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On the synthesis of the Mg_2Ni alloy by mechanical alloying

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Abstract

The synthesis of the hydrogen-storage alloy Mg_2Ni has been carried out through a single-step mechanical alloying employing an energy ball mill. The synthesized ball-milled Mg_2Ni alloy has been found to exist in the form of fine (nano) particles with sizes of about 40 Å. The nanoparticle form has been found to lead to easy activation for hydrogenation by annealing at 300 °C (about 10^{-4} Torr vacuum) for 30 min and hydrogen uptake has been found to commence from the first cycle itself.

Keywords: Synthesis; Mechanical alloying; Hydrogen storage

1. Introduction

Mechanical alloying has recently emerged as a novel technique for alloy formation [1,2]. The resulting alloy can be either crystalline, amorphous or quasi-crystalline [3]. One of the unique uses of mechanical alloying is to make alloys of entirely immiscible metals, e.g. the Cu–V system [2]. In the early developments of the ball milling technique, it has been frequently used to amorphize alloys. Recent developments include its use in making several kinds of alloys, particularly those in which the heat of mixing is negative and therefore a thermodynamic driving force is provided in a natural way. Heat of mixing being negative, however, is not a limiting criterion; alloys such as Cu–Ta and Cu–V [2] with a positive heat of mixing have also been made by this technique. Yet another use of the technique is to make nanocrystalline metal [4]. Whereas the technique has been used quite extensively, understanding of the process of mechanical alloying is not complete at present. It is suggested that the heat generated due to collision of the balls resulting in continuous fragmentation, coalescence events and the interdiffusion of ingredients of the alloy at the collision sites are the main steps of the process of mechanical alloying.

In the metal hydride systems, surface area and particle size of the material are the important parameters for enhancement in the hydrogen uptake, reduction in the activation time, temperature and pressure, and improvement in the kinetics of the material. One of the important storage materials corresponds to the Mg–Ni system (i.e. Mg_2Ni) which is a low cost hydride system having very high hydrogen absorption capacity (about 3.4 wt.%). However, the major disadvantage of Mg_2Ni is its high activation and desorption temperature (about 300 °C). Since mechanical alloying by ball milling leads to materials in fine-particle form, which may result in reduction of the activation time and temperature, it may be typically suited for the synthesis and formation of the hydrogen-storage material Mg_2Ni.

The present paper deals with the synthesis of Mg_2Ni solely by mechanical alloying employing high energy ball milling and its characterization by X-ray diffraction (XRD), transmission electron microscopy and hydrogen absorption–desorption. It may be pointed out that, even though the synthesis of Mg_2Ni has been achieved earlier through planetary ball milling coupled with hydrogenation [5,6], the present work appears to be the first of its type where the Mg_2Ni synthesis has been covered in a single-step process through high energy ball milling. The Mg_2Ni alloy formed through energy ball-mill-based mechanical alloying is in the form of nanoparticles (about 40 Å) as confirmed through XRD and electron microscopy. It underwent easy hydrogen activation, e.g. it could be hydrogenated even in the first cycle. Investigations have been done to reveal the hydrogen absorption–desorption behaviour of the mechanically alloyed Mg_2Ni and the results have been analysed in terms of the smallness of particle size.

2. Experimental techniques and results

The synthesis of Mg_2Ni was accomplished by ball milling a stoichiometric mixture of Mg (99.8% pure) and Ni (99.9% pure). The magnesium and nickel powders were sieved to

