

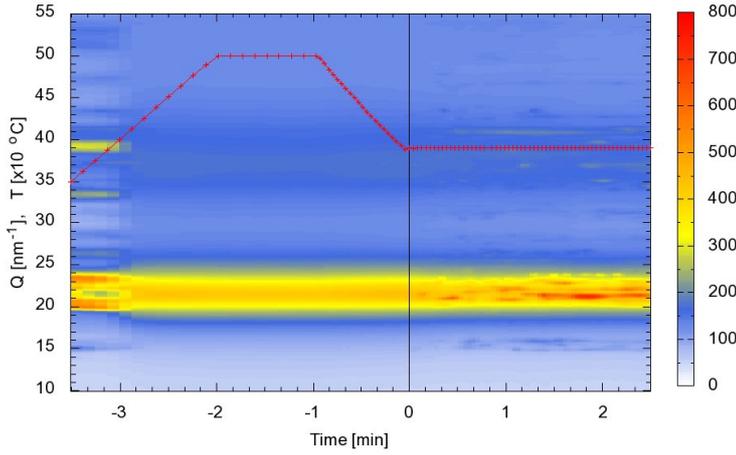


	<b>Experiment title:</b> The study of glass formation and glass transition by in-situ XRD	<b>Experiment number:</b> HD-229
<b>Beamline:</b> ID11	<b>Date of experiment:</b> from: 10.4.2008 to: 14.4.2008	<b>Date of report:</b> 15.6.2009
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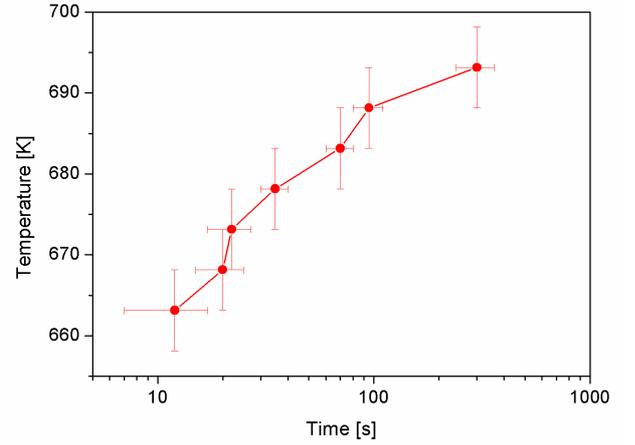
## Report:

The temperature-/time-resolved microstructure evolution of the selected Zr-based ( $Zr_{48}Cu_{45}Al_7$ ) and La-based ( $La_{62}Al_{14}(Cu_{5/6}Ag_{1/6})_{14}Ni_5Co_5$ ) bulk metallic glass (BMG) during non-isothermal heating was investigated by *in-situ* angular-dispersive X-ray diffraction (XRD) at the ID11 undulator beamline in ESRF (Grenoble, France). The bulk sample in the form of thin rod was mounted in quartz capillary having an outer diameter of 1 mm. Annealing was done in Ar-protective atmosphere using hot stage Linkam THMS 600 [1]. X-ray diffraction patterns were collected upon constant-rate heating up to 873 K followed by controlled cooling. Heating and cooling rates were fixed to 10 K/min. The synchrotron radiation wavelength was set to  $\lambda = 0.140873 \text{ \AA}$ . The diffraction experiments were carried out in the Debye-Scherrer geometry.  $LaB_6$  standard was used to calibrate the sample-to-detector distance and tilt of the imaging plate relative to the beam path. The sample was illuminated for 3 s by well collimated incident beam having cross section of  $0.7 \times 0.3 \text{ mm}^2$ . XRD patterns were collected using a fast CCD detector (FRELON 2k16) carefully mounted orthogonal to the x-ray beam. The delay between consecutive patterns, due to read-out time of the CCD (2048 pixels  $\times$  2048 pixels) and write-time to hard-disc was 1 s. The two-dimensional XRD patterns were integrated to the Q-space using the software package FIT2D [2] after dark-current and spatial distortion corrections.

Temperature-Time-Transformation (TTT) diagram of  $LaAlCuAgNiCo$  BMG was determined using one piece of rod sample, which was repeatedly melted by annealing up to 500 °C (773 K). Each time we heated sample up to 500 °C with 100 K/min. Then we hold at 500 °C for 1 min. Afterward we cooled down to desired temperature with the maximum cooling rate of 120 K/min (actually the limit of the oven we have used). After reaching desired temperature, isothermal annealing started for a given time while taking XRD patterns every few seconds. As an example Figure 1 shows series of XRD patterns acquired during such ramp. The temperature profile is depicted with red crosses connected with the red line. One can see that just few



