

## New Mg-based alloy obtained by mechanical alloying in the Mg–Ni–Ge system

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### Abstract

The mechanical alloying (MA) of the 2Mg–0.5Ni–0.5Ge mixture at room temperature under argon atmosphere was investigated. The crystal structure, morphology and thermal stability of the products were characterized by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis and differential scanning calorimetry. A new alloy in the Mg–Ni–Ge system was synthesized by MA of the 2Mg–0.5Ni–0.5Ge mixture and by the combination of MA and subsequent thermal treatment. No evidence of the formation of Ni–Ge compounds was observed. The new ternary alloy can be considered isostructural with Mg<sub>3</sub>Ni<sub>2</sub>M-type compound, with a *F* cubic cell and a lattice parameter *a*=11.521 Å. Thermal studies show that the Mg–Ge–Ni alloy is stable upon heating up to 500 °C.

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### 1. Introduction

Magnesium is considered attractive as a hydrogen storage material, due to its lighter weight, its higher hydrogen storage capacity (7.6 wt.%) and its lower price compared with other metals. However, magnesium is inadequate to be used in hydrogen storage applications due to its high hydrogen desorption temperature and relatively slow hydrogen absorption/desorption kinetics. When Ni is used as an alloying element forming Mg<sub>2</sub>Ni or amorphous MgNi, an enhancement in the hydriding/dehydriding kinetics has been reported [1–3]. For this reason, different efforts to substitute Mg or Ni by a third element (M) to form ternary materials such as Mg<sub>2</sub>Ni<sub>1–x</sub>M<sub>x</sub> [4,5], Mg<sub>2–x</sub>M<sub>x</sub>Ni [6,7] or MgNi<sub>1–x</sub>M<sub>x</sub> [8,9] are being developed.

Some evidence about the formation of ternary alloys type Mg<sub>2</sub>Ni<sub>1–x</sub>M<sub>x</sub> [4,5] or Mg<sub>2–x</sub>M<sub>x</sub>Ni [6,7] has been reported. Aymard et al. [4] have prepared the Mg<sub>2</sub>Ni alloy and Mg<sub>2</sub>Ni<sub>0.7</sub>Co<sub>0.3</sub> ternary alloy through the combination

of mechanical alloying (MA) followed by thermal treatment. The alloy with Mg<sub>2</sub>Ni<sub>0.7</sub>Co<sub>0.3</sub> composition presents the Mg<sub>2</sub>Ni hexagonal structure with partial substitution of Ni by Co. Zhang et al. [5] have synthesized Mg<sub>2</sub>Ni<sub>1–x</sub>Zr<sub>x</sub> (0<*x*<0.3) alloys by ball milling-diffusion method (BDM). These Mg<sub>2</sub>Ni<sub>1–x</sub>Zr<sub>x</sub> alloys have the same hexagonal crystal structure as that of Mg<sub>2</sub>Ni, with changes in the lattice parameters with ‘*x*’. The partial replacement of Ni by Zr in Mg<sub>2</sub>Ni leads to improvements in the desorption kinetics and also to a decreasing of the desorption enthalpy and the decomposition temperature. Liang et al. have prepared Mg<sub>2</sub>Ni and Mg<sub>1.9</sub>Ti<sub>0.1</sub>Ni alloy by MA [6]. The Mg<sub>1.9</sub>Ti<sub>0.1</sub>Ni alloy has similar lattice parameters to Mg<sub>2</sub>Ni, due to the small difference in the atomic radii between Mg and Ti. Moreover, Mg<sub>1.9</sub>Ti<sub>0.1</sub>Ni alloy shows an improvement in the hydrogen absorption/desorption kinetics with respect to Mg<sub>2</sub>Ni. Guangle et al. [7] have produced alloys with nominal compositions Mg<sub>1.7</sub>Ti<sub>0.3</sub>Ni<sub>0.8</sub>Mn<sub>0.2</sub> and Mg<sub>1.5</sub>Al<sub>0.5</sub>Ni by a combination of high pressure/temperature conditions. They determined that Mg<sub>2–x</sub>M<sub>x</sub>Ni (M=Al, Ti) alloy is a multiphase system composed of Mg<sub>2</sub>Ni, Mg, M–Ni compounds, MgO and Mg<sub>3</sub>Ni<sub>2</sub>M, a new cubic phase. This recent study is the only one where an A<sub>2</sub>B-type hexagonal structure is not obtained by substitution of A or B.

