

반응성분쇄에 의해 CoO를 첨가한 Mg의 수소저장특성

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Hydrogen-storage Properties of CoO-Added Mg by Reactive Grinding

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ABSTRACT

We tried to improve the H₂-sorption properties of Mg by mechanical grinding under H₂ (reactive grinding) with CoO. The sample Mg+10wt.%CoO as prepared absorbs 1.25wt.% hydrogen and the activated sample absorbs 2.39wt.% hydrogen for 60min at 598K, 11.2barH₂. The reactive grinding of Mg with CoO increases the H₂-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 H₂-sorption rates by making cracks on the surface of Mg particles and reducing the particle size of Mg.

주요기술용어 : H₂-sorption properties of Mg, CoO addition(CoO를 첨가한 수소저장특성), Reactive grinding(반응성 분쇄), Hydriding rates(수소화물형성속도), Dehydriding rates(수소화물분해속도), Particle-size distribution(입도분포).

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 slow¹⁾. A lot of work to ameliorate the reaction kinetics of magnesium with hydrogen has been done by alloying certain metals with magnesium²⁻¹⁰⁾, by mixing metal additives with magnesium¹¹⁾, by plating nickel on the surface of magnesium¹²⁾.

Song¹³⁾ 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 alloying¹⁴⁻¹⁶⁾ 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.¹⁷⁾ reported that mechanical alloying in H₂(Reactive Mechanical Grinding) for a short time(2h) 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 tried to improve the hydrogen sorption properties of Mg by mechanical grinding under H₂ (reactive grinding) with CoO.

10wt.%CoO (total weight = 8g) in a stainless steel container (with 17 hardened steel balls, total weight = 72g) closed in a hermetic way. The average particle size of CoO was 294 μ m. All the handlings were performed in a glove box under Ar in order to prevent oxidation. The mill container was then evacuated to primary vacuum (10-4bar) prior to filling with high purity hydrogen gas (11bar). The disc rotation speed was fixed to 200 rpm for all the experiments. The experimental procedure was as follows ; 15 min of milling, 5 min of rest, 15 min of milling, refilling with H₂ gas (11bar). This procedure was repeated until the total expected milling time 2h was reached.

The hydriding apparatus has been described previously¹⁸⁾. 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 and for the

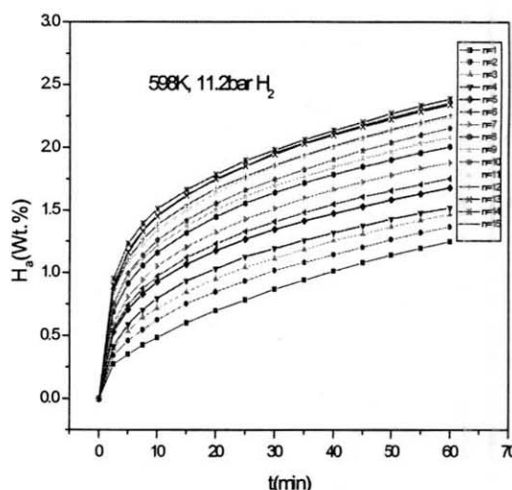


Fig. 1. Variations in Ha by Mg+10wt.%CoO as a function of time t under 11.2bar H₂ at 598K according to the number of hydriding-dehydriding cycles n.

2. Experimental details

Pure Mg powder was mixed with

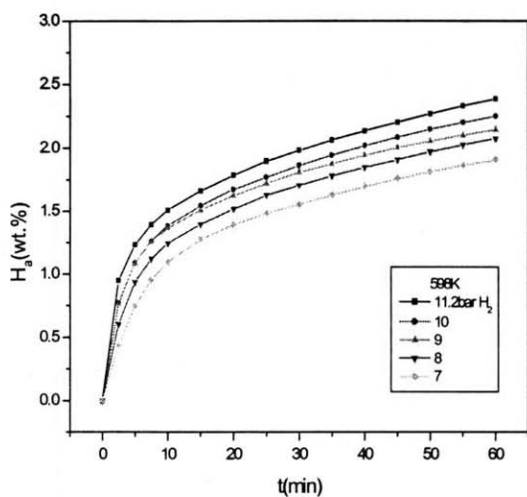


Fig. 2. H_a versus t curves for activated Mg+10wt.%CoO at 598K under various hydrogen pressures.

samples after hydriding-dehydriding cycling. The microstructures were observed by SEM (scanning electron microscope).

