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Journal of Alloys and Compounds 217 (1995) 245–249

Journal of
ALLOYS
AND COMPOUNDS

Hydrogen absorption in nanocrystalline Mg_2Ni formed by mechanical alloying

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Received 13 April 1994; in final form 11 July 1994

Abstract

High-energy ball milling has been used to produce nanocrystalline Mg_2Ni with grain sizes of about 20–30 nm. Results on the hydrogen storage characteristics of the material are presented. Enhancements were found in the kinetics of hydrogen absorption and in the activation pretreatment. Nanocrystalline Mg_2Ni readily absorbs hydrogen at temperatures lower than 250 °C. Further improvements (i.e. absorption at room temperature with relatively good kinetics) have been effected by additional surface modification with Pd catalyst.

Keywords: Hydrogen absorption; Mechanical alloying; High-energy ball milling; Kinetics

1. Introduction

Many metallic materials are known to form hydrides reversibly. Intermetallic Mg_2Ni with its high hydrogen capacity (up to 3.6 wt.%) is amongst the prime candidates for hydrogen storage systems. However, under normal conditions (i.e. at room temperature and atmospheric pressure) Mg_2Ni does not absorb hydrogen. The usual hydrogenation conditions are: 250–350 °C and hydrogen pressure of 15–50 bar. Below about 250 °C hydrogen absorption does not occur for all practical purposes. Moreover, even for absorption above 250 °C Mg_2Ni must be activated prior to hydrogenation. Activation usually involves annealing at a higher temperature (325 °C) under higher hydrogen pressure (20 bar). The activation process has to be repeated several times to obtain reproducible absorption/desorption characteristics [1]. Improvement of the hydrogenation conditions of Mg_2Ni is therefore essential to produce a suitable material for practical hydrogen storage.

We show below that nanocrystalline alloys (with grain size below 100 nm) combine good hydrogen absorption characteristics with enhanced mechanical properties. The nanocrystalline material was obtained by high-energy ball milling. This technique is typically used to prepare nanocrystalline material by a cyclic mechanical deformation of the pre-melted alloy. However, using this technique one may also form the alloy directly from the elemental components. In the case where the melting temperatures of the components are very different, such as Mg_2Ni, this offers a very considerable advantage.

2. Experimental methods

In order to produce Mg_2Ni, ball-milling of elemental powders of Ni (99.9%, 400 mesh) and Mg (99.8%, 5–100 mesh) was performed in a laboratory high-energy mill Spex 8000 (from Spex Industries, Inc., Edison, NJ). Powder mixtures were milled in a hardened steel vial under a purified argon atmosphere. The handling of the samples was carried out under argon in a glovebox. Alloying of Mg_2Ni with e.g. Cu was performed by a partial replacement of the nickel powder by Cu (up to 25 at.%) in the initial powder mixture. Catalytic modification of the surface of the Mg_2Ni powder was carried out by introducing small amounts of Pd (less than 1 wt.%) to the powders in the course of the ball-milling process.

The ball-milled powders were characterized by X-ray diffraction using a Nicolet–Stoe powder diffractometer (Cu Kα radiation). The microstructures and phase compositions of the ball-milled material were studied using a Philips CM20 (200 kV) transmission electron microscope equipped with an energy-dispersive X-ray analysis system (EDAX 9900) with a thin Be window.

0925-8388/95/$09.50
SSDI 0925-8388(94)01348-9

Hydrogen sorption properties of the ball-milled powders were investigated by a computer-controlled gas titration apparatus [2]. Samples of Mg_2Ni were hydrogenated at various temperatures. After evacuation and heating up to the required temperature, hydrogen gas was admitted and the changes of hydrogen pressure as a function of time were measured, thus providing information on the absorption kinetics. Pressure–concentration isotherms were determined by an automatic step-by-step admission of hydrogen, at the times when the pressure change in measuring volume was less than 1×10^{-5} bar s^{-1}.

3. Results and discussion

3.1. Alloy formation

Mg_2Ni is difficult to prepare by conventional metallurgy because of the great difference in melting temperatures and hence vapor pressures of Mg and Ni. Mechanical alloying by ball-milling avoids melting of the elements and forms the compound through solid-state reaction. Although ball-milling is quite a common technique, published results on ball-milled Mg and Ni powders have not yet been shown to produce single-phase, stoichiometric Mg_2Ni [3,4]. Previously the formation of Mg_2Ni was observed only during hydriding–dehydriding or sintering of ball-milled Mg–Ni powders [3].

