JOURNAL OF MATERIALS SCIENCE 27 (1992) 1417–1419

Verification of the rate-controlling steps in the hydriding reaction of Mg_2Ni

M.Y. SONG
Department of Materials Engineering, Chonbuk National University, 664-14 1ga Deogzindong Chonju Chonbuk, 560-756, Korea

H.R. PARK
Department of Chemical Technology, Chonnam National University, 300 Yongbongdong Bukgu Kwangju, 500-757, Korea

The rate-controlling steps in the hydriding reaction of Mg_2Ni are verified by comparing the incubation periods in the hydriding reaction of the Mg_2Ni alloy and a mechanically-alloyed mixture of 2Mg and Ni, by using gas mixtures of hydrogen and argon, and by varying the sample weight in the hydriding reaction.

1. Introduction

Mg_2Ni is considered a promising candidate for use as a hydrogen storage material together with FeTi and $LaNi_5$. In a previous work [1] the hydriding kinetics of the Mg_2Ni alloy were studied between 543 and 583 K from 2.5–8 bar H_2. The hydriding reaction of Mg_2Ni progresses by a nucleation and growth mechanism. Under relatively low hydrogen pressures, the nucleation of the Mg_2Ni hydride controls the hydriding rates. After nucleation, the rate-controlling step is analysed to be the forced flow of hydrogen molecules through pores, interparticle channels or cracks of the sample, involving heat-transfer control.

In this work, nucleation control of the hydriding rate of the Mg_2Ni alloy using the Mg_2Ni alloy and a mechanically alloyed mixture of 2Mg and Ni, forced flow control using gas mixtures of hydrogen and argon, and heat-transfer control by varying the sample weight in the hydriding reaction, were verified.

2. Experimental procedure

The hydrogen was purified by passing through a column filled with magnesium chips maintained at 823 K. Magnesium powder (− 50 mesh, 99.8 % purity) and nickel (− 325 mesh, 99.9 % purity) were used.

To prepare the Mg_2Ni alloy, a mixture of magnesium and nickel in the proportions corresponding to the composition $Mg_{2.05}$ Ni was pressed under 3 ton cm^{-2} (290 MPa) for 2 min in a vacuum. This composition was chosen because during the reaction a small quantity of magnesium was evaporated. The pellet was then melted under an argon atmosphere of 3 bar (0.3 MPa) at 1173 K for 1 h in a molybdenum crucible. After grinding and pressing under argon, it was annealed at 973 K for 60 h under an argon atmosphere. Magnetic measurements showed that the sample exhibited paramagnetic behaviour, and very small amounts of $MgNi_2$ and MgO as impurities were detected from the X-ray diffraction patterns. A back-scattering electron micrograph revealed some inclusions of a nickel-rich phase (probably $MgNi_2$) in the Mg_2Ni matrix.

A mechanically alloyed mixture of 2Mg and Ni was prepared in a planetary mill with an acceleration of about 60 ms^{-2}. Portions of the mixture (3g) of 2Mg and Ni were stirred together with 200 g stainless steel balls (diameter 4 mm) in the planetary mill under argon for 30 min. The resulting samples contained 0.5%–1% Fe.

The apparatus for hydriding was previously described elsewhere [2]. The hydrogen pressures were maintained nearly constant during the hydriding reaction by compensating the reactor for the absorbed hydrogen from the standard volume.

3. Results and discussion

The Mg_2Ni alloy and the mechanically alloyed mixture of 2Mg and Ni were activated sufficiently (about 15 hydriding–dehydriding cycles at 573 K under 0–7 bar (0.7 MPa) hydrogen pressure). With the hydriding–dehydriding cycles the Mg_2Ni phase developed in the mechanically alloyed mixture, and its quantity remained nearly constant after about the eighth hydriding–dehydriding cycle. After activation, 73 % Ni in the mechanically alloyed mixture was transformed into Mg_2Ni. This value was obtained by measuring the quantity of hydrogen desorbed under a hydrogen pressure under which the magnesium hydride is stable and only the Mg_2Ni hydride can be decomposed.

