Report on the Helmholtz-Zhejiang University Research Collaboration Program in the time period of 2007-2009

The Zhejiang University-Helmholtz Research Collaboration Program entitled "Investigation of Metallic Glasses under Stress by Synchrotron Radiation Techniques" initiated in 2006 for a time period of five years, was approved in 2007 by the Helmholtz Association. A budget of 487,500 EUR for the first three years (March 2007 to February 2010) was granted to the program in 2007. After the first three-year period, an international evaluation report to the program will be conducted, which will be used for the Helmholtz Association to decide whether to continue the Helmholtz-Zhejiang University research collaboration program. During the last three years, the Laboratory of New-Structured Materials, Zhejiang University, and the Hard X-ray Scattering group, DESY, have been intensively working on all the activities planned in the framework on the collaboration program. A summary is listed as follows:

1. Research activities

1.1 Deformation of bulk metallic glasses

In the last three year, we discovered an intrinsic plastic $Cu_{45}Zr_{46}Al_7Ti_2$ bulk metallic glass (BMG) with high strength and superior compressive plastic strain of up to 32.5 %, which was successfully fabricated by copper mold casting [10]. The correlation of mechanical properties with atomic structure of the BMG was investigated by using Synchrotron Radiation techniques. The superior compressive plastic strain is attributed to a large amount of randomly distributed free volume, induced by Ti minor alloying, which results in extensive shear band formation, branching, interaction and self-healing of minor cracks. In order to confirm the idea of free-volume effect on mechanical behavior of BMGs proposed, we further carried out a study on CuZrAl BMG and indeed revealed that the plasticity of the BMG can be tailored by introducing different amounts of free volume in BMGs[15]. These results demonstrate that introducing free volume to BMGs could be one promising way to improve plasticity of BMGs. In addition, we explored various possibilities to overcome the restriction of limited plastic deformation and lack of work-hardening of BMGs. We successfully achieved large macroscopic compressive plastic deformation (over 15%) and work-hardening-like behavior in a monolithic BMG through tailoring loading stress distribution experimentally [12]. We explored a new method to study tension behavior of BMG by in situ XRD under tension to quantitatively determine elastic properties of BMGs [13] and a new method to characterize residual stress in BMGs was developed [16]. The uniaxial tensile behavior of four BMGs has been investigated [20]. It is found that the local strain is basically homogeneously distributed at low stress. However, heterogeneity appears obviously when the stress is close to the fracture strength. The amplitude of fluctuation in local strain for these four BMGs could relate to the distribution of excess free volume within the medium range order. This might be a precursor for the formation of shear bands.

1.2 Atomic structure and phase transformation of metallic glasses

Atomic structures of several metallic glasses ($Cu_{64.5}Zr_{35.5}$, $Cu_{61.8}Zr_{38.2}$, $Cu_{46}Zr_{46}Al_8$, $Zr_{70}Ni_{30}$ and $Zr_{70}Cu_{30-x}Pd_x$ (x = 0, 1, 5, 10, 20 and 30 at.%) have been investigated by a combination of state-of-the-art experimental techniques (synchrotron radiation-based x-ray diffraction (XRD) and extended x-ray absorption fine structure (EXAFS)) with computational methods (reverse Monte Carlo (RMC) and *ab initio* molecular dynamics (VASP) simulation) [3-5,13,14]. Three-dimensional (3D)

atomic configurations of the studied metallic glasses have been established. Icosahedron-like clusters are detected in the studied metallic glasses. The amorphous-to-amorphous phase transition induced by pressure is a very active field in materials science and condensed matter physics, and the nature of the transition is still an open question. In this program, we discovered that LaCe-based bulk metallic glass exhibits a sudden change in compressibility, which might originate from the Kondo coupling between 4f spin and conductive electrons due to the addition of cerium [1]. Such an effect has never been reported in any bulk metallic glasses yet. 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. This seems to be the first observation of an amorphous-to-amorphous phase transition in bulk metallic glassy systems. In addiation a new Ce_3Al solid solution alloy was discovered originating from $Ce_{75}Al_{25}$ metallic glass under pressure [19].