3. Results and discussions

Fig. 1 shows the variations of weight percentage of hydrogen H_a absorbed by Mg+10wt.%CoO as a function of time t (min) under 11.2bar H_2 at 598K according to the number of hydriding-dehydriding cycles n . The percentages of absorbed hydrogen H_a are expressed with respect to the sample weight. As the number of hydriding-dehydriding cycles increases, the hydriding rates increase. After the 14th hydriding cycle the hydriding rates decrease. It is considered that the activation is accomplished after the 14th hydriding cycle. The H_a value after 60min is 2.39wt.% at $n=14$.

Fig. 2 shows the H_a versus t curves for the activated Mg+10wt.%CoO at 598K under various hydrogen pressures. As the hydrogen

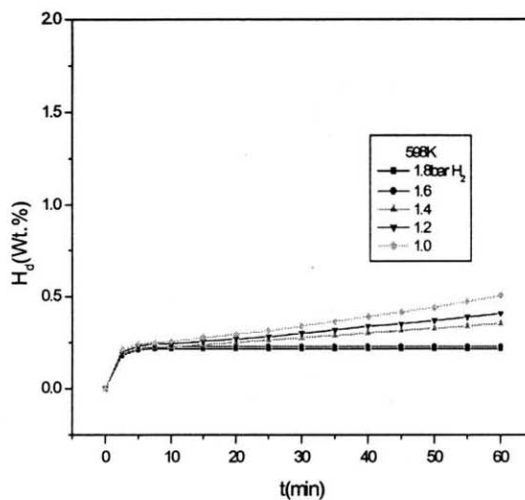


Fig. 3. H_d versus t curves for activated Mg+10wt.%CoO at 598K under 1.0-1.8bar H_2 .

pressure increases, the hydriding rate becomes higher.

The reactive grinding of Mg with CoO 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. 3 gives the variations in the weight percentage of the desorbed hydrogen with respect to the sample weight, H_d (wt.%), by the activated Mg+10wt.%CoO at 598K under 1.0-1.8bar H_2 . Before obtaining these curves, the sample was hydrided under 11.2bar H_2 for 2h at 598K. As the hydrogen pressure decreases, the dehydriding rate becomes higher.

Fig. 4 shows the H_a vs. t curves and H_d vs. t curves at various temperatures under similar hydrogen pressures.

Fig. 5 shows the X-ray (CuK α) power diffraction pattern of Mg+10wt.%CoO (a) as

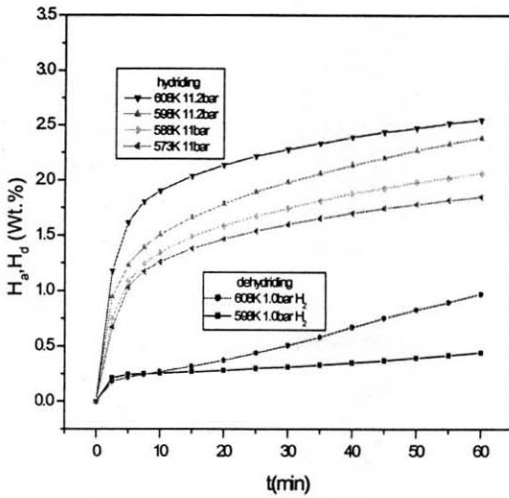


Fig. 4. H_a vs. t curves and H_d vs. t curves at various temperatures and under similar hydrogen pressures.

prepared and (b) after 14 hydriding-dehydriding cycles (at 598K, 0-11.2bar H_2 for 22 days). The sample as prepared contains Mg and small amounts of MgH_2 , MgO and CoO. The sample after 14 cycles contains MgH_2 , Mg and small amounts of CoO and MgO.

Fig. 6 gives the microstructures observed by SEM for the sample Mg+10wt.%CoO; (a) as prepared and (b) after 47 hydriding-dehydriding cycles. The Mg particles in the sample as prepared have similar sizes whose shapes are spherical or oval-like. The sample after cycling has small particles and large particles with many defects on the surface. The sample Mg+10wt.%CoO after cycling has many small particles, and cracks are observed in the large particles. The expansion and contraction of Mg with hydriding-dehydriding cycling is considered to lead to the formation of many defects and cracks and the diminution of the particle size.

