Structure, Mechanical Properties and Post-processing of Nano-structured Metallic Glasses

Dissertation

zur Erlangung des akademischen Grades eines

Doktor-Ingenieurs

(DR.-ING.)

der Fakultät für Ingenieurwissenschaften,
Informatik und Psychologie der Universität Ulm

von

Yue Dong

aus Hegang, China

Gutachter: Prof. Dr. Hans-Jörg Fecht
Prof. Dr. Alex Dommann
Prof. Dr. Jian-Zhong Jiang

Amtierender Dekan: Prof. Dr.-Ing. Maurits Ortmanns

Ulm, 04.12.2020
Prof. Dr. Hans-Jörg Fecht
Institute of Functional Nanosystems, University Ulm, Albert-Einstein Allee 47, 89081 Ulm, Germany

Prof. Dr. Alex Dommann
"Materials meet Life", Swiss Federal Laboratories for Materials Science and Technology, Lerchenfeldstrasse 5, 9014 St.Gallen, Switzerland

Prof. Dr. Jian-Zhong Jiang
International Center for New-Structured Materials, State Key Laboratory of Silicon Materials and School of Materials Science and Engineering, Zhejiang University, 310027 Hangzhou, China
Parts of this dissertation are already published in the following articles:


Table of Contents

1. INTRODUCTION AND MOTIVATION ................................................................................. 1

1.1. GLASSES AND GLASS FORMATION ........................................................................... 3
  1.1.1. DEFINITION OF GLASSES ............................................................................... 3
  1.1.2. GLASS TRANSITION .................................................................................... 3

1.2. METALLIC GLASSES ................................................................................................. 10
  1.2.1. SYNTHESIS OF METALLIC GLASSES ............................................................... 10
  1.2.2. RESEARCH METHODS ON STRUCTURE OF METALLIC GLASSES ....................... 14
  1.2.3. STRUCTURAL RELAXATION AND REJUVENATION OF METALLIC GLASSES ............ 14

1.3. MECHANICAL PROPERTIES OF METALLIC GLASSES .............................................. 17
  1.3.1. ELASTIC PERFORMANCE ............................................................................. 17
  1.3.2. PLASTIC DEFORMATION AND SHEAR BANDS ................................................. 18
  1.3.3. DEFORMATION ON HETEROGENEOUS BMGs .................................................. 23
  1.3.4. PLASTIC DEFORMATION TREATMENTS ON METALLIC GLASSES ....................... 25

1.4. RESEARCH MOTIVATION ......................................................................................... 29

2. EXPERIMENTAL PROCEDURES .................................................................................... 31

2.1. MATERIALS USED IN THIS RESEARCH ................................................................. 33
  2.2. SAMPLE PREPARATION ..................................................................................... 35
    2.2.1. STRUCTURAL RELAXATION ....................................................................... 35
    2.2.2. THERMAL CYCLING TREATMENT ............................................................... 35
    2.2.3. HIGH-PRESSURE TORSION (HPT) ............................................................... 35

2.3. THERMAL ANALYSIS ............................................................................................ 37

2.4. STRUCTURAL CHARACTERIZATION ...................................................................... 38
  2.4.1. X-RAY DIFFRACTION (XRD) ....................................................................... 38
  2.4.2. SCANNING ELECTRON MICROSCOPY (SEM) .................................................. 38
  2.4.3. TRANSMISSION ELECTRON MICROSCOPY (TEM) ........................................... 39
  2.4.4. SYNCHROTRON RADIATION X-RAY ANALYSIS ............................................. 40
  2.4.5. THREE DIMENSIONAL ATOMIC PROBE TECHNIQUE (3D-APT) ......................... 42

2.5. MECHANICAL PROPERTIES MEASUREMENTS ...................................................... 43
  2.5.1. ULTRASOUND PULSE-ECHEL TECHNIQUE .................................................... 43
  2.5.2. VICKERS HARDNESS .................................................................................. 43
  2.5.3. NANOINDENTATION .................................................................................... 44
  2.5.4. IN-SITU TENSILE/COMPRESSION TEST ....................................................... 47

3. EXPERIMENTAL RESULTS ......................................................................................... 49

3.1. STRUCTURE OF NANOSTRUCTURED BMGs ............................................................ 51

3.2. PROPERTIES OF NANOSTRUCTURED BMGs ....................................................... 56
  3.2.1. THERMAL PROPERTIES ............................................................................. 56
  3.2.2. MECHANICAL PROPERTIES ...................................................................... 56

3.3. ANNEALING TREATMENT ON HOMOGENEOUS AND NANOHETEROGENEOUS BMGs .................................................. 59
  3.3.1. EFFECT OF ANNEALING ON THERMAL PROPERTIES OF HOMOGENEOUS BMGs .................................................. 60
3.3.2.  EFFECT OF ANNEALING ON THERMAL PROPERTIES OF NANOHETEROGEOUS BMGs ........................................ 61
3.3.3.  EFFECT OF ANNEALING ON MECHANICAL PROPERTIES ........................................................................... 62
3.4.  THERMAL CYCLING TREATMENT ON HOMOGENEOUS AND NANOHETEROGEOUS BMGs .................. 63
3.4.1.  EFFECT OF THERMAL CYCLING ON STRUCTURES AND THERMAL PROPERTIES ...................................... 63
3.4.2.  EFFECT OF THERMAL CYCLING ON MECHANICAL PROPERTIES .............................................................. 64
3.5.  SEVERE PLASTIC DEFORMATION ON HOMOGENEOUS AND NANOHETEROGENEOUS BMGs ............... 67
3.5.1.  EFFECT OF SEvere PLASTIC DEFORMATION ON STRUCTURE AND THERMAL PROPERTIES .................. 67
3.5.2.  EFFECT OF SEvere PLASTIC DEFORMATION ON MECHANICAL PROPERTIES ........................................... 70

4.  DISCUSSION .................................................................................................................................................. 75

4.1.  EFFECT OF COBALT ON THERMODYNAMICS OF SUPERCOOLED LIQUID ................................................. 77
4.2.  MECHANICAL PROPERTY ENHANCEMENT OF NANOSTRUCTURED BMGs ............................................. 80
4.2.1.  IMPROVED ELASTIC PROPERTIES ........................................................................................................ 80
4.2.2.  SHEAR BAND BEHAVIOR DURING PLASTIC DEFORMATION .............................................................. 83
4.3.  STRUCTURE RELAXATION OF BMGs DURING ANNEALING ....................................................................... 85
4.3.1.  STRUCTURE RELAXATION OF BMGs AT DIFFERENT TEMPERATURES .................................................. 85
4.3.2.  STRUCTURE RELAXATION OF BMGs WITH DIFFERENT LIQUID “FRAGILITY” ........................................ 87
4.4.  FREE VOLUME AND MECHANICAL BEHAVIOR OF THERMALLY CYCLED BMGs ................................... 91
4.5.  ENHANCEMENT MECHANISM OF SEVERE PLASTIC DEFORMATION OF BMGs .................................... 94
4.5.1.  INCREASED FREE VOLUME AND IMPROVED TENSILE PLASTICITY ...................................................... 94
4.5.2.  SHEAR BAND AND CRACK BEHAVIOR DURING TENSION .................................................................... 98
4.5.3.  HPT EFFECT ON RESIDUAL STRESS AND POISSON’S RATIO ............................................................... 102

5.  SUMMARY AND CONCLUSION .................................................................................................................. 105

REFERENCES ...................................................................................................................................................... 111
PUBLICATIONS .................................................................................................................................................... 127
CONFERENCE CONTRIBUTIONS ...................................................................................................................... 128
ACKNOWLEDGEMENT ........................................................................................................................................ 129
LIST OF ACRONYMS ......................................................................................................................................... 131
LIST OF FIGURES ................................................................................................................................................. 133
CURRICULUM VITAE .......................................................................................................................................... 137
1. Introduction and Motivation
1.1. Glasses and glass formation

1.1.1. Definition of glasses

The word “glass” comes from Indo-European gel- or ghel-, which is a host of color adjectives and refers to shiny substance later. The oldest Egyptian glasses found in tombs were produced in 7000 B.C. by combination of sea salt, burned bones and sands. Because of their high hardness, the man-made glasses were first used to shape the sharp edges of tools. The glass blowing was invented around the first century B.C. After that, glass products were improved dramatically and widely used as window panes, bottles and so on [1-3].

Silicate glasses are the oldest and most popular types of glasses. At the beginning, silica was thought as a required component for glasses and used to define glasses. However, it is a mistake. Many kinds of glasses without silica have been developed. It is found that all the glasses have two common characteristics. First, in contrast to crystalline materials (Figure 1(a)), glasses do not exhibit atomic long-range order (Figure 1(b)). Their atomic structure is not completely random. Short to medium-range order can be detected in the range of a few to a few tens of atoms. With this special structure, glasses show very different mechanical performance with the crystalline materials (such as the mentioned high hardness). Second, glasses exhibit time-dependent glass transformation behavior [4,5].

![Figure 1 Schematic diagram of crystal structure (a) and amorphous structure (b).](image)

1.1.2. Glass transition

It is known that, by avoiding the nucleation, liquid can be supercooled below its melting point. But the liquid cannot be supercooled without limitation. The difference in entropy $\Delta S_f$ between the liquid and corresponding crystalline solid decreases with the reduction in the
temperature. \( \Delta S_f \) will become zero at the Kauzmann temperature. This means that a paradox arises, whereby the entropy of the supercooled liquid can be lower than that of the crystalline phase with further cooling [6,7]. In order to terminate this, a solidification process must take place before reaching this temperature, known as the glass transition [8]. The calculated entropies of crystal and liquid aluminum are shown in Figure 2 [9]. A Kauzmann temperature of 225 K is obtained. Glass transition is a transition in which a supercooled liquid freezes into a solid configurationally during cooling.

![Figure 2](image-url)

**Figure 2** The entropy of liquid and crystalline aluminum as function of temperature in the stable and metastable regime. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature, Nature, [9], Copyright 1988.

The crystallization homogeneous nucleation rate \( I_{ss} \) can be written as Equation (1)

\[
I_{ss} = \frac{A}{\eta(T)} \exp \left[ -\frac{16\pi \sigma^3}{3k_B T [\Delta G^{l-x}(T)]^2} \right]
\] (1)
where $\eta(T)$ is the liquid shear viscosity, $\sigma$ is interfacial energy between crystalline nucleus and liquid, $k_B$ is Boltzmann constant, $\Delta G^{l-x}(T)$ is activation energy for an atom addition to a cluster, $A$ is a temperature-independent constant. From this equation, a temperature-time-transformation (TTT) diagram can be obtained as a “C” shape, as shown in Figure 3. When crystallization is suppressed by kinetic constraints (e.g. fast cooling), an amorphous solid is formed by glass transition as the arrow in Figure 3 indicates.

![Figure 3 Temperature-Time-Transformation (TTT) diagram of crystallization and glass transition.](image)

The heat capacity $C_p$ of liquid is always higher than that of the corresponding crystalline solid, as shown in Figure 4. It is known that the change rate of entropy $S$ is

$$
\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}
$$

(2)

The difference in entropy between the liquid and the crystalline solid $\Delta s_m$ (melting entropy) can be written as Equation (3)

$$
\Delta s_m = \int_{T_K}^{T_m} \frac{\Delta C_p}{T} dT
$$

(3)

where $T_m$ is the melting temperature and $T_K$ is the Kauzmann temperature [10].

An obvious difference in the specific heat change as a function of temperature of supercooled liquid can be observed in Figure 4 (a) and (b). A peak close to $T_g$ can be distinguished for the $\text{Au}_{53.2}\text{Pb}_{27.6}\text{Sb}_{19.2}$ supercooled liquid. This type of glass-forming liquid is defined as “fragile”
liquid. Its relaxation process is consistent with the Vogel–Fulcher law. The viscosity $\eta$ change of the “fragile” liquid can be described as Equation (4), when the temperature decreases towards some characteristic temperature $T_0$

$$\eta = A \exp \left( \frac{B}{T - T_0} \right)$$

(4)

where $A$ and $B$ are constants independent of temperature [12].

On the contrary, in Figure 4 (b), Zr$_{41}$Ti$_{13}$Cu$_{13}$Ni$_{10}$Be$_{23}$ supercooled liquid shows a different change trend of specific heat, in which no peak can be observed; such a liquid is defined as “strong”. Different from the “fragile” liquid, its viscosity change can be described by the Arrhenius form function.

---

*Figure 4 Specific heat of glassy, supercooled liquid and crystalline state of (a) Au$_{53.2}$Pb$_{27.6}$Sb$_{19.2}$ alloys and (b) Zr$_{41}$Ti$_{13}$Cu$_{13}$Ni$_{10}$Be$_{23}$ alloys. Modified with permission of The Japan Institute of Metals, Copyright 1995, from [11].*
\[ \eta = A \exp \left( \frac{E}{k_B T} \right) \]  

(5)

where \( A \) and \( E \) are temperature-independent constants and \( k_B \) is Boltzmann’s constant. The viscosity changes of both types of liquid as a function of temperature are shown in Figure 5 [13].

The different liquid “fragility” can be understood by the energy landscape model, which describes the energy change of the structure as a function of different configurations of an N-body system [14]. Figure 6 shows schematic diagrams of the energy landscapes of “strong” and “fragile” liquids. The vertical axis indicates the potential energy, and the horizontal axis shows the configurational coordinates. The “strong” liquid with Arrhenius behavior has constant activation energy (\( E \) in Equation (5)) [15]. In contrast, the activation energy of “fragile” liquid, which deviates from Arrhenius behavior, fluctuates within a wide range; this leads to a highly heterogeneous landscape [16].
Studies have shown that this thermodynamic property of a liquid is related to its glass-forming ability. “Stronger” liquids tend to show better glass-forming ability, due to the inhibitory effect on crystal nucleation and growth kinetics [17,18]. The common used oxide glasses, such as fused silica, have very slow kinetics of crystal nucleation and growth, such that the liquids can be easily supercooled far below their melting points. Thus the products made of them are easy to produce. However, it is difficult for metallic systems, due to their much faster crystallization kinetics compared with oxides. Metallic liquids of conventional metals and alloys are very unstable, such that they can crystallize under the melting point in as short a period as several microseconds (the nose tip temperature on TTT curves is very close to Y-axis). When they solidify into low-energy phases, an equilibrium structure, which is the crystalline lattice, is easily reached [19,20].

The feature of supercooled liquid is also linked to the mechanical properties of the formed glass. A relationship was found between the “fragility” of certain supercooled liquids and the elastic moduli of the formed metallic glasses, as Equation (6):
where \( m \) is the steepness index as a measure of fragility, and \( B \) and \( G \) are the bulk and shear moduli, respectively [21]. Furthermore, metallic glasses formed by “fragile” supercooled liquid tend to exhibit higher Poisson’s ratios \( v \) [22] which indicates better ductility.
1.2. Metallic glasses

1.2.1. Synthesis of metallic glasses

For most metallic systems, extremely high cooling rates above $10^5$ K/s are required to avoid the phase transition from liquid to crystalline solid. Metallic glasses were first observed in 1959 at California Institute of Technology in a study on extended solid solubility by rapid quenching ($10^7$ K/s) of the Au–Si binary system from the liquid phase with sample thicknesses of a few micrometers [23,24]. Due to the requirement of very high cooling rates, metallic glasses should have a very small thickness in at least one direction. This hinders their potential application as structural materials [25]. In next decades, many studies have been performed to obtain stable metallic supercooled liquids with slow crystallization kinetics. It has been found that alloys with relatively slower glass-forming critical cooling rate and better glass-forming ability should (1) be multicomponent (have more than two elements), due to the reduced energetic advantage of ordered structure by the increase in the configurational entropy of the supercooled liquid; (2) have a larger mismatch of atomic radius between elements (above 12%), leading to a higher atomic packing density such that crystallization requires a greater volume increase; (3) have negative mixing enthalpy among the main elements, which accelerates the atomic diffusivity and reduces the crystallization nucleation rate; and (4) have deep eutectic composition, which can form a stable liquid at low temperature [19,26,27]. Critical cooling rates for glass transition of different systems are shown in Figure 7.

![Critical cooling rate and reduced glass transition temperature $T_g/T_E$ of glasses with different compositions.](image-url)
Thin foils and ribbons of metallic glasses were produced by melt-spinning technique (Figure 8 (a)) with cooling rate of $10^5$–$10^6$ K/s, developed in the 1960s. After more than three decades of efforts, the synthesis of samples with sizes of even more than 20 mm, so-called bulk metallic glasses (BMGs), by direct copper-mold casting is possible (Figure 8 (b)). Several series of BMGs have been developed with critical cooling rates slower than $10^3$ K/s. Inoue and co-workers at Tohoku University discovered the BMG formers based on zirconium, magnesium, and lanthanum [28-30]. At Caltech, Johnson and co-workers also developed a series of Zr-based BMGs [31-32]. Zr-based BMGs have high glass-forming ability, which can be used in sporting goods and structural components. Mg-based BMGs are biodegradable, which has potential applications as bone implants. Pd-based BMGs have good damage tolerance with high strength–toughness combinations [33-36].

**Figure 8** Schematic diagram of MGs synthesis methods: (a) melt-spinning and (b) water cooled copper-mold suction casting.

Crystalline materials have much wider application range compared with amorphous materials. Although the glass structure has been known for one thousand years, most of their applications are restricted to lenses and windows [37]. The main reason is that the microstructures of crystalline materials (such as lattice defects, grains size, and chemical composition distribution) can be modified by various methods to control their properties. In order to make the BMGs microstructure modification possible, the principle of nanoglasses has recently been proposed. As shown in Figure 9, the idea is to generate glasses with glassy/glassy interfaces (the white region) between adjacent regions (the black region) as controllable defects [38,39].
Several methods have been developed to produce nanoglasses. Inert-gas condensation was first investigated. Nanometer-sized glassy clusters are first evaporated from the target material into the inert gas atmosphere (Helium); then they consolidate on the surface of a rotating liquid nitrogen-cooled cylinder. Nanometer-sized glassy powders can be obtained by stripping the condensed nanometer-sized glassy clusters off the substrate. It is followed by the consolidation process, containing two steps: First, the powders are pre-consolidated in an ultra-high vacuum system. The resulting sample is shaped like a disc (e.g., about 0.5 mm in thickness and about 5 mm in diameter). Second, this disc is compacted under high pressure (up to 5 GPa). To avoid oxidation, the high pressure consolidation process should be an in-situ procedure using inert gas condensation, as shown in Figure 10 (left). Nanoglasses consisting of Au-La, Fe-Si, Ni-Ti, Sc-Fe etc. have been synthesized by this method [38-41]. The Sc$_{75}$Fe$_{25}$ nanoglass films synthesized by inert-gas condensation have strain enhanced from 5% to 10% compared with the homogeneous ribbons with the same composition and lower yield stress due to the softer interfaces [42]. Magnetron sputtering is another possible method. The schematic illustration is shown in Figure 10 (right). A negative potential is applied to the target, acting as cathode. Electrons are repelled from the target. They collide with Ar atoms, forming Ar$^+$ ions. These Ar$^+$ ions are then accelerated in the magnetic field and collide with the target. In this way, atoms in the target are ejected and deposit on the substrate. Nanoglasses produced by it, such as Au-based metallic glass, have similar structures and properties to those prepared by inert-gas condensation [43,44]. Furthermore, it is found that working pressure of Ar affects the films structure: homogeneous at low working pressures and nanostructured with mesoscopic hills and nanometer-sized-columns at higher working pressures, as shown in
Figure 11 [49]. Severe plastic deformation can also generate nanoglasses by controlling the free volume distribution, which always concentrate in shear bands [45,46]. It was reported recently that nano-BMGs could also be produced as nanometer-scale multiphase glassy structures by phase separation with certain special compositions [47,48]. In this work, Co was introduced into ZrCuNiAl BMGs system. The positive enthalpy of mixing between Cu and Co can be the driving force for phase separation.

Figure 10 Schematic illustration of nanoglasses preparation methods: inert gas condensation (left) and magnetron sputtering (right).

Figure 11 SEM images of the top view of sputtered Au_{40}Cu_{28}Pd_{5}Ag_{7}Si_{20} thin films, deposited on clean Si <100> at working pressures of Ar of (a) 0.4, (b) 4 and (c) 10 Pa and cross section at working pressures of (d) 0.4, (e) 4 and (f) 10 Pa. Modified from [49], Copyright 2018, with permission from Elsevier.
1.2.2. Research methods on structure of metallic glasses

X-ray diffraction (XRD) and electron diffraction are powerful tools to analyze the crystalline structure of alloys. While, due to the lack of long-range order, the information we can obtain by diffraction on metallic glasses is much less. Some other experimental methods are developed to characterize the amorphous structures. The pair distribution function (PDF) describes the atomic distance distribution. It can be calculated from XRD results. PDF reflects the short-range order of metallic glasses which can also be used to analyze the free volume change [50]. Extended X-ray absorption fine structure (EXAFS) analysis is a method to investigate the nearest-neighbor atoms of one element in the material. Topological structures of metallic glasses, including the coordinate number and Voronoi polyhedra changes, can be analyzed by EXAFS [51]. Small-angle X-ray scattering (SAXS) is sensitive for the nanometer-scale heterogeneity. It can determine the size and shape of nanoparticles in composite metallic glasses [52]. Simulation is also an effective method to study amorphous structures. Such as, molecular dynamics (MD) simulation is to investigate the atomic structure by calculation with predefined potentials. First principles are also used in some simulations for ab initio calculations [53].

To better understand the amorphous structure of metallic glasses, several structural models have been proposed, including the hard spheres dense random packing model, trigonal prism model, and chemical twinning model [54-56]. However, all these models have limitations and most of them are valid only for binary systems [57,58]. The description of metallic glass structures, especially for multicomponent materials, is still difficult.

1.2.3. Structural relaxation and rejuvenation of metallic glasses

Annealing is a commonly used heat treatment applied to traditional alloys, which is to heat to a suitable temperature, hold for a certain time, and then allow to cool. In annealing, dislocation density is decreased, internal stress is released, and average grain size is changed. A structure with lower Gibbs free energy is obtained. The purpose of annealing is to reduce the materials’ hardness, making them more workable and ductile. The annealing treatment has particular effect on amorphous structure. In this research, I only focus on the effect of low-temperature annealing below the $T_x$ of samples, because of the fragility of the intermetallic compounds formed at high temperature. Increased temperature can enhance
the mobility of atoms. Thus, the heating on metallic glasses usually leads to a structural relaxation process, resulting in a structure closer to equilibrium [59]. For most cases, structural relaxation is related to the change in heat capacity, annihilation of the excess free volume and embrittlement of the samples [60,61].

