ESRF	**Experiment title:** Microstructure and local atomic correlations in bulk-amorphous Zr-Ti-Be-Ni-Cu alloys	**Experiment number**: HS-942
Beamline: ID01	**Date of experiment**: from: 06/10/1999 to: 13/10/1999 and from: 10/05/2000 to: 16/05/2000	**Date of report**: 15/10/2001
Shifts: 21 + 21	**Local contact(s)**: Dr. A. Mazuelas & Dr. P. Boesecke	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. A. Wiedenmann*, Dr. A. Hoell*, Dr. M.-P. Macht

Hahn-Meitner-Institute, Department of structural research, Glienicker Strasse 100, D-14109 Berlin, Germany

Dr. J.-P. Simon*, Dr. F. Bley*, Dr. F. Livet*

Université de Grenoble, B.P. 75, F-38042 St. Martin d'Hères, France

Report:

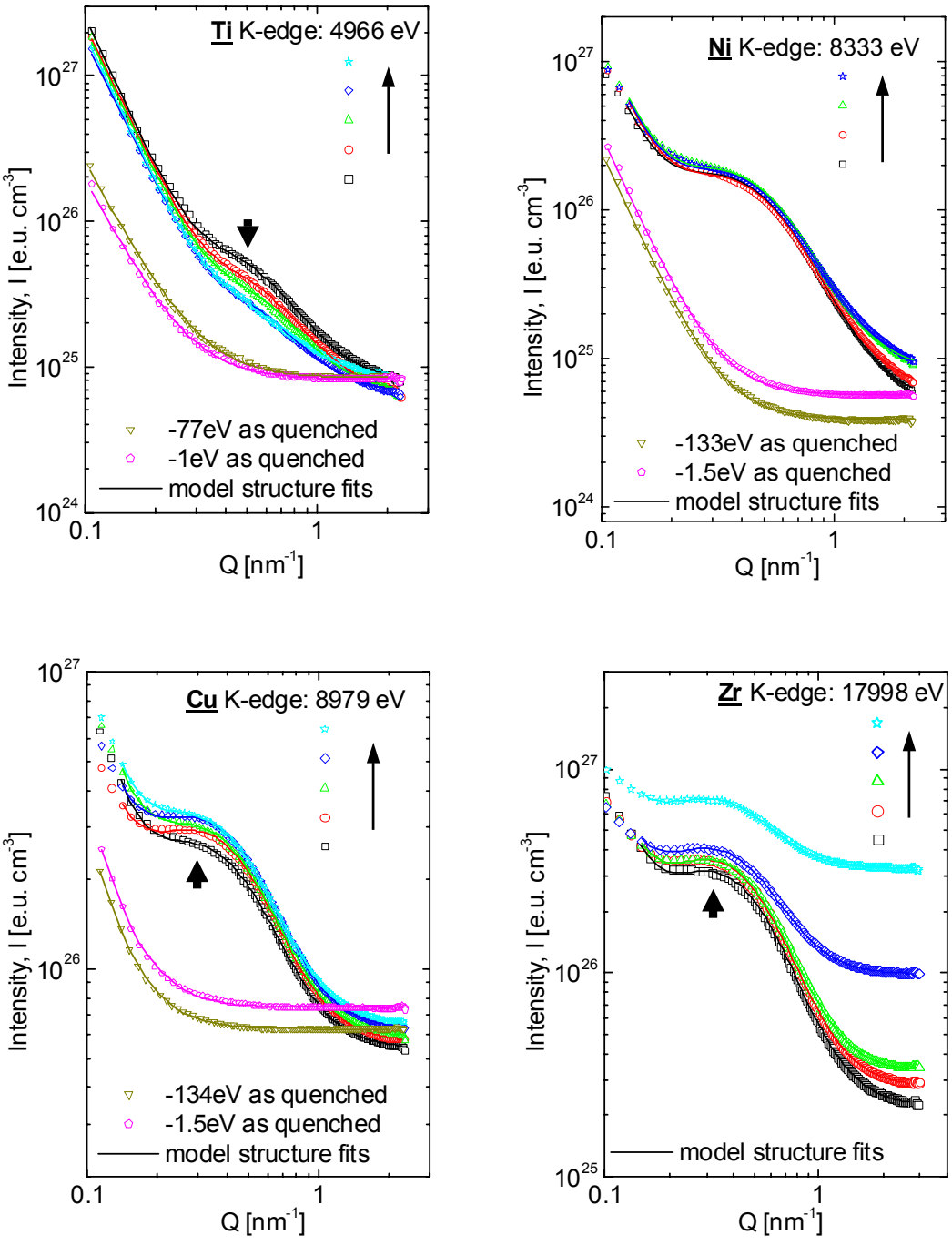
New metallic alloys of the compositions $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ have recently been developed which permits the formation of large bulky ingots at low cooling rates [1]. These materials reveal strong resistance against crystallisation in the supercooled liquid (SCL) state in a wide range of about 50 K above the glass temperature, T_g = 593 K. Previous studies of the evolution of the microstructure upon heat treatments by combining small angle neutron (SANS), wide angle neutron scattering, X-ray diffraction, transmission electron and field ion microscopy gave clear evidence of a decomposition in the SCL state into two amorphous phases: Nanosized droplets with radii between 3 and 6 nm are embedded in the amorphous matrix [2-7].

