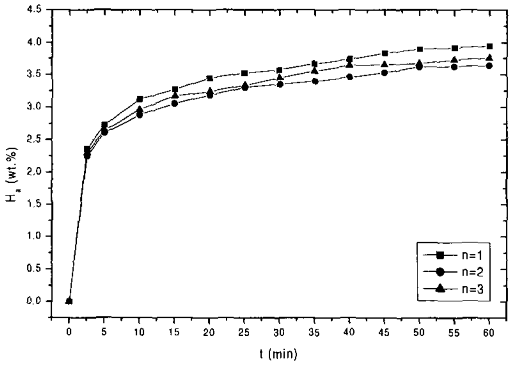

Fig. 3. Variations of Ha versus t curves of Mg 1 10wt.%MnO at 593K, 12 bar H_2 according to the number of cycles n.

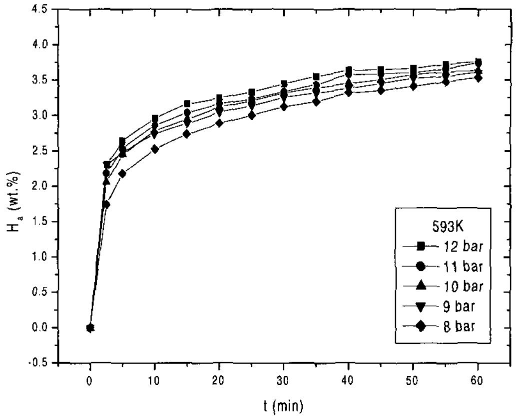

Fig. 4. Ha versus t curves of Mg10wt.% MnO under various hydrogen pressures at 593K.

Fig. 1 shows the X ray (CuKα) powder diffraction patterns of Mg-10wt.%MnO as prepared by milling at the revolution speed of 250 rpm for 2 h with weight ratio of sample to ball 1/45. The samples as prepared contain Mg, MnO and a small amount of MgH_2.

Fig. 2 gives the microstructure observed by SEM for Mg-10wt.%MnO as prepared by milling at the revolution speed 250 rpm for 2 h with ratio of sample to ball 1/45. The samples have both small and large particles. The large particles have cracks with MnO on the surface.

Fig. 3 shows the variations of weight percentage of hydrogen Ha absorbed by Mg-10wt.%MnO as a function of time t(min) at 593K, 12 bar H_2 according to the number of hydriding dehydriding cycles n. The percentages of absorbed hydrogen Ha are expressed with respect to the sample weight. As the number of hydriding dehydriding cycles increases, the hydriding rates decrease. It shows that hydriding dehydriding cycling for activation is not required. The Ha value after 10min is 3.12 wt.% and that after 60 min is 3.95 wt.% at the first cycle.

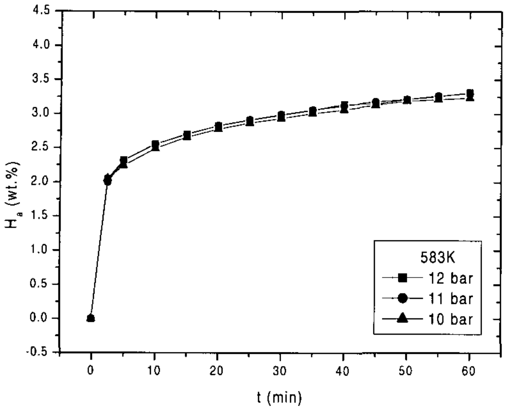

Fig. 5. Ha versus t curves of Mg wt.% MnO under various hydrogen pressures at 583K.

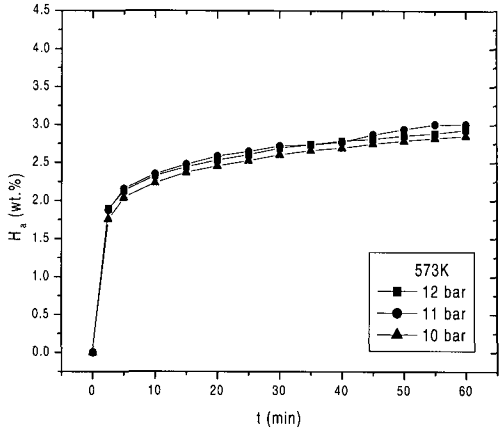

Fig. 6. Ha versus t curves of Mg 10wt.% MnO under various hydrogen pressures at 573K.

