X-RAY DIFFRACTION STUDY ON THE FORMATION OF ULTRAFINE NANOSTRUCTURES BY CRYSTALLIZATION OF METALLIC GLASSES

N. Mattern

Institut für Festkörper- und Werkstofforschung Dresden, Postfach, D-01171 Dresden

ABSTRACT

The influence of iron addition on the crystallization behavior of Zr$_{65}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$ bulk metallic glass was investigated by X-ray diffraction. Addition of iron in amorphous (Zr$_{65}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$)$_{100-x}$Fe$_x$ ($0 \leq x \leq 20$) leads to a changed crystallization sequence and to the formation of nanocrystals. The formation of a cubic NiTi$_2$-type phase (S.G. Fd 3m, $a_0=1.22$ nm) is the first step of crystallization in amorphous alloys with iron contents $x \geq 1$. Depending on the iron content the average crystallite size decreases to the nanometer regime. Ultrafine nanoclusters of down to 2 nm in size are formed as the first step of crystallization for amorphous Zr$_{52}$Al$_6$Cu$_{14}$Ni$_8$Fe$_{20}$. The 2 nm clusters grow by Ostwald ripening during isothermal annealing up to 5 nm average crystallite size. Atomic pair correlation functions of the nanostructured states as well as transmission electron microscopy are in agreement with results from Rietveld refinement.

INTRODUCTION

Crystallization of an amorphous precursor is a possible route to prepare new materials. Metastable crystalline phases, quasicrystals, and nanostructures may be formed upon annealing. Nanocrystals are possible if a high nucleation rate is combined with a low growth rate. For example, this can be achieved by the addition of elements like Au or Nb in Fe-based metallic glasses [1]. Compared to the amorphous alloy the nanocrystalline state may offer improved properties as it was found for nanocrystalline soft magnetic alloys [2]. Nanocrystalline composites with high strength have also been obtained upon crystallization of Zr-based bulk glasses containing different additions such as Ti or Pd [3,4]. In this paper we report on the crystallization behavior of a Zr$_{65}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$ bulk glass originally developed by Inoue et al. [5] which was modified by iron additions. The influence of the iron content on the phase formation and microstructure was studied in detail. The possibility of formation of an ultrafine nanocrystalline microstructure in this Zr-based system will be shown.

EXPERIMENTAL

Amorphous (Zr$_{65}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$)$_{100-x}$Fe$_x$ ($0 \leq x \leq 20$) ribbons 10 mm in width and 25 µm in thickness were prepared by means of rapid quenching from the melt using a single-roller melt-spinner under argon atmosphere. The thermal behavior was investigated in a Netzsch DSC 404 differential scanning calorimeter (DSC) with a heating rate of 40K/min. Pieces of the ribbons were isothermally annealed at different temperatures $T_A$ under argon atmosphere. X-ray diffraction (XRD) patterns of the annealed samples were recorded by means of a Philips PW 3020 Bragg-Brentano diffractometer using CuK$\alpha$ radiation. To analyze the short-range order the scattering curves were measured up to 270 nm$^{-1}$ at the high-energy beam-line BW5 of the storage ring DORIS ($\lambda=0.10776$ Å). TEM images and electron diffraction patterns were obtained using a Philips CM200FEG microscope.
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RESULTS AND DISCUSSION

![Graph showing thermal behavior](image1)

Fig. 1: Thermal behavior of amorphous (Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10})_{100-x}Fe_x alloys as obtained from DSC (the glass transition temperature T_g and the crystallization temperature T_x1 are defined as the onset temperatures of the glass transition and the first crystallization peak, respectively). For all the iron-containing alloys, a cubic phase of the NiTi_2-type (S.G. 227) forms in the first step of crystallization. (a_0 = 1.22 nm). The formation of a metastable cubic phase with NiTi_2 structure was reported earlier for melt-spun NiZr_2 and CoZr_2 ribbons [6,7] and, more recently, for bulk glass-forming Zr-Ni-Al-Cu alloys [8-10]. The chemical composition of the NiTi_2-type phase in the iron containing samples is unknown but probably all elements of the alloy are present. Cubic NiZr_2 may have an extended solid solution range between nickel and other metal atoms. In our case the solution of iron is indicated by the variation of the lattice constant a_0 with the iron content. The temperature window where this metastable phase exists becomes extended with increasing iron content. Obviously, the addition of iron stabilizes the metastable "big cube phase".

