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Amorphization reaction during mechanical alloying: influence of the milling conditions

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Amorphous Ni–Zr powders have been prepared by mechanical alloying of elemental crystalline powders. The glass-forming range has been determined in detail at different milling intensities. Depending on the milling conditions, at least partial crystallization of the formerly amorphous material can occur from 66 to 75 at% Ni, due to a temperature rise during milling at high intensity. In comparison with isothermal annealing experiments at various temperatures on completely amorphous powder, a relation between milling temperature and milling time is shown. This confirms the similarity of the amorphization process during mechanical alloying with the solid-state interdiffusion reaction in alternating crystalline multilayers.

1. Introduction

Within the last few years a lot of interest has been focused on the preparation of amorphous alloys by mechanical alloying. Starting from elemental crystalline powders a large number of alloy systems, for example Ni–Nb [1], Ni–Ti [2], Cu–Ti [3], and several transition metal–Zr systems [4], have been investigated. (For a recent review, see [5].) During the early stages, ball milling produces powder particles with a characteristically layered microstructure due to cold welding and repeated mechanical deformation [2, 4, 6]. Further milling leads to an ultrafine composite, and finally a true alloying by a solid-state interdiffusion reaction occurs, leading to a homogeneous amorphous alloy [7]. Detailed experiments in the Ni–Ti [2], Cu–Ti [3], Fe–Zr [8], Co–Zr [9, 10], and Ni–Zr [11–13] systems show that a successful amorphization is possible over a wide composition range in the central part of the binary phase diagram.

The interdiffusion reaction can be understood by considering the different free enthalpies of the layered compound of the pure elements, the amorphous phase and the competing intermetallic phase. As is well known, the thermodynamically stable state of a system is determined by a minimum in the free enthalpy, G. In metallic systems, the free enthalpy of the crystalline state is always lower than the free enthalpy of the amorphous state. On the other hand, the amorphous state is metastable, i.e. an energy barrier has to be overcome in order to crystallize amorphous metals. The principle of forming amorphous metals by a solid-state reaction is based, then, on first establishing a crystalline initial state having a high free enthalpy, G_0 [14]. For example, this can be achieved by the formation of the already mentioned layered microstructure during the early stages of milling if the alloy system has a negative free enthalpy of mixing. The free enthalpy, G_0, of the layer system can be reduced either by forming the metastable amorphous phase or by forming a crystalline intermetallic phase. The crystalline equilibrium phase is, of course, preferred energetically. The decisive factor is, however, the kinetics of the phase formation. For this purpose the timescales of all possible reactions must be taken into consideration. The formation of the amorphous phase is then possible, and probable, if the reaction to the amorphous phase proceeds substantially faster than the reaction to the crystalline phase. At the same time, however, the amorphous phase must not crystallize under the given conditions as the reaction proceeds, i.e. the reaction temperature, T_r, must be markedly below the crystallization temperature.

Because different authors apply different types of milling equipment and different experimental conditions, it is important to know how amorphization by mechanical alloying is influenced by the milling conditions. Therefore, in the present work the rotational velocity of the planetary ball mill used in the experiments was varied. By this, the intermetallic equilibrium phase Ni_3Zr appears in the composition range from 66 to 75 at % Ni in the case of intense milling [11]. To clarify this, the total peak temperatures reached within the powder particles during milling for the intensity settings 3, 5 and 7 were calculated following the procedure proposed by Schwarz and Koch [15] and using hitting velocities of the balls as derived by Magini [16] from a detailed analysis of the ball motion during milling. The results, listed in Table I,

