Spinodal decomposition of Ni-Nb-Y metallic glasses studied by in situ Small Angle X-Ray Scattering

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The ternary Ni-Nb-Y system exhibits an extended miscibility gap in the liquid [1]. By means of rapid quenching (melt spinning) the decomposed melt can be frozen into a phase separated metallic glasses [2]. Figure 1 shows the X-ray diffraction pattern (CoKα-radiation) of a Ni₇₀Nb₁₅Y₁₅ metallic glass characterized by diffuse maxima only. For such glassy Ni-Nb-Y alloys with Ni > 60 at% early stages of phase separation are obtained having fluctuation in nm dimensions with no visible contrast in TEM images (Fig. 1). In this case Small Angle X-ray Scattering (SAXS) enables to extract quantitative parameters of the heterogeneous microstructure [3]. The frozen in glassy structure is in a metastable state and changes upon heating. The aim of this work was to investigate the decomposition behaviour of a Ni₇₀Nb₁₅Y₁₅ metallic glass at elevated temperature in the supercooled liquid state well below the crystallization temperature.

In order to analyze the decomposition, in-situ SAXS measurement were performed at the B1 beam-line at the DORIS storage ring at HASYLAB/DESY Hamburg. A heating stage under vacuum was used for the in-situ measurements at elevated temperatures. The in situ measurements were performed at an energy of 8269 eV in the vicinity of the K-absorption edge of Ni. The used sample-detector distance of 3635 mm covered a q-range (q=4πsinθ/λ) between 0.5 and 6.0 nm⁻¹. In total for the sample and the background measurements a beam time of 30 min was accumulated per pattern. The scattering curves were calibrated into macroscopic scattering cross sections via the reference measurements in units of cross section per unit volume [cm²/cm³]=[cm⁻¹].

The SAXS patterns recorded during isothermal annealing at T=748 K are shown in Figure 3 as a function of time. For comparison the room temperature data of the sample before heating are also given (circles). The SAXS patterns show a maximum at q_max = 1.2 nm⁻¹. The occurrence of the maximum in the SAXS curves is an indication of the presence of high density of electron density fluctuations with a dominant correlation length in the Ni₇₀Nb₁₅Y₁₅ metallic glass. Using the relationship ζ = 2π/q_max between correlation length ζ and

![Figure 1: XRD patterns of as-quenched and heat treated Ni₇₀Nb₁₅Y₁₅ glasses](image1)

![Figure 2: TEM image and electron diffraction pattern of Ni₇₀Nb₁₅Y₁₅ glass (as-quenched)](image2)
peak maximum one obtains $\zeta = 5$ nm for $\text{Ni}_{70}\text{Nb}_{15}\text{Y}_{15}$ glass. With increasing time, the height or integral intensity of the maximum $q_{\text{max}} = 1.2$ nm$^{-1}$ becomes more pronounced. A similar behaviour of the SAXS intensities is observed for an other sample measured at $T=723$ K. Figure 5 shows the integral intensities of the SAXS curves as a function of time. The intensity increases exponentially for the early stage as can be seen from the semi-logarithmic plot. Later the growth diminishes and converges to a stationary stage. Both SAXS curves can be transformed into each other by a scaling factor describing the same thermally activated process of decomposition. As expected, a higher decomposition rate was measured for the in-situ measurement performed at the higher temperature. The retention of the amorphous state of the samples during heat treatment was proven by subsequent XRD measurements of the heat-treated SAXS samples (Fig. 1).

The structure formation by spinodal decomposition is usually described by the Cahn-Hillard theory [4]. The decomposition is initiated via the spontaneous formation and subsequent growth of coherent composition fluctuations. An exponential time law is derived for the scattered intensity from the linear Cahn-Hillard theory which is in agreement with the observed dependence of $I(q)$ during early stages. At later stages, the stationary state of the concentration amplitude is reached and the composition profile may change into a square-like shape which gives reason for the deviation from the exponential growth of the SAXS intensity. It is worth to notice that the position of the maximum of $I(q)$ does not change with annealing time (Fig. 3, 4). This means, that the fluctuation length remains constant during the decomposition, which points to the spinodal decomposition as mechanism in Ni-Nb-Y glasses.

References