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Cooperative hydriding properties in a nanostructured Mg_2Ni–H system

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Abstract

A nanostructured Mg_2Ni–H system was prepared by reactive mechanical grinding (RMG) of Mg_2Ni under a H_2 gas pressure of 1 MPa during various time periods from 5 to 4800 min. The structural and hydriding properties of the products obtained were examined by X-ray diffraction, thermal analysis, SEM and TEM. The experimental results showed the existence of cooperative dehydriding phenomena in intra- and inter-grain regions which have about the same volume fractions. Dehydrogenation from distorted inter-grain regions in nanostructured Mg_2Ni–H prepared by RMG for 60 min occurs at the same temperature as hydrogen leaves the intra-grain region of crystalline $Mg_2NiH_{0.3}$. Elastic interactions in nanostructured materials are important for the understanding of such cooperative dehydriding phenomena.

Keywords: Nanostructure; Mg_2Ni–H; Hydrogen storage; Cooperative hydriding phenomena

1. Introduction

Recently, much attention has been paid to make materials nanostructural and to give them new functions. In the first approximation, a nanostructured material can be regarded as containing both single-crystalline intra-grain regions and non-equilibrium deformed inter-grain regions, which have similar volume fractions. Therefore, hydriding properties of nanostructured materials are different from those of crystalline or amorphous ones, both with respect to thermodynamic and kinetic aspects, as reported by Mütschele and Kirchheim [1,2]. One of their unusual properties is the enhancement of hydrogen solubility compared to crystalline materials, which may be due to the large hydrogen content of the inter-grain regions [2,3]. Another is the enhancement of hydrogen diffusivity dependent on hydrogen concentration [2,4], which may be due to the hydrogen behaviour in the inter-grain regions. These results indicate that the hydriding properties of nanostructured materials are dominated by the deformed inter-grain regions at the interface of nm-size crystallites.

In this paper, we will review our recent results on the structural and hydriding properties of a nanostructured Mg_2Ni–H system prepared by reactive mechanical grinding (RMG) under a hydrogen atmosphere [5–9], and we would like to propose that it is possible to design new types of nanostructured materials which show high capacity (more than ~2 wt.%) and dehydriding temperature lower than 150 °C. Recently it was shown that the kinetics of hydrogenation were strongly improved in nanocrystalline Mg_2Ni formed by mechanically grinding in an argon atmosphere [10].

2. Results

Fig. 1 shows X-ray diffraction patterns of the Mg_2Ni–H system at room temperature after mechanical grinding (RMG) under a H_2 gas pressure of 1 MPa for various periods from 5 to 4800 min [5]. Without mechanical grinding, we notice that the $Mg_2NiH_{0.3}$ phase is formed at room temperature only after 720 min under a H_2 gas pressure of 1 MPa, as shown in Fig. 1 (see ‘0 min’ scan). On the other hand, the $Mg_2NiH_{0.3}$ phase forms easily by mechanical grinding of Mg_2Ni at room temperature for only 5 min under a H_2 gas pressure of 1 MPa, as shown in Fig. 1 (see ‘5 min’) scan, indicating that the mechanical grinding process strongly promotes the formation of the $Mg_2NiH_{0.3}$ phase. As the grinding times are increased to 60 min, the X-ray diffraction peaks broaden and the intensities gradually decrease, but the peak positions do not change. The peak broadening does not progress for grinding periods longer than 60 min. These results indicate that the intra-grain crystallites consist of the $Mg_2NiH_{0.3}$ phase independent of the grinding period, while the size of these crystallites decreases with increasing grinding time

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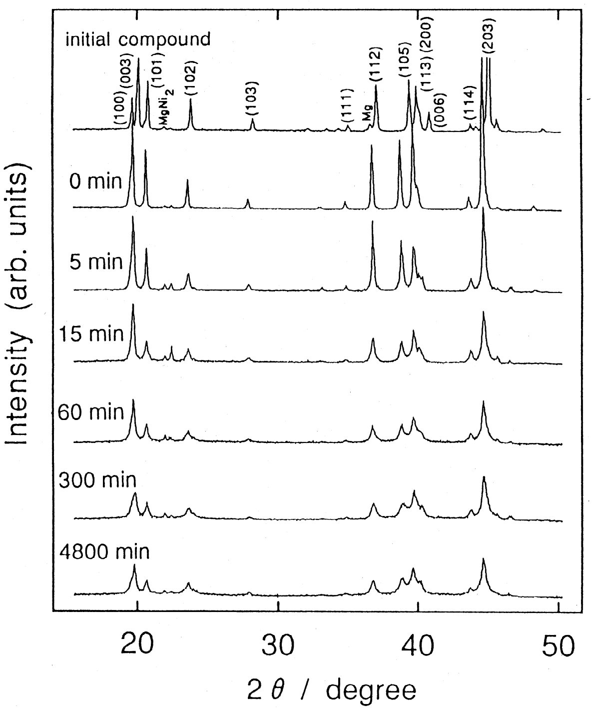