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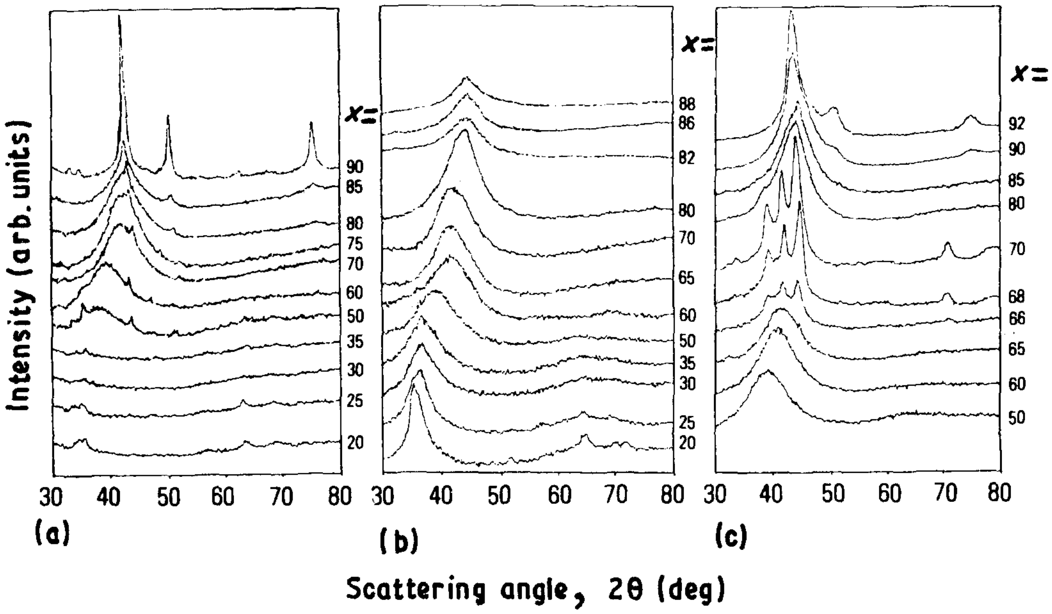

Figure 1 X-ray diffraction patterns of several Ni_xZr_{100-x} samples after 60 h mechanical alloying: (a) milling intensity 3; (b) milling intensity 5; (c) milling intensity 7.

show a good agreement with the rough estimate of the total peak temperatures published in a former paper [11].

In this paper the thermal conditions during milling with both isothermal annealing experiments on amorphous $Ni_{70}Zr_{30}$ powder and the characteristic reaction times of alternating crystalline multilayers amorphized by solid-state interdiffusion reaction are compared to show the similarity of both preparation techniques. It becomes evident that in terms of the above-mentioned solid-state reaction mechanism, the temperature rise during mechanical alloying is sufficient to enable an interdiffusion reaction. For high milling intensities the temperature can rise above the crystallization temperature, resulting in at least partially crystallized material.

2. Experimental procedure

The mechanical alloying was performed in a conventional planetary ball mill (Fritsch "Pulverisette 5") using elemental nickel and zirconium powders. (For further details, see [11].) The samples were characterized by X-ray diffraction using a Siemens D500 diffractometer in reflection geometry with Cu$K\alpha$ radiation ($\lambda = 0.154$ nm). The thermal analysis was carried out in a DSC 7 Perkin–Elmer differential scanning calorimeter at a heating rate of 40 °C min^{-1} under a purified argon atmosphere. Isothermal annealing experiments were also performed in the DSC. Furthermore, the microstructure was characterized by transmission electron microscopy using a Siemens Elmiskop 101 microscope operated at 100 kV. For this, the powder was compacted and the resulting samples ion-beam thinned in a Technics ion mill.

