DEVITRIFICATION OF MECHANICALLY ALLOYED Zr-Ti-Nb-Cu-Ni-Al GLASSY POWDERS STUDIED BY TIME-RESOLVED X-RAY DIFFRACTION

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Abstract. The crystallization of mechanically alloyed $Zr_{67}Ti_{6.14}Nb_{1.92}Cu_{10.67}Ni_{8.52}Al_{5.75}$ glassy powder is investigated by time-resolved X-ray diffraction. The powder displays a multi-step crystallization behavior characterized by the formation of a metastable nanoscale quasicrystalline phase during the first stage of the crystallization process. At higher temperatures, coinciding with the second crystallization event, the amorphous-to-quasicrystalline transformation is followed by the precipitation of the tetragonal Zr_2Cu phase (space group I4/mmm) and the tetragonal Zr_2Ni phase (space group I4 /mcm). The transformations are gradual and the quasicrystals and the subsequent phases coexist over a temperature interval of about 25K.

1. INTRODUCTION

More than fifty years ago Frank proposed that the local atomic structure of the metallic liquids may be organized in a non-crystallographic fashion (i.e. icosahedral) [1]. The occurrence of the icosahedral short-range order (SRO) has also been invoked to explain the formation of quasicrystals (QC) by devitrification of glassy materials [2]. In this view, the icosahedral SRO characterizing the metallic melt is *quenched-in* during solidification and subsequently it promotes the formation of the quasicrystalline phase, which is characterized by an aperiodic translational symmetry. Indeed, investigations on the crystallization of Zr-based metallic glasses suggest that icosahedral SRO precedes the formation of quasicrystals upon devitrification [3]. In addition, the observation that, in contrast to the glassy alloys produced by liquid quenching, binary $Zr_{70}Pd_{30}$ glassy alloys prepared by mechanical alloying (MA) [4,5] do not undergo QC forma-

tion upon partial crystallization indirectly supports this assumption. This might suggest that the formation of quasicrystals from glassy precursors is limited to glassy materials formed directly from the liquid phase. It has been shown for the MA Zr-Ti-Nb-Cu-Ni-Al glassy powders [6] that oxygen contamination during milling affects QC formation by selectively reacting with Zr and consequently by driving the chemical composition of the glassy phase out of the range suitable for QC formation [6]. The contamination drawback can be bypassed by the addition of an appropriate amount of elemental zirconium to the MA powder. The resulting variation of composition changes the crystallization behavior inducing the formation of the QC phase [6]. This demonstrates that if a particular short-range order is necessary for the formation of quasicrystals, it can be achieved also by solid-state processing.

In this work, the crystallization of the QC-forming $Zr_{67}Ti_{6.14}Nb_{1.92}Cu_{10.67}Ni_{8.52}Al_{5.75}$ glassy powders

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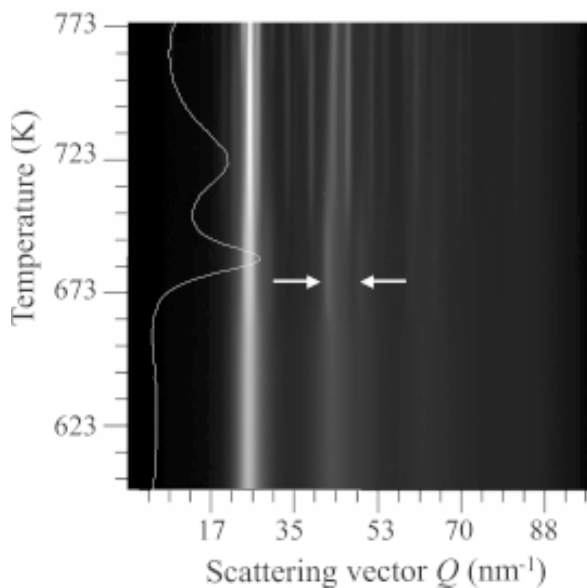
Fig. 1. Two-dimensional image and corresponding DSC scan (white line) of the mechanically alloyed $Zr_{67}Ti_{6.14}Nb_{1.92}Cu_{10.67}Ni_{8.52}Al_{5.75}$ glassy powders. The arrows indicate the diffraction signals belonging to the quasicrystalline phase at $Q_p = 43$ and 49 nm^{-1}.

produced by MA has been further investigated by time-resolved X-ray diffraction. The aim of our study of the temperature dependence of the structure of glassy powder is determination of the temperature ranges of stability of the different phases formed during heating.