Fig. 1. X-ray diffraction patterns (CuKα radiation) at room temperature of the Mg_2Ni–H system prepared by mechanical grinding under a H_2 gas pressure of 1 MPa [5].

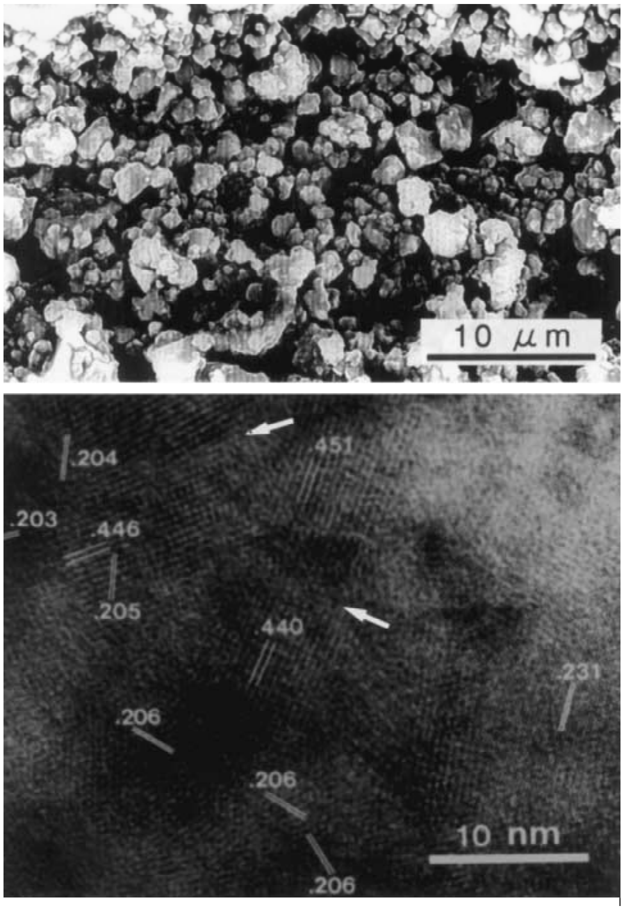

Fig. 2. SEM (top) and high-resolution TEM (bottom) images of the Mg_2Ni–H system ground under a H_2 gas pressure of 1 MPa for 60 min [6]. Arrows in the TEM images indicate inter-grain regions.

and remains almost constant after grinding times longer than 60 min.

In order to determine the volume fractions of the intra-grain and inter-grain regions in the Mg_2Ni–H system, we took SEM and TEM pictures for samples obtained by RMG for 60 min. As can be seen from the SEM images shown in Fig. 2 the sample consists of particles having a size of several micrometers. Microscopically, we can see lattice fringes in the TEM image of the interior of the particles thinned by focusing ion beam (FIB) cutting methods shown at the bottom of Fig. 2. From the TEM pictures one can deduce that each particle is composed of epitaxial Mg_2NiH_x ($x<0.3$) having an average crystallite size of ~15 nm (intra-grain region) and deformed Mg_2NiH_y inter-grain regions having an average thickness of ~1.5 nm between the intra-grains [6]. The average intra-grain size estimated by TEM is in good agreement with that estimated from the peak broadening in the X-ray diffraction patterns [7] as well as that estimated by experiments of small-angle scattering of neutron (SANS) for the Mg_2Ni–D system [8]. In order to estimate the specific surface area of the products, we also performed a BET examination for this system. The result confirmed that there were little pores or cracks introduced by milling under a hydrogen pressure of 1 MPa [7]. From the results of derivative thermogravimetry of the Mg_2Ni–H system (DTG profile in Fig. 3), we can deduce that the hydrogen content as obtained by integrating the DTG profile increases as the RMG time increases to 60 min, and remains constant for grinding times longer than 60 min, reaching $x=1.8$ for Mg_2NiH_x [5]. This result suggests that a large fraction of hydrogen in the Mg_2Ni–H system occupies the deformed inter-grain regions, and not the intra-grains. Nevertheless, it is of interest to note that the dehydriding reaction for samples prepared during grinding periods shorter than 60 min occurs at almost the same temperature at which the hydrogen in the intra-grain crystallites $Mg_2NiH_{0.3}$ is desorbed (around 440 K). However, we also notice that a two-step dehydriding process occurs for grinding times longer than 300 min, suggesting that the dehydrogenation reaction is weakened for the longer grinding times. Since the volume fraction of the inter-grain region does not change for grinding times longer than 60 min, it seems likely that the atomic configurations in the inter-grain regions are changed by longer grinding times so as to produce stable hydrogen sites. In this context it should be noted that the temperature corresponding to the second peak in DTG for 4800 min is close to the dehydrogenation temperature of Mg_2NiH_4. This is due to the onset of a transformation of deformed Mg_2NiH_y in the inter-grain regions to Mg_2NiH_4 around 480 K, which