In order to evaluate the unknown compositions and volume fractions of these phases, we combined Anomalous Small Angle X-ray Scattering (ASAXS at the beamline ID01) investigations and SANS experiments (V4 instrument, HMI, Berlin).

Starting from one ingot of the as quenched homogeneous amorphous bulk glass samples of different thickness of about 10 μm, 30 μm and 100 μm with polished surfaces were used in order to optimise the X-ray scattering effect in the regions of the different absorption edges. One sample of each thickness was annealed simultaneously in the SCL state at 643 K for 9 h. The x-ray energy has been tuned below the energy of the K-edges of Ti, Ni, Cu and Zr giving rise to a change of the scattering contrast, when the corresponding elements are distributed non-uniformly in the alloy. The beamline was operated under complete vacuum conditions without any absorbing window in the x-ray beam, excluding the window of the 2-dimensional gasfilled detector. The sample – detector distances were chosen as a function of energy such that a momentum transfer range of 0.1 $nm^{-1} < Q < 2\ nm^{-1}$ with $Q = 4\pi\sin(\Theta/2)/\lambda$ was covered. The scattering intensities were corrected for background and detector efficiencies and normalised to electron scattering units by comparing the scattering intensity of the samples with that of a calibrated glassy carbon. Including EXAFS for energy calibration and sample transmissions all necessary correction measurements took about more than half the time.

A rotating wheel sample changer was used during the first experiment in 1999. Different experimental problems caused that the contrast variation measurements remained unfinished. The detector had to be changed to enhance the efficiencies at low energies. Additionally, one monitor counter and the reproducibility of the sample positions yielded to non-systematic errors of the transmission and of the absolute intensities. An unexpected synchrontron shutdown which ends the experiment yields to a lost of four shifts.

Because of the described problems we got the opportunity to repeat this experiment. In preparation of the second experiment in 2000, the ID01 group and we improved parts, to overcome the mentioned problems. Therefore, a new sample changer was constructed [8] and the monitor counter was exchanged. Directly behind the new sample changer a moveable large area diode should allows reproducible transmission measurements.
The new experiment in 2000 proved, that the instrument and software improvements were successful, and yielded more stable experimental conditions and reproducible sample positions as well as transmissions.
Four or five scattering curves were measured at different energies below each of the four edges of Ti, Ni, Cu or Zr. The final absolute scaled intensity curves, extracted from both experimental dates, are shown as a function of the scattering vector in the four figures.



Figures: ASAXS scattering intensities near the denoted edges of the as quenched and the annealed sample. The directions of the arrows show the direction of energy increase while approaching the edges. The thick arrows mark the anomalous scattering effect, observed for Ti, Cu and Zr. The lines are the results of the fits using the derived structural model [9].

In the heat-treated sample a variation of the scattering signals at the Ti, Cu and Zr edges were found whereas no variation occurred at the Ni edge. All ASAXS scattering patterns could be well described by a unique model consisting of a size distribution of spherical droplets surrounded by a depletion zone. The energy depending variation of the contrasts between core, shell and matrix allowed the composition fluctuation to be reconstructed. Additionally, the contrast parameters obtained from the SANS data revealed that also Be (which is not accessible for X-rays) takes part in the amorphous decomposition. Ti and Be behave oppositely in the core as well as in the shell of the particles [9]. Finally, the model of relative composition fluctuations is given in [9].

Despite the two dates of experiment, there was no time left for the proposed feasibility test to measure the wide-angle scattering around the K-edge of Zr.

References

[1] Johnson, W.L., Peker, A.; Appl. Phys. Lett. 63 (1993) 23425.
[2] Wiedenmann, A., Keiderling, U., Macht, M.-P., Wollenberger, H.; Mat. Science Forum 225-227 (1996) 71.
[3] Wiedenmann, A., Liu, J.M.; solid st. comm. 100 (1996) 331.
[4] Liu, J.M., Wiedenmann, A., Gerold, U., Wollenberger, H.; phys. stat. sol. (b) 199 (1997) 379.
[5] Hermann, H., Wiedenmann, A., Uebele, P.; Physica B241-243(1998)352-354.
[6] Macht, M.P., et al; Mat. Science Forum 225-227 (1996) 65.
[7] Gerold, U., Wiedenmann, A., Bellissent, R., Macht, H.-P., Wollenberger, H.; Nanostruc. Mat. 12(1999) 605.
[8] Metzger, T.H., Mazuelas, A., Boesecke, P., et al, The Anomalous Scattering Beamline ID01 at the ESRF, SRI-conference, Berlin, 2000.
[9] Hoell, A., Bley, F., Wiedenmann, A., Simon, J.P., Mazuelas, A., Boesecke,P.; Composition fluctuations in the demixed supercooled liquid state of.$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$: a combined ASAXS and SANS study, Scripta Mater, 44 (2001) 2335-39.