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In the present study, we produce a new ternary alloy in the Mg–Ni–Ge system by MA of the 2Mg–0.5Ni–0.5Ge mixture at room temperature under argon atmosphere. An alternative route for the production of this alloy is also reported. Studies of the morphology, structure and thermal stability of the novel ternary alloy were carried out. Considering that no Mg–Ni–Ge ternary phase diagram exists to the knowledge of these authors, we provide information about the existence of a stable ternary alloy in the Mg–Ni–Ge system.

## 2. Experimental

Elemental Mg granules (purity higher than 99.9%) and Ni and Ge powders (purity 99.9%) were mixed with a composition 2Mg–0.5Ni–0.5Ge. The mixture was mechanically milled under argon atmosphere using a Uni-Ball-Mill II apparatus (Australian Scientific Instruments), which has an external magnetic field controlling the ferromagnetic steel balls movement. The ball-to-powder ratio was 44:1. All handling was performed in a glove box

under dry argon. The argon pressure inside the container was 0.1 MPa.

The container was opened at regular intervals of time to remove a small amount of powder for monitoring structural and morphological changes. Structural changes were

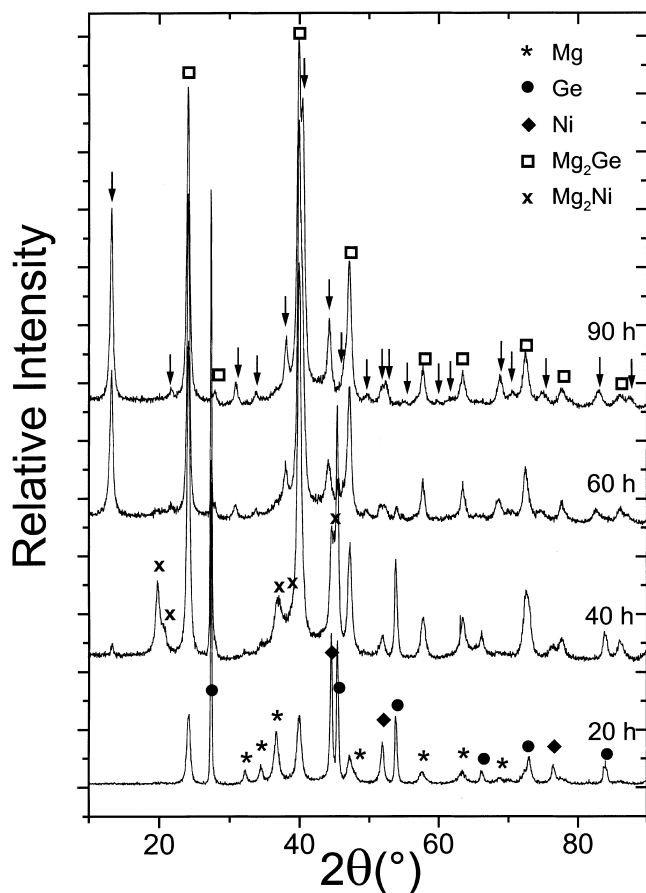
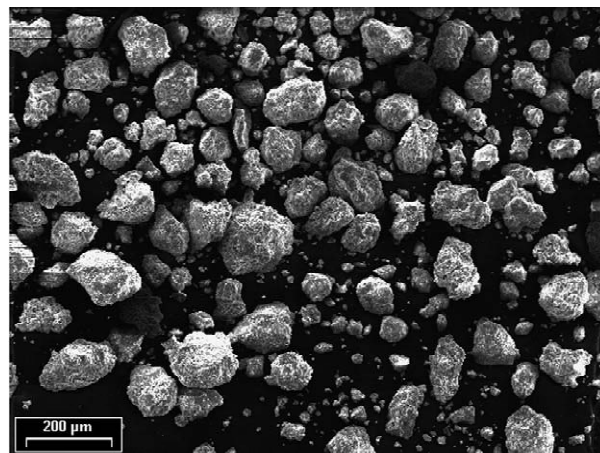
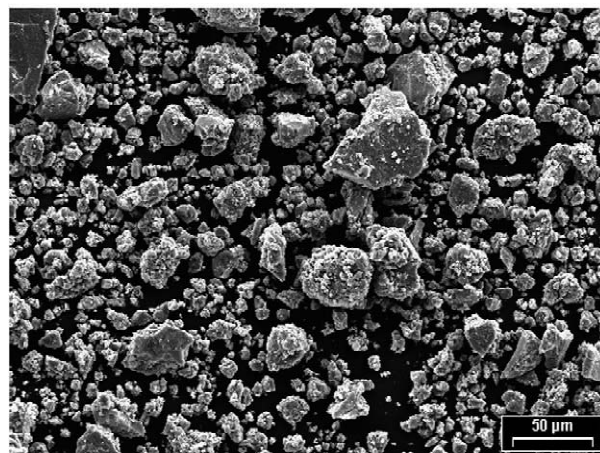


