EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

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.

ESRF	**Experiment title:** Investigation of nanoscale heterogeneities and short-range order changes in mechanically loaded glassy alloys	**Experiment number**: HD 613
Beamline: ID 11	**Date of experiment**: from: 26.03.2013 to: 2.04.2013	**Date of report**: 2.07.2013
Shifts: 21	**Local contact(s)**: Dr VAUGHAN Gavin, Dr WRIGHT Jonathan Paul	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. STOICA Mihai*
Prof. ECKERT Jürgen
Dr. SCUDINO Sergio*
Director YAVARI A.R.

Report:

In general, the formation and the stability of condensed matter are closely related to their atomic structure. Nevertheless, the structure of metastable alloys- in particular BMGs- is poorly known and, as a result, the atomic origins of the glass forming ability (GFA) of BMGs have not been well understood. The problem becomes more complicated when considering a nanocomposite instead of a BMG, since in this case a glassy matrix and nanocrystals- or even clusters of several thousands of atoms- coexist. The BMGs usually deform very slightly via localized shear-transformation zones (STZs) and shear-band mechanisms, and immediately suffer a catastrophic failure. Upon mechanical deformation, the BMGs may become anisotropic. Some BMGs may develop nanocrystalline structure directly upon mechanical loading, twin, and then plastically deform. The length scale of the transformation is usually less than few hundreds of nm. In-situ measurements using focussed hard synchrotron x-rays may put in evidence this mechanism. Besides, using a similar approach, the residual stress can be mapped in the deformed and/or prestressed/pre-strained glassy samples.

The room temperature ductility of BMGs is usually disappointedly low due to shear localization. This is a consequence of strain softening, a phenomenon that originates from shear-induced dilation that causes plastic strain to be highly localized in shear bands. Shear localization is particularly critical under quasistatic tensile loading, where generally a single shear band propagates catastrophically through the material soon after yielding. So far, significant tensile ductility has been reported only for sub-microscopic samples of ~100 nm and for testing at high strain rates. Recently our research group [1] developed CuZrbased BMGs, which polymorphically precipitate nanocrystals during deformation. The formation of such structural heterogeneities hampers shear band generation and results in macroscopically detectable plastic strain and work hardening. The precipitation of nanocrystals and their subsequent twinning can be understood in terms of a deformation-induced softening of the instantaneous shear modulus. This novel deformation mechanism is believed to be not only limited to CuZr-based BMGs but it may also promote ductility in other BMGs. For example, our very last mechanical tests on Fe-based BMGs corroborate this conclusion [2]. The structure and in particular the SRO of the Fe-based glasses were previously investigated at ID11 during the experiment HD482 (see the submitted report, as well as ref. [2]). Several properties of amorphous materials including fatigue, fracture, and component performance are governed by the magnitude of strain fields around heterogeneities, such as local compositional variations, crystalline inclusions, voids, or cracks. Recently, we succeeded to calculate the strain tensor of a BMG under tensile stress [3] by evaluating the shift of the main amorphous maximum in the reciprocal space by x-ray diffraction using synchrotron radiation. We believe that this method can be successfully applied in order to map the residual stresses and nanoscale heterogeneities in BMGs induced by elastic and/or plastic deformation [4]. It was also observed that some Fe-based BMGs with small Cu additions may become ductile. The reason is believed to be the segregation of Cu nanoclusters during casting or mechanical loading. The scientific literature lacks on systematic studies related to this aspect.

During the experiment several BMG samples were in-situ investigated (i.e. in compression), as well as after different mechanical treatments: scan around a shear band or around small plastic deformation created by indentation, in order to quantify the residual stress. The experiments were done by using a very fine beam, i.e. focussed down to 5 µm x 150 nm.

The first example is presented in Fig. 1, which shows for comparison the shifting in the main broad peak positions Q1 between an as-cast and indented Zr-based BMG sample.

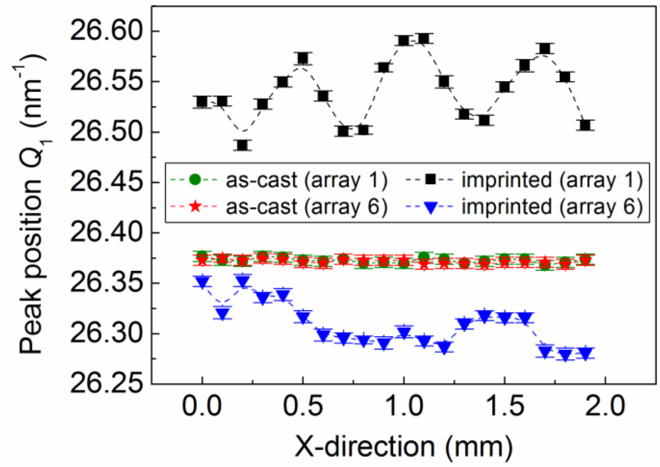

Fig. 1 The shift of the Q1 positions, comparison between as-cast and indented Zr-based BMG. For simplicity it was plot only one point out of 100 experimental points (for this emasurement a very fine focussed beam was used).

As a result of the plastic deformation, the amorphous peaks of the imprinted glass are shifted compared to the as-cast material. The magnitude of the shift depends on the position probed, as shown in Fig. 1, where the values of Q1 for the imprinted glass oscillate periodically along the X-direction. Arrays of XRD patterns taken near the imprinted surface (e.g. array 1, 100 µm beneath the imprinted surface) show higher Q1 values than the as-cast glass, whereas arrays taken at larger distances (e.g. array 6, 600 µm beneath the imprinted surface) exhibit lower values of Q1 compared to the as-cast glass. In contrast, no significant variation of Q1 occurs in the corresponding arrays of the as-cast glass, which indicates that the starting as-cast sample is structurally homogeneous.

