

# Time-resolved SAXS study on decomposition and crystallization in bulk amorphous alloys

Jörg F. Löffler\*, William L. Johnson\*, P. Thiyagarajan<sup>†</sup>, and Soenke Seifert<sup>‡</sup>

\*California Institute of Technology, Pasadena, CA 91125 USA

<sup>†</sup>Argonne National Laboratory, Argonne, IL 60439 USA

## Introduction

In the last decade, new multicomponent metallic glass-forming systems have been developed, which have a high thermal stability and excellent glass-forming ability [1]. These new ‘bulk amorphous alloys’ can be produced with cooling rates of less than 100 K/s in dimensions of 1 cm or more. Thus, they open new opportunities to study physical properties in the undercooled melt. Small-angle neutron scattering (SANS) resolves decomposition and nanocrystallization at temperatures near the calorimetric glass transition temperature,  $T_g$  [2]. This is in contrast to simple classical nucleation theory, which predicts a very small nucleation rate resulting in a rather coarse-grained microstructure. In order to understand the crystallization pathway in these alloys, which is crucial for the development of new bulk amorphous alloys, we performed additional *in situ* small-angle x-ray scattering (SAXS) experiments.

## Results and Discussion

We investigated in detail the Cu-Ti-based bulk glass-forming alloy Vit101 ( $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ ) and the Zr-based alloy Vit105 ( $\text{Zr}_{52.5}\text{Ti}_5\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}$ ) by isothermal annealing at temperatures between  $T_g$  ( $\approx 673$  K) and 923 K. Figure 1 gives an example for Vit101 annealed at 673 K. A clear interference maximum is visible at  $Q_{\text{max}} \approx 0.075 \text{ \AA}^{-1}$ . This value is much higher than the one measured by SANS, which is about  $0.015 \text{ \AA}^{-1}$  [3]. To heat the sample to 673 K, it was first held at a temperature of 623 K, *i.e.* 50 K below  $T_g$ . Surprisingly, the SAXS intensity changed before this temperature. Figure 2 gives an example for Vit105 annealed at 708 K. The interference maximum is superimposed with the surface scattering of the 50  $\mu\text{m}$  thick sample. However, the maximum can still be estimated to be at around  $0.03 \text{ \AA}^{-1}$ . This value is only slightly higher than the one measured by SANS [3]. In both alloys, the interference maxima are observed in a very broad temperature range up to 110 K (Vit105) and 150 K (Vit101) above  $T_g$ . In addition, in Vit101, two maxima are observed in a temperature range between 761 K and 779 K. Furthermore, at temperatures above 823 K, the intensity in Vit101 changes drastically and  $Q_{\text{max}}$  shifts very rapidly to lower  $Q$  values with increasing annealing time.

As has been described in [2], the interference maxima give evidence for decomposition and nanocrystallization in these alloys. Furthermore, the two maxima resolved in Vit101 give evidence that a second nanocrystalline phase forms during the isothermal annealing. At higher temperatures, Oswald ripening occurs. Future work addresses the question as to why x-rays and neutrons resolve different values of  $Q_{\text{max}}$ . Vit101 was annealed for 15 hours at 673 K before the SANS measurement was performed, whereas the *in situ* SAXS measurement was only performed for 0.5 hours. Thus, one may speculate that the shift in  $Q_{\text{max}}$  is due to

different annealing times. However, Figure 1 shows that a shift in  $Q_{\text{max}}$  only occurs in the first 5 minutes. Thus, neutrons and x-rays likely resolve different crystallization kinetics in these alloys.

A very interesting result is the fact that the decomposition phenomena first occurs far below  $T_g$ . A more detailed investigation of this phenomenon, in conjunction with additional transmission electron microscopy (TEM) experiments, may give new insight into the nature of the glass transition. Furthermore, the effects of Oswald ripening occurring at high temperatures can be ideally studied in these alloys.

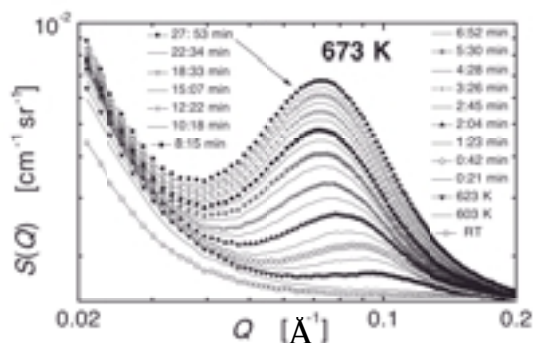


Figure 1: SAXS intensity data of Vit101 annealed for 30 minutes at 673 K. The sample was heated from room temperature (open squares) by adjusting the furnace for 3 minutes at 603 K (solid line) and for 1 minute at 623 K (down triangles). Surprisingly, a small intensity change is already visible at this temperature, which is 50 K below  $T_g$  (!). After that, the heater was adjusted to 673 K. The sample reached this temperature after 83 seconds (solid line).

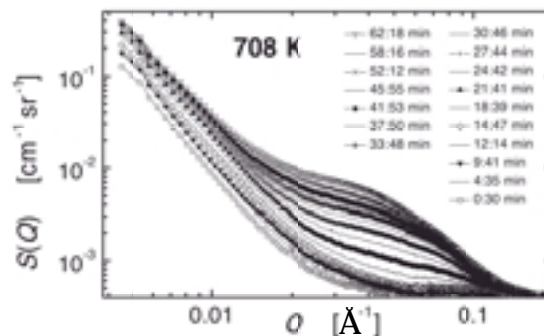


Figure 2: SAXS intensity data of Vit105 annealed for one hour at 708 K. The annealing times are given in the figure.

## Acknowledgments

This work was supported by the Department of Energy (DOE) (DEFG-03-86ER45242) and Alexander von Humboldt Foundation (J. L.). It also benefited from the use of the Advanced Photon Source funded by DOE, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38.

## References

- [1] A. Peker and W.L. Johnson, *Appl. Phys. Lett.* **63**, 2342 – 2244 (1993).
- [2] J.F. Löffler, P. Thiyagarajan, and W.L. Johnson, J. *Appl. Crystallogr.* (to appear in April 2000); see also *Mater. Sci. Forum* (in press).
- [3] J.F. Löffler *et al.*, in preparation.