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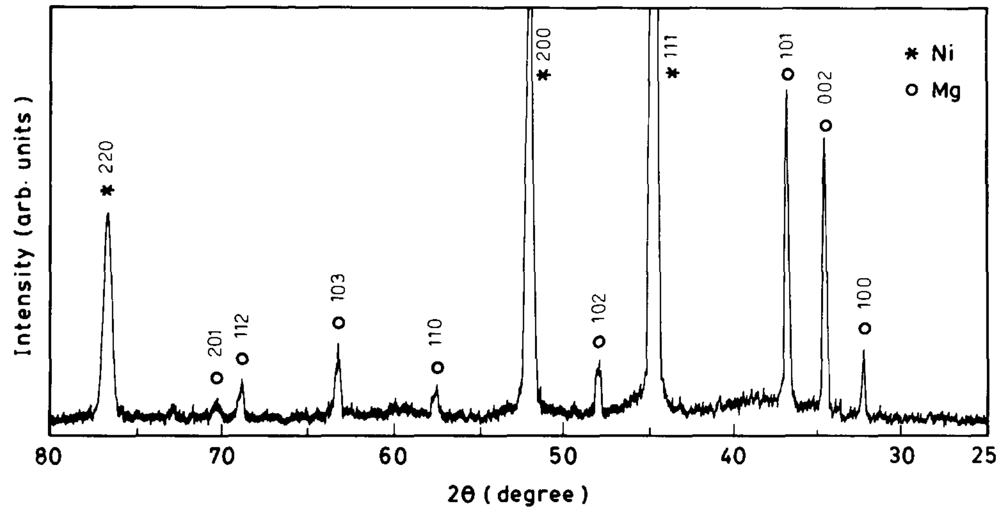

Fig. 1. X-ray diffractograph of the initial mixture of elemental magnesium and nickel.

achieve a particle size of about 100 μm. The mixture was ball milled for 100 h, at room temperature, in an argon atmosphere with milling speed of 40 rev min^{-1}. The high energy ball mill used here was fabricated indigenously and was based on a somewhat modified version of the mill designed by Benjamin [7]. It has a cylinder of inner diameter about 5.6 cm, volume about 400 ml having an impeller and 40 steel balls of diameter about 0.95 cm. The volume fraction of the balls with reference to the tank was approximately 0.35.

In order to monitor the possible alloy formation, a small amount (0.5 gm) of the ball-milled material was intermittently taken out from the ball mill at time intervals of 50, 80 and 100 h. From a series of experiments, it was found that these time periods were most appropriate for checking the possible alloy formation. These small quantities were subjected to XRD characterization employing a Philips PW 1710 X-ray diffractometer equipped with graphite monochromator and working with Cu Kα radiation ($\lambda = 1.5418$ Å). Fig. 1 is a representative XRD pattern of the mixture of 2Mg–Ni before ball milling which as expected showed separate elemental peaks corresponding to magnesium and nickel. Fig. 2 shows the X-ray diffractogram of the mixture ball milled for 50 h. Extensive analysis of these results revealed that the peaks corresponding to magnesium almost disappeared, and those of nickel decreased in intensity and got broadened (increased full width at half-maximum (FWHM)). These features suggest the commencement of diffusion of magnesium into nickel which leads to alloy formation. Fig. 3 shows the XRD pattern of the sample ball milled for 80 h. It reveals that along with the Mg_2Ni (hexagonal, $a \approx 5.19$ Å, $c \approx 13.21$ Å, Laves phase) some free nickel is also present. It may be noticed that the peaks corresponding to nickel ($d \approx 2.03$, 1.76 and 1.24 Å) have no significant change in intensity but these become sharper (i.e. with decreased FWHM).