TABLE I Intensity settings, corresponding hitting velocities (according to [16]) and kinetic energies of the 10 mm balls, and total peak temperatures during milling in the planetary ball mill

	Intensity setting		
	3	5	7
Hitting velocity (m sec^{-1})	2.3	3.3	4.3
Kinetic energy (10^{-2} J)	1.2	2.4	4.1
Total peak temperatures (°C)	117	217	353

3. Results and Discussion

In order to determine the glass-forming range, the X-ray diffraction patterns were used to obtain a first qualitative description as shown in Fig. 1a to c for intensity settings 3, 5 and 7, respectively. From the patterns shown in Fig. 1b the glass-forming range was roughly estimated to extend from 20 to 30 at % Ni to 75 to 85 at % Ni, respectively. For an exact determination of the terminal compositions of the amorphous phase, various physical properties were measured as a function of composition [11]. From these results it was found that glass formation by mechanical alloying in the Ni–Zr system is, in general, possible from 27 to 83 at % Ni. This agrees well with calculations of the metastable phase diagram by Bormann *et al.* [17] predicting a glass-forming range from 33 to 83 at % Ni by using the Calphad technique, and by Miedema calculations performed by Weeber and Bakker [13] predicting 24 to 83 at % Ni. On the nickel-rich side, the experimentally determined value exactly coincides with the value predicted by both theoretical techniques, whereas on the zirconium-rich side, the experimental value lies between the values of the two theoretical procedures, but the results are still very close.

Furthermore, the strong influence of the milling intensity on the amorphization process has been investigated by several experiments. Within 60 h of milling no complete amorphous powder was obtained for milling intensity 3 (see Fig. 1a). Obviously the deformation of the powder particles was not severe enough and the resulting temperature not high enough for a complete solid-state reaction under these conditions. Otherwise, peaks of the intermetallic equilibrium phase Ni_3Zr are seen from 66 to 75 at % Ni after powder milling at intensity 7 (see Fig. 1c). From

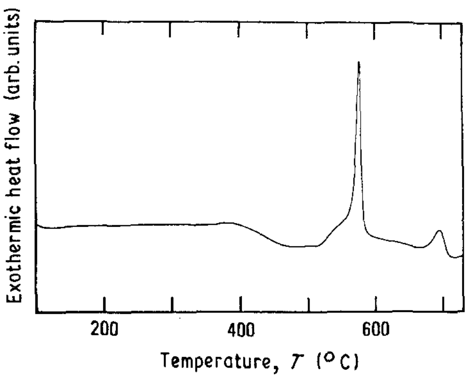

Figure 2 DSC scan of amorphous $Ni_{68}Zr_{32}$ powder at a heating rate of 40 °C min^{-1}.

the appearance of this intermetallic phase it is concluded that at least a partial crystallization has occurred.

It is still an open question why the hexagonal Ni_3Zr phase appears instead of the expected pseudo-orthorhombic $Ni_{21}Zr_8$ and the A-centred orthorhombic $Ni_{10}Zr_7$ equilibrium phases that should be formed at this composition range according to the equilibrium phase diagram. Probably the formation of Ni_3Zr is kinetically more favoured than the decomposition of the amorphous phase into the two structurally more complex pseudo-orthorhombic lattices. For comparison, completely amorphous $Ni_{68}Zr_{32}$ shows two exothermic peaks during a DSC run with 40 °C min^{-1} up to 730 °C (see Fig. 2). At 577 °C the amorphous phase crystallizes into Ni_3Zr and a second crystallization step at 697 °C leads to the formation of the equilibrium phases $Ni_{21}Zr_8$ and $Ni_{10}Zr_7$ as shown in Fig. 3. Probably Ni_3Zr forms quite easily by crystallization of the amorphous phase because of its simple crystal structure. This might be different for other compositions, explaining why partial crystallization only occurs from 66 to 75 at % Ni but not over the whole composition range at this milling intensity. To obtain greater insight into the progress of alloying at intensity 7, $Ni_{68}Zr_{32}$ powder was examined after different milling times by X-ray diffraction. Starting with elemental nickel and zirconium, after 4 h milling, the typical broad maximum of the amorphous phase shows up in the diffraction pattern (see Fig. 4). Further milling for up to 12 h leads to a completely amorphous powder with no indications of an intermetallic phase. Therefore, the partial crystallization of the material observed after 60 h seems to be due to a strong temperature increase during further milling.

