Plasticity Enhancement of Composite and Nanoscaled Metallic Glasses

D. Şopu, M. Stoica, J. Eckert

published in

NIC Symposium 2018
K. Binder, M. Müller, A. Trautmann (Editors)

Forschungszentrum Jülich GmbH,
John von Neumann Institute for Computing (NIC),
Schriften des Forschungszentrums Jülich, NIC Series, Vol. 49,
ISBN 978-3-95806-285-6, pp. 281.
http://hdl.handle.net/2128/17544

Plasticity Enhancement of Composite and Nanoscaled Metallic Glasses

Daniel Şopu[1,3], Mihai Stoica[2], and Jürgen Eckert[3]

[1] Institute of Materials Science, Technische Universität Darmstadt,
Jovanka-Bontschits-Str. 2, 64287 Darmstadt, Germany
E-mail: sopu@mm.tu-darmstadt.de

[2] Laboratory of Metal Physics and Technology, Department of Materials, ETH Zurich,
8093 Zurich, Switzerland
E-mail: mihai.stoica@mat.ethz.ch

[3] Erich Schmid Institute of Materials Science, Austrian Academy of Sciences,
Jahnstraße 12, 8700 Leoben, Austria
E-mail: juergen.eckert@unileoben.ac.at

Under tensile loading at low temperature metallic glasses generally fail in a brittle manner. So far, significant tensile ductility has been observed if heterogeneities, such as crystalline secondary phases, are introduced into the glassy matrix or when reducing the size of metallic glass samples down the nanoscale regime. Here, we perform molecular dynamics simulations on $Cu_{64}Zr_{36}$ composite structures reinforced with B2 CuZr nanowire and investigate how the martensitic phase transformation and the distribution of these precipitates influence the mechanical deformation mechanisms. Additionally, we provide an atomistic understanding of the deformation mechanisms of metallic glass nanowires and differentiate the extrinsic size effects and aspect ratio contribution to plasticity.

1 Introduction

Bulk metallic glasses (BMGs) have gained a great deal of interest due to advantageous mechanical properties, such as high yield strength and a large elastic limit[1]. Despite the great potential of BMGs to be used as structural materials the inverse strength-ductility-functionality problem, namely, materials either have high strength but lack ductility (i.e. are brittle and hard to form) or they are highly ductile but lack strength, significantly limits the application of these materials. However, significant ductility can be attained when heterogeneities, such as crystalline secondary phases[2], pre-induced shear bands[3], soft glass-glass interfaces[4,5] or pores[6] are introduced into the metallic glass. The role of soft heterogeneities is to introduce strain concentrations which act as initiation sites for shear bands, resulting in the formation of a highly organised pattern of multiple shear bands.

A straightforward strategy to improve the plasticity of BMGs is to synthesise BMG matrix composites[7]. The composite materials are heterogeneous microstructures combining a glassy matrix with crystalline secondary phases[2]. The interactions between the reinforcing second phase and shear bands (SBs) significantly retards fracture. The enhanced ductility is attributed to those composites reinforced with a high volume fraction of ductile crystalline phase. Nevertheless, a high volume fraction of soft precipitates improves the ductility of the composites but sacrifices their strength[8]. On the other hand, CuZr-based BMG composites reinforced with B2 CuZr precipitates show extraordinary plasticity together with work hardening capability in compression tests. It was suggested that B2 crystallites exhibit a martensitic transformation from a B2 to a B19' structure, which is reversible and renders it a shape-memory alloy[9], and which is the reason for the pronounced work hardening of this phase[10]. Because the understanding of the deformation mechanism of BMG composites reinforced with martensitic inclusion is still incomplete, a theory on the shear band nucleation and interaction with martensites on the atomic scale is highly desirable.

The second strategy to gain significant tensile ductility is to reduce the length scale of the glassy samples. A transition from brittle behaviour to tensile ductility and homogeneous plastic flow has been observed in nano-sized metallic glasses with dimensions of the order of 100 nm[11]. However, other studies showed that plastic deformation in compression is always size-independent and localised in shear bands[12]. Moreover, simulation results support the picture of size-independent shear banding until sample dimensions approach the shear band thickness[13]. It is believed that the different mechanical responses are reflected sensitively in the processing route of how the wires are made. The long exposure to high-energy ions incurred during FIB milling was claimed to affect the structure and properties of nanowires, inducing the unusual room temperature ductility[14]. As we will see in this study, two characteristics are important for the deformation behaviour under tensile load of nano-sized metallic glasses: the aspect ratio (length to diameter ratio, L:d) and the structure of the nanowire[6]. Moreover, we will show that by modifying the atomic structure of a brittle nanowire through systematic structural rejuvenation, in terms of creating free volume and disturbing the short-range order (SRO), enhanced tensile ductility can be attained.