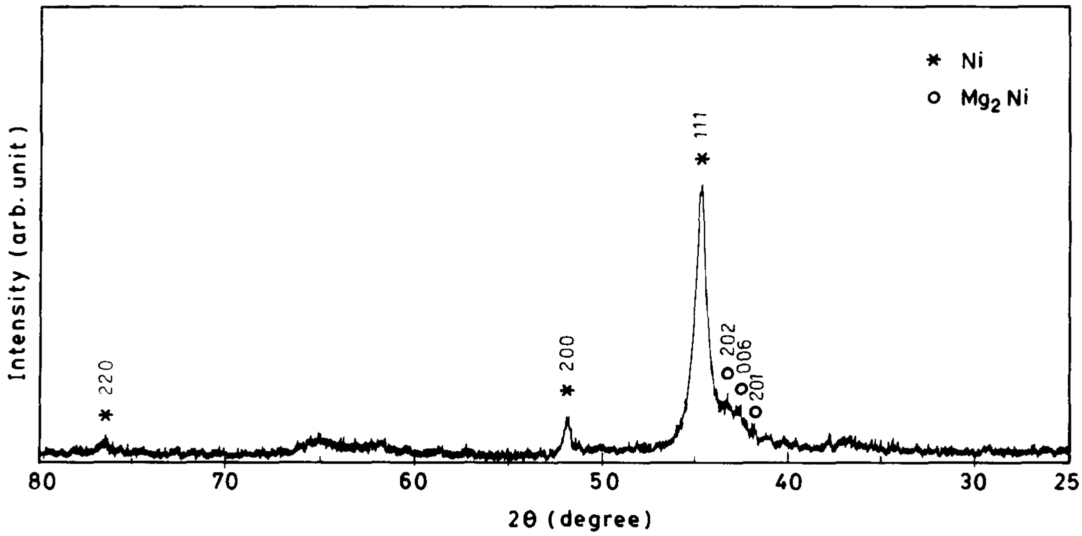

Fig. 2. X-ray diffractograph of the mixture ball milled for 50 h. Alloy formation has commenced as evidenced by the appearance of extra peaks which could be identified as coming from Mg_2Ni.

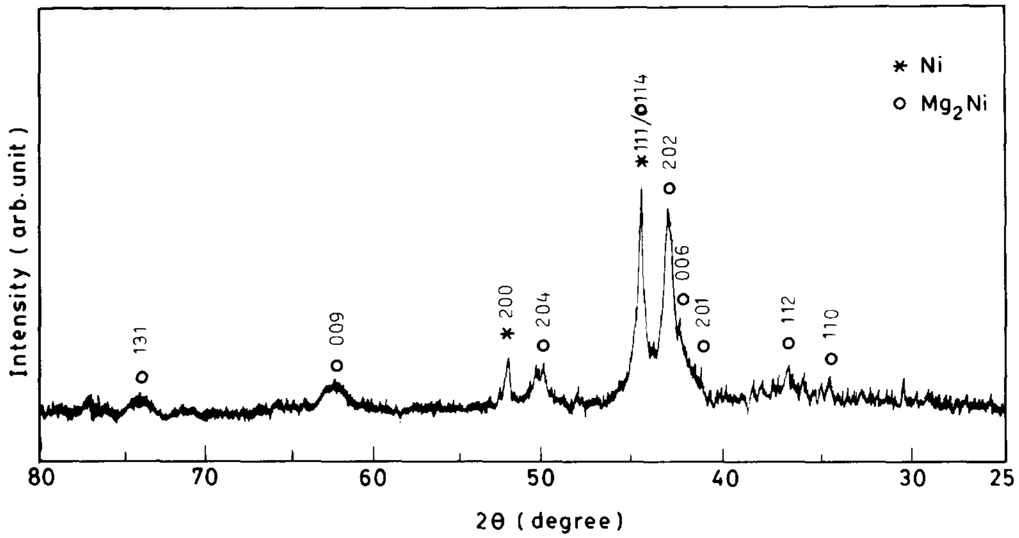

Fig. 3. X-ray diffractograph of the mixture ball milled for 80 h. The appearance of the peaks corresponding to Mg_2Ni can be noticed.

Finally, the XRD pattern for a sample ball milled for 100 h is depicted in Fig. 4. This pattern reveals the clear and prominent peaks of Mg_2Ni with some free nickel. Thus the XRD characterization revealed that the Mg_2Ni alloy formation resulted after about 100 h of ball milling the elemental mixtures.

