Glass-forming range in mechanically alloyed Ni-Zr and the influence of the milling intensity

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Amorphous Ni-Zr powders have been prepared by mechanical alloying from crystalline elemental powders. The glass-forming range has been determined by x-ray diffraction, differential scanning calorimetry, and saturation magnetization measurements. From 27 to 83 at. % Ni the powders become amorphous. This shows that deep eutectics do not play any role, contrary to amorphization by melt spinning. Crystallization temperatures, crystallization enthalpies, and wave numbers Q_p, obtained from x-ray diffraction investigations, are compared with the data received for rapidly quenched samples. In addition, the effect of the milling intensity on the glass formation has been studied for the first time. If the intensity is too high, crystalline intermetallic phases are formed. On the other hand, the powder needs an extended milling time to become completely amorphous if the milling intensity is too low. Conclusions on the actual temperature of the individual particle during mechanical alloying and on the glass-forming process are drawn from these results.

I. INTRODUCTION

It has recently been shown that amorphous powders can be prepared by mechanical alloying. Starting from the 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 Ref. 5.) During the early stages of milling the powder particles are cold-welded and a characteristically layered microstructure is formed which gets more and more refined with extended milling time.[2,4,6] This increases the interfacial area between the two elements. The interfaces are very clean and finally a true alloying by a solid-state reaction at these interfaces sets in if this reaction is favored by a negative enthalpy of mixing.[7] If the temperature where the solid-state reaction takes place is lower than the crystallization temperature of the amorphous phase, this metastable phase is formed. In this way, for example, amorphous Fe-Zr has been formed over a wide concentration range[8] which is not restricted to deep eutectics in the phase diagram where melt spinning preferentially forms amorphous metals in the Fe-Zr system.

For Ni-Zr, amorphization by solid-state reaction has been observed using several different experimental techniques such as vapour deposition,[9] jelly roll technique,[10] and mechanical alloying.[4,8,11] In this paper we determine the glass-forming range in this alloy system by means of measuring several different physical properties. Additionally we show that the milling intensity strongly affects the amorphization process, which has not been investigated so far.

II. EXPERIMENT

The samples are prepared from elemental powders obtained from Ventron GmbH. The Ni powder with a particle size of 1–3 μm and the Zr powder with a particle size smaller than 177 μm, are mixed and sealed under argon atmosphere (less than 1-ppm O_2 and H_2O) in a cylindrical steel container together with the steel balls. The total mass of the powder is 30 g. The mechanical alloying is performed in a conventional planetary ball mill (Fritsch "Pulverisette 5") with a ball to powder weight ratio of 15:1. In order to produce completely amorphous powders in the middle concentration range, the milling was performed for 60 hours. To avoid oxidation, the steel container was not opened during the experiment. The ball milling was performed with the intensity settings 3, 5, or 7 corresponding to calculated velocities of the hitting balls of 2.5, 3.6, or 4.7 ms^{-1} (or to kinetic energies of 1.4×10^{-2}, 2.9×10^{-2}, or 4.9×10^{-2} J of each ball). The x-ray investigations were performed in a Siemens D 500 diffractometer in reflection geometry using Cu$K\alpha$ radiation ($\lambda = 0.154$ nm). The crystallization temperatures and enthalpies were measured in a differential scanning calorimeter (Perkin-Elmer DSC 7) at a heating rate of 40 K/min. The saturation magnetization was determined from measurements in a vibrating sample magnetometer at 1 T at room temperature.

III. RESULTS

A. X-ray diffraction

The x-ray diffraction patterns of several Ni$_x$Zr$_{100-x}$ samples after 60 h of mechanical alloying at milling intensities 3, 5, and 7, respectively, are shown in Figs. 1(a)–1(c). For most of these samples the sharp crystalline lines have almost completely disappeared and the typical broad diffuse maxi-
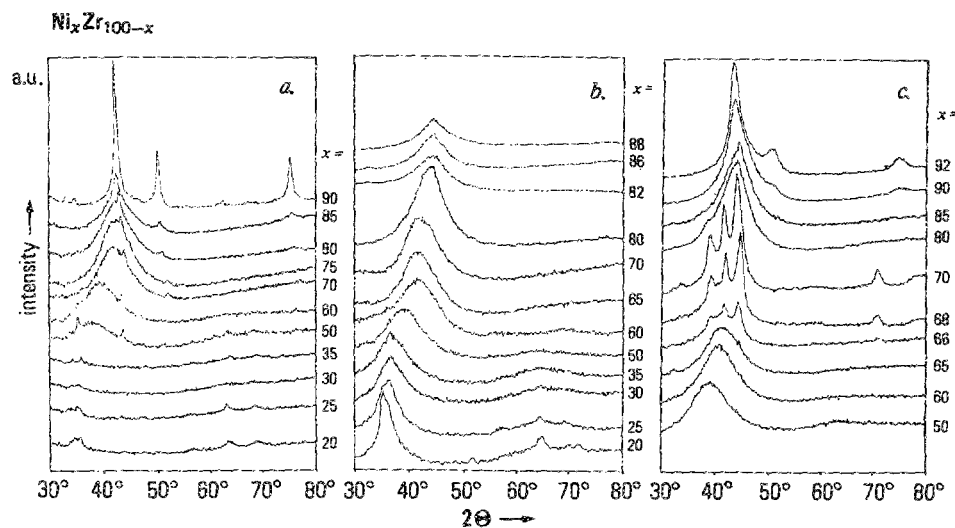
FIG. 1. X-ray patterns of several Ni_xZr_{100-x} samples after 60 h of mechanical alloying: (a) milling intensity 3; (b) milling intensity 5; (c) milling intensity 7.