However, under the ball-milling conditions (high-energy mill and high ball-to-powder mass ratio) used in the present work, stoichiometric Mg_2Ni was formed directly. Fig. 1 shows X-ray powder diffraction spectra illustrating the formation of Mg_2Ni by mechanical alloying. Fig. 1(a) shows X-ray diffraction pattern for the starting material: a mixture of the elemental Ni and Mg. Fig. 1(b) presents an intermediate stage of mechanical alloying reaction (after 26 h of ball-milling); Mg_2Ni compound with some unreacted elemental Mg and Ni. The final product of the solid-state reaction is pure Mg_2Ni, with no traces of Mg or Ni (Fig. 1(c)). The final diffraction pattern exhibits broadening of the peaks characteristic for nanocrystalline material. Microstructure and electron diffraction pattern of the as-ball-milled Mg_2Ni powder are shown in Fig. 2. The average grain size as determined by electron microscopy is about 20–30 nm.

The studies of ball-milled powder mixtures of Mg and Ni showed that the rate of Mg_2Ni formation by mechanical alloying depends strongly on the applied milling parameters. Under a low mass ratio of balls to powder (R) the formation of Mg_2Ni was relatively slow. For example, ball-milling with ball-to-powder ratio $R=0.6$ gives only a very small amount (a few percent) of Mg_2Ni phase after 100 h of milling. The more effective conditions we found for the formation of Mg_2Ni phase using a vibratory mill (SPEX 8000) were: $R=5$, milling time = 60 h.

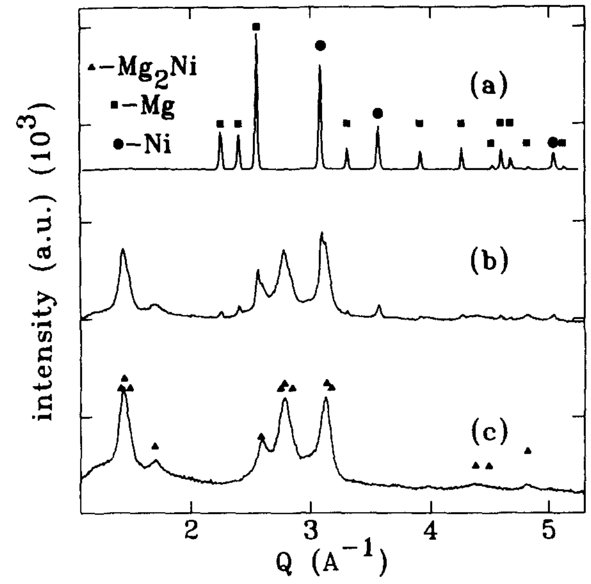

Fig. 1. X-ray diffraction patterns for Mg–Ni powders: (a) initial state (elemental powders mixture); (b) after 26 h of milling; (c) after 66 h of milling: nanocrystalline Mg_2Ni.

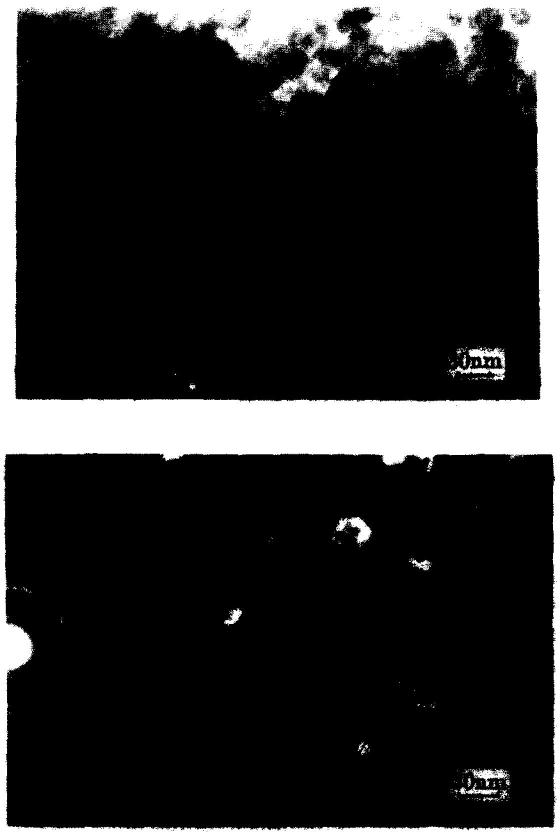

Fig. 2. TEM image (bright and dark field image) and electron diffraction pattern for nanocrystalline Mg_2Ni.