The reactive grinding of Mg with MnO increases the hydriding rates by facilitating nucleation (by creating defects on the surface of the Mg particles and by the additive) and by reducing the particle size of Mg and thus by shortening the diffusion distances of hydrogen atoms.

Fig. 4 shows the Ha versus t curves at 593K under various hydrogen pressures for Mg-10wt.%MnO milled with the weight ratio of sample to ball 1/45. As the hydrogen pressure increases, the hydriding rate becomes higher.

Fig. 5 and Fig. 6 show the Ha versus t curves under various hydrogen pressures at 583K and 573K, respectively, for Mg-10wt.%MnO milled with the weight ratio of sample to ball 1/45.

Fig. 7 gives the variations in the weight percentage of the desorbed hydrogen with respect to the sample weight, Hd(wt.%), at 593K under 1.0 1.8 bar H_2 by Mg-10wt.%MnO milled with the weight ratio of sample to ball 1/45. Before obtaining these curves, the sample was hydrided under 12 bar H_2 for 1 h at 593K. As the hydrogen pressure decreases, the dehydriding rate becomes higher. The hydrided sample desorbs 2.12 wt.% hydrogen at 593K, 0.8 bar H_2 for 60 min.

Fig. 8 shows a Pressure Composition Isotherm for Mg-10wt.%MnO at 593K. Before obtaining the data for the curve, the sample was hydrided for about 65 hours at 593K. The data points were obtained every two hours. The hydrogen storage capacity at 593K is about 5.73 wt.%. The isotherm shows a plateau at about 1.6 bar H_2.

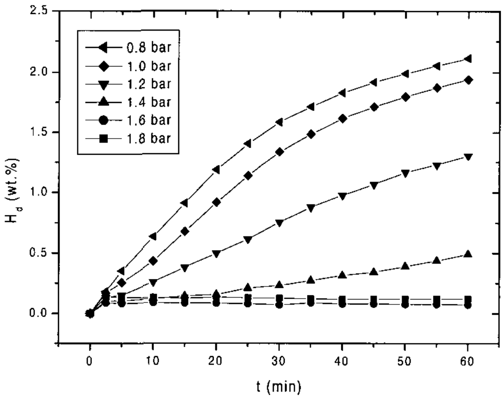

Fig. 7. Hd versus t curves of Mg wt.% MnO under various hydrogen pressures at 593K.

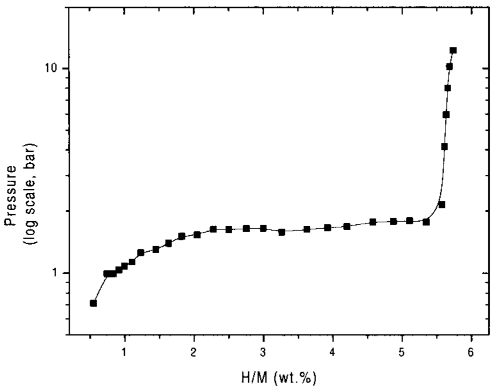

Fig. 8. Pressure composition isotherm of Mg 10 wt.%MnO H2 system at 593K.

From the results of hydriding rates and microstructure, it is considered that the hydriding dehydriding cycling increases the H_2 sorption rates by facilitating nucleation(by creating defects on the surface of the Mg particles), by making cracks on the surface of Mg particles and reducing the particle size of Mg and thus by shortening the diffusion distances of hydrogen atoms.

4. Conclusions

The samples Mg-10wt.%MnO were prepared by mechanical grinding under H_2 (reactive mechanical grind) with weight ratio of sample to ball 1/45 at a revolution speed 250 rpm for 2 h. The sample Mg-10wt.%MnO prepared likewise does not require hydriding dehydriding cycling for activation. It absorbs 3.12 wt.% hydrogen for 10 min and 3.95 wt.% hydrogen for 60 min at the first cycle at 593K under 12 bar H_2. The sample desorbs 2.12 wt.% hydrogen at 593K, 0.8 bar H2 for 60 min. The reactive grinding of Mg with MnO increases the H_2 sorption rates by facilitating nucleation(by creating defects on the surface of the Mg particles and by the additive), by making cracks on the surface of Mg particles and reducing the particle size of Mg and thus by shortening the diffusion distances of hydrogen atoms. Hydriding dehydriding cycling increases the H_2

surface of Mg particles and reducing the particle size of Mg.

