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- fill in a separate form for each project or series of measurements.
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- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Early stages of phase separation and crystallization in Al-based metallic glasses.	**Experiment number**: ME-1178
Beamline: ID2	**Date of experiment**: from: 30/09/2005 to: 03/10/2005	**Date of report**: 09/02/2006
Shifts: 9	**Local contact(s)**: Dr. Michael SZTUCKI	*Received at ESRF:*

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Report:

The objective of the ME-1178 experiment was investigation of early stages of nanocrystallization in a group of Al-based amorphous alloys. Our previous results obtained at ID2 during the ME-758 experiment indicated that nanocrystalization process is initated and controlled by spinodal decomposition of amorphous phase occuring on length scale of about 10 nm. While the ME-758 data covered mostly the late stages of nanocrystallization process, we were lacking information on the early stages of transformation. We believed that ME-1178 would provide strong evidence supporting our previous assumption of phase separation occuring in the glassy phase leading to nanocrystalline microstructure formation.

Aluminum-based metallic glasses containing rare earth (RE) and rare earth and transition metals (TM) additions are known to exhibit excellent mechanical properties [1,2]. These properties can be further improved by thermal annealing to obtain ultra-fine (~10 nm) primary fcc-Al nanocrystals of density about 10^{23} m^{-3} embedded in an amorphous matrix. The nanocrystalline microstructure requires high nucleation frequency and low growth rate. Nanocrystallization of the Al-based glasses was previously attributed to heterogeneous nucleation [3], quenched-in nuclei [4] and new type of homogeneous nucleation [5]. Results based on electron microscopy suggesting amorphous phase separation in Al-Gd-La-Ni glass were also reported [6]. Our recent works based on results obtained in the framework of the ESRF experiments [7,8,9] have shown that amorphous phase separation underlies the nanocrystallization of Al-based metallic glasses. In this report we present results from *in-situ* small-angle and wide-angle X-ray scattering (SAXS/WAXS) measurements performed for a group of amorphous Al-RE and Al-RE-TM alloys (RE=Y, Nd, Sm, Gd, Tb, Dy, Pr; TM=Fe, Ni, Co) produced using the "melt-spinning" technique. The measurements were carried out at much lower temperatures and using longer acquisition times compared to ME-758 experiment. In the following part of this report, a detailed description of results obtained for $Al_{91}Gd_9$ binary amorphous alloy will be given. These results are representative for most of the investigated alloys.

An ingot of $Al_{91}Gd_9$ alloy was prepared from pure elements using arc melting device. Amorphous samples in form of 25 μm thick ribbons were obtained by rapid quenching using the "melt-spinning" method. The liquid alloy was ejected by argon pressure onto the surface of a massive copper wheel spinning at rate of 33 m/s. The incident beam wavelength of λ=1.00 Å was used in the experiment. Small pieces of as-quenched ribbons were sealed in glassy capillaries under argon atmosphere. Samples were placed in a hot-stage holder between the incident beam and SAXS/WAXS detectors. The annealing temperature was reached with 90 K/min heating rate. The q-range covered 0.07 – 1.85 nm^{-1} ($q = (4\pi/\lambda)\sin\theta$, where θ is the scattering angle) in case of SAXS while WAXS measurements covered 4 – 44 deg of 2θ range. In order to achieve similar sensitivity of both methods, the gain levels of SAXS and WAXS detectors were kept at approximately equal values during whole experiment.

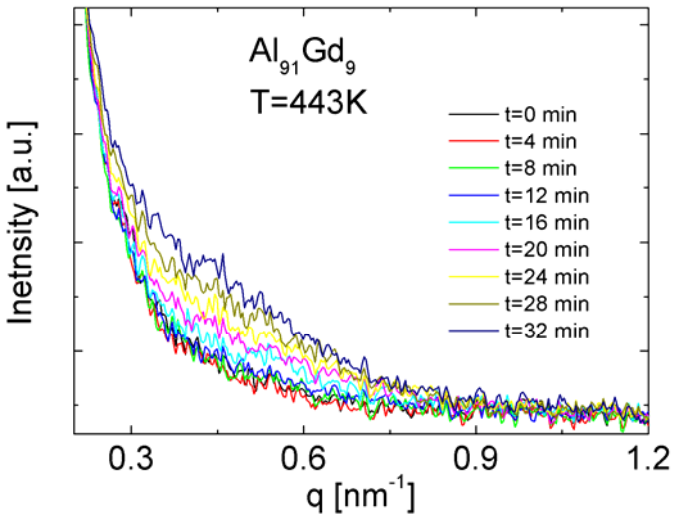

Figure 1

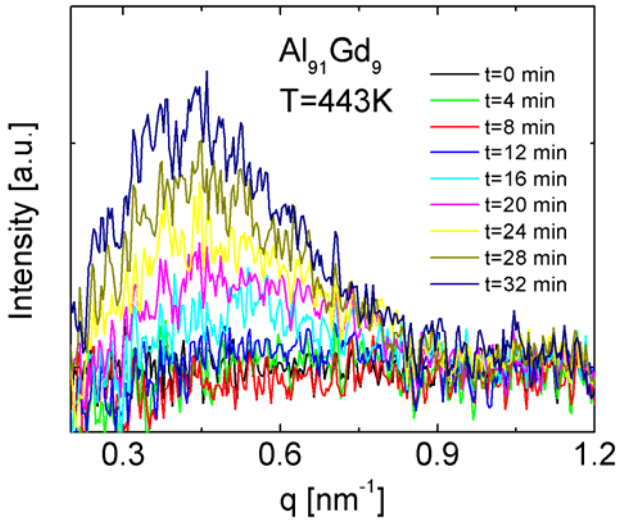

Figure 2

Figure 1 shows evolution of small-angle spectra during annealing of $Al_{91}Gd_9$ at 443 K. During initial 12 minutes no changes in SAXS spectra were detected. This constant signal contribution significant at low q is attributed to sample surface imperfections. After the initial transient, a continuous increase of SAXS intensity is visible. **Figure 2** presents the data re-plotted after subtraction of constant intensity contribution. It can be seen that a characteristic maximum develops in the small-angle region indicating regularity in spatial arrangement of the scattering objects. The maximum is initially centered at about 0.55 nm^{-1} corresponding to 11.5 nm in real space. As the transformation progresses, the position of the SAXS peak shifts progressively towards the origin in q-space. Simultaneously taken WAXS spectra (**Figure 3**) do not show any changes