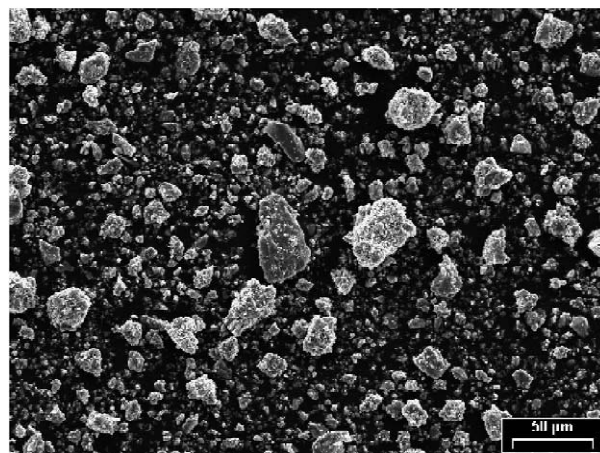
Fig. 1. XRD patterns of the 2Mg–0.5Ni–0.5Ge mixture milled under argon as a function of milling time. Arrows indicate the Mg–Ge–Ni alloy peaks.



(A)



(B)



(C)

Fig. 2. Wide area SEM micrographs of the 2Mg–0.5Ni–0.5Ge mixture after MA for different milling times. (A) 4 h, (B) 40 h, and (C) 200 h.

studied using X-ray diffraction (PW 1710/01, Philips Electronic Instruments). The particle morphology was characterized by scanning electron microscopy (SEM 515, Philips Electronic Instruments) and the different phases were identified by energy dispersive X-ray analysis (EDX, Philips Electronic Instruments). The thermal behavior of the samples was studied by differential scanning calorimetry (DSC 2910, TA Instruments) using a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  and argon flow rate of  $18\text{ ml min}^{-1}$ .