3.2. Hydrogen sorption

Ball-milled nanocrystalline Mg_2Ni shows better hydrogen sorption properties than the conventional polycrystal. The as-produced powder readily absorbs hydrogen with no activation, achieving the final hydrogen content of about $x \approx 3.4$ wt.% after the first hydrogenation cycle at 300 °C (Fig. 3). In subsequent cycles, absorption kinetics are reproducibly about four times faster than for conventionally activated polycrystalline material. For example, half time for reaction with hydrogen at 7 bar is about 1 min for ball-milled material as compared to about 4 min for conventional Mg_2Ni [5].

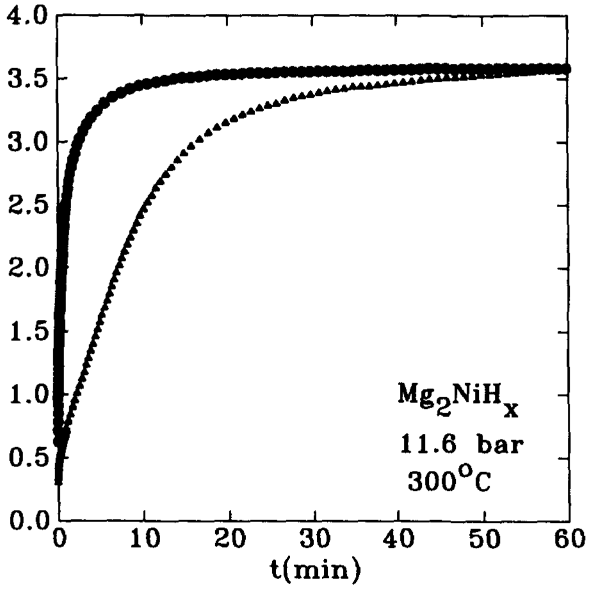

Fig. 3. Rate of hydrogen absorption of as-ball-milled Mg_2Ni at 300 °C: ▲, in the first absorption cycle (no prior activation); ●, in subsequent reproducible cycles. Absorption of two hydrogen atoms is 7 min and 0.3 min respectively.

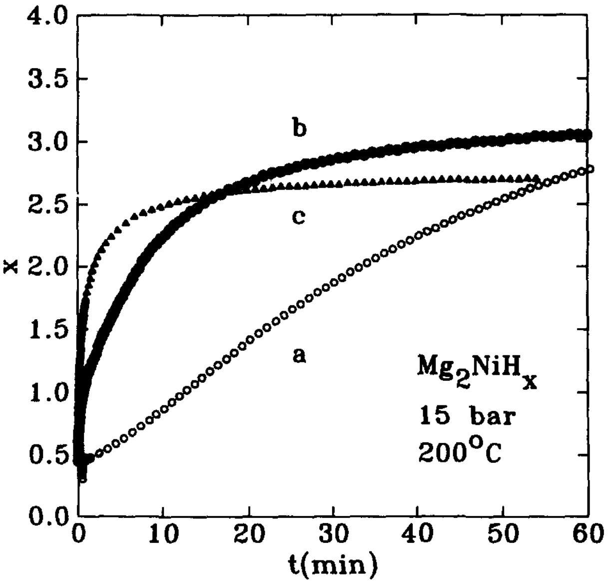

Fig. 4. Rate of hydrogen absorption (at 200 °C): (a) as-ball-milled Mg_2Ni (fresh); (b) ball-milled Mg_2Ni stored in air for several months; (c) nanocrystalline Mg_2Ni with Pd catalyst.

