

**Abschlussbericht (Sachbericht)**

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| <b>Förderinstrument:</b>           | <b>Sondermaßnahmen</b>   |
| Impulsfonds-Förderkennzeichen      | IK-Ch-002  |
| Projekttitle                       | Investigation of Metallic Glasses under Stress by Synchrotron Radiation Techniques |
| Federführende/r Wissenschaftler/in | Dr. Hermann Franz  |
| Helmholtz-Zentrum                  | DESY   |
| Gesamtlaufzeit                     | 01.03.07-31.08.12  |

**1) Fortschritt des im Antrag beschriebenen Arbeitsprogramms**

*Berichten Sie kurz und allgemeinverständlich über die wesentlichen Ergebnisse. Waren Abweichungen vom Arbeitsprogramm notwendig?*

This report summarized the results of the very successful cooperation between Zhejiang University, Hangzhou, PR China, and DESY, Hamburg, Germany, on the topic of *“Investigation of Metallic Glasses under Stress by Synchrotron Radiation Techniques”*. In five years, from 2007 to 2012, more than 90 papers in reviewed journals have been published. Some of the results are still under evaluation, so that the project will continue to produce contributions to the research field even after the end of the funding period. Based on the exceptional success we are currently investigating pathways to continue this well established cooperation.

Besides scientists and post-docs several students have been involved, both at Zhejiang University and at DESY. Scientists from Zhejiang University have been trained in the use of Synchrotron Radiation based experimental techniques during long term visits at DESY. In addition every year several mutual short term visits have been arranged. Results have been presented on various national and international conferences and seminars.

Most important achievements have been the development of several new and innovative alloys with optimized glass forming abilities, the unraveling of structure - property relations, correlation of microscopic and macroscopic deformation mechanism, and the development of advanced data collection and evaluation procedures.

In the following a short description on the most important achievements will be presented.

**I. Atomic structures of metallic glasses**

Atomic structures of a wide range of metallic glasses (La-based, CuZr, CuZrAl, ZrNi, NiNbZr, ZrCuPd, FeCoNbB, and many more) have been investigated by a combination of advanced 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) [3-5,14,15]. Three-dimensional atomic configurations of the studied metallic glasses have been established. Icosahedron-like clusters have been detected in many of the studied metallic glasses. The question about the nature of the amorphous-to-amorphous phase transition induced by pressure, a very active field in materials science and condensed matter physics, has been tackled. 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 before. This seems to be the first observation of an amorphous-to-amorphous phase transition in bulk metallic glassy systems. The origin for the crossover was detected to be delocalization of f

electrons under pressure. One new Ca-Al metallic glass system with non-f electron also demonstrates an amorphous-to-amorphous crossover due to a charge transfer from s or p electrons to d orbital. Based on atomistic structural data the group at Zhejiang University developed the largest Zr-based bulk metallic glass prepared by copper mold casting with 73 mm diameter[64]; the largest rare-earth based BMG rods prepared by copper mold casting with a critical diameter of 35 mm [2] and a novel ZrCu-based bulk metallic glass with at least 20 mm diameter[12].

## II. Structural evolution of BMGs under stress

We discovered an intrinsic plastic CuZrAlTi bulk metallic glass with high strength and superior compressive plastic strain of up to 32.5 %. The correlation of mechanical properties with atomic structure of that alloy 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[16]. 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 [13]. We explored a new method to study tension behavior by *in situ* XRD under tension to quantitatively determine elastic properties and a new method to characterize residual stress in BMGs was developed [14]. These new tools for structural characterization were successfully applied to four BMGs [27]. 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 several 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. Conclusions drawn for structure data could be supported by molecular dynamics simulations of stress-strain behavior [94].

## Publications related to the project

### 2007

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La-based bulk metallic glasses with critical diameter up to 30 mm  
Acta Materialia **55**, 4409 (2007)
3. X.D. Wang, J. Bednarcik, K. Saksli, H. Franz, Q.P. Cao, J.Z. Jiang  
Tensile behaviour of bulk metallic glasses by in-situ high energy X-ray diffraction  
Applied Physics Letters **91**, 081913 (2007)
4. L. Yang, S. Yin, X.D. Wang, Q.P. Cao, J.Z. Jiang, K. Saksli, H. Franz  
Atomic structure in Zr<sub>70</sub>Ni<sub>30</sub> metallic glass

Journal of Applied Physics **102**, 083512 (2007)

5. L. Yang, J.Z. Jiang, K. Saksl, H. Franz

Origin of pre-peak in  $Zr_{70}Cu_{29}Pd_1$  metallic glass

Journal of Physics: Condensed Matter **19**, 476217 (2007)

6. X.D. Wang, L. Yang, J.Z. Jiang, K. Saksl, H. Franz, H.J. Fecht, Y.G. Liu, H.S. Xie

Enhancement of plasticity in Zr-based bulk metallic glasses

Journal of Materials Research **22**, 2454 (2007)

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Tension and stress relaxation behavior of a La-based bulk metallic glass

Journal of Materials Research **22**, 3303 (2007)

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

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

Journal of 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, J.Z. Jiang

Ultrahigh-strength binary Ni-Nb bulk glassy alloy composite with good ductility

Journal of Alloys and Compounds **443**, 105 (2007)

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Microstructure and crystallization in  $Cu_{50}Zr_{45}Al_5$  metallic glass

Journal of Alloys and Compounds **441**, 185 (2007)

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Acta Materialia **56**, 1785 (2008)

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Journal of Applied Physics **104**, 093519 (2008)

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Acta Materialia **60**, 4136 (2012)

82. Y.K. Fang, J.Z. Jiang  
High-pressure effects on Ti-Zr-Ni metallic glass and its corresponding quasicrystal  
Journal of Non-Crystalline Solids **358**, 3212 (2012)

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In vitro investigation of novel Ni free Zr-based bulk metallic glasses as potential biomaterials  
Materials Letters **75**, 74 (2012)

84. X.P. Nie, Q.P. Cao, Z.F. Wu, X.D. Wang, S.Q. Ding, J.Z. Jiang  
The pitting corrosion behavior of shear bands in a Zr-based bulk metallic glass  
Scripta Materialia **67**, 376 (2012)

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Thermal oxidation effect on corrosion behaviour of  $Zr_{46}Cu_{37.6}Ag_{8.4}Al_8$  bulk metallic glass  
Intermetallics **22**, 84 (2012)

86. L.Y. Chen, Z. Xue, Z.J. Xu, R.X. He, X.P. Nie, Q.P. Cao, X.D. Wang, S.Q. Ding, J.Z. Jiang  
Cu-Zr-Al-Ti bulk metallic glass with enhanced glass forming ability, mechanical properties, corrosion resistance and biocompatibility  
Advances in Engineering Materials **14**, 195 (2012)

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Does an icosahedral short-range order prevail in glass-forming Zr-Cu melts?  
Europhysics Letters **100**, 56002 (2012)

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Identification of Curie point in Fe-based metallic glasses using in-situ hard X-ray diffraction  
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89. D. Qu, A. Mizuno, M. Watanabe, J. Bednarcik, J. Shen  
Undercooling behavior of Zr-Cu-Ni-Al bulk metallic glasses investigated by in situ synchrotron high energy X-ray diffraction  
Materials Science and Engineering A **555**, 36 (2012)

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Experimental and thermodynamic assessment of the Gd-Zr system  
CALPHAD **39**, 27 (2012)

91. C. Hostert, D. Music, J. Bednarcik, J. Keckes, J. M. Schneider  
Quantum mechanically guided design of  $Co_{43}Fe_{20}Ta_{5.5}X_{31.5}$  (X=B, Si, P, S) metallic glasses  
Journal of Physics: Condensed Matter **24**, 175402 (2012)

92. G. Wang, N. Mattern, J. Bednarcik, R. Li, B. Zhang, J. Eckert  
Correlation between elastic structural behavior and yield strength of metallic glasses  
Acta Materialia **60**, 3074 (2012)

93. J. Bednarcik, L. Y. Chen, X. D. Wang, J. Z. Jiang, H. Franz  
Mapping the Strain Distributions in Deformed Bulk Metallic Glasses Using Hard X-Ray Diffraction  
Metallurgical and Materials Transactions A **43**, 1558 (2012)

**2013**

94. X.D. Wang, H.B. Lou, J. Bednarcik, H. Franz, H.W. Sheng, Q.P. Cao, J.Z. Jiang  
Structural evolution in bulk metallic glass under high-temperature tension  
Applied Physics Letters **102**, 051909 (2013)

**2) Finanz-/Zeitplan**

*Können Sie Finanz- und Zeitplan einhalten oder sind Anpassungen notwendig?*

Finanz- und Zeitplan wurden eingehalten.

**3) Strategischer Mehrwert**

*Welchen strategischen Mehrwert für die Helmholtz-Gemeinschaft hat das Vorhaben bisher erreicht oder inwieweit ist er absehbar?*

Das Forschungsprojekt stärkt die Zusammenarbeit mit der Volksrepublik China, einem der strategische Partner der Helmholtzgemeinschaft. Durch den regelmässigen Austausch werden Beziehungen zu den Kollegen and der Zhejiang Universität gepflegt, aber auch Kontakte zu anderen Universitäten z.B. in Nanjing und Shanghai geknüpft. Längerfristige Besuche chinesischer Kollegen am DESY tragen zur erfolgreichen Durchführung von Forschungsprojekten bei. Das wird auch durch die grosse Anzahl von gemeinsamen Publikationen und die erfolgreiche Zwischenbegutachtung dokumentiert. Durch das gemeinsame Projekt haben wir Zugang zu den Präparationslabors an der Universität Zhejiang, und können deren weltweit einmalige Expertise in der Entwicklung von massiven metallischen Gläsern nutzen. Langfristig trägt diese Kollaboration mit chinesischen Wissenschaftlern zu einer Intensivierung der wissenschaftlichen Zusammenarbeit bei.

**4) Drittmittel**

*Wurden Drittmittel eingeworben? Wenn ja, von wem und in welcher Höhe?*

Es wurden keine weiteren Drittmittel eingeworben.