Metallic glasses have two types of relaxation processes at different temperatures: the primary α relaxation and the secondary β relaxation. α relaxation is responsible for the glass transition phenomenon that takes place mainly at temperatures above $T_g$. β relaxation can initiate at lower temperatures, which is the principal source of dynamic behavior in the glass structure [62,63]. Subtle structural changes, including topological and chemical short-range order changes, mainly take place during β relaxation by nearest-neighbor length scale atomic rearrangements [64,65]. No obvious change can be detected by XRD or TEM. Glasses with more significant β relaxation often have more activated shear transformation zones (STZs) during deformation [66]. Relaxation can be studied by dynamical mechanical analysis (DMA), DSC, or scanning tunneling microscopy. DMA is most commonly used, due to its sensitivity to atomic rearrangement. Glasses with pronounced β relaxation usually have relatively higher Poisson’s ratio $\nu$, indicating better ductility [67].

More complex thermal treatments, i.e. thermal cycling, have been developed to optimize alloys’ mechanical properties, such as superalloys applied in the aerospace industry, which need to undergo four or more different heat-treatment operations to obtain the demanded properties. Quenching followed by an annealing process is also widely used to modify the mechanical properties of steels. The annealing treatment can release the internal stresses introduced by quenching. Not only high-temperature thermal cycling, but also cryogenic treatment (with liquid nitrogen) has been applied on traditional materials to improve their properties [68,69].

The influence of thermal cycling on metallic glasses was first studied to simulate the service environment of Earth orbit. In low Earth orbit, the spacecraft periodically enters and emerges from Earth’s shadow region, resulting in a surface temperature cyclic variation of approximately −100 – 100 °C [70]. This research shows that, for Ti-based BMGs, thermal cycling treatments lead to structural relaxation, which is similar to an annealing effect but weaker [71]. The opposite effect, structural rejuvenation, was observed on samples treated by lower temperature thermal cycling (liquid nitrogen – room temperature). The reason is the heterogeneity of glasses due to the heterogeneous dynamic in liquids prior to the glass
transition [72]. Due to the spatially varying thermal expansion coefficient in their heterogeneous structures, the internal stresses induced by temperature changes during thermal cycling lead to atomic rearrangement and rejuvenation [73], which results in a more disordered structure with higher energy and higher free volume content. As published [74], La-based metallic glasses cycled 15 times showed an increased relaxation enthalpy before glass transition in DSC measurements (as shown in Figure 12), indicating the rejuvenation. Zr-based BMGs have improved compression plasticity after thermal cycling. Thermal cycling treatment can also affect the magnetic properties of Fe-based metallic glasses. The easy axis of Fe$_{80}$Si$_{8.75}$B$_{10}$Cu$_{1.25}$ metallic glass ribbons was rotated toward the ribbon plane by three cycles between liquid nitrogen and room temperatures. By this treatment, the saturation flux density was increased from 1.46 to 1.55 T and the coercivity was decreased from 9.21 to 8.54 A/m [75].

Figure 12 Differential scanning calorimetry of La$_{55}$Ni$_{20}$Al$_{35}$ metallic glasses. (a) An exotherm during relaxation can be observed. (b) Comparison of as-cast and cycled (liquid nitrogen – room temperature) samples. (c) The change of exotherm as a function of cycle number. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature, Nature, [74], Copyright 2015.
1.3. Mechanical properties of metallic glasses

1.3.1. Elastic performance

Because there is not lattice dislocation slip system as in crystalline metals, metallic glasses manifest high elastic strain, which is approximately 2% before yielding [76]. Their yield strengths can be close to the theoretical strengths of metals, which are much higher than those of conventional alloys. The yield strengths of Cu-based and Zr-based BMGs are approximately 2 GPa. Fe-based BMGs show 4 GPa [77]. For some Co-based BMGs, it can reach 5.5 GPa [78]. Elastic moduli, such as Young’s modulus $E$, reflect the material stiffness and interatomic bond. Young’s moduli of metallic glasses with different compositions are markedly different, between 25 GPa and 200 GPa [82], as shown in Figure 13 [79]. For Zr-based BMGs, they are of approximately 90 GPa – 120 GPa.

![Figure 13 Bulk modulus $K$ and Young’s modulus $E$ of BMGs with different compositions. Modified from [82], Copyright 2012, with permission from Elsevier.](image-url)

Poisson’s ratio $\nu$ describes the expansion or contraction of a material in directions perpendicular to the direction of loading. The value of Poisson's ratio $\nu$ is the amount of transversal expansion divided by the amount of axial compression, as the equation $\nu = \frac{-d\varepsilon_{\text{trans}}}{d\varepsilon_{\text{axial}}}$, where $\varepsilon_{\text{trans}}$ is transverse strain, $\varepsilon_{\text{axial}}$ is axial strain. It is an important parameter and related to the structure and properties of glass materials. Normally, metallic glasses with high $\nu$ have good ductility [80,81]. Zr-based BMGs have $\nu$ values of approximately 0.34 – 0.37. The $\nu$ values of various glasses are shown in Figure 14 [82]. The shear modulus/bulk modulus
ratio (μ/B) can also reflect the ductility of MGs. The lower ratio (μ/B), the better the plastic properties of the BMGs [83].

![Figure 14 Bulk modulus, shear modulus, and Poisson’s ratio ν of different BMGs. Reprinted from [82], Copyright 2012, with permission from Elsevier.]

1.3.2. Plastic deformation and shear bands

Plastic deformation in crystalline alloys is basically achieved through the sliding/climbing of dislocations. Dislocations are crystallographic defects or irregularities within a crystal structure which can move by breaking the atoms bonds from one of the surrounding planes and rebonding with the atoms at the terminating edge. During cold-working, the dislocation density increases. The consequent increasing overlap between the strain fields of adjacent dislocations gradually increases the resistance to further dislocation motion, resulting in the work-hardening effect. Work-hardening makes the delocalized plastic strain spread out across the entire sample relatively easily. However, BMGs have a different deformation mechanism [84]. Because of no dislocation in amorphous structure, plastic deformation can be only achieved by the atomic jumps in localized regions, which are called shear bands. There are two stages during the formation of shear bands. The first is the generation of regions available for shearing by rejuvenation, i.e. the activation of shear transformation zones (STZs). The second stage is the synchronous shear of atoms along the rejuvenated planes [85]. STZs are local regions involving a group of atoms with much larger atomic displacements than in the surrounding matrix, which can rearrange spontaneously and cooperatively to
accommodate the applied shear strain [86-88]. STZs cannot be experimentally observed. However, their existence has been confirmed by computer simulations [89]. Non-affine displacement fields can be found around STZs, including a few tens to one hundred atoms. The intensity of the field decreases sharply with increasing distance from the center. There are no well-defined boundaries. STZs have an average approximate size of 1 nm with an activation energy of several tens of electronvolts.

The regions with larger structural disorder, more free volume, and higher atomic level stress are more likely to generate STZs [90-92]. STZs appear around these defects firstly due to the stress concentration during the deformation. Different from the dislocations in crystalline materials, isolated STZs cannot move. Metallic glasses with a larger STZ volume tend to have higher Poisson’s ratio and better ductility as shown in Figure 15, due to the more homogeneous deformation with multiple rejuvenated planes [93].

When the STZ region is sufficiently large, a rejuvenated plane, shear band, forms and propagates through the material, as shown in Figure 16. It has more disordered structure than the remaining part, with a thickness of 10 nm – 20 nm. The nucleation and propagation of shear bands play a dominant role in the deformation, yielding, and fracture of metallic glasses. The structure and temperature changes in shear bands affect the mechanical properties of BMGs [94].
The direct experimental detection of atomic structural change in shear bands is difficult. Other methods have been used to investigate shear bands. Their different atomic-range order shows different corrosion resistance form the rest of the material. Similar to grain boundaries in crystalline alloys, the positions of shear bands can be revealed by etching on well-polished BMGs samples, due to their lower corrosion resistance [95,96]. Diffraction results and positron annihilation spectroscopy of severely deformed BMGs with high-density shear bands showed larger average atomic distance and increased free volume compared with the non-deformed or relaxed samples [97]. In one study [98], high-resolution transmission electron microscopy (HRTEM) was used to analyze the structure in individual shear bands. A lower density of shear bands with a thickness of 10-100 nm was observed by the transmission electron microscopy (TEM) contrast, which is coincident with the diffraction results and positron annihilation spectroscopy. Thus, it can be concluded that volumetric dilation occurs in association with shear band formation. The free volume change in shear bands is not the only reason for this effect; it is rather more complex [99]. The broadening of the first amorphous halo in the diffraction pattern indicates more disordered structure. Computer simulations of the atomic-range order show that icosahedral clusters and five-fold bonding are reduced significantly in shear bands [100,101]. This structure is very similar to supercooled liquid, except for the anisotropy introduced by deformation [85]. Thermal stress during annealing or thermal cycling could produce samples with rejuvenated isotropic structure.

The temperature change in shear bands is complex and important for understanding the deformation mechanism. It is known that metallic glasses have higher elastic strain limits compared with crystalline alloys (~0.2%). Much more elastic energy can be stored in metallic...
glasses. During yielding, the dissipation of this energy is only in the shear bands, which represent a very small fraction of the entire volume. Therefore, substantial temperature increases within the bands are possible [102,103]. This can be confirmed by the melting of a thin film near the shear bands offset, which was sputtered on the sample surface prior to deformation [104]. This is also the reason for the appearance of vein patterns on the fracture surface of BMGs. The increased temperature can reduce the viscosity within the bands, leading to more serious “work-softening”. Thus, hot shear bands in metallic glasses are always associated with catastrophic mechanical failure [105]. Infrared thermography was used to measure the temperature change in shear bands. A model describing the relationship among temperature increase $\Delta T$, position from the shearing plane $x$, and time $t$ was also put forward as Equation (7):

$$\Delta T = \frac{H}{2\rho C_p \sqrt{\pi \alpha t}} \exp \left( \frac{-x^2}{4\alpha t} \right)$$

where $H$ is the energy release of shear bands, $\rho$ is density of the material, $C_p$ is the specific heat capacity, and $\alpha$ is the thermal diffusivity [104]. If the plastic deformation takes place at low temperature (such as $-25$ °C), the behavior of shear bands becomes stick–slip sliding, which is a cycle of arrest alternating with rapid shearing and a sharp load drop [106]. Due to the shear bands with smaller shear offset, metallic glasses show better plasticity at lower temperatures [107].

Nano-scaled crystallization in shear bands is reported. The mechanism of it is still under debate. The mentioned localized temperature rise is a possible reason. However, this rapid heating does not allow sufficient time for nucleation and growth. The configuration change in structure by strain and increased free volume are more important. For some Cu-Zr based bulk metallic glasses, this nanocrystallization can block the propagation of shear bands and force the proliferation. The initiation of new shear bands needs higher stress, leading to a “work-hardening” effect which is favorable for ductility.

The size effect of BMG samples is also an important factor for the shear band behavior during deformation. Reducing the samples size is helpful to avoid the transition to hot shear bands [108]. Research [94] shows that when cylindrical samples of $\text{Zr}_{64.13}\text{Cu}_{15.75}\text{Ni}_{10.12}\text{Al}_{10}$ BMG are compressed, those with small diameters (1–2 mm) exhibit stable sliding of shear bands with limited velocities. Meanwhile, there is no significant temperature increase in these slow shear bands. Thus, the samples show good plasticity. On the contrary, for sample sizes as large as
3–4 mm, the sliding velocities of shear bands increase with time without constraint, due to the significant temperature increase. The temperature in shear bands can reach $T_g$, leading to liquid-like behavior of shear bands and work-softening of the sample. The fracture surface of the samples can also confirm this size effect, whereby stable sliding of shear bands results in a smooth surface.

During plastic deformation of BMGs, dilatation takes place in the shear bands by the coalescence of free volume, leading to the formation of voids. With further increase of the strain, a crack forms when the offset of a shear band exceeds the limit. Instead of the interatomic bonds breaking in crystalline materials, the break of local atomic clusters leads to crack propagation in BMGs. The toughness of materials depends on the energy release at cracks tips. If the stored elastic energy can dissipate in a large volume of materials by various process (such as sliding of dislocations), the material will be tough. If the energy concentrates in a small region, the cracks tips will become instable easily. For BMGs, high elastic energy concentrates at the cracks tip. Most of BMGs are brittle materials.

The typical fracture morphology of BMGs are shown in Figure 17. Vein patterns can be observed due to the melting on the fracture surface. Molten drops can even appear during fast fracture because of the concentration of high elastic energy [94]. The larger and deeper veins (Figure 17 (a)) indicate better ductility of BMGs compared with the samples with smoother fracture morphology (Figure 17 (b)).

![Figure 17 Fracture surfaces of two Zr-based BMGs.](image)

In summary, because of the lack of mobile defects in BMGs, their flow stresses are much higher than those of crystalline alloys, and close to their theoretical values. However, the generation of free volume and local adiabatic heating in shear bands leads to “work-softening” effect during deformation. It results in the localization of plastic deformation in a thin band,
which causes instability. Different from the interatomic bonds breaking in crystalline alloys, local atomic clusters breaking in metallic glasses easily leads to crack growth and consequently early failure [107].

1.3.3. Deformation on heterogeneous BMGs

In order to apply the BMGs as structural materials, stable shear bands and homogeneous deformation are expected. With strict conditions, such as high temperature (0.9 $T_g$) or very slow strain rate, the homogeneous flow (even Newtonian flow) can take place by the diffusion of atoms in the entire glassy samples, while this is impossible for the room temperature application. It has been found that increasing the density of shear bands in the BMG can lead to more homogeneous energy release and lower temperature in each band. Furthermore, these shear bands interact with each other, resulting in inhibition of sliding. Thus, blocking the sliding of shear bands during deformation by embedded heterogeneities should be effective for the improvement of the ductility of metallic glasses [84].

As discussed above, nanoglass is a new developed structure [109,110]. It has the following features, which are beneficial to mechanical properties: (1) Because of the enhanced atomic misfit, increased free volume in the glass/glass boundaries can offer more STZs and shear band initiation sites, making the plastic deformation homogeneous. (2) The propagation of shear bands can be hindered by the relative higher density of glassy clusters. The shear bands cannot slide unrestricted, resulting in a serrated shear and improving ductility [111]. MD simulations of Cu$_{50}$Zr$_{50}$ metallic glasses and nanoglasses show that their uniaxial tensile ductility improves with the decreasing glassy “grain” size. The softer interfaces offer more shear band initiation sites, leading to more homogeneous deformation. The denser clusters can further hinder the sliding of shear bands, resulting in improved plasticity. Even superplastic deformation can occur when the glassy “grain” size decreases to 5 nm, due to the homogeneous elastic energy release and uniformly distributed STZs [112]. Special magnetic properties can also be introduced by the nanoglass structure. Research on Fe$_{90}$Sc$_{10}$ nanoglass shows that it exhibits ferromagnetism. The reason is that the ferromagnetic interface regions polarize the glassy “grains” at low temperature [113].

Recent research reveals that the amorphous structure change during annealing could be more complicated than people thought [114,115]. From neutron diffraction analysis, it is found that
two different regimes can be distinguished in β relaxation. The first regime is quick and observable by DSC, which is related to the inter-atomic distances. The second regime affects local chemical ordering, which could lead to phase separation. This can be revealed by small-angle neutron scattering analysis [114]. Research [115] shows that nanoscale spatial structural heterogeneity changes during β relaxation can be observed directly by amplitude modulation dynamic atomic force microscopy. For example, a maximum point can be observed on the scattering curve at \( \sim 0.029 \, \text{Å}^{-1} \) for annealed Vitreloy 105 metallic glasses [116]. Chemical decomposition between Zr and Cu was also detected in annealed Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_5\) BMG as shown in Figure 18, in which Cu-rich clusters formed with size of \( \sim 100 \, \text{nm} \).

![Figure 18 In-situ TEM images of (a) as-cast and (b) annealed Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_5\) BMG samples. Decomposition by annealing is obvious. The framed areas on both pictures indicate that the observation is on the same sample and the same position. Reprinted from [117], Copyright 2008, with permission from Elsevier.](image)

With this heterogeneous structure, the plasticity of annealed (at 623 K) Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_5\) BMGs is improved significantly as shown in Figure 19 [117,118], with the formation of multiple shear bands. The magnetic properties of metallic glasses can also be optimized by annealing. In
Fe$_{80.8}$Cu$_{1.2}$B$_{10}$P$_8$ metallic glass, Mössbauer spectroscopy analysis showed Fe$_3$B-like chemical order; short-range order tended to transform to an FeB-like atomic arrangement during structural relaxation, leading to an increase of Fe clusters, which can improve the magnetic properties [119].

![Figure 19](image)

Figure 19 (a) Compression stress–strain curves of as-cast and annealed Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_5$ BMG samples. SEM images of the sample surfaces after compression test. (b) SEM images of indentations on both samples. Increased shear bands can be observed on the annealed sample. Reprinted from [117], Copyright 2008, with permission from Elsevier.

1.3.4. Plastic deformation treatments on metallic glasses

Cold-rolling, hot-forging, and equal channel angular pressing are all widely used plastic deformation treatments for crystalline materials in industry [120,121]. Apart from obtaining suitable product shapes, they can also lead to dislocation density change and grain refinement, modifying the structure and properties of materials. As discussed above, localization of plastic
deformation is one of the most important problems for applications of BMGs, which leads to brittle failure. The reason is the strain-softening behavior that the plastically deformed regions (shear bands) have more free volume, becoming softer than the rest of the BMGs. The following plastic deformation is more likely to occur in the pre-existing shear bands. Thus, one potential means of enhancement is to delocalize the plastic deformation by introducing more pre-existing shear bands in BMGs. More shear bands with different orientations could form in the following plastic deformation, thereby achieving a more homogeneous deformation throughout the whole sample. Therefore, some pre-mechanical treatments could be effective for the improvement of plasticity of BMGs [122].

Shot-peening of BMGs was studied by Y. Zhang et al. [123]. Young’s modulus and hardness were reduced on the edge region near the surface on the cross-section, due to the introduced pre-existing shear bands. Its plasticity was improved under compression with more shear bands forming on the sample surface. In the imprint treated BMGs, the deformed regions by linear teeth became softer due to the introduced shear bands with increased free volume [124]. The tensile plastic strain of the treated sample was increased by 0.9%. Cold-rolling of metallic glasses was also investigated. As reported [125], the soft inhomogeneities in the introduced pre-existing shear bands can stabilize the deformation and improve the plasticity of Zr$_{64.13}$Cu$_{15.75}$Ni$_{10.12}$Al$_{10}$ BMGs. Two-direction rolling can efficiently produce shear bands with conjugated directions. The intersection of these shear bands leads to work-hardening under tension. However, a shortcoming of these three treatments is that their affected region is near the surface, such that pre-existing shear bands can be induced only near the surface. Thus, the mechanical properties of only thin samples can be improved effectively.

Severe plastic deformation is a newly developed technique of metal-forming, in which a very large plastic strain can be applied to bulk alloys under high pressure without changing the sample shape [126,127]. Ultrafine grained (1–1000 nm) and even nanostructured materials with high-angle grain boundaries can be produced [128]. Severe plastic deformation was first performed in the 1930s by Percy Williams Bridgman [129]. However, it did not draw attention until the 1980s, which people found it could be used for the grain refinement of alloys [130]. Then, a number of different severe plastic deformation techniques have been innovated and reported. High-pressure torsion (HPT) is a severe plastic deformation technique developed for the modification of materials, which was first proposed to study the deformation of different elements under high pressure [129]. A photo of the HPT treatment device is shown in Figure
Twenty years ago, this technique became a research hotspot because of its outstanding effect on grain refinement [130]. HPT is more efficient to obtain high-angle grain boundaries compared with other methods. Not only bulk materials but also powders can be used to prepare samples by HPT [131,132]. During HPT, the cut thin-disk sample is placed between upper and lower anvils under an applied pressure of 4–6 GPa. One anvil rotates and then the disk is deformed by shearing. The disk does not break apart and the sample shape does not change, due to the high pressure and constraint of the anvils. The strain can be controlled by the number of rotations. Research [133] shows that a special structure is formed in warm HPT-treated C45 steel, which is mixture of elongated and equiaxed ferritic grains with cementite lamellas at the interfaces. This treatment significantly improves the mechanical properties of C45 steel. The tensile strength is larger than 2100 MPa. The plastic strain can reach 3.7%.

![Photograph of HPT device (Institute of Nanotechnology, KIT).](image)

The effect of HPT on BMGs was also investigated recently. Synchrotron radiation XRD measurements showed that, after HPT treatment, the atomic order was reduced and the free volume was increased in BMGs with various compositions (such as Au-based [50] and Zr-based [134] BMGs), known as rejuvenation. This rejuvenation can lead to improvement of the plasticity of treated BMGs by reducing the velocity of shear bands sliding in nanoindentation measurements [135]. In HPT-treated Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_{5} BMGs, work-hardening behavior
and enhanced tensile ductility can be observed because of the heterogeneous structure with HPT-introduced shear bands [136]. It is also accompanied by the development of residual stress due to the inhomogeneous plastic flow with a strain gradient. Hardness is sensitive to the change of stress state. The tensile stress in the sample center causes softening, and the compressive stress leads to hardening on the edge of the HPT-treated BMGs [137]. Nanocrystallization could occur in BMGs with certain compositions, such as Cu₆₀Zr₃₀Ti₁₀, Nd₁₁.₈Fe₈₂.₃B₅.₉, and Ti₅₀Ni₂₅Cu₂₅, during HPT due to the heating effect and topological structure change [138,139]. α-Fe nanocrystals smaller than 10 nm are induced by HPT in Nd₉Fe₈₅B₆ BMGs. After subsequent annealing, they showed enhanced magnetic properties with increases of 13% in remanence and 19% in coercivity, as compared with the samples prepared only by annealing [140].

Until now, all the reported studies focused only on the treatments of relatively homogeneous BMGs. It will be interesting to perform a systematic study on annealing/thermal cycling/severe plastic deformation treatments of nanometer-scale phase-separated BMGs. This work reports results of these post-proceedings on the nano-structured Zr₅₅.₇Ni₁₀Al₇Cu₁₉Co₈.₃ BMG, with the aim to enhance its tensile mechanical properties. For comparison, these proceedings are also performed on the Zr₆₄Ni₁₀Al₇Cu₁₉ BMG with a relatively homogeneous structure.
1.4. Research motivation

Because of the special structure, metallic glasses has some excellent mechanical properties, such as high strength, high elastic strain, high wear and corrosion resistance. But the lack of plasticity is a prevalent problem, which seriously restricts their applications. In this research, BMGs with various microstructures were synthesized. Various post-treatments were also carried out on the BMGs to further improve their ductility and meet the application requirements.

