Pergamon

Materials Research Bulletin 35 (2000) 1989–1998

Materials
Research
Bulletin

Fast amorphization reaction in ZrNi system prepared by mechanical alloying

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(Refereed)
Received 13 October 1999; accepted 28 February 2000

Abstract

The amorphous phase of ZrNi system was obtained by mechanical alloying (MA) of elemental crystalline powders in an inert atmosphere. The time required to achieve the amorphous state was 5 h. In contrast with all previous reports on this system, this amorphization time is considerably shorter. X-ray diffraction and differential scanning calorimetry (DSC) measurements were used to assess the amorphous state. Moreover, the comparison of the ZrNi alloy produced by MA with another prepared by fast quenching (FQ) confirmed that the final structure of the MA sample is fully amorphous. The reduced radial distribution function G(r) obtained by a Fourier transform of the structure factor S(Q) showed that a single amorphous phase formed at the end of the amorphization reaction. Further MA results in the recrystallization of the ZrNi alloy. Recrystallization takes place at a milling time even shorter than any reported milling time to obtain an amorphous phase in this system. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: A. Amorphous materials; A. Alloys; C. X-ray diffraction; C. Differential scanning calorimetry (DSC)

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1. Introduction

The mechanical alloying (MA) of metallic powders using a high-energy ball mill is considered to be a powerful tool for the production of metallic alloys with a wide range of compositions [1,2]. Alloys consisting of early–late transition metals produced by the MA technique (such as ZrPd [3], TiNi [4], HfNi, Hf–Cu [5], and HfPd [6]) are good examples of such alloys. One of the basic problems associated with the production of

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PII: S0025-5408(00)00396-2

such alloys is establishing whether the end product obtained by this technique has a truly amorphous structure on an atomic scale. X-ray diffraction can be used to study the structure and provide useful information on such a scale. In the present work, $Zr_{65}Ni_{35}$ was prepared by MA to investigate the formation of amorphous phases. This system was chosen for this study because previous studies [7] of this system involved progressively long MA times. Such prolonged MA periods are not expected in this system, for two reasons. First, the ZrNi system is very well known for its substantial negative heat of mixing. Second, Ni is expected to diffuse very quickly in Zr based on the volume ratio, which is $V_{Ni}/V_{Zr} = 0.38$.

2. Experimental

The first series of samples were prepared by the MA technique. Parent powders of the Zr and Ni elements were mixed and mechanically alloyed in a hardened steel vial of a Spex mixer (model 8001) using a charge of 4 g and two ½″ steel balls. The balls to powder ratio was 4.15:1. To avoid oxidation, milling was carried out under an argon atmosphere. Each sample was put in the steel vial in a glove box, flushed with argon several times, then sealed and put in the mixer. During the milling process care was taken not to open the vial to extract part of the sample for X-ray analysis. Instead, the progress of the amorphization reaction was monitored at the end of each milling run. However, the possibility of oxygen contamination cannot be ruled out completely. The alloy was found to transform to an amorphous phase at a milling time of 5 h.

The second sample was prepared by the fast quenching (FQ) technique. Parent ingots of $Zr_{65}Ni_{35}$ samples were produced using Zr and Ni wires. These ingots were melt-spun at high wheel speed (~4500 rpm) into metallic glass ribbons in an atmosphere of purified argon. The ribbons produced were typically 25 μm thick and 1–2 mm wide. To study the amorphization reaction, a JEOL X-ray diffractometer with Cu target was used. To derive the radial distribution function, a Philips PW 1050 vertical goniometer was used with a graphite curved-crystal monochromator and molybdenum Kα radiation ($\lambda = 0.711$ Å). DSC measurement was carried out with a Perkin-Elmer TAC 7/DX. The samples were heated at a heating rate of 20 K/min under a flow of purified argon. The X-ray data analysis followed a conventional scheme with the subtraction of the instrumental background, correction to the Compton scattering. The corrections also involved the normalization to the total structure factor S(Q). A program was written to transform the S(Q) to the radial distribution function using a Fourier transform.