2 Computational Methods

To understand the underlying mechanisms and achieve an atomistic level description of the deformation mechanism, molecular dynamics (MD) simulation proved useful at this stage. MD computer simulations using the software LAMMPS[15] were used to capture the competing deformation mechanism in martensitic inclusions and glassy matrix of the composite and to discriminate between the extrinsic size effects and aspect ratio contribution to the plasticity of nanowires. The $Cu_{64}Zr_{36}$ glass was simulated using the Finnis-Sinclair type potential by Mendelev *et al.*[16]. A metallic glass cubic cell containing 8000 atoms was produced by quenching it from the melt to 50 K with a cooling rate of 10^{10} K/s. Samples of different dimensions will be then obtain by replicating this glassy block. Uniaxial tensile tests were conducted on all systems at 50 K with a constant strain rate of 4×10^{7} $1/s$. The atomic scale deformation mechanisms were analysed by visualising the local atomic shear strain μ^{Mises}[17] and Common Neighbour Analysis (CNA)[18], calculated with the OVITO analysis and visualisation software[19].

3 Metallic Glass Composites Reinforced with Shape Memory Alloys

We investigated the deformation chain reaction in shape memory BMG composites in order to understand the reason for the enhanced ductility and work-hardening observed in these type of composites[20]. To that end we prepared a slab-shaped $Cu_{64}Zr_{36}$ glass sample with dimensions of $L_x \times L_y \times L_z$ = 36 x 7.5 x 84 nm^3 and a total number of 1296000 atoms by

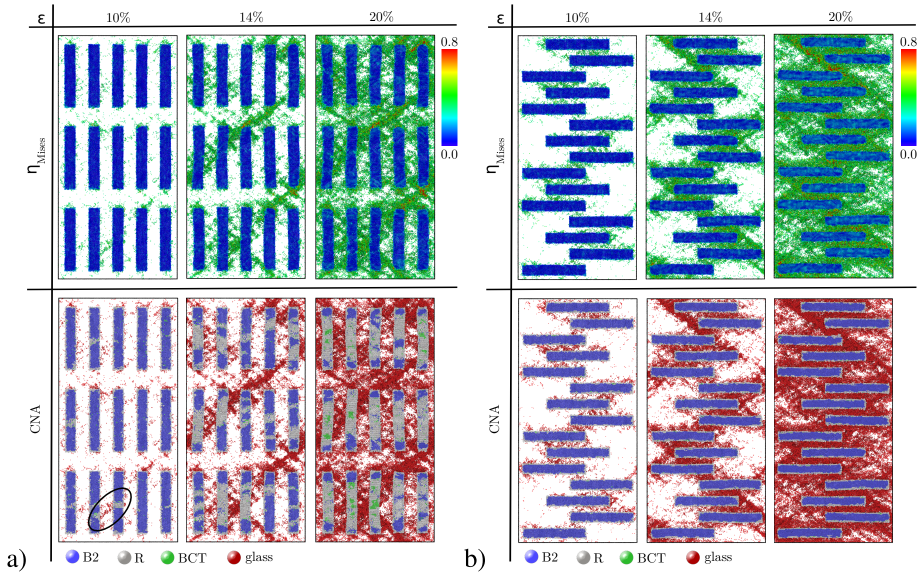

Figure 1. Local atomic shear strain and CNA for $Cu_{64}Zr_{36}$ BMG composites containing 15 CuZr B2 nanowires distributed along (a) and normal (b) to the deformation direction. In order to capture the stress-induced martensitic transformation in the B2 crystalline phase only half of the structure and those atoms with an atomic strain higher than 0.3 are shown. Figures taken with permission from Ref. 21.

replicating the initial glassy block. Two 3D-periodic bulk composites are constructed by inserting 15 B2 CuZr nanowires of cross-sectional dimensions of 3.22×3.22 nm^2 and a length of 19.4 nm into the monolithic glass while deleting the glassy atoms which overlap to the crystalline ones.

