

Zwischenbericht (Sachlicher Teil)  
Helmholtz-Zhejiang University Research Collaboration  
“Investigation of Metallic Glasses under Stress by Synchrotron Radiation Techniques”  
IK-CH-002

In the year 2007, both the Laboratory of New-Structured Materials, Zhejiang University, and the Hard X-ray Scattering group, DESY, have been busy starting the activities planned in the framework on the collaboration program entitled “Investigation of Metallic Glasses under Stress by Synchrotron Radiation Techniques”.

All topics described in the research plan have been worked on.

### 1) Atomic structures of metallic glasses

Several diffraction experiments using high energy synchrotron radiation have been conducted at beamline BW5 of DORIS. Atomic structures of  $Zr_{70}Ni_{30}$  and  $Zr_{70}Cu_{30-x}Pd_x$  ( $x = 0, 1, 5, 10, 20$  and  $30$  at.%) metallic glasses were investigated in addition by EXAFS at the Ni and Zr K-edge and by reverse Monte Carlo simulation. Distributions of coordination number (CN) and Voronoi clusters were analyzed by Voronoi tessellation method. In the  $Zr_{70}Ni_{30}$  metallic glass the average CN of atoms was obtained to be 11.4 together with the average CN of Zr and Ni atoms of 11.8 and 10.6, respectively. It is found that Z11 Kasper polyhedra and distorted icosahedra are the favoured structural units in  $Zr_{70}Ni_{30}$  metallic glass. The discrepancy in atomic structure between  $Zr_{70}Ni_{30}$  metallic glass and its corresponding crystalline (or quasi-crystalline) phases can explain the fact that  $Zr_{70}Ni_{30}$  metallic glass does not transform to neither icosahedral nor fcc  $Zr_2Ni$  phase during the solidification process. In  $Zr_{70}Cu_{30-x}Pd_x$  ( $x = 0, 1, 5, 10, 20$  and  $30$  at.%) metallic glasses, a pre-peak arising in the low  $Q$  range of  $S(Q)$  in  $Zr_{70}Cu_{29}Pd_1$  metallic glass was detected whereas no pre-peak was observed in the other samples. The origin of the pre-peak is identified to be the medium-range order around Pd atoms occupying octahedral-like cluster in the metallic glass. When a pre-peak in  $S(Q)$  exists for metallic glasses containing heavy metal elements with low concentration (such as noble metal or rare earth elements), medium-range order, centred with these heavy atoms, occurs in metallic glasses.

### 2) Structural evaluation of BMGs under stress

Ductility is one essential prerequisite for many applications of bulk metallic glasses. We investigated the correlation of mechanical properties with atomic structure of bulk metallic glasses using Synchrotron Radiation techniques. We performed in situ high energy X-ray diffraction to detect the tensile behaviour of two  $Zr_{62}Al_8Ni_{13}Cu_{17}$  and  $La_{62}Al_{14}(Cu_{5/6}Ag_{1/6})_{14}Co_5Ni_5$  bulk metallic glasses. Based on the diffraction data, the tensile elastic modulus and Poisson's ratio have been accurately evaluated. Such experiments confirm that the XRD technique is suitable to study tension behaviour of bulk metallic glasses. No excess free volume appears in the fractured region. However, a drastic change in atomic-level strains is found in the La-based BMG along the tensile direction, while a tiny crystalline component is detected in the fracture region of Zr-based BMG, which may be the different factors leading to the catastrophic failure of them, respectively.

We also studied compression behaviour of monolithic Zr-based bulk metallic glasses and found that a minor adjustment in Zr/Ni concentration ratio can dramatically enhance the plasticity of monolithic Zr-based bulk metallic glasses, from only about 2.2% for  $Zr_{65}Al_8Ni_{10}Cu_{17}$  BMG to 14% for  $Zr_{62}Al_8Ni_{13}Cu_{17}$  BMG. No deformation-induced nano-crystallization appears in a 55% strained  $Zr_{62}Al_8Ni_{13}Cu_{17}$  BMG (without catastrophic failure after failure) while pre-existing nano-crystals in  $Zr_{65}Al_8Ni_{10}Cu_{17}$  BMG result in its limited plasticity. Also note that the stability of  $Zr_{62}Al_8Ni_{13}Cu_{17}$  BMG against crystallization upon deformation is rather higher than  $Zr_{65}Al_8Ni_{10}Cu_{17}$  BMG. As determined by X-ray diffraction using synchrotron radiation, the enhanced plasticity of  $Zr_{62}Al_8Ni_{13}Cu_{17}$  BMG seems to be related to the relative homogeneity of the amorphous structure.

