

SPECIAL ISSUE ARTICLES

MECHANICAL ALLOYING OF Mg-Ge BASED MIXTURES
UNDER HYDROGEN AND ARGON ATMOSPHERES

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Abstract - The effect of milling atmosphere and milling time on the nature and composition of milled products is investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and differential scanning calorimetry (DSC). The milling of the 2Mg-Ge mixture under argon and hydrogen allows the formation of Mg₂Ge. The MgH₂ hydride is also formed after milling both 2Mg-Ge and 2Mg-0.5Ge-0.5Ni mixtures under hydrogen. The formation of Mg₂Ni during the milling of the 2Mg-0.5Ge-0.5Ni mixture under argon and the formation of MgH₂ under hydrogen make the formation kinetics of Mg₂Ge slower. The DSC measurements indicate that the decomposition temperature of MgH₂ is 250 °C. The presence of Ge and Ge-Ni reduces in more than 200 °C the MgH₂ decomposition temperature respect to pure MgH₂. The Mg hydriding process during the mechanical alloying is improved by the presence of Ni in the starting mixture.

Keywords - Mechanical alloying, Mg-Ge mixture, Mg-Ni mixture, magnesium hydride, mechanosynthesis.

I. INTRODUCTION

Mechanical alloying (MA) is a solid-state powder processing method by which different alloys, ceramics, amorphous materials, intermetallics, etc., are synthesized at room temperature (Koch, 1992; Froes *et al.*, 1995; Lü and Lai, 1998). MA involves two processes, *cold welding* between particles which are continuously impacted by the balls, and *fracturing* of the cold welded particles under the collision (Koch, 1992; Lü and Lai, 1998). These processes enable powder particles to be always in contact with each other creating new atomically clean surfaces and minimizing the diffusion distance. Without cold welding, the particles will not be bonded together by interdiffusion, while too

much cold welding will lead to an increase in particle size and no formation of clean surfaces for diffusion. Therefore the balance between cold welding and fracturing is essential for a successful MA. The possible predominance of a process is in part due to the nature of particles. Ductile materials can be easily deformed plastically under compressive loading, whereas hard particles tend to resist the attrition and compressive forces.

MA has been successfully employed for fabrication of several metallic alloys that can not be prepared by traditional melting and casting techniques. The technique provides a way to overcome the usual difficulty of formation of new alloys using a starting mixture of low and high melting temperature elements, as example Mg-Si (Riffel and Schilz, 1998) and Mg-Ni (Singh *et al.*, 1995). In the present work, we study the production of Mg based alloys, of stoichiometry 2Mg-Ge and 2Mg-0.5Ge-0.5Ni, by MA. We examine the effect of milling atmosphere and milling time on the MA process of the ductile (Mg) - brittle (Ge and Ni) mixture. The structural and microstructural characteristics as well as the thermal stability of milled materials were analyzed by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and differential scanning calorimetry (DSC).

II. EXPERIMENTAL

Elemental powders of magnesium, germanium and nickel (purity greater than 99.9%) were used. The powders were mechanically milled under argon (99.995 %, AGA, Argentina) and hydrogen (99.995 %, Air Liquid, Argentina) using a Uni-Ball-Mill II apparatus (Australian Scientific Instruments). The 2Mg-Ge and 2Mg-0.5Ge-0.5Ni mixtures together with ferromagnetic steel balls were put into a stainless steel container and closed in an argon glove box. In all experiments, about 6 g of starting materials were used, giving a ball to powder weight ratio of 44:1. The pressure inside

