ESRF	**Experiment title:** In-the-beam Amorphisation and Crystallisation of New Bulk Glass-Forming Alloys	**Experiment number:** HS-299
Beamline: ID11	**Date of Experiment:** from: 24 Nov. 1997 to: 01 Dec. 1997	**Date of Report:** 11 Aug. 1998
Shifts:	**Local contact(s):** Dr Petra Rejmankova	*Received at ESRF :* 13 AOUT 1998

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Report: The minimum objective of this experiment of a kind never previously undertaken, was to design and test an experimental set-up to perform real-time monitoring of the crystallisation of bulk glass-forming alloys during heating from the amorphous state and during cooling of the liquid alloy.

Eperimental methods:

Samples with rectangular sections and thicknesses of 2 mm were cut out of bulk amorphous ingots and after surface cleaning, were sealed in multi-stage quartz crucibles. Above the samples a strangulation supported pure Zr getter plates flame-heated after sealing in order to absorb any remaining oxygen. The ID1 1 beam energy used was 90 keV. Crucibles containing the bulk glass samples were vertically placed between the incident beam and a two-dimensional detector at a distance of 41.6 cm. The beam cross-section had a diameter of 0.2 mm. A high frequency generator was rented for induction heating of the samples on the ID1 1 for the duration of HS-299. An induction coil was placed above the samples while an infrared pyrometer monitored sample temperature. Transmitted intensity indicated that good quality diffraction spectra could be obtained after acquisition times of 1.5 seconds but the signal processing on ESRF computer facilities required an additional 1.5 seconds such that spectra could be obtained every 3 seconds. Figure 1 shows the experimental setup for this first series of measurements on ID1 1

Experimental Results

Figure 2 shows diffraction spectra obtained for a bulk amorphous $Zr_{55}Cu_{30}Al_{10}Ni_5$ during heating up to melting. The numbers correspond to those of successive frames with the heating starting with frame Zr2. The temperature during heating was monitored by the pyrometer. Crystallisation begins on frame Zr6. The heating rate up to crystallisation is about 40 K/s assisted by the exothermic release of the heat of crystallisation ΔH_{cryst}. The heating up to melting is subsequently slower because of the dissipation of ΔH_{cryst} and endothermic absorption of the enthalpy of melting ΔH_m and of the order of 6 K/s. Figure 3 shows the the main peaks of the spectra with increasing T. Between frames Zr7 and Zr24 there is only a slight displacement towards higher angles that could signify some rejection of the larger Zr atoms. However, with frame 25, the main peaks 1 and 2 of frames Zr7 to Zr24 disappear over a time of only 6 seconds and are replaced by main peaks 3 and 4 identified as the (103) and the (110) peaks of tetragonal Zr_2Cu. The previous phase (main peaks 1 and 2) is therefore metastable.

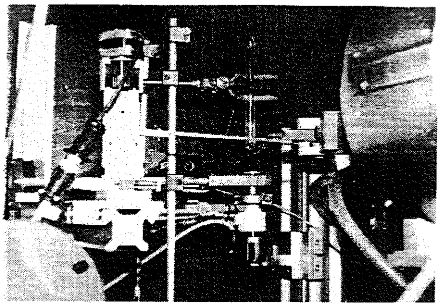

Figure 1: Experimental setup on ID1 1

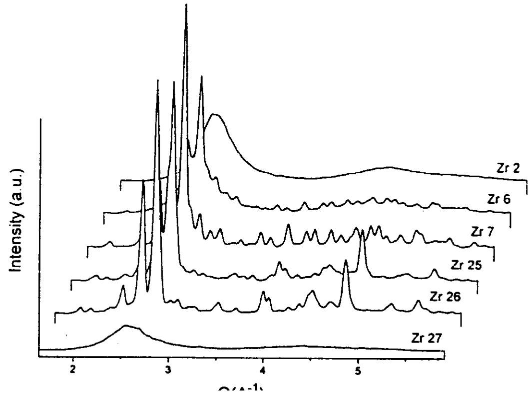

Figure 2: Spectra of bulk amorphous $Zr_{55}Cu_{30}Al_{10}Ni_5$ during heating up to melting.

Figure 4 compares crystallisation during heating of the amorphous phase (frame **Zr5**) just evoqued with the crystallisation of the liquid phase (frame Zr29) during cooling which leads to direct nucleation and growth of Zr_2Cu (peaks 3 and 4). The metastable phase (peaks 1 and 2) is not detected [l-2].

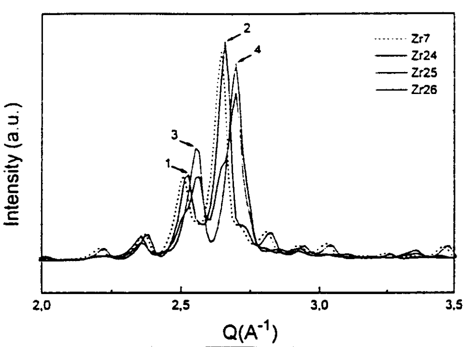

Figure 3: Evolution of the main Bragg peaks of fig. 2 with increasing T.

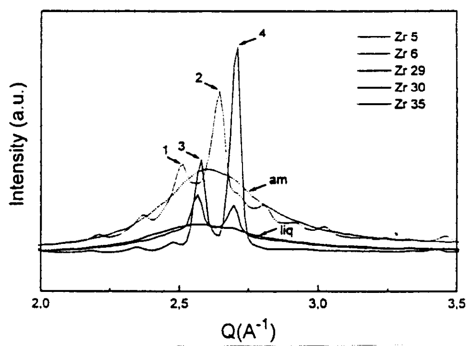

Figure 4: Comparison of crystallisation during heating of amorphous $Zr_{55}Cu_{30}Al_{10}Ni_5$ (frame Zr5) and cooling of the liquid alloy (Zr29).

Conclusions

An new experimental set-up in the transmission geometry was successfully tested to conduct real-time detection of nucleation and growth of crystalline phases from amorphous and liquid states of bulk glass-forming alloys for the **first** time. Crystallisation of amorphous $Zr_{55}Cu_{30}Al_{10}Ni_5$ occurs via nucleation and growth of a metastable phase that transforms to equilibrium tetragonal Zr_2Cu before melting. However,nucleation of the metastable phase is not obtained during cooling of the liquid alloy and Zr_2Cu forms directly. These differences (which were reproduced) are being modelled by homogeneous nucleation of the metastable crystallites from the amorphous state and heterogeneous nucleation of tetragonal **Zr2Cu** from the liquid state. Another exciting experimental window of opportunity was unveiled by in-the-beam amorphisation of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ in bulk thicknesses [3].

References

[1] "Detection of the onset of crystallisation from the bulk glass and the liquid states using synchrotron radiation" Yavari A.R., Inoue A., LeMoulec A., Rejmankova P. and Kvick A., *European Union Conf. on Nanocrystallisation,* Grenoble 1998, in press.

[2] "Crystallisation of $Zr_{55}Cu_{30}Al_{10}Ni_5$ from the Bulk Glass and the Liquid States" Yavari A.R., Botta Filho W-J., Inoue A., LeMoulec A., Rejmankova P. and Kvick A., International Conference on Glasses, Mato Grosso, Bonito, Brezil, August 24 au 29, 1998 (*J. Non-Cyst. Solids*)

[3] submitted for publication 1998.