Microstructural evolution during mechanical alloying of Mg and Ni

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Abstract

This study investigates the microstructural evolution during mechanical alloying of Mg and Ni, and during subsequent heat treatments of SPEX milled powders. The milling was performed under an inert argon atmosphere, employing two different ball-to-powder ratios (BPR): 10:1 and 20:1. It was observed that a large number of defects were produced during the first hours of milling. These defects led to the amorphization of part of the system, and promoted an extensive refinement of the microstructure as well. Later on, the formation of the Mg2Ni compound due to the crystallization of the amorphous phase was observed. The microstructural details showed us that a possible complete sequence of phase transformations during milling of pure Mg and Ni could be: Mg(c) + Ni(c) → Mg(nc) + Ni(nc) → amorphous + Ni(nc) + Mg(nc) → Mg2Ni(nc), where c and nc stand for crystalline and nanocrystalline, respectively. On the other hand, subsequent heat treatments of the milled powder showed that the amorphous phase could also be transformed into Mg2Ni by heating. Finally, the knowledge of the evolution of the microstructure during milling and annealing were combined to propose an optimal processing route to efficiently obtain the Mg2Ni compound.

Keywords: Nanocrystalline; Mechanical alloying; Mg, Ni

1. Introduction

Metallic hydrides have been extensively investigated in the past few years due to their potential application as hydrogen storage materials. These materials are characterized by a high hydration capacity, and a fast hydration and de-hydration kinetics [1]. Among all the metallic elements, Mg exhibits the most elevated hydration capacity through the formation of MgH2, which is capable of storing 7.6 wt.% of hydrogen [1,2]. Mg also has the advantage of being abundant, low cost and low density. However, Mg is highly reactive and forms a surface oxide layer that hinders the formation of the hydride compound, hence increasing the activation energy for hydration. This last point translates into higher hydration temperatures and pressures, or slower kinetics of hydration [3,4]. Therefore, finding ways of improving the hydration kinetics of Mg has been one of the main challenges faced by researchers in this area. In this line of thought, two approaches focusing in two different aspects have been followed to increase its kinetics of hydration: (a) changes in chemical composition, and/or (b) new materials processing techniques. As a result of the first approach effort, the intermetallic compound Mg2Ni has been proposed as an alternative hydrogen storage material [5–8]. The Mg2Ni compound can combine with hydrogen to form the Mg2NiH4 hydride, which in turn has a lower hydration capacity than Mg, 3.6 wt.% H, but a much faster hydration kinetics [9,10]. Regarding materials processing, Mg2Ni has been traditionally produced by fusion, and hence it is difficult to obtain high quality Mg2Ni because of the large differences in melting point and vapor pressure between Mg and Ni [11]. However, it is now possible to avoid the inherent difficulties of the fusion technique by using mechanical alloying [3,12–14]. This is so because the reaction between Mg and Ni takes place in solid state and, more importantly, the compound obtained possesses microstructural characteristics such as nanocrystallinity [4,15,16] that are more suitable for hydrogen absorption [17–19].
Another important characteristic of mechanical alloying is the possibility of developing different kinds of amorphous alloys and compounds. Obtaining amorphous materials, however, is not unique to this process. In fact, the first reports on amorphous metallic alloys were published by Buckel and Hilsch [20] in 1952, working on deposition from the vapor phase. Later, the work of Dovesi and coworkers [21] in 1960 on rapid quenching of the Au–Si eutectic alloys created an enormous driving force to study amorphous alloys. In the case of materials produced by mechanical alloying, the amorphization phenomenon in alloys and intermetallic compounds has been documented since the early 1980s [22]. However, in spite of the amount of work done since then, the sequence of events leading to the formation of the amorphous phases during mechanical alloying is still under discussion [22–24]. In the particular case of the Mg–Ni system, the existence of an amorphization process during mechanical alloying has also been detected [25,26]. Although it has been postulated that the amorphous phase may act as a precursor for the crystalline compound, the role that the initial elements play on the formation of this new amorphous phase is not completely understood yet.