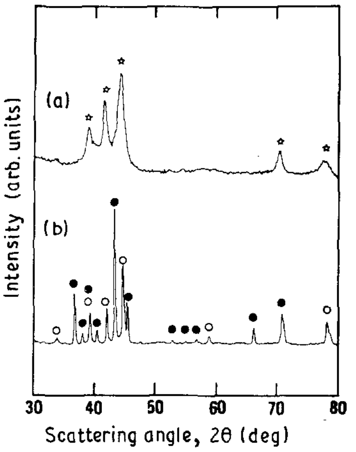

Figure 3 X-ray diffraction patterns for $Ni_{68}Zr_{32}$, (a) after the first, and (b) the second crystallization step. (☆) Ni_3Zr, (○) $Ni_{10}Zr_7$, (●) $Ni_{21}Zr_8$.

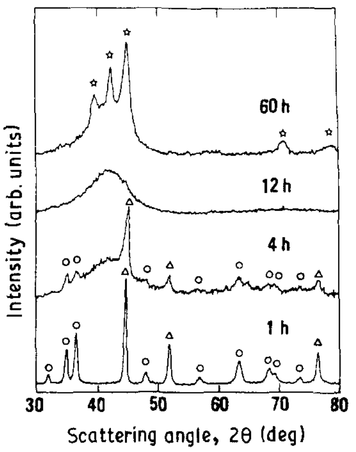

Figure 4 X-ray diffraction patterns for $Ni_{68}Zr_{32}$ after different milling times at intensity 7. (○) α-Zr, (△) Ni, (☆) Ni_3Zr.

The propagating crystallization can be monitored not only by X-ray diffraction but also by DSC. Fig. 5 shows a plot of the crystallization temperature, T_x (defined as the peak position of the first exothermic peak during a DSC run), of $Ni_{68}Zr_{32}$ powder after different milling times. Between 4 and 12 h, T_x increases slightly due to the increasing homogeneity of the material during further milling. This homogenization has been already shown in the diffraction patterns of Fig. 4. After 12 h milling, a significant decrease in T_x can be observed. The value achieved after a milling time of 72 h is characteristic for the crystallization of an amorphous $Ni_{50}Zr_{50}$ alloy. Obviously the sustained precipitation of Ni_3Zr subsequently lowers the nickel content in the remaining amorphous phase. This is also indicated by a shift of the peak position of the amorphous maximum to lower diffraction angles in the X-ray diffraction patterns (not shown in this work). Therefore, it is concluded that crystallization during extended milling becomes easier because of the lower crystallization temperature of the amorphous phase with about 50 at % Ni and the existence of already formed Ni_3Zr precipitates.

A similar result has been obtained for $Ni_{70}Zr_{30}$. Milling for 60 h at intensity 5 leads to a completely

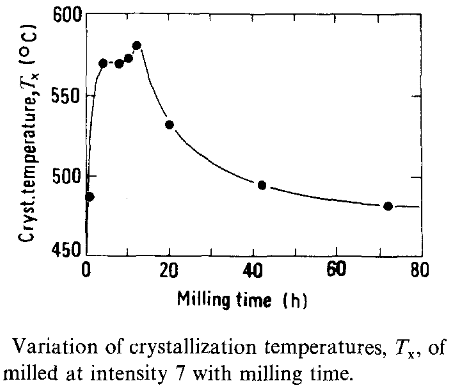

Figure 5 Variation of crystallization temperatures, T_x, of $Ni_{68}Zr_{32}$ powder milled at intensity 7 with milling time.

