

**STUDY OF MECHANICAL BEHAVIORS AND STRUCTURES OF
BULK METALLIC GLASSES WITH HIGH-ENERGY
SYNCHROTRON X-RAY DIFFRACTION**

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DEDICATION

This dissertation is dedicated to my wife, Fengxia Zhu, my parents, Dongfu Jiang and Shuying Wang, my brother and sister-in-law, Ling Jiang and Jialuo Liu, my sister and brother-in-law, Wei Jiang and Siwei Chen, my father- and mother-in-law, Yingsheng Zhu and Yinmei Hu, and the rest of my family and friends, for their love, encouragement, and support.

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ABSTRACT

This dissertation addresses two critical issues in the mechanical behaviors and structures of bulk-metallic glasses (BMGs): (1) the effect of composition, fabrication method, and pretreatment of plastic deformation on mechanical properties and structures of BMGs; (2) the mechanical response and structural evolution of BMGs in the elastic and plastic region.

$(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ amorphous alloys were used to study the effect of composition on mechanical properties and structures of BMGs. The $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ alloy exhibits lower yield stress and Young's modulus, higher Poisson's ratio, worse thermal stability, and better plasticity than $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$. Both the topological and chemical effects of Al addition account for the differences of mechanical and physical properties between them.

A $\text{Zr}_{55}\text{Ni}_5\text{Al}_{10}\text{Cu}_{30}$ glass-forming alloy with injection casting (the melting temperatures are 1,550 K and 1,250 K, respectively) and with suction casting was fabricated. The results indicate that despite their amorphous structures, the suction-casting samples exhibit a lower yield stress, lower Young's modulus, and larger plastic strain than the injection-casting samples (the melting temperature is 1,550 K) due to more quenched-in free volumes in suction casting, which results from the higher cooling rate.

The inhomogeneous plastic deformation in $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BMG samples was introduced by four-point-bend fatigue. There is almost no difference of the stress-strain behaviors between the deformed and undeformed samples. Elastostatic compression was used to introduce homogeneous deformation in $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ BMG samples. The

preloaded samples are softer with decreases of yield strength and Young's moduli. Anisotropy was observed in the preloaded samples despite their small magnitudes, which even occurred at a relatively low temperature and applied stress level.

The structural evolution of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ BMG in the elastic region was analyzed with anisotropic pair density function. The analysis of the first shell of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass confirms the structural changes in the elastic region. The bond reorientation leads to direction dependent changes in the chemical short-range order. The structural evolution in the plastic region of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ BMG is investigated as well. The serrations were observed for both the stress-displacement and full width at half maximum-displacement curves. The excess free volume was measured, which increases with increasing the displacement.

TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION.....	1
CHAPTER 2: REVIEW OF LITERATURE.....	4
2.1. Development of Bulk Metallic Glasses.....	4
2.2 Deformation.....	6
2.2.1 Deformation Mechanisms	6
2.2.2 Elastic Deformation	14
2.2.3 Plastic Deformation	16
2.3 Structure of Bulk Metallic Glasses.....	22
2.4 Mechanical Response of Metallic Glasses using In-Situ High Energy X-ray Diffraction	26
2.4.1 Diffraction-Data Treatment and Theoretical Background.....	27
2.4.2 Strain Analysis from Tensile Tests and Reciprocal Space.....	29
2.4.3 Strain Analysis from Compression Tests and Reciprocal Space.....	31
2.4.4 Strain Analysis from the Real Space.....	33
2.4.5 Analysis of Structural Anisotropy.....	35
2.4.6 Peak-Width Analysis	37
2.4.7 The Accuracy of Determining Strain in Amorphous Alloys with In- Situ High-Energy X-Ray Diffraction	40
CHAPTER 3: THE EFFECT OF COMPOSITION ON PROPERTIES AND STRUCTURES OF CUZRAL BULK METALLIC GLASSES	43
3.1 Introduction.....	43
3.2 Experimental Procedure	45
3.3 Results.....	47
3.4 Discussions.....	53
3.5 Summary	57
CHAPTER 4: THE EFFECT OF FABRICATION METHODS ON MECHANICAL BEHAVIORS AND STRUCTURES OF A ZR₅₅NI₅AL₁₀CU₃₀ BULK METALLIC GLASS	59
4.1 Introduction.....	59
4.2 Experimental Procedure	61
4.3 Results and Discussions.....	64
4.4 Summary	69
CHAPTER 5: THE EFFECT OF PLASTIC-DEFORMATION HISTORY ON THE SUBSEQUENT PROPERTIES AND STRUCTURES OF BULK METALLIC GLASSES	70
5.1 Introduction.....	70
5.2 Experimental Procedure	72
5.3 Results and Discussions.....	77
5.4 Summary	84
CHAPTER 6: STRUCTURAL EVOLUTION OF A ZR₇₀CU₆NI₁₆AL₈ BMG UNDER COMPRESSION.....	85
6.1 Introduction.....	85

6.2	Experimental Procedure	87
6.3	Results and Discussions.....	88
6.4	Summary	96
CHAPTER 7: CONCLUSIONS		97
CHAPTER 8: FUTURE WORKS.....		101
REFERENCES		103
APPENDIX		113
VITA		177

LIST OF TABLES

Table 1.	The values for Young's Modulus E and Poisson's ratio ν for the metallic glasses in the literatures [20].....	114
Table 2.	Elastic constants measured from the x-ray (XR) and resonant ultrasonic spectroscopy (RUS) measurements: Young's modulus, E and Poisson's ratio, ν	115
Table 3.	The glass transition temperature (T_g), the onset crystallization temperature (T_x), the supercooled region (ΔT), and the structural relaxation exothermic heat (ΔH_0) for the IC (1550), IC (1250), and SC glass-forming alloys.	116
Table 4.	Plastic strain, yield stress, Young's modulus (E), and Poisson's ratio (ν) of the IC (1550), IC (1250), and SC glass-forming alloys.	117
Table 5.	Direction-dependent r_i and coordination numbers N_i of nearest neighbourhood in $Zr_{70}Cu_6Ni_{16}Al_8$ glass under compressive stress.	118

LIST OF FIGURES

Figure 1.	Critical casting thickness for glass formation as a function of the year the corresponding alloy was discovered [2].	119
Figure 2.	Free-volume model. Top: Plastic flow; Bottom: Free-volume evolution. [9].....	120
Figure 3.	Shape of the assumed interlayer shear resistance of a metallic glass: solid curve after Foreman and dotted curve actually using a linear approximation. [17].....	121
Figure 4.	A diffuse shear transformation inside a spherical volume element, Ω_f is favored at high temperatures $T > 0.68T_g$. [17].....	122
Figure 5.	A more intense shear transformation in a disk-shaped volume element, which is favored at low temperature. [17]	123
Figure 6.	A sketch of a typical in-situ high-energy synchrotron x-ray diffraction experiment. [20].....	124
Figure 7.	(a) Diffraction image as recorded by the MAR 345 2D image plate detector for $Zr_{64.13}Cu_{15.75}Ni_{10.12}Al_{10}$ BMG. The polar coordinates (s, φ) and the axis of tensile deformation are depicted. (b) X-ray diffraction pattern resulting from integration among the polar coordinates (s, φ) of the image presented in (a). [20]	125
Figure 8.	Change in the first peak position with applied tensile stress observed in the tensile ($\varphi = 90^\circ$) and transversal ($\varphi = 0^\circ$) direction. [20]	126
Figure 9.	Angular dependence of the strain determined at various stages of tensile deformation. The full line denote fits of the experimental data to equation. [20].....	127
Figure 10.	Stress-strain curves for different strain tensor components. The lines correspond to the fit of the data to a linear function starting from the origin of the coordinate system. [20].....	128
Figure 11.	Strains determined from the diffraction data of tensile/transverse directions. In addition, the tensile stress-strain curves of $Zr_{62}Al_8Ni_{13}Cu_{17}$ and $La_{62}Al_{14}(Cu_{5/6}Ag_{1/6})_{14}Co_5Ni_5$ BMGs are also included for comparison. [23]	129
Figure 12.	Strain vs. applied stress of $Cu_{50}Zr_{50}$ glass measured by XRD and mechanical testing. [25].....	130
Figure 13.	Evolution of elastic strain components of (a) $Zr_{55}Cu_{20}Ni_{10}Al_{10}Ti_5$ and (b) $Cu_{47.5}Zr_{47.5}Al_5$ during loading. The increment of ε_{11} and ε_{22} strains deviates from linearity on atomic scale before the onset of macroscopic yielding. [24].....	131
Figure 14.	Pair correlation function $g(r)$ calculated from the $S(Q)$. Inset: shift in the first peak in $g(r)$ to smaller r with increasing compressive stress. [22].....	132
Figure 15.	Pair distribution function $G(r)$ of as-cast and tensioned samples for $Zr_{62}Al_8Ni_{13}Cu_{17}$ and $La_{62}Al_{14}(Cu_{5/6}Ag_{1/6})_{14}Co_5Ni_5$ BMGs. [21]	133
Figure 16.	(a) Deconvolution of the first coordination shell into two Gaussians for an unloaded sample and (b) at different stages of deformation. [20]	134

Figure 17. Atomic density $\rho(r, \chi = 0)$ of $\text{Cu}_{50}\text{Zr}_{50}$ glass in the tensile direction vs. load. [25].....	135
Figure 18. Strain vs. applied load of $\text{Cu}_{50}\text{Zr}_{50}$ glass determined from the shift of maxima positions r_i of $\rho(r, \chi)$. [25].....	136
Figure 19. The change of width [full width at half maximum (FWHM)] with applied stress for the “plastic” $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ is higher than for the macroscopically “brittle” $\text{Zr}_{55}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}\text{Ti}_5$. [24].....	137
Figure 20. Change in the widths (FWHM) of the two overlapping peaks in the RDF. [22].....	138
Figure 21. Schematic view of the scattering setup for in-situ compression tests.....	139
Figure 22. DSC traces of $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ glass-forming alloys at a heating rate of 20 K/min.	140
Figure 23. Evolution of elastic strain components of $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ glass-forming alloys during loading in the elastic region.	141
Figure 24. The change of width [full width at half maximum (FWHM)] with the applied stress for $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ glass-forming alloys.....	142
Figure 25. Uniaxial compression stress-strain curves of $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ glass-forming alloys at a strain rate of $8 \times 10^{-4} \text{ s}^{-1}$	143
Figure 26. Histogram showing the polyhedral fractions with various Voronoi indices for Cu-centered and Al-centered polyhedral.	144
Figure 27. Zr-Cu-Al combinations in the shell of (a) Cu-centered FI and (b) Al-centered FI in $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$, respectively.	145
Figure 28. The schematic view of (a) injection casting and (b) in-situ suction casting.	146
Figure 29. Schematic view of the scattering setup for ex-situ measurement.	147
Figure 30. The high-energy synchrotron x-ray results of the IC (1550), IC (1250), and SC samples, and the corresponding diffraction patterns shown in the inset of (b) SC sample and (c) IC (1250) sample.	148
Figure 31. DSC traces of the IC (1550), IC (1250), and SC samples tested under a continuous argon flow at a heating rate of $20 \text{ K} \cdot \text{min}^{-1}$. The inset is an enlargement in the temperature range around the glass transition temperature.	149
Figure 32. Uniaxial compression stress-strain curves of the IC (1550), IC (1250), and SC samples at a strain rate of $4 \times 10^{-4} \text{ s}^{-1}$ at room temperature.	150
Figure 33. Evolution of elastic strain components of the IC (1550) and SC samples during compressive loading in loading direction.....	151
Figure 34. The shear-band morphology on side surfaces of fractured rods of (a) IC (1550) and (b) SC.	152
Figure 35. The schematic view of the fatigue treatment.	153
Figure 36. Shear band morphology for (a) the compressive and (b) tensile-side surfaces of section a in $(\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30})_{99}\text{Y}_1$, respectively.	154
Figure 37. The evolution of strains in loading and transverse directions with the applied	

stress for inside-pin and outside-pin samples in $(\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30})_{99}\text{Y}_1$, respectively.	155
Figure 38. Strain determined from $G(r)$ at several stresses for inside-pin and outside-pin samples in $(\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30})_{99}\text{Y}_1$, respectively.	156
Figure 39. The change of width [full width at half maximum (FWHM)] with the.....	157
Figure 40. Shear band morphology for tensile-side surface of section a in $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$	158
Figure 41. The evolution of strains in loading and transverse directions with the applied stress for inside-pin and outside-pin samples in $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$, respectively.	159
Figure 42. The change of width [full width at half maximum (FWHM)] with the applied stress for inside-pin and outside-pin samples in $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$, respectively.	160
Figure 43. The evolution of strains in loading directions with the applied stress for inside-pin and outside-pin samples in $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$, respectively.	161
Figure 44. The difference in scattering intensity, $\Delta S(Q)$, for the preload samples of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ in loading direction plane for two measurement geometries, respectively, in the first group.	162
Figure 45. The difference in scattering intensity, $\Delta S(Q)$, for the preload samples of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ in loading direction plane for two measurement geometries, respectively, in the second group.	163
Figure 46. Structure factor $S(Q, \varphi=90^\circ)$ of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass as a function of load.	164
Figure 47. Strain vs. applied stress of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass along loading and transverse directions.	165
Figure 48. Change of isotropic structure factor S_0 vs load and anisotropic structure factor S_2 of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass.	166
Figure 49. Anisotropic pair density functions (PDFs) $\rho_2(r)$ of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass under different loads.	167
Figure 50. Anisotropic PDFs $\rho_2(r)$ and first derivative of $\rho_0(r)$ of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass at 1200 MPa.	168
Figure 51. The strains obtained by fitting the anisotropic part, $\rho_2(r)$ and the first derivative of the isotropic PDF, $\rho_0(r)$ with the equation (37) at different stress levels for $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass.	169
Figure 52. Direction dependence of nearest neighbourhood of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass; (a) 0MPa, (b) 1200 MPa.	170
Figure 53. The evolution of strains in loading and transverse directions with the applied stress to plastic region for the sample 2 of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass.	171
Figure 54. The evolution of stress and the change of FWHM in the loading direction with the displacement for the sample 2 of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass.	172
Figure 55. The rate of change of FWHM on the change of stress as function of the displacement in the loading direction for the sample 2 of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass.	173
Figure 56. The curve of stress vs. strain in the loading direction for the sample 2 of	

	Zr ₇₀ Cu ₆ Ni ₁₆ Al ₈ glass.	174
Figure 57.	Measured peak position of the first scattering maxima in (a) the loading and (b) transverse directions as a function of the displacement for the sample 2 of Zr ₇₀ Cu ₆ Ni ₁₆ Al ₈ glass.	175
Figure 58.	Measured excess free volume in the sample 2 of Zr ₇₀ Cu ₆ Ni ₁₆ Al ₈ glass as a function of the displacement.	176

CHAPTER 1: INTRODUCTION

In the past decade, much interest has been drawn upon bulk-metallic glasses (BMGs) [1, 2], which can be fabricated up to a bulk size (over 1 mm) by chilling gas or liquid phases, through avoiding the crystallization processes. Without any long-range order, BMGs exhibit excellent physical, chemical, and mechanical properties. [1-5] A combination of the ability of being fabricated to a bulk size and excellent properties makes BMGs as potential structural materials. [3, 6, 7]

At high stress levels and low temperatures, BMGs normally present inhomogeneous deformation, which is characterized by the formation of localized shear bands, followed by the rapid propagation of these shear bands, and finally sudden fracture of materials. [8-10] While the homogeneous deformation of amorphous alloys is typically believed to occur only at low stresses and high temperatures (usually $\sim 70\%$ of glass transition temperature, T_g) [9]. However, recently Lee's group demonstrated that a homogeneous flow of amorphous alloys is feasible in their bulk form, especially when subjected to a stress below the global yield strength at room temperature. [11-16] Although a free-volume model [9], shear transformation zone model [17], and local-density-function theory [18] were proposed, the mechanism of deformation for BMGs is still not fully understood.

Almost 50 years passed since the first amorphous alloy was discovered. However, the structure model of metallic glasses is still a great challenge for the science community and not resolved.