In Fig. 1(a) the local atomic shear strain together with the CNA are presented for the case of the BMG composite with nanowires arranged along the deformation direction (z-direction), and we will call this throughout the paper Clongitudinal. For better visualisation just half of the sample and only the nanowires and those atoms of the glassy matrix with an atomic strain higher than 30% are shown. At a strain of 10% shear transformation zones (STZ) start forming around the amorphous-crystalline interface. Additionally, some nanowires show a stress-induced martensitic transformation from the B2 phase to an intermediated R-phase. Under the applied strain small embryonic SBs nucleate at the interface and propagate through the glass but, they are immediately blocked by the next nanowires. Once the SB hits the next nanowire the stress at the tip of the SB induce phase transformation in the crystalline phase (see Fig. 1(a)). Moreover, these embryonic shear bands continue to transform leading to broadening of the shear bands. The deformation mechanism described in MD simulations closely resemble to the one observed in experiments by Chen *et al.*[22]. CuZr-based BMG composites show extraordinary plasticity together with work hardening capability in compression tests. The width increase of a shear band reduces the elastic shear stress and shear strain in the vicinity of the nanowires, and thereby impedes the further propagation of the shear band because higher applied force will be required to maintain the shear stress that can keep the shear flow continuously along the band. Hence, even at a strain of 20% none of these embryonic SBs become critical being confined between the crystalline nanowires, ensuring a homogeneous deformation of the BMG composite. In addition, all nanowires show martensitic transformation under uniaxial tension. In Fig. 1(a), bottom panel, it can be seen that all nanowires partially transform from the B2 phase (blue atoms) to an intermediate R-phase (gray atoms) and finally, from the R-phase to the body-centred-tetragonal phase (BCT) coloured in green.

Based on these results an interesting question arises: how does the stress-induced phase transformation affect the deformation mechanism of BMG composite? In order to answer the question we have constructed a composite with the same number and type of nanowires but with a different spatial distribution that under loading will show no martensitic transformation. Basically, the nanowires are now distributed normal to the loading direction (named Ctransversal) as can be seen in Fig. 1(b). Although the Ctransversal composite was deformed following the same procedure as in the first case of the Clongitudinal composite, the plastic behaviour suffers great modifications. First, it can be easily seen that plastic strain in Ctransversal is more localised than in Clongitudinal composite which means a higher probability for SB slip activation. The martensitic transformation in the systematically distributed nanowires distributes homogeneously the applied strain and widens the plastic zone. Besides, the strain is highly localised in the Ctransversal composite and confined between the nanowires. Secondly, there is a big difference in the number of atoms involved in plastic deformation when compared the two composites. The lacking of phase transformation in the crystalline phase, which is normally driven by the elastic energy release, resulted in a higher fraction of percolated STZs in the Ctransversal composite and, consequently, an increased probability for the formation of mature shear bands.

4 Metallic Glass Nanowires

4.1 Effect of Aspect Ratio

Next, we studied the transition from brittle to ductile behaviour observed in metallic glass nanowires[23]. Hence, cylindrical-shaped metallic glass nanowires were prepared via bulk cutting from a sample obtained by replicating the initial quenched $Cu_{64}Zr_{36}$ glassy block. For this case, periodic boundary condition was only imposed along the axial direction, while the lateral directions were left free.

Fig. 2 shows the stress-strain curves of two nanowires with a diameter of $d = 20$ nm and aspect ratio of 3 and 12.5, respectively, together with a sequence of snapshots of the local atomic shear strain evolution during deformation. Regardless of the aspect ratio, within the elastic regime, both nanowires behaved in the same manner. Once the maximum stress is overcome, the two nanostructures show radically different plastic regimes. Although in both cases plastic deformation starts at almost the same strain level of 9% and is localised in shear bands, only the nanowire with the high aspect ratio fail catastrophically under tensile load following the sudden initiation and propagation of one shear band. This is consistent with the stress drop to zero in the stress-strain curve, as illustrated in Fig. 2. Moreover, despite the fact that three shear bands nucleate, only one of them goes critical mediating the plasticity of the long nanowire. With decreasing the aspect ratio, a shear band sets in, but the slip is arrested and the nanowire undergoes a finite stress drop. The nanowire will continue to deform plastically and the shear band will develop extensively