The powder ball milled for 100 h was characterized for its hydrogenation-dehydrogenation behaviour by monitoring the *P-C-T* curves. The alloy was activated by heating up to 300 ± 1 °C in vacuum of 10^{-4} Torr for 30 min. Thereafter hydrogenation was carried out at the same temperature at a pressure of 30 kgf cm^{-2}. Fig. 5 represents a typical first-cycle *P-C* desorption curve at a temperature of 300 °C from the Mg_2Ni powder ball milled for 100 h. The weight per cent of hydrogen desorbed by mechanically alloyed Mg_2Ni in the first cycle was found to be only 0.8%. It increased with cycling (3 h, 30 kgf cm^{-2}, 300 °C) and reached a value of 3.2 wt.% in the fifth cycle as shown in Fig. 6. Although the mechanically alloyed powder shows only 0.81 wt.% of hydrogen desorption in the first cycle, this in comparison to other versions of mechanically alloyed Mg_2Ni corresponds to a higher storage capacity. In contrast, the Mg_2Ni alloy prepared by melting and sintering showed desorption only after 13 hydriding cycles [8]. However, the previous results for the mechanically alloyed Mg_2Ni show desorption only after ten hydriding cycles [5,6]. The excellent hydrogen desorption of the mechanically alloyed Mg_2Ni (ball milled for 100 h) may be attributed to the increased surface area corresponding to small particles (or isolated grains) resulting from continuous fragmentation in the ball milling process. In

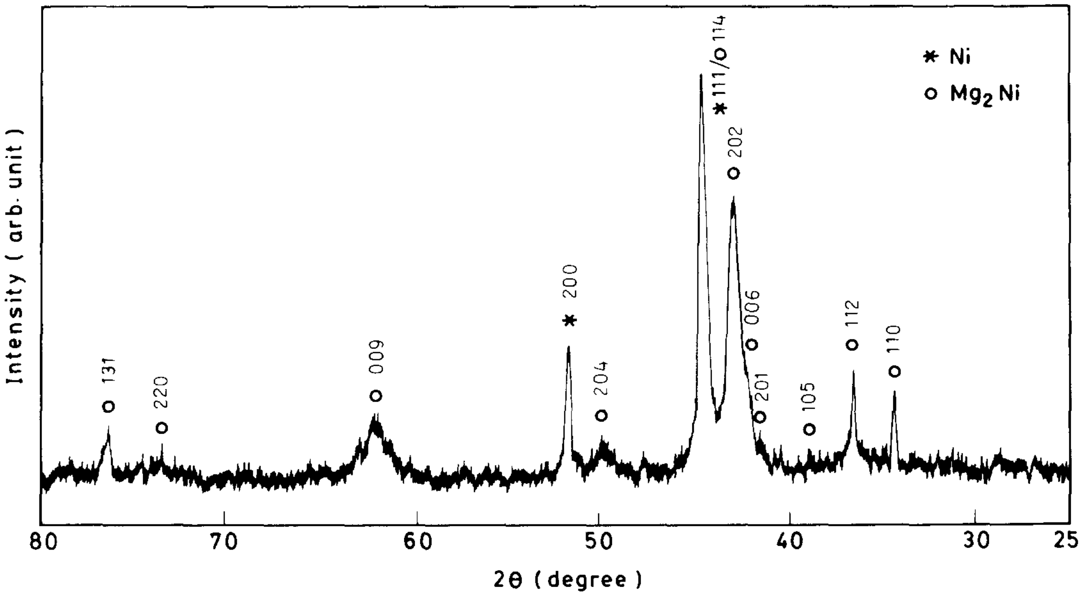

Fig. 4. X-ray diffractograph of the mixture ball milled for 100 h. XRD peaks corresponding to well-developed Mg_2Ni indicating nearly complete alloy formation have been outlined and can be clearly seen.