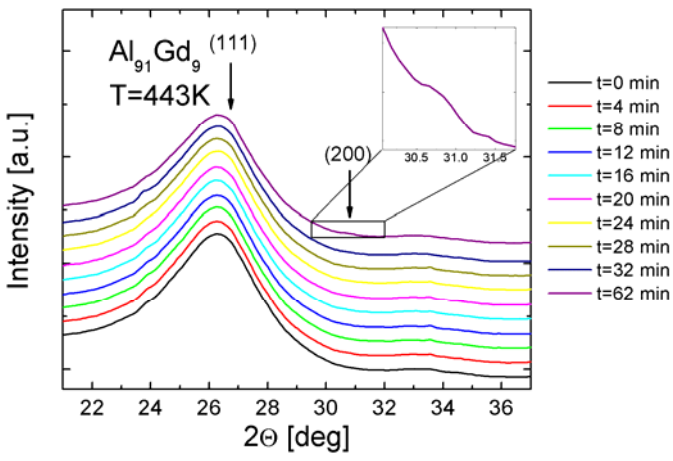

Figure 3

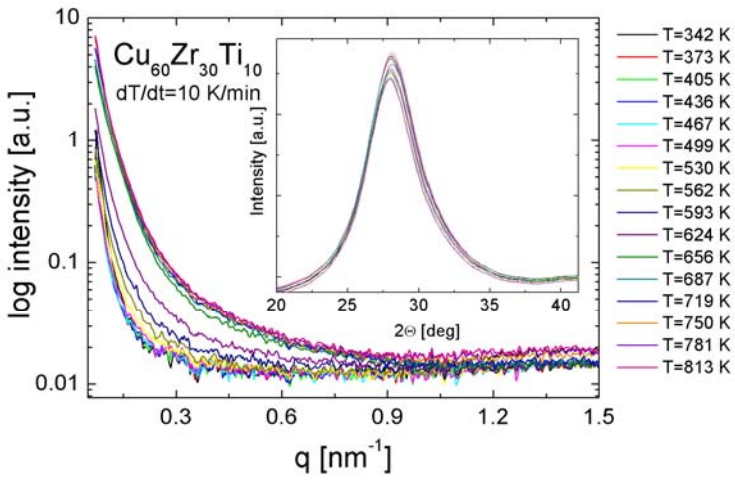

Figure 4

during initial 32 minutes and exhibit a typical "halo" pattern providing evidence of still fully amorphous character of the sample. The positions of (111) and (200) fcc-Al Bragg peaks are indicated by arrows. After 32 min the traces of diffraction peaks of fcc-Al nanocrystalline phase begin to appear on the "halo" pattern. After 62 min the peaks can be clearly distinguished in the WAXS spectra (see inset in **Figure 3**). Within the experimental conditions, we have estimated the minimal detectable crystalline volume fraction to be 0.05%.

As shown in this report, the amorphous phase separation takes place prior to any crystallization event. According to our previous works [8,9] an initially homogenous amorphous alloy decomposes by spinodal mechanism into Al- and RE-rich zones. As demonstrated above, in the early stage of transformation both decomposed phases remain stable against crystallization. After the initial transient, the nucleation of the fcc-Al phase takes place inside the Al-rich regions. The size of the crystals is constrained by the size of the Al-rich regions leading to formation of a microstructure consisting of nanocrystals embedded in the amorphous matrix [8,9].

The ME-1178 experiment supports our previous results concerning nanocrystallization in Al-based metallic glasses. Focusing the on early stages of the transformation, we have managed to obtain experimental evidence of amorphous phase separation prior to devitrification. This is the first experimental result of the X-ray scattering methods confirming decomposition of the glassy phase. Our observations indicate that phase separation must be considered as a potentially possible mechanism of nanocrystallization in other families of metallic glasses. Inspired by the results obtained for Al-based alloys we performed the SAXS/WAXS analysis during isochronal heating of the amorphous $Cu_{60}Zr_{30}Ti_{10}$ bulk glass forming alloy which is know to undergo crystallization on nanometer scale [10]. Significantly, we have detected a considerable increase of SAXS intensity, while WAXS spectrum did not exhibit any traces of crystalline peaks (see **Figure 4**). The increase occurs in temperature range of 590-650 K and suggest formation of compositional fluctuations in the amorphous state. The presence of compositional fluctuations may explain formation of the ultra-fine nanocrystalline structure in $Cu_{60}Zr_{30}Ti_{10}$ glass.

The amorphous phase separation and it's influence on subsequent crystallization in metallic glasses attracts significant attention recently. The results obtained during ME-1178 experiment open new perspective on mechanism of nanocrystallization of metallic glasses. Further studies of amorphous phase separation in different amorphous metallic alloys are required in order to fully establish the relation between the phase separation and nanocrystallization phenomena.

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