

Shuaidan Lu, Shuchen Sun\*, Xiaoxiao Huang, Xiaoping Zhu, Ganfeng Tu and Kuanhe Li

# Glass-forming ability and mechanical properties of a $\text{Zr}_{52.8}\text{Cu}_{29.1}\text{Ni}_{7.3}\text{Al}_{9.8}\text{Y}_1$ bulk metallic glass prepared by hereditary process

DOI 10.1515/gps-2015-0039

Received May 22, 2015; accepted July 20, 2015; previously published online August 13, 2015

**Abstract:** Zr-based bulk metallic glass possesses the highest potential as a structural material among metallic glasses. However, the production conditions have a great effect on its glass-forming ability (GFA) and mechanical characteristics. In this paper, an attempt was made to find the effect of a hereditary structure on the GFA and mechanical properties of a solid  $\text{Zr}_{52.8}\text{Cu}_{29.1}\text{Ni}_{7.3}\text{Al}_{9.8}\text{Y}_1$  bulk metallic glass in order to evaluate a novel process of using binary alloys as precursors, which have a hereditary relation to the aim metallic glass (MGs). When the quenching temperature is below the threshold overheating temperature, the hereditary process can improve the GFA and compressive strength obviously. At a quenching temperature of 1523 K, the hereditary process can improve the supercooled liquid region  $\Delta T_x$  from 33 K to 55 K and the compressive strength from 1555 MPa to 1652 MPa.

**Keywords:** bulk metallic glass; compressive strength; hereditary process; precursors; Zr-based.

## 1 Introduction

The discovery of bulk metallic glasses has stimulated widespread research enthusiasm because of their technological promise for practical applications and scientific importance in understanding glass formation and glass phenomena [1–4]. Specifically, bulk metallic glasses exhibit a rare and tantalizing combination of traits of

higher fracture strength, fracture toughness and elasticity, than their crystalline counterparts, which makes them one of the strongest engineering materials known, and because they can occupy a peculiar thermodynamic middle ground between solid and liquid, they can be processed like plastics into nanoscale textures, seamless hollow containers, and other shapes that are impossible to make with traditional metals [3, 4]. However, the major limitation of their commercial use is high cost and process requirements [4].

As a consequence, only a minute fraction of potential bulk metallic glass properties have been explored thus far. To improve the potential properties, more efficient techniques and methods are required [5–8]. In the last decade, most researches have focused on utilizing unique combinations of elements to improve the glass-forming ability (GFA) and mechanical properties of metallic glass. However, the properties of metallic glasses are closely related to the microstructure of metallic liquids. It is known that the non-crystalline structure is expected to be retained if the liquids can be quenched at a sufficiently high cooling rate to suppress the formation of equilibrium crystalline phases. So, the change of metallic liquid is made in the search for better properties of metallic glasses. And the studies have been focusing on the discussions about the microheterogeneity from different master alloys, its relations with macro-properties [9–12].

In this paper, we focus on exploring a hereditary process of preparing a  $\text{Zr}_{52.8}\text{Cu}_{29.1}\text{Ni}_{7.3}\text{Al}_{9.8}\text{Y}_1$  bulk metallic glass using binary precursors. The selected binary precursors at deep eutectic points can effectively reduce the smelting temperature, and the precursors can lower the smelting temperature of the aim product. The short and middle range order in precursors can be inherited by the metallic liquid and glass under a certain temperature. In addition, the GFA and mechanical properties of aim bulk metallic glasses prepared by the hereditary process and conventional process are evaluated and contrasted. This work demonstrates that preparing a  $\text{Zr}_{52.8}\text{Cu}_{29.1}\text{Ni}_{7.3}\text{Al}_{9.8}\text{Y}_1$  bulk metallic glass from binary precursors can be effective in improving the GFA and mechanical properties.

\*Corresponding author: Shuchen Sun, School of Materials and Metallurgy, Northeastern University, Shenyang, Liaoning 110819, P. R. China, e-mail: sunsc@smm.neu.edu.cn

Shuaidan Lu, Xiaoxiao Huang, Xiaoping Zhu, Ganfeng Tu and Kuanhe Li: School of Materials and Metallurgy, Northeastern University, Shenyang, Liaoning 110819, P. R. China