3. Results and discussion

3.1. X-ray diffraction study

Fig. 1 represents the X-ray diffraction pattern of the $Zr_{65}Ni_{35}$ samples after 0 h (parent sample), 2 h, and 5 h of mechanical alloying. Fig. 1a shows characteristic diffraction peaks

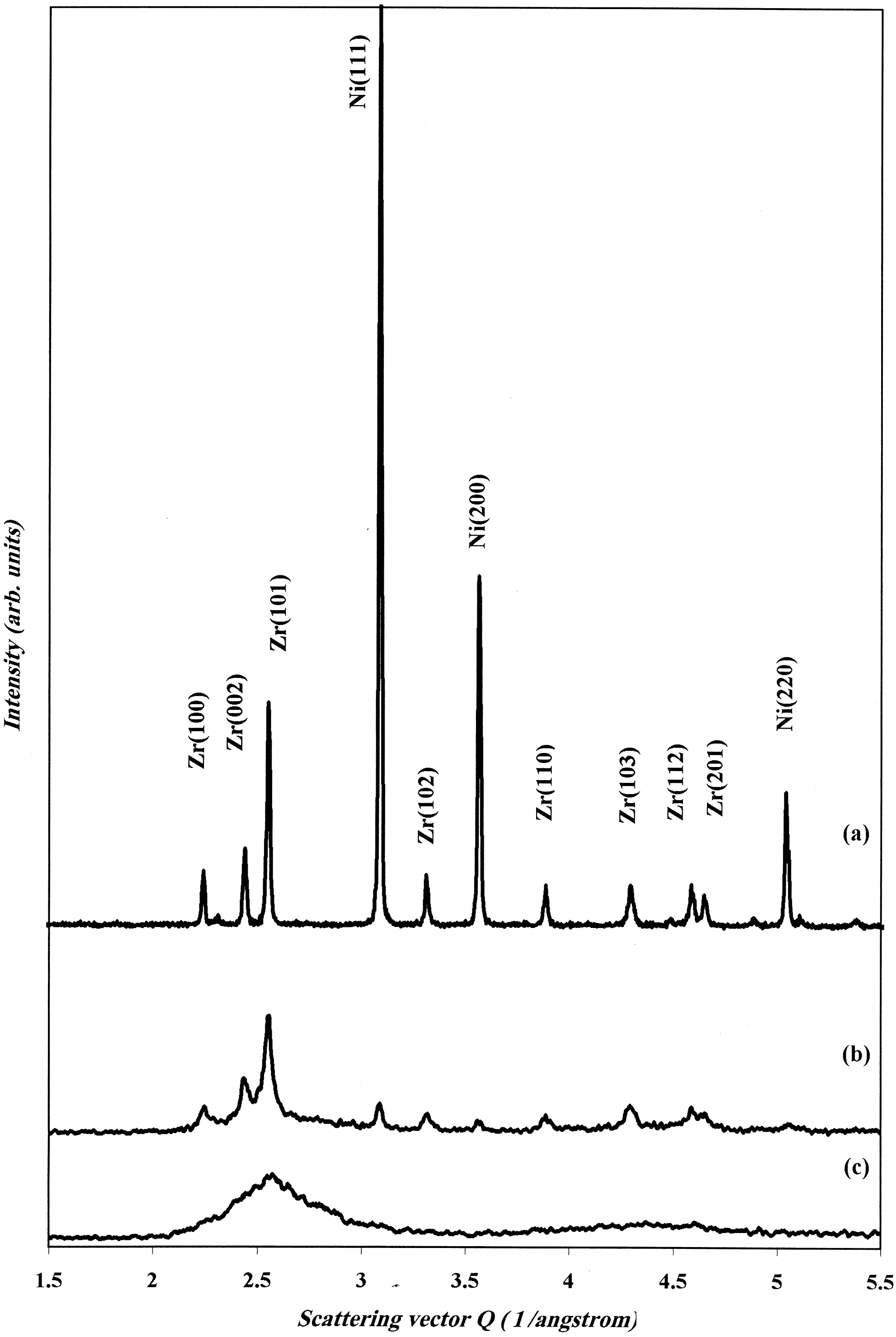

Fig. 1. X-ray diffraction patterns for (a) $Zr_{65}Ni_{35}$ parent powders, (b) after 2 h of MA, and (c) after 5 h of MA.