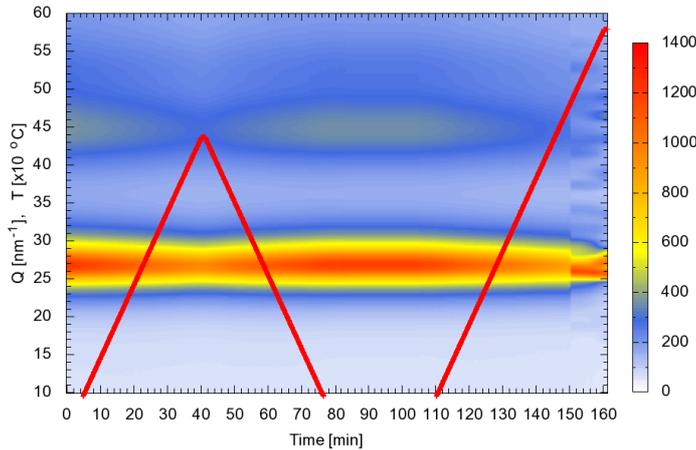
**Fig.1** The red curve shows the temperature ramp during in-situ experiment (every cross on the curve corresponds to one XRD pattern). The series of XRD patterns acquired at ID11. Heating and cooling were done at 100 °C/min and 120 °C/min, respectively



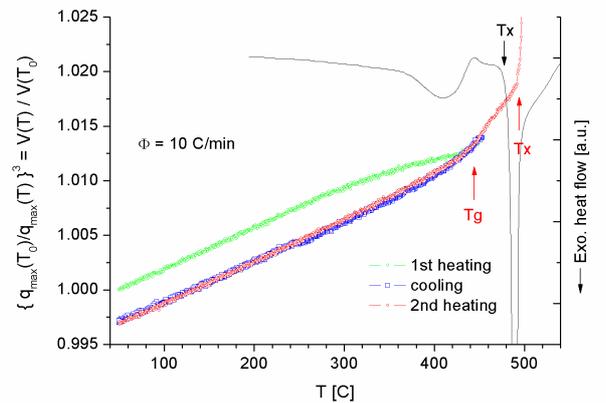
**Fig.2** TTT-diagram of LaAlCuAgNiCo BMG as obtained from consecutive isotherms measured at different temperatures using in-situ XRD.

seconds after reaching 390 °C, the first sharp peaks appear. Actually temperature of 390 °C appeared as the lowest temperature at which we could observe some measurable time delay. For lower temperatures crystallization immediately started when reaching given temperature after cooling from 500 °C. Figure 2 shows TTT-diagram of LaAlCuAGNiCo BMG as obtained from consecutive isotherms measured at different temperatures using in-situ XRD. It should be noted here that although we made longer isothermal annealings above 420 °C (693 K) we could not observe beginning of crystallization.

Further we studied the thermal stability of Zr-Cu-Al BMG as a function of heating profile. We simply acquired series of XRD patterns during constant-rate heating (10 K/min) from room temperature up to 450 °C followed by cooling down to room temperature. Then we again heated the sample at 10 K/min up to 600 °C. Figure 1 shows series of XRD patterns acquired during such thermal treatment.



**Fig.3** The series of XRD patterns acquired during constant-rate heating (10 K/min) up to 600 °C. The red curve shows the temperature ramp during in-situ experiment.



**Fig.4** The thermal expansion of amorphous phase as determined from the temperature behaviour of principal peak position  $q_{max}=q_{max}(T)$  using equation (1). DSC curve traced at 10 K/min is also shown.

For a given set of XRD patterns (below crystallization temperature) we fitted the principle peak profile using equation (1) and thus constructed the temperature dependence of the peak profile. We were interested in the temperature dependence of the peak position,  $q_{max}=q_{max}(T)$  since the relative change of the peak position with temperature is closely related to the thermal expansion by

$$\left\{ \frac{q_{max}(T_0)}{q_{max}(T)} \right\}^3 = \left\{ \frac{V(T)}{V(T_0)} \right\} = \{1 + \alpha_{th}(T - T_0)\} \quad (1)$$

where  $\alpha_{th}$  is the volume coefficient of thermal expansion below  $T_g$  as long as no structural change occurs and corresponds to the temperature slope or derivative of the reduced mean atomic volume  $\{V(T)/V(T_0)\}$  at  $T$ , with the reference  $T_0$  corresponding to room temperature [3]. As can be seen from Fig.4 thermal cycling reveals hysteresis, which is due to relaxation phenomena related to the annealing below  $T_g$ . The coefficient  $\alpha_{th}$  of volume thermal expansion is  $(3.79 \pm 0.01) \times 10^{-5}$  1/K. Furthermore, observed transition temperatures are in good agreement with differential scanning calorimeter measurements.

[1] <http://www.linkam.co.uk/>

[2] A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch, and D. Häusermann, *High Press. Res.*, Vol. **14** (1996) p. 235.

[3] A.R. Yavari et al. / *Acta Materialia* 53 (2005) 1611–1619