The goals of this research are as follows:

- To synthesize and analyze the BMGs with nanoheterogeneous structure.
  A phase separation method was used to produce as-cast inhomogeneous BMGs by addition of Co into ZrCuNiAl BMGs system. The positive enthalpy of mixing between Cu and Co (Table 1) can be the driving force for phase separation. Their structures were studied by synchrotron radiation XRD, EXAFS analysis, TEM, etc.

<table>
<thead>
<tr>
<th>Atomic bonds</th>
<th>Enthalpy of mixing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-Co</td>
<td>-41 kJ/mol</td>
</tr>
<tr>
<td>Zr-Cu</td>
<td>-23 kJ/mol</td>
</tr>
<tr>
<td>Zr-Ni</td>
<td>-49 kJ/mol</td>
</tr>
<tr>
<td>Zr-Al</td>
<td>-44 kJ/mol</td>
</tr>
<tr>
<td>Cu-Co</td>
<td>+6 kJ/mol</td>
</tr>
</tbody>
</table>

- To investigate the mechanical properties of the nano-structured BMGs.
  The elastic moduli were measured by an ultrasound pulse-echo technique. Nanoindentation with Berkevich and spherical indenter was utilized to investigate the changes in hardness and elastic strain limit. In-situ compression tests were carried out under scanning electron microscopy (SEM) to obtain the stress–strain curves and observe the behavior of shear bands during plastic deformation.
• To understand the structural relaxation in the nano-structured BMGs. Homogeneous and nanoheterogeneous BMGs samples were treated by annealing and thermal cycling. The effects of annealing temperature, time, number of cycles were studied. Differential scanning calorimetry (DSC) was conducted to measure the thermal property changes of the BMGs. A free volume model was used to analyze the effects of thermal treatments. Their mechanical properties were also measured.

• To study the effect of severe plastic deformation on the BMGs. High pressure torsion treatments were carried out on both-type BMGs samples. The effects of deformation degree (the number of torsions) on crystallization, shear band behavior, and free volume evolution in amorphous structures were investigated by TEM and synchrotron radiation XRD.

• To further improve the plasticity of the BMGs. In-situ compression/tension tests were conducted on the as-cast and treated two-type BMGs samples. The behaviors of shear bands and cracks were observed by SEM. Nanoindentation was used to measure the hardness change. The deformation mechanism was discussed.

This dissertation includes five chapters. Chapter 1 presents an introduction to BMGs and the research motivation. Chapter 2 describes the employed materials. The processing, structural characterization, and mechanical property measurement methods are also presented. All the experimental results are shown in Chapter 3, including the structures and properties of the as-cast BMGs and treated BMGs with different processing. In Chapter 4, the change mechanisms of the structure and properties of the homogeneous and nanoheterogeneous BMGs under different treatments are discussed. Chapter 5 includes a summary of this work and an outlook for further research.
2. Experimental Procedures
2.1. Materials used in this research

As discussed in the introduction part, many BMGs series have been developed. Noble-metal-based BMGs were first synthesized in the 1980s, such as Au_{55}Pb_{22.5}Sb_{22.5} [141] and Pd_{40}Ni_{40}P_{20} [142]. Since then, Fe-, Cu-, Ti-, Mg-, Zr-, and La-based BMGs were discovered with good glass-forming ability. In 1991, a Zr-Al-Ni-Cu BMG was prepared by casting with 15 mm critical thickness [143]. Some commercial BMGs have been developed based on it, such as Vitreloy 105 (Zr_{52.5}Ti_{5}Cu_{17.9}Ni_{14.6}Al_{10}). By controlling the elastic moduli and Poisson’s ratio \( \nu \) of BMGs, W.H. Wang et al. found some compositions based on the Zr-Al-Ni-Cu system, as shown in Table 2, which showed high Poisson’s ratio and good glass forming ability [144].

Table 2 Glass transition temperature \( T_g \), crystallization \( T_x \), density \( \rho \), Young’s modulus \( E \), shear modulus \( G \), bulk modulus \( K \), and Poisson’s ratio \( \nu \) of several Zr-Al-Ni-Cu BMGs. Republished with permission from The American Association for the Advancement of Science [144].

<table>
<thead>
<tr>
<th>BMG</th>
<th>( T_g ) (K)</th>
<th>( T_x ) (K)</th>
<th>( \rho ) (g/cm(^3))</th>
<th>( E ) (GPa)</th>
<th>( G ) (GPa)</th>
<th>( K ) (GPa)</th>
<th>( \nu )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr_{61.88}Cu_{18}Ni_{10.12}Al_{10} (S1)</td>
<td>653</td>
<td>744</td>
<td>6.649</td>
<td>80.12</td>
<td>29.10</td>
<td>108.33</td>
<td>0.377</td>
</tr>
<tr>
<td>Zr_{64.13}Cu_{15.75}Ni_{10.12}Al_{10} (S2)</td>
<td>643</td>
<td>745</td>
<td>6.604</td>
<td>78.41</td>
<td>28.46</td>
<td>106.63</td>
<td>0.377</td>
</tr>
<tr>
<td>Zr_{62}Cu_{15.3}Ni_{12.3}Al_{10} (S3)</td>
<td>652</td>
<td>748</td>
<td>6.615</td>
<td>79.65</td>
<td>28.89</td>
<td>109.03</td>
<td>0.378</td>
</tr>
<tr>
<td>Inoue’s Zr_{61.88}Cu_{18}Ni_{10.12}Al_{10}</td>
<td>652</td>
<td>748</td>
<td>6.642</td>
<td>82.96</td>
<td>30.27</td>
<td>106.65</td>
<td>0.355</td>
</tr>
</tbody>
</table>

In this work, the Zr_{64}Ni_{10}Al_{7}Cu_{19} system was selected as a basis and added cobalt to replace zirconium, Zr_{64-x}Ni_{10}Al_{7}Cu_{19}Co_{x} (\( x = 0–16 \)). The enthalpy of mixing between cobalt and copper is positive (6 kJ/mol), and the enthalpy of mixing cobalt and zirconium is highly negative (−41 kJ/mol) [145]. Our aim is to achieve an inhomogeneous structure or even nanoglass to further improve the mechanical properties of the BMGs by the positive enthalpy of mixing between elements. At the same time, the glass-forming ability should not be excessively reduced.

Ingots with compositions of Zr_{64-x}Ni_{10}Al_{7}Cu_{19}Co_{x} (\( x = 0–16 \)) were prepared by arc-melting of the pure elements (above 99.5%) under an argon atmosphere. In order to obtain samples with homogeneous composition, the ingots were remelted for five times. Then, each ingot was melted and casted into a water-cooled copper mold by suction. Different shapes of samples were prepared, including disks with diameter of 10 mm, thickness of 0.8 mm and rods with
diameter of 2 mm, length of 40 mm. All the casted samples were grinded using 400, 800, 1200, and 2000 grit SiC papers with an appropriate abrasive and lubrication to remove the surface layer. Then, the samples were cut by a diamond cutting machine for further measurements and treatments.
2.2. Sample preparation

2.2.1. Structural relaxation

As discussed above, annealing on metallic glasses usually leads to more relaxed structure. While, for certain BMGs with special compositions, annealing could also introduce non-affine thermal strain due to the inhomogeneity in the glassy structure, resulting in the increased free volume and improved ductility. In this work, structural relaxation of samples with composition $Zr_{64-x}Ni_{10}Al_7Cu_{19}Co_x$ were conducted by annealing in a DSC device. Different annealing temperature around the glass transition temperature $T_g$ was utilized, with a heating rate of 160 K/min. The samples were held at the temperature for 10 h with flowing high-purity Ar to avoid oxidation.

2.2.2. Thermal cycling treatment

In order to introduce non-affine thermal strain and avoid the annihilation of free volume in the amorphous structure at the same time, low-temperature thermal cycling treatment was performed on the nanoheterogeneous BMG samples composed of phases with different thermal expansion coefficients. The homogeneous $Zr_{64}Ni_{10}Al_7Cu_{19}$ BMG samples were also treated as a reference. The samples were inserted into liquid nitrogen (77 K), held for 1 min, and then placed in boiling water (373 K) for 1 min. These cycles were performed for 1–160 times. A device was designed to complete this treatment automatically. The structural and property changes of the treated samples with different cycling numbers were then analyzed.

2.2.3. High-pressure torsion (HPT)

HPT is a technique to carry out severe plastic deformation of samples by introducing torsional strain under high quasi-hydrostatic pressure. In this work, we expect that HPT treatment of BMGs could introduce pre-existing shear bands with increased free volume to enhance their plasticity. The different effects of severe plastic deformation on homogeneous and nanoheterogeneous samples are interesting. BMGs samples were prepared as disks with 0.5 mm thickness and 10 mm diameter. They were placed between a fixed anvil and a rotating anvil under a pressure of 6 GPa, as shown in Figure 21.
It is worth noting that the processing regimes including hydrostatic pressure, processing temperature, and deformation strain make an important contribution to HPT processing and successfully improving the properties of samples. For steels, the employed hydrostatic pressure should be 4.5–6 GPa. Due to the high strength of BMGs, the hydrostatic pressure applied in this work is 6 GPa. As discussed earlier, a high temperature could lead to free volume annihilation in BMGs, which is harmful to their plasticity. Therefore, the HPT treatments were only processed at room temperature. The deformation strain was controlled by changing the number of HPT rotations. In order to study the effects of deformation degree on the structure and properties of BMGs, 2, 5, 10, and 20 HPT rotations were carried out on both homogeneous and nanoheterogeneous BMGs samples.
2.3. Thermal analysis

With the increase of temperature, BMGs samples undergo several types of physical transformation, including structural relaxation and crystallization. During these transitions, more or less heat is needed to maintain the same temperature as the reference. For example, crystallization is an exothermic process for BMG. Therefore, the sample requires less heat flowing to raise its temperature at the same rate as the reference. Differential scanning calorimeter (DSC) is a technique applied for the measurement of the heat flow difference between the sample and reference to analyze the physical process.

In this work, samples were cut from the as-cast and treated Zr$_{64-x}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_x$ BMGs disks at a position approximately 2 mm from the center (the same as the tensile test samples) for DSC measurements (Perkin Elmer Pyris 1). The heating range is 353–853 K with a heating rate of 20 K/min under flowing high-purity Ar. Each sample was measured twice. The final result was the baseline subtracted from the heat flow of the first heating.
2.4. Structural characterization

2.4.1. X-ray diffraction (XRD)

XRD is a well-developed technique for the analysis of the crystalline structure of materials. From the peak position, the interplanar spacing can be calculated by Bragg’s law:

\[ 2d \sin \theta = n\lambda \]  

(8)

where \( d \) is the spacing between diffracting planes (interplanar spacing), \( \theta \) is the scattering angle (the peak position on the XRD pattern), \( n \) is a positive integer, and \( \lambda \) is the wavelength of the X-ray. The average grain size of materials can be estimated from the peak width. The relative height of peaks reflects the texture in the structure. Residual stresses can also be analyzed by the shifts of the XRD peaks.

For glassy materials, less information can be obtained from normal XRD, due to the amorphous structure. Normally, it can be only used to check whether the materials are fully amorphous or not. If there is no sharp diffraction peaks on the pattern, but rather only a halo, it can be concluded that the crystalline content is less than 5%. Some other information can be obtained by calculation on the XRD results. For example, the position of the maximum point on the peak reflects the atomic packing density. The degree of atomic disorder in an amorphous substance is related to the width of the XRD diffraction peak.

In this work, Cu-Kα radiation (Siemens D 5005 operating at 40 kV) XRD analysis was first performed on all the BMG samples with different compositions and different treatments. In order to obtain more information from the amorphous structure, synchrotron radiation XRD were also utilized on selected samples, for which the X-ray has shorter wavelength and higher intensity. Structure factors and pair distribution functions can be obtained from the results, which are further discussed in the following section.

2.4.2. Scanning electron microscopy (SEM)

When electrons interact with atoms near the surface of a sample, various types of signals can be produced, including secondary electrons, backscattered electrons, X-rays, etc. Secondary electrons are emitted from the atoms very close to the sample surface, which can reveal its morphology. The emitted backscattered electrons and X-rays are related to the atomic
number Z of the elements in the sample. SEM is to scan the surface of a sample with a focused electron beam to obtain images of the surface topography or composition.

In this work, the chemical composition distributions of as cast BMGs samples were investigated by backscattered electrons imaging and energy dispersive spectrometer (EDX). Secondary electrons imaging analysis was used to observe the evolution of shear bands, propagation of cracks and fracture morphologies of samples under compression or tension by a high-resolution field-emission SEM (Leo-1550, ZEISS, Germany).

2.4.3. Transmission electron microscopy (TEM)

TEM is a technique in which an electron beam transmits through a thin sample (less than 100 nm), interacting with it and forming a diffraction pattern or image. The electrons are emitted from a tungsten filament or needle at a high voltage. The electron beam is then manipulated and focused by a magnetic field. Electron diffraction is a powerful tool for the analysis of the fine structure of crystalline materials. However, similar to XRD measurements, the pattern of electron diffraction through glasses is only a halo, due to the lack of atomic long-range order in the amorphous structure. TEM images have high resolution because of the short de Broglie wavelength of electrons, which can reflect the atomic arrangement of materials.

In this work, TEM imaging were used to observe the nano-structure in BMGs, including nano-glassy clusters, nano-crystalline particles and shear bands. Besides the high resolution TEM images, high angle annular dark field (HAADF) image of the nano-heterogeneous sample were also taken in a scanning transmission electron microscope (STEM) mode. HAADF is an annular dark field image formed only in very high angle, incoherently scattered electrons (Rutherford scattering from the nucleus of the atoms), as opposed to Bragg scattered electrons, is highly sensitive to variations in the atomic number of atoms in the sample (contrast $\sim Z^{1.7}$) [147]. The measurements were carried out using aberration-corrected FEI Titan 80/300 TEM operated at 300 kV. Selected samples were prepared by mechanical grinding and low-angle Ar-ion milling. TEM foils from HPT samples were taken from the same location as tensile and DSC specimens, which are at a distance of 1-2 mm from the sample center.
2.4.4. Synchrotron radiation X-ray analysis

When charged particles are accelerated radially, electromagnetic radiation is emitted. Synchrotron radiation is achieved by forcing electrons to travel in a curved path using a magnetic field and then accelerate them to the X-ray emission range. It was first found in a collider in high-energy physics research. Compared with the Cu target (Cu-K\(\alpha\)) X-ray (\(\lambda \sim 1.54\) Å) the synchrotron radiation X-ray has higher brilliance, wider wavelength range, and shorter pulses.

As discussed earlier, very little information can be obtained from the diffraction results of an amorphous structure by Cu-K\(\alpha\) X-ray radiation. While, the structure factors of the short-range order structure can be obtained by the synchrotron radiation XRD analysis, because of the short wavelength. The principle of this measurement is similar with the Cu target XRD. First, the raw data of diffraction pattern is gotten. After subtracting the background and container scattering, the diffraction intensity \(I(Q)\) in \(Q\) space can be obtained by integration. Software fit2d can be used for this raw data processing. By further calculation and correction on absorption, polarization and Compton scattering, the structure factor \(S(Q)\) is obtained. The pair distribution function (PDF, \(G(r)\)) in real space is the Fourier-transformed structure factor \(S(Q)\). Software PDFgetX2 is a powerful tool to analyze these diffraction results. In this work, synchrotron radiation XRD was carried out on selected samples with 0.12 Å wavelength in DESY, Hamburg.

The X-ray absorption of a sample increases dramatically when the energy of the incident ray matches the binding energy of an electron of an element in the sample, leading to a drop in the transmitted X-ray intensity, which is called the absorption edge. Each element has its X-ray absorption spectroscopy, which is a set of absorption edges corresponding to the different binding energies of its electrons. Because the measurement of X-ray absorption spectroscopy requires a tunable X-ray wavelength, the synchrotron radiation X-ray source is necessary. Extended X-ray absorption fine structure (EXAFS) spectra are in a range of 500–1000 eV from an absorption edge of an element on the absorption-coefficient–energy graph, as shown in Figure 22. For an element, its surrounding atoms can be described as scattering points for the incident X-ray. This backscattering results in an interference pattern, which is a modulation of the measured absorption coefficient, leading to oscillations in the EXAFS spectra. Thus, information of the chemical coordination environment of the central absorbing element can be obtained by analyzing the EXAFS results. First, the X-ray absorption curve should be
normalized. Then the intercepted extended X-ray absorption spectra is modulated as wave function \( \chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)} \), where \( \mu(k) \) is the measured absorption coefficient, \( \mu_0(k) \) is the ideal absorption coefficient, \( k \) is optoelectronic wave vector. By Fourier transform on \( \chi(k) \), the radial distribution function can be obtained in real space. Several software have been developed to help analyze the EXAFS, such as Athena and Winxas. In this work, some selected samples were grinded to a thickness of approximately 30 µm. EXAFS analysis was carried out in SSRF, Shanghai. Radial distribution functions were obtained with Zr atom and Co atom as the center atom.

Figure 22 X-ray absorption spectrum.

When an X-ray travels through a sample, elastic scattering occurs at small angles (approximately 0–4°) if there is nanoscale density inhomogeneity in the material. Thus small-angle X-ray scattering (SAXS) measurements can be taken to analyze the size, shape, and distribution of the nanoparticles. The smaller the recorded angle, the larger is the particle size (1–100 nm). The employed X-ray should be a hard X-ray with a wavelength of 0.07–0.2 nm. Therefore, this measurement can only be conducted by synchrotron radiation X-ray. In this work, the as-cast Zr\textsubscript{55.7}Ni\textsubscript{10}Al\textsubscript{19}Cu\textsubscript{19}Co\textsubscript{8.3} BMG sample was grinded to approximately 30 µm. The SAXS measurement was performed in BSRF, Beijing.
2.4.5. Three dimensional atomic probe technique (3D-APT)

APT measurement is to observe the individual atoms on a sample surface by removing and identifying the ions. 3D view can be rebuilt by computer methods which includes billions of atoms from the sharp tip sample. It is powerful to characterize the nanometer size structure in materials, such as thin films structure, grain boundaries and nano-scale phase separation. In this work, the atomic spatial distribution of the amorphous alloys was analyzed with 3D-APT instrument (CAMECA LEAP 5000XR) at a temperature of 60K. Needle shaped samples were prepared by focused ion beam technique (FIB).
2.5. Mechanical properties measurements

2.5.1. Ultrasound pulse-echo technique

The propagation velocity of ultrasound waves in a solid medium depends on its elastic properties. In this technique, a pulse-echo experiment is used to measure the propagation velocity $v$ and the absorption coefficient $\alpha$ of the wave. It is popularly used in different fields, such as materials and medical science, with a result deviation as low as 0.1%. Ultrasound waves can be reflected at the interface between two materials, such as metal and air. The frequency used in the tests is 6 MHz, which is produced and received by piezoelectric transducers. With an oscillograph, the propagation velocities of longitudinal waves $c_L$ and transverse waves $c_T$ can be obtained. Then, the elastic moduli of the material can be calculated from the Equations (9) – (13):

$$c_L = \sqrt{\frac{\lambda + 2\mu}{\rho}}$$  \hspace{1cm} (9)

$$c_T = \sqrt{\frac{\mu}{\rho}}$$  \hspace{1cm} (10)

$$G = \mu$$  \hspace{1cm} (11)

$$v = \frac{\lambda}{2(\lambda + \mu)}$$  \hspace{1cm} (12)

$$E = 2(1 + v)G$$  \hspace{1cm} (13)

where $\rho$ is the density of the material, $\lambda$ and $\mu$ are Lame’s elastic constants, $E$ is Young’s modulus, $G$ is shear modulus, and $v$ is Poisson’s ratio of the material.

In this research, each sample was measured five times to obtain the average value. However, the HPT-treated samples were too thin (0.4 mm) for the ultrasound pulse-echo measurement. Their elastic moduli were estimated by nanoindentation results, which will be discussed later.

2.5.2. Vickers hardness

Indentation is a widely applied method for the measurement of mechanical properties of materials, which has been developed for several decades. Indentation tests were first used by Brinell in the 20th century. Traditional indentation tests include the Brinell test, Vickers test, Rockwell test, etc., which are adopted as industrial test methods. The Vickers test, with a small
diamond square-based pyramidal indenter, is usually used for nondestructive hardness measurements of thin samples or thin films. During the measurement, an indenter is forced into the sample surface with a load 1–100 g for a certain time. The hardness HV can be calculated as

\[ HV = \frac{P}{A} \]  

(14)

where \( P \) is the applied load on the indenter, \( A \) is the surface area of the resulting indent. \( A \) can be calculated from Equation (15):

\[ A = \frac{d^2}{2 \sin\left(\frac{136^\circ}{2}\right)} \]  

(15)

where \( d \) is the average length of the diagonals of the resulting indent, which can be measured by optical microscopy. Thus, HV can be obtained as

\[ HV \approx \frac{1.845P}{d^2} \]  

(16)

In this study, polished samples were measured by a Micromet 5103 Vickers microhardness device from Buehler. Each test was repeated for 8–10 times and the average value of HV was calculated.

2.5.3. Nanoindentation

In recent years, with the development of materials science including surface science and nanomaterials science, nanoscale properties have received much attention. With the recent development of measurement systems, nano-newton loads and nanometer displacements can be measured accurately. Nanoindentation becomes an important tool for the measurement of mechanical properties at small volumes. A typical nanoindentation load–displacement curve is shown in Figure 23. Both elastic and plastic deformation occur with the pressing of the indenter into the sample surface. Only the elastic part of the displacement is recoverable in the withdrawal process of the indenter.
Figure 23 Typical load–displacement curve of nanoindentation measurement on a sample. Modified from [148], Copyright 2002, with permission from Elsevier.

Hardness and the elastic modulus are the most frequently measured mechanical properties by nanoindentation. The load on indentation divided by the contact area of the impression is defined as the nanoindentation hardness, which can be obtained as

$$H = \frac{P_{\text{max}}}{A}$$  \hspace{1cm} (17)

where $P_{\text{max}}$ is the maximum load and $A$ is the contact area of the indentation. For an indenter whose geometry is known, the projected contact area $A$ is a function of the contact depth $h$, $A = F(h)$. At the peak load, $A = F(h_c)$.