In the present work, the microstructural evolution during milling of Mg and Ni, and during subsequent heat treatments, is studied. The influence of the processing parameters on the phases present at any given time, the formation of an amorphous phase, and the complete sequence of phase transformations leading to the formation of Mg$_2$Ni are also studied. Finally, an alternative route for manufacturing Mg$_2$Ni that involves heat treatment after milling is also studied. This last manufacturing route could be very attractive because it avoids the long milling times necessary for the formation of the intermetallic Mg$_2$Ni using only mechanical alloying.

2. Experimental

Elemental powders of Mg (98% purity) and Ni (99% purity) were mechanically alloyed in a SPEX mill, model 8000D, equipped with stainless steel balls and vials under an inert argon atmosphere. The charge consisted of 50 wt.% of each element, and two different ball-to-powder ratios (BPR) were employed: 10:1 and 20:1. X-ray diffraction (XRD) measurements were carried out in a Siemens D5000 diffractometer using Cu Kα radiation. Differential scanning calorimetry (DSC) measurements were performed in a TA Instruments machine, model 2920 DSC. All the samples were DSC-scanned from 293 to 673 K using a heating rate of 10 K/min under a nitrogen atmosphere. The activation energy of the phase transformations was determined by the Kissinger method using five different heating rates (5, 10, 20, 30 and 50 K/min). The internal microstructure of the powder was studied using a Philips CM-12 transmission electron microscopy (TEM) operated at 100 kV, whereas the powder size and morphology was studied using a Philips XL 30 S-FEG scanning electron microscopy (SEM) equipped with an EDS system.

3. Results

3.1. Powder size and distribution

Fig. 1 shows the powder after 3 h of milling for two different BPRs (10:1 and 20:1). It can be seen that, in both cases, the powder has a bimodal size distribution composed of large agglomerates of ~100 μm, and small, heavily deformed particles of ~10–20 μm. In fact, the large agglomerates are made of several of the small, deformed particles welded together. These two types of particles are commonly seen in the early stages of high-energy milling of ductile materials, and are the product of a continuous cycle of plastic deformation, welding and fracturing [27]. Regarding the powder size distribution, it is worth noting that the two distributions seen in Fig. 1 are very similar to each other, even though the BPRs are quite different. This microstructural feature indicates that the presence of the large agglomerates within a powder population depends more on the milling time than on the BPR. Finally, and after several hours of milling, fracturing becomes the most relevant event due to the inherently brittle nature of the
Mg$_2$Ni intermetallic compound, hence reducing the overall powder size and narrowing the powder size distribution.

3.2. X-ray diffraction

The XRD spectra of samples milled for 3 and 8 h and with ball-to-powder ratios of 10:1 and 4:1 are shown in Fig. 2 (the complete results obtained with a BPR of 4:1 can be found elsewhere [26]). It can be observed that while the Mg and Ni peaks are well defined in the sample milled for 3 h using the lower BPR (4:1), the sample milled with a higher BPR (10:1) presents just one broadened peak located in the 2\(\theta\) region that otherwise contains three Mg peaks corresponding to the (1 0 0), (0 0 2) and (1 0 1) planes. This peak broadening, as it will be discussed later, may be related to an amorphization process previous to the detection of the compound Mg$_2$Ni. It can be also seen in Fig. 2 that only Mg and Ni peaks are detected after 8 h of milling using a BPR of 4:1, but Mg, Ni and Mg$_2$Ni are detected after the same period of time using a BPR of 10:1 instead. If we define the detection time as the time necessary to detect the presence of the (0 0 3) plane of Mg$_2$Ni in the XRD spectrum, the detection times for BPRs of 10:1 and 4:1 are 8 and 29 h, respectively [26] (not shown in the XRD spectra).

Another characteristic shown by the XRD spectra in Fig. 2 is that, during the first hours of milling, the Mg peaks lowered their intensity and increased their extent of broadening due to the cumulative plastic deformation. As it was mentioned before, this led to the presence of only one broad peak in the diffraction zone corresponding to the (1 0 0), (0 0 2) and (1 0 1) Mg planes after 8 h of milling. However, the Ni peaks are hardly affected after the same 8 h of milling (the (1 1 1) and (2 0 0) Ni peaks are still clearly distinguishable). Therefore, the evolutions of Mg and Ni during milling are clearly different, and the process has a greater influence on the evolution of Mg than on that of Ni.