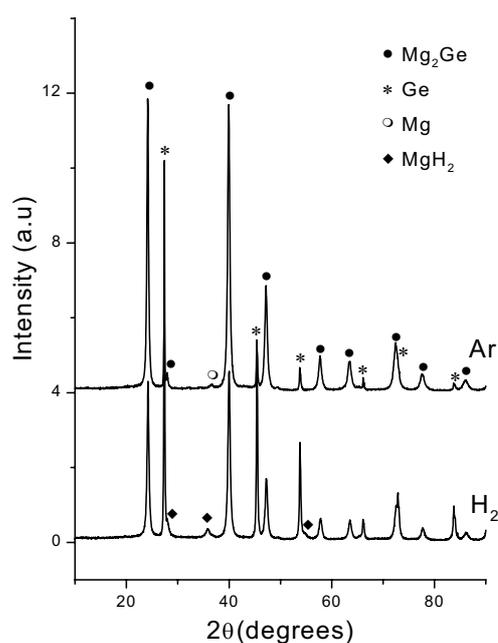


Fig. 1: XRD patterns of the 2Mg-Ge mixture milled during 24 h.

the container was 1 atm for milling under argon and 5 atm when milling under hydrogen.

At regular intervals, the container was opened in an argon glove box and a small amount of powder was taken for analysis by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and differential scanning calorimetry (DSC). The X-ray powder diffraction was performed on a Philips PW 1710/01 instrument with $\text{CuK}\alpha$ radiation (graphite monochromator). Scanning electron microscopy (SEM 515, Philips Electronic Instruments) was used to characterize the microstructure. The thermal behavior of the samples was studied by DSC (DSC 2910, TA Instruments) using a heating rate of $25^\circ\text{C min}^{-1}$ and an argon flow rate of 18 ml min^{-1} .

III. RESULTS

A. MA of the 2Mg-Ge mixture under argon and hydrogen

Figure 1 shows the XRD patterns corresponding to the 2Mg-Ge mixture milled 24 h under argon and hydrogen. After 24 h of milling under argon, we observe the formation of Mg_2Ge (JCPDS Powder Diffraction Data Card N° 02-1135), whereas only the most intense reflections of Ge (JCPDS Powder Diffraction Data Card N° 04-0545) and Mg (JCPDS Powder Diffraction Data Card N° 35-0821) are still detected. In hydrogen

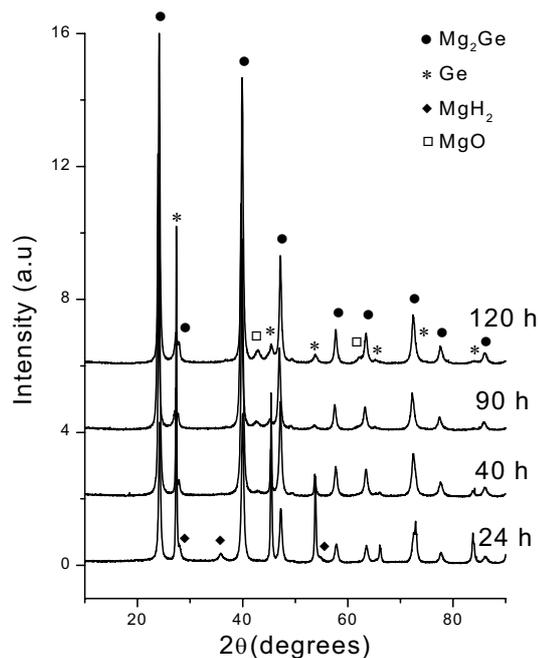


Fig. 2: XRD patterns of the 2Mg-Ge mixture milled under hydrogen for different times.

atmosphere the behavior is different. Although we also observe the Mg_2Ge formation, the comparison of the relative intensities of Mg_2Ge diffraction peaks in each atmosphere suggests that Mg_2Ge has been formed in higher proportion in argon atmosphere. In addition, we also observe the formation of MgH_2 (JCPDS Powder Diffraction Data Card N° 12-0697) simultaneously with the formation of Mg_2Ge .