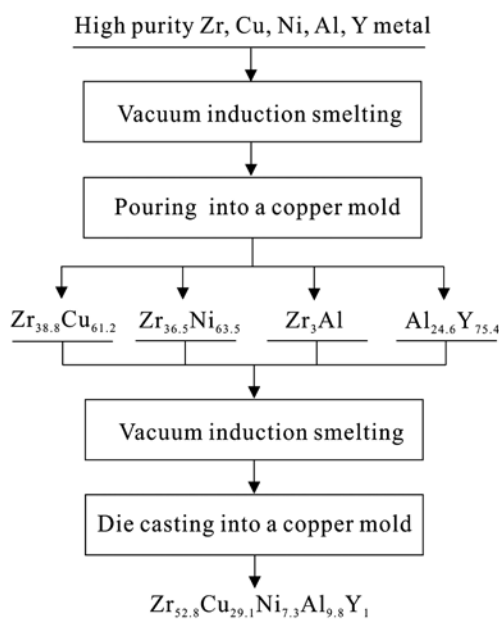
## 2 Materials and methods

The  $\text{Zr}_{52.8}\text{Cu}_{29.1}\text{Ni}_{7.3}\text{Al}_{9.8}\text{Y}_1$  metallic glass was selected as the objective in the current study. According to the principle of deep eutectic point, the  $\text{Zr}_{36.5}\text{Cu}_{63.5}$ ,  $\text{Zr}_{38.8}\text{Ni}_{61.2}$ ,  $\text{Zr}_3\text{Al}_1$  and  $\text{Al}_{24.6}\text{Y}_{75.4}$  binary alloys were selected as the precursors to smelt  $\text{Zr}_{52.8}\text{Cu}_{29.1}\text{Ni}_{7.3}\text{Al}_{9.8}\text{Y}_1$  metallic glass. The melting points and smelting temperatures of binary alloys are shown in Table 1. The smelting temperatures are selected at 100 K above the melting points, which are also much lower than the conventional metallic glass smelting temperatures. All alloys were smelted with a mixture of pure metals by using the medium-frequency induction furnace, and die casted into a copper mold with 3 mm thickness. The hereditary and conventional processes of preparing metallic glass were both used and their respective GFA and flexure strength were analyzed and contrasted. The high purity metals are supplied by Boyu nonferrous metal Co., Ltd., Shenyang, China. And the device is supplied by Jinzhou Hangxing Vacuum Equipment Co., Ltd., Jinzhou, China.

The hereditary process of preparing metallic glass is shown in Figure 1. High purity Zr (99.0 wt.%), Cu (99.99 wt.%), Ni (99.99 wt.%), Al (99.99 wt.%), Y (99.0 wt.%) metal were mixed according to the binary alloy ( $\text{Zr}_{41}\text{Cu}_{59}$ ,  $\text{Zr}_{36}\text{Ni}_{64}$ ,  $\text{Zr}_{73}\text{Al}_{27}$  and  $\text{Al}_{88}\text{Y}_{12}$ ) components ratio and smelted by using the medium-frequency induction furnace; they were then die casted into a copper mold. Next, the binary alloys obtained from quenching were mixed and smelted again as precursors to prepare the aim metallic glass. The solid binary alloys have a

**Table 1:** The melting points and smelting temperatures of binary alloys.

Binary alloy	$\text{Zr}_{36.5}\text{Cu}_{63.5}$	$\text{Zr}_{38.8}\text{Ni}_{61.2}$	$\text{Zr}_3\text{Al}_1$	$\text{Al}_{24.6}\text{Y}_{75.4}$
Melting point (K)	1343	1158	1261	1233
Smelting temperature (K)	1443	1258	1361	1333



**Figure 1:** The hereditary process of preparing  $\text{Zr}_{52.8}\text{Cu}_{29.1}\text{Ni}_{7.3}\text{Al}_{9.8}\text{Y}_1$  bulk metallic glass using precursor.

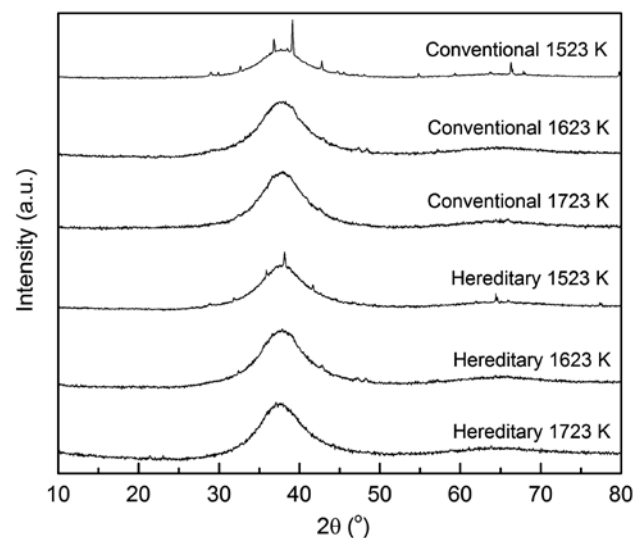
hereditary relation to the formation of an amorphous structure. The conventional process of preparing metallic glass was mixing the five kinds of purity metals and smelting them directly.