mum of the amorphous state appears. For the amorphous samples the broad diffuse x-ray peak of the amorphous phase slightly shifts to higher diffraction angles with increasing Ni content. The peak position represented by the wave number $Q_p = 4\pi \sin\theta/\lambda$ is related to the mean nearest-neighbor distance in these alloys. In Fig. 2 the Q_p values of the mechanically alloyed samples are compared with data obtained for melt-spun samples.[12] The wave numbers show a good agreement between the mechanically alloyed and the melt-spun samples. Whereas the samples in the middle concentration range are perfectly amorphous, the samples with less than 35 at. % and more than 70 at. % Ni show some irregularities at the amorphous peak, or even crystalline peaks [see Fig. 1(b); the samples with $x \geqslant 82$ have a smaller intensity because a different detector slit was used]. These peaks become more evident towards the very Zr-rich composition range and, on the other hand, towards the very Ni-rich composition range, too, and are identified to be due to elemental Zr or Ni.

Although the x-ray diffraction patterns can only give a qualitative description, there are some significant differences between samples of the same composition prepared at different milling intensities. For milling intensity 5 the amorphous phase extends from about 30 at. % to about 83 at. % Ni [Fig. 1(b)] whereas samples milled at intensity 7 show intermetallic peaks from $x = 66$ to 75 [Fig. 1(c)]. For

intensity 3 milling for 60 h is not sufficient for complete amorphization [Fig. 1(a)].

B. Crystallization

The crystallization behavior of powder prepared at milling intensity 5 is shown in Fig. 3 where the DSC scans up to 730 °C are plotted for several samples. For some compositions a second crystallization reaction or a phase transformation is detected at higher temperatures. The crystallization temperatures T_x derived from the first exothermic peak of the DSC scans, are plotted as a function of Ni content in Fig. 4. Whereas T_x varies over more than 150 °C in the middle concentration range, it remains nearly constant in the alloys with less than 27 and more than 80 at. % Ni. Fig. 4 also shows the crystallization temperatures of rapidly quenched amorphous Ni-Zr alloys.[13] Taking the different heating rates into account, the T_x of the mechanically alloyed samples is about 10–20 °C higher than that of the rapidly quenched samples, which is due to about 2 at. % oxygen in the mechanically alloyed Ni-Zr powder.[14] Although the crystallization temperatures show the same concentration
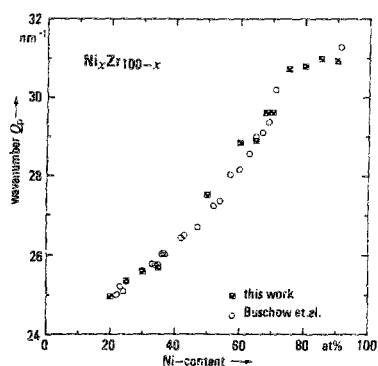

FIG. 2. Wave number Q_p of mechanically alloyed amorphous Ni-Zr vs Ni content, in comparison with results obtained for rapidly quenched samples by Buschow *et al.* (see Ref. 12).
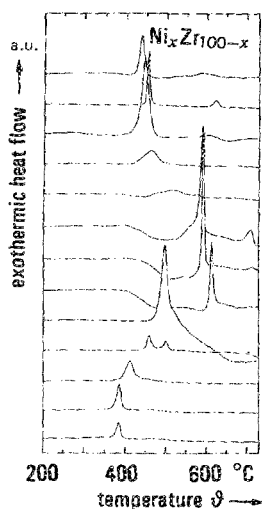

FIG. 3. DSC scans of several Ni_xZr_{100-x} samples at a heating rate of 40 K/min.