1.3 Development of novel bulk metallic glasses

We developed the second largest bulk metallic glass: La-based BMG rods prepared by copper mold casting [2] with a critical diameter of 35 mm and a novel ZrCu-based bulk metallic glass with at least 20 mm [11] diameter. We further investigated composition optimization, thermal properties, physical properties and glass-forming ability (GFA) of new families of La-based and ZrCu-based bulk metallic glasses. We reveal the origin of the high GFA in both systems, which is attributed to the smaller difference in Gibbs free energy between amorphous and crystalline phases. Several new Ni-based and Fe-based BMGs were also developed during the program [8,9,17,18,21,22].

2. Manpower

1) In the last three years, Zhejiang University has put 2 staff members (40%), 2 postdocs (100%), 7 ph.d. (100%) and 4 master (100%) students to work on the present research project. The Hard X-ray Scattering group, DESY, has put 2 staff member (20%), 1 postdoc (80%) and 1 ph.d. student (100%) to work on the present research project. Within this program, 6 students finished their thesis at Zhejiang University (4 Ph.D. and 2 master).

3. Meeting and exchange visiting

Prof. Jianzhong Jiang visited DESY for two weeks in 2007, one week in 2009. Dr. Xiaodong Wang worked at DESY for 8 months in 2007, 3 months in 2008 and 1 month in 2009. Mr. H.B. Lou (ph.d. student), Dr. L Yang and Prof. Y.Z. Fang worked at DESY for 1 month in 2009. Dr. H. Franz visited Zhejiang University for one week every year. Prof. Jianzhong Jiang was invited to give talks at eight international conferences on the subject (ISMANAM2007, 2008, and 2009, RQ13, BMG6 and WPI-Europe BMG, Lightweight BMGs, TMS conferences). Dr. Xiaodong Wang attended three international conferences on the subject (e.g., ISMANAM2007 and 2009, BMG7) with oral presentations. Dr. J. Bendnarcik attended three international conferences on the subject (IWNCS2008, ISMANAM2009 and RQ13) with oral presentations. In addition, four members from Zhejiang university attend five BMG conferences in China. Both sides exchanged their research results also via e-mail. Three conferences were held at Zhejiang University during this program:

(1) “International Conference on Pressure Science”, 11-13 May, 2007. (about 120 participants).

(2) “International Conference on Applications of Synchrotron Radiation Techniques”, 23-24 October, 2007. (about 90 participants).

(3) “International Conference on Amorphous Alloys”, 19-23 November, 2008. (about 100 participants).

4. Background of the collaboration project

The Peoples Republic of China is, besides Russia and the European Union, a strategic partner of the Helmholtz Association. This is reflected for example by the Helmholtz office established in Bejing.

Joint research projects are an efficient tool to strengthen this partnership. By regular exchanges of the members of the collaborating groups a deeper understanding for the respective scientific and cultural traditions and rules is created. This is however not limitted to the partners within the program but also extends to collaborating institutes on both sides. In particular extended visits promote the scientific exchange. The exchange program offers access to the excellent preparation laboratories at Zhejiang University and in return offers chineese colleagues assisted use of the facilities available at DESY. This has to be seen also as training for young scientists to prepare for the use of the newly built Shanghai Light Source (SSRF) currently under commissioning.

After finishing their visit to DESY young chineese scientists are capable of supporting useres on advanced instrumentation at synchrotron light sources.

In the long range perspective this collaboration strengthens the scientific collaboration between the Peoples Republic of China and Germany, a partnership of strategic importance in particular in view of the chineese participation in the European Free Electron Laser Facility XFEL.