Recently, high-energy synchrotron x-ray diffraction provides a novel way to investigate the mechanical response and structural evolution of BMGs simultaneously. In 2005, the measurement of the strain distribution by synchrotron radiation was first established by Poulsen et al. in a brittle $\text{Mg}_{60}\text{Cu}_{30}\text{Y}_{10}$ BMG. [19] After that, some work [20-26] has been done on various BMG systems either under the compressive or tensile load. The tensors of the strain are extracted from the data both in the reciprocal and real space. However, the elastic constants calculated from the tensors of the strain are different from the measurement of the resonant ultrasonic spectroscopy. The structural evolution in the elastic region under loading is more direct from the real space. Most of the work [20-23] assumes that the structure is still isotropic when the data is analyzed in the real space, which is not the case since the sample becomes anisotropic under the applied load. Very few studies [25-26] investigated the structural evolution in the elastic region with the anisotropic pair density function (PDF). Using this analysis method of the anisotropy pair density function, Mattern et al. [25] investigated $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{65}\text{Zr}_{35}$ under tensile loading. They found topological rearrangements within the atomic nearest-neighbor environment in the elastic region. Wang et al. [26] observed the similar results in $\text{Cu}_{64.5}\text{Zr}_{35.5}$ in the case of compressive stresses.

However, it is very difficult to study the structural evolution of BMGs in the plastic region at room temperature with in-situ high-energy synchrotron x-ray diffraction, since the BMG has a very limited plastic strain. To our knowledge, there is no report on this issue so far.

In this dissertation, with the technique of high-energy synchrotron diffraction, the effect of composition, fabrication method, and pretreatment of plastic deformation on

the mechanical properties and structures of BMGs will be investigated. The structural evolution in the elastic region will be explored with the method of the anisotropic PDF. Moreover, the structural evolution in the plastic region will be the first time to be addressed from the data in the reciprocal space.

Intellectual Merit: This research explores the mechanical response and structural evolution in the elastic and plastic region of BMGs under a compressive load with high-energy synchrotron x-ray diffraction. The present study will (i) develop a novel approach to obtain the strain tensors in BMGs, (ii) further the fundamental understanding of the deformation mechanisms of the BMGs, and (iii) promote the application of the high-energy synchrotron x-ray diffraction on the research in BMGs.

Broader Impacts: The dissertation work contributes to the fundamental knowledge in the mechanical response and structural evolution in the elastic and plastic regions of BMGs. The effect of composition, fabrication method, and pretreatment of plastic deformation on the mechanical properties and structure of BMGs are systemically investigated. In particular, the anisotropic PDF is used to analyze the structural evolution in the elastic region of the BMG, giving a more novel and accurate way to understand the deformation mechanisms. Specifically, the structural evolution in the plastic region is the first time to be investigated with high-energy synchrotron x-ray diffraction. Therefore, the dissertation provides the useful information for the BMG-research community, especially in the area of the mechanical response and structural evolution of BMGs using the technique of high-energy synchrotron x-ray diffraction.

CHAPTER 2: REVIEW OF LITERATURE

2.1. Development of Bulk Metallic Glasses

For the last several thousands years, the conventional bulk metallic materials are being widely used in our daily life and their importance remains unchanged even at present. These conventional bulk metallic materials exhibit a three-dimensional periodic atomic configuration. However, a number of bulk amorphous materials with the absence of the long-range periodicity and related grain structure can be fabricated by rapid solidification from gas or liquid phases, through bypassing the crystallization processes. In these glasses, atoms are randomly packed, which form a specific structure with the short and medium range orders but without the long-range order. [27] The major bonding types in glasses include ionic, covalent, van der Waals, hydrogen, and metallic bonding. In which, a glass mainly formed through the metallic bond is named a metallic glass, which is comparatively a newcomer to the amorphous materials group. [28]

Metallic glasses, also named as amorphous alloys or glassy alloys, were first synthesized in the Au-Si system by Duwez at the California Institute of Technology (Caltech) in 1960, using a rapid-solidification technology. [29] The rapid quenching techniques that they developed for chilling metallic liquids can provide a cooling rate as high as 10^5 - 10^6 K/s. As a result, the process of nucleation and growth of crystalline phases could be constrained to achieve a frozen liquid configuration at room temperature and yield a metallic glass. The significance of Duwez's work was that their method permits large quantities of an alloy to be made into a glassy state, compared to other methods, for example, vapor condensation. Investigating on the formation, structure, and

properties of metallic glasses started to attract increasing attentions because of their fundamental scientific importance and engineering application potentials [30-32].

In the 1960s, Chen and Turnbull successfully fabricated amorphous alloys of ternary Pd-Si-N with N = Ag, Cu, or Au. The thicknesses of these Pd-Si-N glassy alloys could be up to 1 mm [31]. In addition, Chen systematically investigated Pd-Si-based, Pd-P-based, and Pt-P-based alloys in 1974 and developed these ternary glassy alloys with a critical casting thickness on 1-3 mm by quenching the melt, contained in a drawn fused quartz capillary, into water [32]. If a critical size of the metallic glass is above 1 mm, the metallic glass is defined as a bulk-metallic glass (BMG). The first bulk metallic glass was the ternary Pd-Cu-Si alloy prepared by Chen. In the beginning of 1980s, the Turnbull group re-investigated Pd-Ni-P alloys. They were able to make glassy ingots of $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ with a diameter of 5 mm by successfully decreasing heterogeneous nucleation [33]. In 1984, the Turnbull group had extended the critical casting thickness to 1 cm by processing the Pd-Ni-P melt in a boron oxide flux [34]. There is no doubt that the formation of the Pd-based BMG is an exciting achievement. However, due to the high cost of the Pd element, the investigation on this system only interested the academic field. The development of new BMG systems with lower cost and greater critical thickness intrigues the more activity of the research community.

In the late 1980s, Inoue et al. successfully developed new multicomponent-alloy systems comprised mainly of common metallic elements with lower critical cooling rates [35-36]. They investigated the rare-earth-based system and found an exceptional glass-forming ability (GFA) in La-Al-Ni and La-Al-Cu alloys [35]. By casting the alloy melt in water-cooling copper molds, they were able to fabricate fully glassy alloys with critical

thicknesses of several millimeters, even several centimeters in quaternary and quinary systems [37], such as Mg-Cu-Y and Mg-Ni-Y alloys, along with a family of multicomponent Zr-based BMGs (e.g., Zr-Cu-Ni and Zr-Cu-Ni-Al BMGs) [38, 39].

In the early 1990s, the Johnson group started the search for BMG glass compositions with good GFA and successfully discovered the quinary system of Zr-Ti-Cu-Ni-Be. For example, in 1993, Johnson and Peker developed the quinary glassy alloy of $\text{Zr}_{41.2}\text{Cu}_{12.5}\text{Ni}_{10}\text{Ti}_{13.8}\text{Be}_{22.5}$ with significantly lower critical cooling rates down to 1 K/s [40]. This alloy is commonly referred as VITRELOY 1 (Vit 1), the first commercial BMG. The finding of Vit 1 alloy together with the work of the Inoue group can be considered as the beginning of the structural applications of bulk metallic glasses.

Starting with the first metallic glass developed by Duwez et al., the history of metallic glasses is almost 50 years. The critical casting thickness increased by more than three orders of magnitudes in the past 50 years as shown in Figure 1 [2]. Over the last two decades, significant achievements have been made in exploring the metallic-glass alloy system. Numerous metallic glasses have been developed, including Zr- [41, 42], Ni- [43, 44], Ti- [45, 46], Mg- [47, 48], Cu- [49, 50], Al- [51, 52], Fe- [53, 54], La- [35], and Pd- [55, 56] based alloy systems.

2.2 Deformation

2.2.1 Deformation Mechanisms

2.2.1.1 Free-Volume Model [9]

A classical model on the mechanism of deformation in metallic glasses is so called as the “free-volume” model, developed by Turnbull and co-workers [57, 58] and

applied to the case of glass deformation by Spaepen [9]. The free volume is defined as the average atomic volume minus the average atomic volume in the ideally-ordered structure. It is the excessive volume that atoms can freely move in.

In this model, the deformation is viewed as a series of discrete atomic jumps in the glass, and these jumps are obviously favored to have a nearest neighbor environment of high free volumes as shown in Figure 2. These sites can more readily accommodate the atom with the volume of v^* . It is assumed that the atomic positions before and after the jump are relatively stable with the minimum local free energy. The activation-energy barrier of motion, ΔG^m , is necessarily supplied to make the atom jump. Without the applied stress, the activation barrier is obtained from thermal fluctuations. The rate of forward jumps of an atom across the activation barrier equals that of backward jumps. This is the basic microscopic-diffusion mechanism. When the glass is under the applied external force, for example, shear stress, the activation-energy barrier that the atom jumps is biased in the direction of the force. In other word, the number of forward jumps is larger than the number of backward jumps. This trend results in a net forward flux of atoms and forms the basic mechanism of a flow. Quantitatively, the flux can be expressed as follows. When all the atoms in a specimen, under the deformation of shear, make one jump (≈ 1 atomic diameter) in the direction of the shear, this would result in a macroscopic shear strain ($\gamma \approx 1$). If only a fraction of atoms jump, the shear-strain rate, $\dot{\gamma}$ is the fraction of atoms that make forward jumps per second. The $\dot{\gamma}$ can be written as

$$\dot{\gamma} = (\text{fraction of potential jump sites}) \times (\text{a net number of forward jumps on each of those sites per second}) \quad (1)$$

Based on Cohen and Turnbull' theory, the probability, $p(v)dv$, of finding an atom with a free volume between v and $v + dv$ can be calculated as:

$$p(v)dv = \frac{\alpha}{v_f} \exp\left(-\frac{\alpha v}{v_f}\right)dv \quad (2)$$

Where α is a geometrical factor between 1/2 and 1, and v_f is the average free volume of an atom. If an atom is a potential jump site, its free volume must be larger than the effective hard-sphere size of the atom, v^* . Thus, the total probability that an atom is on a potential jump site can be written as:

$$\int_{v^*}^{\infty} \frac{\alpha}{v_f} \exp\left(-\frac{\alpha v}{v_f}\right)dv = \exp\left(-\frac{\alpha v^*}{v_f}\right) \quad (3)$$

Of course, a factor of Δf is needed, considering the flow in homogeneity. Δf is the fraction of the sample volume in which potential jump sites can be found. For a homogeneous flow, all the atoms contribute to the flow, $\Delta f = 1$. However, for an inhomogeneous flow, the plastic flow is localized in very thin shear-band regions, $\Delta f \ll 1$. Therefore, the fraction of potential jump sites is:

$$\Delta f \exp\left(-\frac{\alpha v^*}{v_f}\right) \quad (4)$$

If a shear stress of τ is applied on an atom, when this atom makes a jump, the work done is $\tau\Omega$ where Ω is the atomic volume. The free energy of the atom after the jump is, therefore, decreased by $\Delta G = \tau\Omega$. Then, the net number of forward jumps per second can be calculated as the difference between a forward flux over an activation barrier, $\Delta G^m - \Delta G/2$, and a backward flux over an activation barrier, $\Delta G^m + \Delta G/2$. The net number of forward jumps per second per potential jump site is given by:

$$\nu[\exp(-\frac{\Delta G^m - \tau\Omega/2}{kT}) - \exp(-\frac{\Delta G^m + \tau\Omega/2}{kT})] \quad (5)$$

where ν is the frequency of the atomic vibration ($\sim$ Debye frequency).

Substituting Equations (4) and (5) into (1), the strain rate can be given as:

$$\dot{\gamma} = \frac{\partial \gamma^p}{\partial t} = \Delta f \exp[-\frac{\alpha \nu^*}{\nu_f}] 2\nu \sinh(\frac{\pi\Omega}{2kT}) \exp[-\frac{\Delta G_m}{kT}] \quad (6)$$

This is the general flow equation, which is applicable for both homogeneous and inhomogeneous deformation of glasses.

2.2.1.2 Shear-Transformation-Zone Model [17]

In 1979, Argon proposed a shear-transformation-zone model. It discusses a mechanism of plastic flows in metallic glasses in which strain is produced by local shear transformations nucleated under the applied stress and the assistance of thermal fluctuations in regions around free-volume sites of the glass structure. In this model, the fundamental unit process underlying deformation is a local rearrangement of atoms that can accommodate shear strains. This local rearrangement is referred to as “a local inelastic transition” or more commonly “a shear-transformation zone (STZ)”. The STZ is a local cluster of atoms that undergoes an inelastic shear distortion from one relatively low-energy configuration to another such configuration, crossing an activated configuration of higher energy and volume. Argon discussed this theory, based on the temperature below the T_g . At high temperatures ($0.6T_g \leq T \leq T_g$) the transformation is a diffuse rearrangement producing a relatively small local shear strain in a roughly spherical region. At low temperatures ($0 \leq T \leq 0.6T_g$), the transformation is in a narrow disk-shaped region and resembles closely the nucleation of a dislocation loop.

High-temperature low-stress mechanism: when the liquid is rapidly cooled below T_g , the free-volume state of the structure remains largely frozen-in. In this range, the deformation is isoconfigurational, and the large-strain plastic flow is dominated by the kinetics of the rearrangement of the atoms in regions around free-volume sites. In order to compute the specific form of the activation free enthalpy for the shear-transformation process, it can be assumed that the binding is largely metallic, the shear resistance of the structure across a plane resembles that of a close-packed metal, and a skewed sinusoidal curve can nicely represent this resistance shown in Figure 3. Furthermore, for convenience of operation, a smoothly varying skewed sinusoidal resistance can be replaced by the linearized and discontinuous form.

The important parameters of this interlayer shear resistance include: the initial slope, which is taken to be equal to the shear modulus, μ , of the glass, the ideal shear resistance, τ , and the period, d , which is taken to be equal to the nearest neighbor distance given by the position of the first peak in the radial distribution function. The flow unit is taken as a region of volumes, Ω_f , consisting of a free-volume site and its immediate surroundings. It is assumed that under an applied shear stress, σ , a relatively diffuse internal rearrangement of atoms around the free-volume site occurs, as depicted in Figure 4 and results in a local shear strain of γ_0 in this region. This type of shear transformation in a spherical region of size, Ω_f , can increase the elastic strain energy by $\Delta\varepsilon$:

$$\Delta\varepsilon = \frac{7-5\nu}{30(1-\nu)} \mu \gamma_0^2 \Omega_f \quad (7)$$

Here ν is Poisson's ratio. This elastic-strain-energy increment is short lived and will be dissipated soon, resulting in a loss of memory for the initial state in the first region. Thus, the shear strain rate at a low stress ($\sigma \ll \tau$) can be given by

$$\dot{\gamma} = \alpha \gamma_0 \nu_G \exp\left(-\frac{\Delta \varepsilon + \gamma_0 \tau \Omega_f}{kT}\right) \sinh\left(\frac{\sigma \gamma_0 \Omega_f}{kT}\right) \quad (8)$$

In this equation, the effect of a “back flux” of reverse transformations against the applied stress is also incorporated. ν_G is the normal mode frequency of the flow unit along the activation path. α incorporates numerical constants and the steady state volume fraction of flow units contributing to the plastic flow. The strain rate could be rewritten as:

$$\dot{\gamma} = \alpha \gamma_0 \nu_G \exp\left(-\beta A \frac{T_g}{T}\right) \sinh\left(\frac{\sigma}{\tau}\right) \left(\frac{T_g}{T}\right) \left(\frac{\tau}{\mu} A\right) \quad (9)$$

where $\beta = \left(\frac{7-5\nu}{30(1-\nu)}\right) \gamma_0 + \frac{\tau}{\mu}$ $A = \frac{\mu \gamma_0 \Omega_f}{kT_g}$, and τ/μ is the ideal elastic-shear strain at

which the ideal shear strength is reached.