Fig. 1 shows the variation of the incubation periods, t_i, in the hydriding reaction of the activated samples as a function of the hydrogen pressure, P_0, at 543 K. The incubation period of the mechanically alloyed mixture is shorter than that of the Mg_2Ni alloy. This indicates

0022–2461 © 1992 Chapman & Hall

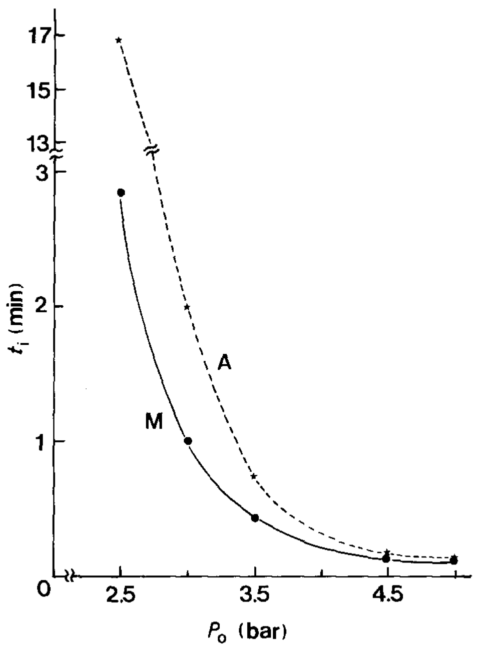

Figure 1 Variation of the incubation periods, t_i, in the hydriding reaction as a function of hydrogen pressure, P_0, at 543 K for the Mg_2Ni alloy (curve A) and for the mechanically-alloyed mixture of 2Mg and Ni (curve M).

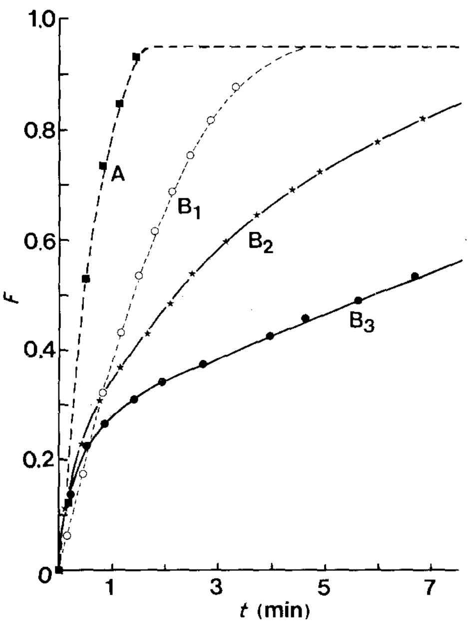

Figure 2 Variation of the reacted fraction, F, as a function of time, t, at 573 K: (A) under 7 bar H_2, and under 7 bar H_2 mixed with a quantity of argon corresponding, respectively, to a pressure of (B_1) 0.7 bar, (B_2) 1.0 bar and (B_3) 1.3 bar.

that the nucleation of the hydride is more favoured in the mechanically alloyed mixture than in the Mg_2Ni alloy.

The principal effects of treatment in the planetary mill on the mixture of 2Mg and Ni are considered to be an enlargement of surface area and an increase in the number of defects on the surface and in the interior of the sample. The expansion and contraction of the lattice during the hydriding–dehydriding cycles favour the diminution of the particle size and can create defects. On the contrary, the effect of annealing during the hydriding–dehydriding cycles can cause a decrease in the surface area by sintering and the reduction in the number of defects.

The defects created on the surface and in the interior of the sample and/or nickel and magnesium (which have not been transformed into Mg_2Ni) can be the sites of nucleation for the Mg_2Ni hydride.

Probably the more numerous defects created in the mechanically alloyed mixture can be considered to promote the nucleation of the Mg_2Ni hydride and to bring about the results shown in Fig. 1, supporting nucleation control of the hydriding rates of Mg_2Ni under relatively low hydrogen pressures.

The flow of the gas phase is considered to be a possible rate-controlling step when the particles are small, and/or the particles are porous, and the reaction rates are large. The particles of the activated Mg_2Ni are small (about 3 μm) and porous [1]. The hydriding rates are very large. In fact, the time of reaction corresponding to $F = 0.5$ is about 3 min under 7 bar H_2 at 573 K (equilibrium plateau pressure = 4.16 bar).

Fig. 2 shows with time, t(min), the variation of reacted fraction, F, in the hydriding reaction of the activated Mg_2Ni alloy at 573 K (A) under 7 bar H_2, and under 7 bar H_2 mixed with a quantity of argon corresponding, respectively, to a pressure of (B_1) 0.7 bar, (B_2) 1.0 bar and (B_3) 1.3 bar. The quantity of the sample is 0.25 g. We can observe that the hydriding rates decrease remarkably as the partial pressure of argon increases. This shows that the intrinsic process is not the rate-controlling step in the hydriding reaction of the activated Mg_2Ni alloy, and this supports that the forced flow of hydrogen molecules, one of the extrinsic processes, controls the hydriding rates. As the partial pressure of argon increases, the number of argon molecules increases and the hydrogen molecules collide more frequently with argon molecules during mass transport of hydrogen molecules up to the surface of the sample. So the flow of hydrogen molecules is interrupted and the hydriding rates decrease. The ensemble of these confirmations proves that the forced flow of hydrogen molecules is the rate-controlling step in the hydriding reaction of the activated Mg_2Ni.

