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Evolution of Nanocrystalline Structures Using High Energy Ball Milling of Quaternary $Mg_{1.75}Nb_{0.125}C_{0.125}Ni$ and Binary Mg_2Ni

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High energy ball milling of two initial quaternary and binary powder mixtures of $Mg_{1.75}Nb_{0.125}C_{0.125}Ni$ and Mg_2Ni has been carried out in pure argon atmosphere for the synthesis of nanocrystalline powders based on Mg_2Ni intermetallic compound. A planetary ball mill was employed using a ball to powder weight ratio of 20:1 for various milling time of 5, 10, 15, 20, 30 and 60 h. Characterization of the crystal structure of the milled products using X-ray diffractometry exhibited the formation of Mg_2Ni-based nanocrystallites after ≈ 5 h of milling for the both powder mixture. However, its volume fraction was greater in the case of quaternary powder mixture than that of binary one. In addition, an amorphous phase was detected in the milled products; its volume fraction showed increase by increasing milling time. The calculated mean crystallite size of Mg_2Ni structure showed decrease by increasing the milling time following the Williamson–Hall procedure and was found to be ≈ 8 and 10 nm after 20 h of milling for the initial powder mixture of $Mg_{1.75}Nb_{0.125}C_{0.125}Ni$ and Mg_2Ni, respectively.

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1. Introduction

High energy ball milling is considered as an important technique for the production of nanocrystalline compounds with extended solid solubilities. The growing interest for this technique is due to the possibility of obtaining materials with unique chemical, physical and mechanical properties. During high energy ball milling, solid state reactions take place in the initial powder mixture by repeated mechanical deformations caused by ball–powder–ball and ball–powder–chamber collisions. Numerous structural defects are created which increase the kinetic of elemental interdiffusion. Furthermore, the ball collisions cause fracturing and cold welding of the elementary particles, forming clean interfaces at atomic scale. Strain is introduced into the lattice and as a result, crystals fracture into smaller pieces.

Ball milling process has been successfully applied to the synthesis of various materials such as dispersion strengthened alloys and equilibrium intermetallic phases. As nonequilibrium processing method, it can be utilized to produce large quantities of materials at relatively low cost. These materials have already given rise to great interest in many applications such as magnetic, catalysis and hydrogen storage materials [1, 2].

Using current storage materials, it is not possible to exceed capacity of 2 wt% H_2, whereas for instance, magnesium can store 7 wt% H_2. Unfortunately, MgH_2 is very stable and too much energy has to be expended in releasing the hydrogen. Alloying magnesium with other elements could lower the stability of the hydride without reducing the capacity to an unacceptable value. Magnesium and nickel form two stable intermetallic compounds; Mg_2Ni and $MgNi_2$. $MgNi_2$ does not react with hydrogen, at least in the crystalline state [3]. Mg_2Ni alloy has been known to absorb a large amount of hydrogen, up to 3.6 wt% [1–3].

It is already well known that during high energy ball milling or mechanical alloying of Mg–Ni alloys an amorphous phase forms, which upon further milling results as nanocrystallites [4]. It is also established that microstructure of Mg alloys has a strong influence on their hydrogen characteristic [2–4]. The purpose of the present work is to investigate the effect of Nb and C additive on the kinetic of formation of the mechanically alloyed Mg_2Ni-based crystal structure using two initial powder mixtures with stoichiometric compositions of $Mg_{1.75}C_{0.125}Nb_{0.125}Ni$ and Mg_2Ni.

2. Experimental procedures

Magnesium tears, Ni, C and Nb powders with a purity ≈ 99.5 wt% were used as the starting materials. High energy ball milling was performed using a planetary ball mill with a rotation speed of 600 rpm. Two elemental powder mixtures with different compositions of Mg_2Ni and $Mg_{1.75}C_{0.125}Nb_{0.125}Ni$ were prepared (Table). A ball/powder weight ratio of 20:1 was adjusted for 5, 10, 15, 20, 30 and 60 h of milling. Two powder mixtures were milled in separate tempered steel vials with steel balls ($\phi = 20$ mm) under an argon gas atmosphere.

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TABLE

Chemical composition of the two powder mixtures.