The XRD spectra from samples milled for 3, 5, 8 and 10 h using BPRs of 20:1 and 10:1 are shown in Fig. 3. It can be seen that when the BPR is 20:1, the detection time for the Mg$_2$Ni compound can be as short as 3 h. Therefore, as it was seen before, the higher the BPR, the shorter the detection time. Similarly, the broadening of the Mg peak due to the possible amorphization process is still present. However, by employing such an elevated BPR (20:1), it was not possible to identify clearly the changes produced by the milling process on Mg, at least at the times selected in this study. On the other hand, the evolution of Ni using a BPR of 20:1 is different than when the BPR was 10:1. It is now possible to observe the changes induced by the milling process on the (1 1 1) and (2 0 0) peaks of Ni, particularly after 5 h. These changes involve peak broadening and intensity lowering (both indications of grain refinement). Another feature shown in Fig. 3 is that the Mg and the Mg$_2$Ni peaks overlap in the sample milled with a BPR of 20:1, but now the (1 1 1) Ni peak also overlaps with the (2 0 3) Mg$_2$Ni peak, and the (2 0 0) Ni peak almost completely disappears. These last two features were not observed in the sample milled with a BPR of 10:1, i.e., the higher energy involved when the BPR is 20:1 was able to greatly modify the microstructure of both Ni and Mg (and not just Mg as when the BPR was 10:1).

Regarding the evolution of the intermetallic compound Mg$_2$Ni, after being detected at the early stages of milling by the presence of the (0 0 3), (1 0 2), (1 1 2) and (2 0 0) planes in the XRD spectrum, the number of detected planes gradually increases with milling time, implying that an increasing amount of Mg and Ni is being transformed into Mg$_2$Ni. These changes continue until no peaks associated to Mg and Ni are detected, and the number of detected Mg$_2$Ni planes no longer changes (approximately after 14 h of milling).

3.3. Differential scanning calorimetry

The DSC curves corresponding to samples milled for 3, 8 and 10 h using a BPR of 10:1 present two exothermic peaks during heating (Fig. 4). It is observed in these scans that as the milling time increases, the peak temperature of each reaction
shifts towards lower temperatures, and the first exothermic reaction tends to disappear. Also, these DSC curves show a remarkable change of behavior after 8 h of milling; and this time corresponds to the detection time for Mg$_2$Ni (using XRD).

Similarly, the DSC curves corresponding to samples milled for 3, 8 and 10 h using a BPR of 20:1 also present two exothermic reactions (Fig. 5). The difference, however, is that the first peak disappears much faster than when the BPR is 10:1 (implying a much faster kinetics). Furthermore,
the first reaction peak tends to overlap with the second in as short as 7 h of milling. These changes and their relationship with the phases present in the samples will be discussed in the next section.

3.4. Microstructure

In order to observe the microstructural changes during milling, backscattered electron (BSE) images were taken from the cross-section of the milled powder. Fig. 6(a) shows the microstructure in cross-section of a large agglomerated particle taken from a sample milled for 3 h using a BPR of 10:1. It can be seen that the agglomerated powder is composed of flaky-shaped, heavily deformed particles, and that the chemical composition, revealed by the difference in the gray scale in BSE image, is quite heterogeneous throughout the powder (EDS analyses showed that the Ni content ranged from 39 to 81 wt.%, depending on the region). On the other hand, the cross-section micrograph taken from the powder milled for 10 h using a BPR of 20:1 shows a much more homogeneous microstructure (Fig. 6(b)). The heavily deformed particles and the large differences in gray contrast are no longer observed. In fact, EDS analyses showed that in this case the Ni content varied from 46 to 50 wt.%. The microstructure of Mg observed by TEM in a sample milled for 10 h using a BPR of 10:1 is shown in Fig. 7. It can be seen that the grain size is less than 15–20 nm, while the SAD diffraction pattern shows very diffuse rings with two main contributions: nanocrystals and a possible amorphous precursor phase. It is also worth mentioning that the same small grain sizes were observed in Mg milled for less time. On the other hand, the microstructure of Ni in a sample milled for 5 h using a BPR of 20:1 consisted mainly of grains with an average size of ~100–200 nm, and the SAD diffraction pattern shows definite spots instead of diffuse rings (Fig. 8). Therefore, the Ni grain structure has not been broken down to the level at which Mg is broken down (~20 nm), reinforcing the idea of Mg being more rapidly changed than Ni during milling. However, the grain structure of Ni is further refined after long periods of milling (>10 h), reaching values similar to that of Mg (~20–30 nm) (Fig. 9). Finally, and independent of the milling time, the grain size of the intermetallic compound Mg$_2$Ni (as it first appears) is approximately 20 nm (Fig. 10).