Table 1
The $Zr_{65}Ni_{35}$ weighting factors W_{ij} of the partial structure factors (PSFs) for X-ray radiation

W_{ij} of the PSFs $S_{ij}(Q)$		
W_{ZrZr}	W_{ZrNi}	W_{NiNi}
0.528	0.397	0.075

from the hexagonal α-Zr structure (with lattice constants $a = 3.23$ Å and $c = 5.15$ Å), and from the cubic Ni (with lattice constant $a = 3.54$ Å). The most intense peaks are the (101) reflection of Zr and the (111) reflection of Ni, as expected. All the peaks in Fig. 1a can be indexed to the crystalline Zr or Ni. No additional diffraction peaks from ZrNi were observed throughout the amorphization reaction.

It is clearly seen that all the Bragg peaks of Ni overshadowed those of Zr, but disappeared within 2 h of mechanical alloying (Fig. 1b). After 5 h of milling (Fig. 1c), the X-ray diffraction pattern no longer shows any residual crystalline peaks, and the material has transformed completely to an amorphous phase. To confirm that the mechanical alloyed $Zr_{65}Ni_{35}$ sample reached a complete amorphous phase on an atomic scale, it was compared with another sample of the same composition prepared by the fast quenching technique, which is the conventional technique for the production of amorphous phases. The two samples can be compared on two levels: first, on the Q-space structure level [represented by the structure factor S(Q)], and second, on the real space structure level [represented by the radial distribution function G(r)].

3.1.1. The structure factor S(Q)

The total structure factor S(Q) can be written in terms of the partial structure factors $S_{ij}(Q)$ according to the Faber-Ziman formulations [8], as follows:

$$S(Q) = \frac{C_{ZrZr}^2\phi_{Zr}^2 S_{ZrZr}(Q) + 2C_{Zr}C_{Ni}\phi_{Zr}\phi_{Ni}S_{ZrNi}(Q) + C_{Ni}^2\phi_{NiNi}^2 S_{NiNi}(Q)}{<\phi>^2} \tag{1}$$

where C_{Zr} and C_{Ni} are the concentrations of Zr and Ni elements, respectively, ϕ_{Zr} and ϕ_{Ni} are the scattering amplitudes, i.e., the atomic form factor *f* for X-rays (corresponding to the limit $Q = 0$), and $<\phi> = C_{Zr}\phi_{Zr} + C_{Ni}\phi_{Ni}$. Therefore, S(Q) for $Zr_{65}Ni_{35}$ is written as

$$S(Q) = W_{ZrZr}S_{ZrZr}(Q) + W_{ZrNi}S_{ZrNi}(Q) + W_{NiNi}S_{NiNi}(Q) \tag{2}$$

From the values of the weighting factors W_{ij} (Table 1), it can clearly be seen that Zr–Zr and Zr–Ni atomic correlations are the major contributors to the total S(Q), with the Ni–Ni atomic correlations being 7.5% of the total. Fig. 2 shows the S(Q) for $Zr_{65}Ni_{35}$ prepared by MA (Fig. 2a) and FQ (Fig. 2b). The two curves are quite similar, and exhibit the same main features. All the main broad peaks of the two samples are at nearly the same scattering vector Q (where $Q = 4\pi \sin(\theta/2)/\lambda$, θ being the scattering angle and λ the X-ray wavelength). This confirms two important findings. First, the MA sample reached a completely amorphous phase after 5 h of mechanical alloying. To date, this is