### 3. Results and discussion

#### 3.1. MA of the 2Mg–0.5Ni–0.5Ge mixture under argon

The XRD patterns of Fig. 1 show the evolution of the phases during the MA of 2Mg–0.5Ni–0.5Ge mixture as a function of milling time. The intensity of the diffraction peaks of magnesium (JCPDS Powder Diffraction Data Card N° 35-0821) clearly reduces and the width of the peaks increases with milling time due to plastic deformation. The nickel diffraction peaks (JCPDS Powder Diffraction

Data Card N° 04-0850) disappear after 60 h of milling, whereas the most intense reflections of Ge (JCPDS Powder Diffraction Data Card N° 04-0545) are still detected. The  $\text{Mg}_2\text{Ge}$  (JCPDS Powder Diffraction Data Card N° 02-1135) and  $\text{Mg}_2\text{Ni}$  (JCPDS Powder Diffraction Data Card N° 35-1225) phases are formed after 20 and 40 h of MA, respectively. The  $\text{Mg}_2\text{Ni}$  peaks disappear after 60 h of milling, whereas an important set of diffraction peaks is unidentified and associated with the formation of a Mg–Ni–Ge alloy. At 90 h, two phases are clearly identified:  $\text{Mg}_2\text{Ge}$ , which appears from 20 h of milling, and a Mg–Ni–Ge alloy, which starts forming at 40 h of milling, as indicated by the presence of the diffraction peak at  $2\theta=13.2^{\circ}$ . No changes in the formed phases are observed by additional milling up to 200 h. The formation of Ni–Ge compounds is not detected.

MA of the 2Mg–0.5Ni–0.5Ge mixture generates a reduction in the particle size with the milling time. Fig. 2A–C show the particle size distribution for samples milled for 4, 40 and 200 h, respectively. The sample milled for 4 h (Fig. 2A) shows a wide particle size distribution

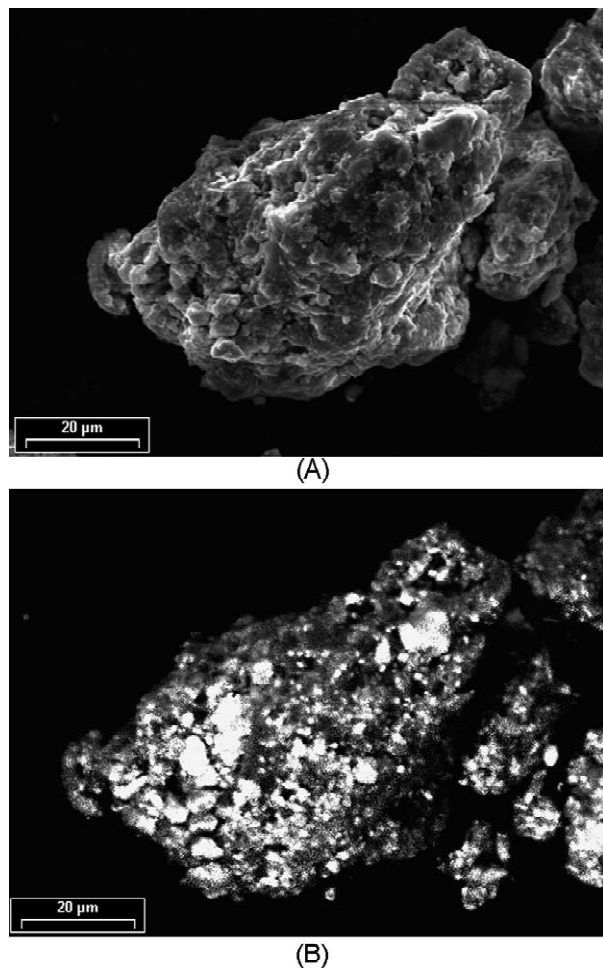


Fig. 3. SEM micrographs of the 2Mg–0.5Ni–0.5Ge mixture after 4 h of MA. (A) Secondary electron image; (B) backscattered electron image.