Figure 24 Schematic diagram of a cross-section of a nanoindentation measurement. Modified from [148], Copyright 2002, with permission from Elsevier.
The function form, $F$, can be established through experiments. In order to determine $h_c$, we know from Figure 24 that

$$h_c = h - h_s$$

(18)

Sneddon’s expression (Equation (19)) can be used to obtain $h_s$ for a conical indenter

$$h_s = \frac{(\pi - 2)}{\pi} (h - h_f)$$

(19)

The term $(h - h_f)$ means that only the elastic portion is included. Through Sneddon's force–displacement, we can obtain that at peak load

$$h - h_f = 2 \frac{P_{max}}{S}$$

(20)

where $S = dP/dh$ is the experimentally measured initial unloading contact stiffness. Therefore,

$$h_s = 2(\pi - 2) \frac{P_{max}}{\pi S} = \varepsilon \frac{P_{max}}{S}$$

(21)

For the flat punch, $\varepsilon$ is 1.0, for the conical punch $\varepsilon$ is 0.72, and for the Berkovich indenter, $\varepsilon$ is 0.75. The unloading curve can be described as Equation (22):

$$P = B(h - h_f)^m$$

(22)

where $B$ and $m$ are constants. The values of $m$ are 1, 2, and 1.5 for flat, conical and spherical punch geometries, respectively. At peak load, we can obtain

$$S = \left(\frac{dP}{dh}\right)_{h=h_{max}} = Bm(h_{max} - h_f)^{m-1}$$

(23)

For a Berkovich indenter,

$$A = 24.56h^2$$

(24)

Because of the lack of plastic behavior, the elastic modulus of the sample can be calculated from the initial unloading contact stiffness, $S = dP/dh$, which is the slope of the initial part of the unloading curve. So,

$$S = 2\beta \sqrt{\frac{A}{\pi E_r}}$$

(25)

where $S$ is the experimentally measured initial unloading contact stiffness. $A$ is the projected contact area of the indentation. $\beta$ is an indenter geometry depended constant ($\beta$ of the Berkovich indenter is 1.304). $E_r$ is a reduced modulus, which is defined because of the elastic deformation on the indenter. It is given by the Equation (26):

$$E_r = \frac{1 - v^2}{E} + \frac{1 - v_i^2}{E_i}$$

(26)
where $E$ is Young’s modulus and $\nu$ is Poisson’s ratio of the sample. $E_i$ and $\nu_i$ are the elastic modulus and Poisson’s ratio of the indenter, respectively [148].

In this research, nanoindentation measurements with a Berkovich indenter were conducted on all the well-polished samples using a MTS NANO Indenter XP testing system. Each sample was measured 10–15 times at different positions. For the HPT-treated samples, the measurements were from their center to edge to analyze the hardness and modulus changes as functions of the deformation degree. Each position was measured at least three times. The maximum displacement was 2000 nm.

To study the elastic deformation process, nanoindentation measurements by a spherical indenter with diameter of 2.3 μm were also performed on selected polished samples. With this indenter, the elastic deformation depth (50-100 nm) is much larger than the measurements with Berkovich indenter, because of the less stress concentration. Thus, accurate elastic strain limit can be obtained by a first pop-in event method [146]. Ten indentation tests were performed on each sample at different positions with a loading rate of 0.5 mN s$^{-1}$ and maximum load of 20 mN.

2.5.4. In-situ tensile/compression test

Tensile and compression tests are important for mechanical properties analysis of materials. A stress–strain curve can be obtained from a calculated load–displacement curve. From the stress–strain curve, the elastic modulus, strength, and ductility of the materials can be obtained. The stress and strain have the relations (27), (28):

\[
\sigma = \frac{P}{A_0} \tag{27}
\]

\[
\varepsilon = \frac{\Delta L}{L_0} \tag{28}
\]

where $\sigma$ is the normal stress, $P$ is the applied load, $A_0$ is the original cross-sectional area, $\varepsilon$ is the normal strain, $\Delta L$ is the length change of the sample, and $L_0$ is the original length of the sample.

For BMGs, the shear band behavior is crucial for their mechanical performance, which has significant effects on the plastic deformation and crack propagation. Thus, in-situ tensile/compression testing under SEM is a powerful tool to observe the formation and sliding of shear bands during deformation and analyze the mechanical property changes in BMG.
samples. It should be noticed that the BMGs we studied here are much harder than the steel made test stage. On the load–displacement curve (Figure 25 (b)), the initial elastic deformation part is unreliable due to the deformation of the sample holder. The accurate elastic strain of samples can be estimated by directly measuring the sample length change from SEM images during testing, as shown in Figure 25 (c). The plastic displacement on the curve is reliable, as it is entirely localized on the thin samples.

In this research, tensile samples were cut as a dog-bone shape with a 2 mm × 1 mm × 0.3 mm narrow middle. The HPT-treated samples were cut from the disks at the same position as the DSC samples (2 mm from the center) which have the same strain state. The compression samples were prepared as cylinders with length 2 mm and diameter 1 mm. The in-situ tests were conducted in a high-resolution field-emission SEM (Leo-1550, ZEISS, Germany) with a MicroDAC (Kammrath and Weiss) tensile/compression test stage (Figure 25 (a)). The strain rate was $5 \times 10^{-5}$ s$^{-1}$ until the fracture of the samples. The load–displacement curves and sample surface images were recorded at the same time during the test (Figure 25 (b) and (c)). All the measurements were repeated twice to ensure the repeatability of the observed results. Standard compression tests were also conducted with strain of rate $10^{-4}$ s$^{-1}$ on the samples with length of 4 mm and diameter of 2 mm.

Figure 25 (a) In-situ tensile test stage. (b) Load–displacement curve obtained during test (deformed $Zr_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3}$ sample by HPT for two rotations). (c) SEM image obtained during original test.
3. Experimental Results
3.1. Structure of nanostructured BMGs

The structures of the as-cast Zr$_{64-x}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_x$ (x = 0–16 at.%) samples with 2 mm diameter were first studied by XRD (with Cu-Kα radiation). From the XRD patterns in Figure 26, it can be found that samples with Co content lower than 8.3 at.% are fully amorphous. The crystalline Zr$_{64-x}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_x$ alloys are rather brittle. Therefore, in this research, I focus on the BMG samples with composition Zr$_{64-x}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_x$ (x = 0–8.3 at.%). Disc shape samples (φ 10mm, h 0.8mm) were also casted, which are full amorphous [149]. The maximum points (obtained by Gaussian fitting) on the XRD curves shift right to higher 2θ value with the increasing Co content. For Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$, it is at 36.58°, which moves to 37.12° when the Co content reaches 8.3%. This indicates a denser structure. It is coincident with the mass density change measured by Archimedes’ method which increases from 6.78±0.01 g/cm$^3$ to 6.88±0.01 g/cm$^3$ as shown in Table 3 [149].

![Figure 26 XRD patterns of BMGs with composition Zr$_{64-x}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_x$ (x = 0–16 at.%). Modified from [149].](image)

Synchrotron radiation XRD with short wavelength (0.124 Å) can characterize the finer atomic structure of BMGs. As introduced in Chapter 2, the structure factor as a function of wave vector, S(Q), can be obtained from the diffraction intensity data. All the as-cast samples with five different compositions have similar S(Q) in Figure 27. Pair distribution functions (G(r)) are the Fourier transformation of S(Q) as shown in Figure 28. As shown on the magnified image of the first peaks (Figure 28 (b)), it can be observed that with increasing Co content, the first peak amplitude is reduced and the height of its left-side shoulder (r ≈ 2.72 Å) increases. This
means that the addition of Co in this BMG leads to the rearrangement of the atomic packing and formation of new topological structure with shorter atomic bonds, resulting in reduced average atomic distance [149].

![Figure 27 (a) Structure factors of Zr$_{64-x}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_x$ (x = 0–8.3 at.%) BMG samples and (b) magnification of the first peaks on their structure factors (DESY, Hamburger). Modified from [149].](image1)

![Figure 28 (a) Pair distribution functions (PDFs) and (b) magnification of the first peaks on PDFs, of Zr$_{64-x}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_x$ (x = 0–8.3 at.%) BMG samples (DESY, Hamburg). Modified from [149].](image2)

To investigate the newly formed topological structure and chemical ordering, EXAFS analysis is carried out for certain selected BMG samples (Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$, Zr$_{60}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_4$, and Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_8.3$). The radial distribution functions of these three samples with Co or Zr as the center element (Co-K edge or Zr-K edge) were obtained. As shown in Figure 29 (a), on the Co-K edge EXAFS results, no change can be detected for either the Zr$_{60}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_4$ or Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_8.3$ BMGs, indicating that the atomic surrounding environment around Co is...
not influenced by changing the Co content. This means that the newly formed topological structure is not changed in the BMG samples with different Co content. As shown in Figure 29 (b), the height of Zr-Zr bond peak (2.90 Å) reduces with the increase in the Co content. Meanwhile, the peak height of Zr-Ni, Zr-Cu, or and Zr-Co bonds (their bond lengths are similar and cannot be distinguished from each other on the curves) increases. Furthermore, the maximum point of this peak (Zr-Ni, Zr-Cu, or and Zr-Co bonds) shifts left from 2.48 Å to a smaller value of 2.41 Å, indicating the reduced atomic bond length. Thus, it can be known that, in the new topological structure, Zr-Zr bonds are replaced by the formed shorter and stronger Zr-Co bonds, resulting in a reduced average atomic distance in the Zr$_{64-x}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_x$ (x = 0–8.3 at.%) BMGs [149].

\[ \text{Figure 29 Extended X-ray absorption fine structure (EXAFS) of (a) Co K-edge data and (b) Zr K-edge data, of selected Zr}_{64-x}\text{Ni}_{10}\text{Al}_7\text{Cu}_{19}\text{Co}_x (x = 4 \text{ and } 8.3) \text{BMG samples (SSRF, Shanghai). Modified from [149].} \]

To analyze the element distribution, Zr$_{64-x}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_x$ (x = 0–8.3) BMGs were studied by SEM (secondary electron imaging and backscattering electron imaging). However, only homogeneous structure for all samples can be detected on the micrometer scale. Then, TEM was further used to investigate the structure of the Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ and Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMG samples on the nanometer scale. As shown in Figure 30, the electron diffraction patterns show that both samples have fully amorphous structure. In the HRTEM images, a difference can be observed that a relatively homogeneous structure was detected in the as-cast Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ sample, whereas nanometer-scale amorphous clusters are clearly detected in the as-cast Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ sample. Nanoscale phase separation (5–10 nm) seems likely.
to take place in the Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMG sample, because of the positive enthalpy of mixing between copper and cobalt [149].

![Figure 30 TEM images of two BMG samples (a) Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ and (b) Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$.](image)

As introduced in the last chapter, compared with normal TEM analysis, HAADF is more sensitive to the composition change in materials. Figure 31 shows the HAADF image of the two-type samples mapped by STEM. It is found that elements with higher Z (Zr) enrich in the structure (bright points) of Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMG, which further verify the nanometer-scale phase separation [147].

![Figure 31 High-angle annular dark-field imaging of as cast samples (a) Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ and (b) Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMGs.](image)

SAXS is a powerful method to analyze the size of the nanometer-scale second phase in materials. Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMG sample with 30 μm thickness were polished for SAXS
with an incident beam with wavelength of 0.154 nm. Scattering patterns were acquired in transmission geometry by a 2D detector. The 2D images were integrated azimuthally, corrected for background scattering and normalized. The resulting scattering intensity I(Q) was plotted as a function of the scattering vector Q. Figure 32 shows the SAXS results for the Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMG sample. A peak can be observed at $Q = 0.6 \text{ nm}^{-1}$, indicating the nano-scale heterogeneity.

![Figure 32 X-ray small-angle scattering result of Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ sample (BSRF, Beijing).](image-url)
3.2. Properties of nanostructured BMGs

3.2.1. Thermal properties

To study the thermal properties of the homogeneous and nanoheterogeneous BMGs, DSC analysis was conducted. The results in Figure 33 show that the cobalt component significantly affects the thermal properties of the samples. The single crystallization peak of the Zr$_{64}$Ni$_{10}$Al$_{7}$Cu$_{19}$ BMG at 723 K separates into two. The glass transition temperature $T_g$ of the alloys shifts right from 648 to 675 K with increasing Co content, because of the stronger atomic bonds. Meanwhile, the first crystallization temperature decreases (from 723 to 701 K), resulting in the reduced thermal stability of the supercooled liquid ($T_{x1} - T_g$ gets smaller with Co content). The second crystallization peaks move to higher temperature. The thermal parameters of the Zr$_{64-x}$Ni$_{10}$Al$_{7}$Cu$_{19}$Co$_x$ ($x = 0$–8.3) BMGs are listed in Table 3.

![DSC curves](image1)

Figure 33 (a) DSC curves, (b) glass transition temperature $T_g$ of Zr$_{64-x}$Ni$_{10}$Al$_{7}$Cu$_{19}$Co$_x$ ($x = 0$–8.3 at.%) BMGs as a function of Co content. Modified from [150], with the license “CC-BY 4.0” (https://creativecommons.org/licenses/by/4.0/).

3.2.2. Mechanical properties

The ultrasound pulse-echo technique with a pulse frequency of 2.25 MHz was first utilized to analyze the mechanical property changes of the BMGs. The measured results are shown in Table 3. It can be seen that, similar as the $T_g$ change, both Young’s moduli and hardness of these BMGs increase monotonically with the Co content. The change of Poisson’s ratio is more complicated, such that it first reduces from 0.391±0.002 for the Zr$_{64}$Ni$_{10}$Al$_{7}$Cu$_{19}$ BMG to 0.385±0.002 for the BMG sample with composition Zr$_{58}$Ni$_{10}$Al$_{7}$Cu$_{19}$Co$_6$ and then increases to 0.393±0.002 when the Co content reaches 8.3%. The change in the ratio of shear modulus to
bulk modulus ($\mu/B$) is opposite, which increases from 0.235±0.003 to 0.250±0.003 and then decreases to 0.231±0.003.

Figure 34 shows the stress–strain curves of the Zr$_{64-x}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_x$ ($x = 0$–8.3) BMG samples of length 4 mm and diameter 2 mm obtained by a standard compression test with strain rate $10^{-4}$ s$^{-1}$. Each measurement was repeated for three times. The elastic property changes are interesting. It is shown in Table 3 that Young’s moduli of the samples increase with the Co content from 76±2 MPa to 85±2 MPa. Meanwhile, the maximum elastic strain also increases to 2.6% when the Co content is 8.3%. It can be confirmed by nanoindentation analysis which will be further discussed in the next chapter. The plastic strain decreases first with increasing Co content (up to 6%) from 3±0.5% to 1.5±0.5%. For the Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMG, the ductility improves markedly such that its plastic strain reaches approximately 4±0.5% [149]. This is coincident with the change tendency of Poisson’s ratio and $\mu/B$ [180,181].

**Table 3 Parameters of Zr$_{64-x}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_x$ ($x = 0$–8.3) BMGs: $T_g$, $T_{x1}$, $T_{x2}$, $T_m$, $T_i$, $E$, $\nu$, $\mu/B$, density, and hardness.**

<table>
<thead>
<tr>
<th>C(Co) (at%)</th>
<th>$T_g$ (K)</th>
<th>$T_{x1}$ (K)</th>
<th>$T_{x2}$ (K)</th>
<th>$T_m$ (K)</th>
<th>$T_i$ (K)</th>
<th>$E$ (GPa)</th>
<th>$\nu$</th>
<th>$\mu/B$</th>
<th>Density (g/cm$^3$)</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>648±3</td>
<td>723±3</td>
<td>-</td>
<td>1103±3</td>
<td>1185±3</td>
<td>76±2</td>
<td>0.391±0.002</td>
<td>0.235±0.003</td>
<td>6.78±0.01</td>
<td>5.3±0.1</td>
</tr>
<tr>
<td>2.7</td>
<td>654±3</td>
<td>710±3</td>
<td>730±3</td>
<td>1106±3</td>
<td>1194±3</td>
<td>79±3</td>
<td>0.390±0.002</td>
<td>0.237±0.003</td>
<td>6.82±0.01</td>
<td>5.5±0.1</td>
</tr>
<tr>
<td>4</td>
<td>668±3</td>
<td>710±3</td>
<td>748±3</td>
<td>1108±3</td>
<td>1203±3</td>
<td>80±2</td>
<td>0.388±0.002</td>
<td>0.241±0.003</td>
<td>6.85±0.01</td>
<td>5.9±0.2</td>
</tr>
<tr>
<td>6</td>
<td>670±3</td>
<td>706±3</td>
<td>769±3</td>
<td>1115±3</td>
<td>1223±3</td>
<td>82±2</td>
<td>0.385±0.002</td>
<td>0.250±0.003</td>
<td>6.86±0.01</td>
<td>5.9±0.1</td>
</tr>
<tr>
<td>8.3</td>
<td>675±3</td>
<td>701±3</td>
<td>794±3</td>
<td>1121±3</td>
<td>1268±3</td>
<td>85±3</td>
<td>0.393±0.002</td>
<td>0.231±0.003</td>
<td>6.88±0.01</td>
<td>6.2±0.1</td>
</tr>
</tbody>
</table>
Figure 34 Standard compression stress–strain curves of Zr$_{64-x}$Ni$_{10}$Al$_3$Cu$_{19}$Co$_x$ ($x = 0–8.3$) BMGs. Modified from [149].
3.3. Annealing treatment on homogeneous and nanoheterogeneous BMGs

In our previous research, we tried to prepare the nanoscale crystalline–amorphous composite structure by high-temperature annealing. A Zr\textsubscript{55.7}Ni\textsubscript{10}Al\textsubscript{7}Cu\textsubscript{19}Co\textsubscript{8.3} BMG sample was heated to 733 K (between its first and second crystallization peaks). An XRD spectrum (Figure 35) of this sample exhibits clear signs of crystallinity. To further investigate the microstructure of the annealed specimen, a TEM investigation was performed. Figure 36 shows a TEM bright-field image of such a specimen. Nanoscale crystalline grains can be observed.

Figure 35 XRD of Zr\textsubscript{55.7}Ni\textsubscript{10}Al\textsubscript{7}Cu\textsubscript{19}Co\textsubscript{8.3} BMG sample annealed at 733 K.

Figure 36 TEM bright-field image of Zr\textsubscript{55.7}Ni\textsubscript{10}Al\textsubscript{7}Cu\textsubscript{19}Co\textsubscript{8.3} BMG annealed at 733 K.

Although the structure was obtained as designed, the mechanical properties of the sample were not as wished. Because of the brittleness of the formed crystalline phase, no plastic strain could be detected under compression testing. Thus, in the following research, I focused
on the effect of low-temperature annealing, i.e. annealing at temperatures below the crystallization temperature $T_x$ of the samples.

As discussed above, low temperature annealing could change the structure of BMGs and improve their mechanical properties by introducing the thermal stress and non-affine strain. In this work, isothermal annealing was utilized on Zr$_{64-x}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_x$ BMGs. The samples were rapidly heated (160 K/min) to a fixed temperature and then held for 10 h. XRD and DSC were used to analyze the structural changes. The mechanical properties of the annealed BMGs were measured by nanoindentation and compression testing.

### 3.3.1. Effect of annealing on thermal properties of homogeneous BMGs

Homogeneous Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ BMG samples were annealed at various temperatures within the range of 606–658 K ($T_g$ of the sample is 648 K). Thermal property was firstly measured by DSC (Figure 37), which is sensitive to the thermal properties change. Annealing introduces an endothermic overshoot (enthalpy recovery) on the DSC curves at ~670 K, as shown in Figure 37 (b). The height of this overshoot increases at first and then decreases with further increases in the annealing temperature. The maximum of the peak shifts to a higher temperature with the increasing annealing temperature. The crystallization processes are affected only by high-temperature annealing (i.e. 627 K, 637 K, 648 K and 658 K, as shown in Figure 37 (c)). Figure 37 (c) shows that with the increase of annealing temperature, the crystallization exothermic peak keeps stable first and then shifts to a lower temperature when the annealing temperature is higher than 627 K. It shifts from 748 K to 737 K by annealing at 658 K with the reduction of peak height and increase of peak width. The crystallization enthalpy is unaffected.

![Figure 37](https://example.com/fig37.png)

*Figure 37 (a) DSC curves, (b) Changes in the heat flow above $T_g$. The cross on the curve is the annealing temperature, (c) Changes in the crystallization peak on the DSC curves, of Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ BMG samples annealed at different temperatures. Modified from [150], with the license “CC-BY 4.0” (https://creativecommons.org/licenses/by/4.0/).*
3.3.2. Effect of annealing on thermal properties of nanoheterogeneous BMGs

Samples with various Co contents were annealed at different temperatures below $T_g$ (563 K and 583 K). Figure 38 shows the DSC curves of the as cast and annealed samples. It can be seen that at these temperatures, annealing has no effect on the crystallization processes of these BMGs that their crystallization temperature and enthalpy are not changed. While, the structural relaxation process below $T_g$ is affected. As marked by arrow in Figure 38 (b), the low-temperature (563 K) annealed nanoheterogeneous BMG sample ($Zr_{55.7}Ni_{10}Al_7Cu_{19}Co_{8.3}$) has an endotherm-reducing event around 380 K. This phenomenon cannot be observed on the DSC curve of the annealed homogeneous sample ($Zr_{64}Ni_{10}Al_7Cu_{19}$). After high-temperature (583 K) annealing, there is no endotherm-reducing event for both $Zr_{64}Ni_{10}Al_7Cu_{19}$ and $Zr_{55.7}Ni_{10}Al_7Cu_{19}Co_{8.3}$ samples. The endothermic overshoot on $Zr_{64}Ni_{10}Al_7Cu_{19}$ BMG (marked by arrow in Figure 38 (c)) becomes less obvious with the increase in Co content. The reason for the difference of thermal properties between the annealed homogeneous and nanoheterogeneous BMGs will be discussed in detail in the next chapter.

![Figure 38 (a) DSC curves of the as-cast BMGs, (b) DSC curves of the BMGs annealed at 563 K, (c) DSC curves of the BMGs annealed at 583 K, with different Co compositions.](image-url)
3.3.3. Effect of annealing on mechanical properties

An interesting change can be observed on the nanoindentation-measured hardness. It is reported that the hardness of BMGs usually increases after annealing, due to the free volume annihilation [165]. Nanoindentation analysis shows that the hardness of the BMG samples increases for 0.3–0.4 GPa by annealing (563 K) when their Co content is lower than 8.3%. While the hardness of the Zr$_{55.7}$Ni$_{10}$Al$_{7}$Cu$_{19}$Co$_{8.3}$ sample is reduced from 6.2±0.2 to 6.0±0.2 GPa as shown in Figure 39. After high-temperature annealing (583 K), the hardness of all samples increases.

![Figure 39 Nanoindentation hardness of unannealed and low-temperature annealed (563K) BMGs samples with different Co content. Reprinted from [150], with the license “CC-BY 4.0” (https://creativecommons.org/licenses/by/4.0/).](image)

Because of this unusual softening, improved plasticity of the annealed (563 K) Zr$_{55.7}$Ni$_{10}$Al$_{7}$Cu$_{19}$Co$_{8.3}$ BMG sample was expected. Then it was subjected to a compression test. Unfortunately, the plastic strain was small as show in Figure 40.