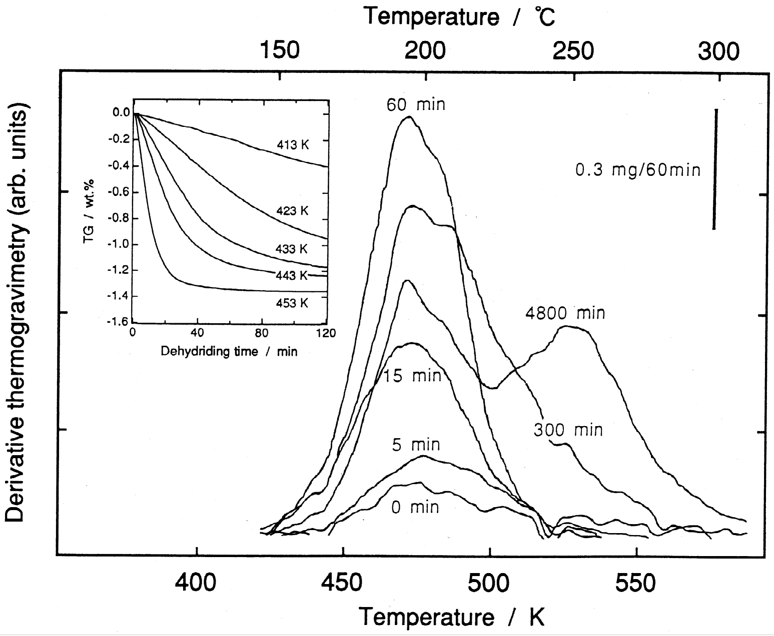

Fig. 3. Derivative thermogravimetry (DTG) profiles of the Mg_2Ni–H system ground under a H_2 gas pressure of 1 MPa for various periods at increasing temperature (5 K min^{-1}) in an argon atmosphere. The inset shows the dehydriding kinetics of the Mg_2Ni–H system prepared by mechanical grinding (60 min) under a hydrogen atmosphere [7].

occurs with an increase of temperature because of the slower dehydriding reaction associated with longer grinding times. Thus, the dehydrogenation reaction is fastest in product obtained by RMG for 60 min. In the inset of Fig. 3 are shown the dehydrogenation kinetics at various temperatures of the Mg_2Ni–H system obtained by RMG for 60 min. The dehydriding reaction proceeds even at 413 K and 90% of dissolved hydrogen is dehydrogenated within 30 min at 453 K [7].

3. Discussion

The large amount of dissolved hydrogen in the nanostructured Mg_2Ni–H system is considered to be due to the high solubility of hydrogen in the deformed Mg_2Ni inter-grain regions. We now estimate the dissolved hydrogen concentration H_c (wt.%) in the deformed inter-grain regions. The total content of dissolved hydrogen H_t after 60 min grinding time is given by the following expression:

$$\begin{aligned} H_t &= 1.4\ \text{wt.\%} \\ &= \{1 - V_{int}\ (60\ \text{min})\} \times 0.3(\text{wt.\%}) + V_{int}\ (60\ \text{min}) \\ &\quad \times H_c\ (\text{wt.\%}) \end{aligned} \tag{1}$$

where V_{int} is the volume fraction of the deformed inter-grain region. The first term on the right hand side is the hydrogen capacity of the intra-grain regions and the second one is that of the inter-grain regions. Using the following relation [1],

$$V_{int} = 3I_t/C_s \tag{2}$$

we obtain $V_{int} = 0.30$. Here, I_t is the average thickness of the inter-grain regions (~1.5 nm) and C_s is the average crystallite size (15 nm) after 60 min grinding. From this we found a value of 4.0 wt.% in the deformed Mg_2Ni inter-grain region, from Eq. (1), which is almost the same as that in the Mg_2NiH_4 phase. Thus, the high hydrogen content of 4.0 wt.% in the inter-grain region corresponds well to the strong contrast in deuterium content between intra-grain and inter-grain regions as obtained by SANS experiments of nanostructured Mg_2Ni–D. These estimations confirm that ~85% of hydrogen in the Mg_2Ni–H sample formed by RMG (60 min) are absorbed in the deformed inter-grain regions [7].