With the aim of evaluating the Mg_2Ge formation degree as a function of milling time, we analyze the phase evolution during MA of the 2Mg-Ge mixture. Under argon atmosphere, we do not observe significant changes in the phases with the milling time. However, the Mg_2Ge formation is not complete even after 330 h of milling, coexisting Ge and MgO (JCPDS Powder Diffraction Data Card N° 45-0946) as residual phases for longer milling times. Figure 2 shows the XRD patterns of 2Mg-Ge mixture after MA under hydrogen for different times. The presence of MgH_2 is not observed for milling times longer than 24 h. Further milling produced an increase in the intensity of the Mg_2Ge diffraction peaks respect to the corresponding ones of Ge. However, both Ge and MgO phases are detected at 120 h of milling, in a similar way to argon atmosphere (Fig. 2).

B. MA of the 2Mg-0.5Ge-0.5Ni mixture under argon and hydrogen

Figure 3 shows the XRD patterns of the 2Mg-

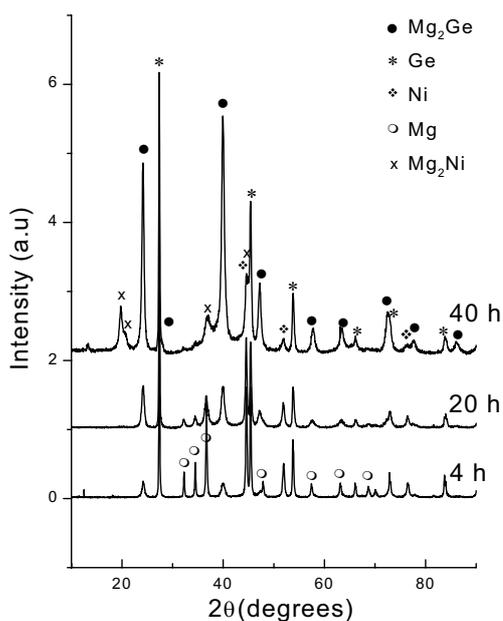


Fig. 3: XRD patterns of the 2Mg-0.5Ge-0.5Ni mixture milled under argon.

0.5Ge-0.5Ni mixture milled under argon for different times. We observe the Mg_2Ge formation in the initial period of milling (4 h). The presence of Mg_2Ge is even more clear after 20 h by the increase of the relative intensities of the (111, $2\theta = 23.86^\circ$) and (220, $2\theta = 39.89^\circ$) diffraction peaks corresponding to the magnesium germanide. The intermetallic Mg_2Ni is formed after 40 h of milling (JCPDS Powder Diffraction Data Card N° 35-1225).

To analyze the effect of the milling atmosphere we perform the MA of the 2Mg-0.5Ge-0.5Ni mixture under hydrogen. Figure 4 shows the evolution of the phases during MA as a function of milling time. Similarly to the 2Mg-Ge mixture milled under hydrogen (Fig. 1), we observe both Mg_2Ge and MgH_2 formation. The presence of MgH_2 is even detectable after 40 h of milling. The presence of $\text{NiH}_{1.11}$, NiH_2 or Mg_2NiH_4 hydrides is not observed.

C. DSC measurements

In order to analyze the thermal stability of MgH_2 produced by MA under hydrogen from both 2Mg-Ge and 2Mg-0.5Ge-0.5Ni mixtures, we perform the DSC measurements showed in Fig. 5. As a reference, we also present the thermal behavior of pure MgH_2 produced after the same milling treatment (Gennari *et al.*, 2001). Figure 5 (curve “a”) shows the DSC curve for the pure Mg powder milled 20 h under hydrogen. The MgH_2 decompo-