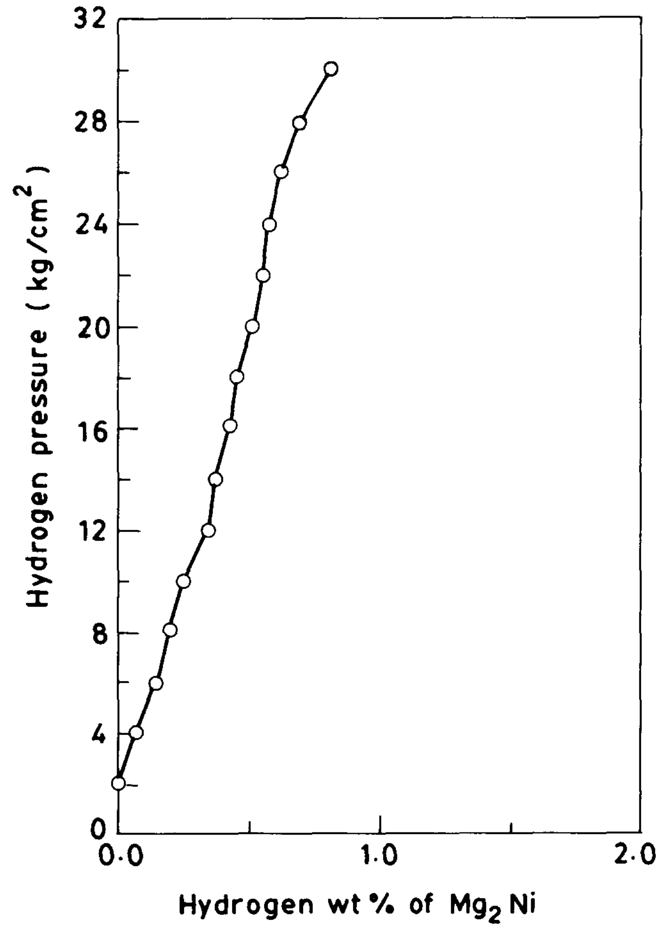

Fig. 5. *P–C* desorption curve for the sample ball milled for 100 h and activated at 300 °C in vacuum (10^{-4} Torr) for 30 min (see text).

addition to this, the effect of the Mg_2Ni–Ni biphasic nature of the material may also lead to the improved hydrogenation characteristics. Apparently further experimentation would be required to separate out the influence of the particle size and biphasic nature of the material.

The mechanically alloyed Mg_2Ni was also subjected to microstructural characterization using the transmission electron microscopic technique. Fig. 7 shows a representative selected-area diffraction powder pattern of the mechanically alloyed Mg_2Ni where all lines can be attributed to Mg_2Ni (hexagonal, $a \approx 5.19$ Å, $c \approx 13.21$ Å). This again confirms the formation of Mg_2Ni. Fig. 8 shows the dark field image of the mechanically alloyed material exhibiting particle (isolated grains) size of about 40 Å. It may be suggested that in the process of mechanical alloying the continuous fragmentation of particles leads to occurrence of isolated grains (Fig. 8) and owing to their small size they become capable of absorbing and desorbing right from the first cycle.

3. Discussion

One of the striking aspects of the present work is that here Mg_2Ni is synthesized in a single-step process, i.e. by ball milling alone, whereas other investigators report the formation of Mg_2Ni by a two-step process, i.e. ball milling which was carried out only for 5–30 min coupled with hydrogenation–dehydrogenation [5,6]. In these studies the hydrogenation, which is an exothermic reaction (formation enthalpy about −63 kJ (mol H_2)$^{-1}$), and also dehydrogenation, which would require heating up to at least 300 °C, involved high temperature and hence would lead to solid state diffusion. The alloy formation would therefore embody solid state diffusion. Alloying by ball milling is a result of powdering the ingredients and their interdiffusion. In the present case described above, the particle size of the ball-milled mixture is about 20–40 Å. The ultimate so-small size of particles is presumably due to repeated fragmentation which is more favourable for the type of mill used here than for high energy ball mills [7]. Indeed, the property of the particles being so small facilitates the interdiffusion because the diffusion coefficient for the very small particles is much larger than that for the usual bulk materials [9] and also because the total distance required for diffusion reduces. This should be considered in conjunction with the fact that, when the mixture of the ingredients is fractured and coalescence occurs between the balls, the temperature increases due to loss of kinetic energy of the balls. The increase in temperature varies, depending on the type of the ball mill and the operating parameters, e.g. rotation speed, dimensions of different parts of the mill etc. Indeed the rise in temperature can be as high as 400 °C [10]. This in turn promotes the diffusion. Thus we propose that the increased temperature of very fine powdered ingredients, enhanced diffusion and reduced distance required for diffusion taken together would make the observed alloying understandable.