2. EXPERIMENTAL

Glassy powders with nominal compositions $Zr_{67}Ti_{6.14}Nb_{1.92}Cu_{10.67}Ni_{8.52}Al_{5.75}$ were produced by mechanical alloying using a Retsch PM400 planetary ball mill and hardened steel balls and vials. All sample handling was carried out in a glove box under purified argon atmosphere (less than 1 ppm O_2 and H_2O). The powders were milled for 100 h at a ball-to-powder mass ratio of 13:1 using a milling speed of 150 rpm. The amount of iron and oxygen were found to be about 0.1 and 0.3 wt.%, respectively. The thermal stability was investigated by differential scanning calorimetry (DSC) at a heating rate of 40 K/min under a continuous flow of purified argon. The time-resolved synchrotron X-ray studies were performed at the Advanced Photon

Source (APS) at Argonne National Laboratory. Diffraction data were collected at a constant heating rate of 40 K/min in order to compare the structural evolution with the thermal stability investigated by DSC (for further details see Ref. 7).

3. RESULTS AND DISCUSSION

The results of the X-ray diffraction experiments as a function of temperature for the MA $Zr_{67}Ti_{6.14}Nb_{1.92}Cu_{10.67}Ni_{8.52}Al_{5.75}$ powder are summarized in the two-dimensional image presented in Fig. 1, together with the corresponding DSC scan. Note, Fig. 1 comprises a sequence of individual scans collected at different temperatures illustrating diffracted intensity vs. Q (scattering vector = $4\pi\sin\theta/\lambda$); increased brightness reflects increased diffracted intensity. Analyzing Fig. 1 reveals the overall time-resolved crystallization behavior and thus provides preliminary general information about the structural transformations that occur during heating. At low temperature, below the first crystallization event, only two bright lines belonging to the amorphous phase are visible. These lines are rather broad, indicating the diffuse nature of the scattering from the amorphous structure. At intermediate temperatures that correspond to the first exothermic DSC peak, the diffraction data show a clear transition from the amorphous to a quasicrystalline structure. In this temperature range the diffraction signal at about $Q_{p1} = 26$ nm^{-1} becomes brighter and narrower, whereas the signal at $Q_{p2} = 43$ nm^{-1} is shifted to lower Q values with increasing temperature. Moreover, an additional bright line belonging to the QC phase is visible at about $Q_{p3} = 49$ nm^{-1}. At higher temperatures, coinciding with the second crystallization event, the amorphous-to-quasicrystalline transformation is followed by the precipitation of the high-temperature phase(s). The transition is gradual and the quasicrystals and the subsequent phase(s) coexist over a temperature interval of about 25K. In this coexistence region, Q_{p2} is again shifted to higher Q values whereas Q_{p3} finally disappears.
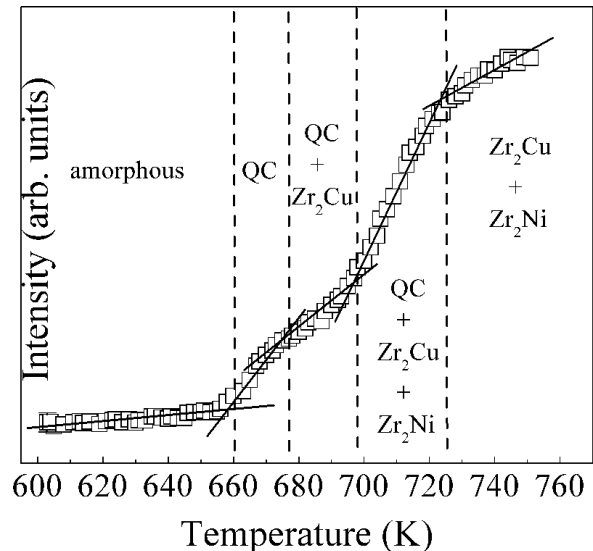
In order to clarify the devitrification sequence of the powder, selected diffraction data recorded at temperatures between 663 and 773K (corresponding to the crystallization events) are shown in Fig 2. In these plots, the pattern of the amorphous phase recorded at low temperature was used as background and subtracted from the total intensity of subsequent scans obtained at higher temperatures to remove the diffraction contribution due to the amorphous phase and also to highlight
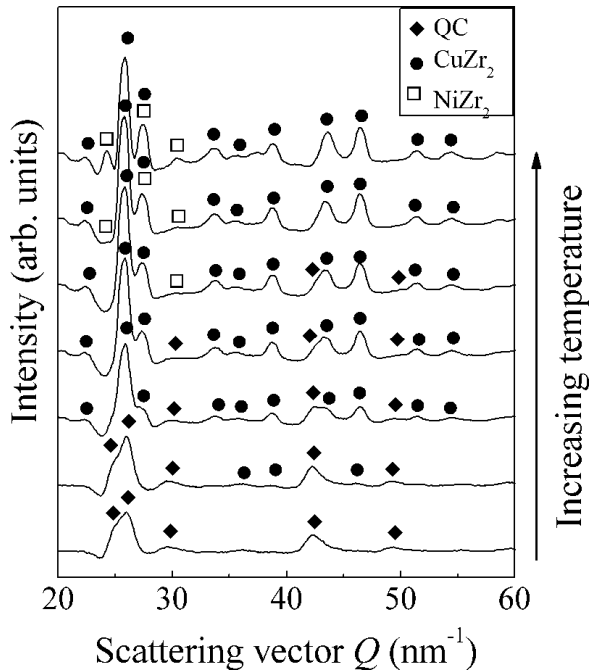
Fig. 2. Diffraction data recorded at temperatures between 663 and 773K (corresponding to the crystallization events). In these plots, the pattern of the amorphous phase recorded at low temperature was used as background and subtracted from the total intensity of subsequent scans obtained at higher temperatures.