![Figure 40 In-situ compression stress–strain curve of the low-temperature annealed (563K) Zr$_{55.7}$Ni$_{10}$Al$_{7}$Cu$_{19}$Co$_{8.3}$ BMG sample.](image)
3.4. Thermal cycling treatment on homogeneous and nanoheterogeneous BMGs

In order to introduce the non-affine thermal strain and avoid the annihilation of free volume during annealing, low-temperature thermal cycling treatments on BMGs have been developed. In some research [74], it leads to the structural rejuvenation with the increasing free volume in some relative homogeneous BMGs and improves their ductility. Thus, with the difference in thermal expansion coefficient between various phases, more pronounced improvement on nanoscale heterogeneous BMGs is wished. In this work, thermal cycling between liquid nitrogen and boiling water temperatures was performed 1, 4, 8, 10, 15, 20, 40, 80, and 160 times on \( \text{Zr}_{64}\text{Ni}_{10}\text{Al}_{7}\text{Cu}_{19} \) and \( \text{Zr}_{55.7}\text{Ni}_{10}\text{Al}_{7}\text{Cu}_{19}\text{Co}_{8.3} \) samples. XRD and DSC were performed on all the treated samples to analyze their structural changes. Their mechanical properties were also measured by the ultrasound pulse-echo technique, nanoindentation, Vickers hardness measurement, and in-situ tension test.

3.4.1. Effect of thermal cycling on structures and thermal properties

As shown in Figure 41, both the homogeneous \( \text{Zr}_{64}\text{Ni}_{10}\text{Al}_{7}\text{Cu}_{19} \) and nanoheterogeneous \( \text{Zr}_{55.7}\text{Ni}_{10}\text{Al}_{7}\text{Cu}_{19}\text{Co}_{8.3} \) samples remained fully amorphous after thermal cycling that no crystalline peak was observed in the XRD results. The position of the maximum point on the XRD curves did not change with the number of cycles, which is at \( 2\theta = 36.58^\circ \) for \( \text{Zr}_{64}\text{Ni}_{10}\text{Al}_{7}\text{Cu}_{19} \) and \( 2\theta = 37.12^\circ \) for \( \text{Zr}_{55.7}\text{Ni}_{10}\text{Al}_{7}\text{Cu}_{19}\text{Co}_{8.3} \). From the DSC results (Figure 42), it can be seen that the crystallization processes of the samples are not affected, with an unchanged \( T_g \) and \( T_x \).

Figure 41 X-ray diffraction patterns of thermal cycling treated samples with different cycling number (a) \( \text{Zr}_{64}\text{Ni}_{10}\text{Al}_{7}\text{Cu}_{19} \) and (b) \( \text{Zr}_{55.7}\text{Ni}_{10}\text{Al}_{7}\text{Cu}_{19}\text{Co}_{8.3} \).


3.4.2. Effect of thermal cycling on mechanical properties

The mass densities of samples were measured by Archimedes’ method. As shown in Figure 43, no obvious changes with different cycling numbers were detected, which are all within the results deviation range. Same as the as-cast state, the densities of cycled Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ and Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ samples are around 6.78±0.01 g/cm$^3$ and 6.88±0.01 g/cm$^3$ respectively, as shown in Figure 43.

![Figure 42 DSC curves of (a) Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ and (b) Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ as-cast and treated BMGs with different numbers of thermal cycles.](image)

![Figure 43 Density change of both samples as a function of thermal cycling number.](image)

The ultrasound pulse-echo technique was used to measure the Young’s moduli (Figure 44 (a)), shear moduli (Figure 44 (b)), and Poisson’s ratio (Figure 44 (c)) of the treated samples. All of them show little change compared with the uncycled samples. The Young’s modulus of the
treated samples with and without Co remain around 76±2 and 85±2 GPa, respectively. The shear modulus of the two samples are close, which are 27.5±1 and 28.5±1 GPa. No effect of thermal cycling is observed on them. The unchanged Poisson’s ratio (within the results deviation range) with a mean value of 0.392±0.002 and 0.393±0.002 shows that the ductility of the samples could not be affected by the thermal cycling either. The Vickers hardness of the samples is stable with different thermal cycling treatments (Figure 44 (d)). The value is always around 455±10 HV for Zr64Ni10Al7Cu19 samples and 470±10 HV for Zr55.7Ni10Al7Cu19Co8.3 samples.

**Figure 44 Changes of (a) Young’s moduli, (b) shear moduli, (c) Poisson’s ratio, (d) Vickers hardness of both samples as a function of thermal cycling number.**

Tensile testing was carried out on a cycled (150 times) nanoheterogeneous Zr55.7Ni10Al7Cu19Co8.3 sample to detect its plasticity change. As shown in Figure 45, there is no improvement in the ductility after thermal cycling that the plastic strain is 0%.
Figure 45 Stress–strain curve of the thermal cycling (150 times) treated Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMG sample by in-situ tensile test.
3.5. Severe plastic deformation on homogeneous and nanoheterogeneous BMGs

As introduced above, severe plastic deformation treatment could improve the mechanical properties of both crystalline alloys and metallic glasses. For amorphous structure, a more disordered structure with more free volume could form during this treatment, leading to more shear bands initiation in the following plastic deformation. This large number of introduced shear bands can lead to more homogeneous deformation and improve ductility of BMGs.

HPT is a new technique developed for the severe plastic deformation treatment of materials. In this work, HPT was carried out on as-cast Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ and Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ samples for 2, 5, 10, and 20 rotations. The effect of the deformation degree on the structure and properties of homogeneous and nanoheterogeneous BMGs was investigated. All the samples had no cracks formed during severe plastic deformation treatments.

3.5.1. Effect of severe plastic deformation on structure and thermal properties

Figure 46 shows XRD patterns of all severely plastically deformed (HPT-treated) samples. Except the broad peaks, no sharp crystalline diffraction peaks can be observed for all samples, meaning that all the samples remain amorphous after HPT treatment.

Figure 46 XRD patterns of as-cast and HPT-treated samples with different deformation degrees (a) Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ and (b) Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$. Reprinted from [151], with the license “CC-BY 4.0” (https://creativecommons.org/licenses/by/4.0/).
Figure 47 and Figure 48 show TEM images of samples before and after severe plastic deformation. Relatively homogeneous structure was detected in the as-cast Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ sample while nanometer scale glassy clusters are clearly detected in the as-cast Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ sample, which have been analyzed above. TEM images in Figure 47(c)(d) and Figure 48(c)(d) reveal that after HPT for 2 rotations, Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ MG sample remains relative homogeneous while significant changes take place for the Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ MG sample. The nanometer scale crystalline particles appear as bright points on the dark field image for the Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ sample in Figure 48(c). The reason for the formation of nanocrystalline particles in Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ sample induced by HPT is the less thermal stability of its supercooled liquid ($\Delta T_{x_1}$-$T_g$ is as small as 26K). More induced shear bands (SBs) can also be observed on the TEM images of Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ sample as compared to the Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ sample after 2-rotation HPT. It should be noticed that more nanocrystalline particles are found along SBs as compared to the matrix, because of high degree plastic deformation in SBs during HPT. With further increasing deformation degree (up to 20 rotations), no obvious changes were detected by TEM in Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ sample, while homogenization of the glass structure was observed in Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ sample (Figure 48(e)) due to the deformation-accelerated diffusion and temperature rise during the high deformation degree HPT. It will be further discussed in the next chapter. Slight growth in the size of nanocrystalline particles was also observed on Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ sample (diameter 5-10 nm, marked by arrows and circles in Figure 48(e)(f)). The content of nanocrystalline particles is small, most likely less than 5%, so that they cannot be detected by conventional XRD and DSC measurements [151].
Figure 47 TEM images of Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ (a) Dark-field image of as-cast sample. (b) Bright-field HRTEM image of as-cast sample. (c) Dark-field image of deformed sample by HPT for two rotations. (d) Bright-field HRTEM image of deformed sample by HPT for two rotations. (e) Dark-field HRTEM image of deformed sample by HPT for 20 rotations. (f) Bright-field HRTEM image of deformed sample by HPT for 20 rotations. Modified from [151], with the license “CC-BY 4.0” (https://creativecommons.org/licenses/by/4.0/).

Figure 48 TEM images of Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ (a) Dark-field image of as-cast sample. (b) Bright-field HRTEM image of as-cast sample. (c) Dark-field image of deformed sample by HPT for two rotations. (d) Bright-field HRTEM image of deformed sample by HPT for two rotations. (e) Dark-field HRTEM image of deformed sample by HPT for 20 rotations. (f) Bright-field HRTEM image of deformed sample by HPT for 20 rotations. Modified from [151], with the license “CC-BY 4.0” (https://creativecommons.org/licenses/by/4.0/).
DSC measurements performed for all severe plastic deformed samples reveal HPT treatments do not affect the crystallization processes for both-type MGs with no obvious change on glass transition temperature, $T_g$, $T_x$ and crystallization enthalpy as shown in Figure 49 and Table 4. Because the nanocrystalline content in Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ sample is too small, the change in the thermal properties cannot be observed either, as they are within the the results deviation range [151].

![DSC curves of (a) Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ and (b) Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ as-cast and treated BMGs samples with different HPT rotation numbers. Modified from [151], with the license “CC-BY 4.0”](https://creativecommons.org/licenses/by/4.0/).

![Table 4 Thermal parameters of $T_g$, $T_{x1}$, $T_{x2}$, $T_b$ first crystallization enthalpy $\Delta H_{x1}$, and second crystallization enthalpy $\Delta H_{x2}$ of Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ and Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMG samples before and after HPT process (N = 2, 5, 10, 20). Reprinted from [151], with the license “CC-BY 4.0”](https://creativecommons.org/licenses/by/4.0/).

<table>
<thead>
<tr>
<th></th>
<th>Zr$<em>{64}$Ni$</em>{10}$Al$<em>7$Cu$</em>{19}$</th>
<th>Zr$<em>{55.7}$Ni$</em>{10}$Al$<em>7$Cu$</em>{19}$Co$_{8.3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ascast</td>
<td>N=2</td>
</tr>
<tr>
<td>$T_g$ (K)</td>
<td>648±3</td>
<td>649±3</td>
</tr>
<tr>
<td>$T_{x1}$ (K)</td>
<td>720±3</td>
<td>723±3</td>
</tr>
<tr>
<td>$T_{x2}$ (K)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$T_b$ (K)</td>
<td>1182±3</td>
<td>11±3</td>
</tr>
<tr>
<td>$\Delta H_{x1}$ (J/g)</td>
<td>-60±2</td>
<td>-59±2</td>
</tr>
<tr>
<td>$\Delta H_{x2}$ (J/g)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3.5.2. Effect of severe plastic deformation on mechanical properties

As discussed above, the compression plasticity of the Zr-based BMGs is obviously improved by the introduction of nanoscale heterogeneity that the compression plastic strain of the
Zr\textsubscript{55.7}Ni\textsubscript{10}Al\textsubscript{7}Cu\textsubscript{19}Co\textsubscript{8.3} BMG can reach 4%. However, its tensile plasticity is still low, less than 0.1%. Annealing and low-temperature cycling treatments have been tried on the BMGs. Although the structures were changed, neither of them was helpful to improve the tensile plasticity of the BMGs. Better tensile performance of HPT treated samples is wished.

SEM images and a load-displacement curve can be obtained during in-situ tension test. The tension stress-strain curves of as-cast and HPT treated samples are shown in Figure 50. Each measurement was repeated for three times and the deviation of the experimental results is smaller than 0.2%. Similar as the results reported in many other publications [153-155], both as-cast MGs show almost no plastic strain in tension, 0% for Zr\textsubscript{64}Ni\textsubscript{10}Al\textsubscript{7}Cu\textsubscript{19} and 0.07% for Zr\textsubscript{55.7}Ni\textsubscript{10}Al\textsubscript{7}Cu\textsubscript{19}Co\textsubscript{8.3} MGs samples, respectively. The deformation concentrates in one or two major SBs. Different from compression process, these SBs extend to cracks easily under tensile load which leads to catastrophic fracture very fast after yielding. It is slightly improved on as-cast Zr\textsubscript{55.7}Ni\textsubscript{10}Al\textsubscript{7}Cu\textsubscript{19}Co\textsubscript{8.3} sample because of the inhibition of SB propagation by the nanometer scale second phase. After HPT for 2 rotations, the tensile ductility of both samples is improved significantly, 0.5±0.1% for Zr\textsubscript{64}Ni\textsubscript{10}Al\textsubscript{7}Cu\textsubscript{19} MG and 0.9±0.1% for Zr\textsubscript{55.7}Ni\textsubscript{10}Al\textsubscript{7}Cu\textsubscript{19}Co\textsubscript{8.3} MG. Plastic strain of 0.9% is a high value for MGs under tension with slow strain rate and at room temperature. While the plastic strain of both relative homogeneous and nano-structured MGs samples decrease to 0.1% ~ 0.3%, when the HPT deformation degree further increases (N=5, 10, 20) [151].

Figure 50 Tensile stress–strain curves of Zr\textsubscript{64}Ni\textsubscript{10}Al\textsubscript{7}Cu\textsubscript{19} and Zr\textsubscript{55.7}Ni\textsubscript{10}Al\textsubscript{7}Cu\textsubscript{19}Co\textsubscript{8.3} samples before and after HPT process. Modified from [151], with the license “CC-BY 4.0” (https://creativecommons.org/licenses/by/4.0/).
Nanoindentation with a Berkovich indenter was also performed on all the as-cast and HPT-treated disc samples from their center to edge regions to analyze the mechanical property changes. The nanoindentation hardness radial distributions of the untreated and treated Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ samples are shown in Figure 51 (a). It can be seen that the values of all samples are similar in the central region (0–0.5 mm from the center) due to the low shear strain ($\gamma = \frac{2\pi NR}{h}$) with small $R$. While, the hardness in the outer region (0.5–2.5 mm from the center) increases with the deformation degree, which reaches 6.3±0.1 GPa for the sample treated by 20 rotations of HPT. In the edge region (more than 2.5 mm from the center), the value of the nanoindentation hardness decreases due to the microcracks appearing during severe plastic deformation in the edge of the sample. Figure 51 (b) shows the radial distribution of the nanoindentation hardness values of the as-cast state and all the HPT-treated nanoheterogeneous samples (Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$). Its change tendency is different from that of the homogeneous Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ samples. In the outer region, the hardness value reaches a maximum (6.4±0.1 GPa) by two rotations HPT treatment and no further enhancement can be detected with further increasing the rotation number (5, 10, 20 rotations). No hardness reduction can be observed in the edge region of these samples due to their better ductility, indicating that microcracks did not appear during severe plastic deformation.

![Figure 51 Nanoindentation hardness distribution of as-cast and HPT-treated (rotation number $N = 2, 5, 10, \text{ and } 20$) (a) Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ and (b) Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMG samples.](image)

The Young’s modulus radial distributions of all samples are shown in Figure 52 (a) and (b). Similar to the hardness value changes, the heterogeneous structure is more sensitive for the low-degree deformation. After two turns of deformation, Young’s modulus of the Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ sample increases from 84±2 to 92±2 GPa and no further enhancement
was detected with further increasing the deformation degree. However, Young’s modulus of the Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ sample increases from 78±2 to 83±2, 85±2, 87±2, and 89±2 GPa after HPT for 2, 5, 10, and 20 rotations, respectively.

Figure 52 Young’s modulus distribution of as-cast and HPT-treated (rotation number N = 2, 5, 10, and 20) (a) Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ and (b) Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMG samples.
4. Discussion
4.1. Effect of cobalt on thermodynamics of supercooled liquid

As discussed in Chapter 1, the thermodynamics of supercooled liquids are related to their glass-forming ability and the mechanical properties of the formed BMGs. “Fragile” liquid tends to have lower glass-forming ability, but form BMGs with better ductility. “Strong” liquid has the opposite characteristic [21,22]. The fragility index of a liquid $m$ is defined as Equation (29):

$$ m = \frac{d \log_{10} \eta(T)}{d \left( \frac{T_g}{T} \right)} \bigg|_{T=T_g} \quad (29) $$

where $\eta(T)$ is the viscosity, $T_g$ is the glass transition temperature. For “strong” liquid, it can be described by the Arrhenius form equation (Equation (5)) [156,157]. Then, fragility index $m$ can be expressed as Equation 30:

$$ m = \frac{E}{k_B T_g \ln 10} \quad (30) $$

where $E$ is the activation energy for local cooperative rearrangement at $T_g$, $k_B$ is Boltzmann’s constant. Alternatively, for “fragile” liquid, the viscosity is described by the Vogel–Fulcher–Tamman relation (Equation (4)) [158,159]. Then, $m$ can be described as Equation (31)

$$ m = \frac{B T_g}{\ln 10 (T_g - T_0)^2} \quad (31) $$

where $B$ and $T_0$ are fitting parameters that can be obtained from the heating rate dependence of glass transition temperature $T_g$, as Equation (32) [170]

$$ \beta = C \exp \frac{B}{T_0 - T_g} \quad (32) $$

where $\beta$ is the continuous heating rate and $C$ is a constant [160].

In order to analyze the effect of the Co component on the “fragility” of the glass-forming liquids, different heat rates $\beta$ (0.167, 0.333, 0.667, and 1 K/s) were used in DSC for each sample to measure the change in $T_g$. The measured $T_g$ and calculated $m$ are shown in Table 5.

It can be seen that there is no visible difference on fragility index $m$ for these alloys with various cobalt content, which are all around 40 with large error bars. The reason is the high thermal stability of “strong” liquids. Their $T_g$ fluctuation with heating rate is small compared with “fragile” glass forming liquids such as Pd-based liquids ($m$~65) [82,170], making this measurement and calculation difficult. For BMGs forming liquids, the value of $m$ is within 30~70 and a small value indicates “strong”. Glass forming liquids of all $\text{Zr}_{64-x}\text{Ni}_{10}\text{Al}_7\text{Cu}_{19}\text{Co}_x$
BMGs are “strong” relatively. As introduced, viscosity of “strong” liquid can be described by the Arrhenius form equation (Equation (5)). More accurate fragility index $m$ of $\text{Zr}_{64-x}\text{Ni}_{10}\text{Al}_7\text{Cu}_{19}\text{Co}_x$ alloys could be obtained by Equation (30).

<table>
<thead>
<tr>
<th>Co content (%)</th>
<th>$T_g$ (K) $\beta=0.167$ K/s</th>
<th>$T_g$ (K) $\beta=0.333$ K/s</th>
<th>$T_g$ (K) $\beta=0.667$ K/s</th>
<th>$T_g$ (K) $\beta=1$ K/s</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>644±3</td>
<td>648±3</td>
<td>656±3</td>
<td>662±3</td>
<td>40±7</td>
</tr>
<tr>
<td>2.7</td>
<td>651±3</td>
<td>654±3</td>
<td>664±3</td>
<td>668±3</td>
<td>41±7</td>
</tr>
<tr>
<td>4</td>
<td>664±3</td>
<td>668±3</td>
<td>675±3</td>
<td>681±3</td>
<td>42±7</td>
</tr>
<tr>
<td>6</td>
<td>667±3</td>
<td>671±3</td>
<td>679±3</td>
<td>683±3</td>
<td>41±8</td>
</tr>
<tr>
<td>8.3</td>
<td>672±3</td>
<td>675±3</td>
<td>685±3</td>
<td>690±3</td>
<td>42±7</td>
</tr>
</tbody>
</table>

In Equation 30, $E$ is the activation energy for local cooperative rearrangement, related with shear modulus and characteristic shoving volume. Shear modulus of a material is affected by its atomic arrangement. A relationship between the fragility index $m$ and the steepness $\lambda$ of the left-hand side of the first peak on pair distribution function of BMG, was given by [161] as Equation (33)

$$m = \frac{E}{k_B T_g \ln 10} = \frac{V_c C_G}{k_B T_g \ln 10} \left[ 1 + (2 + \lambda) \alpha T T_g \right]$$

(33)

where $\alpha_T$ is the thermal expansion coefficient, for ZrNiAlCu system, $\alpha_T T_g = 7.4 \times 10^{-3}$ [186]. $V_c$ is the characteristic atomic volume, which is related with the shear transformation zone (STZ) volume $V_{STZ}$, $V_c = \frac{1}{320} V_{STZ}$ [76,161]. As discussed in Section 1.3.2. and shown Figure 15, STZ volume $V_{STZ}$ is relevant with Poisson’s ratio $\nu$. Hence all the $\text{Zr}_{64-x}\text{Ni}_{10}\text{Al}_7\text{Cu}_{19}\text{Co}_x$ alloys should have similar $V_c$, because of their very close $\nu$ values (0.388 - 0.393, as shown in Table 3). $C_G$ is a constant independent of $T$ [161]. The fragility index $m$ of $\text{Zr}_{64}\text{Ni}_{10}\text{Al}_7\text{Cu}_{19}$ has been studied and published as 35 [21,82]. Thus, knowing the steepness $\lambda$ of the left-hand side of the first peak on their the pair distribution function (as shown in Figure 53 (a)), the $m$ values of $\text{Zr}_{64-x}\text{Ni}_{10}\text{Al}_7\text{Cu}_{19}\text{Co}_x$ glass forming liquids can be obtained as shown in Figure 53 (b). It can be seen that the liquids becomes more “fragile” with increasing Co content.
This change is coincident with some other research [21,22] that “fragile” liquid has worse glass-forming ability due to the thermodynamic driving force for crystal nucleation [11]. The critical diameter of the Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMG is 2 mm, whereas for the Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ BMG, it is more than 5 mm. A fully amorphous structure cannot even be formed with further increased Co content (10% and 16%). BMGs formed by “fragile” liquid usually show higher Poisson’s ratio $\nu$ and better ductility [82,164]. This is the reason for the improved compression plasticity (4%) of the Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMG. Their mechanical performance will be further discussed in the following section.
4.2. Mechanical property enhancement of nanostructured BMGs

4.2.1. Improved elastic properties

From the stress–strain curves of the as-cast BMGs samples in Figure 34, the maximum elastic strain in the compression test increases with Co content. It would be very interesting if the change tendency were true. Because their Young’s moduli, as shown in Table 3, also increase with the increasing Co content, which means that the stored recoverable elastic energy would increase dramatically. However, it is worth noting that due to the experimental loading conditions (such as inevitable shape changing of the sample holder), the obtained maximum elastic strains calculated from the stress–strain curves are relatively inaccurate.