For the high-temperature mechanism, the strain-rate sensitivity exponent, m , can be defined as:

$$m = \left(\frac{\partial \ln \dot{\gamma}}{\partial \ln \sigma}\right)_T = \left(\frac{\sigma}{\tau}\right) \left(\frac{T_g}{T}\right) \left(\frac{\tau}{\mu} A\right) \coth\left(\frac{\sigma}{\tau}\right) \left(\frac{T_g}{T}\right) \left(\frac{\tau}{\mu} A\right) \quad (10)$$

Low-temperature high-stress mechanism: The Bragg experiment and computer simulation demonstrate that the shear transformation at high stresses becomes more intense but narrows down to a region between two short rows of 4-6 atoms around a free-volume site depicted in Figure 5. This process closely resembles the nucleation of a dislocation loop that does not expand. Such alternation in the local shear transformation can be expected under high stresses, which permits the attainment of larger local shear

strains in small regions, around free volume sites. The energetically-favored transformation configuration is in the shape of a thin disk containing the shear-transformation direction in its plane. In this case, the elastic-strain-energy increment, $\Delta\epsilon$, due to the transformation is that of a circular dislocation loop of a radius, R ,

$$\Delta\epsilon = \frac{\mu(\Delta x)^2 R(2-\nu)}{4(1-\nu)} \left(\ln \frac{4\alpha R}{d} - 2 \right) \quad (11)$$

where Δx is the relative shear displacement across the plane of the loop between a stable and an unstable equilibrium positions of the configuration under the combined effect of the applied stress. The shear resistance of the structure, d , is the nearest neighbor distance in the glass, and α is a core cut-off parameter (≈ 1 for the type of binding appropriate for close-packed metals). The plastic deformation rate can be given by:

$$\dot{\gamma} = \dot{\gamma}_G \exp\left(-\frac{\Delta G^*}{kT}\right) \quad (12)$$

ΔG^* is the activation energy under a large applied shear stress, and it is more complicated than in the high-temperature mechanism. $\dot{\gamma}_G$ presents a very similar composition and magnitude as the pre-exponential term for the high-temperature mechanism.

The free-volume model views the deformation as a series of discrete atomic jumps in the glass. These jumps are obviously favored near sites of high free volumes, which can more readily accommodate them. Due to the diffusion-like character of the process, the characteristic energy scale in the free-volume model is of the order of the activation energy for diffusion, $\sim 15 - 25 kT_g$ [9, 58, 59], which is quite similar to the lower end of the range for the expected energy of an STZ operation. However, the activation energy in two models corresponds differently. In the STZ model, the activation

energy corresponds to a subtle redistribution of many atoms over a diffuse volume, while the activation energy in the free-volume model corresponds to a more highly localized atomic jump into a “vacancy” in the glass structure. [8] Mechanisms in both models may occur homogeneously throughout a glass body or in a localized mode during the formation of a shear band. Despite differences in the conceived atomic motions underlying the shear-transformation-zone model and the free-volume model and differences in the macroscopic mechanical response between these two cases, the deformation mechanism is, at least nominally, the same. The atomic-level mechanisms, including STZ and free-volume models, provide the basis for a more quantitative understanding of the deformation of metallic glasses.

However, recently Egami [60] pointed out that the free-volume model is a phenomenological theory, based upon the experimental observations. Although it is able to explain some mysteries of glasses and liquids beautifully, for example, viscosity changes greatly over a relatively small temperature range just above T_g , the free-volume model in its original form does not work well for metallic glasses. The most important parameter in the free-volume theory is the ratio of the critical value of the free-volume to accept an atom, v^* , to the atomic volume, v_a , v^* / v_a . The theory assumes that this value is close to unity. In reality, it is about 0.8 for van der Waals liquids and much less than 1, is close to 0.1 for metallic liquids. Moreover, the validity of the free-volume concept is obvious for systems of hard spheres (HS). For a hard sphere to move in a close-packed structure, there must be extra space between the spheres, otherwise they are trapped in the cage made by neighbors and cannot move. However, in the case of metals, the atoms, which are soft and squeezable, are able to move without a free space, simply by

squeezing in. Thus, the relevance of the free-volume concept is less obvious for metal systems with softer interatomic potentials. Based on the above discussion, caution should be taken when the free-volume theory is used for metallic glasses. Other theories, such as the local-density-function theory, are under development. In the future, more realistic and accurate microscopic and atomistic description of metallic glasses may be available, based on local structural fluctuations.

2.2.2 Elastic Deformation

Elastic deformation is a change in the shape of a material at low stresses, which is recoverable after the stress is removed. This type of deformation involves stretching of the bonds, but the atoms do not slip past each other. Thus, it is easy to understand that the ability of elastic deformation will be related to the atom-bond strength. In general, the force, F , which holds atoms together, can be defined as [61]

$$F_{ij} = \frac{dU_{ij}}{dr} \quad (13)$$

where U_{ij} is the potential energy between two atoms, which can be presented as

$$U_{ij} = -\frac{A}{r^n} + \frac{B}{r^m} \quad (14)$$

here r is the distance between i and j atoms, respectively. A , n , B , and m are constants. The first and second energy terms come from an attractive and repulsive interaction, respectively. An equilibrium position is achieved, when U_{ij} has a minimum value. In a similar way, the forces can also be divided into the attractive force and the repulsive

force. Under the equilibrium condition, U is minimized, and atoms reside at $r = r_0$ with $F = 0$.

The elastic modulus is proportional to the stiffness, which is defined as the slope of the F-r curve and shown in Equation:

$$ElasticModulus \propto S = \frac{d^2U}{dr^2} \quad (15)$$

The modulus will decrease as the inter-atom distance increases.

BMGs are usually considered to be elastically isotropic. Isotropic materials have two independent elastic constants, Young's modulus (E), and Poisson's ratio (ν). However, from a more fundamental point of view, it is reasonable to consider the bulk modulus (B) and shear modulus (μ), which represents the response to hydrostatic and shear stresses, respectively. The bulk modulus involves bond stretching or compression only, while the shear modulus involves bond distortion. Compared to their crystalline counterpart with a similar composition, the bulk modulus of amorphous alloys is typically about 6% smaller [62]. For crystals, the bulk modulus increases with increasing the curvature of the interatomic potential energy well and decreases with increasing the equilibrium separation between atoms. [63] The density of a metallic glass is slightly lower than its crystalline counterpart (around a 0.5 – 2 % difference). Thus, accordingly on average, the interatomic spacing is slightly larger in the glass. [8] If it is assumed that the short-range order and, hence, the cohesive forces are not significantly different between the crystal and the metallic glass, the difference in the bulk modulus can be explained adequately by the difference in the atomic separation. In contrast, the response of metallic glasses to shear stresses is significantly different from that of crystals. Both μ

and E are around 30% smaller in amorphous alloys than in the crystals. [62, 64-67] Such a large difference can not be explained on the basis of a change in the atomic spacing alone. [68] It is believed that the difference is a result of how the local environment influences atomic rearrangements in response to shear stresses. [69] Metallic glasses have a wider range of atomic environments and slightly less dense packing, allowing the local atomic displacement, which benefits the increase of the macroscopic strain.

In metallic glasses, the response to shear stresses may include not only atomic displacements but also an anelastic reshuffling of the atomic near-neighbors. Although the fraction of atoms involved in these events (i.e., an anelastic STZ operation) may be small, the local strains are large enough that their cumulative effect contributes to the macroscopic strain significantly. [70]

2.2.3 Plastic Deformation

The plastic deformation of metallic glasses is through the operation of STZs and the redistribution of free volumes, which can result in an accumulation of local strains. These local events (STZs and a redistribution of free volumes) can be distributed homogeneously or inhomogeneously in time and space under the effect of the temperature, the applied strain rate, and the glass condition. The homogeneous deformation can be divided into the steady-state flow and non-steady state flow. In the steady-state flow, a homogeneous flow is a balance between the structural disordering and ordering, e.g., the free-volume creation and annihilation. The basic phenomenology of flow is, therefore, given by the biased accumulation of local STZ strains. While for a non-steady state flow, a homogeneous flow occurs with the structural evolution, i.e., a net

gain or loss of free volumes can occur during deformation. At high temperatures and low applied stresses, flow is Newtonian, i.e., the strain rate is proportional to stress [71]. However, at higher applied stress levels, the stress sensitivity of deformation drops rapidly, and the flow becomes non-Newtonian. Both of the cases discussed above are at high temperatures and present as homogeneous deformation. This transition from the Newtonian to non-Newtonian flow is also promoted by a decrease in temperature. The deformation becomes inhomogeneous. The divergence from the Newtonian behavior corresponds to a decreasing rate sensitivity and a corresponding decline in the flow stability.

At high stress levels and low temperatures, BMGs present inhomogeneous deformation, which is characterized by the formation of localized shear bands, followed by the rapid propagation of these shear bands, and finally a sudden fracture of materials. [8-10] Although a large amount of plastic strains is accumulated at these localized areas (i.e., shear bands), the entire plastic deformation of the specimen is generally very low (~2-3%). Shear-band formation is generally thought as a direct consequence of strain softening. In metallic glasses, there are many potential causes for strain softening and localization, including the local production of free volumes due to the flow dilatation, local evolution of structural order due to STZ operations, and the redistribution of internal stresses associated with the STZ operation, and local heat generation. As the stress increases, strains are first accommodated elastically, until the stress level increases enough to activate the plastic flow in a local region (i.e., shear bands). The increased rate of strain accumulation in a shear band is accompanied by strain softening. The partitioning of the strain rate into a shear band occurs over a finite range of the applied

macroscopic strain and the strain in the band quickly becomes very large. When the applied strain is fully accommodated by the shear accumulated with the band, relaxing the stress. After a single shear band operates and arrests, the successive shear banding can operate upon continued straining, which help accommodate the further deformation of the material. As a result of this strain localization, load-displacement curves exhibit characteristic patterns of flow serration. For a displacement-controlled experiment, the serrations are represented as load drops. For a load-controlled experiment, the serrations are registered as the displacement bursts. For both cases, each serration is a relaxation event associated with the formation of a shear band. The process of shear localization is very important in the metallic-glass research, since the formation of the shear bands will affect the strength and especially the ductility, which is directly related to the application of BMGs.

Another source of shear localization in metallic glasses is considered as thermal effects in localized regions. The estimates of the local temperature rise resulted from the local heating ranged from less than 0.1 K to a few thousand K. [72] Leamy and co-workers [73] first proposed that shear-banding events are essentially adiabatic phenomena. But this idea was quickly criticized by others, based on that the rapid thermal conduction would limit the temperature rise in a thin shear band. [74] Schuh and co-workers [8] first assumed that shear-banding events are adiabatic and, then, calculated some of their properties to compare these to the experimental measurements. They found that if shear bands in metallic glasses were primarily adiabatic, then either the displacement rates or the shear-band thicknesses would be much greater than the experimental observations. Thus, it seems unlikely that shear localization in metallic

glasses is driven primarily by thermal softening. Despite the discussion above, significant increases in temperature do occur during shear-banding events. Wright et al. [75] estimated the temperature increase in a single shear band due to the local adiabatic heating by quantitatively measuring the serrated plastic flow of $\text{Zr}_{40}\text{Ti}_{14}\text{Ni}_{10}\text{Cu}_{12}\text{Be}_{24}$ (at.%) and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ (at.%) under compressive loading. The predicted temperature increases only a few degrees Celsius. Lewandowski et al. [72] estimated the temperature rise associated with shear banding by fusible-coating Vitreloy 1 samples with a low-melting-point metal, tin. They provided the direct evidence of a temperature rise of 200 K in the operating shear bands, at least near the surface.

The structure and behavior of shear bands are the focus interests when the inhomogeneous deformation is studied. The direct structural characterization of the shear bands is desirable, although it is a significant challenge. Shear bands typically comprise only a small volume fraction of a deformed specimen, and bulk-characterization techniques average over both the shear bands and the remaining undeformed region of the material. However, scattering techniques have been used to study heavily cold-worked specimens, providing the evidence for structural disordering. [76-79] Transmission-electron-microscopy (TEM) is a possible method to characterize the structural feature of the individual shear bands, for example, the thickness of shear bands. TEM observations indicate that shear bands in metallic glasses are only 10-100 nm thick, [80-82] which is quite small, compared to adiabatic shear bands in crystalline metals, which are typically 10-100 μm thick [83]. Based on the abundant experimental evidence, there is the significant shear-induced dilatation of the structure for both homogeneous and inhomogeneous deformation. This dilatation usually contributes to a plastic flow via the

reduced viscosity. [8] The direct evidence for dilatation is from measurements of density changes of metallic glasses as a result of plastic deformation. Density decreases of 0.1-0.2% have been observed upon the extensive inhomogeneous deformation.[84, 85] These observed density changes are large, compared with ~0.01% dilatation of crystalline alloys [86], but small in comparison to many polymers. It should be noted that if, as is commonly assumed, deformation and, thus, dilatation are restricted to the shear bands, then by making reasonable approximations as to the number density and thickness of shear bands, the dilatation inside the shear bands themselves must be quite large (>10%) [85]. The same situation is for the strain energy density, which is also quite high [87]. The combination of these observations tells us that even in the inhomogeneous regime, plastic deformation may not be restricted to the shear bands, or that shear bands are more diffuse than usually thought. The change in the free volume during both homogeneous and inhomogeneous deformation can be measured indirectly but quantitatively by studying the structural relaxation near the glass transition using a differential-scanning calorimetry (DSC) [88]. For example, an increase in the free volume with increasing the degree of the inhomogeneous deformation has been observed. Positron-annihilation techniques are considered as powerful tools for studying open-volume regions in solid materials. [89] The early work using this technique showed that the plastic deformation of metallic glasses resulted in an increase in the positron lifetime, which is consistent with a greater degree of open volumes in the amorphous structure [79, 90]. Another kind of information can be achieved from positron-annihilation measurements is to discern the local chemical environment around open-volume regions. Another feature of the structure of shear bands is the possible presence of voids, which is believed to result from the

coalescence of excess free volumes in the shear band once deformation stops. For example, Donovan and Stobbs [91] observed the sub-nanometer-scale voids in shear bands, when the specimen is under tension loading, not under compressive loading. Jiang and Atzmon [82] reported similar observations for shear bands formed on the initially tensile side of ribbons deformed by bending, followed by unbending, but observed no voids on the initially compressive side of the same ribbons. This trend indicates that the hydrostatic components of stress play a role in affecting the void nucleation. Besides the structure features discussed above, the formation of nano-crystals inside shear bands have been observed in metallic glasses. An example of such nano-crystals formed is reported by Jiang and Atzmon during bending of an $\text{Al}_{90}\text{Fe}_5\text{Gd}_5$ glass. [82] The mechanism why nano-crystals form inside shear bands in metallic glasses is still not clear and under debate. The popular explanation is that localized heating of the shear band possibly causes crystallization, considering the increase temperature in shear-band regions. However, Demetriou and Johnson [92] argued that the driving force for nucleation decrease with increasing the temperature, which means that the elevated temperature alone is not a sufficient explanation. If there are no pre-existing nuclei to grow, it is not clear that the rapid heating and cooling inside a shear band allow sufficient time for nucleation. Thus, the thickness of the shear band is important because it, along with the strain rate and the thermal conductivity of the alloy, determines the time scale available for crystallization.

2.3 Structure of Bulk Metallic Glasses

The atomic structure is the basis for the understanding the nature of the metallic glasses. The term “structure” can be understood from different angles. Firstly, it means a topological structure (or order), which describes the arrangement of atoms according to the constraint of filling the three-dimensional space. Secondly, it also means a chemical structure (or order), which describes the mutual arrangement of the atoms of the different components forming an alloy. Thirdly, the structure further comprehends the short-range structure and the medium range structure. The amorphous state of metallic glasses can be placed together with the liquid state between the gaseous and crystalline states. All the state can be described in terms of a packing of structural units. In the gaseous state, the structural units are the molecules, which are far away from one another. In the amorphous state, the structural units are closely packed, but mutually rotated and distorted. In the crystalline state, the structural units are elementary cells, which are arranged periodically along the three directions of a coordinate system in the real space. The metallic glasses were found to have an amorphous structure with a high degree of densely and randomly packed atomic configurations.