**Impuls- und Vernetzungsfonds**

**Einfacher Verwendungsnachweis**

Federführendes Zentrum:

Deutsches Elektronen-Synchrotron,  
 DESY  
 Notkestr. 85  
 D-22607 Hamburg

|  |                    |                  |
|--|--------------------|------------------|
|  |                    |                  |
| <table style="width: 100%;"> <tr> <td style="width: 50%;"><b>Förder-Nr.:</b></td> <td style="width: 50%;"><b>IK-CH-002</b></td> </tr> </table> | <b>Förder-Nr.:</b> | <b>IK-CH-002</b> |
| <b>Förder-Nr.:</b>   | <b>IK-CH-002</b>   |                  |

Zwischennachweis

Verwendungsnachweis (Schlussnachweis)  
 für den Zeitraum 01.03.2007 bis 31.08.2012

Partner Institut:  
 Zehjiang University

Alle Beträge in Euro (€)

| 1<br>Position                                    | 2<br>Abgerechnet  | 3<br>Anerkannt |
|--|-------------------|----------------|
| Personal   | 366.555,60        |                |
| Sachmittel (inkl. Reisen)                        | 47.774,94         |                |
| Investitionen (Anschaffungskosten)               | 44.616,58         |                |
| Weiterleitungen an Dritte insgesamt <sup>1</sup> | 357.500,00        |                |
| Sonstiges  | 0,00              |                |
| <b>Summe:</b>                                    | <b>816.447,12</b> |                |

|   | Nachgewiesen    | Anerkannt |
|---|-----------------|-----------|
| <b>4 Abgerechnet insgesamt (Summe von Spalte 2)</b> | 816.447,12      |           |
| <b>5 Eigenmittel</b>                                | 0,00            |           |
| <b>6 Erhaltene Zahlungen aus dem Impulsfonds</b>    | -812.500,00     |           |
| <b>7 Kassenbestand aus Vorjahr</b>                  |                 |           |
| <b>8 Kassenbestand zum 31.08.2012 (Mehrbedarf)</b>  | <b>3.947,12</b> |           |

Zutreffendes bitte ankreuzen:

- Wir bestätigen, dass die Partner die Verwendung der an sie weitergeleiteten Mittel aus dem Zuwendungsvertrag nachgewiesen haben.
- Die Bestimmungen des Zuwendungsvertrages sind beachtet worden. Die Ausgaben waren notwendig. Es ist wirtschaftlich und sparsam verfahren worden. Die vorstehenden Eintragungen sind richtig und vollständig und stimmen mit den Büchern und Belegen überein.

.... Hamburg, den 27.12.2012.....  
 Ort, Datum

.....  
 Unterschrift(en) U. Wolfram, Leiter Finanzabteilung

Deutsches Elektronen-Synchrotron  
 Ein-Ebenen-Synchrotron- und Licht-Wellenlängen-Gemeinschaft  
 Notkestraße 85 | 22607 Hamburg | Tel. 040 8998-0



Sachlich richtig | rechnerisch richtig

(mit ..... den ..... Euro)

....., den .....

.....  
 Unterschrift(en)

Intervention:

<sup>1</sup> Bei mehreren Partnern bitte auf separatem Blatt einzeln ausweisen.

## Usage List

Helmholtz Research Centre:

Deutsches Elektronen-Synchrotron, DESY  
Notkestr. 85  
D-22607 Hamburg

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Partner Institut:

Zhejiang University,  
310027 Hangzhou,  
P.R. China

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Name of the Helmholtz Project: Investigation of Metallic Glasses under Stress by  
Synchrotron Radiation Techniques

Funding No: VH- IK-Ch-002

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Received funds from DESY : 357,500 €

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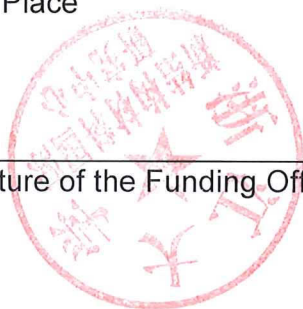
Costs appeared in the time period: 2007-2012

|                                       |                       |          |
|---------------------------------------|-----------------------|----------|
| Personal costs                        | <u>82,135</u>         | €        |
| Travel costs                          | <u>39,068</u>         | €        |
| Costs for workshops, conferences, etc | <u>6,307</u>          | €        |
| Other direct costs                    | <u>242,348</u>        | €        |
| <b>Total costs</b>                    | <b><u>369,858</u></b> | <b>€</b> |

2012-11-10, hangzhou

Date, Place

Signature of the Funding Office



Signature of Leading Scientist

**Impuls- und Vernetzungsfonds**

**Einfacher Verwendungsnachweis**

Federführendes Zentrum:

Deutsches Elektronen-Synchrotron (DESY)  
 Notkestr. 85  
 D-22607 Hamburg

|                              |
|------------------------------|
|                              |
| <b>Förder-Nr.: IK-CH-002</b> |

Partner Institut:

Zhejiang University

Zwischennachweis  
 Verwendungsnachweis (Schlussnachweis)  
 für den Zeitraum **01.01.2007 bis 31.12.2007**

Alle Beträge in Euro (€)

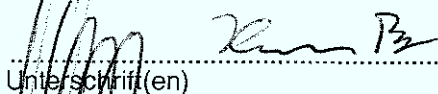
| 1  | 2                 | 3         |
|--|-------------------|-----------|
| Position   | Abgerechnet       | Anerkannt |
| Personal   | 47.071,90         |           |
| Sachmittel (inkl. Reisen)                        | 2.633,00          |           |
| Investitionen (Anschaffungskosten)               | 0,00              |           |
| Weiterleitungen an Dritte insgesamt <sup>1</sup> | 81.500,00         |           |
| Sonstiges  | 0,00              |           |
| <b>Summe:</b>                                    | <b>131.204,90</b> |           |

|   | Nachgewiesen    | Anerkannt |
|---|-----------------|-----------|
| <b>4 Abgerechnet insgesamt (Summe von Spalte 2)</b> | 131.204,90      |           |
| 5 Eigenmittel                                       | 0,00            |           |
| 6 Erhaltene Zahlungen aus dem Impulsfonds           | 135.417,00      |           |
| 7 Kassenbestand aus Vorjahr                         | 0,00            |           |
| <b>8 Kassenbestand am 31.12.2007 (Guthaben)</b>     | <b>4.212,10</b> |           |

Zutreffendes bitte ankreuzen:

- Wir bestätigen, dass die Partner die Verwendung der an sie weitergeleiteten Mittel aus dem Zuwendungsvertrag nachgewiesen haben.
- Die Bestimmungen des Zuwendungsvertrages sind beachtet worden. Die Ausgaben waren notwendig. Es ist wirtschaftlich und sparsam verfahren worden. Die vorstehenden Eintragungen sind richtig und vollständig und stimmen mit den Büchern und Belegen überein.

...Hamburg, den 18. März 2008.....  
 Ort / Datum

  
 Unterschrift(en)

Deutsches Elektronen-Synchrotron DESY  
 in der Helmholtz-Gemeinschaft  
 Notkestraße 85 - 22607 Hamburg - Tel. 040 / 89 98-0

Sachlich richtig | rechnerisch richtig

(mit \_\_\_\_\_ Euro)

....., den .....

Unterschrift(en)

Intervention:

<sup>1</sup> Bei mehreren Partnern bitte auf separatem Blatt einzeln ausweisen.

## Usage List of Funds

Name of the project: Investigation of Metallic Glasses under Stress by Synchrotron Radiation Techniques

IK-Ch-002

Costs of the project partner(s) Zhejiang University in the fiscal year 2007 :

|                                       |                      |          |
|---------------------------------------|----------------------|----------|
| Personal costs                        | <u>13,558</u>        | €        |
| Travel costs                          | <u>8,634</u>         | €        |
| Costs for workshops, conferences, etc | <u>1,057</u>         | €        |
| Other direct costs                    | <u>58,329</u>        | €        |
| <b>Total costs</b>                    | <b><u>81,578</u></b> | <b>€</b> |

Total funds sent by DESY to the partner(s) or received by the partner 81,475 €

Brief description of the activities (achieved goals, time schedule and perspectives):

In the year 2007, the group, Laboratory of New-Structured Materials, Zhejiang University, has been pursuing all research activities planned in the Zhejiang University-Helmholtz Research Collaboration Program with a project entitled "Investigation of Metallic Glasses under Stress by Synchrotron Radiation Techniques". The summary of all activities are expressed as follows:

### **1. Research activities**

1.1 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 by reverse Monte Carlo simulation combining with x-ray diffraction, Ni and Zr K-edge extended x-ray absorption of fine structure measurements [1,2]. 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 [3], which might be the first observation of amorphous-to-amorphous phase transition in bulk metallic glassy systems.

1.2 Tensile behaviors 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 (BMGs) were studied [4]. The tensile elastic modulus and Poisson's ratio have been accurately evaluated. Such experiments confirm that the XRD technique is suitable to study tension behavior of bulk metallic glasses. We also studied compression behavior of monolithic Zr-based bulk metallic glasses [5] 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. Tension and stress relaxation behaviors of a  $La_{62}Al_{14}Cu_{11.7}Ag_{2.3}Ni_5Co_5$  bulk metallic glass (BMG) as a function of isothermal annealing time have been investigated [6]. We found that annealing at 373 K below the glass transition temperature (423 K) of the BMG alloy, causes an increase of special heat difference at glass transition and density of the alloy, indicating a reduction of free volume in the BMG alloy with annealing time.

1.3 We developed the second largest bulk metallic glass: 35 mm  $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$  BMG rod by copper mold casting [7]. The origin of the high GFA enhanced by the Ag and Ni-Co substitution were investigated from the kinetic, structural and thermodynamic points of view. It is found that high GFA is attributed to the smaller difference in Gibbs free energy between amorphous and crystalline phases in the pseudo quaternary alloy system. The developed La-based BMG alloys with high GFA, low glass-transition temperatures and relatively

wide supercooled liquid regions should be useful for both scientific and engineering applications. We also developed the Ni-based ternary bulk metallic glasses with critical diameter up to 3 mm in Ni-Nb-Zr system using a strategy for catching the best glass former based on relative glass forming ability of alloys [8].

## 2. Manpower

Zhejiang University has put 1 staff member, 1 postdoc, 2 ph.d. and 3 master students to work on the present research project. They worked hard and obtained many interesting results, which have been published in the international recognized journals.

## 3. Meeting and exchange visiting

In the year 2007, Prof. Jianzhong Jiang visited HasyLab, Hamburg for two weeks and Dr. Xiaodong Wang worked at HasyLab, Hamburg for 8 months. Dr. H. Franz visited Zhejiang University for one week. Both sides exchanged their research results often via visiting and e-mail.