The heat of formation of the Mg_2Ni hydride and that of chemisorption of hydrogen are the cause of the increase in the temperature during the course of the hydriding reaction. The heat of formation of the Mg_2Ni hydride is about -61.5kJ/mol H_2 [1]. The heat of chemisorption of hydrogen on the surface of nickel is about -126kJ mol^{-1} [3]. The increase in temperature during the reaction decreases the hydriding rate by raising the equilibrium plateau pressure and causing a diminution of the difference between hydrogen pressure and the equilibrium plateau pressure, which is related to the hydriding driving force.

The heat transfer depends on several factors: the intrinsic properties of the hydride (thermal conductivity of the sample, particle size, form or porosity for the porous samples), the parameters exterior to the sample (thermal conductivity of the reactor, precision of the temperature controller), and the quantity of

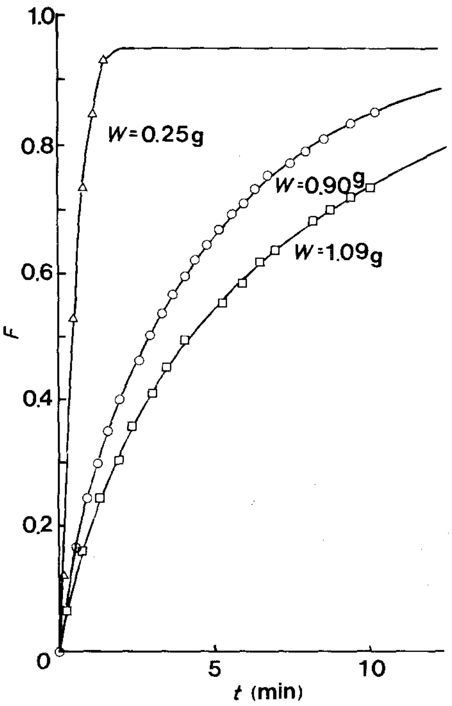

Figure 3 Variation of the reacted fraction, F, with time, t, at 573 K under 7 bar H_2 for different quantities, W, of sample.

sample. The particles of the activated Mg_2Ni form porous agglomerates [1]. The thermal conductivity of the Mg_2Ni hydride is small (about 0.63 J $m^{-1}s^{-1}K^{-1}$ at 298 K under 5 bar H_2) compared, for example, with that of FeTi hydride (about 1.34 J $m^{-1}s^{-1}K^{-1}$) [4].

Fig. 3 shows the variation of the reacted fraction, F, as a function of time, t (min), for various quantities, W, of sample at 573 K under 7 bar H_2. The greater the quantity of the sample, the smaller the hydriding rate. As the quantity of the sample increases, the quantity of the hydrogen absorbed per unit time increases and thus the exothermic heat becomes larger. This results in a larger temperature increase in a sample of larger quantity. This larger temperature increase decreases the hydriding rate more in the sample of larger quantity. The results of Fig. 3 prove that the heat transfer is also a rate-controlling step of the hydriding reaction of the Mg_2Ni alloy.

4. Conclusion

The rate-controlling steps are verified in the hydriding reaction of Mg_2Ni: (1) the control of the nucleation of the Mg_2Ni hydride using the Mg_2Ni alloy and a mechanically alloyed mixture of 2Mg and Ni, (2) the control of the forced flow of hydrogen molecules using gas mixtures of hydrogen and argon, and (3) the heat-transfer control by varying the sample weight.

Acknowledgement

The financial support of the Korean Ministry of Education Research Fund for Advanced Materials in 1989 is gratefully acknowledged.

References

1. M. Y. SONG, M. PEZAT, B. DARRIET, J. Y. LEE and P. HAGENMULLER, *J. Mater. Sci.* **21** (1986) 346.
2. M. Y. SONG, M. PEZAT, B. DARRIET and P. HAGENMULLER, *J. Solid State Chem.* **56** (1985) 191.
3. G. C. BOND, "Catalysis by Metals" (Academic Press, London, 1962) p. 105.
4. L. J. SWARTZENDRUBER, G. C. CARTER, D. J. KAHAN, M. E. READ and J.R. MANNING, Preprint 2nd World Energy Conference, Zürich, August 1978.

Received 6 February
and accepted 7 June 1991