Although the first amorphous alloy was discovered almost 50 years ago, the structure model of metallic glasses is still a great challenge for the scientific community and not resolved. The early structural models range from the microcrystallite to the continuous random type. Proposed microcrystalline models are usually assembled of misoriented microcrystals with diameters averaging five to ten atomic spacing. [93] Usually, it is assumed that the spatial orientations of the crystallites are completely uncorrelated. The continuous-random model has its essential structural-element

configurations, which are noncrystallographic. Such different configurations can be incorporated into periodic space-filling arrangements when combined with each others. The earliest continuous-type model was the random network proposed by Zachariasen [94] and applied to covalently-bound glasses. In such a structure, the full interatomic connectivity is maintained but with a substantial dispersion of bond angles about some average value. The densest-random-packing (DRP) model, an analog to the random-network model, is originally developed for centrosymmetrically-bonded monatomic systems. Such structures were assembled from hard spheres, which are known to model real monatomic systems surprisingly well. The most conspicuous feature of the DRP structure is the prevalence of configurations in which the centers of four contacting spheres form tetrahedra with nearly regular shapes. Later, several modifications to the DRP model [95] have been made to extend its applications. For example, two sphere diameters were used to describe the structure of alloys which make this model applicable to simple multi-systems. [96] Also, in contrast to hard-sphere, soft-repulsive potentials were used in the model. [69]

Both random network and densely random-packed model structures are constructed on the basis of a single algorithm, which is applicable at all stages of the building block of the model. In contrast to such continuous random modeling, an amorphous solid might be formed by small and ordered, but noncrystalline, clusters. The motivation for forming this structure may derive from the energetic preference under the operation of centrosymmetric short-range interatomic forces. [93] The local structure can be described, using topological analyses based upon the study of Voronoi polyhedra. It is assumed that the assemblies of the lowest potential energy would be those composed

entirely of regular polyhedra which have the highest density per atom. But space cannot be wholly filled by the stacking of those densely-packed polyhedra alone. To form a crystalline closed-packed structure, it is necessary to include the less dense and more energetic polyhedral configurations. However, in assembling a small, in contrast to an infinite, number of atoms, small distortions of the polyhedra from regularity can be much more prominent to help construct the amorphous structure. This idea has been reported by some researchers and proven by computer simulations. [97] It must be pointed out that although the polyhedral analysis is very useful for understanding the amorphous structure, it could be misleading when one attempts to consider the relation between the local structure and the physical properties. For example, Egami et al. [98] reported that only in network systems, such as amorphous SiO_2 , is the topology of the atomic bonding itself physically more meaningful than the distortion of the environment. However, in an ideal metallic system, it is the distortion of the symmetry of the local environment, as well as the local stress, which is likely to be more important in determining many of the physical properties than the topology of bonding.

When considering the building block of the amorphous structure, besides the topology packing of the atoms, other factors should be kept in mind too. Chen and Clark [99] pointed to the X-ray evidence for the existence of a short-range chemical order between the first-nearest neighbor atom pairs in metallic glasses and melts and attributes the easy glass formability to the enhancement of cohesion in the liquid/glass resulting from strong, chemical bonding between unlike nearest neighbors. Nagel and Tauc [100] reported that electronic factors could affect the stability of the structure of certain metallic glass.

Early structural models were based on randomness, but were modified to acknowledge that the nearest-neighbor atomic environment displayed order similar to that in competing crystalline structures. However, attempts to define the structure of the metallic glass beyond the nearest-neighbour shell have continued to be unsuccessful. [101] Until recently, a description of how clusters of atoms interconnect to generate medium-range order is available. Miracle [102] proposed dense packing of overlapping atomic clusters as the fundamental scheme for metallic glasses. In his model, an arbitrary “face-centered-cubic” (Fcc) lattice of clusters is chosen to achieve a high density. But a strain factor has to be introduced to limit the coherence of such a lattice to the 1 - 1.5 nm scale in order to maintain a long-range disorder to keep the materials glassy. Without resorting to a predetermined structural model, Sheng et al. [103] instead use reverse Monte-Carlo simulations [104], based on the experimental X-ray diffraction and absorption data, as well as ab initio simulations of molecular dynamics [105] to solve the three-dimensional structure of binary metallic glasses. In order to investigate the short- to medium-range details of the BMG structure, they firstly determined the three-dimensional positioning of the atoms of the glasses. The number of nearest neighbours in an atomic cluster can be determined, using a technique know as Voronoi tessellation [106]. It is found that the basic units of the short-range order that emerges are various polyhedra of around 9 to 13 atoms, with a solute atom in the middle. The precise form of these polyhedral clusters is controlled by the ratio of the effective sizes of solute and solvent atoms, and, thus, changes according to the elemental constituents of the glass. A flexibility of a moderate variation in coordination numbers allows for a more efficient packing of “soft” atoms without requiring an Fcc structure. After mapping out the three-

dimensional positions of the clusters, they determined the topological packing of the clusters with a technique known as common neighbor analyses. The results showed that the clusters pack with an appreciable icosahedral medium-range order, regardless of the short-range order within the clusters. Like the Fcc-packing model of Miracle, this icosahedral packing of clusters generates cavities similar to those in the randomly and densely packing model [107], into which additional solute species of different sizes may be introduced [108]. This feature allows bulk metallic glasses to form.

2.4 Mechanical Response of Metallic Glasses using In-Situ High Energy X-ray Diffraction

Many methods have been developed and used to investigate the deformation mechanisms characteristic of BMGs. Ex-situ uniaxial tests (compression and tension) are usually performed to study the mechanical behaviors of BMGs. A great amount of information about mechanical behaviors can be achieved from ex-situ tests, such as the elastic limit, yield stress, and plastic strain of BMGs under different loading modes. More details of deformation mechanisms characteristic of BMGs have been studied. For example, the serrated flow can be characterized from stress-strain curves. The spatiotemporality of shear banding and the fracture mode can be examined with scanning electron microscopy (SEM). The structure of shear bands can be studied with transmission electron microscopy (TEM). Recently, characterization of amorphous materials by diffraction methods for the purpose of strain scanning was established by Poulsen and co-workers [19]. Characterizing the strain distribution in metallic glasses is crucial for understanding the deformation mechanisms of them.

2.4.1 Diffraction-Data Treatment and Theoretical Background

Most of metallic-glass studies using in-situ high energy X-ray diffraction was performed, using different synchrotron sources as follows: Advanced Photon Source (APS) at the Argonne National Laboratory, USA; the European Synchrotron Radiation Facility (ESRF) Grenoble, France; or HASYLAB at the Deutsches Elektronen-Synchrotron (DESY) Hamburg, Germany. The x-rays used for these experiments were monochromatic hard x-rays with energies at 80 - 100 Kev.

The direct information achieved from diffraction of metallic glasses is the elastic scattering intensity, $I(Q)$, as a function of the scattering vector, Q , which is defined as $4\pi\sin\theta/\lambda$, where θ is half of the scattering angle (see Figure 6), and λ is the wave length of the radiation. The structure factor can be written as:

$$S(Q) = \frac{I(Q)}{N\langle f(Q) \rangle^2} \quad (16)$$

where N is the number of atoms, $f(Q)$ is the atomic-scattering factor for x-rays, and the angular brackets indicate averaging over the composition of the materials [22]. The real-space structural information is the PDF, $g(r)$, in which r is the distance from an average atom located at the origin. It can be available by Fourier transforming $S(Q)$. Another very important function related to PDF is the radial distribution function (RDF), which is defined as $4\pi r^2 g(r)$. With this definition, the coordination number of a particular atomic shell of interest can be obtained by integrating the RDF over a suitably chosen range of r .

When a metallic glass is subjected to forces that create a macroscopic stress, both $S(Q)$ and $g(r)$ will change accordingly. For uniaxial loading (compression or tension), the changes in the real space is easy to expect. The compressive stress will tend

to move atoms close in the loading direction, and, thus, a peak in $g(r)$ for that direction will move to smaller values of r for a tensile stress, the opposite should happen. In the reciprocal space, Q is expected to shift toward higher values in the case of the compressive stress and lower values when the sample is tensioned. By analogy with the simple definition of the engineering strain, the strain for an applied stress, σ , can be written as:

$$\varepsilon_i(\varphi_i, \sigma) = \frac{Q(\varphi_i, 0) - Q(\varphi_i, \sigma)}{Q(\varphi_i, \sigma)} \quad (17)$$

which is angle-dependent. In the transverse direction, a strain of the opposite sign can be expected due to the Poisson's effect. A typical diffraction image of a metallic-glass sample is shown in Figure 7. The amorphous structure is proved by the absence of any sharp and clear ring. Then the diffraction pattern is integrated upon the polar coordinates (s, φ) . The integration can be done by dividing the entire circle into sections based on the divided angle. For example, the entire circle can be divided into 36 sections of 10° each. The data integration can be done with the use of the *FIT2D* software [109] and after the integration of the intensity curves will be corrected for the background, polarization, and inelastic Compton scattering. Figure 7b presents a typical diffraction pattern after integrating the diffraction image. The structure factor, $S(Q)$, can be calculated based on the equation with the help of the *PDFgetX2* software package [145]. Once the load is applied, the round concentric halos from Figure 7a become elliptical, and the asymmetry increases as the load increases. The angular variation of the strain can be fitted with the following equation [20]:

$$\varepsilon(\varphi, \sigma) = \varepsilon_{11} \sin^2 \varphi + \varepsilon_{12} \sin \varphi \cos \varphi + \varepsilon_{22} \cos^2 \varphi \quad (18)$$

With the equation, the strain tensor can be determined, and the axial, ε_{11} , tangential, ε_{22} , and in-plane shear component, ε_{12} , can be derived. In Figure 6, $\varphi = 90^\circ$ corresponds to the axial stress, and $\varphi = 0^\circ$ corresponds to the tangential stress. Components not in the plane perpendicular to the incoming beam can be determined by rotating the specimen around an axis perpendicular to the incoming beam. The similar analysis works in the real space. However, Dmowski and Egami [110] pointed out that due to the presence of the structural anisotropy, PDF should be expanded into a spherical harmonics, otherwise systematic errors may occur especially in the first neighborhood.

2.4.2 Strain Analysis from Tensile Tests and Reciprocal Space

Stoica et al. [20] investigated the strain distribution in the $\text{Zr}_{64.13}\text{Cu}_{15.75}\text{Ni}_{10.12}\text{Al}_{10}$ BMG by in-situ tensile tests under synchrotron radiation. The symmetric circular broad diffraction pattern proved the glassy structure for the samples prior to applying the tensile stress. With increasing the tensile load, it becomes elliptical. To describe such changes more quantitatively, the authors constructed a set of symmetrized intensity distributions, as described previously and traced the change in the first peak position as a function of the azimuth angle, φ , and tensile stress, σ . The experimental scatter of the measured strain values at each different stress level is shown in Figures 8 and 9 [20]. From Figure 8 [20], it is proved that the asymmetry of the first diffuse maximum increases with increasing the load. The decrease in the peak position with increasing the tensile stress reflects the fact that atoms move apart along the tensile direction. An opposite behavior is observed in the transverse direction. Figure 9 [20] shows the angular variation of the strain at a given stress, σ , as calculated from the

relative change in the position of the first peak using Equation (18). The fit of the experimental data to Equation (18) gives the axial and tangential components of the strain tensor, ε_{11} and ε_{22} , respectively. The stress-strain curves for different strain-tensor components are shown in Figure 10 [20]. The curves all present a linear behavior within the experimental error, which indicates the elastic deformation for the investigated specimens. The maximum axial strain (ε_{11}) is $1.50 \pm 0.01\%$. The elastic modulus determined in the tensile mode is $E_{11} = 94 \pm 1$ GPa, and the experimentally-determined Poisson's ratio, $\nu = -\varepsilon_{22} / \varepsilon_{11}$, is 0.325 ± 0.01 .

Wang et al. [23] detected the tensile behaviors of $\text{Zr}_{62}\text{Al}_8\text{Ni}_{13}\text{Cu}_{17}$ and $\text{La}_{62}\text{Al}_{14}(\text{Cu}_{5/6}\text{Ag}_{1/6})_{14}\text{Co}_5\text{Ni}_5$ BMGs using in situ high-energy x-ray diffraction. The tensile modulus and Poisson's ratio can be accurately evaluated. The strains determined from the diffraction data of tensile/transverse directions are shown in Figure 11 [23]. It can be seen that there is a good linear behavior and basically no sign of yielding. By linearly fitting the points and calculating the ratio of strains between the transverse and tensile directions for each alloy, the tensile elastic modulus and Poisson's ratio were obtained, about 83 GPa and 0.37 for the $\text{Zr}_{62}\text{Al}_8\text{Ni}_{13}\text{Cu}_{17}$ BMG and 34 GPa and 0.36 for $\text{La}_{62}\text{Al}_{14}(\text{Cu}_{5/6}\text{Ag}_{1/6})_{14}\text{Co}_5\text{Ni}_5$ BMG, respectively.

Using the same method, Mattern et al. [25] measured amorphous ribbons with the compositions of $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{65}\text{Zr}_{35}$ under tensile loading. The results for $\text{Cu}_{50}\text{Zr}_{50}$ are presented in Figure 12 [25]. Again, a good linear behavior up to the highest value before the fracture of the strain with the applied stress can be observed, and no sign of plastic deformation was observed either. The Young's modulus and the Poisson's ratio

were calculated directly from the slopes of the components, ε_{11} and ε_{22} , vs. stress and turned out to be $E = 63$ GPa and $\nu = 0.31$, respectively.

2.4.3 Strain Analysis from Compression Tests and Reciprocal Space

The evaluation of a strain distribution by synchrotron radiation was established by Poulsen et al [19]. They measured a brittle $\text{Mg}_{60}\text{Cu}_{30}\text{Y}_{10}$ BMG under a compressive load. A good linear dependence of the strain as a function of the applied stress was found, and the sample failed at the end of the elastic regime.

Hufnagel et al. [22] investigated $\text{Zr}_{57}\text{Ti}_5\text{Cu}_{20}\text{Ni}_8\text{Al}_{10}$ BMGs loaded in uniaxial compression. The samples were loaded incrementally from 0 MPa to 1,080 MPa (approximately 60% of the yield stress for this alloy) and back to zero stress, and the diffraction patterns were recorded at various stresses where the load was held for the x-ray exposure. Instead of $I(Q)$, $S(Q)$ was used to analyze the strain variation. As the compressive stress increases, the first peak in $S(Q)$ shifts to a larger Q in the loading direction. The opposite trend was present for $S(Q)$ in the transverse direction. Compared to tensile tests, the axial component, ε_{11} , and the tangential component, ε_{22} , of the strain tensor become negative and positive, respectively. The stress-strain curves indicated that the strain increases linearly with increasing the compressive stress. A straight-line fit to both loading and transverse directions and then diagonalized can yield an elastic modulus of $E = 87 \pm 2$ GPa and Poisson's ratio of $\nu = 0.34 \pm 0.01$, which are both in a reasonable agreement with the macroscopic measurements on closely related amorphous alloys.

Das et al. [24] applied compressive loads on two different BMGs beyond the elastic region to measure strain tensors by high-energy x-ray diffraction to study the

plastic yielding phenomena. These two typical amorphous alloys were chosen as “plastic” $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ and “brittle” $\text{Zr}_{55}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}\text{Ti}_5$ BMGs. After loading, the diffraction patterns changed from a circular feature of the unloaded state to the elliptical nature of the ring, which indicates a decrease of the atomic spacing of the nearest neighbors along the loading direction. The data analysis has been performed, using $I(Q)$ in a reciprocal space. At each stress level, a peak function was used to fit the first maximum to determine the peak shifts with respect to the unloaded condition. The evolution of the different atomic-scale strain components (ε_{11} , ε_{22} , and $\gamma_{12} = \varepsilon_{12}$) with the applied stress for $\text{Zr}_{55}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}\text{Ti}_5$ and $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ is shown in Figure 13 [24], respectively. For the $\text{Zr}_{55}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}\text{Ti}_5$ BMG, the strain components, ε_{11} and ε_{22} , increase with increasing the load. However, the shear component, γ_{12} , remains close to zero. After 1,400 MPa, the increment of ε_{11} and ε_{22} strain components slightly deviates from linearity, and the sample failed at 1,740 MPa, which is similar to the observed macroscopic yielding (MY) of this alloy at 1,727 MPa. The $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ BMG behaved a very similar way. However, the deviation of the linear relationship starts at around 1,200 MPa and finally, the elastic strain saturates at 1,506 MPa. The test was stopped at 1,700 MPa at a plastic strain of about 0.6 % - 0.7 %. According to the earlier report that the measured microscopic yield stress is 1,547 MPa for $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$, the stress required for macroscopic yielding under compression and the saturation of the elastic strain at the atomic scale are consistent for both investigated alloys.

