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Effect of the milling energy on the production and thermal stability of amorphous $Mg_{50}Ni_{50}$

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ABSTRACT

The effect of milling energy on the amorphisation process and subsequent thermal crystallization of $Mg_{50}Ni_{50}$ was investigated. The amorphous $Mg_{50}Ni_{50}$ was produced using a planetary mill (medium energy) with a ball to material weight ratio of 13:1, and a SPEX mill (high energy) with a ball to material weight ratio of 20:1. The results obtained by means of X-ray diffraction showed that it is possible to obtain an amorphous $Mg_{50}Ni_{50}$ alloy, through both milling processes, starting of Ni powders and Mg turnings. However, the amorphisation process requires more time in the planetary mill (80–90 h) than in the SPEX mill (15–20 h), due to the difference in energy level and milling mechanism between these mills. The phase evolution during the amorphisation process is practically independent of the mill energy. In this way, it was observed that the mill conditions promoted an extensive refinement of the microstructure during the first hours of milling. The defects produced during this time led to the amorphisation of part of the system. This amorphous precursor suffers a mechanically induced crystallization into Mg_2Ni, which is subsequently destabilized into amorphous $Mg_{50}Ni_{50}$. Based on the results obtained, it is proposed that the formation of amorphous precursor during mechanical milling of Mg and Ni is a characteristic of the Mg–Ni system, over a wide composition range, rather than of a particular composition. In relation to the thermal crystallization of the amorphous produced, the results of the differential thermal analysis applied to the amorphous samples showed that the formation enthalpy for both amorphous is the same, however, the amorphous produced in a planetary mill presented higher crystallization temperatures and apparent activation energies than the amorphous produced in a SPEX mill. The last behavior would be related with iron contamination coming from the erosion of the milling media. Finally, it is possible to conclude, that under the experimental condition employed, the amorphous phases produced in a planetary and SPEX mill, are structurally and energetically similar.

1. Introduction

The mechanical alloying (MA) process developed by Benjamin et al. [1,2] in the early 1970s, is now recognized as a versatile technique for obtaining oxide-dispersion-strengthened superalloys [1], intermetallic compounds [3,4], supersaturated solid solutions [5] and amorphous phases [6], among others.

The variables which control the transformation stages of the initial elements into final phases during the MA process are not clear yet. However, previous works [7,8] have indicated that the transformation stages could depend on the chemical composition and milling conditions.

On the other hand, the last investigations made on the field of hydrogen storage materials, have showed that in addition to the chemical composition, the microstructure is a relevant variable in the hydriding and dehydriding behavior of these materials. In this way, the study of the amorphous phases and nanostructured composites has been increased in the recent years [9–19].

Amorphous $Mg_{50}Ni_{50}$, produced by MA, has showed a marked improvement in the hydriding–dehydriding kinetics compared to Mg_2Ni and ball-milled Mg_2Ni [20,21]. In order to maintain the improved hydrogen storage properties upon cycling, the thermal stability of amorphous structures must be considered. In the present work, amorphisation phase evolution during the MA of an equiatomic mixture of Mg and Ni, and subsequent thermal crystallization of the amorphous alloys as functions of milling energy (medium and high energy) has been studied.

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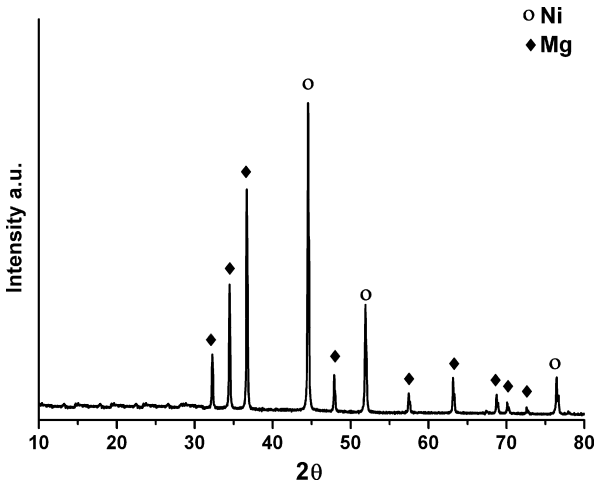

Fig. 1. XRD pattern of initial mixture of Mg and Ni in a 1:1 atomic proportion.

2. Experimental

Amorphous $Mg_{50}Ni_{50}$ was produced by MA, of Mg turnings (98 wt.% pure, supplied by Aldrich with particle size below 4 mesh) and Ni powder (99.99 wt.% pure, supplied by Fluka with a particle size below 250 mesh) in a 1:1 atomic proportion, in a medium energy Fritsch Pulverisette 5 planetary mill, with a ball to powder weight ratio of 13:1, and, in a high energy SPEX 8000 D mill, with a ball to powder weight ratio of 20:1. Both milling processes were performed in discontinuous way consisting of 1 milling hour followed by rest period of 0.5 h. In order to prevent the alloys oxidation during milling, the powder mixtures were sealed under Ar. The mechanically alloyed powders were characterized by X-ray diffraction (XRD) in a Shimadzu XRD-600 diffractometer using Cu Kα radiation. Thermal stability was determined by means of differential scanning calorimetry (DSC) in a SDT 2960 and DSC 2920, TA instruments, devices. The size and morphology of the powder was studied using a Jeol 5410 scanning electron microscope (SEM).