Four people from Zhejiang university also performed synchrotron radiation experiments at KEK in Japan.

Two workshops were held at Zhejiang University. They are

(1) "International Workshop on Pressure Science", 11-13 May, 2007.

(2) "International Workshop on Applications of Synchrotron Radiation Techniques", 24 October, 2007.

## 4. Time schedule and perspectives

In the year 2008, we will continue our effort to study the correlation of mechanical properties with atomic structure of bulk metallic glasses using Synchrotron Radiation techniques. Simple systems, e.g., CuZr BMG, will be studied by using a combination of state-of-the-art experimental techniques (synchrotron radiation-based XRD, XAFS and neutron diffraction) and computational techniques (reverse Monte Carlo (RMC) and ab initio molecular dynamics simulation) to resolve the atomic-level structure of metallic glasses. We expect to deduce three-dimensional atomic configuration of the CuZr BMG, which will link with mechanical behaviour of the BMG. Based on results obtained in the year 2008, new mechanism for mechanical behaviour of BMG will be proposed. We expect that about 8 research articles will be published in the international recognised journals.

In the year 2008, we will put 2 staff members, 2 postdocs and 3 ph.d. and 3 master students to work on the present research project. Exchange visiting will be arranged between both sides. One workshop will be held at Zhejiang University.

## 5. References

- [1] L. Yang, S. Yin, X.D. Wang, Q.P. Cao, J.Z. Jiang, K. Saksl and H. Franz, J. Appl. Phys. **102**, 083512 (2007).
- [2] L. Yang, J.Z. Jiang, K. Saksl and H. Franz, J. Phys. Condens. Matter. **19**, 476217 (2007)
- [3] 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, Proceedings of the National Academy of Sciences (PNAS) **104**, 13565 (2007)).
- [4] X.D. Wang, J. Bednarcik, K. Saksl, H. Franz, Q.P. Cao and J.Z. Jiang, Appl. Phys. Lett. **91**, 081913 (2007).
- [5] X.D. Wang, L. Yang, J.Z. Jiang, K. Saksl, H. Franz, H.J. Fecht, Y.G. Liu and H.S. Xie, J. Mater. Res. **22**, 2454 (2007).
- [6] 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, J. Mater. Res. **22**, 3303 (2007).
- [7] Q.K. Jiang, G.Q. Zhang, L. Yang, X.D. Wang, K. Saksl, H. Franz, R. Wunderlich, H. Fecht, and J.Z. Jiang, Acta Mater. **55**, 4409 (2007)
- [8] L.Y. Chen, H.T. Hu, G.Q. Zhang, and J.Z. Jiang, J. Alloys and Compounds **443**, 109 (2007)

2008,3,6

Date

Signature of funding office

Signature of leading scientist

**Impuls- und Vernetzungsfonds**

**Einfacher Verwendungsnachweis**

Federführendes Zentrum:

Deutsches Elektronen-Synchrotron,  
DESY  
Notkestr. 85  
D-22607 Hamburg

|                              |
|------------------------------|
|                              |
| <b>Förder-Nr.: IK-CH-002</b> |

Partner Institut:

Zhejiang University

Zwischennachweis  
 Verwendungsnachweis (Schlussnachweis)  
 für den Zeitraum 01.01.2008 bis 31.12.2008

Alle Beträge in Euro (€)

| 1<br>Position                                    | 2<br>Abgerechnet  | 3<br>Anerkannt |
|--|-------------------|----------------|
| Personal   | 56.258,83         |                |
| Sachmittel (inkl. Reisen)                        | 3.536,00          |                |
| Investitionen (Anschaffungskosten)               | 0,00              |                |
| Weiterleitungen an Dritte insgesamt <sup>1</sup> | 72.000,00         |                |
| Sonstiges  | 0,00              |                |
| <b>Summe:</b>                                    | <b>131.794,83</b> |                |

|   | Nachgewiesen      | Anerkannt |
|---|-------------------|-----------|
| <b>4 Abgerechnet insgesamt (Summe von Spalte 2)</b> | 131.794,83        |           |
| 5 Eigenmittel                                       | 0,00              |           |
| 6 Erhaltene Zahlungen aus dem Impulsfonds           | -162.500,00       |           |
| 7 Kassenbestand aus Vorjahr (Guthaben)              | -4.212,10         |           |
| 8 Kassenbestand am 31.12.2008 (Guthaben)            | <b>-34.917,27</b> |           |

Zutreffendes bitte ankreuzen:

- Wir bestätigen, dass die Partner die Verwendung der an sie weitergeleiteten Mittel aus dem Zuwendungsvertrag nachgewiesen haben.
- Die Bestimmungen des Zuwendungsvertrages sind beachtet worden. Die Ausgaben waren notwendig. Es ist wirtschaftlich und sparsam verfahren worden. Die vorstehenden Eintragungen sind richtig und vollständig und stimmen mit den Büchern und Belegen überein.

Hamburg, den 27.03.2009 .....

Ort, Datum

.....

Unterschrift(en)

Sachlich richtig | rechnerisch richtig

(mit ..... Euro)

..... den .....

Unterschrift(en)

Intervention:

Deutsches Elektronen-Synchrotron  
Ein Forschungszentrum der Helmholtz-Gemeinschaft  
Notkestr. 85 | 22607 Hamburg | Tel. 040 8998-0



<sup>1</sup> Bei mehreren Partnern bitte auf separatem Blatt einzeln ausweisen.



## Usage List of Funds

Name of the project: Investigation of Metallic Glasses under Stress by Synchrotron Radiation Techniques

IK-Ch-002

Costs of the project partner(s) ZhejiangUniversity  
in the fiscal year 2008 \_\_\_\_\_ :

|  |                     |
|--|---------------------|
| Personal costs   | __17,906__ €        |
| Travel costs   | __9,477__ €         |
| Costs for workshops, conferences, etc                                    | __1,000__ €         |
| Other direct costs   | __43,972__ €        |
| <b>Total costs</b>   | <b>__72,355__ €</b> |
| Total funds sent by DESY to the partner(s)<br>or received by the partner | __72,000__ €        |

Brief description of the activities (achieved goals, time schedule and perspectives):

In the year 2008, the group, Laboratory of New-Structured Materials, Zhejiang University, has been pursuing all research activities planned in the Zhejiang University-Helmholtz Research Collaboration Program with a project entitled "Investigation of Metallic Glasses under Stress by Synchrotron Radiation Techniques". The summary of all activities are expressed as follows:

### **1. Research activities**

#### **1.1 Deformation of bulk metallic glasses**

We discovered an intrinsic plastic  $\text{Cu}_{45}\text{Zr}_{46}\text{Al}_7\text{Ti}_2$  BMG with high strength and superior compressive plastic strain of up to 32.5 %, which was successfully fabricated by copper mold casting [1]. The correlation of mechanical properties with atomic structure of the BMG was investigated by using Synchrotron Radiation techniques. It is found that the superior compressive plastic strain is attributed to 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. The mechanism of plasticity presented here suggests that the creation of large amount of free volume into BMGs by minor alloying or other methods might be a new promising way to enhance plasticity of BMGs. In order to confirm the idea of free-volume effect on mechanical behavior of BMGs, we further report the improvement of plasticity in a ternary monolithic CuZrAl BMG caused by large amount of randomly-distributed free volume induced during solidification using high cooling rate [2]. It reveals that the plasticity of BMGs can be indeed tailored by introducing different amounts of free volume in BMGs. These results demonstrate that introducing free volume to BMGs could be one promising way to improve plasticity of BMGs. We also successfully achieved large macroscopic compressive plastic deformation (over 15%) and work-hardening-like behavior in a monolithic BMG through tailoring loading stress distribution experimentally [3]. To uncover the influence of the preexisting/residual stress on mechanical behavior of BMGs, we performed microvickers indentation studies of a stressed BMG [4]. The preexisting stress was introduced by bending. The results show that the nominal hardness decreases with preexisting tensile stress and increases with preexisting compressive stress. The real hardness decreases with preexisting tensile stress, but does not increase obviously with preexisting compressive stress. The finite element analysis indicates that the strong hardness dependence on stress results from the large elastic limit of BMGs. The compressive stress induced the formation of high density

shear bands, which results in softening, reducing the enhancement of hardness induced by applied compressive stress. The results obtained in this work are helpful to understand the mechanical behavior of BMGs. The relationship of hardness difference vs. applied stress reported here indicates that indentation technique might be a promising method to characterize residual stress in BMGs.

### 1.2 Development of novel bulk metallic glasses

Our group at Laboratory of New-Structured Materials, Zhejiang University, developed the a novel ZrCu-based bulk metallic glass at least 20 mm [5] together with the formation of about 25 gram amorphous metallic ingots in a wide Zr-(Cu,Ag)-Al composition range using conventional arc-melting machine. The effect of Ag addition on glass forming ability of the quaternary alloy has been systematically investigated from the structural, thermodynamic and kinetic points of view. The origin of high glass forming ability in the studied system is attributed to denser local atomic packing and the smaller difference in Gibbs free energy between amorphous and crystalline phases of Zr-(Cu,Ag)-Al BMGs (for  $Zr_{46}(Cu_{4.5/5.5}Ag_{1/1.5})_{46}Al_8$ ,  $\Delta G_{f,s}=1.5$  kJ/mol). The alloy shows good thermal and mechanical properties: glass-transition temperature  $T_g=703$  K, relatively wide supercooled liquid region  $\Delta T_x=72$  K, high activation energy for crystallization  $E_a=3.0$  eV, fragility parameter  $m=49$ , yield strength 1822 MPa, fracture strength 2163 GPa, Vicker's hardness  $533\pm 3$ , density  $7.177$  g/cm<sup>3</sup>, Young's modulus 92 GPa, shear modulus 33.8 GPa, and Poisson ratio 0.367. It also exhibits high corrosion resistance in H<sub>2</sub>SO<sub>4</sub> solution. The combination of high glass forming ability (critical sizes for BMG more than 20 mm), relatively wide supercooled liquid region  $\Delta T_x=72$  K, excellent mechanical properties (up to 2100 MPa fracture strength and about 28 % compressive plasticity), high corrosion resistance (in H<sub>2</sub>SO<sub>4</sub> solution), with cheap and environment-friendly raw materials enables to make the newly-developed Ni-free Zr-(Cu,Ag)-Al BMG alloys as promising engineering materials. We studied the effect of the fourth element on glass forming ability (GFA) in Ni-Nb-Zr-X (X=Ti, Ta, Fe, Cu, Co, V, Y, Mo, Sn, Al, Si) BMG system [6]. Among these elements, Co addition can increase GFA of the Ni-Nb-Zr BMG system. The best glass former is Ni<sub>57</sub>Nb<sub>33</sub>Zr<sub>5</sub>Co<sub>5</sub> alloy with critical diameter of 3.5 mm. The corrosion rate of this alloy is approximately one order of magnitude less than that of the stainless steel in aggressive 6 M HCl open to air at room temperature. This alloy exhibits high  $T_g$  of 866 K, supercooled liquid region  $\Delta T_x$  of 45 K, compressive fracture strength of 2.9 GPa, 1 % compressive plasticity, and excellent corrosion resistance as compared to stainless steel. Furthermore, we studied quaternary Fe<sub>72-x</sub>M<sub>x</sub>Y<sub>6</sub>B<sub>22</sub> (M= Ni, Co and Mo) BMGs [7]. It is found that a fully amorphous Fe<sub>68</sub>Mo<sub>4</sub>Y<sub>6</sub>B<sub>22</sub> cylindrical rod with 6.5 mm in diameter can be prepared by copper mold injection. These alloys have a high glass transition temperature of about 900 K with high fracture strengths up to about 3 GPa although they are still brittle. Magnetic measurements reveal that they are ferromagnetic at ambient temperature with low coercive force of about 2 A/m, saturation magnetization of about 0.7 T and effective permeability of about 7000 at 100 kHz. The newly-developed Fe-based quaternary alloys exhibit excellent combination properties: superior glass forming ability (GFA), high glass transition temperature, and soft magnetic properties, which could have potential applications in electronic industries.