The specimens prepared were analyzed by X-ray diffraction (XRD) (X'Pert Pro, PANalytical Corporation, the Netherlands) with Cu  $K\alpha$  radiation. Differential scanning calorimetry (DSC) was performed using a TG-DSC (SDTQ600, TA Instruments, USA) in an argon atmosphere with heating rates of 20 K/s and the sample mass of  $20 \pm 1$  mg. The flexure strength was measured by using an all-powerful material test machine (AG-X 100kN, Shimadzu Corporation, Japan).

## 3 Results and discussion

Figure 2 shows the XRD patterns of samples cast at different quenching temperatures by using two types of processes. It can be seen that all of the XRD patterns mainly consist of two broad diffuse peaks between diffraction angles  $30^\circ$ – $45^\circ$  and  $55^\circ$ – $75^\circ$ , respectively. There is no apparent crystalline phase corresponding to the sharp crystallization peak, indicating that this sample is in the amorphous structure. When the quenching temperature is controlled at 1523 K, although its pattern shows broad diffuse backgrounds, but the amorphous diffuse peak are shape, the amorphous diffuse peak of 1523 K is sharper than that of 1523 K, showing that it has the trend of further crystallization, and the trend of further crystallization of 1523 K is more obvious. Thus, the threshold overheating temperature for a fully amorphous structure of  $\text{Zr}_{52.8}\text{Cu}_{29.1}\text{Ni}_{7.3}\text{Al}_{9.8}\text{Y}_1$  bulk metallic glass is at least 1623 K, below which it may have an intersection with the crystallization position.

The DSC curves of  $\text{Zr}_{52.8}\text{Cu}_{29.1}\text{Ni}_{7.3}\text{Al}_{9.8}\text{Y}_1$  bulk metallic glass prepared by two processes are shown in Figure 3. All

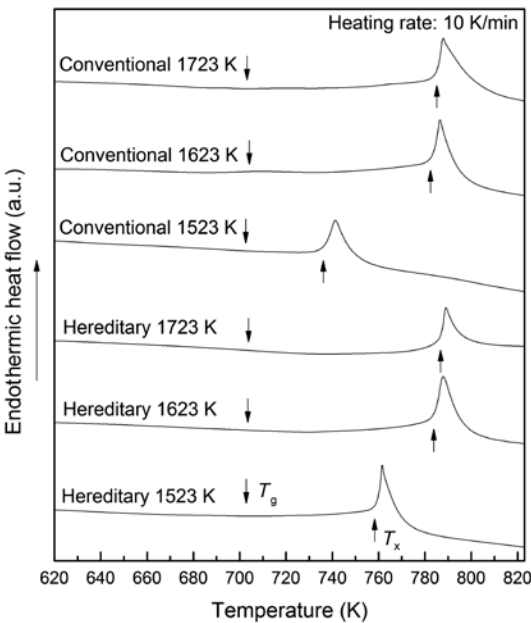


**Figure 2:** X-ray diffraction patterns of metallic glasses quenching at different temperatures and processes.

samples show an endothermic event, which is characteristic of glass transition. For the purpose of comparison, the specific temperatures of the six kinds of alloys quenching at different temperatures and processes are listed in Table 2.

The specific temperature  $T_x$  and  $\Delta T_x$  of the samples with lower quenching temperature clearly decline, which means that the short-term thermal stability of these samples is improved by using the hereditary process. The hereditary process in the content range investigated does not evidently influence the basic form of the DSC curves at different quenching temperatures, however, the specific temperature  $T_x$  and  $\Delta T_x$  of the samples at a high quenching temperature evidently rises, which means that the short-term thermal stability of the metallic glass is enhanced by overheating [13, 14].