2.4.4 Strain Analysis from the Real Space

The strain analysis can also be done using the data from the real space. After the structure factor, $S(Q)$, is calculated, the pair distribution function, $g(r)$, can be obtained by Fourier transforming $S(Q)$. Hufnagel et al. [22] investigated the variations of $g(r)$ of $\text{Zr}_{57}\text{Ti}_5\text{Cu}_{20}\text{Ni}_8\text{Al}_{10}$ BMGs at different stages of compressive deformation, shown in Figure 14 [22]. As expected, the first peak in $g(r)$ shifts to a smaller r with increasing the load along the loading direction. It is a challenge to extract the strain from the peak shift for the data in the real space. Because the peak positions in $g(r)$ are difficult to determine accurately due to the asymmetry of the peaks at a low r and the broadness of the peaks at a high r , which leads to a significant scatter in the measured strain. Hufnagel et al. [22] proposed a more robust technique, which focused not on the tops of the peaks, but on the places where $g(r) = 1$. These crossing points are less sensitive to the effects of the asymmetry and can be accurately determined even for peaks at a large r . Hufnagel et al. [22] reported that there is no dependence of strain on r rather than a strong dependence on length scale, which was reported by Poulsen and co-workers [19]. However, it is interesting that the strain determined from the lowest value of r at which $g(r) = 1$ is consistently smaller in magnitude than that determined at larger values of r . This trend is believed to be related to the asymmetry of the peaks and the changes in the interatomic bonding lengths. Wang et al. [21] observed similar phenomena in four BMGs of $\text{Zr}_{62}\text{Al}_8\text{Ni}_{13}\text{Cu}_{17}$, $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$, $\text{Zr}_{48}\text{Cu}_{43}\text{Al}_7\text{Ag}_2$, and $\text{La}_{62}\text{Al}_{14}(\text{Cu}_{5/6}\text{Ag}_{1/6})_{14}\text{Co}_5\text{Ni}_5$, and results are shown in Figure 15 [21]. The strain in a r range of below 4 Å is smaller than that in a larger r range. In addition, the local strain increases in a homogeneous way when the stress is low. The fluctuation in the local strain becomes more distinct when the stress

increases, which mainly appears in the two ranges of about 4 - 8 and 10 - 14 Å. This trend could be linked with different responses from clusters and superclusters in BMGs, respectively. Especially, the large oscillation in the range of 10 - 14 Å could indicate the high open volume existing between the superclusters and suggest a redistribution of free volumes.

Another possible way to deal with the asymmetry of the peaks of $g(r)$ is to deconvolute the peaks to analyze atomic pairs in detail. For example, Stoica et al. [20] investigated the variations of $g(r)$ of the $\text{Zr}_{64.13}\text{Cu}_{15.75}\text{Ni}_{10.12}\text{Al}_{10}$ BMG during different stages of deformation. They deconvoluted the first RDF peak, which corresponds to the first coordination shell. Although it is not possible to identify the atomic pairs contributing to the first peak in the RDF, they made some reasonable approximation for the $\text{Zr}_{64.13}\text{Cu}_{15.75}\text{Ni}_{10.12}\text{Al}_{10}$ alloy. First, since the contribution of each atomic pair to the RDF is weighted by the atomic-scattering factors of the elements and by their concentration, the influence of Al can be neglected due to its low atomic number and presence at relatively low concentration. Second, the separation of the atoms in each pair is related to the sum of their atomic radii. The contributions of Cu and Ni are indistinguishable, considering their nearly the same size (1.28 and 1.25 Å for Cu and Ni, respectively). So only two partials [Zr-(Cu,Ni) and (Zr-Zr)] are the dominant atomic pairs which constitute the first coordination shell of the PDFs and need to be resolved. Figure 16 shows the result of the deconvolution for the first shell of the undeformed $\text{Zr}_{64.13}\text{Cu}_{15.75}\text{Ni}_{10.12}\text{Al}_{10}$ [20]. The center of the first peak was estimated to be at 2.68 Å corresponding to Zr-(Cu,Ni) atomic pairs. The second peak is centered at 3.14 Å originating from Zr-Zr atomic pairs. Seen from Figure 16 [20], both peaks shift toward

higher r values with increasing the tensile stress, which proves that the tensile stress increases the average atomic distances along the loading direction. Similar results were reported in other metallic glasses by Hufnagel and co-workers. The average atomic distances along the loading direction became smaller in the case of a compressive load.

2.4.5 Analysis of Structural Anisotropy

The above strain analysis in the real space assumed that the structure is isotropic or the structure anisotropy is ignored when the load is applied. However, in reality, it is that the structure anisotropy will definitely be introduced in the case of an applied load. Dmowski and Egami [110] pointed out that in the presence of the structural anisotropy, the calculation of the pair density function, $\rho(r)$, using the usual sine-Fourier transformation of the structure factor may result in systematic errors, especially in the first neighbourhood. In this case, the directionally-dependent pair-density function and analogously the structure factor can be expressed by the expansion into spherical harmonics [110-112]. Thus, the $S(Q)$ and the $\rho(r)$ can be separated into two components, i.e., the isotropic structure factor, $S_0(Q)$, and isotropic pair-density function, $\rho_0(r)$, and anisotropic components of the structure factor, $S_l(Q)$ and pair-density function, $\rho_l(r)$, respectively. Neglecting order terms of $l > 2$, the components can be calculated from the structure factors in the loading and transverse directions

$$S_0(Q) = \frac{\sqrt{4\pi}}{3} [S(Q, \varphi = 90^\circ) + 2S(Q, \varphi = 0^\circ)] \quad (19)$$

$$S_2(Q) = \sqrt{\frac{16\pi}{45}} [S(Q, \varphi = 90^\circ) - S(Q, \varphi = 0^\circ)] \quad (20)$$

The components of $\rho_l(r)$ are then related by a transformation

$$\rho_l(r) = \frac{(i)^l}{2\pi^2} \int S_l J_l(Qr) Q^2 dQ \quad (21)$$

where J_l is the spherical Bessel function with $J_0(Qr) = \sin(Qr)/Qr$, and $J_2(Qr) = [3/(Qr)^3 - 1/Qr] \sin(Qr) - 3/(Qr)^2 \cos(Qr)$.

The atomic density of any direction, φ , is then given by

$$\rho(r, \varphi) = \rho_0(r) \sqrt{\frac{1}{4\pi}} + \rho_2(r) \sqrt{\frac{5}{16\pi}} (3 \sin^2 \varphi - 1) \quad (22)$$

Using this analysis method of the anisotropy pair density function, Mattern et al. [25] measured amorphous ribbons with the compositions of $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{65}\text{Zr}_{35}$ under tensile loading. The calculated atomic density functions of the $\text{Cu}_{50}\text{Zr}_{50}$ glass in the tensile direction with and without the stress are shown in Figure 17 [25]. It can be seen that besides the shift of the maxima positions, the shape of the first maximum corresponding to the nearest neighbourhood is changed. The authors determined the positions of the maxima of $\rho(r)$ using a Gaussian function fitting. The relative shift of the different maxima, r_i , of the pair distribution functions is shown in Figure 18 [25]. The direction-dependent strain values behave quite similar for the maxima at $r > 0.4$ nm. The slopes are in reasonable agreement with the strain result in the reciprocal space shown in Figure 12 [25].

By deconvoluting the first RDF peak, which corresponds to the first coordination shell, two partials of Cu-(Zr,Cu) and Zr-Zr atomic pairs are resolved to estimate the variation of the coordination numbers. For the Cu-(Zr,Cu) pairs, the coordination number decreases in the loading direction but increases in the transverse direction, and an opposite behavior

occurs for the Zr-Zr pairs. The coordination number changes reflect the topological rearrangements within the atomic nearest-neighbor environment in the elastic region. However, the total coordination numbers of the Cu-(Zr,Cu) and the Zr-Zr atomic pairs remain almost constant, respectively. It means that, for Zr-Zr pairs, the bond reorientation is processed by breaking the bonds in the transverse direction and reforming new bonds in the loading direction, and the opposite behavior occurs for Cu-(Zr,Cu) pairs. This bond reorientation leads to a direction-dependent changes in the chemical short-range order, which is associated with the structural change in the nearest-neighbor of BMGs. Wang et al. [26] observed the similar results in $\text{Cu}_{64.5}\text{Zr}_{35.5}$ in the case of compressive stresses.

2.4.6 Peak-Width Analysis

Unlike the crystalline materials, the physical nature of the reciprocal- and real-space distribution-function-peak width changes during deformation in amorphous materials remains unclear. Also, to my knowledge, there are very few studies done to address this feature. Egami et al. [113] showed the importance of atomic-level stresses in describing the structure of amorphous solids. The local hydrostatic pressure, p , described the local-density fluctuations and can be simply defined as

$$p = -\frac{1}{3}(\sigma_1 + \sigma_2 + \sigma_3) \quad (23)$$

where σ_1 , σ_2 , and σ_3 are the three principal stresses. Srolovitz and Egmai [18] examined the relationship between the $g(r)$ and the hydrostatic pressure variance, $\langle \Delta p^2 \rangle^{1/2}$, for a single-component model structure with molecular dynamic simulations. From their analysis, they determined that the width of the first peak in the $g(r)$ decreased as the

variance in p decreased. Das et al. [24] investigated the strain dependence of the width of the first peak in $I(Q)$ for “brittle” $\text{Zr}_{55}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}\text{Ti}_5$ and “plastic” $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ BMGs, which were loaded in uniaxial compression. The results are shown in Figure 19 [24]. It was found that in their measurements, the width of the first peak in $I(Q)$ along the longitudinal direction (parallel to the loading axis) decreased with increasing the compressive stress, while the peak widths in the transverse direction (normal to the loading axis) increased with increasing the compressive stress. In addition, the change of width under stress is significantly higher in the plastic $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ than in the brittle $\text{Zr}_{55}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}\text{Ti}_5$. The authors believed that the greater width change in the plastic BMG is related to more homogeneous distribution of free volumes and more averaging of the local hydrostatic stress, which leads to a more homogenous activity of the STZs. Those results indicate that the greater width change of the diffraction peak in one BMG may indicate better plasticity. Hugnagel et al. [22] examined the stress dependence of the RDF peak width for a $\text{Zr}_{57}\text{Ti}_5\text{Cu}_{20}\text{Ni}_8\text{Al}_{10}$ BMG loaded in uniaxial compression. Using a two-Gaussian-peak model to fit the first shell, they found that the peak widths of the RDF corresponding to atomic correlations along the longitudinal direction decreased with increasing the compressive stress, while the peak widths in the transverse direction increased with the increasing compressive stress shown in Figure 20 [22]. Also, the magnitude of the increase in the peak widths in the transverse direction was less than the decrease in the longitudinal direction by a factor approximately equal to Poisson’s ratio. Based on Suzuki and Egmai’s report [70], Hugnagel et al. [22] pointed out that with increasing the load, the average hydrostatic stress $\langle p \rangle$ increases, but the overall p

becomes more uniform. The local p for the regions with the locally large dilatation is closer to the overall mean $\langle p \rangle$, thus reducing $\langle \Delta p^2 \rangle^{1/2}$ and causing the observed sharpening of the peaks in $g(r)$ and RDF. According to Srolovitz and Egmai's model [18], their studies on peak width were under being not strained. Ott et al. [114] examined the effects of applied compressive and tensile strains on $\langle \Delta p^2 \rangle^{1/2}$ and the peak widths of $\text{Cu}_{64.5}\text{Zr}_{35.5}$ by combining the high-energy x-ray diffraction and molecular dynamic (MD) simulations. The results showed that the width of the first peak in total $S(Q)$ for the longitudinal direction decreased with increasing tensile stress and increased, to a lesser extent, for the transverse direction, while, under uniaxial compression, the width of the first peak in total $S(Q)$ for the longitudinal direction increased with increasing compressive stress and decreased for the transverse direction. However, the peak widths of the total reduced-pair-distribution function, $G(r)$, responded in an opposite manner than the peak widths for the total $S(Q)$. The widths of the first peak in the total $G(r)$ and $S(Q)$ are strongly dependent on the elastic response of the different partial-pair correlations. The effects of the different bond stiffnesses are particularly important. The MD simulations of amorphous $\text{Cu}_{64.5}\text{Zr}_{35.5}$ alloys deformed under applied uniaxial and hydrostatic strains showed that the widths of the first peaks in the total- and partial-PDF do not necessarily exhibit the same strain dependencies as the variance in hydrostatic pressure. For the model deformed uniaxially, the variance in the hydrostatic pressure does not demonstrate any obvious strain dependence. For the model strained hydrostatically, a length-scale dependence of the atomic displacements can significantly affect the changes of the peak widths during the elastic deformation.

2.4.7 The Accuracy of Determining Strain in Amorphous Alloys with In-Situ High-Energy X-Ray Diffraction

Table 1 summarizes the values of Young's modulus, E , and Poisson's ratio, ν , for the metallic glasses reported in the literatures [19, 20, 22-25]. The data are extracted from three kinds of methods: using the high-energy synchrotron x-ray radiation and using ultrasound methods, or macroscopic tensile/compression tests. It can be seen from the Table 1 that basically, there always are differences in the constants measured using the high-energy synchrotron x-ray radiation and ultrasound methods. For the first time, Poulsen and co-workers [19] demonstrated that the theoretical considerations used in their work are essentially correct, by measuring the elastic strain and strain distribution in a Mg-based BMG. There is a linear relationship between the strain measured in both reciprocal and real spaces and uniaxial stress. The strain measured from the first-peak shifts in $I(Q)$ agreed well with the strain calculated based on the macroscopic measurements of Young's modulus, E . In the real space, the strain calculated from $g(r)$ in the lower r range is smaller than in the higher r range, where the calculated strain asymptotically approached the one calculated from the $I(Q)$ peak position. i.e., the strong dependence on r . Poulsen et al. [19] attributed this observation to the unspecified "structural rearrangement on the length scale of 4 - 10 Å". Hufnagel and co-workers observed similar results in a Zr-based BMG. However, the r -dependence effect is much smaller than that reported by Poulsen et al [19]. They proposed that "the difference between the stiffnesses of the nearest-neighbor atomic environment and that over longer length scales can be attributed to the effect of topological rearrangements in the nearest-

neighbor environment of a relatively small fraction of the atoms, without the need to invoke significant structural rearrangements over longer length scales”.

Stoica and co-workers [20] considered that BMGs can be divided into two groups based on if they are intrinsically brittle and plastic in compression. From Table 1, it is clear that in the case of “nondeformable” or intrinsically brittle BMGs, the constants measured from ultrasonic and tensor analyses are almost similar, indicating a similar elastic behavior of each atomic shell. However, in the case of plastically-deformable BMGs, the elastic constants measured with two types of the methods show large differences, reflecting the different stiffness of each atomic shell. In addition, a range of local atomic environments of the atoms exists in a glassy material. As a consequence of the disorder, the fluctuation of inter-atomic distances may occur, which leads to variations of the atomic-level stress. Mattern et al. [25] confirmed the anelastic changes of the short-range order by analyzing the first neighborhood of CuZr binary glasses under tensile stresses in the elastic region. The response of the nearest neighborhood upon loading leads to the directional changes in the chemical short-range order.

Very recently, Mendelev et al. [115] utilized MD simulations to test the reliability of strain values obtained from diffraction data for amorphous alloys. The simulation results for one-component and binary systems indicated that the estimated strain from the experimental diffraction data most likely is not exact, either underestimated or overestimated, due to a small degree of atomic relaxations and varying degrees on both the individual atom-pair interactions and the source of radiation for a specific diffraction experiment (i.e., x-rays vs. neutrons).

All the above discussions together may tell us the accuracy of determining strain in amorphous alloys with in-situ high energy x-ray diffraction and explain the differences in mechanical behavior observed at the microscopic level (high-energy x-ray) and at the macroscopical level.