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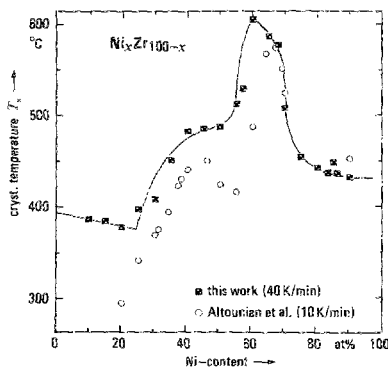
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FIG. 4. Crystallization temperature of mechanically alloyed Ni-Zr vs Ni content in comparison with results obtained for rapidly quenched samples by Altounian et al. (see Ref. 13).

dependence for more than 27 at. % Ni, the rapidly quenched samples show a monotonic decrease for smaller Ni contents, whereas the T_x values of the mechanically alloyed samples are almost constant. Therefore, the terminal composition of the amorphous phase is $Ni_{27}Zr_{73}$. For lower Ni contents a two-phase region exists consisting of the amorphous phase and elemental Zr. A similar analysis has been performed for the Ni-rich compositions, too, showing almost constant crystallization temperatures for more than about 80 at. % Ni. From this fact it may be concluded that a two-phase material consisting of the amorphous phase and elemental Ni is formed.

C. Magnetization measurements

To check the remaining elemental Ni portion we measured the saturation magnetization of the powders. Since no intermetallic phases are detected in the x-ray diffraction patterns and amorphous Ni-Zr is not magnetic at room temperature, measuring the saturation magnetization M_s provides direct information on the residual content of elemental Ni in the milled powders. In Fig. 5 the saturation magnetization of the mechanically alloyed powders versus Ni content is shown for the three different milling intensities and compared with the calculated magnetization for an unmilled Ni-Zr composite (dashed line). Depending on the milling intensity there is a magnetization background for samples up to 85 at. % Ni which is attributed to residual elemental Ni not completely reacted during the mechanical alloying. For more than 85 at. % Ni the magnetization shows a sharp increase due to a bigger amount of remaining elemental Ni. This means that on the Ni-rich side both the amorphous
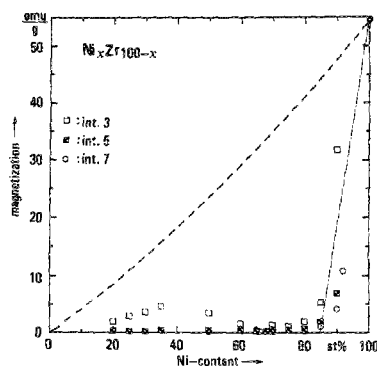

FIG. 5. Comparison of the saturation magnetization of mechanically alloyed Ni-Zr with calculated values for the unmilled powder mixture (dashed line).

phase and the Ni-rich phase coexist, which must be interpreted as the existence of a two-phase region where the amorphous phase is in a metastable equilibrium with almost pure Ni. It is likely that this Ni-rich phase exhibits an increased solubility range compared to the stable crystalline phases of the equilibrium phase diagram as it has been found before for mechanically alloyed Ni-Ti (Ref. 2) and Fe-Zr.[15] The limiting composition of the amorphous phase can be estimated by the lever rule to be about $Ni_{85}Zr_{15}$. As shown in Fig. 5, there are no significant differences for samples milled at intensity 5 and 7. Compared to the unmilled powder mixture the M_s values are strongly reduced in the middle concentration range and for Zr-rich compositions and show nearly the same increase for Ni-rich alloys. On the other hand, the samples milled at intensity 3 show much higher values in the middle concentration range. Obviously, the powders do not become completely amorphous and the high values of the saturation magnetization are caused by a high amount of residual elemental Ni. Only from $x = 60$ to 75 the portion of the amorphous phase seems to be larger, as the decrease of the saturation magnetization shows.

IV. GLASS-FORMING RANGE

In order to estimate the glass-forming range, the x-ray diffraction patterns shown in Fig. 1 can give a first qualitative hint. Although it is not possible to determine an accurate value, the terminal composition of the amorphization range must be somewhere between 20 and 30 at. % Ni and 75 to 85 at. % Ni, respectively. For this purpose it is better to measure various physical properties of the samples as a function of composition within the glass-forming range and within the two-phase regions between amorphous and crystalline phase. Intrinsic physical properties, for example, the crystallization temperature or the superconducting transition temperature, depend on composition within the homogeneity range of the amorphous phase and are constant in the two-phase regions. On the other hand, extrinsic physical properties such as the crystallization enthalpy of the amorphous phase or the saturation magnetization of the Ni-rich phase also depend on the composition within the amorphous phase, but show a proportionality to the amount of the amorphous phase determined by the lever rule in the two-phase regions.

