Zwischenbericht (Sachbericht)

Fördermaßnahme:	
Förder-Nr.: IK-Ch-002	Titel des Vorhabens: Investigation of Metallic Glasses under Stress by Synchrotron Radiation Techniques
Federführender Wissenschaftler: H. Franz	
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Activity report for IK-Ch-002 2008

In 2008 we were intensively working on bulk metallic glasses (BMGs). Special emphasis was placed at the study of relaxation phenomena, glass transition and glass forming ability of novel BMGs. Further we were extensively working on understanding of deformation mechanisms of selected Zr- and Cu-based BMGs.
Since DORIS III had a long shutdown due to the upgrade of the pre-accelerator chain in the period between January and August 2008 we performed part of our experimental work at the synchrotron source ESRF (Grenoble, France). Two proposals were submitted and both were granted beam times at the beamlines ID11 and ID15B.

The group at the Laboratory of New-Structured Materials, Zhejiang University, developed a novel ZrCu-based bulk metallic glass with critical diameter of at least 20 mm. The formation of about 25 gram amorphous metallic ingots was demonstrated in a wide Zr-(Cu,Ag)-Al composition range using a conventional arc-melting machine. The effect of Ag addition on the glass forming ability of the quaternary alloy has been systematically investigated from the structural, thermodynamic and kinetic points of view. The origin of the high glass forming ability (GFA) 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. The alloy shows good thermal and mechanical properties: glass-transition temperature T_g=703 K, wide supercooled liquid region ΔT_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, density 7.177 g/cm^3, Young's modulus 92 GPa, shear modulus 33.8 GPa, and Poisson ratio 0.367. It also exhibits high corrosion resistance in H_2SO_4 solution. The combination of high GFA (critical sizes for BMG more than 20 mm), relatively wide supercooled liquid region, excellent mechanical properties (about 28 % compressive plasticity), with cheap and environment-friend raw materials makes the newly-developed Ni-free Zr-(Cu,Ag)-Al BMG alloys a promising engineering materials.

In parallel some work was dedicated to Ni-based BMGs. The combination of superior properties and low material cost make also Ni-based BMGs a promising system for applications as engineering materials. However, the critical size of Ni-based BMGs is much smaller compared to other BMGs. We studied the effect of the fourth element on the GFA in Ni-Nb-Zr-X (X=Ti, Ta, Fe, Cu, Co, V, Y, Mo, Sn, Al, Si). Among these elements Co increases the GFA of the Ni-Nb-Zr BMG system. The best glass former is $Ni_{57}Nb_{33}Zr_5Co_5$ with a critical diameter of 3.5 mm. The corrosion rate of this alloy is approximately one order of magnitude less than that of 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 ΔT_x of 45 K, compressive fracture strength of 2.9 GPa, 1 % compressive plasticity. The combination of high thermal stability, high strength with compressive plasticity and excellent corrosion resistance suggests these alloys for industrial applications. Furthermore, the addition of Sn to Ni-Nb-Zr-Co alloy is effective for enhancing the stability of the supercooled liquid. The maximum supercooled liquid region of 85 K is obtained in $Ni_{57}Co_5(Nb_{33/38}Zr_{5/38})_{33}Sn_5$.

We further studied quaternary $Fe_{72-x}M_xY_6B_{22}$ (M= Ni, Co and Mo) BMGs. It was found that a fully amorphous $Fe_{68}Mo_4Y_6B_{22}$ 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 an excellent combination of properties: superior glass forming ability, high glass transition temperature, and soft magnetic properties, which could have potential applications in electronics industries.

Ductility is one essential prerequisite for many applications of bulk metallic glasses. That is why currently lots of effort goes into experiments aiming at the understanding of the plastic behaviour of BMGs. In the year 2008, we discovered an intrinsic plastic BMG ($Cu_{45}Zr_{46}Al_7Ti_2$) with high strength and superior compressive plastic strain of up to 32.5 %, which was successfully fabricated by copper mold casting. The correlation of mechanical properties with atomic structure of the BMG was investigated by using Synchrotron Radiation techniques. Within a beam time at ID15B of ESRF we studied the tensile deformation of Zr-based BMGs using in-situ high-energy x-ray diffraction. Special emphasis was laid on the influence of defects like shear bands on the deformation parameters. It is found that the superior compressive plastic strain can be 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. It is suggested that the creation of a large amount of free volume into BMGs by minor alloying or other methods might be a 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 a high cooling rate. It reveals that the plasticity of BMGs can be indeed tailored by introducing different amounts of free volume in BMGs.

In this year, we further explore 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 [3]. Numerical analysis was also carried out to investigate the stress distribution under the same mechanical condition. It is shown that loading induced stress gradient is responsible for the achievement mentioned above. To uncover the influence of the preexisting/residual stress on mechanical behavior of BMGs, we performed microvickers indentation studies of a stressed BMG. 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 indicates that indention might be a promising method to characterize residual stress in BMGs.

BMGs produced usually contain three or more elements. However, simpler systems are of great interest, fundamentally as well as technologically, since they facilitate the determination of atomic structure for a given BMG. Recently, binary Cu-Zr BMGs have been synthesized. It was found that the glass forming ability in the system strongly depends on compositions, even down to 1 at.%. Thus, to determine the atomic structure of binary Cu-Zr BMG becomes very important. Atomic structures of $Cu_{64.5}Zr_{35.5}$ BMG, together with the eutectic composition $Cu_{61.8}Zr_{38.2}$ for 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 atomic configuration of the binary $Cu_{64.5}Zr_{35.5}$ BMG is established. It is found that icosahedron-like clusters are dominant in both MGs. However, icosahedron-like clusters centred by Cu atoms are slightly denser packed and less distorted in $Cu_{64.5}Zr_{35.5}$, 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 determined 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. Atomic structures of $Cu_{46}Zr_{46}Al_8$ BMG, together with binary $Cu_{50}Zr_{50}$ MG ribbon for comparison, have been investigated. Based on the three dimensional atomic configuration of the ternary $Cu_{46}Zr_{46}Al_8$ BMG, we attempted to explain the high GFA from three aspects of the 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.

The thermal stability of pseudo-quaternary La-Al-(Cu,Ag)-(Ni,Co) bulk metallic glasses was investigated using in-situ high-energy x-ray diffraction. Using a high-speed x-ray camera (time resolution of 2 seconds) we could observe the kinetics of the glass transition and crystallization at heating rates up to 100 K/min. Furthermore we succeeded with the determination of a decent fraction of its time-temperature-transformation diagram. As a by-product we observed a thermal hysteresis when cycling La-based BMGs between room temperature and glass transition temperature. Comparing as cast and pre-annealed samples we concluded that the hysteresis effect is due to quenched in defects.

Publications

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Participation in conferences, workshops…

J.Z. Jiang: 13th International Conference on Rapidly Quenched and Metastable Materials, Dresden, Germany

Inter. Syposium on Amorphous Alloys, Hangzhou, P.R. China

J. Bednarcik: 13th International Conference on Rapidly Quenched and Metastable Materials, Dresden, Germany

9th International Workshop on Non-Crystalline Solids, Porto, Portugal

H. Franz: Inter. Syposium on Amorphous Alloys, Hangzhou, P.R. China