The lack of long-range order in metallic glasses enables yield strength closer to theoretical limits but reduces plastic deformation which is inhomogeneous, concentrated in narrow shear bands. The in-situ formation of a softy secondary phase in the glassy matrix can overcome this drawback with a better balance between strength and plasticity. The two most promising families of bulk metallic glass composites with significant deformability are Ti-Zr-Be-based and CuZr-based. The former precipitates β-(Ti,Zr) dendrites in the glassy matrix whereas the latter forms spherical precipitates of the cubic B2-CuZr phase. The plastic deformation starts in the softy secondary phase, which will induce the formation of a heterogeneous stress distribution in the glass matrix with stress concentration and formation of multiple shear bands. The precipitates also act as a barrier for the fast movement of shear bands, avoiding earlier fracture. Both B2 and β-(Ti,Zr) may undergo martensitic transformation during deformation depending on composition and it will result in a more stable deformation with work-hardening behaviour. The search for new bulk metallic glass composites without toxic elements as Be and with enhanced mechanical properties is of fundamental interest in order to widen their range of application and optimize their performance by understanding the correlation between phase formation, microstructure and mechanical properties. We discovered very recently a new family of TiCu-based BMG composites with advanced mechanical properties [5] which combines the softy cubic B2-(Ti,Zr)(Cu,Ni) phase within the glassy matrix. The structural transformation in these composites during uniaxial compression tests was analyzed by in-situ high energy X-ray diffraction and the results for a $Ti_{45}Cu_{41}Ni_9Zr_5$ rod are shown in Fig. 2. The as-cast sample consists basically of two phases: the cubic B2-(Ti,Zr)(Cu,Ni) and amorphous phase. Fig. 2 shows that this cubic phase undergoes a martensitic transformation to the orthorhombic B19-(Ti,Zr)(Cu,Ni) during deformation. The in-situ XRD results show that the B2 phase starts to transform around 620 ± 50 MPa, which is earlier than the measured yield strength (around 1500 ± 50 MPa). This proves that the B2 phase deforms first than the glass matrix as suggested in our previous paper. The martensitic transformation of the B2 to the B19 phase contributes to the large ductility observed for these composites and can also explain their work-hardening behaviour.

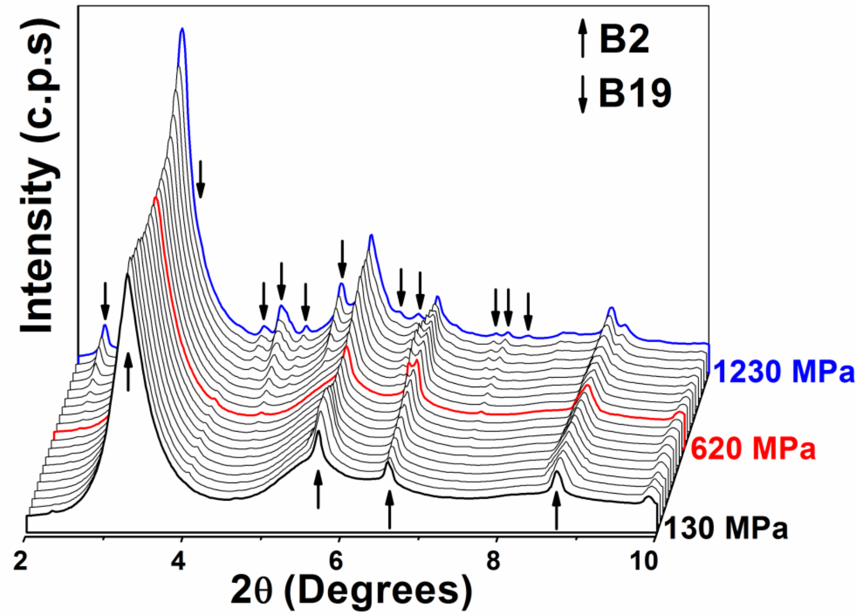

Figure 1 – In-situ XRD results obtained during compression of a 1 mm diameter $Ti_{45}Cu_{41}Ni_9Zr_5$ rod. The cubic B2-(Ti,Zr)(Cu,Ni) phase transforms to the orthorhombic B19-(Ti,Zr)(Cu,Ni) during deformation, which contributes to the large ductility and work-hardening behaviour observed for these composites. For this experiment the very fine focused x-ray beam passed through one single B2 crystal.

References

[1] S. Pauly *et al.*, “Transformation-mediated ductility in CuZr-based bulk metallic glasses”, Nat. Mater. vol. 9, p. 473, 2010.
[2] A. Seifoddini *et al.*, “New $(Fe_{0.9}Ni_{0.1})_{77}Mo_5P_9C_{7.5}B_{1.5}$ glassy alloys with enhanced glass-forming ability and large compressive strain”, Mater. Sci. Eng. A. vol. 560 p. 575 (2013)
[3] M. Stoica *et al.*, “Strain distribution in $Zr_{64.13}Cu_{15.75}Ni_{10.12}Al_{10}$ bulk metallic glass investigated by in situ tensile tests under synchrotron radiation“, J. Appl. Phys. vol. 104, 013522, 2008.
[4] M. Stoica *et al.*, “Mechanical Response of Metallic Glasses: Insights from In-situ High Energy X-ray Diffraction“- Research Summary, JOM vol. 62, p. 76, 2010.
[5] P. Gargarella, S. Pauly, K.K. Song, J. Hu, N.S. Barekar, M. Samadi Khoshkhoo, A. Teresiak, H. Wendrock, U. Kühn, C. Ruffing, E. Kerscher, J. Eckert, Acta Materialia, 61 (2013) 151-162.