Fig. 3. Temperature dependence of the height of the diffraction peak at Q_p = 26 nm^{-1}, where the amorphous, QC and tetragonal Zr_2Cu phases display the most intense diffraction peaks.

the coherently scattering phases. At low temperatures, corresponding to the first crystallization event, only a few broad diffraction peaks are visible, signifying the presence of an ordered structure of nanometer scale dimensions. The comparison with previously reported data [6] clearly indicates that this first crystallization product is an icosahedral quasicrystalline phase. With an increase of temperature the primary diffraction peak sharpens and increases its intensity. Subsequently, additional peaks that can be assigned to the tetragonal Zr_2Cu phase (space group I4/mmm) appear. In the same temperature range, the intensity of the QC diffraction signals is reduced and further diffraction peaks belonging to the tetragonal Zr_2Ni phase (space group I4/mcm) become visible. Finally, at higher temperatures, the QC phase is no longer visible and only the tetragonal phases coexist.

Additional information to better understand the structure evolution upon heating was obtained by evaluating the temperature dependence of the in-

tensity of the first scattering peak. Fig. 3 shows the temperature dependence of the height of this peak at about Q_p = 26 nm^{-1}, where the amorphous, QC and tetragonal Zr_2Cu phases display the most intense diffraction peaks. Comparing the data in Fig. 3 together with the corresponding results in Fig. 2 reveals a clear correlation between the slopes of the curve at different temperatures and the phase evolution during heating. At low temperature in the amorphous region, the curve displays a linear relation that slightly increases with temperature, probably due to structural relaxation. Within this temperature interval no indication of glass transition can be detected. This behavior is different from that observed for the $Zr_{52}Ti_5Cu_{18}Ni_{15}Al_{10}$ alloy, which, in contrast, displays a linear decrease of the intensity and a clear change of the slope at the glass transition temperature [8]. At the crystallization temperature T_{x1} = 655K, where the quasicrystals form, the slope $dI(Q_p)/dT$ displays an abrupt change as a result of the appearance of a coherently scattering phase. At about 670K, the slope changes again due to the precipitation of the tetragonal Zr_2Cu phase, which brings an additional contribution to the intensity of the first peak. At about 690K, in correspondence to the formation of the tetragonal

Zr_2Ni phase, the second slope change is followed by a third one. In contrast to the previous ones, the third slope change is more marked. This is most likely due to the contribution of the Zr_2Cu phase to the overall peak intensity, which increases with increasing temperature, while the contribution due to the QC phase is reduced (Fig. 2). From about 720K the slope is progressively reduced due to the disappearance of the QC and finally the intensity reaches an almost constant value.

4. SUMMARY

The crystallization of mechanically alloyed $Zr_{67}Ti_{6.14}Nb_{1.92}Cu_{10.67}Ni_{8.52}Al_{5.75}$ glassy powder has been investigated by time-resolved X-ray diffraction. The results reveal a complex crystallization behavior characterized by the sequential formation of a metastable nanoscale quasicrystalline phase, tetragonal Zr_2Cu and tetragonal Zr_2Ni phases. The transformations are gradual and the temperature ranges of stability of the different phases overlap partially.

ACKNOWLEDGEMENTS

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