Nominal composition	Mg [g]	Ni [g]	Nb [g]	C [g]
Mg_2Ni	2.95	3.56	–	–
$Mg_{1.75}Nb_{0.125}C_{0.125}Ni$	2.42	3.34	0.66	0.09

Determination of crystal structures of the milled products were carried out employing X-ray diffraction (XRD) technique on a Phillips X'Pert Pro diffractometer using a monochromatic Cu K_α radiation. Morphology and chemical analysis of the starting materials and the milled products were characterized using scanning electron microscopy (SEM), CamScan model MV2300, equipped with an energy dispersive spectrometer (EDS).

3. Results and discussion

The appearance of the starting materials is shown in Fig. 1; Mg tears with ≈ 1 mm length, Nb powder of irregular shape, C — flake shape and Ni — spherical powder. Figure 2 shows the XRD patterns of the milled products after different milling times. Diffraction peak intensities of Mg, Ni, C and Nb showed decrease by increasing milling times. In addition, gradual peak broadening was observed. Moreover, reflections related to the formation of Mg_2Ni crystal structure were detected; these showed higher intensities in the case of quaternary product than those of binary ones (i.e., the volume fraction of the intermetallic compound is greater in the quaternary product than that of binary one).

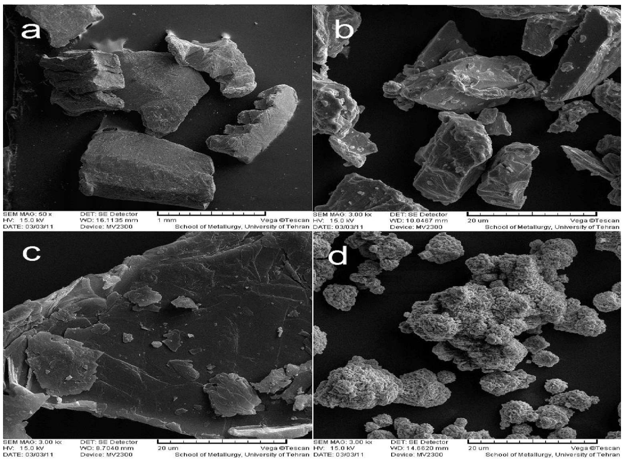

Fig. 1. SEM micrographs of the starting materials: (a) Mg tears, (b) Nb, (c) C, and (d) Ni powders.

In the case of binary powder mixture, diffraction peaks of Ni and Mg were observed after 5 h of milling. The milled product consisted of dominant mixture of Ni, Mg and substantial Mg_2Ni crystal structures. Peaks of Mg_2Ni phase with relative low intensities indicate the beginning of the alloying process. After 10 h of milling of Mg_2Ni powder mixture, four main peaks of Mg_2Ni-based crystal structure appear. The peak broadening indicates that the crystallite size decreases rapidly at the beginning of milling and then levels off. In addition, this can be due to an increase in the specific area of the powder and an increase in the number of lattice defects caused by the mechanical milling. After 5 h of milling, no peak related to C and Nb can be observed. However, broadened Ni peaks were detected.

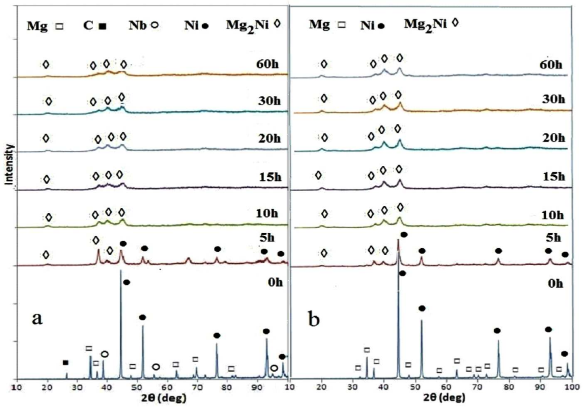

Fig. 2. XRD patterns of (a) Mg_2Ni and (b) $Mg_{1.75}C_{0.125}Nb_{0.125}Ni$ powder mixtures after various milling times.