To get accurate elastic strain limits (maximum elastic strain) of the as-cast BMGs samples with composition \( \text{Zr}_{64-x}\text{Ni}_{10}\text{Al}_{7}\text{Cu}_{19}\text{Co}_x \) (\( x = 0–8.3 \) at.%), the first pop-in method [146] was carried out on them by nanoindentation with a spherical indenter. Compared with the normally used Berkovich indenter, much larger elastic deformation depth (50-100 nm) can be obtained because of the less stress concentration, which is more helpful for the investigation of the elastic performance of materials. The first pop-in event corresponds to a transition from perfectly elastic to plastic deformation [146]. Thus, the elastic strain limit, corresponding to the displacement before the first pop-in (the yield depth), can be analyzed by nanoindentation measurements with relatively high accuracy, as shown in Figure 54. The displacement before the first pop-in in the inset of Figure 54 (a), which are averaged values from ten nanoindentation tests, indeed increases with increasing Co content.

In order to further confirm this effect, the lengths of the samples with and without yield loading were measured in SEM during the in-situ compression. As shown in Figure 54 (b), coincident with the first pop-in analysis by nanoindentation, the in-situ compression tests also reveal the increasing tendency of the elastic strain limit with Co content. The length change measured under SEM shows that the \( \text{Zr}_{55.7}\text{Ni}_{10}\text{Al}_{7}\text{Cu}_{19}\text{Co}_{8.3} \) BMG sample has 2.8% maximum elastic strain, which is higher than many reported values for other BMGs (1.8–2%) [76,107,165]. The reason for the improved maximum elastic strain and high increased Young’s modulus is that the denser nanoscale second phase effectively hinders the shear band propagation, resulting in higher critical activation stresses for shear bands [166]. Figure 54 (c) shows the stored recoverable elastic energies of the \( \text{Zr}_{64-x}\text{Ni}_{10}\text{Al}_{7}\text{Cu}_{19}\text{Co}_x \) (\( x = 0–8.3 \)) BMGs, which were calculated from Equation (34):
where \( E_{\text{per unit}} \) is the stored elastic energy of materials per cubic meter, \( E_Y \) is Young’s modulus, and \( \varepsilon_{\text{ESL}} \) is the maximum elastic strain of the material. As expected, \( E_{\text{per unit}} \) increases dramatically with the increasing of the Co content. For the Zr\(_{55.7}\)Ni\(_{10}\)Al\(_7\)Cu\(_{19}\)Co\(_{8.3}\) BMG, the value is 30–50 times higher than those of aluminum alloys and stainless steel. This high stored recoverable elastic energy gives this BMG good application potential for sports equipment, such as golf clubs and ski poles.
Figure 54  (a) Nanoindentation curves of Zr$_{64-x}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_x$ ($x = 0$–8.3) BMG samples. The inset is the position of the first pop-in event on the curve of each sample. (b) Maximum elastic strain measured from in-situ compression and displacement at the first pop-in event obtained from the (a) inset. (c) Stored recoverable elastic energies for Zr$_{64-x}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_x$ ($x = 0$–8.3) BMGs as a function of Co content. Modified from [149].
4.2.2. Shear band behavior during plastic deformation

As discussed, the nanometer-scale heterogeneity introduced by the addition of Co affects not only the elastic properties but also the plastic behavior of these BMGs, which is reflected in the compression stress–strain curves, Poisson’s ratio, and $\mu/B$ of the $\text{Zr}_{64-x}\text{Ni}_{10}\text{Al}_7\text{Cu}_{19}\text{Co}_x$ ($x = 0–8.3$) BMGs, as shown in Figure 34 and Table 3. In-situ compression experiments under SEM were performed that micrographs and videos could be taken during the deformation to monitor the formation and sliding of shear bands.

Figure 55 shows images of the yielded samples under load. On the surface of the $\text{Zr}_{64}\text{Ni}_{10}\text{Al}_7\text{Cu}_{19}$ BMG sample, all the shear bands have the same orientation (Figure 55 (a)). On the contrary, intersections of shear bands can be observed on the $\text{Zr}_{55.7}\text{Ni}_{10}\text{Al}_7\text{Cu}_{19}\text{Co}_{8.3}$ BMG sample (Figure 55 (c)). The reason for this is the nanoscale phase separation, as shown in Figure 30 and Figure 31. The interfaces in this structure with more free volume lead to more shear bands forming during the compression, resulting in more homogeneous deformation. The propagation directions of these shear bands are altered by the dense second phase [167], as supported by the observation of the shear band intersections, leading to the improvement in the plasticity and strength of the nanoheterogeneous BMG.

While, on the $\text{Zr}_{58}\text{Ni}_{10}\text{Al}_7\text{Cu}_{19}\text{Co}_6$ BMG, only two shear bands propagating through the sample (Figure 55 (b)). The reason is the lower Poisson’s ratio as shown in Table 3. And the nanostructure is not formed due to the low Co content. Thus, the number of shear bands is reduced in the $\text{Zr}_{58}\text{Ni}_{10}\text{Al}_7\text{Cu}_{19}\text{Co}_6$ BMG sample [168,169], leading to the non-homogeneous plastic deformation and brittleness. These observations are coincident with the change of the stress–strain curves shown Figure 34.
Figure 55 In-situ compression SEM images of yielded BMGs samples with compositions (a) Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$, (b) Zr$_{58}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_6$, and (c) Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$. Reprinted from [149].
4.3. Structure relaxation of BMGs during annealing

4.3.1. Structure relaxation of BMGs at different temperatures

To study the effect of annealing on the thermal properties and structure, Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ BMGs were annealed at temperatures around its $T_g$ (606 K – 658 K). An endothermic overshoot appears on the DSC curves of the annealed samples at temperature slightly higher than $T_g$. The peak height increases with the annealing temperature until it reaches $T_g$, and then it starts to decrease with higher annealing temperatures, as shown in Figure 37 (b). This phenomenon was also previously reported in other literature [170]. It is related to the structural relaxation of BMGs.

β-relaxation is known as a precursor for α-relaxation and glass transition, which is the principal source of the dynamics in a glass structure [62,63]. When the temperature is below $T_g$, β-relaxation is dominant (Figure 56), which is to change the topological and chemical short-range order by the nearest-neighbor length scale atomic rearrangements [64,65]. During annealing, more energy barriers can be overcome at higher temperatures (below $T_g$) and thus, the structure arrives at a configuration with a lower energy (deeper minima on the energy landscape). Then, α-relaxation in the following DSC measurement requires a higher activation energy to overcome the higher energy barriers for crystallization. In this way, the endothermic overshoot at 670K (enthalpy recovery) increases with the increase in annealing temperature. In other words, a structure with lower energy is obtained by the low temperature β-relaxation, which has denser atomic packing. Thus, this low-temperature β-relaxation leads to a higher diffusion activation energy for the following α-relaxation, resulting in the appearance of the endothermic overshoot at 670K on the DSC curves. With further increasing the annealing temperature to around $T_g$, α-relaxation will occur during this annealing, accompanied with β-relaxation. Thus, the diffusion activation energy becomes lower, and the endothermic overshoot height on the following DSC measured curve is reduced [150].
Figure 56 Relaxation frequency $f$ change as a function of temperature $T$. Modified from [150], with the license “CC-BY 4.0” (https://creativecommons.org/licenses/by/4.0/).

The different relaxation mechanism at low and high temperature (below $T_g$ and above $T_g$) is also revealed by the heat flow change on the sample as a function of time during annealing. The data can be well fitted with the equation $W(t) = W_0 (1 - e^{-t/\tau})$, where $W_0$ is the increase in heat flow $W(t)$ after an infinite time and $\tau$ is the relaxation time, as shown in Figure 57. The fitted parameters are given in Table 6. The final heat flow, $W_0$, increases from 0.031 to 0.044 W/g with the increase in annealing temperature from 606 to 637 K, which are below $T_g$. The reason is that, at higher temperature, atoms have more energy for diffusion. Thus, higher energy barriers can be overcome, allowing the system to arrive at the structure with the lower energy. The relaxation time $\tau$ also reduces from 56.6 to 38.1 s because of the improved atomic mobility at higher temperature. When the annealing temperature is above $T_g$, the relaxation mechanism changes. Due to the occurrence of $\alpha$-relaxation, the structure has a significantly reduced relaxation time $\tau$, from 38.1 to 9.8 s, compared with the $\beta$-relaxation-dominated process below $T_g$ [150].

Figure 57 Measured heat flow on the Zr$_{64}$Ni$_{10}$Al$_{19}$Cu$_{19}$ BMGs as a function of time during annealing (points) and the fitted curves with equation $W(t) = W_0 (1 - e^{-t/\tau})$. 86
Table 6 Fitting parameters for heat flow on sample as a function of time during annealing, with equation $W(t) = W_0 (1 - e^{-t/\tau})$.

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>$W_0$(W/g)</th>
<th>$\tau$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>606K</td>
<td>0.031</td>
<td>56.6</td>
</tr>
<tr>
<td>616K</td>
<td>0.039</td>
<td>54.2</td>
</tr>
<tr>
<td>627K</td>
<td>0.043</td>
<td>45.9</td>
</tr>
<tr>
<td>637K</td>
<td>0.044</td>
<td>38.1</td>
</tr>
<tr>
<td>648K</td>
<td>0.031</td>
<td>17.8</td>
</tr>
<tr>
<td>658K</td>
<td>0.012</td>
<td>9.8</td>
</tr>
</tbody>
</table>

It can be seen on DSC curves in Figure 37 (c) that the crystallization peak shifts to lower temperatures only after annealing at high temperature. This further confirms that the relaxation mechanism of the $\text{Zr}_{64}\text{Ni}_{10}\text{Al}_{7}\text{Cu}_{19}$ BMG changes that $\beta$-relaxation is no longer dominant and $\alpha$-relaxation starts to play an important role. This perturbation can markedly accelerate crystallization [171]. Furthermore, in this relaxed denser structure, the crystallization process becomes more likely diffusion-controlled instead of nucleation with an increase in the peak width and a reduction in the peak height.

4.3.2. Structure relaxation of BMGs with different liquid “fragility”

To investigate the difference in the annealing effects on homogeneous and nanoheterogeneous BMGs, the DSC results of annealed $\text{Zr}_{64}\text{Ni}_{10}\text{Al}_{7}\text{Cu}_{19}$ and $\text{Zr}_{55.7}\text{Ni}_{10}\text{Al}_{7}\text{Cu}_{19}\text{Co}_{8.3}$ BMGs were compared. As shown in Figure 58, there is an obvious difference in the structure relaxation behavior of the two-type samples. By low-temperature annealing (563 K), the DSC results of the BMGs with Co show an endotherm-reducing event during structure relaxation (380°C-390°C) as shown in Figure 38 (b) and Figure 58 (d), which is more obvious with Co content increasing. With higher annealing temperature, this phenomenon does not appear (Figure 58 (f)). As discussed above, this difference on $\Delta H_{\text{relaxation}}$ reflects the structure change [150].
Some publications [172] argue that this anomalous exothermal is two-step glass transition from the amorphous phase separation. But, in this work, this phenomenon cannot be observed on as-cast heterogeneous samples (Figure 58 (b)). The energy landscape offers a convenient way to consider the structure evolution (Figure 59) [173]. Compared with Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$, Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ supercooled liquid has worse glass forming ability and
the BMG formed by it exhibits better ductility. As discussed in section 4.1 Zr$_{55.7}$Ni$_{10}$Al$_{7}$Cu$_{19}$Co$_{8.3}$ supercooled liquid is more “fragile” [22]. Its potential energy landscape should consist of several deep minima. The quenched samples are frozen at a state, for example, the red point on Figure 59 (a). During the low temperature annealing (563 K), its structure settles into a glassy configuration with lower energy, but not the lowest due to the high energy barrier. In the following heating for DSC measurement, structure transition takes place at a temperature around $T_g$ to get to deeper minima. Some energy is released, resulting the endotherm-reducing event as shown in Figure 58 (d). In high temperature annealing (583 K), the lowest energy phase can be reached and the transition will not happen in the following DSC measurement. Thus the endotherm-reducing event disappears [173]. The Zr$_{64}$Ni$_{10}$Al$_{7}$Cu$_{19}$ supercooled liquid is “stronger” as discussed in section 4.1. The number of deep minima on their potential energy landscape is smaller (Figure 59 (b)).

![Figure 59 Schematic illustration of potential energy landscape of (a) “fragile” liquids, (b) “strong” liquids.](image)

It is reported that, in most cases, the hardness of BMGs increases after annealing due to free volume annihilation [165]. While, nanoindentation analysis shows that the hardness of Zr$_{55.7}$Ni$_{10}$Al$_{7}$Cu$_{19}$Co$_{8.3}$ sample was reduced from 6.2±0.2 to 6.0±0.2 GPa by the low-temperature annealing (563 K). There are two possible reasons for this softening. One is the non-affine thermal strain introduced during annealing, resulting in increased free volume and hardness reduction. The other possible reason is the residual stress which can reduce the measured hardness of the materials.

While, the in-situ compression test shows that the ductility of the low-temperature annealed Zr$_{55.7}$Ni$_{10}$Al$_{7}$Cu$_{19}$Co$_{8.3}$ BMG is not improved as wished. As shown in Figure 60, only one main
shear band formed on the plane of maximum shear stress during compression. It can be known that the free volume content is not increased. Residual stress should be the real reason for the hardness change of the treated BMGs.

Figure 60 In-situ compression SEM images of the low-temperature annealed (563 K) Zr$_{55.7}$Ni$_{10}$Al$_{7}$Cu$_{19}$Co$_{8.3}$ BMG sample at yield point.

Compared with the homogenous BMGs, more residual stress can be introduced in the nano-heterogeneous structure by annealing because of the different thermal expansion coefficients between phases with different chemical composition (Figure 31 (b)), which reduces the measured hardness [137]. The samples without Co or with low Co content (0–6%) have a relatively homogeneous structure and their hardness changes were as normal, i.e., hardening after annealing. By annealing at 583 K (10 h), the hardness of all samples increases, due to the full relaxation at high temperature that the residual stress is released. In the next section, the relationship between free volume and thermal, mechanical properties of BMGs will be discussed in more detail.
4.4. Free volume and mechanical behavior of thermally cycled BMGs

In the last section, the free volume model is mentioned. It is effective for the investigation and prediction of BMGs properties, which has been commonly used [59,84,135]. In most cases, metallic glasses with more free volume exhibit better plasticity, because more shear band initiation positions (more STZs) can lead to more homogeneous deformation. However, the measurement or estimation of the free volume change in BMGs is difficult. Positron annihilation spectroscopy is a method to investigate the structural defects in solids, which can also be used to analyze the free volume in BMGs. The principle of this method is based on the annihilation of positrons by interaction with electrons. Detectable gamma rays are released during this annihilation. While, this measurement experiment, which requires a radioactive positron source ($^{22}$Na) and gamma-ray detector (scintillator), is too complicated for common utilization. The density of BMGs as measured by Archimedes’ method can also reflect the free volume change. But the accuracy of an ordinary balance is not high enough.

Recent studies [59,71,74,135] have shown that the content of free volume in BMGs can be estimated by the heat flow change during DSC measurement. Heating with a temperature lower than $T_g$ can increase the mobility of atoms and annihilate the free volume in BMGs, which still keep as fully amorphous structure but with lower energy and denser atomic packing. So, this reduction in free volume is accompanied by the enthalpy release of BMG samples, which can be reflected as a low-temperature (lower than $T_g$) exothermic effect on the DSC curve. The more free volume a BMG sample contains, the greater should be the released enthalpy on its DSC result. For example, the pre-heated or annealed BMGs, as discussed in the previous section, usually have decreased free volume due to the structural relaxation. Thus, their exothermic effect on the DSC curves become weaker or disappear, as shown in Figure 61 [59].
It has been reported [74] that BMGs have nonuniform thermal expansion coefficients because of the intrinsic nonuniformity in glass structures. Thus, non-affine thermal strain can be introduced by thermal cycling, leading to the more highly disordered structure and increased free volume, known as rejuvenation, resulting in the improved plasticity of BMGs. In this work, a liquid nitrogen–boiling water cycling treatment was carried on both homogeneous and nanoheterogeneous samples. But there is no change in the modulus or plasticity of the treated samples, as shown in Chapter 3.

The free volume changes of the as-cast and thermally cycled BMGs were analyzed by the DSC results in Figure 42. It can be seen that the relaxation enthalpy below $T_g$ is not increased (in Figure 62), meaning that the free volume in the amorphous structure is not affected by thermal cycling as we wished. That is the reason of the unchanged mechanical properties of the treated BMGs. More disordered structure was not formed by thermal strain as we wished.

![Figure 61 Exothermic phenomenon below $T_g$ on DSC results of Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ metallic glasses (a) as-cast, and annealed at different temperatures (b) 600 K, (c) 625 K, (d) 650 K, (e) 675 K, (f) 700 K, (g) 725 K, (h) 750 K. Reprinted from [59], Copyright 2004, with permission from Elsevier.](image-url)
The tensile stress–strain curve of the thermally cycled (150 times) Zr$_{56.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMG sample is shown in Chapter 3. Because of the unchanged free volume content, the result is the same as the as-cast sample, that the tensile plastic strain is still approximately 0%. SEM images were taken during the in-situ tension test. Very few shear bands can be observed on the surface. The main shear band on the plane of maximum shear stress rapidly extended to a crack, as shown in Figure 63.
4.5. Enhancement mechanism of severe plastic deformation of BMGs

4.5.1. Increased free volume and improved tensile plasticity

In the last two sections, free volume model was used to investigate the properties of metallic glasses. The annihilation of free volume by annealing reduces the ductility of BMGs. Thermal cycling treatments cannot change the content of free volume and have no effect on mechanical properties. In this section, the effect of HPT will be discussed.

For Zr-based MGs, a correlation between free volume increase ($\Delta v_f/v$) and structure relaxation enthalpy change ($\Delta H_{fv}$) during DSC measurements was proposed as $\Delta H_{fv} = \beta \cdot (\Delta v_f/v)$, where $\beta$ is constant [59]. Figure 64 (a-b) are the full DSC curves of as-cast and HPT-treated Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ and Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ samples. Figure 64 (c–d) show the enthalpy of relaxation (exothermic phenomenon below $T_g$) in all studied BMGs as a function of HPT rotation number. Due to the looser atomic packing in the interface areas in nanoheterogeneous structure, the as-cast Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMG has higher structural relaxation enthalpy than the as-cast Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ BMG. After 2 rotations HPT treatment, both-type BMGs have increased enthalpy release as compared the as-cast samples, which is more significant for the 2-rotation HPT treated nano-structured Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ MG. ($\Delta H_{fv}$) was increased by 6.4 J/g and 3.4 J/g on nanoheterogeneous and homogeneous MGs, respectively. Three researches have been reported about the measured/calculated values of $\beta$, which are 552±15 kJ/mol [59] and 718.2 kJ/mol [183] for Zr$_{55}$Ni$_{5}$Al$_{10}$Cu$_{30}$ MG, 622.7±20 kJ/mol for Zr$_{41.2}$Ti$_{13.8}$Ni$_{12.5}$Cu$_{10}$Be$_{22.5}$ MG [182]. The accurate $\beta$ value for Zr$_{64-x}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_x$ MGs has not been obtained yet. While the increasing tendency of free volume content is obvious.
Figure 64 Differential scan calorimetry curves of as-cast and HPT-treated (a) Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ and (b) Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMGs with different HPT rotation numbers. Relaxation energy release below $T_g$ of as-cast and HPT-treated (c) Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ and (d) Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMGs with different HPT rotation numbers. Reprinted from [151], with the license “CC-BY 4.0” (https://creativecommons.org/licenses/by/4.0/).

Figure 65 exhibits the structure factor $S(q)$, obtained by synchrotron radiation-based XRD, as a function of the scattering vector $q$, for the as-cast and HPT-treated samples. It is found that 2-rotation HPT treatment results in a peak shift in the first maximum from 2.587 to 2.584 Å$^{-1}$ and 2.620 to 2.614 Å$^{-1}$ for the Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ and Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMGs, respectively. Using the relationship between the first maximum position $Q_{\text{max}}$ and volume $V$, $\left\{Q_{\text{max}}(e^0)^3\right\} \approx \left\{V(e)/V(e^0)\right\}$ [50,174], an increase in average volume for each atom was estimated to be approximately 0.3% and 0.7% for treated Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ and Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ MGs after 2-rotation HPT, respectively. Thus it can be concluded that, after 2-rotations HPT, the treated Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ sample has higher free volume content than that of the Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ sample, which favors for its plasticity. The reason is that more SBs with lower atomic packing density and more free volume can be formed in nano-structured MGs during HPT which has been proved by the in-situ compression test on the as cast samples [151].
By further increasing the rotation number (N=5, 10, 20), the enthalpy of relaxation in both-type MGs decreases (as shown in Table 7) compared with the 2 rotations HPT treated samples, which could be caused by deformation accelerated diffusion and structure relaxation during HPT (N=5, 10, 20). This process is similar as the defect content evolution in alloys with time during ball milling. During ball milling, the deformation-induced defect (defect creation) and deformation accelerated diffusion (defect annihilation), both processes are present, and they compete each other during ball milling. Usually, at initial stage, the deformation-induced defect is dominant while at later stage, deformation accelerated diffusion becomes important, finally a balance often reaches. Although the HPT treatment is not exact the same as ball milling, similar deformation-induced defect and deformation accelerated diffusion both processes should occur too. After 2 rotations HPT, more SBs (could be treated as defects) are formed, i.e., the deformation-induced defect process is dominant. Thus, the enthalpy of relaxation increase in both-type MGs after 2 rotations HPT. With further rotation, deformation accelerated diffusion becomes important, structure relaxation occurs, consequently, resulting in the reduction of the enthalpy of relaxation and free volume. In fact, sample temperature enhancement during rotations by HPT further supports our view that for more rotations by HPT, structural relaxation becomes important. As reported, the temperature in the samples can reach their glass transition temperature $T_g$ during HPT treatment after 2-5 rotations (depending on the rotating speed) [184,185]. Furthermore, the nano-structured Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_8.3$ BMG has less thermal stability than the homogeneous Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$.
BMG. As shown in Table 3, \((T_x - T_g)\) of Zr\(_{55.7}\)Ni\(_{10}\)Al\(_7\)Cu\(_{19}\) sample is only 26 K which is 72 K for Zr\(_{64}\)Ni\(_{10}\)Al\(_7\)Cu\(_{19}\) sample. Thus, nanometer-sized crystalline particles are formed and grew in the nanoscale-heterogeneous MGs during HPT, but cannot be observed in the relatively homogeneous Zr\(_{64}\)Ni\(_{10}\)Al\(_7\)Cu\(_{19}\) BMG.