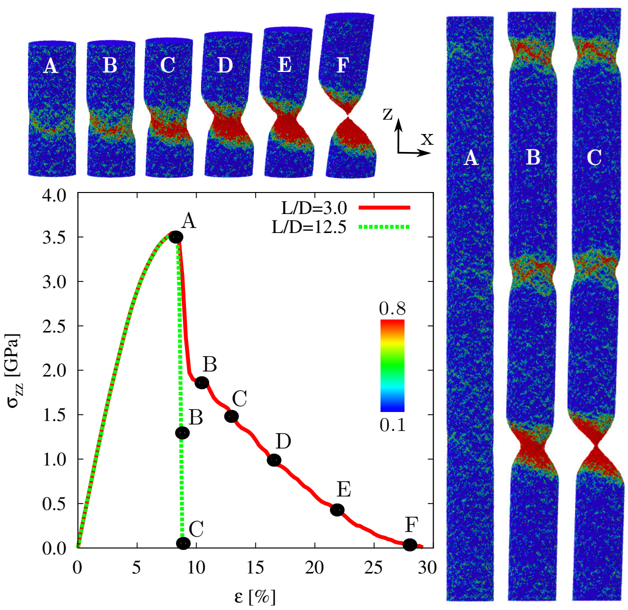

Figure 2. Uniaxial tensile stress-strain curves together the most representative snapshots of the local atomic shear strain along the deformation of two $Cu_{64}Zr_{36}$ glass nanowires with aspect ratio of 3 (panels A to F, up) and 12.5 (panels A to C, at right), respectively. The colour scale indicates the atomic local shear strain. Figure taken with permission from Ref. 23.

and gradually leading to an extended plastic strain of 28% before failure (see Fig. 2) . Based on a simple theoretical model we showed that a complete plastic deformation and fracture under shearing can be achieved only if the aspect ratio of the sample is large enough and inverse proportional to the elongation of the sample[23]. For a $Cu_{64}Zr_{36}$ alloy composition we expect the failure mode transition to occur at critical L:d = 12.5.

4.2 Effect of Structural Rejuvenation

Further, we analysed the effects of structural rejuvenation on the plastic behaviour of metallic glass nanowires. Evidence that irradiation strongly influences the mechanical response of metallic glasses through structural changes and manifested as a decrease in yield stress and ductile-like mode deformation have been experimentally disclosed[24]. Here, the ion irradiation appears to act as an agent for glass rejuvenation manifested as increase in the free volume. Hence, to emulate the irradiated nanowires and, consequently, to simulate the rejuvenation process we randomly remove atoms in the brittle nanowire with high aspect ratio. After diluting by 10 % both structures relax to a density distribution with 2% density difference to the bulk sample in maximum, which matches the flow strain of the homogeneous sample[4]. The difference in the density is also related to the strong variation in the degree of SRO. The common topological feature of SRO in amorphous Cu-Zr is the dominance of Cu-centred full-icosahedral (FI) clusters[25]. These FI units have a high

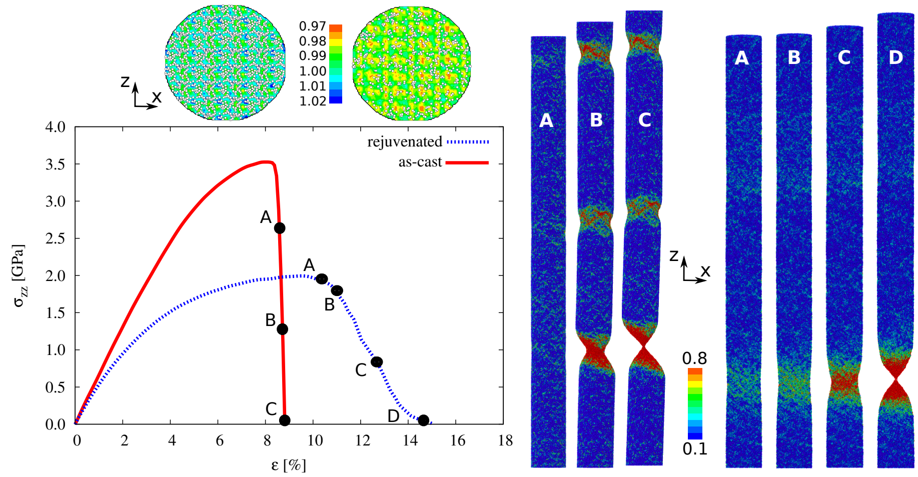

Figure 3. Tensile stress-strain curves together with representative snapshots of the local atomic shear strain along the deformation of the as-cast and rejuvenated nanowires and having an aspect ratio of 12.5. Left hand side panels (A to C) show the localised plastic behaviour in the as-cast nanowire while the right side panels (A to D) display the transition from brittle to extended plastic behaviour when the nanowire is subjected to structural rejuvenation. Contour maps showing the atomic volume distribution relative to the bulk value in the rejuvenated nanowires in comparison to the as-cast sample are shown in the inset of the figure. The circles mark the locations of the FI local motifs within a thin slab of a thickness of 5 nm cut out of the cylindrical nanowires.