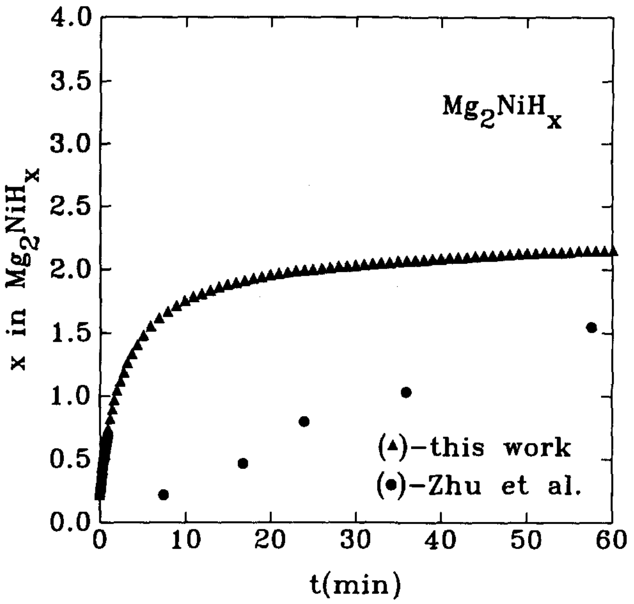

Fig. 5. Rate of hydrogen absorption by nanocrystalline Mg_2Ni with Pd at room temperature (12 bar, without activation) (▲, this work) and by polycrystalline Mg_2Ni etched in HCl (room temperature, 40 bar) (●, from Zhu et al. [12]).

The hydrogen content does not attain, however, the nominal full value of 3.6 wt.% (four atoms per Mg_2Ni) within the applied hydrogenation time, i.e. within 1 h, as is also commonly reported in the literature results. The amount of absorbed hydrogen is usually 3.0–3.45 wt.% in the reported reversible hydrogenation cycles [5,6].

As mentioned, conventional polycrystalline Mg_2Ni absorbs hydrogen (under moderate pressure of hydrogen: less than 20 bar) only at high temperatures, i.e. above 250 °C. At these temperatures a Mg_2NiH_4 hydride forms, which has cubic symmetry, with $a = 0.6490$ nm [7]. This structure of Mg_2Ni is only stable at temperatures higher than 250 °C and transforms upon cooling into a low-temperature Mg_2Ni phase [8]. The low-temperature Mg_2NiH_4 has a more complicated structure (not finally revealed yet): orthorhombic or monoclinic, or perhaps a mixture of the two [8–10]. Hydrogenation of the high-temperature phase of Mg_2NiH_4 is apparently much easier than for the low-temperature phase. Low-temperature Mg_2NiH_4 is very difficult to obtain by direct hydrogenation under moderate pressure conditions. The published results on the hydride formed directly at low temperature were obtained at very high hydrogen pressures, typically by keeping a sample (previously hydrogenated at high temperature) overnight under a pressure of 50 bar [11] or for two days at 200 °C under a pressure of about 120 bar [10]. Our recent experiments on Mg_2Ni powders obtained by ball-milling showed that the nanocrystalline material, as prepared, reacts readily