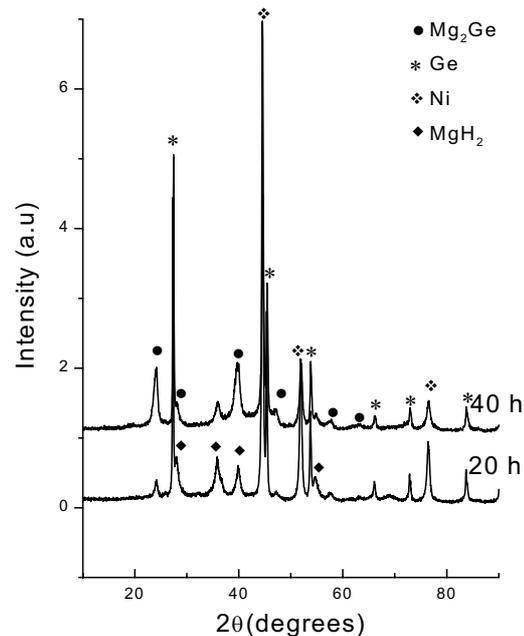


Fig. 4: XRD patterns of the 2Mg-0.5Ge-0.5Ni mixture milled under hydrogen.

sition is indicated by the endothermic peak with an onset temperature of 463°C . For the 2Mg-Ge mixture (curve “b”), we identify a wide endothermic peak starting at 250°C and ending at 470°C . In the case of 2Mg-0.5Ge-0.5Ni mixture (curve “c”), hydride decomposition occurs between 250°C and 340°C . XRD analyses performed on the samples after DSC measurement show the complete MgH_2 decomposition.

D. Morphology evolution during MA

In the Figs. 6 and 7 we present the typical morphology of the 2Mg-0.5Ge-0.5Ni mixture after milling under argon atmosphere. The micrograph 6A (4 h of milling) shows an aggregated particle with laminar structure due to the cold welding phenomena occurring at the initial stage of MA. The backscattered electron image (Fig. 6B) allows to differentiate two zones: Ni and Ge clusters (brightest zone) distributed over the Mg matrix (darkest zone). EDX analyses confirm this element distribution. However, we observe that longer milling times (40 h) introduce significant changes in the powder microstructure. Figure 7A shows an agglomerated particle formed by small grains of about $5\ \mu\text{m}$. The particles become smaller in size due to fracturing process. The backscattered electron image (Fig. 7B) shows an homogeneous distribution of the elements, giving an atomic composition by EDX of 72.7 % Mg, 13.4 % Ge and 13.9 % Ni.

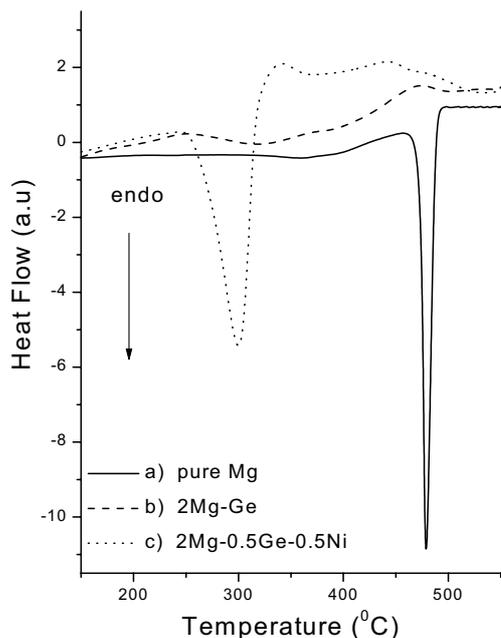


Fig 5: Thermal desorption behavior of MgH_2 formed during the milling under hydrogen. a) pure Mg; b) 2Mg-Ge mixture; c) Mg-0.5Ge-0.5Ni mixture.