3. Results and discussion

3.1. Amorphisation

Fig. 1 shows the X-ray diffraction pattern of the initial mixture of Mg turnings and Ni powders. The initial average crystallite size was calculated using the Scherrer method [22] considering the (1 0 1) Mg plane and (2 0 0) Ni plane. In order to obtain the full width at the half maximum peak intensity, the experimental peaks were fitted using a Lorentz function. The results obtained were corrected considering the instrumental width. Thus, the calculated initial average crystallite sizes for Mg and Ni were of 105 and 80 nm, respectively. Due to that the Scherrer method only consider the crystallite size contribution on the experimental diffraction peak width, the results obtained only represent an inferior limit of crystallite size.

Fig. 2(a) and (b) shows the phases evolution, obtained by means of X-ray diffraction during the amorphisation processes in a planetary and SPEX mills, respectively. In order to observe the amorphisation phase evolution, the X-ray diffraction patterns were normalized.

It can be seen, that the energy applied to the powders by means of planetary milling (medium energy) was enough to produce an amorphous $Mg_{50}Ni_{50}$ alloy, and that the major energy applied by means SPEX milling (high energy) and the consequent increase in the milling temperature, were not sufficient to produce an amorphisation/crystallization cycle, as has been previously reported for other systems [23,24], resulting also in the amorphous $Mg_{50}Ni_{50}$ alloy.

In relation to the amorphisation time, due to the difference in energy level and milling mechanisms (which will be discussed later), the amorphisation process requires more time in the planetary mill (80–90 h) than in the SPEX mill (15–20 h).

Table 1
Calculated average crystallite size for Mg and Ni using Scherrer formula

	Milling time (h)	Average crystallite size (nm)	
		Mg	Ni
As received	–	105	80
Planetary	4	14	23
SPEX	2	12	27

With reference to the phase evolution, it can be seen, that in both milling processes, during the first hours of milling, the Mg peaks lowered their intensity and increased their width in comparison to the Ni peaks. The calculated average crystallite sizes for Mg and Ni, after 4 h of planetary milling and 2 h of SPEX milling, can be seen in Table 1.

The major microstructural refinement reached by Mg in the first hours of milling, could be explained by its crystalline structure. It has been demonstrated [25,26] that the crystallite size attainable by milling depends on the crystallite structure of the material being milled: BCC materials reach the smallest sizes (~9 nm), HCP materials reach somewhat large crystallite size (15–25 nm), and the FCC materials tend to reach the largest crystallite size of all (~25 nm). Since the crystal structure of Mg is HCP and that of Ni is FCC, differences in the crystallite size after milling can be expected.

As the milling continues, the intermetallic Mg_2Ni is detected in a planetary (10 h) and SPEX (5 h) milling. In this case, the Scherrer method could not be applied to measure Mg_2Ni crystallite size because the X-ray diffraction peaks do not have all the requirements for it to be valid, however, considering the width of the peak nearly to $2\theta = 20^\circ$, which is composed by the contribution of the (1 0 0), (0 0 3) and (1 0 1) planes, it is very probable that the Mg_2Ni crystallite size is in nanometer range.

During the Mg_2Ni production by MA, has been previously reported the apparition of an amorphous phase in the first hours of milling called amorphous precursor, because, it can be crystallized by mechanical and thermal way into Mg_2Ni [3,4]. The same behavior has been founded in Mg–B [27] and Ti–Al–Si [28] systems, among others.

In this way, the X-ray diffraction pattern from a sample milled 4 h in a planetary mill shows a raising in the diffraction intensity over the background level, in the regions nearly to the $2\theta \approx 20$ and 40°, which correspond to diffraction position of (0 0 3) and (2 0 0) Mg_2Ni planes. This behavior has been previously reported [3,4], and has been associated as a signal of the amorphous precursor formation.

In order to confirm the existence of this amorphous precursor before the Mg_2Ni detection in mechanical alloying of Mg:Ni in a 1:1 atomic proportion, two samples milled 4 and 2 h in a planetary and SPEX mills, respectively, were analyzed by DSC (Fig. 3(a)), with the aim of detecting a possible crystallization exothermic peak.

By analyzing the calorimetric curves obtained (Fig. 3(a)), and based on previous works [3,4], it can be concluded that the first exothermic reaction around 140 °C, is related with Mg_2Ni crystallization, and a second exothermic event, which took place between 200 and 250 °C, is associated to relaxation, and solid-state reaction between Mg and Ni. The presence of crystalline Mg_2Ni after heat treatment has been confirmed by X-ray diffraction, Fig. 3(b). The difference in the calorimetric curve and the X-ray diffraction patterns, between the sample obtained by planetary and SPEX milling, is related to the amount of amorphous precursor existent in each sample.

Based on the above observations, it is proposed that the formation of amorphous precursor during mechanical milling of Mg and