![Graph showing XRD patterns](image2)

Fig. 2 shows as an example the XRD patterns of the (Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10})_{80}Fe_{20} alloy obtained after isothermal annealing at different temperatures T_A each for 1 hour. The amorphous state remains for annealing temperatures up to T_A = 698 K. Annealing at 723 K ≤ T_A ≤ 773 K leads to the formation of the cubic NiTi_2-type phase (a_0 = 1.22 nm). The strong broadening of the reflections indicates the formation of a nanocrystalline microstructure. The cubic phase and the remaining amorphous phase transform into a tetragonal FeZr_2-type phase (S.G. I4/mmm, No.140) and a cubic NiAlZr phase at T_A ≥ 800 K. In the third step the equilibrium phases are obtained (Fig. 2).

The broadening of the reflections of the cubic NiTi_2-type phase was found to be dependent on the iron content as well as on the annealing time and temperature employed. In general, the reflections become wider with increasing iron content for comparable annealing parameters. Fig. 3 shows the XRD patterns of (Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10})_{100-x}Fe_x alloys annealed for 30 min at T_A = 723 K. Because of the strong overlap of the reflections, Rietveld refinement [11] was applied to evaluate the profile parameters. The reflection profiles were approximated by Pseudo Voigt functions using the Caglioti function \( B^2 = w + v \tan \theta + u \tan^2 \theta \) to describe the dependence of the peak-width B on the diffraction angle 2\theta. The calculated XRD pattern are also shown in Fig. 3 by the solid lines. The angle-dependence of B indicates that the peak broadening is caused by the size effect only.
Fig. 3: XRD of (Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10})_{100-x}Fe_{x} annealed at \( T_A = 723 \) K (meas.: o, calc.: - )

The average crystallite size \( <D> \) was estimated by applying the Williamson-Hall analysis
\[ B^2 \cos^2 \theta = \left( \frac{\lambda}{<D>} \right)^2 + \langle \epsilon \rangle \sin^2 \theta \] [11]. Fig. 4 shows the estimated \( <D> \) values for the samples with different iron contents. The average crystallite size fits well to \( \sqrt{x} \) functional behavior indicating that the number of crystallites \( N \) is proportional to the iron content (\( N \sim x \)).

Depending on composition, annealing temperature and annealing time an average crystallite size \( <D> \) of 2 – 12 nm is calculated. Several data points in Fig. 4 for a given alloy composition correspond to different annealing parameters. Fig. 5 compares some of the XRD patterns of annealed \((Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10})_{80}Fe_{20}\) with the corresponding calculated patterns. The experimental patterns are reproduced best by a superposition of the diagram of the cubic phase with NiTi_{2} structure and an amorphous phase. From these fits, the amorphous volume fraction is estimated to be about 40 \( \pm \) 10 vol\% for the samples annealed at 723 or 773 K, respectively. The diagram of the 723K/1h annealed state differs only slightly from that of the

Fig. 4: Average crystallite size \( <D> \) of the NiTi_{2}-type phase

Fig. 5: XRD of Zr_{52}Al_{6}Cu_{14}Ni_{8}Fe_{20} (fit of amorphous + nanocrystalline phase=solid lines)

Fig. 6: Average crystallite size \( <D> \) in \((Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10})_{80}Fe_{20}\) versus annealing
amorphous as-quenched sample. Diffuse, amorphous-like maxima with a shoulder in the first peak and an enhanced intensity in the second maximum are obtained for the state annealed over the first DSC peak. An average crystallite size $<D> = 2.2$ nm is calculated for the sample annealed at 723K/1h, and $<D> = 4.3$ nm for 773K/1h respectively from the line widths. The small size and the presence of amorphous phase mean that a large number of atoms are situated at the surface of the crystals embedded in the remaining amorphous phase. The differences between calculated and experimental XRD patterns which become larger with reduction in size may be caused by these contributions. On the other hand, changes in the structure of the unit and site disorder may be possible due to size effect. The 2 nm cluster would consists of 4 unit cells only. The diffuse character of the XRD pattern does not allow unique conclusion for this particular structural state. The time dependence of the average crystallite diameter $<D>$ is shown in Fig. 6. The crystallites grow the upon crystallization with time and their average diameter get saturated at values of about 4 - 5 nm. Annealing for longer times lead then to phase transformation of the NiTi$_2$-type phase as discussed before.

TEM images of (Zr$_{65}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$)$_{80}$Fe$_{20}$ annealed at 723 K for 1, 2, 4 and 8 hours are shown in Figs. 7a, b, c, and d, respectively. For the 1 hour annealed state the image is similar to that of the amorphous as-quenched state. The 2 nm crystals or clusters are not resolved in the TEM picture. Small crystallites can be found in the longer annealed samples shown in Figs. 7 b-d. The size of the crystals becomes larger, and a size distribution is observed for longer annealing times. In agreement with the estimation from the XRD data a crystallite size between 2 and 5 nm can be estimated from the images.