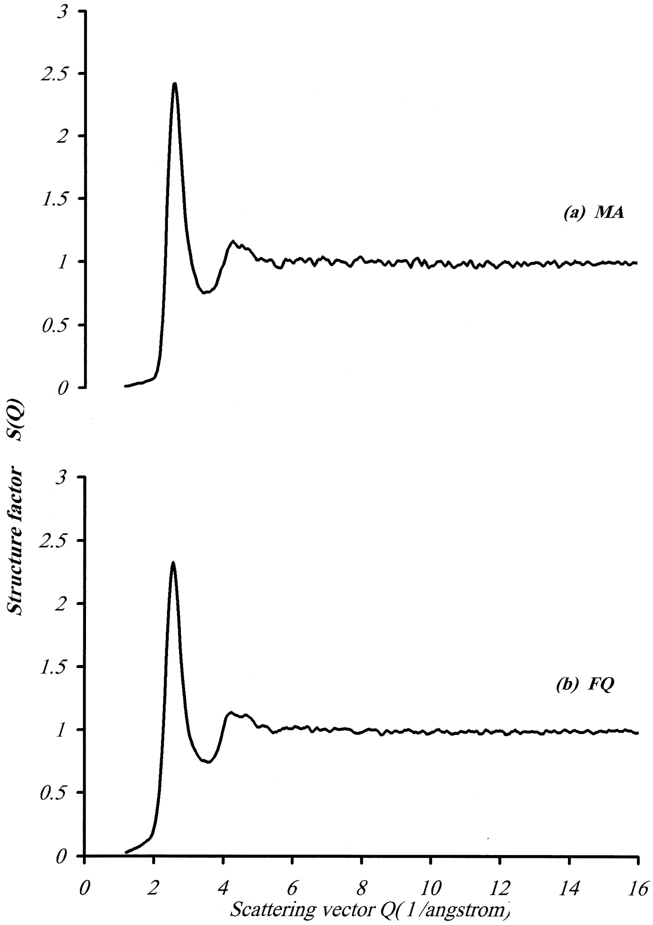

Fig. 2. The structure factor S(Q) derived from the intensity distributions of $Zr_{65}Ni_{35}$ prepared by (a) the MA technique, and (b) the FQ technique.

the shortest time of mechanical alloying to produce amorphous ZrNi phase that has been observed. Second, the alloy has the same final structure (amorphous) regardless of the technique used in producing such an alloy. All the parameters derived from the S(Q) curves in Fig. 2a and b are summarized in Table 2.

Table 2
Summary of parameters measured from the structure factors S(Q) of the MA and FQ $Zr_{65}Ni_{35}$ samples

Preparation technique	Q_1	$S(Q_1)$	Q_2	$S(Q_2)$
FQ	2.61	2.28	4.29	1.15
MA	2.62	2.35	4.30	1.13

Q_1 and Q_2 are the positions of the first and the second peaks, and $S(Q_1)$ and $S(Q_2)$ are the heights of the first two peaks.

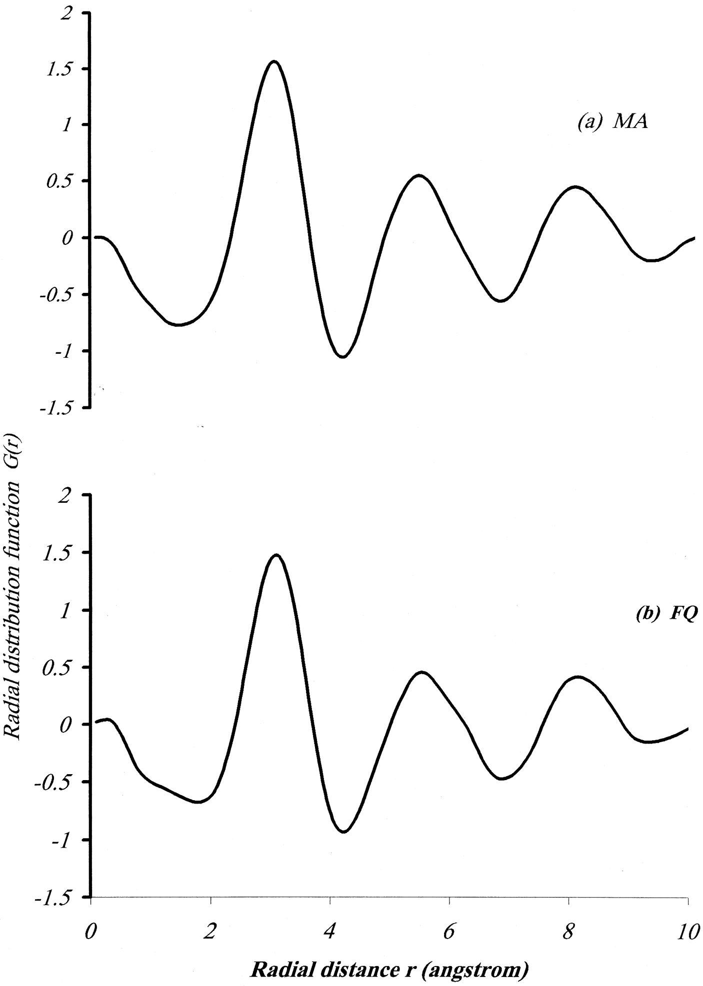

Fig. 3. The reduced radial distribution function G(r) obtained by Fourier transform of the S(Q) for (a) the MA $Zr_{65}Ni_{35}$ sample, and (b) the FQ $Zr_{65}Ni_{35}$ sample.