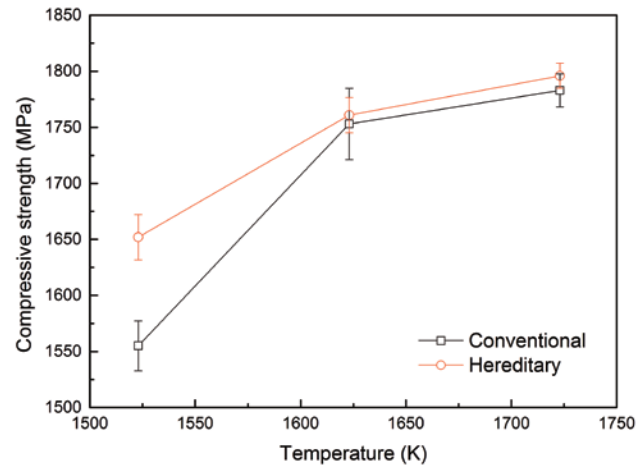
Figure 4 shows the compressive fracture strength dependence of quenching temperatures for 5 mm diameter



**Figure 3:** Differential scanning calorimetry (DSC) curves of metallic glasses quenching at different temperatures and processes.

**Table 2:** Thermodynamic parameters of metallic glasses quenching at different temperatures and processes.

Sample no.	Process	Temperature (K)	$T_g$ (K)	$T_x$ (K)	$\Delta T_x$ (K)
1	Conventional	1523	703	736	33
2	Conventional	1623	704	783	79
3	Conventional	1723	703	785	82
4	Hereditary	1523	703	758	55
5	Hereditary	1623	704	784	80
6	Hereditary	1723	703	786	83