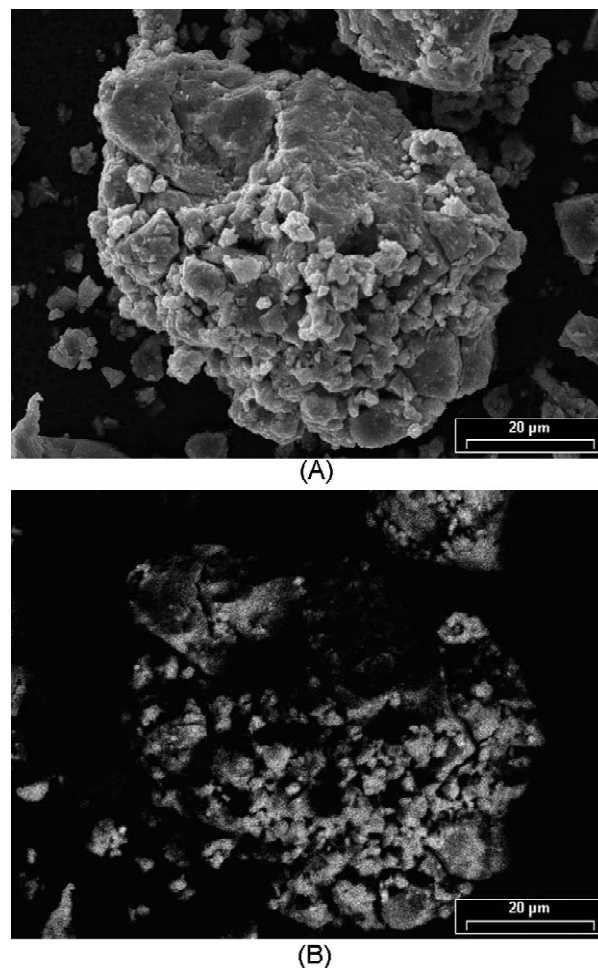


Fig. 4. SEM micrographs of the 2Mg–0.5Ni–0.5Ge mixture after 40 h of MA. (A) Secondary electron image; and (B) backscattered electron image.

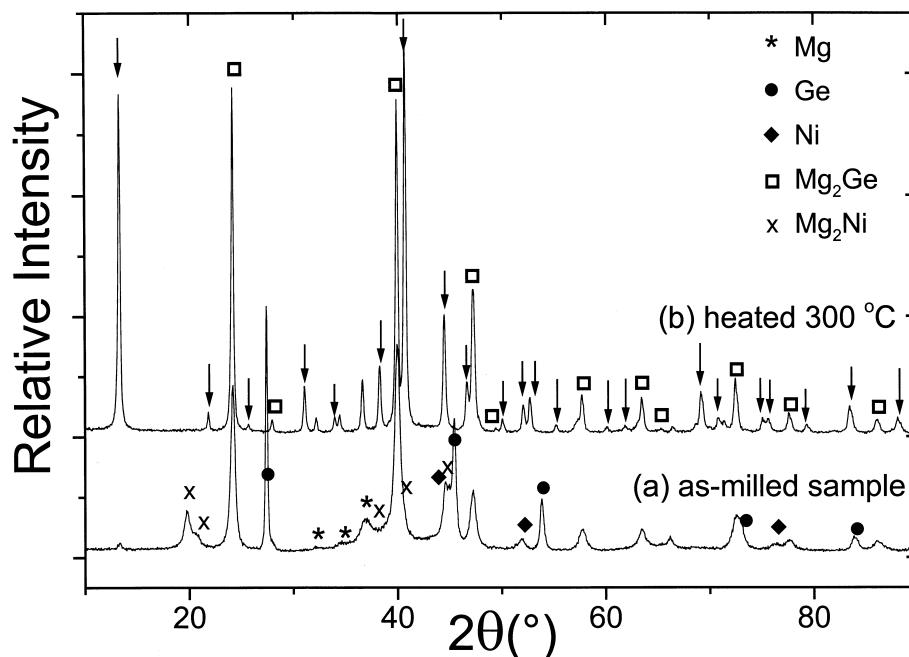


Fig. 5. XRD pattern of the 2Mg–0.5Ni–0.5Ge mixture after: (a) MA for 40 h, and (b) heat treatment at 300 °C for 50 h after milling. Arrows indicate the Mg–Ge–Ni alloy peaks.

from 50 to 170  $\mu\text{m}$ . Additional milling (40 h) produces an important reduction in the particle size due to fracturing process, with sizes lower than 60  $\mu\text{m}$ . After 200 h of milling, we observe a bimodal particle size distribution, with a major proportion of particles around 10–15  $\mu\text{m}$ .