3.1.2. *The real space structure*

The Fourier transform of the total structure factor (measured experimentally) leads to the reduced radial distribution function G(r) representing the structure in real space. The G(r) is given by

$$G(r) = 4\pi r(\rho(r) - \rho_0) = 2/\pi \int_0^{Q_{max}} Q[S(Q) - 1]\sin QrdQ \tag{3}$$

where r is the radial distance from a reference atom, ρ_0 is the average atomic density of the sample, Q_{max} is the maximum measured scattering vector Q. Fig. 3 shows G(r) curves for the MA and FQ $Zr_{65}Ni_{35}$ samples. They consist of a large first peak and broader subsequent peaks. Again, there is excellent correspondence between G(r) curves of the two alloys

Table 3
Parameters measured from the G(r) curves for the MA and FQ $Zr_{65}Ni_{35}$ samples

Preparation technique	r_1	$G(r_1)$	r_2	r_3
FQ	3.05	1.48	5.53	8.13
MA	3.03	1.50	5.50	8.10

The radial distances for the first three peaks and the height of the main peak $G(r_1)$ in the radial distribution function (G(r) are shown.

prepared by MA and FQ techniques. The position of the first maximum peak r_1 gives the average value of the nearest neighbor distance, and it contains contributions from ZrZr, ZrNi, and NiNi pairs depending on the magnitude of the weighting factors of each pair. Some parameters measured from the G(r) curves for the two alloys are given in Table 3. These parameters further confirm the high degree of similarity of the G(r) curves produced by MA and FQ techniques. The first peak position of such curves has almost the same value (see Table 3). This value corresponds well to that expected from the average Goldschmit radius. The Goldschmit radii of ZrZr, ZrNi, and NiNi are $r_{ZrZr} = 3.19$ Å, $r_{ZrNi} = 2.84$ Å, and $r_{NiNi} = 2.49$ Å respectively. Therefore, the average Goldschmit radial position $<r_G>$ of the first peak in the G(r), calculated from the weighted averages of the Goldschmit radii for this alloy, can be written as

$$< r_G > \; = W_{ZrZr} r_{ZrZr} + \frac{\{r_{Zr} + r_{Ni}\}}{2} + W_{NiNi} r_{NiNi} \tag{4}$$

Therefore, according to this equation, the $<r_G>$ value for $Zr_{65}Ni_{35}$ samples equals 3.00 Å. This is in excellent agreement with that of the first (main) peak derived from the G(r) curves for the FQ and MA $Zr_{65}Ni_{35}$ samples (Table 3). This again confirms that the MA $Zr_{65}Ni_{35}$ sample is genuinely amorphous after 5 h of milling.

In a previous study [9], a slight splitting was observed in the first peak of the G(r) curve for the amorphous phases of $Zr_{50}Ni_{50}$ and $Zr_{60}Ni_{40}$ (but not of $Zr_{70}Ni_{30}$ or $Zr_{80}Ni_{20}$) alloy prepared by MA. Such a splitting was attributed to the presence of two amorphous states formed with different kinds of atomic short-range order. No such splitting was observed in either of the two $Zr_{65}Ni_{35}$ samples prepared by FQ and MA techniques in the present work. This means that only a single amorphous homogeneous phase was formed as the end product of the two different preparation techniques.

3.2. DSC measurements

The thermal stability of the amorphous $Zr_{65}Ni_{35}$ system was studied by DSC to determine the crystallization temperature T_x of such a system. Fig. 4 represents a scan by DSC at a heating rate of 20 K/min. A single exothermic peak is observed at a temperature of 753 K. This peak marks the transformation of the single amorphous phase of $Zr_{65}Ni_{35}$ to a crystalline phase. Such a value for T_x is consistent with other thermal studies [9,11] of this system. Moreover, this single peak reconfirms that only a single amorphous phase formed after 5 h of milling in this system.