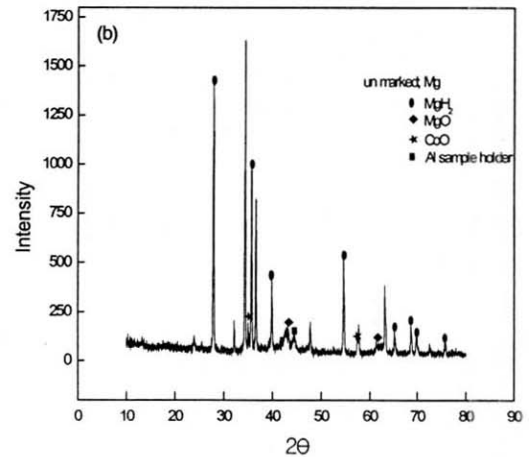
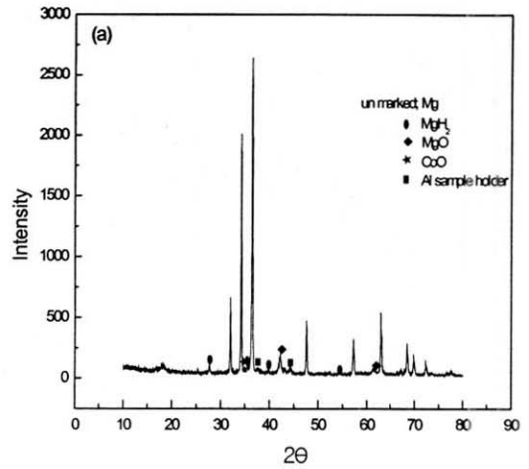


Fig. 5. X-ray (CuK α) powder diffraction pattern of Mg+10wt.%CoO (a) as prepared and (b) after 14 hydriding-dehydriding cycle at 598K

Fig. 7 shows the particle size distribution of the sample Mg+10wt.%CoO (a) as prepared and (b) after 47 hydriding-dehydriding cycles, measured by a particle-size analyzer. For the sample as prepared it is measured two times. The sizes of the particles as prepared are 10-900nm and their medium size 294nm. The sizes of the particles after 47 cycles are 1-600nm and their medium size is about 190nm, showing

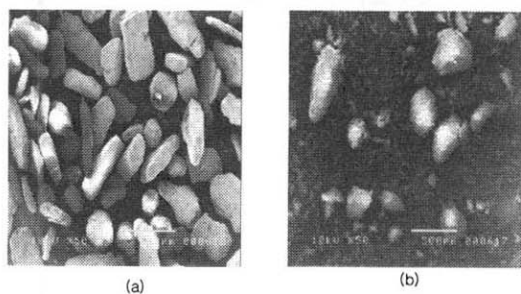


Fig. 6. Microstructures observed by SEM of the sample Mg+10wt.%CoO; (a) as prepared and (b) after 47 hydriding-dehydriding cycles.

that the particles become smaller after cycling. The volume(%) vs. particle size(μm) curve exhibits two maxima around the particle sizes of about 40 and 300 μm , indicating that the sample has two kinds of particles, the smaller particles with about particle size 40 μm and the larger particles with about particle size 300 μm . The curve for the sample after cycling exhibits two maxima around the particle sizes of about 9 μm and 250 μm . These particle sizes for the two maxima are smaller than those for Mg+10wt.%CoO as prepared, indicating that the particles become smaller after hydriding-dehydriding cycling. The specific surface area of the samples after cycling is 0.28 m^2/cm^3 .

From the results of hydriding rates, microstructure and particle size distribution of the samples, 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.