Accordingly, the crystallization temperature as an intrinsic physical property, remains constant for less than 27 at. % Ni as shown in Fig. 4. On the Ni-rich side, T_x is not very sensitive to composition. Therefore, it is not useful to determine the terminal composition of the amorphous phase on this side of the phase diagram from the plot of T_x vs Ni content.

The Zr-rich samples become superconducting at low temperatures and the dependence of the superconducting transition temperatures of these powders can also be applied to determine the terminal composition of the amorphous phase on the Zr-rich side (see Fig. 6). Whereas T_c for rapidly quenched samples decreases with increasing Ni content,[16–18] the mechanically alloyed samples show this behavior only for more than 30 at. % Ni. For less than 25 at. % Ni, T_c is almost constant. (For further details see Ref. 11.)
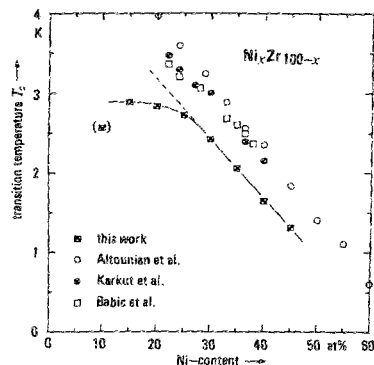
FIG. 6. Superconducting transition temperature T_c, defined as the midpoint of the ac susceptibility transition, for mechanically alloyed Ni_xZr_{100-x} powders, in comparison with the T_c obtained for melt-spun samples by Babić et al., Altounian and Ström-Olsen, and Karkut and Hake. (See Refs. 16–18.)

From this fact and from the crystallization temperature and the x-ray diffraction patterns, it is concluded that for the mechanically alloyed powders a two-phase region of an amorphous phase with the terminal composition of $Ni_{27}Zr_{73}$ and the crystalline ω-Zr phase exists at high Zr content.

For high Ni contents the terminal composition can be determined from the saturation magnetization measurements to be 85 at. % Ni as shown in Fig. 5. This is also confirmed by the x-ray diffraction patterns for milling intensity 5 [Fig. 1(b)] and the crystallization temperature T_x, taking into account some inhomogeneities due to the milling process. Furthermore the crystallization enthalpy strongly decreases for more than 83 at. % Ni, as derived from a plot of the crystallization enthalpy versus Ni content (not shown in this work). This is in good agreement with the terminal composition derived from the saturation magnetization measurements. The decrease of the crystallization enthalpy is due to a more and more reduced portion of the amorphous phase in the two-phase region which reaches up to about 92 at. % Ni.

To consider these results from the point of view of the chemical driving force that governs the amorphization reaction, we calculated the free energy of mixing by using the Miedema model.[19,20] The calculated glass-forming range for an assumed milling temperature of 100 °C is limited from 22 to 67 at. % Ni which is smaller than the experimentally observed existence range. As in several other cases the Miedema model does not give an exact description of the glass-forming range. It is not yet clear if, in general, the Miedema model does not describe the metastable thermodynamic equilibrium sufficiently well or if an additional enthalpy term due to the high defect density after severe deformation or a so-far unspecified atomic mixing term lowers the free enthalpy of the amorphous phase.

A very important parameter of mechanical alloying is the temperature during the milling process. From the x-ray results shown in Figs. 1(b) and 1(c) we conclude that at least a partial crystallization can occur during the mechanical alloying at high milling intensities. Since it has been shown that crystalline intermetallic phases can be amorphized by ball milling[21] the crystallization cannot simply be caused by the milling but it must be an effect of excessive heating during the mechanical alloying. For the samples from $x = 66$ to 75 milled at intensity 7, the intermetallic equilibrium phase Ni_3Zr shows up in the x-ray diffraction

patterns. To clarify this, the peak temperature reached within the powder particles during milling is estimated. Following the procedure proposed by Schwarz and Koch,[22] it is assumed that the particles are deformed by localized shear during a collision between the balls. The normal stress developed is $\sigma_n \approx \rho_b v_s v_r$, where $\rho_b = 8.54$ g cm^{-3} is the density of the steel balls, $v_s = 5800$ ms^{-1} is the speed of a longitudinal wave in steel, and $v_r = 2.5, 3.6$, and 4.7 ms^{-1} for intensity 3, 5, and 7, respectively, is the relative velocity of the balls. The shear process lasts for $\Delta t = 2d/v_s$, where $d = 1$ cm is the diameter of the steel balls and the energy flux dissipated on the glide plane is $F = \sigma_n v_r$. The resulting temperature increase ΔT by the heat flux $F/2$ for time Δt is