packing density and shear resistance[26]. The contour maps of Fig. 3 display the evolution of the FIs clusters together with the atomic volume distribution in the rejuvenated nanowire in comparison to the as-cast one. The fraction of Cu-centred FIs is as low as 14% in the diluted glass compared to average FI value of the as-cast glass of about 22% (with respect to the number of Cu atoms in the system). Hence, the systematic modification of the structure through dilution coupled with the structural softening process observed in the ion-irradiated nanoscaled metallic glasses.

The rejuvenated and as-cast nanowires are deformed following the same procedure as before. The first effect observed after structural rejuvenation is a reduction in the yield stress as shown in Fig. 3. For the nanowire displaying increased structural softening the yield stress decreases from 3.5 to only 2 GPa. As the FI clusters have a high shear resistance[26], a decrease in the total amount of FI clusters can explain the decrease in yield stress. As shown in Fig. 3, the sample experienced obvious necking prior to the final fracture. The necked region enlarged and spread out gradually, and the extensive necking led to a total elongation to failure of 15%, a typical characteristic of ductile deformation. Therefore, we believe that a transition in the mechanical responses of metallic glass nanowires can be attained through structural rejuvenation of a large volume fraction of the sample resulting in a more softer structure that facilitates an entirely distinct mechanism for accommodating plasticity via homogeneous flow at low temperature. The observed transition in the deformation modes are consistent with the experimental prediction, so that, in nanowires that have been subjected to FIB processing or ion irradiation, the plastic behaviour is largely controlled by the irradiated volume of the specimen.

5 Conclusions

The mechanical properties of metallic glasses can be tailored by systematically introducing heterogeneities in the glassy matrix or reducing the size of metallic glass samples down the nanoscale regime. When the heterogeneities have shape memory characteristics BMG composites show enhanced plasticity together with work hardening capability. The competing deformation mechanism in martensitic inclusions and glassy matrix results in the formation of a pattern of broad and delocalised multiple shear bands and a lower fraction of percolated STZs. When the sample length scale is in the range of nanometres, our simulations show that the aspect ratio and the structural rejuvenation play the critical role in the plastic behaviour of metallic glass nanowires. Above a critical aspect ratio, nanowires fail catastrophically under tensile load subsequent to the initiation and propagation of one shear band. Besides, in nanowires with an aspect ratio lower than the critical value the shear slip is arrested and an extended plastic strain is observed. Additional plastic strain can be achieve by changing the structural state of the nanowires in terms of creating free volume and disturbing the short-range order.

Acknowledgements

The authors gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft (DFG) through project grant no. SO 1518/1-1 and the European Research Council under the ERC Advanced Grant INTELHYB (grant ERC-2013-ADG-340025). Computing time was granted within the scope of project HDR10 by the John von Neumann Institute for Computing (NIC) and provided on the supercomputer JUROPA and JURECA at Jülich Supercomputing Centre (JSC).

References

1. A. Inoue, *Stabilization of metallic supercooled liquid and bulk amorphous alloys*, Acta Mater. **48(1)**, 279–306, 2000.
2. J. Eckert, J. Das, S. Pauly, and C. Duhamel, *Mechanical properties of bulk metallic glasses and composites*, J. Mater. Res. **22**, 285–301, 2007.
3. S. Scudino, K. B. Surreddi, and J. Eckert, *Mechanical properties of cold-rolled zr60ti5ag5cu12.5ni10al7.5 metallic glass*, Phys. Status Solidi A **207(5)**, 1118–1121, 2010.
4. D. Şopu, K. Albe, Y. Ritter, and H. Gleiter, *From nanoglasses to bulk massive glasses*, Appl. Phys. Lett. **94(19)**, 191911, 2009.
5. D. Şopu, Y. Ritter, H. Gleiter, and K. Albe, *Deformation behavior of bulk and nanostructured metallic glasses studied via molecular dynamics simulations*, Phys. Rev. B **83(10)**, 100202, 2011.
6. D. Şopu, C. Soyarslan, B. Sarac, S. Bargmann, M. Stoica, and J. Eckert, *Structure-property relationships in nanoporous metallic glasses*, Acta Mater. **106**, 199–207, 2016.
7. C. Fan and A. Inoue, *Improvement of mechanical properties by precipitation of nanoscale compound particles in zr-cu-pd-al amorphous alloys*, Mater. Trans., JIM **38(12)**, 1040–1046, December 1997.