In the case of $Mg_{1.75}C_{0.125}Nb_{0.125}Ni$ powder mixture, formation of Mg_2Ni begins after 5 h of milling. However, its volume fraction was found to be greater than that of the binary one (the latter is associated with relatively lower peak intensities). In addition, XRD results show the formation of an amorphous phase. With further milling, crystallization of amorphous into nanocrystalline Mg_2Ni occurred.

Several hypotheses have to be considered to explain the origin of the mechanically-induced crystallization of amorphous Mg_2Ni during prolonged milling [2]. One factor which can induce amorphous to crystalline transformation during ball milling is the temperature increase in the course of milling process. This could be above the crystallization temperature of the amorphous phase. The crystallization temperature of an Mg–Ni alloy into Mg_2Ni crystal structure was determined to be 324 °C from differential scanning calorimetric measurements [1–6]. The actual temperature of individual particle during ball milling can be high enough to cause crystallization.

SEM observations indicate that particle size decreases with increasing milling time. After milling, particles are reduced in size and an agglomeration of smaller particles occurred (Fig. 3). It is shown that the agglomerates are composed of small particles cold welded together.

The crystallite size and internal strain were calculated from the following equation [5–7]

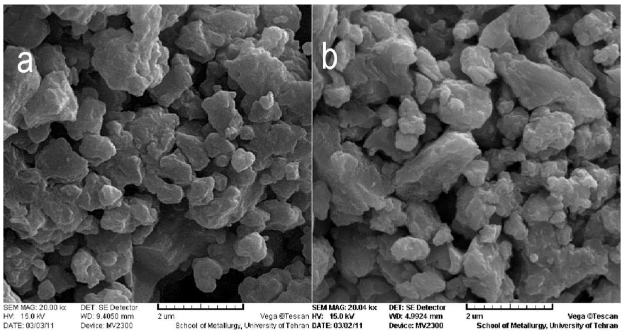

Fig. 3. SEM micrographs of binary and quaternary Mg_2Ni and $Mg_{1.75}C_{0.125}Nb_{0.125}Ni$ milled products after 60 h of milling, respectively.

$$\beta = \frac{0.9\lambda}{t\cos\theta} + \eta\tan\theta\,, \tag{1}$$

where β is the peak widths at half maximum intensity of the reflection with highest intensity, λ is the wavelength, θ is the Bragg angle at maximum intensity, t is the average diameter of crystallites (Å) and η is the lattice strain.

The average Mg_2Ni crystallite size of Mg_2Ni and $Mg_{1.75}C_{0.125}Nb_{0.125}Ni$ milled products were calculated to be about 10 and 8 nm after 20 h of milling, respectively.

4. Conclusions

1. Mg_2Ni-based nanocrystalline powder was produced using high energy ball milling of quaternary and binary elemental mixtures with stoichiometric compositions of $Mg_{1.75}C_{0.125}Nb_{0.125}Ni$ and Mg_2Ni, respectively.
2. The mean crystallite size of Mg_2Ni was found to be smaller in the case of $Mg_{1.75}C_{0.125}Nb_{0.125}Ni$ than that of Mg_2Ni mixture using the same milling conditions.
3. An amorphous phase was formed that its volume fraction increased by increasing milling time.
4. The formation kinetic of Mg_2Ni was found to be higher in the case of $Mg_{1.75}C_{0.125}Nb_{0.125}Ni$ quaternary powder mixture than that of the binary one.

References

[1] I. Okonska, M. Nowak, E. Jankowska, M. Jurczyk, *Rev. Adv. Mater. Sci.* **18**, 627 (2008).

[2] S. Ruggeri, C. Lenain, *J. Alloys Comp.* **339**, 195 (2002).

[3] G. Liang, S. Boily, J. Huot, A. Van Netste, *J. Alloys Comp.* **267**, 302 (1998).

[4] P. Solsona, S. Doppiu, T. Spassov, *J. Alloys Comp.* **381**, 66 (2004).

[5] R.A. Varin, T. Czujko, J. Mizera, *J. Alloys Comp.* **350**, 332 (2003).

[6] T. Spassov, P. Solsona, S. Suriñach, M.D. Baró, *J. Alloys Comp.* **349**, 242 (2003).

[7] H. Inoue, T. Ueda, S. Nohara, N. Fujita, C. Iwakura, *Electrochim. Acta* **43**, 2215 (1998).