### 1.3 Atomic structures of metallic glasses

Recently, binary Cu-Zr BMGs have been synthesized. It was found that the glass forming ability in the system strongly depends on compositions, even narrow down to 1 at.%. Thus, to determine the atomic structure of binary Cu-Zr BMG becomes very important. In this work [8], atomic structures of Cu<sub>64.5</sub>Zr<sub>35.5</sub> BMG, together with eutectic composition Cu<sub>61.8</sub>Zr<sub>38.2</sub> MG ribbon for a comparison, 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). Three-dimensional (3D) atomic configuration of the binary Cu<sub>64.5</sub>Zr<sub>35.5</sub> BMG is established. It is found that icosahedron-like clusters are dominant in both MGs. However, icosahedron-like clusters centered by Cu atoms are slightly denser packing and less distorted in Cu<sub>64.5</sub>Zr<sub>35.5</sub>, which can enhance the glass forming ability by suppressing atomic movements and increasing the structural incompatibility with competing crystalline phases. The atomic arrangements from short to medium range order are envisaged and compared between both glasses. The significant increase in critical size of BMGs from binary Cu-Zr (2 mm) to ternary Cu-Zr-Al (over 5 mm) provides a suitable prototype of BMGs to study the correlation of structure with GFA by using available experimental and computational methods. In this work [9], atomic structures of Cu<sub>46</sub>Zr<sub>46</sub>Al<sub>8</sub> BMG, together with binary Cu<sub>50</sub>Zr<sub>50</sub> MG ribbon for comparison, have been investigated. Based on the atomic configuration of the ternary Cu<sub>46</sub>Zr<sub>46</sub>Al<sub>8</sub> BMG, we explain high GFA of ternary Cu<sub>46</sub>Zr<sub>46</sub>Al<sub>8</sub> alloy from three aspects of atomic structure: (1) rather homogeneous distribution of Al atoms around Cu and Zr atoms, (2) modifying the environment around Cu and Zr atoms away from the local structures of the competing crystalline phase, (3) increasing the amount of icosahedron-like clusters and making their distribution more homogeneous

among different polyhedra in three dimensional space. The atomic arrangements from short to medium range order are explored and a favorable configuration is also mapped for  $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$  BMG with high GFA. We believe that the results obtained here will trigger more atomic structure studies to uncover the nature of GFA for various systems.

## 2. Manpower

Zhejiang University has put 1 postdoc, 3 ph.d. and 4 master students to work on the present research project. They worked hard and obtained many interesting results, which have been published in the international recognized journals.

## 3. Meeting and exchange visiting

In the year 2008, Prof. Jianzhong Jiang visited Hamburg and attended the RQ13 meeting and Dr. Xiaodong Wang worked at Hasylab, Hamburg for about 3 months (October-December 2009). Dr. H. Franz visited Zhejiang University for one week. Dr. J. Bendnarcik attended the RQ13 meeting. Both sides exchanged their research results often via visiting and e-mail. One joint workshop: International Symposium of Amorphous Alloys, was held at Zhejiang University in the time period 19-22 November. About 100 participants attended the meeting and Dr. H. Franz and Prof. J.Z. Jiang both gave one invited talk at the meeting.

## 4. Time schedule and perspectives

In the year 2009, we will continue our effort to study atomic structure, phase transformation and mechanical properties of metallic glasses using Synchrotron Radiation techniques. More systems will be studied by using a combination of state-of-the-art experimental techniques to resolve the atomic-level structure of metallic glasses. We expect to uncover atomic configuration of some metallic glasses. Based on results obtained in the year 2009, new mechanism for mechanical behavior of BMGs will be proposed. We expect that about 8 research articles will be published in the international recognised journals.

In the year 2009, we will put 2 staff members, 1 postdoc and 3 ph.d. and 4 master students to work on the present research project. Exchange visiting will be arranged between both sides. One workshop will be held at Zhejiang University.

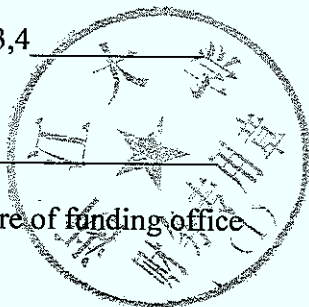
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2009,3,4

Date

Signature of funding office



A handwritten signature in black ink, consisting of several loops and strokes, positioned above a horizontal line.

Signature of leading scientist

## A list of cost

|   |                     |
|---|---------------------|
| <b>1. Personal costs</b>  | <b>__17,906__ €</b> |
| 1 postdoc:  | 7,622 €             |
| 2 ph.d.   | 7,108 €             |
| 3 master students.  | 3,176 €             |
| Zhejiang university puts the 26930 € for one staff, one ph.d. and one master student. |                     |
| <b>2. Travel costs</b>  | <b>__9,477__ €</b>  |
| The cost for Prof. Jianzhong Jiang's visit to Germany:                                | 2,554 €             |
| The flight ticket for Dr. Xiaodong Wang's visit to Hamburg:                           | 1,012 €             |
| The cost for four persons to perform SR experiments at KEK:                           | 5,911 €             |
| <b>3. Costs for workshop, conferences, etc</b>  | <b>__1,000__ €</b>  |
| The cost for one workshop held in Zhejiang University:                                | 1,000 €             |
| <b>4. Other direct costs</b>  | <b>__43,972__ €</b> |
| The cost for some parts for the DSC:  | 1,761 €             |
| The cost for some parts for the compression machine:                                  | 1,921 €             |
| The cost for raw materials:   | 30,756 €            |
| The cost for gas, quatz tube, polishing materials, copper mold etc..                  | 9,534 €             |
| <b>Total costs</b>  | <b>__72,355__ €</b> |
| Total funds sent by DESY to the partner(s)<br>or received by the partner              | <b>__72,000__ €</b> |

**Impuls- und Vernetzungsfonds**

**Einfacher Verwendungsnachweis**

Federführendes Zentrum:

Deutsches Elektronen-Synchrotron,  
DESY  
Notkestr. 85  
D-22607 Hamburg

|                       |
|-----------------------|
| Förder-Nr.: IK-CH-002 |
|-----------------------|

Partner Institut:

Zhejiang University

Zwischennachweis  
 Verwendungsnachweis (Schlussnachweis)  
 für den Zeitraum 01.01.2009 bis 31.12.2009

Alle Beträge in Euro (€)

| 1<br>Position                                    | 2<br>Abgerechnet  | 3<br>Anerkannt |
|--|-------------------|----------------|
| Personal   | 70.224,71         |                |
| Sachmittel (inkl. Reisen)                        | 4.110,36          |                |
| Investitionen (Anschaffungskosten)               | 22.150,00         |                |
| Weiterleitungen an Dritte insgesamt <sup>1</sup> | 55.000,00         |                |
| Sonstiges  | 0,00              |                |
| <b>Summe:</b>                                    | <b>151.485,07</b> |                |

|   | Nachgewiesen | Anerkannt |
|---|--------------|-----------|
| <b>4 Abgerechnet insgesamt (Summe von Spalte 2)</b> | 151.485,07   |           |
| 5 Eigenmittel                                       | 0,00         |           |
| 6 Erhaltene Zahlungen aus dem Impulsfonds           | -162.500,00  |           |
| 7 Kassenbestand aus Vorjahr (Guthaben)              | -34.917,27   |           |
| 8 Kassenbestand zum 31.12.2009 (Guthaben)           | -45.932,20   |           |

Zutreffendes bitte ankreuzen:

- Wir bestätigen, dass die Partner die Verwendung der an sie weitergeleiteten Mittel aus dem Zuwendungsvertrag nachgewiesen haben.
- Die Bestimmungen des Zuwendungsvertrages sind beachtet worden. Die Ausgaben waren notwendig. Es ist wirtschaftlich und sparsam verfahren worden. Die vorstehenden Eintragungen sind richtig und vollständig und stimmen mit den Büchern und Belegen überein.

Hamburg, den 22.04.2010 .....  
Ort, Datum

.....  
Unterschrift(en)

Deutsches Elektronen-Synchrotron  
Ein Forschungszentrum der Helmholtz-Gemeinschaft  
Notkestraße 85 | 22607 Hamburg | Tel. 040 80938-0



Sachlich richtig | rechnerisch richtig

(mit ..... Euro)

....., den .....

.....  
Unterschrift(en)

Intervention:

<sup>1</sup> Bei mehreren Partnern bitte auf separatem Blatt einzeln ausweisen.