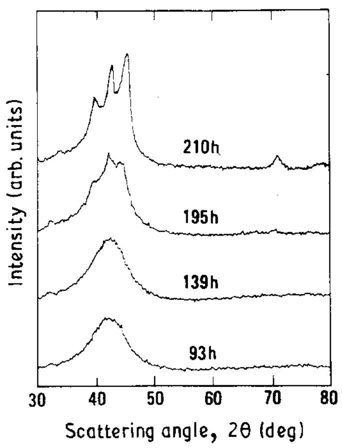

Figure 6 X-ray diffraction patterns for $Ni_{70}Zr_{30}$ after different milling times at intensity 3.

amorphous powder with an X-ray pattern similar to Fig. 1b, that transforms into the partially crystallized material by further milling for 20 h at intensity 7. To check whether this temperature rise during extended milling can be attained for every milling condition, experiments were also performed at low rotational velocities. Fig. 6 shows that complete amorphization of $Ni_{70}Zr_{30}$ requires about 93 h at intensity 3, due to the smooth deformation process and the relatively low reaction temperature, but further milling up to 195 h also produces partially crystallized powder.

Obviously there exists a relation between the actual temperature of the powder particles during the collision caused by different velocities of the hitting balls, and the time necessary to obtain an amorphous or a partially crystallized material. To clarify this, these results were compared with results on isothermally annealed amorphous $Ni_{70}Zr_{30}$ powder. Fig. 7 shows that the portion of crystallized material, P_n, normalized to a completely amorphous powder, increases for higher annealing temperatures due to a faster crystallization reaction at higher temperatures. For example, at 400 °C an annealing of only 5 min is sufficient to produce material with a similar X-ray diffraction pattern as obtained for the $Ni_{70}Zr_{30}$ powder milled for 60 h at intensity 7. It is obvious that at higher temperatures less time is necessary to produce a fixed amount of crystalline material, as shown in Fig. 8, where this fact is demonstrated for the portion of intermetallic phase obtained after 60 h milling at intensity 7. Therefore, we can conclude that heating to crystallization is possible during mechanical alloying. Then amorphization by solid-state reaction can also take place because this reaction is usually much faster, as experiments for layered Ni–Zr composites even with 100 nm thick individual layers have shown [18], where the diffusion rate of nickel in the amorphous Ni–Zr layer has been estimated to be about 2×10^{-15} cm^2 sec^{-1} at 300 °C. Furthermore, Hellstern and Schultz [7] have shown that after about 15 h milling, Fe–Zr powder consists of an ultrafine layered composite with an individual crystallite size of about 20 nm. Obviously, by mechanical alloying, the crystallite size cannot be indefinitely reduced until atomic mixing occurs. Similarly, Hellstern *et al.* [19] recently found that for elemental ruthenium and for the intermetallic phase AlRu, the crystallite size saturates at 12 or 7 nm, respectively. This is explained by considering the Hall–Petch relation which describes the dependence of the yield stress on the grain size. For a small grain size, a very high stress would be required to maintain plastic deformation via dislocation motion. Therefore, it must be assumed that further deformation occurs by a grain-boundary glide mechanism which does not refine the microstructure any more. This means that ball milling does not lead to atomic mixing, but it produces an ultrafine layered microstructure as confirmed by TEM investigations.

Fig. 9 shows bright-field electron micrographs of $Ni_{50}Zr_{50}$ powder after 8 h milling. The typically laminated microstructure produced by repeated fracturing and cold-welding is clearly visible. Furthermore, the amorphous phase has formed by planar growth in between the crystalline nickel and zirconium layers (Fig. 9b) and appears as a grey featureless band in the micrographs. This is in good agreement with results reported by Petzold *et al.* [20]. The formation of the amorphous interlayer is confirmed by the electron diffraction pattern shown in Fig. 10 where besides the reflections of crystalline nickel and zirconium the typical diffuse amorphous ring appears. Obviously there is strong evidence that the glass formation

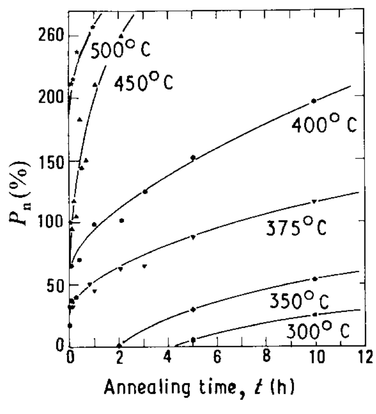

Figure 7 Variation of normalized portion of crystallized material, P_n, with annealing time for different annealing temperatures compared with the portion of crystallized material obtained after milling for 60 h at intensity 7 $Ni_{70}Zr_{30}$.