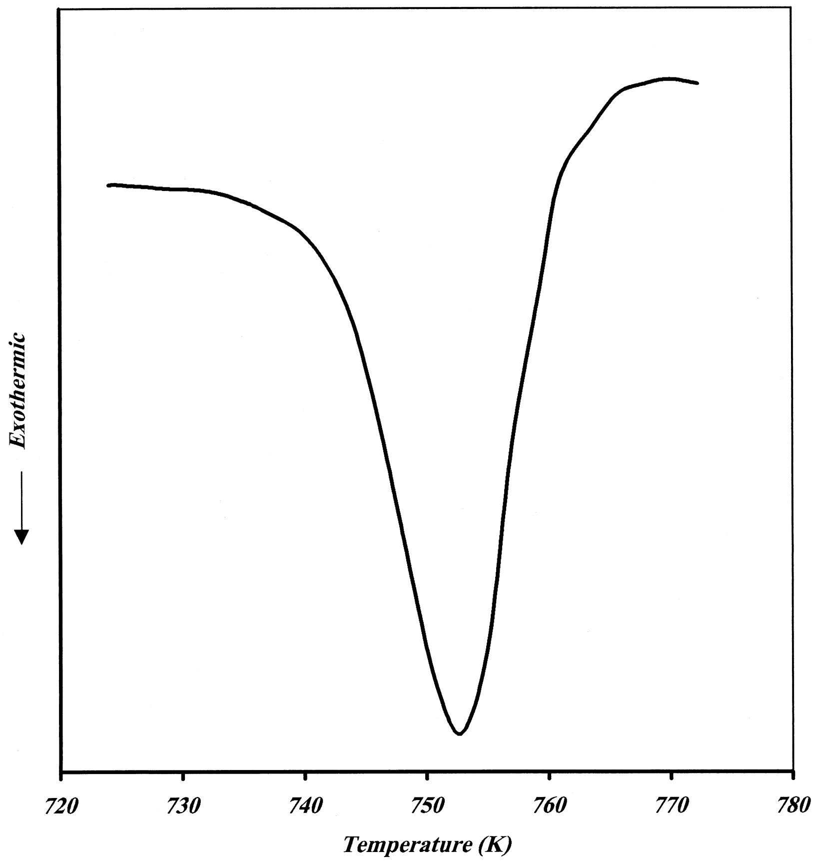

Fig. 4. DSC scan on the $Zr_{65}Ni_{35}$ at a heating rate of 20 K/min. The crystallization temperature T_x is 753 K.

3.3. Recrystallization

Increasing the mechanical milling time leads to recrystallization of the amorphous $Zr_{65}Ni_{35}$ alloy. Fig. 5 shows $Zr_{65}Ni_{35}$ alloy after milling times of 16 and 24 h. These times are much shorter than any time previously reported [7,9,10] to obtain the amorphous phases in this alloy. Because a fully amorphous phase was obtained at a very short milling time (5 h) and recrystallization has already started to occur at 16 h, this means that the short amorphization time can easily be overshot, leading to prolonged milling periods before another amorphous phase forms. Another chance for the occurrence of other amorphous and crystalline phases is possible. Such a cyclic phase transformations (amorphous ⇔ crystalline) was observed in Co–Ti system [10]. Therefore, the prolonged milling periods used previously to amorphize the ZrNi system, such as those (184, 60, and 120 h) used by [7,9,11] respectively, could possibly have been significantly reduced. Therefore, it is essential that the amorphization reactions of alloys prepared by mechanical alloying should be followed very carefully, especially at the early stages of the amorphization reaction. This is very important in order not to lose the first amorphous phase in what may be a long cycle of phase transformations. Minimizing the time of milling serves two purposes: it is