CHAPTER 3: THE EFFECT OF COMPOSITION ON PROPERTIES AND STRUCTURES OF CUZRAL BULK METALLIC GLASSES

The first thing that comes to our minds is the composition, if we discuss what will affect the properties and structures of BMGs. In this Chapter, for $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ BMGs, the elastic properties were characterized by measuring the stress-strain behavior in the elastic-deformation region with high-energy synchrotron x-ray scattering. Meanwhile, plasticity abilities were obtained from the normal uniaxial-compression test. Finally, the local structures were characterized with molecular dynamic (MD) simulations. The combination of the above information allows the discussion of the correlation between the composition and the properties of BMGs.

3.1 Introduction

The CuZrAl glass-forming alloys have received increased attentions because their strength and plasticity appear to be composition-dependent from the recent experimental observation. For example, Kumar and co-workers [116] investigated the $(\text{Cu}_{50}\text{Zr}_{50})_{100-x}\text{Al}_x$ ($x = 2, 5, 6, 8$, and 10 , in atomic percent, at%) glass-forming alloys and found that a minor content deviation can drastically change mechanical properties. Specifically, the yield strengths of the samples with $x = 6, 8$, and 10 increase and meanwhile their plastic strains decrease, compared to the samples with $x = 2$ and 5 . There are some reports to address the reason of the great plasticity of the alloy of $(\text{Cu}_{50}\text{Zr}_{50})_{95}\text{Al}_5$ in this system and it was found that it is related to the nanocrystallization

behavior in this composition. For instance, Kim and co-workers [117] announced that the large plasticity for $(\text{Cu}_{50}\text{Zr}_{50})_{95}\text{Al}_5$ is due to the homogenous distribution of nano-crystals and macroscopic heterogeneities, when the samples were solidified. Kumar et al. [116] gave an explanation that the great plasticity of $(\text{Cu}_{50}\text{Zr}_{50})_{95}\text{Al}_5$ is due to obvious crystallization behaviors in shear-band regions. Recently, Zhu and co-workers [118] found that the microstructure can be closely affected by the solidification condition, and $(\text{Cu}_{50}\text{Zr}_{50})_{95}\text{Al}_5$ glass-forming alloys can exhibit great plasticity with nanocrystals in the amorphous matrix using the normal method of in-situ suction casting. Except the effect of nanocrystals, are there intrinsic structure reasons for a variety of mechanical properties in this $(\text{Cu}_{50}\text{Zr}_{50})_{100-x}\text{Al}_x$ system? With the advantage of ruling out the possibilities, such as extrinsic heterogeneities, nanocrystallization, impurity effects, and surface/internal flaws in the MD-simulation work of Cheng and co-workers [119], the intrinsic resistance to the plastic-flow initiation and the propensity for the onset of softening and strain localization in metallic glasses (MGs) have been investigated. It is concluded in the paper [119] that the properties of CuZrAl MGs are dependent on the alloy composition, which are strongly related to the internal structure. It is not only referred to topological packing, but also bonding and chemical make-up.

Based on the glass-forming-ability (GFA) study of Yu et al. [120] on $(\text{Cu}_{50}\text{Zr}_{50})_{100-x}\text{Al}_x$ ($x = 4, 6, 8, \text{ and } 10$), $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ and $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ exhibit the best GFA. Also, their mechanical properties show the obvious difference [111,116]. Thus, in this study, $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ were selected to study the effect of the composition on the properties and structures of BMGs.

3.2 Experimental Procedure

Sample Preparation

The glass-forming alloys of $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ [atomic percent (at.%)] were prepared by melting a mixture of high-purity Zr [99.9 weight percent (wt.%)], Cu (99.999 wt.%), and Al (99.999 wt.%) in a purified argon atmosphere. In order to obtain the compositional homogeneity, the alloy ingots were remelted several times before being cast into a water-cooled copper mold using an in-situ suction-casting facility. The resulting cylindrical samples are 3 mm in diameter and 50 mm in length. After casting, the rods were reduced to a uniform diameter of ~ 2 mm by centerless grinding and cut to the length: diameter ratio of approximately 2:1. The bar ends were polished in a specially-designed fixture to ensure parallelism.

Differential-Scanning Calorimeter (DSC)

The differential-scanning calorimetry (DSC, Perkin-Elmer DSC7) was used to characterize thermal properties of BMGs. DSC was run for two heating – unheating cycles for each specimen from 323 to 873 K in an argon atmosphere at a heating rate of 20 K/min. The second scan was considered as a base line, since the irreversible thermal activities only happen in the first scan. Any thermal activities associated with the structural evolution during heating were investigated. According to the DSC curves, the glass-transition temperature (T_g) and crystallization temperature (T_x) of the investigated samples could be obtained.

Uniaxial Compression Tests

The cast rods were cut to produce compression samples with an aspect ratio (length/diameter) of 2:1 for the investigation of the mechanical behaviors of BMGs. The ends

of the samples were lapped and polished to ensure the parallelism. A computer-controlled MTS 810 materials test-system servo-hydraulic mechanical-testing machine was used for the compression tests. The machine was aligned prior to use. Strain was recorded using an MTS extensometer. The compression tests were performed in a constant strain rate of $8 \times 10^{-4} \text{ s}^{-1}$.

Resonant Ultrasonic Spectroscopy (RUS) Tests

The RUS is a novel technique developed at the Los Alamos National Laboratory for determining the complete elastic tensor of a solid by measuring its free-body resonances. [122] The mechanical resonances can be calculated for a sample with known dimensions, density, and elastic tensor. In a RUS experiment, the mechanical resonances of a freely-vibrating solid of known shape are measured, and an iteration procedure is used to “match” the measured frequencies with the calculated spectrum. This allows the determination of the full elastic tensor of the solid from a single frequency scan. From the elastic tensor, the elastic module and Poisson’s ratios of the samples were obtained.

In-Situ High Energy Synchrotron X-Ray Diffraction

In-situ high-energy synchrotron x-ray diffraction experiments were performed at the 11-ID-C beam line of the Advanced Photon Source at the Argonne National Laboratory (Argonne, IL). The beam size was $0.3 \times 0.3 \text{ mm}^2$. A digital image plate (MAR 345, with a $100 \times 100 \text{ }\mu\text{m}^2$ pixel size) was positioned 1,400 mm downstream from the sample to record the scattered intensity in transmission through the cylindrical specimens. A two-dimensional ring pattern was recorded on the image plate. Scattering patterns were extracted by azimuthally averaging the ring pattern over an arc of approximately 5° centered on the vertical (loading) and horizontal (transverse) directions using the *FIT2D* software [109]. The specimens were loaded incrementally in uniaxial

compression using a motorized screw-driven load cell. The loading was paused for the data collection during the x-ray exposures. The schematic view of the scattering setup is shown in Figure 21.

MD Simulations

With the embedded-atom-method (EAM) potentials developed by Cheng [123], Dr. E. Bitzek helped us perform MD simulations on systems containing 109,744 atoms for the two compositions of $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$. The original 109,744-atom samples, with a periodic boundary condition (PBC) applied for all three dimensions, were melted and equilibrated at 2,000 K for 2 ns (a time step of 2 fs), and quenched into the glassy states (300 K) at a cooling rate of 30 K ns^{-1} . The temperature and pressure were controlled with the Nose–Hoover thermostat and barostat, respectively. Geometrical analysis on the atomic configurations, using the Voronoi tessellation method [103,106], yields the information about the atomic packing, such as the atomic coordination numbers (CNs), types of coordination polyhedra, etc.

3.3 Results

Thermal properties

Thermal properties of $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ were investigated by measuring DSC curves at a heating rate of 20 K/min, shown in Figure 22. It is found that the samples exhibited an endothermic heat event characteristic of T_g , followed by one exothermic reaction corresponding to T_x of the glass-forming alloy. The T_g and T_x increase monotonically with increasing the Al content, which indicates that $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ has a better thermal stability than $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$.

In-Situ High-Energy Synchrotron X-Ray Diffraction Measurements

For the compression tests on $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ with the in-situ high-energy synchrotron x-ray scattering measurement, the two-dimensional scattering ring pattern recorded on the image plate were extracted by azimuthally averaging the ring pattern over an arc of approximately 5° centered on the vertical (loading) and horizontal (transverse) directions using the *FIT2D* software [109]. The data analysis has been performed by the Q -space method in the reciprocal space, as reported earlier [19]. In the case of each integrated intensity, $I(Q)$, the shift of the first halo is determined with respect to the unload condition. The change of the peak positions in the q space has been measured to be from the average atomic spacing, $d = \frac{2\pi K}{Q_{\max}}$ (where K is a constant that depends on the particular arrangement of the atoms; $Q_{\max}$ is the value of Q where $I(Q)$ has the maximum) [22]. In order to estimate the strain in loading and transverse directions quantitatively, the integrated data have been plotted by considering the average atomic spacing (d) versus the measured $I(Q)$, and a pseudo-Voigt function has been used in order to fit the first halo. The resulting strains at each different stress level can be calculated with the equation of $\varepsilon = \frac{Q_0}{Q_\sigma} - 1$ (where Q_σ and Q_0 are the positions of the first peak in $I(Q)$ under the stress, σ , and zero stress, respectively) [22].

Figure 23 show the evolution of strains in loading and transverse directions with the applied stress for $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$, respectively. It can be seen that there is a linear relationship between the measured strain and applied stress for both

alloys. The strain tensors for both the alloys have been calculated in the linear-elastic region and diagonalized in order to estimate the elastic constants, including the Young's modulus (E) and Poisson' ratio (ν). Table 2 shows elastic constants from x-ray and RUS measurements for $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ alloys. The Poisson' ratio does not vary much for the different measurements but the Young's modulus becomes greater between 9.6 and 9.3 GPA measured from synchrotron x-ray scattering than those measured from RUS for $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ alloys, respectively. The overestimated E means the underestimated elastic strain. Recently, Mendelev et al. [115] tested the reliability of strain values obtained from the diffraction data for the amorphous alloys by utilizing MD simulations. In the authors' opinion, they provided two conclusions. First, the atom relaxation plays an important role in the inexactness of strain measurements from diffraction data, for example, ending up with underestimating the strain for one-component system. Second, in multicomponent systems, the estimated strain from experimental diffraction data most likely is not exact due to the different extents to which the different atom pairs are affected by the applied deformation. Thus, the accuracy of the strain from experimental diffraction data for the multicomponent BMGs also depends on varying degrees on the individual atom-pair interactions. In the literatures [19, 20, 22-25], for multicomponent BMG systems, most cases demonstrate underestimating the strain, i.e., overestimating E .

Peak-Width Analyses

Unlike the crystalline materials, the physical nature of the distribution-function-peak width changes during deformation in amorphous materials remains unclear. Das et al. [24] investigated the strain dependence of the width of the first peak in $I(Q)$ for a

brittle Zr-based metallic glass and a plastic ternary Zr-Cu-Al metallic glass, which were loaded in uniaxial compression. It was found in their measurements that the width of the first peak in $I(Q)$ along the longitudinal direction (parallel to the loading axis) decreased with increasing the compressive stress, while the peak widths in the transverse direction (normal to the loading axis) increased with increasing the compressive stress. Ott et al. [114] examined the stress dependence of the width of the first peak in the total structure factor, $S(Q)$, for a binary Zr-Cu glass loaded in uniaxial tension and compression. They found that the width of the first peak in $S(Q)$ for the longitudinal direction decreased with increasing the tensile stress and increased, to a lesser extent, for the transverse direction, while, under uniaxial compression, the width of the first peak in $S(Q)$ for the longitudinal direction increased with the increasing compressive stress and increased for the transverse direction. In our case, with increasing the stress, the full width at half maximum (FWHM) of the first peak of $I(Q)$ increases along the loading direction and decreases along the transverse direction for both $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ glass-forming alloys as shown in Figure 24. Moreover, there is no obvious difference for the peak-width change for both alloys considering the scattering data points.

Mechanical properties

Figure 25 presents the room-temperature compressive stress-strain curves of the as-cast specimens. The stress-strain curves are characteristic of a large elastic limit of about 2% for glass-forming alloys, followed by a yielding point and a serrated plastic deformation. Unsurprisingly, The specimen of $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ exhibits a yield strength of 1,700 MPa, a little higher than that of $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$, 1,650MPa. There is almost no

plasticity for $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$, While for $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$, it has a considerable plastic strain of around 1.5%.

MD Simulation Analyses

The inherent structure of the 109,744-atom metallic glass was then analyzed by sorting out the nearest-neighbor environment of each of the atoms of all the species present, in terms of Voronoi (coordination) polyhedra [103]. Based on the analysis results, the structure is best described by the Voronoi polyhedra centered on the smaller species (e.g., Cu and Al). Figures 26(a) and (b) display the populations of the five most populous types for Cu-centered and Al-centered polyhedral as follows: $\langle 0, 3, 6, 1 \rangle$, $\langle 0, 2, 8, 0 \rangle$, $\langle 0, 2, 8, 1 \rangle$, $\langle 0, 2, 8, 2 \rangle$, and $\langle 0, 0, 12, 0 \rangle$, respectively. It can be seen from the Voronoi indices that most Cu/Al atoms have a coordination number (CN) near 12, and their coordination polyhedra are dominated by a fivefold symmetry and icosahedral types. The icosahedra with the Voronoi index $\langle 0, 0, 12, 0 \rangle$ have complete fivefold environment and are called as the full icosahedra, in which the center atom bonds with 12 neighbors, and each and every of the 12 pairs has 5 common-neighbor atoms [124]. These pairs are referred to as “fivefold bonds.” However, $\langle 0, 3, 6, 1 \rangle$, $\langle 0, 2, 8, 0 \rangle$, $\langle 0, 2, 8, 1 \rangle$, and $\langle 0, 2, 8, 2 \rangle$ are considered as defective icosahedra. For the Cu-centered icosahedra, the number of FI in $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ increases to 7,780, compared to 7,411 in $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$. However, the numbers of defective icosahedra, $\langle 0, 3, 6, 1 \rangle$, $\langle 0, 2, 8, 0 \rangle$, and $\langle 0, 2, 8, 1 \rangle$, in $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ decrease, compared to those in $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ in spite of the almost same of $\langle 0, 2, 8, 2 \rangle$ in both compositions. For the Al-centered icosahedra, all the numbers of icosahedra of $\langle 0, 3, 6, 1 \rangle$, $\langle 0, 2, 8, 0 \rangle$, $\langle 0, 2, 8, 1 \rangle$, $\langle 0, 2, 8, 2 \rangle$, and $\langle 0, 0,$

12, 0> increase in $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$, compared to those in $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$, especially from 1,853 to 2,445 for <0, 0, 12, 0>.

Figures 27(a) and (b) show dominant Zr-Cu-Al combinations that are observed to make up the first neighbor shells of the Cu-centered and Al-centered FI, respectively. Since these FI consist of multiple species with different sizes and chemical properties, it should be kept in mind that they can not be considered as perfect in a geometric sense. As they are not even identical throughout the sample, but share one thing in common: the complete fivefold environment. This feature of “full but not perfect/identical” is important, because the complete fivefold environment enhances the transition barrier to crystals [125]. As a result, the amorphous state is rendered more stable. For the Cu-centered icosahedra, the six Zr-Cu-Al dominant combinations are 5-6-1, 5-7-0, 6-5-1, 6-6-0, 7-4-1, and 7-5-0. It is not surprising that with increasing the Al content the numbers of Al-involved combinations of 5-6-1 and 6-5-1 increase, while the numbers of the Al-absent combinations of 5-7-0, 6-6-0, and 7-5-0 decrease. For the Al-centered icosahedra, the five Zr-Cu-Al dominant combinations are 5-7-0, 6-6-0, 7-5-0, 8-4-0, and 9-3-0, all of which are the Al-absent combinations, indicating that the Al-Al bonds are difficult to form. It is reasonable considering that the content of Al is small. Compared to $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$, the numbers of all the dominant combinations in $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ increase. The above local structure information indicates that the packing density of $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ is higher than that of $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$.

Of all the Cu atoms in the MG configuration of $(\text{Cu}_{50}\text{Zr}_{50})_{100-x}\text{Al}_x$ ($x = 6$ and 8), the fraction encaged in such FI, $f_{\text{ico}(\text{Cu-centered})}$, is about 21%. Of all the nearest-neighbor bonds around Cu, the fraction of fivefold bonds, $f_{555(\text{Cu-centered})}$, is as high as around 60%.