4. Discussion

The BPR is a very important parameter in the milling process because it determines the number of collisions that occur inside the mill. Therefore, it follows that the amount of energy put into the system, and also the time necessary to obtain a particular phase, both are function of the BPR. For instance, Suryanarayana et al. [28] carried out experiments in SPEX mill using a mixture of Ti–33 at.% Al, obtaining an amorphous phase after 7, 2 and 1 h, using BPRs of 10:1, 50:1 and 100:1, respectively. This relationship between milling time, BPR and phase formation can also be observed in the present study. As it was mentioned before, the microstructural changes during the first hours of milling encompass the refinement of Mg and Ni; although their degree of refinement is quite different from each other (Fig. 2). Using the Sherrer’s method
to measure the grain size, samples milled using a BPR of 4:1 had a Mg grain size of less than 10 nm after 22 h [25]. However, the Sherrer’s method could not be applied to measure Mg grain sizes in samples milled using BPRs of 10:1 or 20:1 because the XRD peak broadening did not meet all the requirements for it to be valid. Therefore, the Mg and Ni grain sizes were measured using transmission electron microscopy. After 5 h of milling using a BPR of 20:1, the Mg grain size is \( \sim 15-20 \text{ nm} \), while the Ni grain size is \( \sim 100-200 \text{ nm} \) (Fig. 8). Consequently, the grain size of Mg is refined much faster than that of Ni. This could be explained by their crystalline structures. It has been demonstrated [29,30] that the grain size attainable by milling depends on the crystal structure of the material being milled: BCC materials tend to reach the smallest sizes (\( \sim 9 \text{ nm} \)), HCP materials reach somewhat larger grain sizes (15–25 nm), and FCC materials tend to reach the largest grain sizes of all (\( \sim 25 \text{ nm} \)). Since the crystal structure of Mg is HCP and that of Ni is FCC, we can expect to see differences in the grain size after milling. On the other hand, the breaking down of the microstructure during milling is governed by the balance between dislocation generation and recovery from an-
nihilation and recombination [30], hence the microstructural evolutions of Mg and Ni are different because the dislocation activity in HCP materials is different than in FCC materials. As a result of these differences, for instance, after 7 h of milling using a BPR of 10:1, Mg forms a very broad peak in the region $2\theta \approx 35-40^\circ$, but Ni does not lower or broaden its peaks (Fig. 11(a)). However, after 7 h of milling using a BPR of 20:1, the Ni peaks have clearly broadened and lowered their intensity (Fig. 11(b)). This means that for Ni to attain the same degree of refinement as Mg, the BPR needs to be doubled (if the milling time is kept the same), reinforcing the idea of the grain size evolution depending on the crystal structure. In any case, the peak broadening of Mg is believed to have two contributions: (a) a very fine grain size, and (b) the formation of an amorphous precursor phase. The SAD diffraction pattern in the TEM micrograph of Fig. 7 shows diffuse rings, commonly seen in amorphous materials. Therefore, the level of refinement of Mg has reached a point at which not only its grain size is very small, but the formation of a Mg-rich amorphous phase has also been promoted. The details of the formation of this amorphous phase are discussed next. Nevertheless, as the milling time increases, more and more Mg reacts to form the amorphous phase, in agreement with previous works [11].