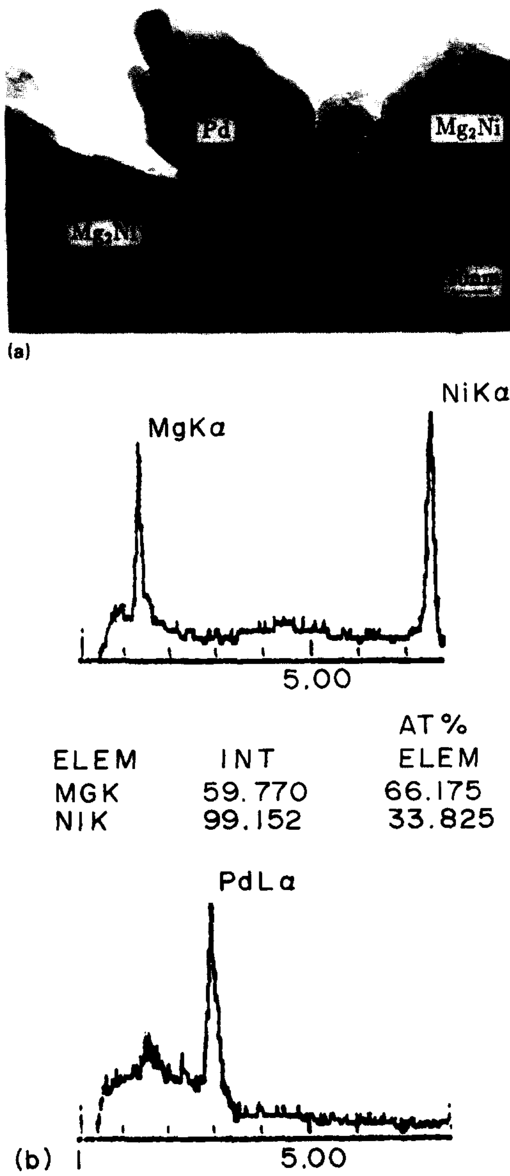

Fig. 6. (a) TEM image of the Mg_2Ni powder surface with Pd cluster, and (b) EDX spectra for the Pd cluster and Mg_2Ni.

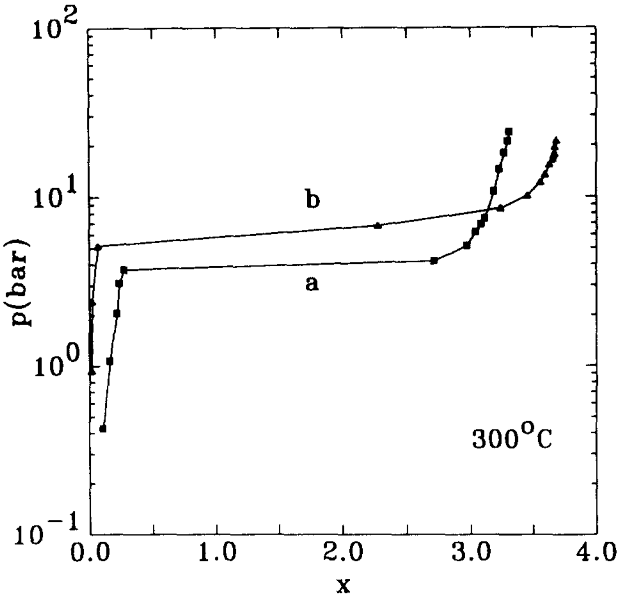

Fig. 7. Pressure–hydrogen concentration isotherms for (a) nanocrystalline Mg_2Ni and (b) nanocrystalline $Mg_2Ni_{0.75}Cu_{0.25}$ measured at 300 °C for absorption.

with hydrogen at temperature 200 °C (and below) and no activation is required (Fig. 4, curve a). However, the kinetics of the absorption at low temperatures are not very fast and only 2 atoms of hydrogen per formula unit can be stored within about 30 min. Even the total amount of hydrogen absorbed in 1 h is quite low, reaching only about 2.7 atoms per Mg_2Ni. It is not clear why nanocrystalline material absorbs less hydrogen at low temperature (lower than the transformation temperature of the hydride). A similar phenomenon has been observed for polycrystalline Mg_2Ni [12]. We presume that it is caused by slow diffusion of hydrogen through the low-temperature hydride phase as it grows.

Interestingly, the samples stored for several months in air after ball-milling show much better hydrogenation characteristics in the first hydrogenation cycle at 200 °C than the freshly prepared samples (curve b in Fig. 4). The kinetics are much faster, and the absorption of 2 atoms of hydrogen can be obtained in 8 min. However, this good absorption characteristic deteriorates gradually over the next three hydrogenation cycles, and the fourth cycle exhibits behavior similar to that of the freshly ball-milled sample. Further cycling shows good reproducibility of the absorption characteristics with no changes in the kinetics. These results can be explained by the effects of sample oxidation (caused by storing in air) on hydrogen absorption. Normally, the presence of the oxide layer drastically reduces hydrogenation ability and poisons the material. Activation annealing (or preheating the nanocrystalline sample to 200 °C to perform hydrogenation) causes cracking and/or decomposition of the oxides. It is known that in Mg_2Ni (with a great difference in affinity to oxygen of Mg and Ni) annealing can cause disproportionation reaction with oxygen [13]. As a result MgO and pure Ni clusters are formed on the powder surfaces. Ni is a good catalyst for hydrogen dissociation and would cause significant enhancement of the surface activity. Unfortunately, this catalytic action of Ni reduces after several hydrogenation cycles of the material.