## Usage List of Funds

Name of the project: Investigation of Metallic Glasses under Stress by Synchrotron Radiation Techniques

IK-Ch-002

Costs of the project partner(s) ZhejiangUniversity  
in the fiscal year 2009 \_\_\_\_\_ :

|  |                |   |
|--|----------------|---|
| Personal costs   | ___ 13,676 ___ | € |
| Travel costs   | ___ 7,240 ___  | € |
| Costs for workshops, conferences, etc                                    | ___ 760 ___    | € |
| Other direct costs   | ___ 33,594 ___ | € |
| <b>Total costs</b>   | ___ 55,270 ___ | € |
| Total funds sent by DESY to the partner(s)<br>or received by the partner | ___ 55,000 ___ | € |

Brief description of the activities (achieved goals, time schedule and perspectives):

In the year 2009, the group, Laboratory of New-Structured Materials, Zhejiang University, has been pursuing all research activities planned in the Zhejiang University-Helmholtz Research Collaboration Program with a project entitled "Investigation of Metallic Glasses under Stress by Synchrotron Radiation Techniques". The summary of all activities are expressed as follows:

### **1. Research activities**

#### **1.1 Metallic glasses under tension**

Mechanical properties of bulk metallic glasses (BMGs) are currently of great interest. One key issue is the failure mechanism of BMGs upon loading, which still remains unclear. Under uniaxial compression or bending conditions, some BMGs exhibit pronounced plasticity. More recently, pronounced tensile ductility for BMG composites was also reported. However, no tensile plasticity has been found so far for monolithic BMGs at ambient temperature and by uniaxial tension. To further understand the evaluation of STZ or the distribution of free volume upon loading, the deformation at the stress close to the fracture strength is greatly concerned. Usually the elastic deformation of BMGs is regarded to be similar to that of most crystalline counterparts, linearly and reversibly. However, some reports show that preloading below the fracture strength of BMGs can enhance excess free volume and produce extended plasticity upon reloading, indicating that some irreversible effect happens in the elastic deformation. We carried out the uniaxial tensile behavior of  $Zr_{62}Al_8Ni_{13}Cu_{17}$ ,  $Cu_{46}Zr_{46}Al_8$ ,  $Zr_{48}Cu_{43}Al_7Ag_2$  and  $La_{62}Al_{14}(Cu_{5/6}Ag_{1/6})_{14}Co_5Ni_5$  bulk metallic glasses (BMGs). Different local atomic responses to tensile stress for four BMGs were investigated by *in situ* high energy x-ray diffraction (HEXRD). 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 largest fluctuation happens in the range of 10 ~ 14 Å that seems the boundary between superclusters, where excess open volume may accumulate. 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. The results obtained in this work suggest that relatively homogeneous atomic packing within the medium range order may promote plasticity of monolithic BMGs, which shed light to design novel BMGs with tensile plasticity.

#### **1.2 Metallic glasses under compression**

Combining one metal with another leads to a range of alloys with properties superior to each individual end member. Since the Bronze and Iron Ages, the quest for new metallic alloys through various chemical and metastable quenching paths has played a crucial role in the advancement of civilizations. The most common type of alloy is a substitutional crystalline solid solution in which atoms of one element randomly substitute for atoms of another element in a crystal structure. The possibilities for substitution, however, are restricted by the classic empirical Hume-Rothery (HR) Rules (1) which require the components have atomic size within 15%, and electronegativity within 0.4 of each other. For instance, the archetypal 4*f* metal Ce alloys with similar rare-earth metals to form “mischmetal” which has unusual pyrophoric properties and strength for a broad range of chemical and physical applications, and the *sp*-bonded light metal Al alloys with similar atoms to form a family of aluminum alloys that have enormous technological importance and application in everyday life, but no known binary substitutional crystalline alloy exists between Ce and Al because their differences of 28% in atomic radii and 0.45 in electronegativity far exceed the HR limit. They can only form stoichiometric compounds in which Ce and Al are chemically ordered and occupy separate crystallographic sites, or metallic glass synthesized by rapidly quenched from melt in which Ce and Al are disordered both chemically and structurally. We carried out compression behavior of Ce<sub>3</sub>Al metallic glass. Using high-pressure at 298 K, we synthesized a face-centered cubic (fcc) disordered alloy of highly dissimilar elements — large Ce and small Al atoms — by compressing the Ce<sub>3</sub>Al metallic glass above 25 GPa. Synchrotron x-ray diffraction, Ce *L*<sub>3</sub>-edge absorption spectroscopy, and *ab-initio* calculations revealed that the pressure-induced Kondo volume collapse and 4*f* electron delocalization of Ce reduced the differences between Ce and Al and brought them within the Hume-Rothery limit for substitutional alloying. The novel alloy remained after complete release of pressure which was also accompanied by the transformation of Ce back to its ambient 4*f* electron localized state and reversal of the Kondo volume collapse, resulting in a non-Hume-Rothery alloy at ambient conditions. The present discovery opens a new route for making novel alloys including Ce-Al alloys of ratios other than 3:1, Ce alloys with other incompatible elements, and other *f*-electron alloys. Such alloys may display a range of unusual and useful mechanical, electronic and magnetic properties and greatly increase the choice of materials for a variety of applications.

### 1.3 Development of Fe-based bulk metallic glasses

In the year 2009 our group at Laboratory of New-Structured Materials, Zhejiang University, focuses our efforts on the development of Fe-based BMGs. This is one of the most important BMG systems because of the low cost and abundance of Fe element in earth. However, the Fe-based BMGs with combination of all the merits (high glass forming ability, high mechanical strength and good plasticity) were rarely reported. In fact, the combination of all the merits is essential/desirable (even imperative) for the wide application of Fe-based BMGs as engineering materials. In this work, we developed a Fe-Co-Nb-B system BMG with enhanced glass forming ability (critical diameter up to 2.5 mm), high glass transition temperature of 821 K, large supercooled region of 58 K, ultrahigh compressive strength of about 4.5 GPa, ultrahigh Vickers hardness of about 13 GPa, and good compressive plastic strain of about 0.6 %, which was searched using a strategy for catching the best glass former based on relative glass forming ability of alloys. The combination of high glass forming ability, high thermal stability, ultrahigh strength and good plasticity makes this alloy of potential applications as a structural material. We further investigated glass forming ability (GFA), mechanical and magnetic properties of Fe<sub>72</sub>W<sub>x</sub>Y<sub>6-x</sub>B<sub>22</sub> (*x*=0, 1, 2 and 3 at. %) and Fe<sub>72-x</sub>W<sub>x</sub>Y<sub>6</sub>B<sub>22</sub> (*x*=1, 2, 3, 4, 5 and 6 at.%) alloys. It is found that fully amorphous Fe<sub>69</sub>W<sub>3</sub>Y<sub>6</sub>B<sub>22</sub> and Fe<sub>68</sub>W<sub>4</sub>Y<sub>6</sub>B<sub>22</sub> cylindrical rods with 4 mm in diameter can be prepared by using copper mold casting. The newly-developed Fe-based quaternary alloys exhibit excellent combination properties: good GFA, high onset crystallization temperature of 970 K, high fracture strength of about 4 GPa, Vickers hardness of about 1000 kg/mm<sup>2</sup>, and good soft magnetic properties at ambient temperature (saturation magnetization of about 0.8 T and coercive force of below 2 A/m), which show potential applications in electronic industries. The effect of W addition on GFA in the Fe-Y-B alloy system is also discussed.

Minor addition of several particular elements, such as Co, Mo, Nb and Y, was found to be an effective way to enhance glass forming ability (GFA) of Fe-based BMGs, while its origin still remains an open question. Recently, a remarkable enhancement of GFA (from about 0.025 to 2 mm) was reported in simple Fe-RE-B (RE= Y, Sc, Dy, Ho, and Er) ternary system by just adding tiny RE (about 4-6 at %). The result raises an interesting question: what are the roles of RE atoms for the enhancement of GFA in the Fe-B system? In this work, we select Fe-Y-B system, as a prototype, to investigate the correlation of GFA with its atomic structure by using extended X-ray absorption fine structure (EXAFS), together with differential scanning calorimetry (DSC) and X-ray diffraction (XRD). Two questions are addressed: (1) why can tiny Y addition enhance GFA and (2) why does more

Y addition (> 7 at.%) deteriorate GFA. It is confirmed that the incorporation of minor large-sized Y atoms promotes the formation of complex  $B_6(Fe,Y)_{23}$  phase, compared with  $Fe_3B$  phase in the Fe-B binary alloy. With further addition of Y (up to 6 at.%), excessive internal strain leads to the distortion of  $B_6(Fe,Y)_{23}$ -like phase and eventually favors the formation of amorphous state during solidification. Consequently, GFA increases from 0.025 mm  $Fe_{78}B_{22}$  thin ribbon to 2 mm  $Fe_{72}Y_6B_{22}$  rod.

## 2. Manpower

Zhejiang University has put 2 postdoc, 3 ph.d. and 4 master students to work on the present research project. They worked hard and obtained many interesting results, which have been published in the international recognized journals.

## 3. Meeting and exchange visiting

In the year 2009, Prof. Jianzhong Jiang visited HasyLab, Hamburg and Prof. Fang Yunzhuang, Dr. Xiaodong Wang, Mr. Luo Hongbo worked at HasyLab, Hamburg for about 2 months (July-August 2009). Dr. H. Franz visited Zhejiang University for one week. Prof. Jianzhong Jiang attended three international conferences giving invited talks. Both sides exchanged their research results often via visiting and e-mail.

## 4. Time schedule and perspectives

In the year 2010, we will continue our effort to study atomic structure, phase transformation and mechanical properties of bulk metallic glasses using Synchrotron Radiation techniques. More systems will be studied by using a combination of state-of-the-art experimental techniques (synchrotron radiation-based XRD, XAFS and neutron diffraction) and computational techniques (reverse Monte Carlo (RMC) and ab initio molecular dynamics simulation) to resolve the atomic-level structure of metallic glasses. We expect to uncover atomic configuration of some metallic glasses. Based on results obtained in the year 2010, new mechanism for mechanical behavior of BMG will be proposed. We expect that about 8 research articles will be published in the international recognized journals.

In the year 2010, we will put 2 staff members, 2 postdoc and 4 ph.d. and 4 master students to work on the present research project. Exchange visiting will be arranged between both sides. One joint workshop: International Conference for Mechanical Properties of Materials, will be planned to be held at Zhejiang University in the time period 24-28 May, 2010.