While all the Al atoms in the MG configuration of $(\text{Cu}_{50}\text{Zr}_{50})_{100-x}\text{Al}_x$ ($x = 6$ and 8), the fraction encaged in such FI, $f_{\text{ico(Al-centered)}}$, is about 51%. Of all the nearest-neighbor bonds around Al, the fraction of fivefold bonds, $f_{555(\text{Al-centered})}$, is as high as around 65%. Thus, Cu-centered and Al-centered icosahedra can be concluded to be the characteristic structural feature in $(\text{Cu}_{50}\text{Zr}_{50})_{100-x}\text{Al}_x$ ($x = 6$ and 8) BMGs.

3.4 Discussions

Based on the above results, $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ exhibit obvious differences of thermal and mechanical properties despite the minor content deviation. The small addition of Al plays a very important role in affecting the properties of this Cu-Zr system. There is no doubt that those differences are associated the structure evolution due to the addition of Al because various mechanical and physical properties are strongly dependent on their internal structures. Although the atomic-level structure of BMGs is elusive, a large amount of work has been done to address it. For example, the “solute-centered quasiequivalent cluster” can be viewed as the basic local structural motif in some binary solute-lean MGs. For multicomponent BMGs, the structure can be described in term of cluster packing, characterized by the icosahedral order. The Cu-Zr binary system has received particular attention because it is among the first metalloid-free metallic glasses, and it can form glasses in a wide compositional range. When we talk about the alloying effect of elements on the structure of BMGs, there are two important kinds. One is purely topological, due to the known atomic-size differences of the elements. The other is the chemistry of the alloy, i.e., the intricate bonding environments. The Cu-Zr metallic glasses exhibit an ideal solution behavior due to the fact that Cu

atoms have a filled 3d shell and, thus, Cu atoms have relatively weak interactions with Zr atoms, leading to a random atomic arrangement in the Cu-Zr amorphous alloys. This weak interaction is reflected by the relatively small enthalpy of mixing (ΔH_{mix}) of -23 kJ/mol between Cu-Zr atoms. Thus, it is believed that the widely-accepted icosahedral short range order (SRO) of Cu-Zr metallic glasses is mainly of topological rather than of chemical origin.

It is known that substituting a few percent of Al for Cu and Zr in the $\text{Cu}_{50}\text{Zr}_{50}$ results in a remarkable improvement of glass-forming ability, as well as pronounced differences in strength and ductility. What is the role of the alloying element of Al?

From the topological view, Al helps promote icosahedral ordering. First, because Al has a radius in between those of Zr and Cu, it is helpful for adjusting the coordination polyhedron around the Cu, which increases the possibility of comfortable arrangements to reach the full icosahedra (FI). This idea is proved from our results of MD simulations. As the addition content of Al increases, the number of FI for the Cu-centered icosahedra in $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ increases to 7,780, compared to 7,411 in $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$. Second, the ideal icosahedral dense packing requires an atomic size ratio, R^* , of 0.902 for a hard-sphere packing model, where $R^* = r_B / r_A$, and r_A and r_B are the atomic radii of the solvent atoms in the nearest-neighbor shell and the center solute, respectively. For the binary Cu-Zr, $r_{\text{Zr}} = 1.58 \text{ \AA}$, $r_{\text{Cu}} = 1.27 \text{ \AA}$, and R^* is 0.804. It indicates that the binary system is not topologically stable/efficient, when Cu is completely surrounded by Zr. However, when Al is added to the binary system, it will be driven to scatter in the Cu-Zr matrix due to the negative ΔH_{mix} of Al with Zr and Cu. Since the atomic size ratio, $r_{\text{Al}} / r_{\text{Zr}}$, is 0.905, which is very close to the ideal ratio of 0.902. It suggests that Al would help

increase the packing efficient. In our study, the Al-centered polyhedra, fivefold bonds are dominant (~ 65%), and the $\langle 0, 0, 12, 0 \rangle$ FI is the most popular (~ 50%). Although ideally Al surrounded by Zr only would be the topologically optimal way for FI packing, it can be unlikely in reality because such Al-Zr icosahedra will result in the local segregation in the MG. In fact, the most Al-centered FI in our simulations have mixed atomic species in the shell. The number of the Al-centered FI in $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ increases compared to $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$. These Al-centered FIs are very important structure features of the CuZrAl system.

More importantly, from the chemical view, the effect of Al makes the ternary system stabler. There is a relatively large enthalpy of mixing (ΔH_{mix}) of -44 kJ/mol between Al-Zr atoms. The dominant electronic interaction leading to the negative mixing enthalpy in Zr and Al is hybridization between Zr d and Al p states. Thus, the covalent bonds form between them, which makes BMGs highly stable and rigid. Also, due to the broad conduction band of Al and the narrow low-lying d band of Cu, the covalent bonds can form between Al and Cu through the hybridization of the s and p Al orbit with the d Cu shell electrons, which will make the Al-Cu bond shortening observed by Cheng et al. [123] This bond shortening makes the Cu neighbor appears closer and “larger” to the centered Al atom. Cu effectively occupies the space around Al just in a similar way as Zr. As a result, the special and shortened Al-Cu bond allows chemistry (stable bonding) and topology (dense packing) to work at the same time, stabilizing and facilitating the formation of the Al-centered FI in the CuZrAl system. The higher the content of Al, the more significant this effect of Al. In other word, the addition of Al not only stabilize the

Cu-Zr system in a topological way but also in a chemistry way. It improves the GFA, making the binary system more strong and less ductile.

In our MD simulation on $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$, the analysis reveals that the structure can be described by the Voronoi (coordination) polyhedral centered around the small species (Cu and Al). The five most populous types for Cu-centered and Al-centered polyhedra are as follows: $\langle 0, 3, 6, 1 \rangle$, $\langle 0, 2, 8, 0 \rangle$, $\langle 0, 2, 8, 1 \rangle$, $\langle 0, 2, 8, 2 \rangle$, and $\langle 0, 0, 12, 0 \rangle$. Among all the Cu-centered polyhedra, the fraction of $\langle 0, 0, 12, 0 \rangle$ FI increases with increasing the Al content, at the expense of other types of coordination polyhedra (such as the CN= 10 $\langle 0, 2, 8, 0 \rangle$ and $\langle 0, 3, 6, 1 \rangle$ types and CN= 11 $\langle 0, 2, 8, 1 \rangle$ type). Many Al atoms themselves become centers of full icosahedra, which boosted the increase of the total population of FI and the atoms involved in them. Those full icosahedra as a prominent structure feature in BMGs has large influence on the properties because they are indeed resistant to the plastic flow, which is demonstrated by the MD simulation work [119]. However, the low-population polyhedra, for example with the Voronoi index $\langle 0, 2, 8, 0 \rangle$ and $\langle 0, 3, 6, 1 \rangle$, can serve as fertile sites for the shear transformation to accommodate plastic deformation. In one word, for the CuZrAl BMG system, this composition-dependent structural ordering can influence the composition-dependent mechanical and physical properties.

It should be noted that despite the result difference of two measurement methods (high-energy x-ray and ultrasonic spectroscopy), there is an accordance with the change trend of the measured Young's modulus and Poisson's ratio, i.e., $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ has a lower Young's modulus and larger Poisson's ratio than $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$. It is believed that those various mechanical and physical properties are strongly dependent on their internal

structures. In our case, with increasing the Al content there is more FIs in $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ than in $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$. Based on pervious research, the elastic properties are correlated with the configurational potential energy (CPE) [126-128]. For example, the lower the CPE, the higher the shear modulus (G). Thereby, it is not difficult to deduce that the lower the CPE, the higher the Young's modulus (E) and the lower the Poisson's ratio based on the equations of $E = 2G(1+\nu)$ and $\nu = (3-2\frac{G}{B})/(6+2\frac{G}{B})$, considering B is not sensitive to the internal atomic configurations. Cheng's MD simulation [129] demonstrated that the FI cluster is a local structural motif that has a lower CPE and a higher configurational transition barrier. Therefore, the population of FI, which determines the CPE, can be taken as the structural origin of the changing elastic constants in $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$. Our observations that the Young's modulus of $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ is lower than that of $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$, while the Poisson' ratio of $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ is higher than that of $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$, are consistent with this explanation from the glass-structure perspective. Of course, the form of more covalent bonds in $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ also accounts for the difference because they make the BMG more rigid.

3.5 Summary

We have observed an obvious difference in the deformation behavior characterized by the x-ray diffraction in the $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ bulk metallic glasses, which is closely correlated to their macroscopic plasticity. The $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ alloy exhibits a lower yield stress and Young's modulus, higher Poisson's ratio, worse thermal stability, and better plasticity ability than $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$. The MD

simulations show that with increasing the Al content, local structure orders of full icosahedra with the dense-packing density increase. More importantly, covalent bonds form due to the addition of Al. Both the topological (dense packing) and chemical (stable bonding) effect of Al addition account for the differences of mechanical and physical properties between $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$.

CHAPTER 4: THE EFFECT OF FABRICATION METHODS ON MECHANICAL BEHAVIORS AND STRUCTURES OF A $\text{Zr}_{55}\text{Ni}_{10}\text{Al}_{10}\text{Cu}_{25}$ BULK METALLIC GLASS

This Chapter discusses another important effect of fabrication methods on the mechanical properties and structures of BMGs. Two methods of injection casting (controlling the melt temperatures at 1,550 K and 1,250 K, respectively) and suction casting were used to fabricate the $\text{Zr}_{55}\text{Ni}_{10}\text{Al}_{10}\text{Cu}_{25}$ glass-forming-alloy samples. The elastic properties were characterized by measuring the stress-strain behavior in the elastic-deformation region with in-situ high-energy synchrotron x-ray scattering. The plasticity abilities were obtained from the normal uniaxial compression test. The structure information was investigated with ex-situ high-energy synchrotron x-ray scattering. DSC measurements reflected the change of free volumes in the samples fabricated with different methods. Based on the above measurements, this Chapter provides the information on how the fabrication methods affect mechanical and structures of BMGs.

4.1 Introduction

BMGs are characterized by their disordered structures and possess many unique properties, such as high hardness and strength, high resistance to corrosion and good magnetic properties. [1, 3-5] However, at high stresses and low temperatures far below the glass-transition temperature, plastic deformation of BMGs is highly localized into narrow shear bands [130, 131], followed by the rapid propagation of these shear bands

across the whole sample and subsequently catastrophic failure with a limited plastic strain (less than 2%). This behavior severely impedes the widespread application of BMGs. The plasticity of BMGs can be enhanced by introducing the heterogeneous structure to form composite materials. Those heterogeneities can be presence of microcrystal [132-136], nanocrystal [137, 138], and/or phase separation [139, 140], which acts as either an initiation site for the formation of shear bands or a barrier to the rapid propagation of shear bands to benefit the improvement of plasticity. Recently, fabrication methods have drawn much attention since they can affect the mechanical properties and structure of glass-forming alloys. There are two dominate methods for the BMG fabrication as follows: injection casting and suction casting. When we deal with the injection casting, solidification of casting is dependent on a few of factors: the melt temperature, injection pressure, the mold material, and the environment atmosphere. Among these factors, the melt temperature is special since it is an efficient and convenient way to change the resulting samples. For example, Mao et al. [141, 142] investigated the effect of the melt temperature on GFA of two Zr-based glass-forming alloys and reported that there exists an optimal casting-temperature range. If the casting temperature is too lower, local-ordering clusters form in the melt, acting as nucleation sites during the following casting process, which destroy the GFA. If casting temperature is too higher, it induces a decrease of the actual cooling rate and leads to the increase of the oxygen content in the melt, which further weakens the GFA of alloys. Kumar et al. [143] did a more detailed study on this optimal casting-temperature range, which leads to form an amorphous structure. They found that the plastic strain increases with an increase in the melt temperature, as long as the samples are monolithic amorphous. The greater plasticity of

the samples fabricated at higher melt temperature seems due to more quenched-in free volumes. The effect of this quenched-in free volume on plasticity was also observed by Chen et al. [144] who investigated a $\text{Cu}_{45}\text{Zr}_{48}\text{Al}_7$ BMG, which was fabricated in different environment atmospheres. The results indicated that the fabrication experiences a higher cooling rate in He than Ar atmosphere, which results in an increase of plasticity led by more quenched-in free volumes in the samples. In this Chapter, we report the free-volume dependence of the plasticity of a BMG fabricated with two fabrication methods of injection casting and suction casting.

4.2 Experimental Procedure

Sample Preparation

The $\text{Zr}_{55}\text{Ni}_5\text{Al}_{10}\text{Cu}_{30}$ (at.%) alloy ingots were prepared by arc melting a mixture of Zr (99.9 wt.%), Cu (99.9 wt.%), Al (99.9 wt.%), and Ni (99.9 wt.%) in a purified argon atmosphere. The 2-mm-diameter cylindrical rods were synthesized by the injection and in-situ suction casting methods. The schematic view of the fabrication methods are shown in Figure 28. The temperature of the melts for injection casting was monitored by the infrared thermoscope, and the two chosen temperatures were 1,550 and 1,250 K. The temperature fluctuation was estimated to be ± 10 K. The three kinds of samples are denoted with IC (1550), IC (1250), and SC, respectively. The resulting cylindrical samples are 2 mm in diameter and 30 mm in length.

DSC

The differential-scanning calorimetry (DSC, Perkin-Elmer DSC7) was used to characterize thermal properties of BMGs. DSC was run for each specimen from 323 to

873 K in an argon atmosphere at a heating rate of 20 K/min. Any thermal activities associated with the structural evolution during heating were investigated. According to the DSC curves, T_g and T_x of the investigated samples could be obtained. In addition, the structural relaxation exothermic heat (ΔH_0) associated with the amount of the free-volume change can be extracted by integrating the exothermic peak area just before the T_g .

Uniaxial Compression Tests

The cast rods were cut to produce compression samples with an aspect ratio (length/diameter) of 2:1 for the investigation of the mechanical behaviors of BMGs. The ends of the samples were lapped and polished to ensure the parallelism. A computer-controlled MTS 810 materials test-system servo-hydraulic mechanical-testing machine was used for the compression tests. The machine was aligned prior to use. Strain was recorded using a MTS extensometer. The compression tests were performed in a constant strain rate of $4 \times 10^{-4} \text{ s}^{-1}$.

RUS Tests

The elastic moduli of the samples were measured with the resonant ultrasonic spectroscopy (RUS)²³.

Ex-Situ High-Energy Synchrotron X-Ray Diffraction

Structures of samples were examined by high-energy synchrotron X-ray diffraction (HESXRD) at the 11-ID-C beam line of the Advanced Photon Source, the Argonne National Laboratory. The measurements were performed in a transmission geometry using an incident X-ray beam energy, E_i , of 115 keV ($\lambda = 0.1078 \text{ \AA}$) and a sample to detector (Mar-345 area detector) distance of 254 mm. The schematic view of

the setup is shown in Figure 29. The x-ray beam cross-section was 0.5 mm×0.5 mm. The detector calibration was done using CeO₂ NIST powder standards. The two-dimensional scattering data sets were integrated about the azimuth to obtain the elastic scattering-intensity, $I(Q)$, where Q is the scattering vector magnitude using *FIT2D* [109] to correct data for detector-geometrical errors due to small angular misalignments, obliqueness, x-ray beam polarization, background intensity, and for the 2D image generation and file-format conversion. A total structure function, $S(Q)$, of the resultant data was conducted with a *PDFgetX2* package [145].

In-Situ High Energy Synchrotron X-Ray Diffraction

In-situ HESXRD was performed in the same beamline under compression using a motorized screw-driven load cell on cylindrical specimens with 2 mm in diameter and 4 mm in height. The load was stepwise increased up to 1,400 MPa in steps of 200 MPa. For in-situ measurements, the x-ray beam cross-section was 0.3 mm × 0.3 mm, and the distance between the samples to the detector was 322 mm. The schematic view of the setup is shown in Figure 21. The two-dimensional scattering patterns under different stress levels were extracted by azimuthally averaging the ring pattern over an arc of approximately 5° centered on the vertical (loading) direction using the *FIT2D* software [109] to obtain $I(Q)$. A pseudo-Voigt function was used to fit the first peak of $I(Q)$. The resulting strains at each different stress level can be calculated with the equation of

$$\varepsilon = \frac{Q_0}{Q_\sigma} - 1 \text{ (where } Q_\sigma \text{ and } Q_0 \text{ are the positions of the first peak in } I(Q) \text{ under a stress, } \sigma, \text{ and zero stress, respectively).}$$

SEM

The shear-band morphology on the side surfaces of fractured specimens was examined, using a Leo 1526 SEM with the energy-dispersive spectroscopy (EDS) to study the deformation mechanisms.