5. List of Publications

1. Q.S. Zeng, Y.C. Li, C.M. Feng, P. Liermann, M. Somayazulu, G.Y. Shen, H.-K. Mao, R. Yang, J. Liu, T.D. Hu, and J.Z. Jiang,
   Anomalous compression behavior in Lanthanum/cerium-based metallic glass under high pressure
   Proceedings of the National Academy of Sciences **104**, 13565 (2007)
2. Q.K. Jiang, G.Q. Zhang, L. Yang, X.D. Wang, K. Saksl, H. Franz, R. Wunderlich, H. Fecht, and J.Z. Jiang,
   La-based bulk metallic glasses with critical diameter up to 30 mm
   Acta Mater. **55**, 4409 (2007)
3. X.D. Wang, J. Bednarcik, K. Saksl, H. Franz, Q.P. Cao and J.Z. Jiang,
   Tensile behavior of bulk metallic glasses by in-situ high energy X-ray diffraction
   Appl.Phys.Lett. **91**, 081913 (2007)
4. L. Yang, S. Yin, X.D. Wang, Q.P. Cao, J.Z. Jiang, K. Saksl and H. Franz,
   Atomic structure in $Zr_{70}Ni_{30}$ metallic glass
   J.Appl.Phys.**102**, 083512 (2007)
5. L. Yang, J.Z. Jiang, K. Saksl and H. Franz,
   Origin of pre-peak in $Zr_{70}Cu_{29}Pd_1$ metallic glass
   J.Phys.Cond.Matter. **19**, 476217 (2007)
6. X.D. Wang, L. Yang, J.Z. Jiang, K. Saksl, H. Franz, H.J. Fecht, Y.G. Liu and H.S. Xie,
   Enhancement of plasticity in Zr-based bulk metallic glasses
   J.Mater.Res. **22**, 2454 (2007)
7. G.Q. Zhang, Q.K. Jiang, X.P. Nie, L.Y. Chen, L.N. Wang, M. Shao, X.D. Wang, Y.G. Liu, H.S. Xie, C.L. Qin, A. Inoue, Y.W. Wang and J.Z. Jiang,
   Tension and stress relaxation behavior of a La-based bulk metallic glass
   J.Mater.Res. **22**, 3303 (2007)
8. L.Y. Chen, H.T. Hu, G.Q. Zhang, and J.Z. Jiang,
   Catching the Ni-based ternary metallic glasses with critical diameter up to 3 mm in Ni-Nb-Zr system
   J.Alloys and Compounds **443**, 109 (2007)
9. L.Y. Chen, Z.D. Fu, G.Q. Zhang, Y.W. Zeng, G.L. Xu, S.L. Zhang and J.Z. Jiang,
   Ultrahigh-strength binary Ni-Nb bulk glassy alloy composite with good ductility
   J. Alloys and Compounds **443**, 105 (2007).
10. L.Y. Chen, Z.D. Fu, G.Q. Zhang, X.P. Hao, Q.K. Jiang, X.D. Wang, Q.P. Cao, H. Franz, Y.G. Liu, H.S. Xie, S.L. Zhang, B.Y. Wang, Y.W. Zeng and J.Z. Jiang,
    New class of plastic bulk metallic glass
    Phys.Rev.Lett. **100**, 075501 (2008)
11. Q.K. Jiang, X.D.Wang, X.P. Nie, G.Q. Zhang, H. Ma, H.-J. Fecht, J. Bendnarcik, H. Franz, Y.G. Liu, Q.P. Cao and J.Z. Jiang,
    Zr-(Cu,Ag)-Al bulk metallic glasses
    Acta Mater. **56**, 1785 (2008)
12. L.Y. Chen, Q. Ge, S.X. Qu, Q.K. Jiang, X.B. Nie and J.Z. Jiang,
    Achieving large macroscopic compressive plastic deformation and work-hardening-like behavior in a monolithic bulk metallic glass by tailoring stress distribution