## 5. References

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2010,4,24

Date

\_\_\_\_\_  
Signature of funding office

  
Signature of leading scientist

A list of cost

|  |                       |
|--|-----------------------|
| 1. Personal costs  | ___13,676___ €        |
| 1 postdoc (partial) :  | 5,823 €               |
| 2 ph.d. (partial)  | 5,430 €               |
| 3 master students (partial)  | 2,423 €               |
| Zhejiang university puts the 26930 € for one staff, two ph.d. and three master students. |                       |
| 2. Travel costs  | ___7,240___ €         |
| The cost for Jianzhong Jiang's visit to Germany, France and Japan for meetings: 3,980 €  |                       |
| The flight tickets for Fang Yunzhuang visit to Hamburg:                                  | 1,236 €               |
| The flight tickets for Xiaodong Wang visit to Hamburg:                                   | 1,012 €               |
| The flight tickets for Luo hongbo visit to Hamburg:                                      | 1,012 €               |
| 3. Costs for workshop, conferences, etc  | ___760___ €           |
| The cost for one workshop held in Zhejiang University:                                   | 760 €                 |
| 4. Other direct costs  | ___33,594___ €        |
| The cost for raw materials:  | 32,549 €              |
| The cost for gas, quartz tube, polishing materials etc..                                 | 1,045 €               |
| <b>Total costs</b>   | <b>___55,270___ €</b> |
| Total funds sent by DESY to the partner(s)<br>or received by the partner                 | ___55,000___ €        |



## Usage List of Funds

Name of the project: Investigation of Metallic Glasses under Stress by Synchrotron Radiation Techniques

IK-Ch-002

Costs of the project partner(s) Zhejiang University  
in the fiscal year 2010 :

|                                       |                      |          |
|---------------------------------------|----------------------|----------|
| Personal costs                        | <u>17,813</u>        | €        |
| Travel costs                          | <u>6,917</u>         | €        |
| Costs for workshops, conferences, etc | <u>1,123</u>         | €        |
| Other direct costs                    | <u>44,218</u>        | €        |
| <b>Total costs</b>                    | <b><u>70,071</u></b> | <b>€</b> |

Total funds sent by DESY to the partner(s)  
or received by the partner 70,000 €

Brief description of the activities (achieved goals, time schedule and perspectives):

In the year 2010, the group, Laboratory of New-Structured Materials, Zhejiang University, has been pursuing all research activities planned in the Zhejiang University-Helmholtz Research Collaboration Program with a project entitled "Investigation of Metallic Glasses under Stress by Synchrotron Radiation Techniques". The summary of all activities are expressed as follows:

### **1. Research activities**

1.1 Atomic structures of  $Zr_{70}Ni_{30-x}Pd_x$  ( $x=0-30$  at.%) and  $Zr_{48}Cu_{45}Al_7$  metallic glasses were investigated by reverse Monte Carlo simulation combining with x-ray diffraction, Cu, Ni, Zr, and Pd K-edge extended x-ray absorption of fine structure measurements [1,2]. Minor Al addition increases closer atomic packing and strong bonding effect, which enhance the glass forming ability in Zr-Cu system. A series of features in  $S(Q)$ s and  $G(r)$ s for  $Zr_{70}Ni_{30-x}Pd_x$  ( $x=0-30$  at.%) metallic glasses suggest that  $Zr_{70}Pd_{30}$  has even higher atomic packing efficiency than  $Zr_{70}Ni_{30}$ . Structural information obtained by reverse Monte Carlo simulation upon experimental data is compared with those calculated according to hard sphere dense packing principle and corresponding crystal phase. Strong bonding effect is determined to be intrinsic character in  $Zr_{70}Pd_{30}$  metallic glass. Electronic structure calculations also confirm the strong bonding.

1.2 Local atomic structures at glassy, supercooled liquid and liquid states for  $La_{62}Al_{14}Cu_{11.7}Ag_{2.3}Ni_5Co_5$ ,  $La_{62}Al_{14}Cu_{24}$  and  $La_{62}Al_{14}Cu_{20}Ag_4$  bulk metallic glasses have been investigated by in situ high temperature X-ray diffraction [3]. We found that the coordination number to be about  $15.1 \pm 0.1$  for the alloy does not depend on temperature up to liquid temperature, while it decreases slightly with temperature for the  $La_{62}Al_{14}Cu_{24}$  and  $La_{62}Al_{14}Cu_{20}Ag_4$  alloys. The  $S(q)$  data recorded at supercooled liquid region can be well described by the Debye theory. For the three alloys, volume expansion coefficient and the slopes of radii variation for the first to third nearest neighboring coordination shells show differences at glassy-to-supercooled liquid transition while no obvious changes were detected at supercooled liquid-to-liquid transition for them. The linear expansion coefficient value ( $1.6 \pm 0.1 \times 10^{-5} K^{-1}$ ) below glass transition temperature deduced from  $S(q)$  data is consistent with that detected by dilatometer ( $1.25 \times 10^{-5} K^{-1}$ ) for the  $La_{62}Al_{14}Cu_{11.7}Ag_{2.3}Ni_5Co_5$  bulk metallic glass.

1.3 Using high-pressure synchrotron x-ray absorption spectroscopy [4], we observed the Ce 4f electron in  $Ce_{75}Al_{25}$

metallic glass transform from its ambient localized state to an itinerant state above 5 GPa. A parallel x-ray diffraction study revealed a volume collapse of about 8.6%, coinciding with  $4f$  delocalization. The transition started from a low-density state below 1.5 GPa, went through continuous-densification ending with a high-density state above 5 GPa. This new type of electronic polyamorphism in densely-packed metallic glass is dictated by the Ce constituent, and is fundamentally distinct from the well-established structural polyamorphism in which densification is caused by coordination change and atomic rearrangement.

## 2. Manpower

Zhejiang University has put 2 staff member, 2 postdoc, 2 ph.d. and 3 master students to work on the present research project. They worked hard and obtained many interesting results, which have been published in the international recognized journals.

## 3. Meeting and exchange visiting

In the year 2010, Dr. Xiaodong Wang worked at HasyLab, Hamburg for 2 months. Mr. Lou Hongbo worked at HasyLab, Hamburg for 2 months. Dr. H. Franz visited Zhejiang University for one week. Both sides exchanged their research results often via visiting and e-mail. Seven people from Zhejiang university also performed synchrotron radiation experiments at APS in USA and SSRF in Shanghai

One conference: The First International Conference on Mechanical Properties of Materials (ICMPM) was held at Zhejiang University in the time period of 24-28 May, 2010. About 150 people from about 12 countries attend the conference. Dr. H. Franz gave us an invited talk at the meeting. We received very positive response from all participates. Thus, in 2011, we will hold the second International Conference on Mechanical Properties of Materials (ICMPM) at Zhejiang University in the time period of 12-15 June, 2011. About the same size will be expected.

## 4. Time schedule and perspectives

In the year 2011, we will continue our effort to study the correlation of mechanical properties with atomic structure of bulk metallic glasses using Synchrotron Radiation techniques. Simple systems, e.g., CeAl, NiNb, CuZr metallic glasses, will be studied by using a combination of state-of-the-art experimental techniques (synchrotron radiation-based XRD, and XAFS) and computational techniques (reverse Monte Carlo (RMC) and ab initio molecular dynamics simulation) to resolve the atomic-level structure of metallic glasses. We expect to deduce three-dimensional atomic configuration of the CeAl, NiNb and CuZr metallic glasses, which will link with mechanical behaviour of the metallic glasses. Based on results obtained in the year 2010, new mechanism for mechanical behaviour of metallic glasses will be proposed. We expect that about 5 research articles will be published in the international recognised journals.

In the year 2011, we will put 2 staff members, 2 postdocs and 3 ph.d. and 3 master students to work on the present research project. Exchange visiting will be arranged between both sides. One workshop: "The Second International Conference on Mechanical Properties of Materials (ICMPM)" will be held at Zhejiang University in the time period of 12-15 June, 2011. About 150 participates will be expected.

## 5. References

1. L. Yang, G.Q. Guo, L.Y. Chen, S.H. Wei, J.Z. Jiang, X.D. Wang, Scripta Mater. 63, 879 (2010)
2. L. Yang, G.Q. Guo, J.Z. Jiang, L.Y. Chen, and S.H. Wei, Scripta Mater. 63, 883 (2010)
3. Q.K. Jiang, Z.Y. Chang, X.D. Wang and J.Z. Jiang, Metallurgical and Materials Transactions A. 41 1634 (2010)
4. Qiao-shi Zeng, Yang Ding, Wendy L. Mao, Wenge Yang, Stas.V. Sinogeikin, Jinfu Shu, Ho-kwang Mao and J.Z. Jiang, Phys. Rev. Lett. 104, 105702 (2010).

2011,5,6

Date

Signature of funding office

Signature of leading scientist

A list of cost

1. Personal costs 17,813 €

1 postdoc: 8,978 €

1 ph.d. 5,672 €

3 master students. 3,163 €

Zhejiang university puts the 33,209 € for one staff and one ph.d. student.

2. Travel costs 6,917 €

The flight ticket for Dr. Xiaodong Wang's visit to Hamburg: 1,058 €

The flight ticket for Mr Lou Hongbo's visit to Hamburg: 1,058 €

The cost for seven persons to perform SR experiments at APS and SSRF: 4,801 €

3. Costs for workshops, conferences, etc 1,123 €

The cost for one conference held in Zhejiang University: 1,123 €

4. Other direct costs 44,218 €

The cost for raw materials: 35,149 €

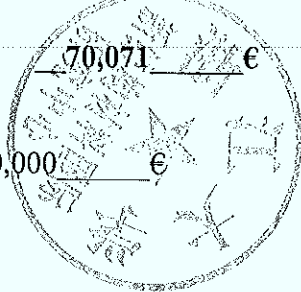
The cost for crucibles: 4,178 €

The cost for gas, quartz tube, copper mold etc.. 4,891 €

**Total costs** 70,071 €

Total funds sent by DESY to the partner(s)  
or received by the partner

70,000 €



**Impuls- und Vernetzungsfonds**

**Einfacher Verwendungsnachweis**

Federführendes Zentrum:

Deutsches Elektronen-Synchrotron,  
 DESY  
 Notkestr. 85  
 D-22607 Hamburg

|                                     |
|-------------------------------------|
|                                     |
| <b>Förder-Nr.:</b> <b>IK-CH-002</b> |

- Zwischennachweis
- Verwendungsnachweis (Schlussnachweis)  
 für den Zeitraum 01.01.2011 bis 31.12.2011

Partner Institut:  
 Zehjiang University

Alle Beträge in Euro (€)

| 1  | 2                 | 3         |
|--|-------------------|-----------|
| Position   | Abgerechnet       | Anerkannt |
| Personal   | 61.305,80         |           |
| Sachmittel (inkl. Reisen)                        | 5.668,86          |           |
| Investitionen (Anschaffungskosten)               | 19.768,33         |           |
| Weiterleitungen an Dritte insgesamt <sup>1</sup> | 70.000,00         |           |
| Sonstiges  | 0,00              |           |
| <b>Summe:</b>                                    | <b>156.742,99</b> |           |

|   | Nachgewiesen | Anerkannt |
|---|--------------|-----------|
| <b>4 Abgerechnet insgesamt (Summe von Spalte 2)</b> | 156.742,99   |           |
| 5 Eigenmittel                                       | 0,00         |           |
| 6 Erhaltene Zahlungen aus dem Impulsfonds           | -162.500,00  |           |
| 7 Kassenbestand aus Vorjahr (Guthaben)              | -63.120,72   |           |
| 8 Kassenbestand zum 31.12.2011                      | -68.877,73   |           |

Zutreffendes bitte ankreuzen:

- Wir bestätigen, dass die Partner die Verwendung der an sie weitergeleiteten Mittel aus dem Zuwendungsvertrag nachgewiesen haben.
- Die Bestimmungen des Zuwendungsvertrages sind beachtet worden. Die Ausgaben waren notwendig. Es ist wirtschaftlich und sparsam verfahren worden. Die vorstehenden Eintragungen sind richtig und vollständig und stimmen mit den Büchern und Belegen überein.

