ESRF	**Experiment title:** Direct observation of structural changes in chemically homogeneous and self-doped metallic glasses upon in-situ ultrafast heating and cooling	**Experiment number**: HC 5088
Beamline: ID13	**Date of experiment**: from: 12/04/2023 to: 15/04/2023	**Date of report**:
Shifts: 9	**Local contact(s)**: Alexey Melnikov	*Received at ESRF:*

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Report:

Bulk metallic glasses (BMGs) are metallic alloys with a disordered atomic arrangement, obtained via rapid cooling from the melt. Due to their unique engineering properties, BMGs have recently become candidates for additive manufacturing methods such as laser powder-bed fusion (LPBF).

During this beamtime, we investigated the crystallization behavior of an industrial-grade Zr-based BMG powder, named ZR01, simultaneously using fast calorimetry and synchrotron X-ray diffraction techniques.

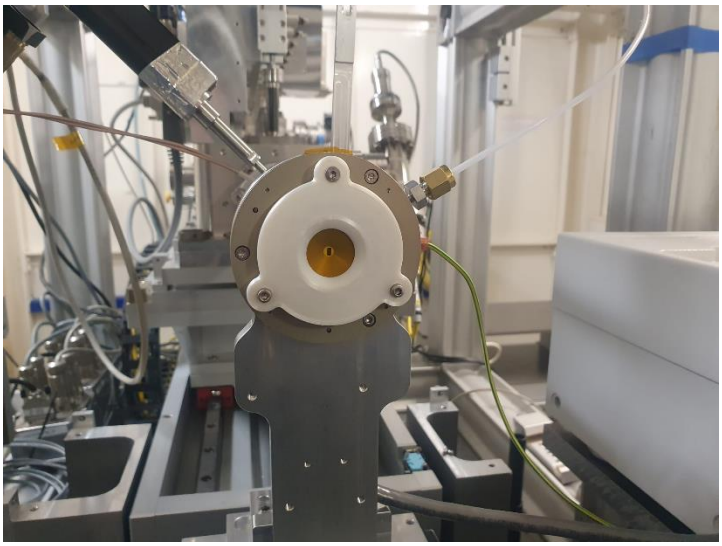
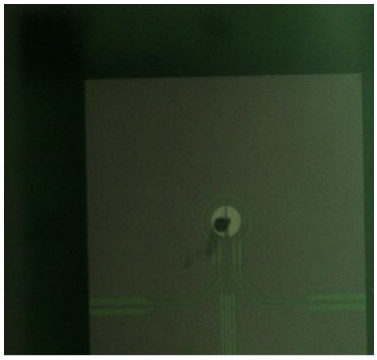


Fig. 1: FDSC external sensor support placed vertically in the beam path. Both sides were closed by a polyimide window to allow sample purging with argon and prevent oxidation.

A commercial Flash DSC 2+ device of METTLER Toledo with an adapted furnace working under Ar flow for *in situ* diffraction was used on ID13. The calorimeter has been modified previously at our home institution to enable its integration into a synchrotron X-ray beamline. The FDSC external sensor support was placed vertically in the beam path, an opening was drilled at the bottom side of the sensor to allow the X-ray beam to reach the sample. Both sides of the support were closed by a polyimide window and the furnace was purged with argon to prevent sample oxidation. The layout of the resulted sample environment is shown in Fig. 1. The front cover of the furnace (white lid in Fig. 1) was 3D-printed on site.