In addition to the particle size reduction, other morphological modifications occur during the milling. Fig. 3A shows a particle after 4 h of milling. This particle has a laminar structure due to the predominance of cold welding phenomena in the initial stage of MA. Two distinct zones are apparent in the backscattered electron image (Fig. 3B). The zones can be identified in the image by the signal intensity, which is a function of each phase's atomic number. Thus, the brightest zone corresponds to Ge and Ni, and the darkest zone to Mg. EDX analyses confirm this elements distribution. Then, at short milling times the particle appears to be composed of cores of Ge and Ni surrounded by Mg matrix. The compositional distribution is in agreement with the XRD results, where Mg, Ge and Ni unreacted phases are detected up to 20 h of milling. Moreover, this phase distribution allows us to understand the absence of Ni–Ge compounds as due to kinetic restrictions. When the milling time increases from 4 h to 40 h, not only the particle size changes (Fig. 2B), but also its morphology (see Figs. 3A and 4A). The particle shown in Fig. 4A appears as an agglomeration of smaller particles of about 5  $\mu\text{m}$ . The backscattered electron image (Fig. 4B) shows a homogeneous distribution of the elements, giving a composition by EDX of 73 at.% Mg, 13 at.% Ge and 14 at.% Ni. The homogeneous distribution of Ge, Ni and Mg is in agreement with the formation of  $\text{Mg}_2\text{Ge}$  and  $\text{Mg}_2\text{Ni}$

Table 1

X-ray powder diffraction peaks obtained for 2Mg–0.5Ni–0.5Ge milled for 40 h and heated at 300 °C for 50 h

<i>hkl</i>	$d_{hkl}$ (Å)	$I/I_0$ (%)
111	6.6335	56
022	4.0665	5
113	3.4690	1
222	3.3201	<1
004	2.8770	8
133	2.6404	3
224	2.3496	16
115, 333	2.2154	100
044	2.0351	34
135	1.9460	11
244	1.9189	15
026	1.8205	2
335	1.7559	7
226	1.7358	10
444	1.6620	2
117, 155	1.6124	2
246	1.5388	2
137, 355	1.4992	2
008	1.4395	1
337	1.4069	2
066, 228	1.3572	16
157, 555	1.3298	6
266	1.3210	3
048	1.2876	1
119, 357	1.2641	6
248	1.2566	6
139	1.2073	3
448	1.1755	1
177, 339, 557	1.1576	13
02 10, 268	1.1294	2
159, 377	1.1135	2
22 10, 666	1.1083	7

compounds detected by XRD at 40 h of milling (Fig. 1).

### 3.2. MA of the 2Mg–0.5Ni–0.5Ge mixture followed by heating

The XRD results shown in Fig. 1 suggest that Mg–Ni–Ge alloy is formed at the expense of Mg<sub>2</sub>Ni (see 40 and 60 h of milling). Bearing this in mind, we perform the heating under argon of the sample milled for 40 h. Fig. 5 shows the XRD patterns of the as-milled sample (Fig. 5a) and the sample after 50 h of heating at 300 °C (Fig. 5b). After thermal treatment (Fig. 5b), the peaks associated with Ni, Ge and Mg<sub>2</sub>Ni disappear, whereas the diffraction peaks of Mg and Mg<sub>2</sub>Ge become sharper. On the other hand, the set of diffraction peaks associated with the ternary alloy are clearly identified (Fig. 5b, see arrows). The appearance of additional peaks to those observed in Fig. 1 for 90 h of milling, such as  $2\theta=25.7^\circ$  and  $2\theta=46.6^\circ$ , is due to the grain growth and relaxation of the lattice strains during heating. Then, a shorter milling of 2Mg–0.5Ni–0.5Ge mixture followed by heating under argon provides an alternative route to Mg–Ni–Ge alloy formation.