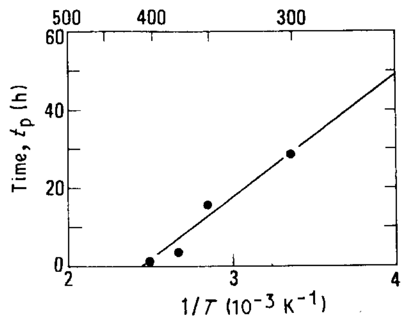

Figure 8 Variation of time t_p necessary to obtain a fixed portion of crystalline material with annealing temperature, $Ni_{70}Zr_{30}$.

TABLE II Constant reaction temperatures, diffusivities (after [21]) and necessary reaction times for a complete amorphization via mechanical alloying

	Temperature °C			
	225	300	325	400
D (cm^2 sec^{-1})	5.3×10^{-17}	2×10^{-15}	1×10^{-14}	7.3×10^{-14}
Reaction time (min)	314	8	1.6	0.2

via mechanical alloying is closely related to the solid-state interdiffusion reaction of evaporated or deformation-produced multilayers. If we apply the interdiffusion mechanism to the amorphization during milling, the important reaction step is the diffusion of nickel through the freshly formed amorphous layer. Thus we can make use of the equation $D_{\mathrm{Ni}} = D_0 \exp(-Q/kT)$ for thermally activated diffusion. Furthermore we can calculate the time, t, necessary for a complete amorphization of the individual layers at certain temperatures according to a parabolic time law for the growth of the amorphous phase. We find a time necessary for a complete reaction of 10 nm thick layers of about 8 min when using $D = 2 \times 10^{-15}$ cm^2 sec^{-1} and a constant reaction temperature of 300 °C. (For further details, see [21].) Table II shows the reaction times for different temperatures, indicating also that a complete amorphization can be achieved within some hours even at quite low temperatures. Therefore, we can conclude that during milling for 60 h the powder has to be at 300 °C for only 0.22% of the whole milling time or at 225 °C for 5.24 h to become completely amorphous.

If we compare this result with the calculated actual temperatures of the powder particles during the collision in the present experiments, it is obvious that we can achieve a complete amorphous material within 60 h of milling at intensity 5. Milling at lower intensities requires longer milling times because of lower temperatures. Therefore, the reaction is not finished within 60 h of milling at intensity 3.