The phenomenon of amorphization during mechanical milling has been reported for more than 20 years. While the early reports concentrated only in the amorphization of intermetallic compounds [22,31], the later ones concentrated in the amorphization during milling of pure elements as well [32]. Similarly, there are several reports stating that when two or more pure elements are mechanically alloyed, and the mixture possesses the same chemical composition than an intermetallic compound, somewhere during milling an amorphous phase will be formed [22,33]. It has been found that the amorphization process is also somehow related to the chemical composition or the type of intermetallic in question. For instance, in the work of Radlinski and Caika [34] it is shown that when Ti–35 at.% Si and Ti–67 at.% Si samples are subjected to the same milling conditions, the complete amorphization occurred only in the Ti-rich alloy, while the alloy with less Ti presented a noticeable broadening of the diffraction peaks, but did not show any sign of amorphization. This was interpreted as the system being composed of a fraction of amorphous phase coexisting with the rest of the material in a nanocrystalline form. Similarly, these authors also showed that there are systems where the formation of intermetallic compounds does not involve the formation of an amorphous phase. For instance, Ti–64 at.% B samples formed a crystalline solid solution before forming the TiB$_2$ compound, and no amorphous phase was detected. However, how the system evolves until it reaches the amorphous state, and under what circumstances the formation of this amorphous phase should be expected are the questions that have not been totally clarified [8,35].

Nevertheless, several different sequences by which an intermetallic compound (crystalline or amorphous) can be obtained by mechanical alloying have been proposed [22,31,34,36]:

- **Route 1:** $mA + nB \rightarrow (A_m B_n)_{\text{amorphous}} \rightarrow (A_m B_n)_{\text{crystalline}}$
- **Route 2:** $mA + nB \rightarrow (A_m B_n)_{\text{amorphous}} \rightarrow (A_m B_n)_{\text{nanocrystalline}} \rightarrow (A_m B_n)_{\text{crystalline}}$
- **Route 3:** $mA + nB \rightarrow (AB)_{\text{solid solution}} \rightarrow (A_m B_n)_{\text{amorphous}} \rightarrow (A_m B_n)_{\text{crystalline}}$
- **Route 4:** $mA + nB \rightarrow (AB)_{\text{solid solution}} \rightarrow (A_m B_n)_{\text{amorphous}} \rightarrow (A_m B_n)_{\text{crystalline}}$
- **Route 5:** $mA + nB \rightarrow (A_m B_n)_{\text{crystalline}} \rightarrow (A_m B_n)_{\text{amorphous}} \rightarrow (A_m B_n)_{\text{crystalline}}$
- **Route 6:** $mA + nB \rightarrow (AB)_{\text{solid solution}} \rightarrow (A_m B_n)_{\text{amorphous}} \rightarrow (A_m B_n)_{\text{crystalline}}$

None of these sequences match our experimental results, so a different sequence is needed to explain the microstructural evolution found here.
Regarding the amorphization in the present study, the results showed that Mg plays a significant role during the formation of the amorphous phase at the early stages of milling. After just a few hours of milling, Mg reaches a grain size of less than 10 nm. At this nanometric range there are more Mg atoms at the grain boundaries than at the grain interior, thereby increasing exponentially its potential reactivity. Therefore, and due to this increased reactivity, the amorphization process might occur via a solid state reaction at the grain boundaries in the contact zone between elemental Ni and Mg. This reaction might be driven by the excess of point and lattice defects created by the deformation, as it has been suggested by Schwarz et al. [32] in the system Ni–Ti.

Contrary to the results reported by Ruggeri et al. [8] and Orimo and coworkers [37,38], the samples in this work did not show complete amorphization. This discrepancy, as proposed by Ji et al. [35], may be due to the fact that the range of chemical compositions used by Ruggeri et al. [8] and Orimo et al. [37] (1:1 atomic ratio) were high in Ni content. For chemical compositions similar to the one used in this work, Ji et al. [35] proposed the following sequence of phase transformations instead:

\[ 2\text{Mg} + \text{Ni} \rightarrow (\text{Mg}_2\text{Ni})_{\text{crystalline}} \]

This sequence, even though it is in agreement with the results obtained in this work, does not indicate the sequence of transformation in between the initial and the final states.