The diffraction peaks indicated belonging to Mg–Ni–Ge alloy (Fig. 5b) are completely indexed on a cubic cell, with  $a=11.521$  Å. The corresponding X-ray powder diffraction data are shown in Table 1. From the systematic extinctions, the possible space groups are determined to be  $Fd\bar{3}m$  and  $Fd\bar{3}$ . Although two compounds are known in the Mg–Ni–Ge system, MgNi<sub>6</sub>Ge<sub>6</sub> (hexagonal,  $P6/mmm$ ) and

Mg<sub>6</sub>Ni<sub>16</sub>Ge<sub>7</sub> (cubic,  $Fm\bar{3}m$ ) [10], none of them reproduce the XRD pattern observed for the ternary alloy (Fig. 5b). On the other hand, we observe that the XRD pattern of the new Mg–Ni–Ge phase is very similar to that of Mg<sub>3</sub>Ni<sub>2</sub>M-type compound recently reported (M=Al, Ti [7]) as belonging to space group  $Fd\bar{3}m$ . Because these compounds exhibit exactly the same systematic extinctions as the phase reported in the present work, this new ternary phase can be considered isostructural with Mg<sub>3</sub>Ni<sub>2</sub>M phases [7]. In addition, the lattice parameter of the Mg–Ni–Ge alloy ( $a=11.521$  Å) is very close to those corresponding to Mg<sub>3</sub>Ni<sub>2</sub>Al ( $a=11.5474$  Å) and Mg<sub>3</sub>Ni<sub>2</sub>Ti ( $a=11.6178$  Å) [7]. The sequence in the lattice parameter values can be correlated with the atomic radii of the third metal in the Mg<sub>3</sub>Ni<sub>2</sub>M ternary alloy, being 1.22 Å for Ge, 1.43 Å for Al and 1.45 Å for Ti [11].

To analyze the thermal stability of the novel Mg–Ni–Ge alloy, we perform DSC measurements under argon flow. Inset plot in Fig. 6 shows a DSC curve obtained from 2Mg–0.5Ni–0.5Ge mixture after MA for 200 h. We observe only an exothermic peak starting at 380 °C and ending at 486 °C, with an associated heat of 79 J g<sup>-1</sup>. In order to clarify the nature of this exothermic phenomena, we perform XRD analyses on samples taken after partial DSC runs. Fig. 6 shows the XRD patterns after different DSC runs stopped at 450 °C (Fig. 6b) and 500 °C (Fig. 6c). For comparison, the XRD pattern of the sample after 200 h of milling is also shown (Fig. 6a). We observe appreciable changes after heating with respect to the reference pattern.