.... Hamburg, den 30.04.2012 .....  
 Ort, Datum

Unterschrift(en) *U. Morfitt*, Leiter Finanzabteilung  
 Deutsches Elektronen-Synchrotron  
 Forschungszentrum der Helmholtz-Gemeinschaft  
 Notkestr. 85 | 22607 Hamburg | Tel. 040 8998-0



Sachlich richtig | rechnerisch richtig

(mit ..... den ..... Euro)

....., den .....

Unterschrift(en)

Intervention:

<sup>1</sup> Bei mehreren Partnern bitte auf separatem Blatt einzeln ausweisen.

# Usage List of Funds

Name of the project: Investigation of Metallic Glasses under Stress by Synchrotron Radiation Techniques

IK-Ch-002

Costs of the project partner(s) Zhejiang University  
in the fiscal year 2011 \_\_\_\_\_ :

|                                       |               |   |
|---------------------------------------|---------------|---|
| Personal costs                        | <u>17,813</u> | € |
| Travel costs                          | <u>5,980</u>  | € |
| Costs for workshops, conferences, etc | <u>1,367</u>  | € |
| Other direct costs                    | <u>56,414</u> | € |

[In the year 2011, raw materials and others get expense]

**Total costs** 81,574 €

Total funds sent by DESY to the partner(s)  
or received by the partner 70,000 €

## Brief description of the activities (achieved goals, time schedule and perspectives):

In the year 2011, the group, Laboratory of New-Structured Materials, Zhejiang University, has been pursuing all research activities planned in the Zhejiang University-Helmholtz Research Collaboration Program with a project entitled "Investigation of Metallic Glasses under Stress by Synchrotron Radiation Techniques". The summary of all activities are expressed as follows:

### **1. Research activities**

1.1 Structural evolution of an Au-based bulk metallic glass (BMG) after severe plastic deformation (SPD) was investigated. The newly-formed glass contains high-density shear bands, a reduced ordering and a concomitant excess free volume determined by SR techniques. Moreover, it exhibits a temperature-independent local structure even in the supercooled liquid region, but a reduced thermal stability reflected in an accelerated crystal nucleation and growth process. These results suggest that SPD modifies the atomic structure of BMGs by localized shear band formation and thus, producing so-called nanoglasses. Constant-rate heating experiments using a fast x-ray camera (time resolution of 2s) reveals detailed information about the thermal stability of the  $\text{La}_{62}\text{Al}_{14}(\text{Cu}_{5/6}\text{Ag}_{1/6})_{14}\text{Ni}_5\text{Co}_5$  (at.%) bulk metallic glass (BMG). Analyzing diffraction patterns in a reciprocal space yields thermal expansion of amorphous alloy providing insight about the thermally activated relaxation effects and kinetics of glass transition. The glass transition appears as a brake in the value of the coefficient of the volume thermal expansion  $\alpha_{th}$ . Furthermore, real space analysis based on reduced pair distribution function  $G(r)$  allows tracing the changes in the local atomic structure of amorphous material during constant-rate heating.

1.2 To be new structural materials, the critical size is always the bottleneck of bulk metallic glasses (BMGs) due to the cooling rate restriction. In the year 2011, we successfully develop a new alloy of  $\text{Zr}_{46}\text{Cu}_{30.14}\text{Ag}_{8.36}\text{Al}_8\text{Be}_{7.5}$ , which can be cast into amorphous rods in 73 mm diameter by copper mould casting. This finding is linked with our understanding of atomic structure of metallic glasses. The strong glass forming ability of this alloy is closely related to the Be addition, which not only suppresses the phase separation happening in the as-cast Be-free BMG but also sustains low Gibbs free energy difference for crystallization. This finding will stimulate more interests in developing BMGs and their industrial applications. Furthermore, we successfully fabricate an intrinsic plastic  $\text{Zr}_{53.8}\text{Cu}_{31.6}\text{Ag}_{7.0}\text{Al}_{7.6}$  bulk metallic glass (BMG) with excellent bending and compressive properties in contrast to the poor plasticity that is usually observed in bulk metallic glasses. No inhomogeneous distribution can be observed. We suggest that the superior compressive and bending plastic strain was attributed to a large amount of randomly distributed free volume after a serial of comparison. The thermal, corrosion and thermal expansion properties, as well as elastic constants for the newly developed ZrCuAgAl BMG, are also presented.



1.3 Glass lacks the long-range periodic order that characterizes a crystal. In the  $Ce_{75}Al_{25}$  metallic glass (MG), however, we discovered a long-range topological order corresponding to a single crystal of indefinite length. Structural examinations confirm that the MG is truly amorphous, isotropic, and unstrained, yet under 25 GPa hydrostatic pressures, every segment of a cm-length MG ribbon devitrifies independently into a face-centered cubic (fcc) crystal with the identical orientation. Using molecular dynamics simulations and synchrotron x-ray techniques, we elucidate that the mismatch between the large Ce and small Al atoms frustrates the crystallization and causes amorphization, but a long-range fcc topological order still exists. Pressure induces electronic transition in Ce which eliminates the mismatch and manifests the topological order by the formation of a single crystal.

## 2. Manpower

Zhejiang University has put 2 staff members, 2 postdocs, 2 ph.d. and 3 master students to work on the present research project. They worked hard and obtained many interesting results, which have been published in the international recognized journals.

## 3. Meeting and exchange visiting

In the year 2011, Prof. Jianzhong Jiang visited HasyLab for one week and Mr. Lou Hongbo worked at HasyLab, Hamburg for 2 months. Dr. H. Franz visited Zhejiang University for one week. Both sides exchanged their research results often via visiting and e-mail. Fifteen people from Zhejiang university also performed synchrotron radiation experiments at SSRF in Shanghai.

One conference: "The Second International Conference on Mechanical Properties of Materials (ICMPM)" was held at Zhejiang University in the time period of 12-15 June, 2011. About 120 people from about 10 countries attend the conference. Dr. H. Franz gave us an invited talk at the meeting. We received very positive response from all participants. Thus, in 2012, we will hold "The Third International Conference on Mechanical Properties of Materials (ICMPM)" at Zhejiang University in the time period of 12-15 November, 2012.

## 4. Time schedule and perspectives

In the year 2012, we will continue our effort to study the correlation of mechanical properties with atomic structure of bulk metallic glasses and liquid melts using Synchrotron Radiation techniques. Simple systems, e.g., CaAl, NiNb, ZrCuAl metallic glasses, will be studied by using a combination of state-of-the-art experimental techniques (synchrotron radiation-based XRD, and XAFS) and computational techniques (reverse Monte Carlo (RMC) and ab initio molecular dynamics simulation) to resolve the atomic-level structure of metallic glasses. We expect to deduce three-dimensional atomic configuration of metallic glasses, which will link with mechanical behaviour of the metallic glasses. Based on results obtained in the year 2011, new mechanism for mechanical behaviour of metallic glasses will be proposed. We expect that about 5 research articles will be published in the international recognised journals.

In the year 2012, we will put 2 staff members, 2 postdocs and 3 ph.d. and 3 master students to work on the project. The Third International Conference on Mechanical Properties of Materials (ICMPM) will be held at Zhejiang University in the time period of 12-15 November, 2012. About 120 participants will be expected.

## 5. References

- 1) Qiaoshi Zeng, Hongwei Sheng, Yang Ding, Lin Wang, Wenge Yang, Jian-Zhong Jiang, Wendy L. Mao, and Ho-Kwang Mao, Long-range topological order in metallic glass, *Science* 332, 1404 (2011)
- 2) X. Wang, Q.P. Cao, Y.M. Chen, K. Hono, C. Zhong, Q.K. Jiang, X.P. Nie, L.Y. Chen, X.D. Wang, and J.Z. Jiang, A plastic Zr-based bulk metallic glass, *Acta Mater.* 59, 1037 (2011)
- 3) X.D. Wang, Q. P. Cao, J.Z. Jiang, H. Franz, J. Schroers, R.Z. Valiev, Y. Ivanisenko, H. Gleiter and H.-J. Fecht, Atomic level structural modifications induced by severe plastic shear deformation in bulk metallic glasses, *Scripta Mater.* 64, 81 (2011)
- 4) H.B. Lou, X.D. Wang, F. Xu, S.Q. Ding, Q.P. Cao, K. Hono and J.Z. Jiang, 73 mm-diameter Bulk Metallic Glass Rod by Copper Mould Casting, *Appl. Phys. Lett.* 99, 051910 (2011)
- 5) J. Bednarcik, M. Sikorski, C. Curfs, X.D. Wang, J.Z. Jiang and H. Franz, Thermal expansion of a La-based bulk metallic glass: insight from in-situ high-energy X-ray diffraction, *J. Phys. Condens. Matter* 23, 254204 (2011)

2012,5,16

Date

Signature of funding office



A handwritten signature in black ink, appearing to read "Jianzhong Jiang".