![Fig. 7: TEM images of (Zr$_{65}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$)$_{80}$Fe$_{20}$ annealed at $T_A=723$ K for a) 1 hour, b) 2 hours, c) 4 hours, and d) 8 hours.](image-url)
To analyze the structure development of (Zr$_{65}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$)$_{80}$Fe$_{20}$ upon annealing in terms of the atomic pair correlation function $g(r)$ the scattering curves were measured in a wide $q$-range ($q=4\pi \sin \theta / \lambda$) up to 270 nm$^{-1}$. Fig. 8 shows the corresponding interference functions $I(q)$ as calculated from the elastic scattered XRD intensities. The $I(q)$ curve of the as-quenched state shows the behavior typical for amorphous metallic alloys with a shoulder in the second diffuse maximum. Oscillations in $I(s)$ can be seen up to 15 Å$^{-1}$ in the experimental data. The scattering curves of the annealed state are clearly different especially in the second maximum and in the maximums at higher $q$-values. The changes in the second maximum of $I(q)$ are much larger between the as-quenched state and the annealed state, but rather similar for all annealed states (Fig. 8). From the interference function $I(q)$ the atomic pair correlation function $g(r) = \rho(r)/\rho_0$ was calculated by the Fourier transform of [12]:

$$4\pi \cdot r \cdot \rho_0 \cdot (g(r) - 1) = \frac{2}{\pi} \int I(s) \cdot s \cdot \sin(s \cdot r) \cdot ds$$

where $\rho(r)$ is the radial atomic pair density distribution function and $\rho_0 = 53$ nm$^3$ is the mean atomic density. Figure 9 shows the calculated $g(r)$ curves. For all these curves two components of the first maximum in $g(r)$ are visible. The second maximum consists of at least three components. The peak positions of the first maximum can be attributed to the zirconium-metal ($r_{Zr-M} = 0.27$ nm) and the zirconium-zirconium ($r_{Zr-Zr} = 0.31$ nm) distances which correspond to the values in crystalline MZr$_2$ and MZr phases [13]. The heights of the components of $g(r)$ change upon annealing. This behavior clearly indicates a complete change of the short-range order of an essential volume fraction after annealing at 723 K. The short-range order is found to be rather similar for all annealed states. To compare the short-range order with that of the NiTi$_2$-type phase a model for a quasicrystalline approximation of the amorphous structure was applied [14]. Fig. 9 also shows the calculated total X-ray pair correlation function $g(r)$. The short-range order of the cubic NiTi$_2$–type phase is found to be similar to the experimental curves for the annealed states, but clearly different to that of the amorphous as-quenched state. With increasing annealing temperature $T_a$ the oscillations in $g(r)$ become more extended to higher $r$-values. If we calculate the correlation length $r_c$, (the value where deviations of $g(r)$ become less than 1% from the average density), then we get $r_c = 1.4$ nm for the as quenched state, $r_c = 1.8$ nm for the 723K annealed state, and $r_c = 3.0$ nm for the 773K annealed state, respectively. The first stage of crystallization of amorphous
(Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10})_{80}Fe_{20} (after annealing at 723K for 1hour) is, therefore nucleation with complete rearrangement of the atoms to form clusters without remarkable growth. Most likely, this is related to significant chemical redistribution of atoms for the formation of the NiTi\textsubscript{2} type nanocrystals. The primary precipitation of clusters corresponds to the first exothermic reaction of the DSC scan. The second step of the crystallization is related to the growth of the clusters. Because the volume fraction of the amorphous phase does not change with time and temperature we conclude that growth mechanism is Ostwald ripening.

Conclusions

Addition of iron in amorphous (Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10})_{100-x}Fe\textsubscript{x} (0 \leq x \leq 20) leads to a changed crystallization behavior. A intermediate cubic NiTi\textsubscript{2}-type phase (S.G. \textit{Fd \bar{3}m}, a\textsubscript{0}=1.22 nm) is formed as the first step of crystallization in amorphous alloys with iron contents $x \geq 1$. Ultrafine nanoclusters of 2 nm in size are formed upon crystallization due to a high nucleation rate combined with a low growth velocity. The comparison of the atomic pair correlation function with results of Rietveld analysis indicates that the ultrafine cluster exhibit the short-range order of the NiTi\textsubscript{2} structure. These clusters or crystallites grow up to 5 - 10 nm with increasing temperature and time as a second stage of crystallization.

References