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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- 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.



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|---|---|--------------------------------------|
| | Experiment title: Spinodal Decomposition versus Nucleation and Growth in Al-based Metallic Glasses | Experiment number: ME 758 |
| Beamline: ID02 | Date of experiment: from: 07/05/2004 to: 10/05/2004 | Date of report: 02 02 2005 |
| Shifts: 9 | Local contact(s): Dr Pierre Panine | <i>Received at ESRF:</i> |
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Report:

The objective of ME-758 experiment was verification of the mechanism of nanocrystallization in Al-based metallic glasses. The work was inspired by the results on the glass crystallization kinetics [1,2] obtained in the framework of the previous ESRF projects.

Aluminum-based metallic glasses containing rare earth (RE) and rare earth and transition metals (TM) additions are known to exhibit promising mechanical properties. These properties can be further enhanced by thermal annealing to obtain ultra-fine (~10 nm) primary fcc-Al nanocrystals of a density of about 10^{22} - 10^{23} m⁻³ embedded in an amorphous matrix. This kind of 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]. Phase separation in Al-Gd-La-Ni glass was reported with nanocrystal nucleating preferentially on the boundaries between the two phases [6]. Here we report results from *in-situ* small-angle and wide-angle X-ray scattering (SAXS/WAXS) measurements performed for the group of amorphous Al-RE and Al-RE-TM alloys (RE=Y, Nd, Sm, Gd, Tb, Dy; TM=Fe, Ni, Co) produced by "melt-spinning" method. All investigated systems exhibited similar SAXS/WAXS spectra evolution. In this report a detailed description of the results obtained for Al₉₂Sm₈ binary alloy will be given as a representative example for most of the investigated systems. The single exception was observed for Al₈₄Y₉Ni₉Co₂ quaternary alloy.

An ingot of Al₉₂Sm₈ alloy was prepared from pure elements using arc melting device. Amorphous samples in form of about 25 μm thick ribbons were obtained by rapid quenching using "melt-spinning" method. The liquid alloy was ejected by argon pressure on the surface of a massive copper wheel spinning at of 33 m/s. The incident beam wavelength used was $\lambda=1.00$ Å. The 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 100 K/min heating rate. The q -range covered $0.07 - 2.1 \text{ nm}^{-1}$ ($q = (4\pi/\lambda) \sin\theta$ and θ is half the scattering angle) in case of SAXS while WAXS measurements covered 5 – 54 deg of 2θ range.

Figure 1 shows the time evolution of SAXS spectra during isothermal annealing at 443 K of an as-quenched sample after subtraction of weak glassy capillary signal. 40 s after reaching the annealing temperature the SAXS intensity $I(q)$ exhibits a growing interference maximum centered at $q = 0.62 \text{ nm}^{-1}$. After 100 s the peak continues to develop growing with time and shifting toward the origin in q space. The presence of a constant signal contribution significant at low q is attributed to scattering from the sample surface imperfections. Simultaneously to the appearance of the SAXS maximum fcc-Al Bragg peaks were found to develop on the initially amorphous halo pattern in the wide-angle regime (**Figure 2**). Similar SAXS/WAXS spectra evolution was observed for other annealing temperatures (453 K and 463 K).

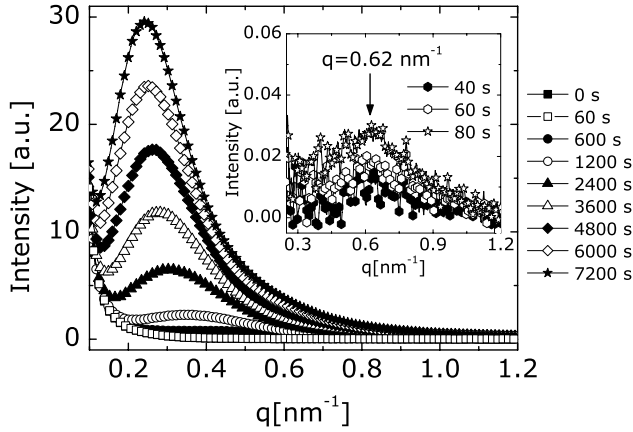


Figure 1

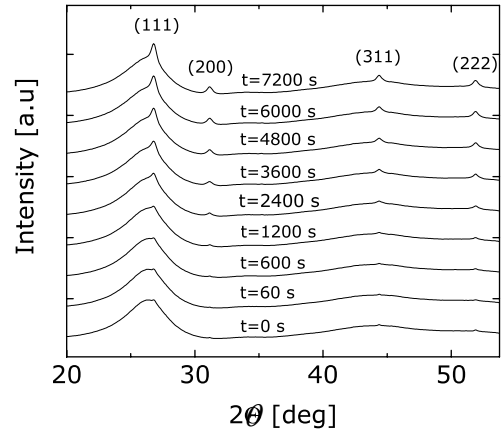


Figure 2

In order to determine the precipitate size the SAXS data were analyzed using the Guinier approximation [7] here $I(q) \propto \exp(R_g^2 q^2 / 3)$ with R_g standing for a radius of gyration. For the spherical precipitates of radius R , $R_g = \sqrt{3/5}R$. **Figure 3** presents the precipitate size evaluated using the Guinier method together with mean crystal size calculated from (200) fcc-Al Bragg peak broadening using standard Scherrer formula. As shown in Fig. 3 the size values obtained from Guinier approximation are always higher than those resulting from Scherrer method. The nanocrystal size determined from TEM micrograph of the sample annealed at 460 K for 1200 s is equal to $11.5 \pm 1.5 \text{ nm}$ which confirms the validity of the WAXS peak broadening method.