$$\Delta T = F(\Delta t/\pi K_0 \rho_p c_p)^{1/2}.$$

For the powder density ρ_p and the specific heat c_p, we used weighted averages of the pure components, giving $\rho_p = 8.2$ g cm^{-3} and $c_p = 394.9$ J kg^{-1} K^{-1} for $Ni_{70}Zr_{30}$. With $K_0 = 5.0$ W m^{-1} K^{-1} we obtain $\Delta T = 80, 167$, and 287 °C for milling intensity 3, 5, and 7, respectively. These values exceed Schwarz and Koch's result[22] by far due to the higher ball velocities. They only refer to the individual collision process and must be added to the overall temperature of the milling container which is about 50, 80, and 120 °C for intensities 3, 5, and 7, respectively. Therefore, the total peak temperatures of the powder particles can reach 130, 247, and 407 °C. For comparison the amorphous powders have been isothermally annealed. At 400 °C an annealing of only 5 min is sufficient to produce partially crystallized material with a similar x-ray diffraction pattern as obtained for the $Ni_{70}Zr_{30}$ powder milled for 60 h at intensity 7. Therefore, we can conclude that the actual temperature of the individual particle during mechanical alloying can in fact be rather high—at least high enough to cause crystallization. Then also amorphization by solid-state reaction can occur since this reaction is usually much faster as DSC results for layered Ni-Zr composites even with 100-nm-thick individual layers have shown.[23]

The various possible transitions between composite, intermetallic phase, and amorphous phase are illustrated in Fig. 7. Starting from a composite of crystalline elements mechanical alloying can produce an amorphous phase. The mechanism responsible for this amorphization is proposed to be similar to the solid-state interdiffusion reaction observed in alternating crystalline multilayers. Perhaps additional energy terms come into play, as mentioned before.[24] Crystallization of the amorphous phase at elevated temperatures transforms this metastable phase into the intermetallic equilibrium phase. On the other hand, it is possible to pro-
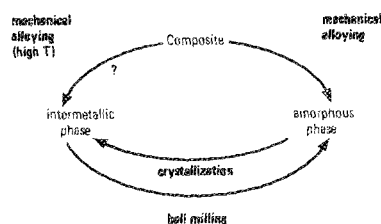

FIG. 7. Schematical illustration of possible transitions between composite, intermetallic phase, and amorphous phase.

duce the amorphous phase by ball milling of the intermetallic phase. In this case the defect density of the equilibrium phase is claimed to rise due to ball milling until its free energy is increased above the free energy of the amorphous phase and therefore the transformation takes place.[22] It also seems possible that mechanical alloying of elemental crystalline powders produces the intermetallic phase by milling at high intensity. We think that this is due to a temperature rise during ball milling up to temperatures above the crystallization temperature of the competing amorphous phase as observed for the samples milled at intensity 7. From our results we can not yet clearly decide whether the observed intermetallic phase is formed by an *in situ* crystallization of a previously formed amorphous phase or, less likely, directly from the composite powders.

The influence of the milling intensity on the reaction product of ball milling is also demonstrated for milling intensity 3 which is obviously too smooth to produce a completely amorphous alloy. Presumably the resulting temperature is not high enough for a complete solid-state reaction and the deformation of the powder particles is not severe enough within 60 h of milling.

V. CONCLUSIONS

We have shown that glass formation by mechanical alloying in the Ni-Zr alloy system is in general possible from 27 to 83 at. % Ni. On both sides of the glass-forming range there exists a two-phase region between the amorphous phase and the elemental crystalline phase. The terminal compositions have been determined by means of examining intrinsic and extrinsic physical properties, since x-ray diffraction only gives a qualitative description of the homogeneity range of the amorphous phase. The measured properties are in good agreement with the data for melt-spun samples at compositions where both melt-spun and mechanically alloyed samples exhibit an amorphous phase. Furthermore, it is shown for the first time, that the amorphization process strongly depends on the milling conditions. Normally the temperature rise during mechanical alloying seems to be high enough to enable an interdiffusion reaction according to a solid-state reaction, and a too intense milling leads to the appearance of the intermetallic equilibrium phase at a composition range from $x = 66$ to 75. This can be explained by a rise of the actual milling temperature to values above the crystallization temperature. On the other hand

the powder does not become completely amorphous within 60 h if the milling conditions are too smooth because then the resulting temperature and the deformation of the powder are not sufficient for a complete solid-state reaction within this time.

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