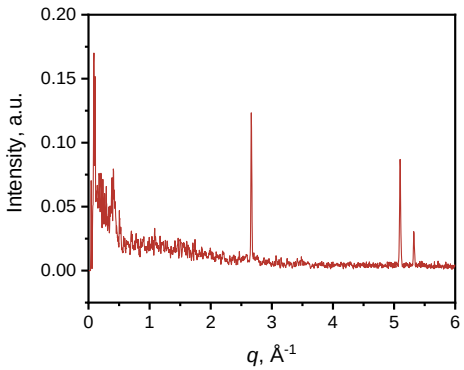
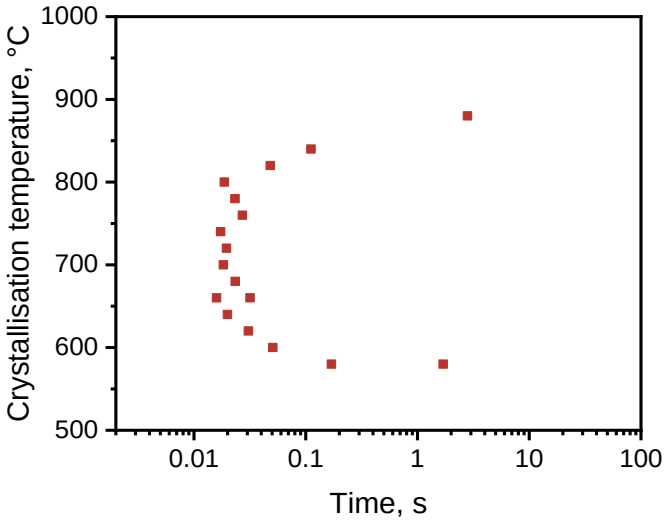


Fig. 2: Left: a single particle of ZR01 alloy on a FDSC chip sensor. The optical micrograph taken in situ before the experiment. Right: an exemplary XRD pattern of a crystallized alloy, 2 ms exposure time.

We performed a series of measurements to determine the time-temperature-transformation (TTT) diagram of the ZR01 alloy *in situ* at the beam energy of 13 keV and beam size of 25 µm × 30 µm. The samples were measured as individual powder particles put on the calorimeter measurement sensor. The samples were fixated using a silicon oil and, after closing the measuring cell, purged by Ar at flow of 40 ml/min for at least 60 minutes. Subsequently, TTT diagrams upon cooling and heating were recorded and corresponding diffraction patterns were measured. The sample size was varied to observe the effect of the size on the crystallization kinetics. The sample size was measured *ex situ* using a SEM after finishing the experiment.

An example of a TTT diagram measured upon heating is shown in Fig. 3 left. The fast crystallization times indicate the presence of nuclei due to quenching of the sample to room temperature before recording the isothermal transformation, and a possible presence of oxides in the sample, which both act as heterogeneous nucleation sites. A SEM micrographs of the sample in Fig. 3 right shows that the sample with diameter of 41 µm cracked during the *in situ* measurement, and reveals columnar radial microstructure. Sample cracking had previously been observed in the case of high crystallinity, which is in accordance with the fact that during a TTT diagram measurement, the sample was crystallized and melted repeatedly. The analysis of the corresponding diffraction patterns is ongoing. An exemplary XRD pattern is presented in Fig. 2 right.

Due to strains in the glassy samples and membrane of the chip sensors, samples often jumped when a



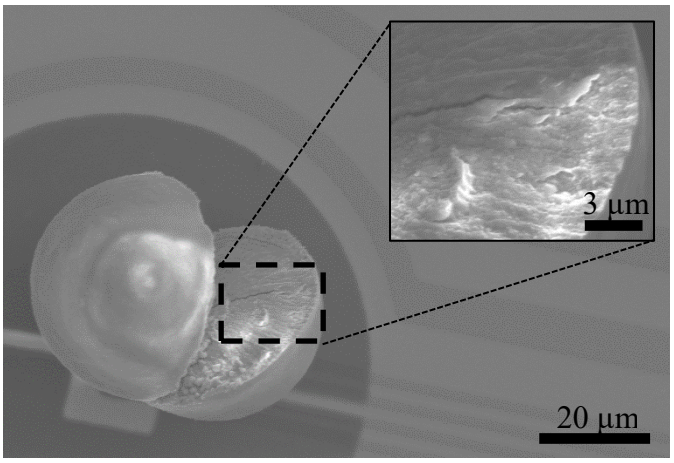


Fig. 3: A time-temperature-trensformation diagram of the sample shown in Figure 2. measured *in situ* (left) and an *ex situ* SE micrograph of the same sample (right). The inset shows the detail of the microstructure and cracking.

measurement is initiated, resulting in sample loss and a new sample must be mounted. Multiple measurements were performed on each sample to achieve a good statistical representation, as the choice of powder particles on the sensor is not representative. A scientific publication is currently in preparation.