In Table 7, it is can be seen that the free volume content change tendency (estimated by structure relaxation enthalpy, structure factor and density) of the studied BMGs and their tensile plastic strain are related, which further confirms that free volume plays an important role for the improvement of ductility of these BMGs. After HPT for two rotations, the shear bands pre-introduced by severe plastic deformation might tolerate the applied strain more homogeneously across the deformed region, avoiding catastrophic failure. Multiple shear bands are formed in these softer regions (more free volume and STZs) during tension and interact with each other. The plastic deformation is more homogeneous, resulting in the enhancement of tensile ductility as we wished. For the 2-rotations HPT-treated BMG Zr\(_{55.7}\)Ni\(_{10}\)Al\(_7\)Cu\(_{19}\)Co\(_{8.3}\) sample, its tensile plastic strain can reach 0.9%, which is a high value for BMGs. Thus, compared with the annealing and thermal cycling treatments, severe plastic deformation (2-rotation HPT) is a feasible method to successfully improve the tensile plasticity of BMGs with nanoheterogeneous structure. However, further increasing the HPT rotation number deteriorates the tension ductility of samples. Because an excessive deformation degree leads to defects annihilation and temperature rise in materials, which is similar to annealing.

<table>
<thead>
<tr>
<th></th>
<th>Zr(<em>{64})Ni(</em>{10})Al(<em>7)Cu(</em>{19})</th>
<th>Zr(<em>{55.7})Ni(</em>{10})Al(<em>7)Cu(</em>{19})Co(_{8.3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile plastic strain (%)</td>
<td>(0) (\pm 0.1) (0.2) (0.2) (0.3)</td>
<td>(0.07) (0.05) (0.05) (0.05)</td>
</tr>
<tr>
<td>Enthalpy of relaxation (J/g)</td>
<td>(-4.9) (\pm 0.5) (-7.1) (\pm 0.5) (-7.3)</td>
<td>(-10.9) (\pm 0.5) (-6.0) (\pm 0.5)</td>
</tr>
<tr>
<td>Position of first maximum (Å(^{-1}))</td>
<td>(2.587) (\pm 0.001) (2.583) (\pm 0.001)</td>
<td>(2.620) (\pm 0.001) (2.617) (\pm 0.001)</td>
</tr>
<tr>
<td>Density (g/cm(^3))</td>
<td>(6.79) (\pm 0.01) (6.79) (\pm 0.01)</td>
<td>(6.88) (\pm 0.01) (6.91) (\pm 0.01)</td>
</tr>
</tbody>
</table>
4.5.2. Shear band and crack behavior during tension

To further investigate the effects of free volume and nano-crystalline particles on the samples tensile deformation, in-situ SEM was used to observe the SBs behavior and cracks evolution on the as-cast and HPT-treated Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ and Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMGs samples. The pre-polished surfaces were smooth except a few scratches and blots. Images in Figure 66 and Figure 67 are from sample surface when the load reaches the yield point. Figure 66 (a) shows that one main SB is formed, propagating through the as-cast Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ sample. On the surface of HPT-treated (N=2) Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ sample (Figure 66 (b)), more SBs appeared under yield stress perpendicular to the tension direction, because of the increased free volume. This phenomenon is similar with the tensile test on rolled MG samples [125]. For the as-cast Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ sample, more than one major SBs were detected, most likely due to the inhibition effect of nanometer-scale second phase during SBs propagation. Its plasticity (0.07%±0.05) is slightly improved as compared with the as-cast Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ sample (0%). The HPT-treated (N=2) Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ sample shows the best plasticity (0.9%±0.1) and the largest free volume content increase, on which multiple SBs are easily observed on the sample surface in SEM image (Figure 67 (b)) [151].

With further increasing the HPT deformation degree (N=5, 10, 20), the number of tension-induced SBs is reduced due to the free volume annihilation as discussed above. For both-type MGs, only two to three SBs can be observed on the surface of the samples under yield stress, as show in Figure 66 (c) and Figure 67 (c). The plasticity of both MGs become worse.
Figure 66 Shear bands on the surface of the Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ sample (a) as-cast, (b) $N = 2$, (c) $N = 20$, under yielding load. Modified from [151], with the license “CC-BY 4.0” (https://creativecommons.org/licenses/by/4.0/).

Figure 67 Shear bands on the surface of the Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ sample (a) as-cast, (b) $N = 2$, (c) $N = 20$, under yielding load. Modified from [151], with the license “CC-BY 4.0” (https://creativecommons.org/licenses/by/4.0/).
Finite element analysis of the tensile tests has been done by Mo Li et al. [175] The calculation results show that heterogeneous free volume dispersion can improve the sample plasticity effectively. In the HPT treated (N=2) Zr_{55.7}Ni_{10}Al_{1}Cu_{19}Co_{8.3} BMG, free volume content is high in the introduced SBs and the formed nano-crystalline particles have little free volume. In this heterogeneous structure, initial deformation started at the soft regions (HPT introduced shear bands), continuing to be localized around their original location. As the deformation continues, the deformation regions are still restricted to their original location although more new deformed regions are created elsewhere. When localized regions have finally developed, the deformation bands do not look smooth and straight, rather rugged and zigzag with many side bands, the localized deformation zones are spread more widely and no through shear band across the sample forms at larger deformation [175]. This simulation is coincident with the experimental results as shown in Figure 67(b). With further increasing HPT rotations (N=5, 10, 20), the free volume dispersion in samples is homogenized [151].

Nanometer-sized crystalline particles (3-10 nm) form and grow in the nanoscale-heterogeneous MGs during HPT, which cannot be observed in the homogeneous MG (Figure 47). For crystalline composite materials, the nanometer scale reinforcements can hinder the sliding of dislocations. To study their effect on the mechanical properties of MGs, nanoindentation measurement results of HPT treated (N = 2) Zr_{64}Ni_{10}Al_{7}Cu_{19} and Zr_{55.7}Ni_{10}Al_{1}Cu_{19}Co_{8.3} BMGs are analyzed. Two smooth curves showed in Figure 68(a) illustrate that both-type MGs have relatively homogeneous deformation. If we focus on the beginning of plastic deformation, some small “serrations” with abrupt increasing of load (marked by arrows Figure 68 (b)) can be observed for Zr_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3} sample. The reason is that the initiated SB is arrested by the nano-crystalline particles. With the increase of load, new SB forms and the deformation continues. This phenomenon cannot be found on treated Zr_{64}Ni_{10}Al_{7}Cu_{19} sample. Instead, some flat “steps” appear on its nanoindentation curve, indicating no obstacle for SBs propagation. It can be further confirmed by the velocity profiles of the indenter as shown in Figure 68(c)(d). Abruptly decelerating and accelerating of the indenter can be seen on the velocity-displacement curve of HPT treated (N = 2)) Zr_{55.7}Ni_{10}Al_{1}Cu_{19}Co_{8.3} BMG at the corresponding displacements of the “serrations” on Figure 68(b), indicating the displacement burst that new SBs activity followed by an increase in load. On the curve of HPT treated (N = 2) Zr-0Co MG, the indenter velocity change is uniform. On
the SEM images (Figure 68(e)(f)), more SBs can be observed around the indentation on HPT treated (N = 2) Zr_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3} BMG [151].

Figure 68 (a) Nanoindentation measurement curves of HPT treated (N=2) Zr_{64}Ni_{10}Al_{7}Cu_{19} BMG and HPT treated (N=2) Zr_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3} BMG. (b) Beginning of plastic deformation on nanoindentation measurement curves of both-type MGs. (c) Velocity profile of the indenter on HPT treated (N=2) Zr_{64}Ni_{10}Al_{7}Cu_{19} BMG. (d) Velocity profile of the indenter on HPT treated (N=2) Zr_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3} BMG. (e) SEM image of indentation on HPT treated (N=2) Zr_{64}Ni_{10}Al_{7}Cu_{19} BMG. (f) SEM image of indentation on HPT treated (N=2) Zr_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3} BMG. Reprinted from [151], with the license “CC-BY 4.0” (https://creativecommons.org/licenses/by/4.0/).

Figure 69 illustrates the SEM images for crack tips on HPT-treated (N=2) Zr_{64}Ni_{10}Al_{7}Cu_{19} and HPT-treated (N=2) Zr_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3} samples just before fracture. It is clear that for the HPT-treated (N=2) Zr_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3} sample, many SBs branching and interacting with each other at the tip are observed, which is not detected for the HPT-treated (N=2) Zr_{64}Ni_{10}Al_{7}Cu_{19} sample. The reason is that, more shear bands were introduced in Zr_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3} sample.
by HPT. During the tension, the crack tips reached these shear bands during propagation, resulting in the newly-formed shear bands. The propagation of the newly-formed shear bands is inhibited again by branching and intersection [176,177]. Thus, the plasticity is improved more obviously (0.07%±0.05% to 0.9%±0.1%) than the relative homogeneous MG (0% to 0.5%±0.1%) [151].

![Figure 69 SEM images of crack tips during tensile tests of the deformed samples (a) Zr64Ni10Al7Cu19 and (b) Zr55.7Ni10Al7Cu19Co8.3 by HPT for 2 rotations. Modified from [151], with the license “CC-BY 4.0”](https://creativecommons.org/licenses/by/4.0/).

It is worth noting that on the stress-strain curves, slight work-hardening can be observed that the yield stress of both-type MGs increases after HPT treatment. The reason is that HPT treatment introduces many SBs in BMG samples which are initiation positions of secondary SBs. During tension test, new SBs are formed and interact with each other, inhibiting further plastic flow and consequently enhance their strengths. It is worth to notice that both “work softening” and “work hardening” could take place on deformed BMGs. For example, work softening is often observed for the low strain samples. Because SBs often propagate along a single direction that the intersection of SBs can be seldom observed by normal plastic deformation treatment. Here HPT was applied, which introduced large and multi-orientations plastic strain on the structure, leading to work hardening for BMGs.

4.5.3. HPT effect on residual stress and Poisson’s ratio

As shown in Figure 51, obvious changing can be observed in the nanoindentation hardness of samples before and after HPT treatment. The reason for this is that the residual stress in the outer region (0.5–2.5 mm from the center) of the HPT-treated samples is compression stress, leading to the increase in the measured hardness value [137]. When the deformation degree
is low (N=2), no obvious hardness increase (5.5 GPa) was detected due to the low internal stress. With further increasing of the deformation degree (rotation number N = 5, 10, 20), the compression residual stress increases, resulting in the increase in hardness. Furthermore, the change tendencies of the homogeneous and heterogeneous BMGs are different. For the Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ samples, the hardness value in the outer region (0.5–2.5 mm from the center) reaches maximum (6.4 GPa) with lower deformation degree (only 2 rotations HPT) compared with the Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ samples (20 HPT rotations). No further hardness enhancement was detected with further increasing the rotation number. It is known that nonuniform plastic deformation is one of the important reasons for the residual stress introduced in structural materials [178,179]. Owing to the phase separation in the Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ sample, the nanometer-scale glassy clusters should have different strengths from the matrix because of their different chemical composition (Figure 31 (b)). Nonuniform plastic deformation takes place in various phases in these heterogeneous-structured BMGs during HPT, resulting in higher residual stress. Thus, in these Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMGs samples, the residual stress reaches maximum after only 2 rotations HPT.

Young’s moduli of the as-cast and HPT-treated Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ and Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ samples were measured by nanoindentation as shown in Figure 52. It should be noted that one need to know the Poisson’s ratio of a material in order to calculate its modulus by

\[
\frac{1}{E_r} = \frac{(1-v^2)}{E} + \frac{(1-v_i^2)}{E_i},
\]

where \(E\) and \(E_i\) are the Young’s moduli of the sample and indenter; \(v\) and \(v_i\) are the Poisson’s ratios of the sample and indenter; and \(E_r\) is the reduced Young’s modulus [148]. Because the thickness of the severely plastically deformed sample (0.4 mm) is too thin to measure the Poisson’s ratio by the ultrasound pulse-echo technique, here we used the value of the as-cast Zr$_{64}$Ni$_{10}$Al$_7$Cu$_{19}$ and Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ samples, \(v = 0.391\) and 0.393, respectively. The deviation of Young’s modulus calculated with various Poisson’s ratios are small, as shown in Figure 70 (a) and (b). Hence the nanoindentation measured Young’s modulus of HPT treated samples should be reliable.
Figure 70 Deviation of Young’s modulus with various Poisson’s ratios on 2 rotations HPT treated samples (a) $\text{Zr}_{64}\text{Ni}_{10}\text{Al}_{7}\text{Cu}_{19}$ and (b) $\text{Zr}_{55.7}\text{Ni}_{10}\text{Al}_{7}\text{Cu}_{19}\text{Co}_{8.3}$.
5. Summary and Conclusion
The goal of this research is to improve the plasticity of BMGs. To achieve it, a composition was first designed to obtain nanoheterogeneous BMGs, which is reported benefit to their ductility. Further treatments were applied to the homogeneous and nanoheterogeneous BMGs, including annealing, thermal cycling, and severe plastic deformation. The structure and mechanical properties of the as-cast and treated samples were studied and discussed comprehensively.

The structures of the as-cast Zr$_{64-x}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_x$ (x = 0–8.3 at%) BMGs were first investigated. TEM images showed that an obvious nanoscale phase separation took place in the glassy structure when the Co content was 8.3%. With further increases in the Co content, crystalline peaks appeared in the XRD patterns of 2-mm-thick samples, due to the reduced glass-forming ability. PDF and EXAFS analysis revealed that a denser topological structure formed, in which stronger Zr-Co atomic bonds replaced Zr-Zr bonds. Nanoscale Zr-rich particles can be observed in the HAADF image of the Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMG.

The nanoheterogeneous structure improved the mechanical properties of the Zr$_{64-x}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_x$ BMGs. Young’s modulus, as measured by the ultrasound pulse-echo technique, increased with Co content because of the stronger atomic bonds. Both nanoindentation and in-situ compression tests confirmed that the elastic strain limit also improved by the addition of Co. The reason for this is the inhibitory effect of the nanoscale second phase on shear band sliding. This means that the stored recoverable elastic energy increases dramatically with the Co content. The Zr$_{55.7}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_{8.3}$ BMG sample also showed improved compression plasticity, which is approximately 4%. From the SEM images taken during in-situ compression tests, it can be observed that more shear bands with different orientations formed and interacted with each other. However, the tensile plastic strains of all samples were still 0%. Different treatments were applied to the samples to further improve their tensile ductility.
Table 8 Young’s modulus, yield stress, elastic strain limit, and compression plastic strain of the Zr$_{64-x}$Ni$_{10}$Al$_7$Cu$_{19}$Co$_x$ BMGs.

<table>
<thead>
<tr>
<th>Co content (at%)</th>
<th>Young’s modulus (GPa)</th>
<th>Yield stress (MPa)</th>
<th>Elastic strain limit (%)</th>
<th>Compression plastic strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>76±2</td>
<td>1610±55</td>
<td>1.8±0.1</td>
<td>2.9±0.3</td>
</tr>
<tr>
<td>2.7</td>
<td>79±3</td>
<td>1670±50</td>
<td>1.9±0.1</td>
<td>3.0±0.3</td>
</tr>
<tr>
<td>4</td>
<td>80±2</td>
<td>1830±42</td>
<td>2.3±0.1</td>
<td>1.5±0.2</td>
</tr>
<tr>
<td>6</td>
<td>82±2</td>
<td>1960±48</td>
<td>2.4±0.1</td>
<td>1.6±0.4</td>
</tr>
<tr>
<td>8.3</td>
<td>85±3</td>
<td>2320±55</td>
<td>2.7±0.1</td>
<td>4.0±0.3</td>
</tr>
</tbody>
</table>

The introduction of non-affine thermal strain was reported as a possible method to improve the plasticity of BMGs. Thus, I applied annealing treatments to the as-cast samples. The structural relaxation process of the BMGs was first analyzed. β-relaxation was dominant in low-temperature annealing. When the temperature was as high as $T_g$, α-relaxation started to play an important role. The nanoheterogeneous BMG has an endotherm-reducing event during relaxation due to the “fragile” supercooled liquid. The raised residual stress can reduce the samples’ hardness. However, the free volume in the structure was annihilated by the enhanced atomic diffusion at high temperature. The plasticity of the annealed BMGs was reduced.

In order to avoid the free volume annihilation, 1–160 cycles of low-temperature thermal treatment (liquid nitrogen – boiling water) were also carried out on these samples. However, the structures and properties of all the samples remained unchanged. The same relaxation enthalpy on DSC curves showed that there was no free volume increase. The reason for this could be that the difference in the thermal expansion coefficient between the phases was insufficient to induce the rejuvenation. The mechanical properties of the treated BMGs were not improved, such that no tensile plastic deformation could be detected.

Severe plastic deformation treatment (HPT) is a newly developed technique for the grain refinement of crystalline alloys. For amorphous materials, it could lead to rejuvenation due to the formed shear bands during deformation, which contain more free volume. In this work, HPT treatments with 2–20 rotations were carried out on the as-cast homogeneous and nanoheterogeneous BMGs. TEM images showed that the structure of the treated
homogeneous BMG samples remained unchanged. However, nanoscale crystalline particles and more shear bands can be observed in the treated heterogeneous BMG samples, due to the different thermal stability and more STZs. DSC results and changes in the structure factors confirmed the increased free volume in the structure treated by two-rotation HPT. This was more obvious on the nanoheterogeneous BMG. As the deformation degree increased further, the free volume was reduced in both samples due to the temperature rising during HPT. The tensile plasticity was coincident with the free volume change, such that both of the samples showed their best performance after two-rotation HPT. In the two-rotation HPT-treated nanoheterogeneous BMG, nanoscale glassy/crystalline particles could inhibit the crack propagation, which further enhanced its ductility. The tensile plastic strain of this sample reached 0.9%.

The BMG materials have been applied in various fields, such as watch industry. Furthermore, National Aeronautics and Space Administration (NASA) has developed Ti-BMG bearings for International Space Station (ISS) by JPL/MIT team in 2015. And Fe-based BMG/composite coatings have been prototyped on the Mars 2020 rover wheel to improve traction. 3D printed Zr-based BMG cutting tools are being tested for possible ice cutting on Europa. Initial tests show promise and self-sharpening behavior. The nano-structured BMGs investigated in this work will have large application potential in the future, because of their outstanding properties.
References


References


References


References


[159] Y. Zhang, H. Hann, “Quantification of the free volume in Zr_{40.6}Cu_{39.3}Al_{17.0}Ag_{8.7} bulk metallic glasses subjected to plastic deformation by calorimetric and dilatometric measurements,” *Journal of Alloys and Compounds*, vol. 488, no. 1, pp. 65-71, 2009. doi: 10.1016/j.jallcom.2009.08.091.

[160] M. Zhu, J. Li, L. Yao, Z. Jian, F. Chang, G. Yang, “Non-isothermal crystallization kinetics and fragility of (Cu_{45}Zr_{47}Al_{17})_{97}Ti_{3} bulk metallic glass investigated by differential


[185] S. Hóbor, Z. Kovács, Á. Révész, “Effect of accumulated shear on the microstructure and morphology of severely deformed Cu_{60}Zr_{30}Ti_{10} metallic glass,” Journal of Alloys

Publications


Conference Contributions

Oral presentations


Y. Dong, H.-J. Fecht, J.-Z. Jiang, R. K. Wunderlich. “Structure and mechanical properties of Zr$_{64-x}$Ni$_{10}$Al$_{7}$Cu$_{19}$Co$_x$ bulk metallic glasses with varying cobalt concentration x=0-16 at.%,” LAM-16, Bonn, 2016.


Poster presentations

Y. Dong, R. Wunderlich, H.-J. Fecht. “Effect of cobalt on the structures and mechanical properties of Zr$_{64-x}$Ni$_{10}$Al$_{7}$Cu$_{19}$Co$_x$ BMGs,” 3$^{rd}$ Sino-German Workshop, Hefei, 2015.


I would like to thank my supervisor, Professor Hans-Jörg Fecht for providing me the opportunity to study in Institute of Functional Nanosystems in University Ulm and the endless support during my PhD project. I benefit a lot from the discussion. It would have been impossible for me to finish this research without his guidance and encouragement.

I would like to express my thanks to Professor Jian-Zhong Jiang from Zhejiang University. In his institute, I obtained a lot of knowledge on synchrotron radiation technique and learnt a lot from his thinking approach. I owe my deep gratitude to Dr. Rainer Wunderlich. I appreciate his good ideas and sound advices throughout my whole work. I would also thank Dr. Qingping Cao. His earnest attitude influence me a lot.

My grateful thanks are extended to Professor Ulrich Herr. I am very impressed by his knowledge in breadth and depth. His constructive suggestions helped a lot in my research. I would also like to thank Professor Carl III Krill for his support. Without his help, I would not have the opportunity to go to the United States for academic exchange.

I would like to thank Mr. Günter Nusser for the machining of samples, Mr. Alexander Minkow for the in-situ SEM measurements and Mr. Jürgen Ankele for equipment maintenance. I wish to thank Dr. Mike Haddad and Dr. Markus Mohr for being very accessible whenever I had needs or questions. I would also thank the academic superintendent and secretary in our institute, Dr. Kai Brühne, Mrs. Helga Faißt and Ms. Monika Menz. I would not study and work smoothly without their support.

I am thankful to my friends and colleagues, Mr. Mingyan Wang, Mr. Runbang Shao, Dr. Pierre Denis, Dr. Andrei Sommer, Dr. Benjamin Riedmüller, Dr. Michael Mertens, Dr. Jules Dake and Mr. Xin Chen for making our office a nice place to work.

In this work, some research cooperation has been done with other institutions. I would like to address thanks to Dr. Xiaodong Wang and Dr. Chao Wang from Zhejiang University for the synchrotron radiation and nanoindentation measurements analysis. I am also thankful to Dr. Johannes Biskupek in TEM group in our university. Thank you for your help in TEM analysis.
want also express my thanks to Dr. Suya Liu and Dr. Julia Ivanisenko from Karlsruhe Institute of Technology (KIT) for the HPT treatments on samples. 

Generous financial support from China Scholarship Council, German Academic Exchange Service DAAD (STIBET Doktoranden) and Deutsches Zentrum für Luft- und Raumfahrt e.V. (DLR ThermoLab VI 50 WM 1759) are gratefully acknowledged.