It is of interest to note that the dehydrogenation from the inter-grain regions in Mg_2Ni–H samples formed by RMG (60 min) occurs at the same temperature at which hydrogen leaves the intra-grain crystallite $Mg_2NiH_{0.3}$. In Fig. 4, the fully desorbed hydrogen content of the nanostructured Mg_2Ni–H system is plotted as a function of the relative cell volume shrinkage of the intra-grain Mg_2NiH_x during the dehydriding process. The latter was deduced from the desorbed hydrogen contents (at 120 min), as shown in the inset of Fig. 3, and the volume changes were estimated from the X-ray diffraction profiles. Fig. 4 shows that the amount of desorbed hydrogen from the product is almost proportional to that desorbed from the intra-grain Mg_2NiH_x phase. This suggests the existence of cooperative dehydriding phenomena between intra-grain and inter-grain regions.

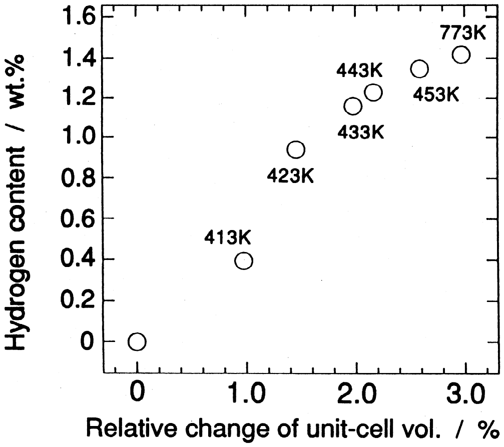

Fig. 4. Hydrogen contents desorbed from nano-structured Mg_2NiH_x prepared by grinding (60 min) as a function of relative cell volume shrinkage of the intra-grain structure Mg_2NiH_x phase during dehydrogenation [7].

As to the mechanisms of such cooperative dehydriding phenomena, we would like to point out the importance of elastic interactions in nanostructured materials, the details of which are schematically shown in Fig. 5. At 440 K, hydrogen is transferred from the intra-grain crystalline $Mg_2NiH_{0.3}$ region to the inter-grain regions because of the instability of dissolved hydrogen in the Mg_2Ni grains. As a result of this transfer, the hydrogen concentration in the inter-grain regions saturates, while the lattice of the intra-grain Mg_2NiH_x region and the deformed inter-grain region cooperatively shrink. These complementary effects lead to an instability of hydrogen in the inter-grain and desorption of hydrogen. This so-called 'cooperative dehydriding reaction', may occur only in specific nanostructured materials.

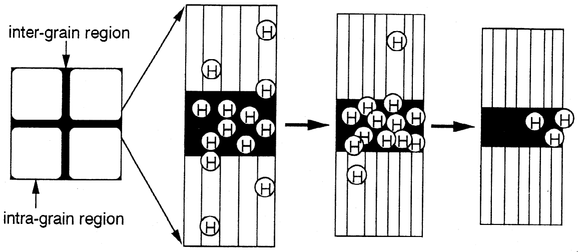

Fig. 5. Schematic diagram of the concept of cooperative dehydriding phenomena.

Finally, we comment on the reversibility of the hydrogen absorption/desorption process. Indeed, the reversibility was examined on a sample which was first ground for 60 min under a hydrogen pressure of 1 MPa, and then dehydrogenated at 453 K, and rehydrogenated at 333 K. The hydrogen content was found to reach up to 1.4 wt.%, which is almost the same as that found during the first run. We can, therefore, conclude that the nanostructured materials are capable of reacting reversibly with hydrogen. However, since the deformed Mg_2NiH_y (y~4.4) phase in the inter-grain regions transforms into the crystalline phase of Mg_2NiH_4 at ~480 K, reversibility is most likely to occur below 480 K.

Acknowledgments

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