In order to elucidate the role of the amorphous precursor in the Mg–Ni system, calorimetric studies have been widely used to study its crystallization [38–40]. In the present study, two exothermic reactions were detected using differential scanning calorimetry (Figs. 4 and 5). It is worth noting that our DSC results did not show the presence of a third exothermic reaction usually related to the formation of the MgNi$_2$ compound. The formation of this compound is not thermodynamically favorable in this study because the Mg content of the amorphous phase found here (70 at.% Mg) is greater than the one found in the amorphous precursor of the MgNi$_2$ compound (50 at.% Mg) [8,38]. These two reactions are related to the formation of Mg$_2$Ni compound, as it is shown next.

The first exothermic reaction is intimately related to the milling process. In fact, when the milling is carried out using a BPR of 10:1, this reaction is detected in all the samples milled for up to 10 h. However, if the BPR is doubled, the same reaction is detected only after 5 h of milling. In other words, this exothermic reaction only occurs when there is a fraction of amorphous phase present in the sample. Fig. 12 corresponds to XRD analyses performed on samples annealed for 1 h after 5 h of milling using a BPR of 20:1. In the as-milled condition (Fig. 3), the material is composed mainly of Mg$_2$Ni and Ni, but when the sample is annealed at 423 K for 1 h, the XRD pattern shows that a small fraction of the sample has been transformed into crystalline Mg$_2$Ni (Fig. 12(a)). Ni, however, is still present in the sample. When the overall energy provided during milling is increased (by either increasing the BPR or the milling time), the fraction of amorphous phase that is transformed during the DSC scan becomes less and less because a greater portion of the sample has already been transformed into Mg$_2$Ni by the milling process. Therefore, it can be said that the absence of first reaction peak observed is associated with the amorphous precursor being mechanically transformed into Mg$_2$Ni.

As of the second reaction, this was first associated to relaxation or grain growth. However, a closer inspection of the data points otherwise. If the sample milled for 5 h using a BPR of 20:1 is annealed at 673 K for 1 h, then the sample is almost 100% Mg$_2$Ni and Ni is no longer detected by XRD (Fig. 12(b)). This could be explained if the Ni remnant reacted (through a thermally activated mechanism) with the Mg that was not used to form the amorphous phase. Therefore, the second exothermic reaction can be interpreted as the thermally activated reaction between nanocrystalline Ni and Mg to form Mg$_2$Ni. Although the details of the second exothermic reaction are not clear yet, the presence of these two reactions

![Fig. 12. XRD of annealed samples, after milling with BPR = 20:1, for (a) 1 h at 423 K, (b) 1 h at 673 K.](image-url)
indicate that the crystallization of the intermetallic compound Mg$_2$Ni is carried out in two stages, in agreement with other studies on metallic glasses [39].

The most important advantage of combining milling and a further annealing treatment is that the overall process of obtaining Mg$_2$Ni becomes far more efficient. This is so because the very long milling times needed to complete transform Ni and Mg into Mg$_2$Ni (14 h using a BPR of 20:1) can now be replaced for a very short milling step (5 h) followed by a 1 h annealing treatment at 673 K. This combined manufacturing process also has the advantage of avoiding the excessive oxidation of Mg during long milling runs.

However, there are differences between the Mg$_2$Ni compound obtained by mechanical milling, and the one obtained by mechanical milling and annealing. As it can be seen in Fig. 13, the number of Mg$_2$Ni planes detected by XRD is different for each sample: the sample milled for 5 h and then annealed at 623 K for 1 h showed more peaks in the XRD spectrum than the one simply milled for 14 h. This could be an indication of some type of texturing present in the milled sample that is absent in the annealed one. In spite of this, the differences between the Mg$_2$Ni compound crystallized by mechanical induction and the one formed by annealing is not fully understood [39,41].