In the present process ball milling itself yields alloy synthesis. It may be pointed out that, whereas the ball milling duration in the present case corresponded to about 100 h, for earlier studies (for example [5,6]) this duration was only 5–30 min. It is worth mentioning that, for the cases where ball milling itself results in alloy synthesis, the duration of ball milling is at least 20 h [1].

In regard to the alloy synthesis through ball milling, there is a general agreement that during ball milling the particles of the ingredients are repeatedly flattened, fractured and rewelded. The continuous fragmentation and coalescence event leads to the formation of alloy [11].

It may be pointed out that there is significant controversy in relation to estimates of temperature rise during ball milling; whereas the estimate of temperature rise given by Schwarz et al. [12] is 30–40 °C, others argue that it would be around 400 °C (see e.g. Ref. [10]). Regardless of the temperature rise the basic process of fragmentation, coalescence and diffusion is expected to be much more vigorous for the ball mill employed in the present investigation (where a vertical ball mill with impeller has been used) [13] than in the conventional planetary-type ball mill. In fact it has been shown that [7] the vertical ball mill has 10 times higher grinding rates than the conventional planetary ball mills. It may be noticed

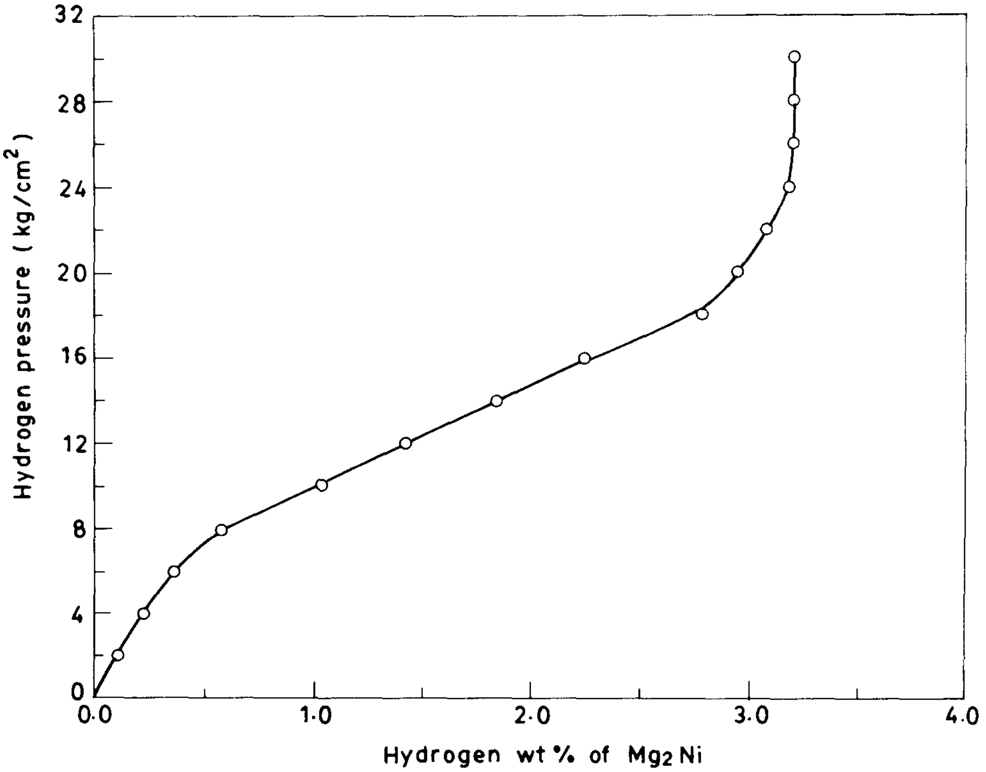

Fig. 6. *P–C* desorption curve for the activated sample which had been ball milled for 100 h, after the fifth cycle. Each cycle consisted of heating the sample to 300 °C at a pressure of 30 kgf cm^{-2} for 3 h.