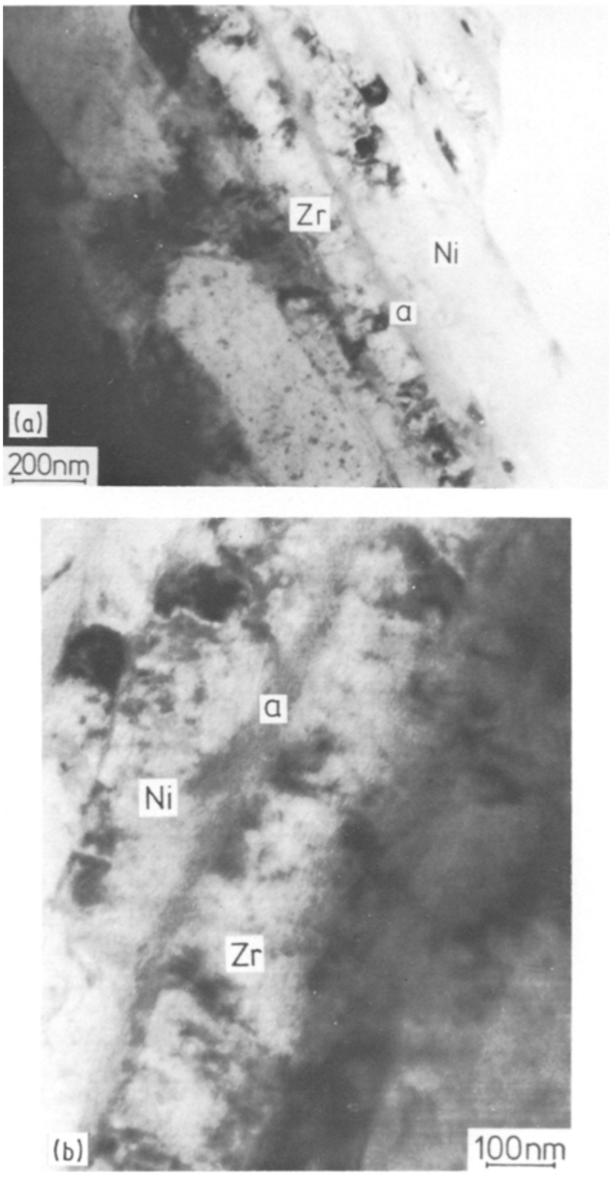

Figure 9 Bright-field transmission electron micrographs of mechanically alloyed $Ni_{50}Zr_{50}$ after 8 h milling. (a) Survey over a larger area of the sample showing the typical layered microstructure. (b) Detail of (a) showing that the amorphous phase (grey featureless band) has formed at the interface in between the elemental layers.

4. Conclusions

It has been shown that amorphization during mechanical alloying occurs via a solid-state interdiffusion reaction of ultrafine layered powder particles produced by repeated cold-welding, deformation and fracturing. The thermal conditions during our experiments are sufficient to produce a completely

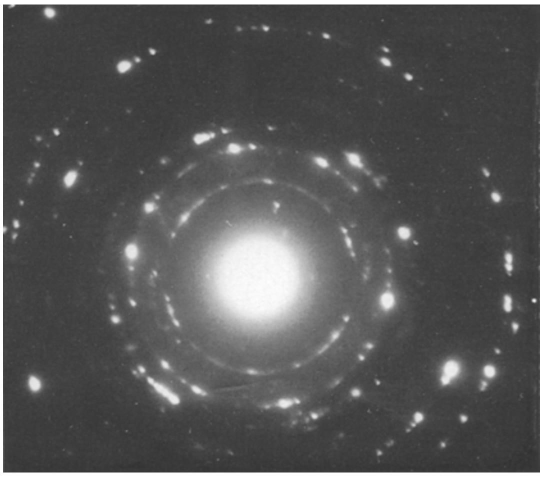

Figure 10 Selected-area electron diffraction pattern of mechanically alloyed $Ni_{50}Zr_{50}$ after 8 h milling. The typical diffuse amorphous halo shows up in addition to reflections of crystalline nickel and zirconium.

amorphous powder from 27 to 83 at % Ni within 60 h of milling at moderate milling intensities. For low milling intensities the reaction temperature decreases and the alloying process is not as effective as for higher intensities. Therefore, longer milling times are required to obtain a completely amorphous material. A too intense milling leads to the appearance of the intermetallic phase Ni_3Zr at a composition range from 66 to 75 at % Ni, due to a rise of the actual temperature during extended milling to values above the crystallization temperature. The formation of the hexagonal Ni_3Zr phase instead of the expected pseudo-orthorhombic equilibrium structures $Ni_{10}Zr_7$ and $Ni_{21}Zr_8$ is thought to be due to kinetic reasons of phase formation. Perhaps kinetic and thermodynamic constraints can also explain why partial crystallization occurs from 66 to 75 at % Ni only, and not over the whole composition range. Comparison of the experiments performed at different milling intensities and times with results obtained from the isothermal annealing of amorphous powder confirms the clear relation between milling temperature and time.

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