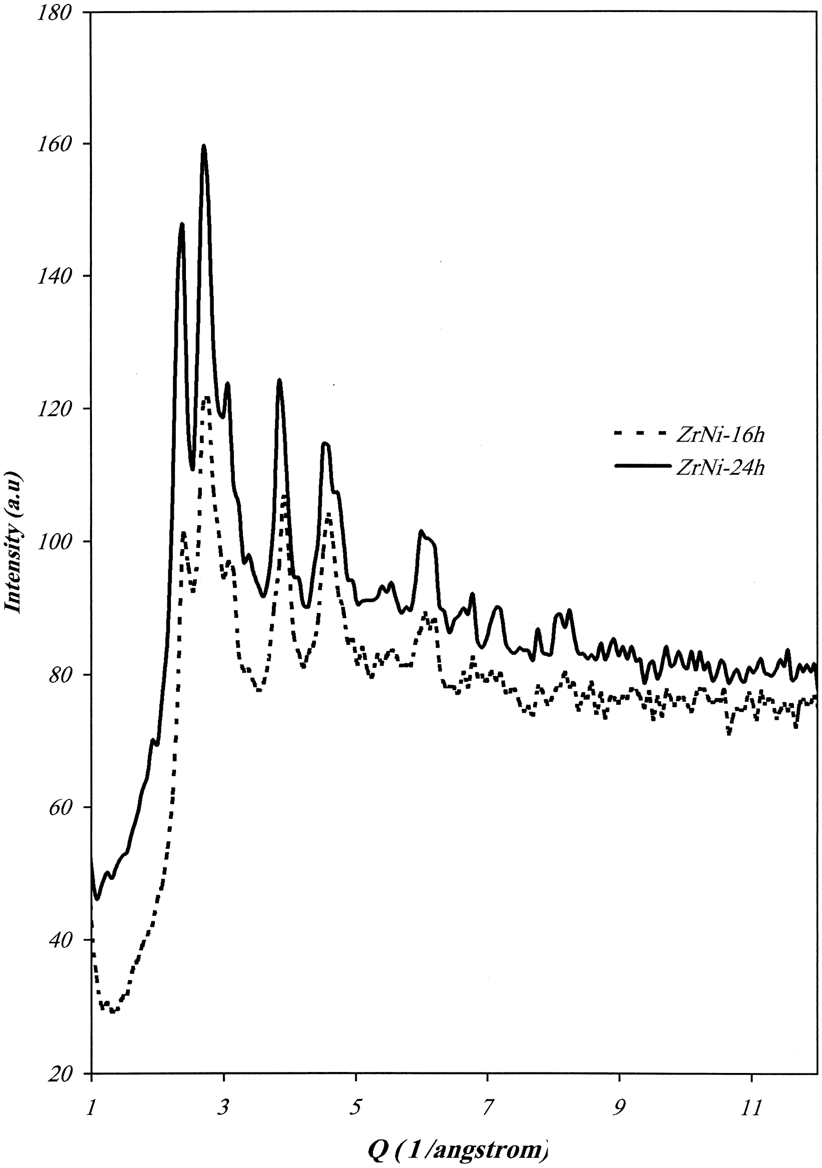

Fig. 5. Recrystallization of amorphous $Zr_{65}Ni_{35}$ after 16 and 24 h of mechanical alloying.

cost effective, and it helps prevent undesirable contamination from the milling tools due to prolonged milling times.

4. Conclusions

Four conclusions can be drawn from the present work. First, a full amorphous phase of $Zr_{65}Ni_{35}$ can be obtained with 5 h of mechanical alloying. Second, the comparison of the

G(r) curve of the MA $Zr_{65}Ni_{35}$ sample to that of the FQ $Zr_{65}Ni_{35}$ sample confirms that the amorphous phase achieved by MA within 5 h is genuine. Third, no splitting was observed in the G(r) curves, which means that only one amorphous state is present in the samples prepared by the two techniques. Finally, and most importantly, the amorphization reactions of alloys prepared by MA should be followed carefully, particularly at the early stages of the MA process, in order not to lose the first amorphous phase of the system under study.

Acknowledgments

I would like to thank the Research Centre of the College of Science, King Khalid University, for partially supporting this project. The DSC and a part of the X-ray measurements were performed at King Abdulaziz City for Science and Technology (KACST). The help of Dr. J. Hefne and Mr. H. Al-Orini of (KACST) is gratefully acknowledged. I would also like to thank Dr. N. Cowlam of the University of Sheffield (UK) for useful discussion, and Mr. J. Newell for performing the fast quenching of the samples.

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