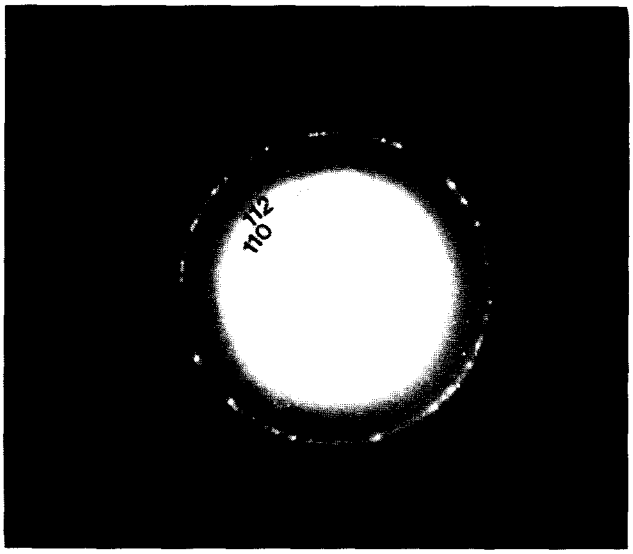

Fig. 7. Electron diffraction pattern exhibiting powder rings corresponding to Mg_2Ni. The indices of reflections are shown.

that, even though the input velocities of balls in a conventional ball mill is greater (about 4.4–6.3 m s^{-1}) than that in an energy ball mill (about 0.8 m s^{-1} [11]), the grinding rates in a conventional mill are slower because of the lengthened time of collision and amount of material compacted per collision. As regards the superior hydrogenation behaviour, e.g. easy activation through annealing at about 300 °C (10^{-4} Torr vacuum) for 30 min, the hydrogen uptake from the first cycle itself is evidently due to the existence of Mg_2Ni alloy in nanoparticle-like fine-particle (about 40 Å) form which provides a larger value of the surface-area-to-volume ratio or easy availability of a surface for activation. It may be mentioned that in similar investigations [5,6] the particle size of

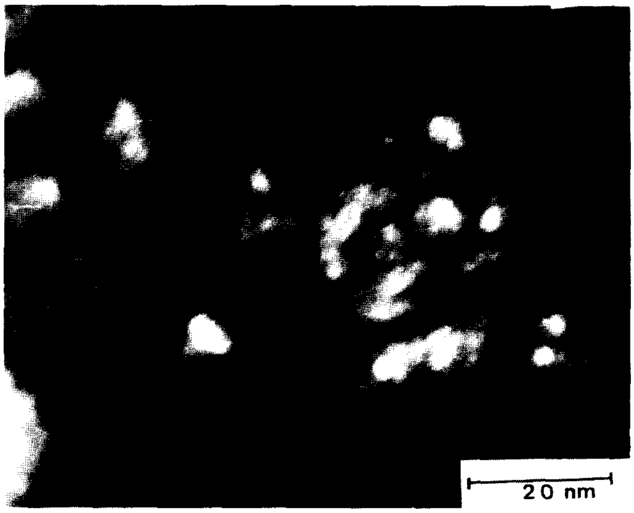

Fig. 8. TEM image of the sample ball milled for 100 h, showing the presence of Mg_2Ni particles of size about 40 Å.

the Mg_2Ni materials after the 58th cycle (H_2 absorption–desorption) is approximately 50 nm as evident from scanning electron microscopy shown in Ref. [6].

4. Conclusions

In the present investigation the hydrogen-storage alloy Mg_2Ni has been synthesized through ball milling of metallic ingredient powders of Mg (99.8%) and nickel (99.9%). A salient characteristic of the present study relates to the fact that, unlike some previous studies where synthesis of Mg_2Ni was achieved through a two-step process involving mechanical alloying (planetary ball mill) and hydrogenation, in the present investigation the synthesis of Mg_2Ni alloy has been achieved in a single-step process embodying mechanical alloying (energy ball mill) alone. It has been shown that this is achieved due to the development of a high energy (vertical drum with impellers) ball mill. Yet another attractive aspect of the present study is that the synthesized Mg_2Ni is in the form of fine (nano) particles with average particle size of about 40 Å. This fine-particle form of Mg_2Ni leads to superior hydrogenation behaviour including easy activation through heating at 300 °C (10^{-4} Torr vacuum) for 30 min duration and hydrogen uptake in the first cycle itself.

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