So far, the sequence of phase transformations that occur during milling can be summarized as follows: at the first stages of milling, both Mg and Ni are heavily deformed, their microstructure refined, and the chemical composition throughout the sample becomes heterogeneous (under-alloyed system). The nanocrystalline Mg later reacts with Ni to form the Mg-rich amorphous precursor. After this stage, a more homogeneous chemical composition is achieved by the combined reaction of the Mg-rich (Mg, Ni) amorphous phase and the remaining Ni. This requires that amorphous phase becomes unstable with respect to the crystalline phase, which eventually occurs due to a steady increase in the store energy produced by the high-energy milling [39]. Finally, as the milling time increases, the chemical composition of the sample approaches that of Mg$_2$Ni. Therefore, the proposed sequence of phase transformations during milling is:

$$\text{Mg} + \text{Ni} \rightarrow \text{Mg}_{amorph} + \text{Ni}_{amorph} \rightarrow \text{amorphous} + \text{Ni}_{amorph} + \text{Mg}_{amorph} \rightarrow \text{Mg$_2$Ni}_{nc}$$

Increasing the BPR to 20:1 does not change this sequence, but it does change the kinetics of the reactions (they are much faster because of the increased energy input). For instance, the majority of the sample consists of Mg$_2$Ni after 3 h milling, although some Ni and Mg are still present.

As the milling continues towards longer times, a different scenario is found. It has been shown that the formation of Mg$_2$Ni during the early stages of milling is greatly influenced by the BPR (changing the BPR can reduce the detection time from 29 to 3 h). However, as the milling progresses, this influence becomes less important (Fig. 3). When the BPR is doubled from 10:1 to 20:1, the detection time is indeed reduced, but still a considerable amount of additional time is needed to complete the transformation from a mixture of amorphous phase, Ni$_{nc}$ and Mg$_2$Ni$_{nc}$ into Mg$_2$Ni$_{nc}$. (actually, almost the same as with 10:1). This implies that

<table>
<thead>
<tr>
<th>BPR</th>
<th>MA Time and Heating Temperature</th>
<th>MA 14h</th>
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<tbody>
<tr>
<td>20:1</td>
<td>2h + 623K 3h + 673K 5h + 623K</td>
<td></td>
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<tr>
<td>10:1</td>
<td>x</td>
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<tr>
<td>5:1</td>
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Fig. 13. Mg$_2$Ni diffracting planes in different samples.
a different phenomenon is affecting the reaction kinetics at the final stages of milling. At the beginning of the milling (or until the detection time), the formation of the compound is kinetically controlled by the refinement of Mg. However, in the final stage (from the detection time until the total transformation into Mg$_2$Ni), the reaction between Ni and the amorphous is the controlling step. This is so because almost all the Mg is used to form the amorphous phase, which is a relatively very fast reaction. If we add the fact that Ni needs to be in a nanocrystalline state for this reaction to take place efficiently, therefore, the formation of Mg$_2$Ni by the reaction between Ni and the amorphous phase is controlled by the rate at which Ni is refined to the nanocrystalline level. Since the refinement of Ni is a slow process (compared to the refinement of Mg), it follows that the overall kinetics of the last stage of milling is slower than that of the early one.

5. Conclusions

The microstructural evolution during high-energy milling of Mg and Ni was analyzed. At the early stages, the main reactions are the grain refinement of Mg and Ni and the partial amorphization of the Mg–Ni mixture. The formation of the amorphous phase was kinetically related to Mg refinement (a relatively fast process), and its chemical composition was found to be rich in Mg. Later on, the crystallization of this amorphous phase was kinetically related to Mg refinement. As a summary, the process. At the later stages of milling, the kinetics of the formation of Mg$_2$Ni is slowed down because it was now related to the lower kinetics of Ni refinement. As a result, the sequence of phase transformations leading to the formation of Mg$_2$Ni during milling can be as follows:

\[ \text{Mg}_n + \text{Ni}_m \rightarrow \text{Mg}_{nm} + \text{Ni}_m \rightarrow \text{amorphous} + \text{Ni}_{m+1} + \text{Mg}_{nm} \rightarrow \text{amorphous} + \text{Ni}_{m+1} + \text{Mg}_n \text{Ni}_{m+1} \]

The combination of mechanical alloying and annealing was able to produce much faster than mechanical alloying alone. The optimized processing route to obtain Mg$_2$Ni was found to be 5 h of mechanical alloying using a BPR of 20:1, and then annealing at 673 K for 1 h.

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