Finally I would like to thank my parents for their support.
## List of Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MG</td>
<td>Metallic glass</td>
</tr>
<tr>
<td>BMG</td>
<td>Bulk metallic glass</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray absorption fine structure</td>
</tr>
<tr>
<td>HPT</td>
<td>High pressure torsion</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High resolution transmission electron microscopy</td>
</tr>
<tr>
<td>PDF</td>
<td>Pair distribution function</td>
</tr>
<tr>
<td>SB</td>
<td>Shear band</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SPD</td>
<td>Severe plastic deformation</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>3DAPT</td>
<td>Three-dimensional atomic probe technique</td>
</tr>
</tbody>
</table>
List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Schematic diagram of crystal structure (A) and amorphous structure (B).</td>
</tr>
<tr>
<td>3</td>
<td>Temperature-time-transformation (TTT) diagram of crystallization and glass transition.</td>
</tr>
<tr>
<td>4</td>
<td>Specific heat of glassy, supercooled liquid and crystalline state of (A) Au53Pb27Sn19 and (B) Zr73Ti13Cu12Ni10Be23 alloys. Modified with permission of the Japan Institute of Metals, copyright 1995, from [11].</td>
</tr>
<tr>
<td>5</td>
<td>Viscosity change of supercooled liquid. “Strong” liquid exhibits Arrhenius behavior with constant activation energy. “Fragile” liquid exhibits super-Arrhenius behavior, such that the activation energy increases with decreasing temperature. Modified from publication [14], copyright 2016, with permission from Elsevier.</td>
</tr>
<tr>
<td>7</td>
<td>Critical cooling rate and reduced glass transition temperature Tg/Tc of glasses with different compositions.</td>
</tr>
<tr>
<td>8</td>
<td>Schematic diagram of MGS synthesis methods: (A) melt-spinning and (B) water-cooled copper-mold suction casting.</td>
</tr>
<tr>
<td>9</td>
<td>Schematic diagram of nanoglass structure. The amorphous interfaces (white region) between amorphous clusters (black region) have more disordered atomic arrangement and more free volume. Adapted by permission from Springer Nature Customer Service Centre GMBH: Springer Nature, Journal of Applied Crystallography, [41], copyright 1991.</td>
</tr>
<tr>
<td>10</td>
<td>Schematic illustration of nanoglasses preparation methods: inert gas condensation (left) and magnetron sputtering (right).</td>
</tr>
<tr>
<td>11</td>
<td>SEM images of the top view of sputtered Au50Cu20Pd5Ag5Si20 thin films, deposited on clean Si &lt;100&gt; at working pressures of Ar of (A) 0.4, (B) 4 and (C) 10 PA and cross section at working pressures of (D) 0.4, (E) 4 and (F) 10 PA. Modified from [49], copyright 2018, with permission from Elsevier.</td>
</tr>
<tr>
<td>12</td>
<td>Differential scanning calorimetry of La65Ni10Al35 metallic glasses. (A) an exotherm during relaxation can be observed. (B) Comparison of as-cast and cycled (liquid nitrogen — room temperature) samples. (C) the change of exotherm as a function of cycle number. Reprinted by permission from Springer Nature Customer Service Centre GMBH: Springer Nature, [74], copyright 2015.</td>
</tr>
<tr>
<td>13</td>
<td>Bulk modulus K and Young’s modulus E of BMGs with different compositions. Modified from [82], copyright 2012, with permission from Elsevier.</td>
</tr>
<tr>
<td>14</td>
<td>Bulk modulus, shear modulus, and Poisson’s ratio of different BMGs. Reprinted from [82], copyright 2012, with permission from Elsevier.</td>
</tr>
<tr>
<td>15</td>
<td>Relationship among STZ volume, Poisson’s ratio, and plasticity of different BMGs. Reprinted from [93], copyright 2008 National Academy of Science.</td>
</tr>
<tr>
<td>16</td>
<td>SEM pictures of shear bands on the surface of a Zr-based BMG during compression deformation. Modified from [149].</td>
</tr>
<tr>
<td>17</td>
<td>Fracture surfaces of two Zr-based BMGs.</td>
</tr>
<tr>
<td>18</td>
<td>In-situ TEM images of (A) as-cast and (B) annealed Zr55Cu30Al10Ni5 BMG samples. Decomposition by annealing is obvious. The framed areas on both pictures indicate that the observation is on the same sample and the same position. Reprinted from [117], copyright 2008, with permission from Elsevier.</td>
</tr>
</tbody>
</table>
FIGURE 19 (A) COMPRESSION STRESS–STRAIN CURVES OF AS-CAST AND ANNEALED ZR$_{64}$Cu$_{19}$Al$_{10}$Ni$_{7}$ BMG SAMPLES. SEM IMAGES OF THE SAMPLE SURFACES AFTER COMPRESSION TEST. (B) SEM IMAGES OF INDENTATIONS ON BOTH SAMPLES. INCREASED SHEAR BANDS CAN BE OBSERVED ON THE ANNEALED SAMPLE. REPRINTED FROM [117], COPYRIGHT 2008, WITH PERMISSION FROM ELSEVIER......................... 25
FIGURE 20 PHOTOGRAPH OF HPT DEVICE (INSTITUTE OF NANOTECHNOLOGY, KIT)............................................. 27
FIGURE 21 SCHEMATIC DIAGRAM OF HPT TREATMENT AND THE SIZE OF THE SAMPLES........................... 36
FIGURE 22 X-RAY ABSORPTION SPECTRUM. ................................................................................................. 41
FIGURE 23 TYPICAL LOAD–DISPLACEMENT CURVE OF NONINDENTATION MEASUREMENT ON A SAMPLE. MODIFIED FROM [148], COPYRIGHT 2002, WITH PERMISSION FROM ELSEVIER................................................. 45
FIGURE 24 SCHEMATIC DIAGRAM OF A CROSS-SECTION OF A NONINDENTATION MEASUREMENT. MODIFIED FROM [148], COPYRIGHT 2002, WITH PERMISSION FROM ELSEVIER................................................. 45
FIGURE 25 (A) IN-SITU TENSILE TEST STAGE. (B) LOAD–DISPLACEMENT CURVE OBTAINED DURING TEST (DEFORMED ZR$_{64}$Ni$_{10}$Al$_{10}$Cu$_{19}$Co$_{3.1}$ SAMPLE BY HPT FOR TWO ROTATIONS). (C) SEM IMAGE OBTAINED DURING ORIGINAL TEST. .................................................................................................................. 48
FIGURE 26 XRD PATTERNS OF BMGS WITH COMPOSITION ZR$_{64}$-xNi$_{10}$Al$_{10}$Cu$_{19}$Co$_{3}$ (X = 0–16 AT.%). MODIFIED FROM [149]................................................................. 51
FIGURE 27 (A) STRUCTURE FACTORS OF ZR$_{64}$-xNi$_{10}$Al$_{10}$Cu$_{19}$Co$_{3}$ (X = 0–8.3 AT.%) BMG SAMPLES AND (B) MAGNIFICATION OF THE FIRST PEAKS ON THEIR STRUCTURE FACTORS (DESY, HAMBURG). MODIFIED FROM [149]................................................................. 52
FIGURE 28 (A) PAIR DISTRIBUTION FUNCTIONS (PDFS) AND (B) MAGNIFICATION OF THE FIRST PEAKS ON PDFS, OF ZR$_{64}$-xNi$_{10}$Al$_{10}$Cu$_{19}$Co$_{3}$ (X = 0–8.3 AT.%) BMG SAMPLES (DESY, HAMBURG). MODIFIED FROM [149].................. 52
FIGURE 29 EXTENDED X-RAY ABSORPTION FINE STRUCTURE (EXAFS) OF (A) CO K-EDGE DATA AND (B) ZR K-EDGE DATA, OF SELECTED ZR$_{64}$-xNi$_{10}$Al$_{10}$Cu$_{19}$Co$_{3}$ (X = 4 AND 8.3) BMG SAMPLES (SSRF, SHANGHAI). MODIFIED FROM [149]................................................................. 53
FIGURE 30 TEM IMAGES OF TWO BMG SAMPLES (A) ZR$_{64}$Ni$_{10}$Al$_{10}$Cu$_{19}$ (X = 0–8.3 AT.%) AND (B) ZR$_{55}$Ni$_{10}$Al$_{10}$Cu$_{19}$Co$_{3}$ BMGS................................................................. 54
FIGURE 31 HIGH-ANGLE ANNULAR FIELD IMAGING OF AS CAST SAMPLES (A) ZR$_{64}$Ni$_{10}$Al$_{10}$Cu$_{19}$ AND (B) ZR$_{55}$Ni$_{10}$Al$_{10}$Cu$_{19}$Co$_{3}$ BMGS................................................................. 54
FIGURE 32 X-RAY SMALL-ANGLE SCATTERING RESULT OF ZR$_{55}$Ni$_{10}$Al$_{10}$Cu$_{19}$Co$_{3}$ SAMPLE (BSRF, BEIJING)............................. 55
FIGURE 33 (A) DSC CURVES, (B) GLASS TRANSITION TEMPERATURE T$_g$, OF ZR$_{64}$-xNi$_{10}$Al$_{10}$Cu$_{19}$Co$_{3}$ (X = 0–8.3 AT.%) BMGS AS A FUNCTION OF CO CONTENT. MODIFIED FROM [150], WITH THE LICENSE “CC-BY 4.0” (HTTPS://CREATIVECOMMONS.ORG/LICENSES/BY/4.0/). ........................................ 56
FIGURE 34 STANDARD COMPRESSION STRESS–STRAIN CURVES OF ZR$_{64}$-xNi$_{10}$Al$_{10}$Cu$_{19}$Co$_{3}$ (X = 0–8.3) BMGS. MODIFIED FROM [149]................................................................. 58
FIGURE 35 XRD OF ZR$_{55}$Ni$_{10}$Al$_{10}$Cu$_{19}$Co$_{3}$ BMG SAMPLE ANNEALED AT 733 K................................................. 59
FIGURE 36 TEM BRIGHT-FIELD IMAGE OF ZR$_{55}$Ni$_{10}$Al$_{10}$Cu$_{19}$Co$_{3}$ BMG ANNEALED AT 733K............................... 59
FIGURE 37 (A) DSC CURVES, (B) CHANGES IN THE HEAT FLOW ABOVE T$_g$, THE CROSS ON THE CURVE IS THE ANNEALING TEMPERATURE, (C) CHANGES IN THE CRYSTALLIZATION PEAK ON THE DSC CURVES, OF ZR$_{64}$Ni$_{10}$Al$_{10}$Cu$_{19}$ BMG SAMPLES ANNEALED AT DIFFERENT TEMPERATURES. MODIFIED FROM [150], WITH THE LICENSE “CC-BY 4.0” (HTTPS://CREATIVECOMMONS.ORG/LICENSES/BY/4.0/). ........................................ 60
FIGURE 38 (A) DSC CURVES OF THE AS-CAST BMGS, (B) DSC CURVES OF THE BMGS ANNEALED AT 563 K, (C) DSC CURVES OF THE BMGS ANNEALED AT 583 K, WITH DIFFERENT CO COMPOSITIONS. ......................... 61
FIGURE 39 NANOINDENTATION HARDNESS OF UNANNEALED AND LOW-TEMPERATURE ANNEALED (563K) BMGS SAMPLES WITH DIFFERENT CO CONTENT. REPRINTED FROM [150], WITH THE LICENSE “CC-BY 4.0” (HTTPS://CREATIVECOMMONS.ORG/LICENSES/BY/4.0/). ........................................ 62
FIGURE 40 IN-SITU COMPRESSION STRESS–STRAIN CURVE OF THE LOW-TEMPERATURE ANNEALED (563K) ZR$_{55}$Ni$_{10}$Al$_{10}$Cu$_{19}$Co$_{3}$ BMG SAMPLE.......................... 62
FIGURE 41 X-RAY DIFFRACTION PATTERN OF THERMAL CYCLING TREATED SAMPLES WITH DIFFERENT CYCLING NUMBER (A) ZR$_{64}$Ni$_{10}$Al$_{10}$Cu$_{19}$ AND (B) ZR$_{55}$Ni$_{10}$Al$_{10}$Cu$_{19}$Co$_{3}$.................. 63
FIGURE 42 DSC CURVES OF (A) ZR$_{64}$Ni$_{10}$Al$_{10}$Cu$_{19}$ AND (B) ZR$_{55}$Ni$_{10}$Al$_{10}$Cu$_{19}$Co$_{3}$ AS-CAST AND TREATED BMGS WITH DIFFERENT NUMBERS OF THERMAL CYCLES. ................. 64
FIGURE 43 DENSITY CHANGE OF BOTH SAMPLES AS A FUNCTION OF THERMAL CYCLING NUMBER. .................. 64
FIGURE 44 CHANGES OF (A) YOUNG’S MODULI, (B) SHEAR MODULI, (C) POISSON’S RATIO, (D) VICKERS HARDNESS OF BOTH SAMPLES AS A FUNCTION OF THERMAL CYCLING NUMBER. .................. 65
FIGURE 50 TENSILE STRESS–STRAIN CURVES OF ZR64Ni19Al7Cu19 AND ZR55.7Ni19Al7Cu19Co8.3 SAMPLES BEFORE AND AFTER HPT PROCESS. MODIFIED FROM [151], WITH THE LICENSE “CC-BY 4.0” (HTTPS://CREATIVECOMMONS.ORG/LICENSES/BY/4.0/). .................................................. 70

FIGURE 51 NANOINDENTATION HARDNESS DISTRIBUTION OF AS-CAST AND HPT-TREATED (ROTATION NUMBER N = 2, 5, 10, AND 20) (A) ZR64Ni19Al7Cu19 AND (B) ZR55.7Ni19Al7Cu19Co8.3 BMG SAMPLES. .............................................. 72

FIGURE 52 YOUNG’S MODULUS DISTRIBUTION OF AS-CAST AND HPT-TREATED (ROTATION NUMBER N = 2, 5, 10, AND 20) (A) ZR64Ni19Al7Cu19 AND (B) ZR55.7Ni19Al7Cu19Co8.3 BMG SAMPLES. .............................................. 73

FIGURE 53 (A) PDF G(R) OF THE ZR64-xNi19Al7Cu19Co x BMGs (DESY, HAMBURGER). INSET IS LOCAL MAGNIFICATION OF THE LEFT-HAND PART OF THE FIRST PEAK. (B) FRAGILITY INDEX M OF THE ZR64-xNi19Al7Cu19Co x BMGS AS A FUNCTION OF CO CONTENT, CALCULATED FROM THE STEEPNESS OF THE LEFT-HAND PART OF THE FIRST PEAK OF THE PDF G(R)................................................... 79

FIGURE 54 (A) NANOINDENTATION CURVES OF ZR64-xNi19Al7Cu19Co x (X = 0–8.3) BMG SAMPLES. THE INSET IS THE POSITION OF THE FIRST POP-IN EVENT ON THE CURVE OF EACH SAMPLE. (B) MAXIMUM ELASTIC STRAIN MEASURED FROM IN-SITU COMPRESSION AND DISPLACEMENT AT THE FIRST POP-IN EVENT OBTAINED FROM THE (A) INSET. (C) STORED RECOVERABLE ELASTIC ENERGIES FOR ZR64-xNi19Al7Cu19Co x (X = 0–8.3) BMGS AS A FUNCTION OF CO CONTENT. MODIFIED FROM [149]. .................................................. 82

FIGURE 55 IN-SITU COMPRESSION SEM IMAGES OF YIELDED BMGS SAMPLES WITH COMPOSITIONS (A) ZR64Ni19Al7Cu19, (B) ZR55.7Ni19Al7Cu19Co8.3, AND (C) ZR33.3Ni19Al7Cu19Co8.3. REPRINTED FROM [149]. ........... 84

FIGURE 56 RELAXATION FREQUENCY F CHANGE AS A FUNCTION OF TEMPERATURE T. MODIFIED FROM [150], WITH THE LICENSE “CC-BY 4.0” (HTTPS://CREATIVECOMMONS.ORG/LICENSES/BY/4.0/). .................................................. 86

FIGURE 57 MEASURED HEAT FLOW ON THE ZR64Ni19Al7Cu19 BMGS AS A FUNCTION OF TIME DURING ANNEALING (POINTS) AND THE FITTED CURVES WITH EQUATION W(T) = W0 (1 − e−T/Τ). .................................................. 86

FIGURE 58 (A) DSC CURVES OF THE AS-CAST BMGS, (B) RELAXATION HEAT FLOW AROUND T0 FOR THE AS-CAST BMGS, (C) DSC CURVES OF THE BMGS ANNEALED AT 563 K, (D) RELAXATION HEAT FLOW AROUND T0 OF THE BMGS ANNEALED AT 563 K, (E) DSC CURVES OF THE BMGS ANNEALED AT 583 K, (F) RELAXATION HEAT FLOW AROUND T0 OF THE BMGS ANNEALED AT 583 K, WITH DIFFERENT CO COMPOSITIONS. MODIFIED FROM [150], WITH THE LICENSE “CC-BY 4.0” (HTTPS://CREATIVECOMMONS.ORG/LICENSES/BY/4.0/). .................................................. 88

FIGURE 59 SCHEMATIC ILLUSTRATION OF POTENTIAL ENERGY LANDSCAPE OF (A) “FRAGILE” LIQUIDS, (B) “STRONG” LIQUIDS. .................................................................................. 89

FIGURE 60 IN-SITU COMPRESSION SEM IMAGES OF THE LOW-TEMPERATURE ANNEALED (563 K) ZR55.7Ni19Al7Cu19Co8.3 BMG SAMPLE AT YIELD POINT. .................................................. 90
FIGURE 61 EXOTHERMIC PHENOMENON BELOW T_G ON DSC RESULTS OF ZR_{64}Cu_{19}Al_{10}Ni_{8} METALLIC GLASSES (A) AS-CAST, AND ANNEALED AT DIFFERENT TEMPERATURES (B) 600 K, (C) 625 K, (D) 650 K, (E) 675 K, (F) 700 K, (G) 725 K, (H) 750 K. REPRINTED FROM [59], COPYRIGHT 2004, WITH PERMISSION FROM ELSEVIER. 92

FIGURE 62 RELAXATION ENERGY RELEASE BELOW T_G OF (A) ZR_{64}Ni_{10}Al_{7}Cu_{19} AND (B) ZR_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3} BMGS AS A FUNCTION OF THE NUMBER OF THERMAL CYCLES. 93

FIGURE 63 IN-SITU TENSION SEM IMAGES OF THE FRACUTED THERMALLY CYCLED (LIQUID NITROGEN-BOILING WATER, 150 TIMES) ZR_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3} BMG SAMPLE. 93

FIGURE 64 DIFFERENTIAL SCAN CALORIMETRY CURVES OF AS-CAST AND HPT-TREATED (A) ZR_{64}Ni_{10}Al_{7}Cu_{19} AND (B) ZR_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3} BMGS WITH DIFFERENT HPT ROTATION NUMBERS. RELAXATION ENERGY RELEASE BELOW T_G OF AS-CAST AND HPT-TREATED (C) ZR_{64}Ni_{10}Al_{7}Cu_{19} AND (D) ZR_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3} BMGS WITH DIFFERENT HPT ROTATION NUMBERS. REPRINTED FROM [151], WITH THE LICENSE “CC-BY 4.0” (HTTPS://CREATIVECOMMONS.ORG/LICENSES/BY/4.0/). 95

FIGURE 65 STRUCTURE FACTORS, S(Q), OF THE AS-CAST AND HPT-TREATED SAMPLES WITH COMPOSITIONS (A) ZR_{64}Ni_{10}Al_{7}Cu_{19} AND (B) ZR_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3} (DESY, HAMBURGER). REPRINTED FROM [151], WITH THE LICENSE “CC-BY 4.0” (HTTPS://CREATIVECOMMONS.ORG/LICENSES/BY/4.0/). 96

FIGURE 66 SHEAR BANDS ON THE SURFACE OF THE ZR_{64}Ni_{10}Al_{7}Cu_{19} SAMPLE (A) AS-CAST, (B) N = 2, (C) N = 20, UNDER YIELDING LOAD. MODIFIED FROM [151], WITH THE LICENSE “CC-BY 4.0” (HTTPS://CREATIVECOMMONS.ORG/LICENSES/BY/4.0/). 99

FIGURE 67 SHEAR BANDS ON THE SURFACE OF THE ZR_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3} SAMPLE (A) AS-CAST, (B) N = 2, (C) N = 20, UNDER YIELDING LOAD. MODIFIED FROM [151], WITH THE LICENSE “CC-BY 4.0” (HTTPS://CREATIVECOMMONS.ORG/LICENSES/BY/4.0/). 99

FIGURE 68 (A) NANOINDENTATION MEASUREMENT CURVES OF HPT TREATED (N=2) ZR_{64}Ni_{10}Al_{7}Cu_{19} BMG AND HPT TREATED (N=2) ZR_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3} BMG. (B) BEGINNING OF PLASTIC DEFORMATION ON NANOINDENTATION MEASUREMENT CURVES OF BOTH-TYPE MGS. (C) VELOCITY PROFILE OF THE INDENTER ON HPT TREATED (N=2) ZR_{64}Ni_{10}Al_{7}Cu_{19} BMG. (D) VELOCITY PROFILE OF THE INDENTER ON HPT TREATED (N=2) ZR_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3} BMG. (E) SEM IMAGE OF INDENTATION ON HPT TREATED (N=2) ZRS_{64}Ni_{10}Al_{7}Cu_{19} BMG. (F) SEM IMAGE OF INDENTATION ON HPT TREATED (N=2) ZR_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3} BMG. REPRINTED FROM [151], WITH THE LICENSE “CC-BY 4.0” (HTTPS://CREATIVECOMMONS.ORG/LICENSES/BY/4.0/). 101

FIGURE 69 SEM IMAGES OF CRACK TIPS DURING TENSILE TESTS OF THE DEFORMED SAMPLES (A) ZR_{64}Ni_{10}Al_{7}Cu_{19} AND (B) ZR_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3} BY HPT FOR 2 ROTATIONS. MODIFIED FROM [151], WITH THE LICENSE “CC-BY 4.0” (HTTPS://CREATIVECOMMONS.ORG/LICENSES/BY/4.0/). 102

FIGURE 70 DEVIATION OF YOUNG’S MODULUS WITH VARIOUS POISSON’S RATIOS ON 2 ROTATIONS HPT TREATED SAMPLES (A) ZR_{64}Ni_{10}Al_{7}Cu_{19} AND (B) ZR_{55.7}Ni_{10}Al_{7}Cu_{19}Co_{8.3}. 104
Curriculum Vitae

Yue Dong

PERSONAL INFORMATION

M/F: Male
Year of Birth: 1988
Place of Birth: Heilongjiang, China

EDUCATION

BACHELOR OF SCIENCE • 2007-2011
Materials Physics
School of Materials Science and Engineering, Dalian University of Technology

MASTER OF ENGINEERING • 2011-2013
Materials Physics and Chemistry
School of Materials Science and Engineering, Harbin Institution of Technology

DOCTOR OF ENGINEERING • 2014-2020
Supervisor: Prof. Hans-Jörg Fecht
Institute of Functional Nanosystems, University Ulm

PROFESSIONAL EXPERIENCE

ACADEMIC ASSISTANT / PROJECT MEMBER • 2014 UP TO PRESENT
Institute of Functional Nanosystems, University Ulm