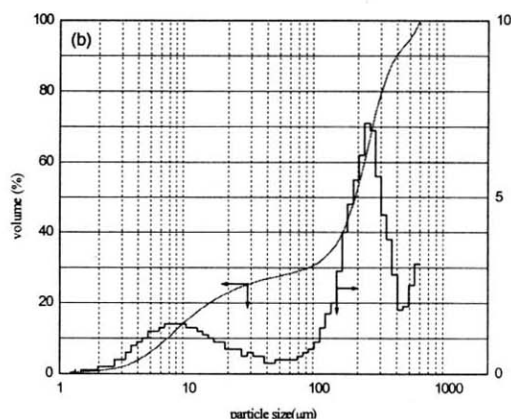
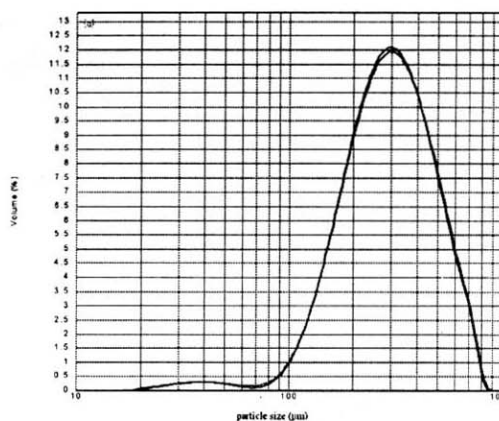


Fig.7. Particle size distribution of the sample Mg+10wt.%CoO; (a) as prepared and (b) after 47 hydriding-dehydriding cycles.

4. Conclusions

We tried to improve the H_2 -sorption properties of Mg by mechanical grinding under H_2 (reactive grinding) with CoO. The sample Mg+10wt.%CoO as prepared absorbs 1.25wt.% hydrogen and the activated sample absorbs 2.39wt.% hydrogen for 60min at 598K, 11.2bar H_2 . The reactive grinding of Mg with CoO 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 H₂-sorption rates by making cracks on the surface of Mg particles and reducing the particle size of Mg.

Acknowledgements

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References

- 1) A. Vose, Metal Hydrides, U.S. Patent 2 Vol. 944, 1961, p. 587.
- 2) J. J. Reilly and R. H. Wiswall, Inorg. Chem Vol. 6, No. 12, 1967; p. 2220.
- 3) J. J. Reilly and R. H. Wiswall Jr, Inorg. Chem, Vol. 7, No. 11, 1968; p. 2254.
- 4) D. L. Douglass, Metall. Trans, A6, 1975, p. 2179.
- 5) M. H. Mintz, Z. Gavra and Z. Hadari, J. Inorg. Nucl. Chem., Vol. 40, No. 12, 1978, p. 765.
- 6) M. Pezat, A. Hbika, B. Darriet and P. Hagenmuller, French Anvar Patent 78 203 82, 1978, Mater. Res. Bull Vol. 14, 1979, p. 377.
- 7) M. Pezat, B. Darriet and P. Hagenmuller, J. Less-Common Met Vol. 74, 1980, p. 427.
- 8) Q. Wang, J. Wu, M. Au and L. Zhang, in Hydrogen Energy Progress V, Proceedings 5th World Hydrogen Energy Conference, Toronto, Canada, Vol. 3, July 1984, edited by T. N. Vezirođlu and J. B. Taylor (Pergamon, New York) pp. 1279-1290.
- 9) E. Akiba, K. Nomura, S. Ono and S. Suda, Int. J. Hydrogen Energy, Vol. 7, No. 10, 1982, p. 787.
- 10) J. M. Boulet and N. Gerard, J. Less-Common Met., Vol. 89, No. 12, 1983, p. 151.
- 11) B. Tanguy, J. L. Soubeyroux, M. Pezat, J. Portier and P. Hagenmuller, Mater. Res. Bull, Vol. 11, 1976, p. 1441.
- 12) F. G. Eisenberg, D. A. Zagnoli and J. J. Sheridan III, J. Less-Common Met., Vol. 74, 1980, p. 323.
- 13) M. Y. Song, J. Mater. Sci 1995;30:1343.
- 14) M.Y. Song, E.I. Ivanov, B. Darriet, M. Pezat and P. Hagenmuller, Int. J. Hydrogen Energy, Vol. 10, No. 3, 1985, p. 169.
- 15) M.Y. Song, E. I. Ivanov, B. Darriet, M. Pezat and P. Hagenmuller, J. Less-Common Met, Vol. 131, 1987, p. 71.
- 16) M.Y. Song, Int. J. Hydrogen Energy, Vol. 20, No. 3, 1995, p. 221.
- 17) J-L. Bobet, E. Akiba, Y. Nakamura and B. Darriet, Int. J. Hydrogen Energy 2000, Vol. 25, 2000, p. 987.
- 18) M.Y. Song, D.S. Ahn, I.H. Kwon, H.J. Ahn, Metals and Materials International, Vol. 5, No. 5, 1999, p. 485.