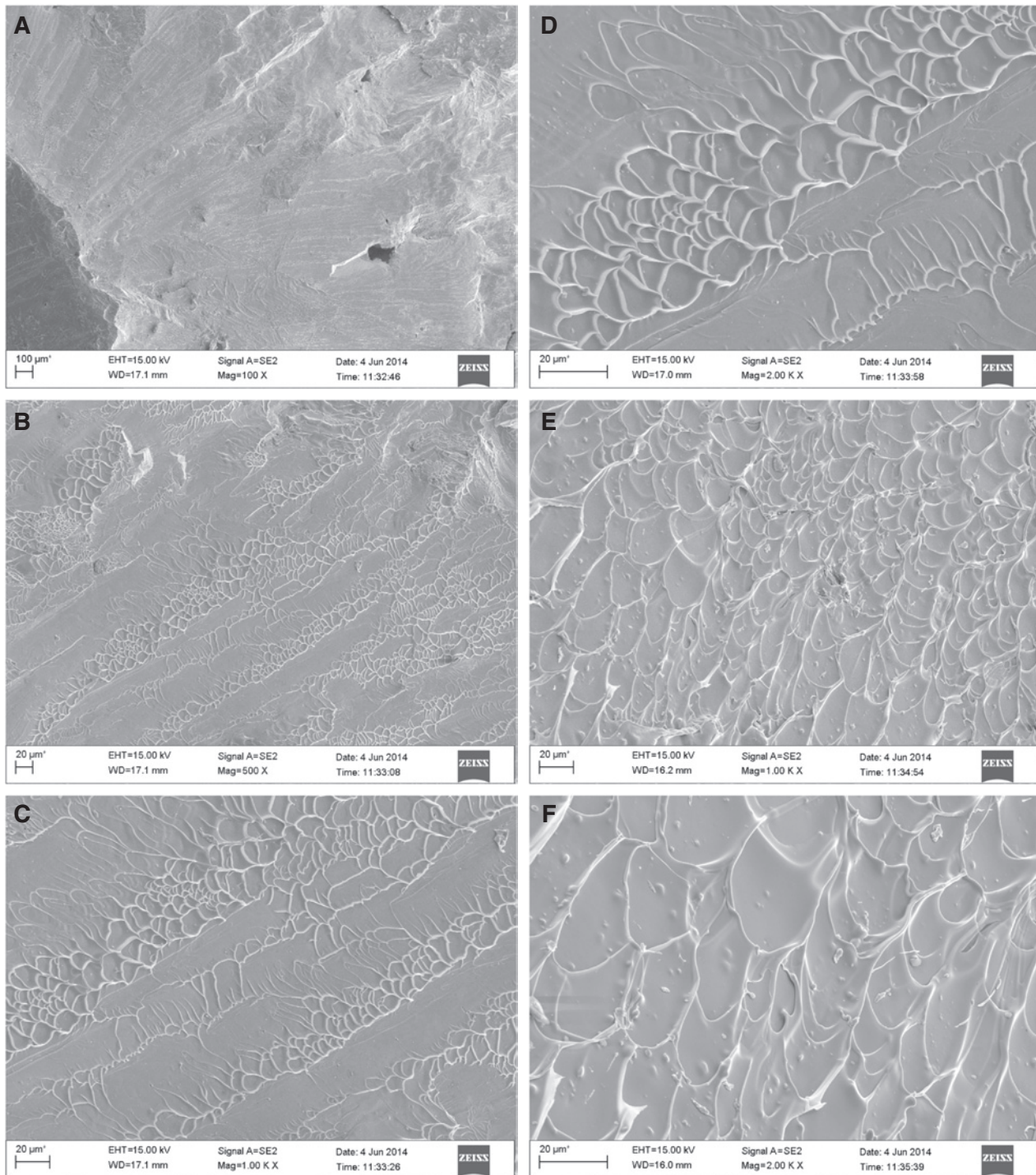


**Figure 4:** The compressive fracture strength dependence of quenching temperatures for  $Zr_{52.8}Cu_{29.1}Ni_{7.3}Al_{9.8}Y_1$  samples.

$Zr_{52.8}Cu_{29.1}Ni_{7.3}Al_{9.8}Y_1$  samples. It is found that the compressive strength increases with the increasing quenching temperature. When the quenching temperature is above the threshold overheating temperature (around 1623 K), there is no obvious change in the compressive strength. When the quenching temperature is 1523 K and below the threshold overheating temperature, the hereditary process can obviously improve the compressive strength from 1555 MPa to 1652 MPa. The compressive strength can reach 1796 MPa at a quenching temperature of 1723 K.

The typical fracture morphology of full bulk amorphous alloy is shown in Figure 5A and B; this is a typical characteristic of fracture feature with well-developed vein-like patterns. It can be seen in Figure 5B that the fracture surface is relatively flat and displays a typical shear fracture feature; such a surface has been widely observed for many other metallic glass samples [15–18]. Further observations show that the typical feature of the fracture surfaces is a vein-like structure, as shown in Figure 5C–F. This vein-like structure spreads over the whole fracture surface and extends along a uniform direction, as marked by arrows in Figure 5C. It is noted that the uniform arrangement of the veins exactly corresponds to the propagation direction of the shear band, which is confirmed by Figure 5E and F. The vein-like structure was attributed to local melting within the main shear bang induced by the high elastic energy in instantaneous fracture [17, 19]. Due to the melting of metallic glass within the main shear bang, the molten metallic glass easily flows and appears in a vein-like structure feature, as clearly shown in Figure 5D and F. For all metallic glasses, their compressive fracture surfaces nearly show the same features, a vein-like structure [20–25]. These veins on the fractography clearly





**Figure 5:** Scanning electron microscopy (SEM) micrographs revealing the compressive fracture of  $\text{Zr}_{52.8}\text{Cu}_{29.1}\text{Ni}_{7.3}\text{Al}_{9.8}\text{Y}_1$  bulk metallic glass. (A) Low magnification, (B) high magnification, (C) magnified picture of local area in (A), (D) magnified picture of local area in (C), (E) magnified picture of local area in (A) and (F) magnified picture of local area in (E).

demonstrate a pure shear fracture process of the different metallic glasses.

Based on the aforementioned results, it is clear that the hereditary process can improve mechanical properties of  $\text{Zr}_{52.8}\text{Cu}_{29.1}\text{Ni}_{7.3}\text{Al}_{9.8}\text{Y}_1$  metallic glass obviously within a

certain temperature range. Because the mechanical properties of metallic glass are mainly determined by composition and microstructure, which to a large extent is related to liquid structure, even a tiny change in the free volume could induce a dramatic effect on material behavior.

## 4 Conclusions

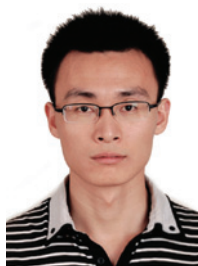
The hereditary process can improve the GFA and compressive strength at a low temperature, which would be significant for us to obtain high GFA and mechanical properties of metallic glass without high temperature melting. At a quenching temperature of 1523 K, the hereditary process can improve the supercooled liquid region  $\Delta T_x$  from 33 K to 55 K and the compressive strength from 1555 MPa to 1652 MPa. The compressive strength can reach 1796 MPa at a quenching temperature of 1723 K. The improvement of the GFA and mechanical properties of metallic glass is attributed to the smaller short-range order in the liquid inherited from the finer microstructure through the binary precursors. This give the hereditary process advantages of lower energy consumption and equipment requirements, which leads to outstanding application potentials.