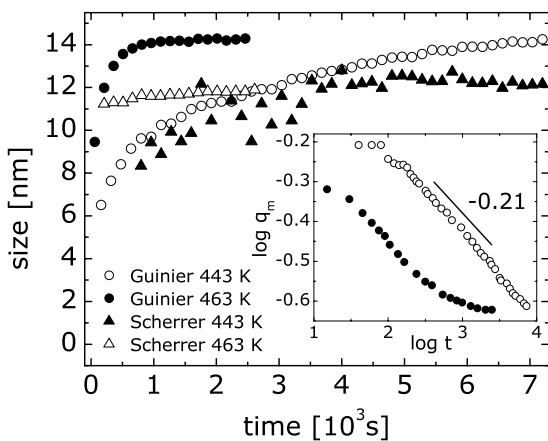


Figure 3

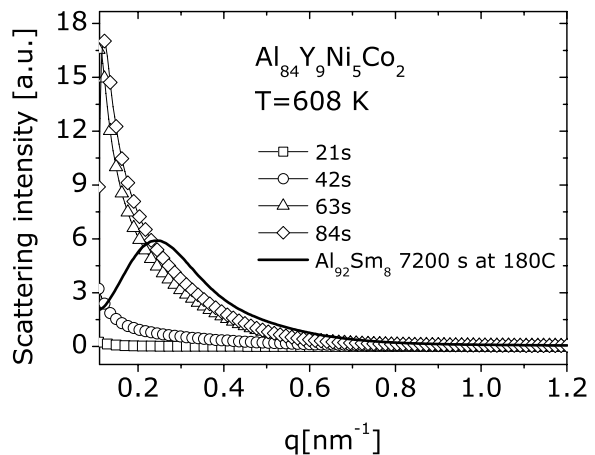


Figure 4

The observed SAXS spectra evolution is reminiscent for phase separation occurring by spinodal mechanism. The existence of a constant compositional wavelength of $2\pi/0.62 \text{ nm}^{-1} = 10 \text{ nm}$ with spontaneously growing amplitude as found in the early stage of transformation at 443 K is consistent with Cahn's linear theory of spinodal decomposition [8]. During the late stages of the decomposition the coarsening of the precipitates occurs which is manifested by the SAXS peak position decay. Many studies

show that shift of the SAXS peak position q_m during the late stages of decomposition can be described by an equation of form $q_m \propto t^{-a}$ [9]. The value of a can be obtained by plotting $\log q_m$ versus $\log t$ (inset in Fig. 3). The plot corresponding to 443 K (open symbols) exhibits wide range of linearity with the slope $a = 0.21$ which is close to exponent values reported in systems undergoing spinodal decomposition [9]. The slope of the plot for 463 K (full symbols) decreases rapidly finally reaching zero which is attributed to advanced crystallization blocking the coarsening process.

Our previous results from X-ray diffraction and TEM [1,2] revealed that $\text{Al}_{92}\text{Sm}_8$ glass devitrification kinetics is controlled by fcc-Al nanocrystals nucleation rate. The glass crystallization proceeds by gradual increase of grain density and decreasing average distance between crystals. At first, such a crystallization model appears to be inconsistent with present SAXS results. This apparent discrepancy can be resolved if one considers a coupling of amorphous phase separation and progressive crystallization of one of the decomposed phases. It can be reasoned that the SAXS interference maximum is partially due to spatially correlated precipitates of Al-rich amorphous phase and partially to nanocrystals nucleating preferentially inside the Al-rich zones. The growth of the crystallites is constrained by the precipitate size because of the samarium atoms with sluggish atomic diffusion outside Al-rich regions. The coarsening proceeds parallel to crystallization which progressively further slows down glass decomposition. We suggest that this mechanism is valid for the following investigated amorphous alloys: $\text{Al}_{90}\text{Y}_{10}$, $\text{Al}_{92}\text{Sm}_8$, $\text{Al}_{90}\text{Gd}_{10}$, $\text{Al}_{91}\text{Tb}_9$, $\text{Al}_{90}\text{Dy}_{10}$, $\text{Al}_{90}\text{Fe}_5\text{Nd}_5$, $\text{Al}_{88}\text{FeNi}_6\text{Nd}_5$, $\text{Al}_{90}\text{Sm}_8\text{Ni}_2$ and $\text{Al}_{85}\text{Y}_{10}\text{Co}_5$.

A single exception from the general crystallization behavior described above was found for the $\text{Al}_{84}\text{Y}_9\text{Ni}_9\text{Co}_2$ amorphous alloy. The distinctive feature of this alloy among other investigated systems is a glass-supercooled liquid transition manifested in the calorimetric measurements during heating. The sample of $\text{Al}_{84}\text{Y}_9\text{Ni}_9\text{Co}_2$ alloy annealed at 608 K exhibited a primary crystallization of fcc-Al phase in WAXS while no interference maximum was found in SAXS region. In spite of the SAXS peak a rapidly growing signal at low angles was observed. **Figure 4** presents the SAXS intensity development during annealing of amorphous $\text{Al}_{84}\text{Y}_9\text{Ni}_9\text{Co}_2$ at 608 K. The SAXS peak observed for $\text{Al}_{92}\text{Sm}_8$ after 7200 s at 443 K is also shown for comparison. It can be reasoned that in case of $\text{Al}_{84}\text{Y}_9\text{Ni}_9\text{Co}_2$ alloy the lack of the SAXS interference maximum indicates a random arrangement of the precipitates suggesting that nucleation and growth mechanism is responsible for the fcc-Al phase formation.

We conclude that amorphous phase separation is a mechanism triggering and controlling nanocrystallization of the large group of Al-based metallic glasses. The model proposed here explains both high nucleation rate and rapid arrest of growth required for nanocrystalline microstructure formation. Further studies on the early stages of the glassy phase separation will allow comparison of the experimental results with the existing models of spinodal decomposition.

References:

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