8. D. C. Hofmann, J. Y. Suh, A. Wiest, G. Duan, M. L. Lind, M. D. Demetriou, and W. L. Johnson, *Designing metallic glass matrix composites with high toughness and tensile ductility* Nature **451(7182)**, 1085–U3, 2008.
9. Yu. N. Koval, G. S. Firstov, and A. V. Kotko, *Martensitic transformation and shape memory effect in zrcu intermetallic compound*, Scripta Metall. Mater. **27(11)**, 1611–1616, 1992.
10. S. Pauly, G. Liu, G. Wang, U. Kühn, N. Mattern, and J. Eckert, *Microstructural heterogeneities governing the deformation of cu47.5zr47.5al5 bulk metallic glass composites*, Acta Materialia **57(18)**, 5445–5453, 2009.
11. H. Guo, P. F. Yan, Y. B. Wang, J. Tan, Z. F. Zhang, M. L. Sui, and E. Ma, *Tensile ductility and necking of metallic glass*, Nat. Mater. **6(10)**, 735–739, 2007.
12. B. E. Schuster, Q. Wei, T. C. Hufnagel, and K. T. Ramesh, *Size-independent strength and deformation mode in compression of a pd-based metallic glass*, Acta Mater. **56(18)**, 5091–5100, 2008.
13. Y. F. Shi, *Size-independent shear band formation in amorphous nanowires made from simulated casting*, Appl. Phys. Lett. **96(12)**, 121909, 2010.
14. L. Liu, M. Hasan, and G. Kumar, *Metallic glass nanostructures: fabrication, properties, and applications*, Nanoscale **6**, 2027–2036, 2014.
15. S. Plimpton, *Fast parallel algorithms for short-range molecular-dynamics*, J. Comput. Phys. **117(1)**, 1–19, 1995.
16. M. I. Mendelev, D. J. Sordelet, and M. J. Kramer, *Using atomistic computer simulations to analyze x-ray diffraction data from metallic glasses*, J. Appl. Phys. **102(4)**, 043501, 2007.
17. F. Shimizu, S. Ogata, and J. Li, *Theory of shear banding in metallic glasses and molecular dynamics calculations*, Mater. Trans. **48(11)**, 2923–2927, November 2007.
18. J. Dana. Honeycutt and Hans C. Andersen, *Molecular dynamics study of melting and freezing of small lennard-jones clusters*, J. Phys. Chem. **91(19)**, 4950–4963, 1987.
19. A. Stukowski, *Visualization and analysis of atomistic simulation data with ovito-the open visualization tool*, Modell. Simul. Mater. Sci. Eng. **18(1)**, 015012, 2010.
20. D. Şopu, M. Stoica, and J. Eckert, *Deformation behavior of metallic glass composites reinforced with shape memory nanowires studied via molecular dynamics simulations*, Appl. Phys. Lett. **106(21)**, 211902, 2015.
21. D. Şopu and K. Albe, *Influence of grain size and composition, topology and excess free volume on the deformation behavior of CuZr nanoglasses*, Beilstein J. Nanotech. **6**, 537–545, 2015.
22. M. Chen, A. Inoue, W. Zhang, and T. Sakurai, *Extraordinary plasticity of ductile bulk metallic glasses*, Phys. Rev. Lett. **96**, 245502, 2006.
23. D. Şopu, A. Foroughi, M. Stoica, and J. Eckert, *Brittle-to-ductile transition in metallic glass nanowires*, Nano Letters **16(7)**, 4467–4471, July 2016.
24. D. J. Magagnosc, R. Ehrbar, G. Kumar, M. R. He, J. Schroers, and D. S. Gianola, *Tunable tensile ductility in metallic glasses*, Sci. Rep. **3**, 1096, 2013.
25. Y. Q. Cheng, E. Ma, and H. W. Sheng. *Atomic level structure in multicomponent bulk metallic glass*, Phys. Rev. Lett. **102(24)**, 245501, 2009.
26. J. C. Lee, K. W. Park, K. H. Kim, E. Fleury, B. J. Lee, M. Wakeda, and Y. Shibutani, *Origin of the plasticity in bulk amorphous alloys*, J. Mater. Res. **22(11)**, 3087–3097, November 2007.