## References

- [1] Wang WH. *Prog. Mater. Sci.* 2007, 52, 540–596.
- [2] Caron A, Wunderlich R, Louzguine-Luzgin DV, Xie G, Inoue A, Fecht HJ. *Acta Mater.* 2010, 58, 2004–2013.
- [3] Byrne CJ, Eldrup M. *Science* 2008, 321, 502–503.
- [4] Chen M. *NPG Asia Mater.* 2011, 3, 82–90.
- [5] Schroers J. *J. Metals* 2005, 57, 35–39.
- [6] Schroers J. *Phys. Today* 2013, 66, 32–37.
- [7] Anderson PW. *Science* 1995, 267, 1615–1616.
- [8] Axinte EM, Chirileanu MPI. *Recent Pat. Mater. Sci.* 2012, 5, 213–221.
- [9] Idzikowski B, Švec P, Miglierini M. *Properties and Applications of Nanocrystalline Alloys from Amorphous Presursors*, Kluwer Academic Publishers: USA, 2003.
- [10] Spaepen F. *Scripta Mater.* 2006, 54, 363–367.
- [11] Wang WH. *Nat. Mater.* 2012, 11, 275–276.
- [12] Torquato S. *Nature* 2000, 37, 341–347.
- [13] Yan ZJ, Li JF, He SR, Wang HH, Zhou YH. *Mater. Lett.* 2003, 57, 1840–1843.
- [14] Zhang SG, Xia MX, Hu GH, Li JG. *J. Non-Cryst. Solids* 2010, 356, 2223–2227.
- [15] Donovan PE. *Mater. Sci. Eng.* 1988, 98, 487–490.
- [16] Sunny G, Prakash V, Lewandowski JJ. *Metall. Mater. Trans. A* 2013, 44, 4644–4653.
- [17] Wright WJ, Samale MW, Hufnagel TC, LeBlanc MM, Florando JN. *Acta Mater.* 2009, 57, 4639–4648.
- [18] He G, Lu J, Bian Z, Chen D, Chen G, Tu G, Chen G. *Mater. Trans., JIM* 2001, 42, 356–364.
- [19] Liu CT, Heatherly L, Horton JA, Easton DS, Carmichael CA, Wright JL, Schneibel JH, Yoo MH, Chen CH, Inoue A. *Metall. Mater. Trans. A* 1998, 29, 1811–1820.
- [20] Guduru RK, Darling KA, Scattergood RO, Koch CC, Murty KL, Bakka M, Shih AJ. *Intermetallics* 2006, 14, 1411–1416.
- [21] Zhang ZF, Eckert J, Schultz L. *Acta Mater.* 2003, 51, 1167–1179.
- [22] Inoue A, Kimura HM, Zhang T. *Mater. Sci. Eng. A* 2000, 277, 294–296.
- [23] Mukai T, Nieh TG, Kawamura Y, Inoue A, Higashi K. *Intermetallics* 2002, 10, 1071–1077.
- [24] Heilmaier M. *J. Mater. Proc. Tech.* 2001, 117, 374–380.
- [25] Subhash G, Dowling RJ, Kecskes LJ. *Mater. Sci. Eng. A* 2002, 334, 33–40.

## Bionotes

Shuaidan Lu



Shuaidan Lu is a PhD student at Northeastern University, China. His primary research interests include metallic glass, metallurgy and material preparation technology. He is currently carrying out research on the preparation of Zr-based metallic glass by the hereditary process.

Shuchen Sun



Shuchen Sun is an Associate Professor and a Master's supervisor at Northeastern University. His research interests include the metallurgy and applications of rare earth, the preparation and application of borides, and bulk metallic glass.

Xiaoxiao Huang



Xiaoxiao Huang is a PhD student at Northeastern University. He is currently carrying out research on the preparation of bulk metallic glass by the hereditary process and TiB<sub>2</sub> by using the chemical vapor deposition method.

**Xiaoping Zhu**

Xiaoping Zhu is a PhD student at Northeastern University. His primary research interests include the metallurgy processing of rare earth, rare earth metal and alloys.

**Kuanhe Li**

Kuanhe Li is a Master's student at Northeastern University. He is currently carrying out research on the preparation of bulk metallic glass.

**Ganfeng Tu**

Ganfeng Tu is a PhD supervisor at Northeastern University and is mainly engaged in the metallurgy and application of rare earth, the preparation and application of alloys, and the comprehensive utilization of metallurgical resources.