Acknowledgements

This research was performed for the Hydrogen Energy R&D Center, one of the 21st Century Frontier R&D Program, funded by the Ministry of Science and Technology.

References

1) D. L. Douglass: "The Formation and Dissociation of Magnesium Alloy Hydrides and Their Use for Fuel Storage in the Hydrogen Car", Metall. Trans., vol. A6, 1975, p. 2179.

2) M. H. Mintz, Z. Gavra and Z. Hadari: "Kinetic Study of the Reaction between Hydrogen and Magnesium, catalyzed by Addition of Indium", J. Inorg. Nucl. Chem, vol. 40, 1978, p. 756.

3) Q. Wang, J. Wu, M. Au and L. Zhang: "The Hydrogen Storage Properties and the Mechanism of the Hydriding Process of Some Multi Component Magnesium Base Hydrogen Storage Alloys", in "Hydrogen Energy Progress V", Proceedings 5th World Hydrogen Energy Conference, Toronto, Canada, July 1984. Vol. 3, edited by T. N. Veziroğlu and J. B. Taylor (Pergamon, New York), 1984, p. 1279.

4) M.Y. Song, M. Pezat, B. Darriet, J. Y. Lee

and P. Hagenmuller: “A Hydriding Kinetic Model of the Mg_2Ni $_2$ System”, J. Mater. Sci., vol. 21, 1986, p. 346.

5) F. G. Eisenberg, D. A. Zagnoli and J. J. Sheridan Ⅲ: “The Effect of Surface Nickel on the Hydriding Dehydriding Kinetics of MgH2”, J. Less Common Met., vol. 74, 1980, p. 323.

6) M.Y. Song: “Improvement in Hydrogen Storage Characteristics of Magnesium by Mechanical alloying with Nickel”, J. Mater. Sci., vol. 30, 1995, p. 1343.

7) M.Y. Song, E.I. Ivanov, B. Darriet, M. Pezat and P. Hagenmuller: “Hydriding Properties of a Mechanically Alloyed Mixture with a composition Mg_2Ni”, Int. J. Hydrogen Energy, vol. 10, No. 3, 1985, p. 169.

8) M.Y. Song, E. I. Ivanov, B. Darriet, M. Pezat and P. Hagenmuller: “Hydriding Dehydriding Characteristics of Mechanically Alloyed Mixtures Mg wt.%Ni(x = 5, 10, 25 and 55)”, J. Less Common Met., vol. 131, 1987, p. 71.

9) M.Y. Song: “Effects of Mechanical Alloying on the Hydrogen Storage Characteristics of Mg x wt.%Ni(x = 5, 10, 25 and 55) Mixtures”, Int. J. Hydrogen Energy, vol. 20, No. 3, 1995, p. 221

10) M.Y. Song: "Development of Mg-10wt.%Ni Hydrogen-Storage Alloy by Mechanical Alloying", J. of the Korean Hydrogen Energy Society, vol. 9, No. 4, 1998, p. 143.

11) J L. Bobet, E. Akiba, Y. Nakamura and B. Darriet: “Study of Mg Ni and Fe) Mixture Elaborated by Reactive Mechanical Alloying Hydrogen Sorption Properties”, Int. J. Hydrogen Energy, vol. 25, 2000, p. 987.

12) M.Y. Song, I.H. Kwon, S.N. Kwon, C.G. Park and J.S. Bae: “Preparation of Hydrogen Storage Alloy Mg wt.%Fe_2O_3 under Various Milling Conditions”, Collected Papers of Korean Hydrogen and New Energy Society Autumn Annual Meeting 2004, p. 293.

13) M.Y. Song, D.S. Ahn, I.H. Kwon, H.J. Ahn: “Development of Hydrogen storage Alloys by Mechanical Alloying Mg with Fe and Co”, Metals and Materials International, vol. 5, No. 5, 1999, p. 485.