Tension and stress relaxation behaviour of a  $La_{62}Al_{14}Cu_{11.7}Ag_{2.3}Ni_5Co_5$  bulk metallic glass as a function of isothermal annealing time have been investigated. We found that annealing at 373 K below the glass transition temperature (423 K) of the BMG alloy, causes an increase of specific heat and density at the glass transition, indicating a reduction of free volume in the BMG alloy with annealing time. Compared with as-cast samples, fracture strength, Vickers hardness, viscosity, Young's modulus, stress relaxation and stability of the annealed BMGs increase with annealing time, which were caused by the reduction of quenched in free volume in the annealed samples. Furthermore, a change of fracture morphology from a mixture of smooth and furrow zones in the as-cast sample to mainly furrow zone in the sample annealed for 8 hours was also observed. All samples exhibit brittle behaviour during tension tests

Since the atomic details of the deformation behavior of BMG is still unclear and presents a "hot topic" in the community, we worked on an upgrade of beamline BW5 enabling us to perform in-situ x-ray diffraction during tensile/compression deformation in a fully automated mode. Additionally the stress rig was modified as to allow for experiments with several 10 microns thick ribbons. First results are promising and show that such in-situ X-ray technique is suitable to study deformation behavior of BMGs.

### 3) Additional work

The amorphous-to-amorphous phase transition induced by pressure is one of the most active fields in materials science and condensed matter physics, and the nature of the transition is still an open question. In this project, we performed in situ room-temperature high-pressure x-ray diffraction (XRD) using synchrotron radiation up to 40 GPa for a LaCe-based bulk metallic glass. It is clear that the position of the broad amorphous peak in the scattering pattern shifts to higher angle with increasing pressure. Analysing this shift a break in the evaluation of the bulk modulus at around 14 GPa was detected. The slopes below and above 14 GPa are different. This suggests that the bulk metallic glass alloy exhibits a sudden change in compressibility, which might be originated from the Kondo coupling between 4f spin and conductive electrons due to the addition of cerium, although it has never been reported in any bulk metallic glasses yet. In addition, we also performed low-temperature resistivity and magnetization measurements for the LaCe-based bulk metallic glass. At low temperatures, the resistivity rapidly increases and a logarithmic temperature dependence below about 12 K, which resembles a Kondo-like magnetic origin scattering problem in Ce-bearing alloys. But, no magnetic dependence of resistivity was observed for the LaCe-based bulk metallic glass. Although the mechanism

of the unusual change in compressibility at about 14 GPa is not completely clear yet, these preliminary experimental results are very encouraging, which seems to be the first observation of amorphous-to-amorphous phase transition in bulk metallic glassy systems. More general and systemic studies on metallic glasses, especially, Ce-based metallic glasses like binary  $Ce_xA_{100-x}$  alloys with different electronic structures ( $x$  covering a wide range) are strongly required and necessary. To elucidate the nature of the possible amorphous-to-amorphous phase transition in metallic systems, we will continue our effort to investigate the nature and possibility of pressure-induced polyamorphic transitions in metallic glasses using in-situ synchrotron radiation XRD technique in the year of 2008.

Results have been published in high impact journals (see below). During the shutdown period at DESY two experiments will be performed at ESRF (already approved). Later this year we will resume the activities at the beamlines BW5 and B2 at DORIS III and in future also on at the new stations at PETRA III.

### Results published in peer reviewed journals

X.D. Wang, J. Bednarcik, K. Saksl, H. Franz, Q.P. Cao, J.Z. Jiang,  
*Tensile behavior of bulk metallic glasses by in-situ high energy X-ray scattering.*  
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X. Ou, W. Roseker, K. Saksl, H. Franz, L. Gerward, X. Xu, G.Q. Zhang, L.N. Wang, J.F. Liu and J.Z. Jiang  
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Journal of Alloys and Compounds **441**, 185 (2007)

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*Enhancement of plasticity in Zr-based bulk metallic glasses.*  
Journal of Materials Research **22**, 2454 (2007)

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*Origin of pre-peak in  $Zr_{70}Cu_{29}Pd_1$  metallic glass*  
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*Anomalous compression behavior of Lanthanum/cerium metallic glass under high pressure*  
Proceedings of the National Academy of Sciences (PNAS) **104**, 13565 (2007)

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*La-based bulk metallic glass with critical diameter up to 30 mm*  
Acta Mater. **55**, 4409 (2007)

L.Y. Chen, H.T. Hu, G.Q. Zhang, and J.Z. Jiang,

*Catching the Ni-based ternary metallic glasses with critical size up to 3 mm in Ni-Nb-Zr system*

J. Alloys and Compounds **443**, 109 (2007)

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