Signature of leading scientist

A list of cost

|  |                     |
|--|---------------------|
| 1. Personal costs  | __17,813__ €        |
| 1 postdoc:   | 8,978 €             |
| 1 ph.d.  | 5,672 €             |
| 3 master students.   | 3,163 €             |
| [Zhejiang university puts the 41,762 € for one staff and one ph.d. student.] |                     |
| 2. Travel costs  | __5,980__ €         |
| The flight ticket for Mr Lou Hongbo's visit to Hamburg:                      | 1,179 €             |
| The cost for fifteen persons to perform SR experiments at SSRF:              | 4,801 €             |
| 3. Costs for workshops, conferences, etc                                     | __1,367__ €         |
| The cost for one conference held in Zhejiang University:                     | 1,367 €             |
| 4. Other direct costs  | __56,414__ €        |
| The cost for raw materials:  | 45,149 €            |
| The cost for crucibles:  | 5,351 €             |
| The cost for gas, quartz tube, copper mold etc..                             | 5,914 €             |
| [In the year 2011, raw materials and others get expense]                     |                     |
| <b>Total costs</b>   | <b>__81,574__ €</b> |
| Total funds sent by DESY to the partner(s)<br>or received by the partner     | __70,000__ €        |

**Impuls- und Vernetzungsfonds**

**Einfacher Verwendungsnachweis**

Federführendes Zentrum:

Deutsches Elektronen-Synchrotron,  
 DESY  
 Notkestr. 85  
 D-22607 Hamburg

|                    |                  |
|--------------------|------------------|
|                    |                  |
| <b>Förder-Nr.:</b> | <b>IK-CH-002</b> |

- Zwischennachweis  
 Verwendungsnachweis (Schlussnachweis)  
 für den Zeitraum 01.01.2012 bis 31.08.2012

Partner Institut:  
 Zehjiang University

Alle Beträge in Euro (€)

| 1  | 2                | 3         |
|--|------------------|-----------|
| Position   | Abgerechnet      | Anerkannt |
| Personal   | 70.799,35        |           |
| Sachmittel (inkl. Reisen)                        | 18.838,42        |           |
| Investitionen (Anschaffungskosten)               | 1.270,08         |           |
| Weiterleitungen an Dritte insgesamt <sup>1</sup> | 9.000,00         |           |
| Sonstiges  | 0,00             |           |
| <b>Summe:</b>                                    | <b>99.907,85</b> |           |

|   | Nachgewiesen    | Anerkannt |
|---|-----------------|-----------|
| <b>4 Abgerechnet insgesamt (Summe von Spalte 2)</b> | 99.907,85       |           |
| <b>5 Eigenmittel</b>                                | 0,00            |           |
| <b>6 Erhaltene Zahlungen aus dem Impulsfonds</b>    | -27.083,00      |           |
| <b>7 Kassenbestand aus Vorjahr (Guthaben)</b>       | -68.877,73      |           |
| <b>8 Kassenbestand zum 31.08.2012 (Mehrbedarf)</b>  | <b>3.947,12</b> |           |

Zutreffendes bitte ankreuzen:

- Wir bestätigen, dass die Partner die Verwendung der an sie weitergeleiteten Mittel aus dem Zuwendungsvertrag nachgewiesen haben.
- Die Bestimmungen des Zuwendungsvertrages sind beachtet worden. Die Ausgaben waren notwendig. Es ist wirtschaftlich und sparsam verfahren worden. Die vorstehenden Eintragungen sind richtig und vollständig und stimmen mit den Büchern und Belegen überein.

.... Hamburg, den 27.12.2012.....  
 Ort, Datum

Unterschrift(en) U. Wolframm, Leiter Finanzabteilung

Sachlich richtig | rechnerisch richtig

(mit \_\_\_\_\_ Euro)

....., den .....

.....

Unterschrift(en)

Intervention:



<sup>1</sup> Bei mehreren Partnern bitte auf separatem Blatt einzeln ausweisen.

## Usage List of Funds

Name of the project: Investigation of Metallic Glasses under Stress by Synchrotron Radiation Techniques

IK-Ch-002

Costs of the project partner(s) Zhejiang University  
in the fiscal year 2012 :

|                                       |              |   |
|---------------------------------------|--------------|---|
| Personal costs                        | <u>1,369</u> | € |
| Travel costs                          | <u>0,820</u> | € |
| Costs for workshops, conferences, etc | <u>1,000</u> | € |
| Other direct costs                    | <u>5,821</u> | € |

**Total costs** 9,010 €

Total funds sent by DESY to the partner(s)  
or received by the partner 9,000 €

### Brief description of the activities (achieved goals, time schedule and perspectives):

In the year 2012, the group, Laboratory of New-Structured Materials, Zhejiang University, has been pursuing all research activities planned in the Zhejiang University-Helmholtz Research Collaboration Program with a project entitled "Investigation of Metallic Glasses under Stress by Synchrotron Radiation Techniques". The summary of all activities are expressed as follows:

#### **1. Research activities**

1.1 Pressure-induced amorphous-to-amorphous configuration changes in Ca-Al metallic glasses (MGs) were studied by performing *in-situ* room-temperature high-pressure x-ray diffraction up to about 40 GPa. Changes in compressibility at about 18 GPa, 15.5 GPa and 7.5 GPa during compression are detected in  $\text{Ca}_{80}\text{Al}_{20}$ ,  $\text{Ca}_{72.7}\text{Al}_{27.3}$ , and  $\text{Ca}_{66.4}\text{Al}_{33.6}$  MGs, respectively, whereas no clear change has been detected in the  $\text{Ca}_{50}\text{Al}_{50}$  MG. The transfer of s electrons into d orbitals under pressure, reported for the pressure-induced phase transformations in pure polycrystalline Ca, is suggested to explain the observation of an amorphous-to-amorphous configuration change in this Ca-Al MG system. Results presented here show that the pressure induced amorphous-to-amorphous configuration is not limited to f electron-containing MGs.

1.2 The issue, composition dependence of glass-forming ability (GFA) in metallic glasses (MG), has been investigated by by systematic synchrotron radiation-based experimental measurements (XRD and XAFS) coupled with theoretical calculations in Cu-Zr and Ni-Nb alloy systems. It is found that the atomic-level packing efficiency strongly relates to their GFA. The best GFA was located at the largest difference in the packing efficiency of the solute-centered clusters between the glassy and crystal alloys in both MG systems. This work provides an understanding of GFA from atomic level and will shed light on the development of new MGs with larger critical sizes.

1.3 On monolithic Ni-Nb metallic glass films, we experimentally revealed 6.6% elastic strain limit by in-situ transmission electron microscopy observations. The origin of high elastic strain limit may link with high free volume in the film, causing the rearrangement of loosely bonded atomic clusters

(or atoms) upon elastic deformation. This high elastic limit of metallic glass films will shed light on new application fields for metallic glasses, and also trigger more studies for deformation mechanism of amorphous materials in general.

## 2. Manpower

Zhejiang University has put 2 staff members, 2 postdocs, 2 ph.d. and 3 master students to work on the present research project. They worked hard and obtained many interesting results, which have been published in the international recognized journals.

## 3. Meeting and exchange visiting

In the year 2012, both sides exchanged their research results often via e-mail. Fifteen people from Zhejiang university also performed synchrotron radiation experiments at SSRF in Shanghai.

One conference: "Workshop on Disordered Alloys" will be held at Zhejiang University in the time period of 13-14 November, 2012. About 60 people will attend the conference. Dr. H. Franz was invited to give an invited talk at the meeting.

## 4. We strongly wish to continue this joint research project.

## 5. References

- 1) H.B. Lou, Y.K. Fang, Q.S. Zeng, Y.H. Lu, X.D. Wang, Q.P. Cao, K. Yang, X.H. Yu, L. Zheng, Y.D. Zhao, W.S. Chu, T.D. Hu, Z.Y. Wu, R. Ahuja and J.Z. Jiang, Pressure-induced amorphous-to-amorphous configuration change in Ca-Al metallic glasses, Nature: Scientific Reports 2, 376; DOI:10.1038/srep00376 (2012)
- 2) Q.K. Jiang, P. Liu, Y. Ma, Q. P. Cao, X. D. Wang, D.X. Zhang, X. D. Han, Z. Zhang and J.Z. Jiang, Super elastic strain limit in metallic glass films, Nature: Scientific Reports, in press.
- 3) L. Yang, G. Q. Guo, L. Y. Chen, C. L. Huang, T. Ge, D. Chen, P. K. Liaw, K. Saksl, Y. Ren, Q. S. Zeng, B. LaQua, F. G. Chen, and J. Z. Jiang, Atomic-scale mechanisms of the glass-forming ability in metallic glasses, Phys. Rev. Lett. 109, 105502 (2012)
- 4) Y. Ma, Q.P. Cao, S.X. Qu, X.D. Wang, and J.Z. Jiang, Effect of structural relaxation on plastic flow in Ni-Nb metallic glassy film, Acta Mater. 60, 3667 (2012)
- 5) Y. Ma, Q.P. Cao, H.F. Zhou, S.X. Qu, D.X. Zhang, X.D. Wang and J.Z. Jiang, Stress state-dependent plastic flow in an amorphous alloy, Acta Mater. 60, 4136 (2012)
- 6) Min Wu, Yunfeng Liang, Jian-Zhong Jiang and John S. Tse, Structure and Properties of Dense Silica Glass, Nature: Scientific Reports 2, 398; DOI:10.1038/srep00398 (2012)

2012,11,10

Date



Signature of funding office

Signature of leading scientist

A list of cost

1. Personal costs \_\_1,369\_\_ €

1 master student. 1,369 €

[Zhejiang university puts another 58,762 € for one staff, two postdocs, two ph.d. and two master students.]

2. Travel costs \_\_0,820\_\_ €

The cost for 3 persons to perform SR experiments at SSRF: 0.820 €

[Zhejiang university puts another 6,145 € for travelling cost]

3. Costs for workshops, conferences, etc \_\_1,000\_\_ €

The cost for one workshop held in Zhejiang University: 1,000 €

[Zhejiang university puts another 4.000 € for the workshop]

4. Other direct costs \_\_5,821\_\_ €

The cost for raw materials: 5,821 €

[Zhejiang university puts another 68,762 € for direct costs]

**Total costs** **\_\_9,010\_\_ €**

Total funds sent by DESY to the partner(s)  
or received by the partner

\_\_9,000\_\_ €