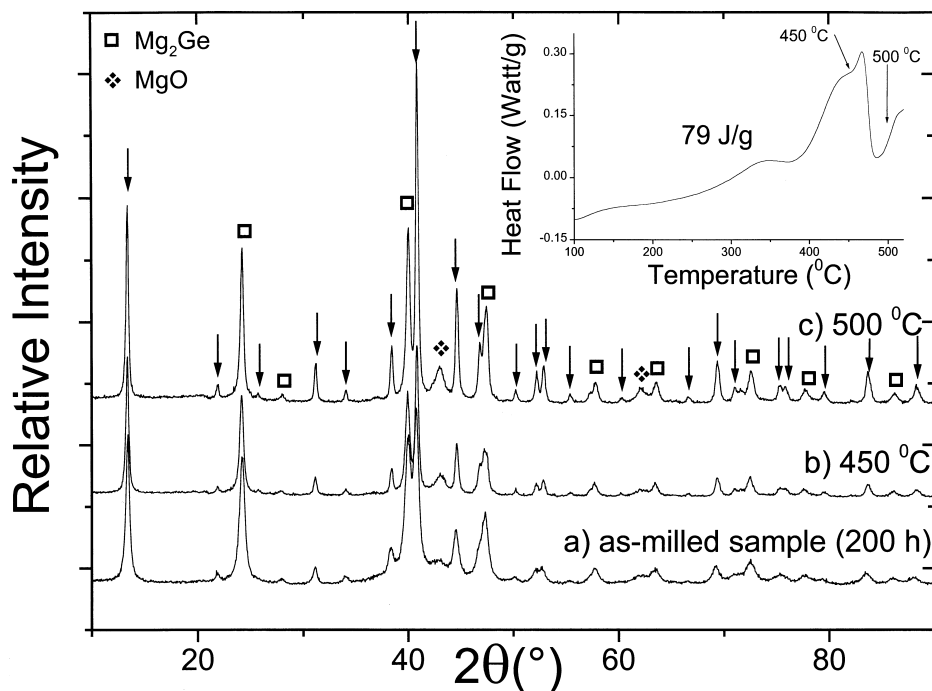


Fig. 6. XRD pattern of the 2Mg–0.5Ni–0.5Ge mixture after: (a) 200 h of MA; (b) same as (a) after DSC run stopped at 450 °C; and (c) same as (a) after DSC run stopped at 500 °C. Arrows indicate the Mg–Ge–Ni alloy peaks. Inset plot shows the DSC curve of the 2Mg–0.5Ni–0.5Ge mixture milled during 200 h.

The diffraction peaks of the sample heated up to 450 °C (Fig. 6b) become sharper and the background improves. In addition, some peaks such as  $2\theta=25.7^\circ$  and  $2\theta=46.6^\circ$ , appear. On the other hand, Mg is oxidized during the heating and the most intense reflections of MgO are detected ( $2\theta=42.9^\circ$  and  $2\theta=62.4^\circ$ ). The XRD pattern of the sample heated up to 500 °C (Fig. 6c) shows narrowing of all the peaks corresponding to ternary alloy (see Table 1). Then, the exothermic peak observed in the inset plot of Fig. 6 can be associated with the crystallization of Mg–Ge–Ni alloy and reveals that this alloy is stable upon heating up to 500 °C.

Therefore, we show experimental evidence about the existence of a new Mg–Ni–Ge alloy with  $\text{Mg}_3\text{Ni}_2\text{M}$ -type cubic structure. Up to today, only two compounds,  $\text{Mg}_3\text{Ni}_2\text{Al}$  and  $\text{Mg}_3\text{Ni}_2\text{Ti}$ , are reported to crystallize into this structure type [7]. However, it is worth mentioning that the cubic  $\text{Mg}_2\text{Ni}_x\text{Co}_{1-x}$  ( $x\leq 0.3$ ) alloy recently reported [12] could be another example, although the authors did not work out completely the structure refinement. The alloys with  $\text{Mg}_3\text{Ni}_2\text{M}$ -type structure (M=Ti, Al, Ge, Co) constitute a new type of potential hydrogen storage alloy.

#### 4. Conclusions

We synthesize a novel Mg–Ni–Ge alloy by MA of the 2Mg–0.5Ni–0.5Ge mixture. No formation of Ni–Ge compounds is detected. An alternative procedure involving MA for short time and subsequent heating also successfully produces the ternary alloy. We show that this ternary alloy

has an  $F$  cubic cell, with lattice parameter  $a=11.521 \text{ \AA}$ , and can be considered isostructural with  $\text{Mg}_3\text{Ni}_2\text{M}$ -type compound. The Mg–Ge–Ni alloy is stable upon heating up to 500 °C under argon flow. Future work should be devoted to the improvement of the production process of this novel alloy and to the study of its interaction with hydrogen and its potential use for hydrogen storage.

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