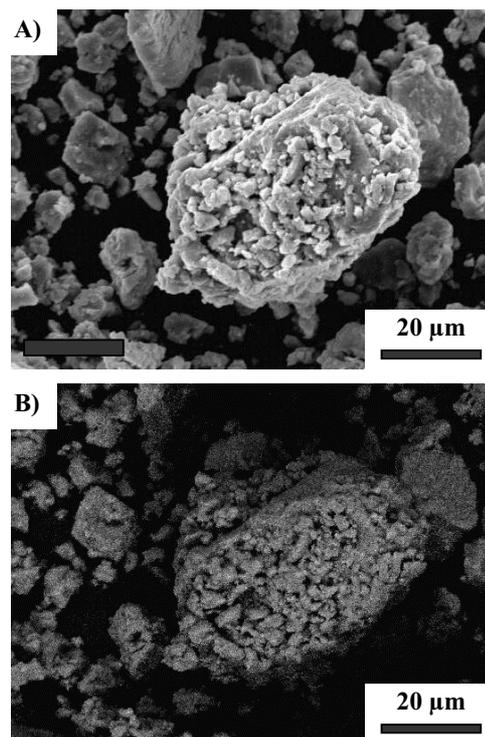


Fig 7: Particle obtained after 40 h of milling of the 2Mg-0.5Ge-0.5Ni mixture under argon

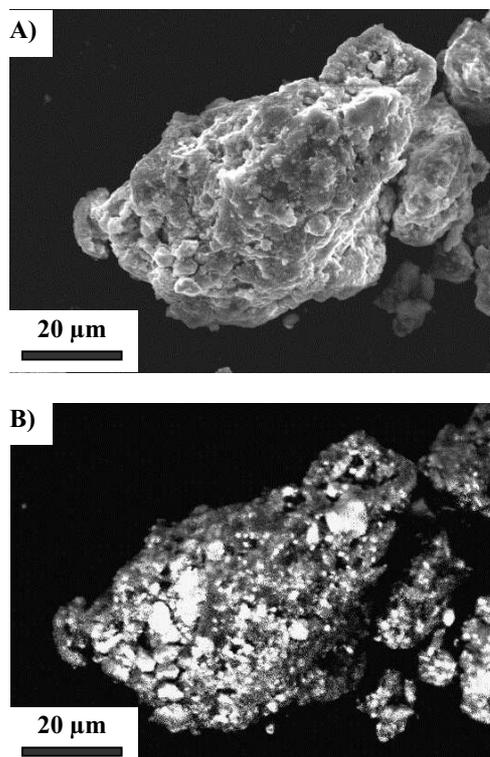


Fig. 6: Particle obtained after 4 h of milling of the 2Mg-0.5Ge-0.5Ni mixture under argon. The brightest phase corresponds to Ge and Ni.

IV. DISCUSSION

From Mg-Ge binary phase diagram (Massalski *et al.*, 1990), we would expect the formation of the stoichiometric Mg_2Ge compound when Mg and Ge are joined in the ratio 2:1 at temperatures lower than 1117 °C. The magnesium germanide has a cubic structure that transforms to the hexagonal crystal structure after exposure to temperatures in the range of 600 to 1200 °C and pressures of 25.3 to 55.7 atm (Dyuzheva *et al.*, 1976). This hexagonal structure can be retained as metastable at room temperature and atmospheric pressure. Considering that it exists a metastable phase with Mg_2Ge composition and that mechanical alloying allows the synthesis of metastable phases due to kinetic restrictions (Koch, 1991; Froes *et al.*, 1995; Lü and Lai, 1998), in all XRD patterns the possible presence of hexagonal Mg_2Ge (JCPDS Powder Diffraction Data Card N° 34-0686) was analyzed.

During the mechanical alloying of the 2Mg-Ge mixture we observe the formation of cubic Mg_2Ge according to the predictions from the binary phase diagram (Figs. 1 and 2). However, we do not observe its complete formation under argon (330 h of milling) and hydrogen atmosphere (120 h of milling), as it is shown by the presence of free Ge after longer milling times. This can be attributed to the