Appl.Phys.Lett. **92**, 211905 (2008)
13. X.D. Wang, S. Yi, Q.P. Cao, J.Z. Jiang, H. Franz, and Z.H. Jin,
    Atomic structure of binary $Cu_{64.5}Zr_{35.5}$ bulk metallic glass
    Appl.Phys.Lett. **92**, 011902 (2008)
14. X.D. Wang, Q.K. Jiang, Q.P. Cao, J. Bednarcik, H. Franz, and J.Z. Jiang,
    Atomic structure and glass forming ability of $Cu_{46}Zr_{46}Al_8$ bulk metallic glass
    J.Appl.Phys. **104**, 093519 (2008)
15. L.Y. Chen, A.D. Setyawan, H. Kato, A. Inoue, G.Q. Zhang, J. Saida, X.D. Wang and J.Z. Jiang,
    Free-volume induced superior ductility in a bulk metallic glass at room temperature
    Scripta Mater. **59**, 75 (2008)
16. L.Y. Chen, Q. Ge, S. Qu, and J.Z. Jiang,
    Stress induced softening and hardening in a bulk metallic glass
    Scripta Mater. **59**, 1210 (2008)
17. H.T. Hu, L.Y. Chen, X.D. Wang, Q.P. Cao, and J.Z. Jiang,
    Formation of Ni-Nb-Zr-X (X=Ti, Ta, Fe, Cu, Co) bulk metallic glasses
    J.Alloys and Compounds **460**, 714 (2008)
18. X.M. Huang, C.T. Chang, Z.Y. Chang, X.D. Wang, Q.P. Cao, B.L. Shen, A. Inoue and J.Z. Jiang,
    Bulk ferromagnetic glasses in the Fe-M-Y-B (M=transition metals) system
    J. Alloys and Compounds **460**, 708 (2008)
19. Q.S. Zeng, Y. Ding, W.L. Mao, W. Luo, R. Ahuja,W. Yang, J.F. Shu, S.V. Sinogeikin, J.Z. Jiang, and H.-K. Mao,
    Novel alloy of incompatible elements
    Proceedings of the National Academy of Sciences **106**, 2515 (2009)
20. X.D. Wang, J. Bednarcik, H. Franz, H.B. Lou, Z.H. He, Q.P. Cao, and J.Z. Jiang,
    Local strain behavior of bulk metallic glasses under tension studied by *in situ* high energy x-ray diffraction
    Appl.Phys.Lett. **94**, 011911 (2009)
21. X.M. Huang, X.D. Wang, Y. He, Q.P. Cao and J.Z. Jiang,
    Are there two glass transitions in Fe-M (M=Mo, W, Nb)-Y-B bulk metallic glasses?
    Scripta Mater. **60**, 152 (2009)
22. Z.Y. Chang, X.M. Huang, L.Y. Chen, M.Y. Ge, Q.K. Jiang, X.P. Nie and J.Z. Jiang,
    Catching Fe-based bulk metallic glass with combination of high glass forming ability, ultrahigh strength and good plasticity in Fe-Co-Nb-B system
    Mater.Sci.Eng. A **517**, 246 (2009)
23. X.P. Nie, X.M. Xu, Q.K. Jiang, L.Y. Chen, Y. Xu, Y.Z. Fang, G.Q. Xie, M.F. Luo, F.M. Wu, X.D. Wang, Q.P. Cao, and J.Z. Jiang,
    Effect of microalloying of Nb on corrosion resistance and thermal stability of ZrCu-based bulk metallic glasses
    J.Non-Crystal.Solids **355**, 203 (2009)
24. Y. Xu, J.Z. Jiang, and X.M. Ge,
    Preparation and Growth Behavior of Amorphous $Pd_{40}Ni_{40}P_{20}$ Film by Electrodeposition
    Journal of Solid State Electrochemistry **13**, 713 (2009)
25. Q.P. Cao, F. Xu, J.W. Liu, LY. Chen, X.D. Wang, J.Z. Jiang, Z.Q. Yao, A. Minkow, K.J. Yang, H.J. Fecht, and S.X. Qu,

Initiation and evolution of shear bands in bulk metallic glass under tension - an in-situ SEM observation

J.Mater.Res. in press

26. L.Y. Chen, Y.W. Zeng, Q.P. Cao, U. Vainio, B.J. Park, Y.M. Chen, Z.L. Zhang, U. Kaiser, X.D. Wang, K. Hono, and J.Z. Jiang,

    Homogeneity of $Zr_{64.13}Cu_{15.75}Ni_{10.12}Al_{10}$ bulk metallic glass

    J.Mater.Res. in press.

27. J. Bednarcik, H. Franz, M. Sikorski, C. Curfs, X.D. Wang and J.Z. Jiang,

    Inverse and real space analysis of thermal expansion of La-based bulk metallic glass using in-situ hard X-ray diffraction

    submitted to APL

6. Master thesis's

H. T. Hu:	Alloying design and properties of Ni-based bulk metallic glasses (2008)
Z. Y. Chang:	Development and properties characterization on Fe-based bulk metallic glasses (2009)

7. PhD thesis's

L. Yang:	Investigation of atomic structure of metallic glasses by synchrotron radiation techniques (2007)
G.Q. Zhang:	Formation of Cu-based bulk metallic glasses and properties (2007)
X.M. Huang:	Preparation, properties and structure of Fe-Y-B based bulk metallic glasses (2008)
L.Y. Chen:	Plastic deformation of monolithic bulk metallic glasses (2009)