Another way to enhance the activity of Mg_2Ni is by catalysis through small additions of palladium. Small amounts of Pd were introduced (less than 1 wt.%) to the powders in the course of the ball-milling process, a method recently applied for producing active nanocrystalline hydrogen absorbers [14,15]. The catalytic action of Pd was found to be extremely effective. Nanocrystalline Mg_2Ni with Pd exhibits much faster absorption kinetics at 200 °C (with no previous activation) than the as-ball-milled samples (reaction half-time of 2 min and 33 min respectively) (Fig. 4, curve c). Moreover, nanocrystalline Mg_2Ni with Pd absorbs hydrogen even at room temperature, without activation. The absorption rate at room temperature is relatively fast, as shown in Fig. 5. More results on the catalytic effects of Pd on hydrogen absorption of nanocrystalline materials will be presented in an upcoming publication.

Fig. 5 also shows results from [12] for the room-temperature absorption of hydrogen by polycrystalline Mg_2Ni powder etched in HCl before hydrogenation at 40 bar. Absorption kinetics are slow; however, after long times (5 h) a capacity of 3 hydrogen atoms per Mg_2Ni can be attained (not shown in the figure). Subsequent cycles exhibited, however, a gradual deterioration of hydrogen absorption [12]. It has been suggested that the surface of the material after etching consists of a porous metallic layer of nickel with high activity for hydrogen dissociation. Rapid degradation of hydrogen absorption capacity with cycling may be caused by disintegration of powder particles and formation of new, less active surfaces [12].

Aoki et al. [16] in a recently published paper showed hydrogen absorption at room temperature by Mg_2Ni ball-milled in argon. The kinetics of hydrogen absorption were somewhat better than for HCl-etched Mg_2Ni and about three times slower than for our nanocrystalline Mg_2Ni with Pd.

Fig. 6(a) shows a TEM image of the nanocrystalline Mg_2Ni powder with an attached Pd particle, which shows that Pd can be effective as a catalyst even when present in the form of small clusters on the surface. EDAX spectra for the Pd particle and Mg_2Ni are shown in Fig. 6(b).

Hydrogen absorption can also be controlled by alloying. Stability of the hydride phase, reaction kinetics and plateau pressure are sensitive to the chemical composition of the material. Substitution of Ni or Mg by other elements (e.g. Al) in Mg_2Ni has been found by Hirata et al. [17] to improve hydrogenation characteristics. Our preliminary results on nanocrystalline ternary alloys (e.g. $Mg_2Ni_{0.75}Cu_{0.25}$) showed that alloying can significantly increase plateau pressure (as can be seen from Fig. 7: plateau pressure has been increased by a factor of 1.7). As a result, the temperature range of hydrogenation cycles for this material can be effectively shifted to lower temperatures. Alloying may offer an alternative for developing a suitable material for hydrogen storage at room temperature.

4. Conclusions

Mg_2Ni in a nanocrystalline form (obtained by ball milling) shows hydrogen absorption characteristics superior to that of the conventional crystal phase.

Activation is much easier (or even unnecessary) because of very active surfaces of the powder created in the ball-milling process.

At high temperatures (about 300 °C) the hydrogen absorption rate is very high, even for the as-made nanocrystalline samples. Absorption rate can be further improved by applying one hydrogenation cycle as a pretreatment.

Nanocrystalline Mg_2Ni exhibits also hydrogen absorption at lower temperatures (for example at 200 °C, i.e. below the temperature of structural transformation of the Mg_2NiH_4 hydride) without any activation.

Modification of the nanocrystalline Mg_2Ni by a small amount of Pd catalyst enhances hydrogen absorption kinetics at 200 °C. Nanocrystalline Mg_2Ni with Pd absorbs hydrogen even at room temperature, without activation and with relatively good kinetics.

Alloying of the ball-milled Mg_2Ni compound by addition of Cu increases plateau pressure. As a result the temperature range of hydrogenation cycles for this material can be effectively shifted to lower temperatures.

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