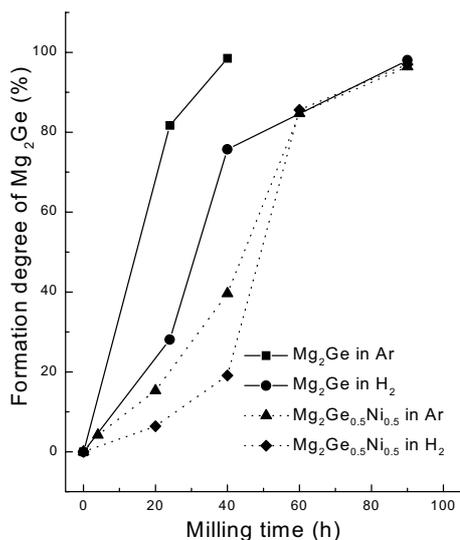


Fig. 8: Formation degree of Mg₂Ge as a function of milling time

loss of Mg due to oxidation and the consequent formation of MgO, detected by XRD (see Fig. 2). The formation of hexagonal Mg₂Ge was not observed during the mechanical alloying of the 2Mg-Ge mixture under argon or hydrogen.

The Mg₂Ge formation degree, A , is calculated from XRD measurements and defined as

$$A = \frac{I_{Mg_2Ge}}{I_{Mg_2Ge} + I_{Ge} + I_{Mg}} \quad (1)$$

where I represents the intensity of the most intense reflection of Mg₂Ge ($d=2,26000 \text{ \AA}$), Ge ($d=3,26600 \text{ \AA}$) and Mg ($d=2,45195 \text{ \AA}$). Figure 8 shows the formation degree of Mg₂Ge as a function of the milling time for the mixtures milled under argon and hydrogen atmospheres. Figure 8 allows us to determine that the 2Mg-Ge mixture milled under argon has associated a greater Mg₂Ge formation degree relative to the 2Mg-0.5Ge-0.5Ni mixture. For comparison of XRD patterns in Figs. 1 and 3, we infer that the Mg₂Ge formation reaction is faster in the mixtures mechanically alloyed with high amount of Ge relative to the initial amount of Mg. The simultaneous presence of Ge and Ni (brittle materials) generates a wide distribution of both materials in a Mg ductile matrix for short milling times (see Fig. 6). In this way, the interdiffusion between Mg-Ge and Mg-Ni is promoted during the cold welding and posterior fracturing. This is demonstrated by the Mg₂Ge and Mg₂Ni formation (Fig. 3) during the MA under argon atmosphere (40 h of milling). The SEM observations (Fig. 7) and the EDX analysis show that

Table 1. Thermodynamic data of some compounds involved in the Mg-Ge and Mg-Ge-Ni systems (Kubaschewski and Alcock, 1979)

| Compound | Formation heat at 298 K (kcal mol ⁻¹) | Formation entropy at 298 K (cal K ⁻¹ mol ⁻¹) |
|----------------------------------|---|---|
| Mg ₂ Ge | -27.5 | 17.4 |
| MgO | -143.7 | 6.4 |
| Mg ₂ Ni | -12.4 | 22.7 |
| MgNi ₂ | -13.5 | 21.2 |
| Ni ₂ Ge | -26.3 | 21.7 |
| MgH ₂ | -18.0 | 7.4 |
| NiH ₂ | 94.0 | 17.6 |
| Mg ₂ NiH ₄ | -15.4 | -29.2 |

Mg, Ge and Ni are homogeneously distributed in each agglomerate after 40 h of milling, in agreement with XRD results (Fig. 3). We do not detect phases belonging the Ge-Ni system from XRD patterns. Although the driving force for the Ni₂Ge is comparable with the corresponding to Mg₂Ge (see Table 1), the morphologic evidence (Fig. 6) supports that the formation of Ni-Ge compounds is not possible due to kinetic restrictions.

Figure 3 shows that the Mg₂Ge formation occurs after 4 h of milling whereas the Mg₂Ni formation requires 40 h of milling. To interpret this behavior, we can compare from Table 1 the formation heat of each compound (considering similar formation entropy for both compounds).

The formation heat of Mg₂Ge is higher than the corresponding to Mg₂Ni and MgNi₂. Then, a greater driving force for the Mg₂Ge formation favors its synthesis respect to the intermetallics in the Mg-Ni system. Taking into account the composition in the starting mixture and the stoichiometric ratio between Mg-Ge and Mg-Ni (2Mg-0.5Ge-0.5Ni), we observe the formation of Mg₂Ge together with Mg₂Ni, both being stable phases of both systems.

On the other hand, Fig. 7 shows that the Mg₂Ge formation degree is greater under argon atmosphere. Considering that heterogeneous reactions may occur if milling is performed in the presence of a reactive atmosphere (Chen and Williams, 1995; Tessier *et al.*, 1998), we can demonstrate that under hydrogen gas-solid reactions occur. This is clear from Figs. 1 and 4, where after the milling of 2Mg-Ge for 24 h and 2Mg-0.5Ge-0.5Ni for 20 h under hydrogen the presence of MgH₂ is identified. The heterogeneous reaction between Mg and hydrogen is favored by the continuous creation of

fresh surfaces and the stress increase as a consequence of the mechanical milling process. In this way the hydrogen can be absorbed onto new surfaces created during milling and react with the metal to form the MgH_2 hydride under further ball impacts (Chen and Williams, 1995).

To characterize the thermal stability of MgH_2 formed after MA process, we analyze the DSC measurements showed in Fig. 5. The proportion of MgH_2 can be calculated using the peak area in the DSC curves (Fig. 5) and the MgH_2 heat of formation given in Table 1 (Kubaschewski and Alcock, 1979). For the curve "a" the calculated proportion of the hydride is about 10 wt.% (Gennari *et al.*, 2001). The proportion of MgH_2 in the 2Mg-Ge mixture (curve "b") is 3.3 wt.%, whereas in the case of the 2Mg-0.5Ge-0.5Ni (curve "c") is 19.1 wt.%. These results suggest that the hydrogen storage capacity is dependent on the presence of additives and/or the presence of compounds as Mg_2Ni . In the milling conditions, the Ni presence in the 2Mg-0.5Ge-0.5Ni mixture can enhance the hydrogen dissociation and recombination over the metallic surface, in agreement with Ivanov *et al.* (1987).

As another interesting result, the MgH_2 formed during MA of the 2Mg-Ge and Mg-0.5Ge-0.5Ni mixtures has a lower decomposition temperature than pure MgH_2 . The onset temperature for pure MgH_2 decomposition is 463 °C (curve "a"), whereas the decomposition temperature of MgH_2 formed by MA of both mixtures is 250 °C (curves "b" and "c"). As the milling time is approximately the same, the structural changes introduced during the milling for the different samples are similar. Then, the reduction in the decomposition temperature is due to the Ge and Ge/Ni presence in the samples (2Mg-Ge and Mg-0.5Ge-0.5Ni mixtures, respectively). Additional studies are being developed in our research group to clarify the role of Ge and Ni on the MgH_2 thermal decomposition.

V. CONCLUSIONS

We analyze the effect of milling time and reaction atmosphere on the phases formed during the MA of the Mg-Ge and Mg-Ge-Ni mixtures. The mechanical milling of the 2Mg-Ge and 2Mg-0.5Ge-0.5Ni mixtures under argon leads to the Mg_2Ge and Mg_2Ge-Mg_2Ni formation, respectively. The formation rate of Mg_2Ge from the 2Mg-0.5Ge-0.5Ni mixture is higher than the corresponding to Mg_2Ni , due to the high formation heat associated to Mg_2Ge .

The formation degree of Mg_2Ge is greater un-

der argon than hydrogen atmosphere for both studied mixtures. We find that the formation of MgH_2 is a competitive reaction with the Mg_2Ge synthesis at short milling times, delaying its formation. The MgH_2 formed after MA of 2Mg-Ge and 2Mg-0.5Ge-0.5Ni mixtures decomposes at lower temperature than pure MgH_2 . This different thermal behavior is due to the presence of Ge and Ge-Ni. The amount of MgH_2 formed is dependent on the presence of Ni, which improves the hydrogen dissociation during the MA and favors the hydride formation.

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