4.3 Results and Discussions

Figure 30(a) shows the HESXRD diffraction patterns of the IC (1550), IC(1250), and SC samples as well as the differences of IC(1250) and SC, compared to IC (1550), respectively. The patterns present much better statistic accuracy and extend further into the Q-space. Two broad maxima, which are characteristic of glassy structures, were observed from the patterns of IC (1550) and SC samples. However, some small diffraction peaks are superimposed on the broad diffuse maxima in the pattern of the IC (1250) sample, which indicates the presence of crystalline phases in the amorphous matrix. Figure 30(b) shows the characteristic two-halo-ring pattern for an amorphous structure in the SC sample. A sharp diffraction ring near the second halo can be obviously observed for IC (1250) sample, as shown in Figure 30(c). We subtracted the curves of IC (1250) and SC samples from the curve of the IC (1550) sample to show the differences, which allow further analysis and phase identification. In spite of no obvious difference between SC and IC (1550) samples, interestingly, the results indicate that these peaks from the difference between IC (1250) and IC (1550) samples match very well to the *CuZr-B2* with a body centered cubic (BCC) structure. Under the lower melt temperature of 1,250 K when the sample was fabricated with injection casting, the crystallization is

easy to happen in the melt liquid. Thus, it is reasonable for the presence of the *CuZr-B2* phase, which is stable above 976.9 K [146] in IC (1250) sample.

Figure 31 shows the DSC thermograms of the IC (1550), IC(1250), and SC samples. The curves of all the samples exhibit an endothermic event characteristic of the glass transition and a supercooled liquid region, followed by exothermic events characteristic of crystallization processes. The thermal properties are summarized in Table 3. The T_g keeps very close for all three samples. However, T_x , of the IC (1550) sample is smaller than those of the IC (1250) and SC samples. As a result, the supercooled region, ΔT , of the IC (1550) sample is smaller than those of IC (1250) and SC samples, which are comparable. ΔT can be an indicator of the thermal stability of the metallic glass [1]. The larger ΔT , the stabler the metallic glass [1]. Thus, the SC sample could exhibit better thermal stability than the IC (1550) sample. Surprisingly, the partially crystallized IC (1250) sample shows comparable ΔT to the SC sample. As aforementioned, the crystalline phase in the IC (1250) sample is a Bcc CuZr-B2 structure, which is a high-temperature stable phase, and would not impair the thermal stability of an amorphous matrix and decrease T_x obviously. The inset in Figure 31 shows the DSC curve near T_g . The exothermic reactions of the IC (1550), IC (1250), and SC specimens signifying the structural relaxation are observed just below the T_g . It is known that this exothermic reaction below the glass transition is the result of the annihilation of free volumes and structural relaxation [147-149]. The change in the free volume is proportional to the heat released during relaxation [147]. The structural relaxation exothermic heat (ΔH_0) for the IC (1550), IC (1250), and SC alloys are 2.3, 0.8, and 2.8 J/g, respectively, which indicates that the SC rod may possess a larger amount of

quenched-in free volume than the IC (1550) and IC (1250) rods. It is easy to understand that the free volume in SC rod is greater than that of IC (1250) rod due to the partial crystallization in the IC (1250) specimen. It is interesting that despite exhibiting an amorphous structure both for IC (1550) and SC alloys, the SC alloy has more quenched-in free volumes than the IC (1550) alloy. The alloy rods of IC (1550) and SC have the same composition and the same size. The differences are the fabrication methods, which may lead to different cooling rates. Santos et al. [150] investigated processing of Ni- and Ti-based BMGs by injection and suction casting and found that the suction casting, despite providing a higher oxygen content than the injection casting, presented better results for maximizing the amorphous diameter/thickness, which is ascribed to the higher cooling rate for the suction processing due to the optimization of the metal/mold contact.

Figure 32 presents the room-temperature compression nominal stress-strain curves tested at a strain rate of $4 \times 10^{-4} \text{ s}^{-1}$ for the IC (1550), IC(1250), and SC samples. The curves have been shifted along the x-axis for clarity. Table 4 compares the plastic strain, yield stress, and the elastic constants of the three alloys. The IC (1550) and IC (1250) samples yield at a very close stress, which is higher than that of SC sample. However, the SC sample fails at a plastic strain of 1.7%, which is obviously greater than those of the IC (1550) and IC (1250) samples. As aforementioned, the BCC *CuZr-B2* crystalline phase in the IC (1250) sample is a high-temperature stable phase and does not impair the thermal stability of the amorphous matrix. Here, it does not impair the mechanical properties of the IC (1250) alloy either, i.e., the IC (1250) sample exhibits the comparable yield stress and plastic strain as the IC (1550) sample. For the IC (1550) and SC samples, both of them exhibit an amorphous structure. However, the SC sample

reveals a lower yield stress and greater plastic strain than the IC (1550) sample. It is most often considered that the plastic flow of metallic glasses is associated with the free volume. The quenched-in free volume as a structural defect is trapped into the glassy state, when a liquid is cooled to form a glass, the quantity of which is, in fact, determined by the cooling rate. [151] Some attempts have been made to investigate the effect of cooling rate on free volumes and mechanical properties of BMGs. For example, Huang et al. [152] found that the smaller size alloy experiencing a faster cooling rate during solidification contains a larger amount of free volumes, resulting in enhanced plasticity upon compressive loading. Chen et al. [144] reported that the $\text{Cu}_{45}\text{Zr}_{48}\text{Al}_7$ BMG rod cast in helium gas atmosphere possesses a larger amount of free volumes, and exhibits enhanced plasticity due to experiencing a higher cooling rate than the same-composition rod cast in an argon-gas atmosphere. In this study, the effect of fabrication methods on the properties was observed. i.e., the rods fabricated with the suction casting contain more quenched-in free volumes and exhibit a lower yield stress and better plasticity than the rods fabricated with injection casting because of the difference of cooling rate of them.

If the amount of quenched-in free volumes is different between IC (1550) and SC samples, their elastic constants should be correspondingly different. We characterized the elastic constants in two ways: the measurements of the stress-strain behavior in the elastic-deformation region with the in-situ high-energy synchrotron x-ray scattering and RUS. Empirically, it is well established that the main part of the first peak in $I(q)$ in a metallic glass contains the information predominantly concerning a medium-range order. [153] Thus, the peak shift of the first peak of $I(q)$ indicates a “microscopic strain” of intermediate range. [154] In order to compare the responses of IC (1550) and

SC samples under compressive load at a smaller length scale, the microscopic stains of them were measured using in-situ HESXRD under compression shown in Figure 33. It can be seen that there is a linear relationship between the measured strain and applied stress for both alloys. The Young's modulus can be estimated by fitting the data with a linear relationship. It turns out that the Young's moduli are 114 GPa and 107 GPa for IC (1550) and SC samples, respectively. The Young's modulus becomes greater between 25 and 21 GPa measured from synchrotron x-ray scattering than those measured from RUS (shown in Table 4) for the IC (1550) and SC samples, respectively. It is known that the difference between those two measurement methods is due to the significant anelastic behavior of BMGs. [115] However, despite the result difference of these two measurement methods, there is an accordance with the change trend of the measured Young's moduli, i.e., the SC sample has a lower Young's modulus than IC (1550). The smaller Young's modulus indicates the sample behavior more softly when it responds against the applied force. It makes sense that this softer sample has more quenched-in free volumes, which acts as defects to decrease the resistance to the applied force.

The shear-band morphology on the side surface of the fractured rods was investigated by SEM, as shown in Figure 34. There are no other shear bands observed except the primary one associated with the fractured surface for the IC (1550) sample. It indicates that the plastic deformation is highly localized in a single shear band. However, multiple shear bands are found for the SC sample, which exhibits larger plastic strains. It is well known that unlike crystalline materials, the plastic deformation of BMGs is highly localized in shear bands, and the plastic strain is totally dominated by the shear-band behavior. Generally speaking, the higher the shear-band density, the better the plasticity.

It is consistent with our observation that the plasticity of the SC alloy with a higher shear-band density is better than that of IC (1550) alloy with a lower shear-band density.

4.4 Summary

We fabricated a $\text{Zr}_{55}\text{Ni}_5\text{Al}_{10}\text{Cu}_{30}$ glass-forming alloy with injection casting (controlling the melt temperature at 1,550 K and 1,250 K, respectively) and with suction casting. The differences of their structures and mechanical properties were investigated. The results indicate that there is a quenched-in CuZr-B2 crystalline phase present in injection-casting samples (the melting temperature is 1,250 K). However, it is a high-temperature stable phase and does not impair the thermal and mechanical properties. The thermal and structural analyses reveal that the injection-casting sample (the melting temperature is 1,550 K) and the suction-casting sample remains an amorphous structure. Despite their amorphous structure, the suction-casting samples exhibit lower yield stresses, lower Young's moduli, and larger plastic strains than the injection-casting samples (the melting temperature is 1,550 K) due to more quenched-in free volumes in suction casting, which results from the higher cooling rate.

CHAPTER 5: THE EFFECT OF PLASTIC-DEFORMATION HISTORY ON THE SUBSEQUENT PROPERTIES AND STRUCTURES OF BULK METALLIC GLASSES

The Chapter discusses the effect of plastic deformation history on the subsequent properties and structure of BMGs. Two kinds of deformation were introduced for BMG samples. One is inhomogeneous plastic deformation introduced by four-point-bend fatigue. The other is homogeneous deformation by elastostatic compression. The subsequent mechanical properties and structures were in-situ characterized with high-energy synchrotron x-ray diffraction.

5.1 Introduction

It is well known that at high stresses and low temperatures far below the glass transition temperature, plastic deformation of BMGs is highly localized into narrow shear bands [130, 131], which makes the deformation inhomogeneous. Bei et al. [155] investigated the effect of pre-strain on subsequent physical and mechanical properties of a brittle metallic glass. By controlling the specimen aspect ratio, compressive strains as high as 80% were obtained in the metallic glass, which introduced profuse shear banding. The authors treated the deformed sample as a composite, consisting of amorphous “grains”, which are relatively hard, surrounded by soft shear-band “boundaries”. A systematic strain-induced softening was observed. The decrease of the hardness and Young’s moduli of the deformed samples indicated the effect of pre-strain on the BMGs.

In general, homogeneous deformation of amorphous alloys is typically believed to occur only at low stresses and high temperatures (usually $\sim 70\%$ of T_g) [9]. However, recently Lee's group demonstrated that a homogeneous flow of amorphous alloys is feasible in their bulk form, especially when subjected to a stress below the global yield strength at room temperature. [11-16] They compressed the samples at a constant stress below their global yield strength and room temperature for prolonged time, which was referred to as "elastostatic compression". It was found that this elastostatic compression can induce the structural disordering, which is irreversible even after the load is removed and is accompanied by the creation of free volumes. Falk et al. [156] proposed a simplified constitutive equation, which permits the prediction of the structural evolution of amorphous solids under shear. In their theory, the structural state is characterized by a dimensionless parameter, χ :

$$C_0 \dot{\chi} = 2\tau \dot{\epsilon}_{pl} (\chi_\infty - \chi) - k(\chi, T) \quad (24)$$

where C_0 is a characteristic quantity of amorphous alloys with units of energy density, χ the dimensionless parameter describing the structural state, χ_∞ the upper limiting value of χ , τ the shear stress, $\dot{\epsilon}_{pl}$ the local deformation rate, and k a thermal relaxation term.

Considering that χ is defined as any structural state, it can be treated as an analog to the excess free volume. In Spaepen's free volume model, χ is defined as the reduced free volume $\chi \equiv v_f / \gamma v^*$, where v_f is the free volume, v^* a critical free volume, and γ a parameter of order unity. In the proceeding of elastostatic compression, the total strain consists of three strain components corresponding to the elastic response (ϵ_E), anelastic response (ϵ_A), and viscoelastic response (ϵ_V). Of these strain components, the

elastic and anelastic strains are fully recoverable upon the removal of the applied load. However, the viscoelastic strain remains unrecoverable, even if the load is removed. Thus, ε_v is the only component that produces a permanent (homogeneous) deformation characterized by a constant flow rate, $\dot{\varepsilon}_v$. Therefore, the local deformation rate ($\dot{\varepsilon}_{pl}$) can be assumed to the same as the homogeneous flow rate ($\dot{\varepsilon}_v$). The values of the maximum shear stress (τ) imposed on the samples can be assumed half the uniaxial compressive stress (σ). At room temperature, the thermal relaxation term (k) can be ignored. Therefore, the equation can be reduced to

$$C_0 \dot{\nu} = \sigma \dot{\varepsilon}_v (\nu_\infty - \nu) \quad (25)$$

Based on Equation (25), the amount of free volume created during the homogeneous deformation is dependent on the parameters: the stress level (σ), homogeneous flow rate ($\dot{\varepsilon}_v$), and exposure time (t) to loading.

In this Chapter, the inhomogeneous and homogeneous deformations were both used to pretreat the BMG samples and, then, subsequent mechanical properties and structure were investigated with high-energy synchrotron x-ray diffraction.

5.2 Experimental Procedure

Sample Preparation

Zr₅₀Cu₄₀Al₁₀ (in at.%) BMGs were prepared, using a ladle-hearth type arc-melt tilt-casting technique. The master-alloy ingots were prepared by arc-melting mixtures of pure Zr, Cu, and Al metals in an argon atmosphere. A special Zr-crystal rod (< 0.05 at.% oxygen) was employed in order to maintain the low-oxygen concentration of the alloys.

The cast rod sample of 10 mm in diameter and 60 mm in length was fabricated by a tilt-casting technique in an arc furnace via a pseudo-floating-melt state before casting to obtain a completely melted state.

(Zr₅₅Al₁₀Ni₅Cu₃₀)₉₉Y₁ BMGs were prepared from high-purity Zr, Al, Ni, Cu, and Y raw materials by arc melting under a Ti-gettered argon atmosphere. The BMGs were fabricated by injection-casting the master alloy into a copper mold. The copper mold is water-cooling, and the cooling rate is around 10 – 100 K/s. the cast samples were 3 mm × 3 mm × 75 mm square bars.

After casting, Zr₅₀Cu₄₀Al₁₀ (in at.%) and Zr₅₅Al₁₀Ni₅Cu₃₀)₉₉Y₁ BMG samples were machined to a rectangular bars with 2.3 mm × 2.3 mm × 25 mm and 2.5 mm × 2.5 mm × 25 mm, respectively, for four-point-bend fatigue treatments.

Zr₇₀Cu₆Ni₁₆Al₈ (in at.%) BMGs were prepared by arc-melting mixtures of pure Zr, Ni, Cu, and Al metals in an argon atmosphere. To avoid oxygen contamination, a special crystal Zr rod (< 100 mass ppm oxygen) was used. The master alloy was completely remelted and cast into a rod shape (3.5 mm in diameter and 30 mm in length) by the arc-tilt-casting method. After casting, the rods were reduced to a uniform diameter of ~2 mm by centerless grinding and cut to the length: diameter ratio of approximately 2:1. The bar ends were polished in a specially-designed fixture to ensure parallelism for the following compression tests and elastostatic compression treatments.

Four-point-bend Fatigue Treatments

The square-bar samples were used for four-point-bend fatigue. The four surfaces were polished using a P 4,000/1,200 grit SiC paper to avoid the surface effect. A MTS 810 was employed for four-point-bend fatigue tests, which were performed with an R

ration (the ratio of the minimum stress/the maximum stress) of 0.1 under a load-control mode, using a sinusoidal waveform at a frequency of 10 Hz. The schematic view of the fatigue is shown in Figure 35. A $(\text{Zr}_{55}\text{Al}_{10}\text{Ni}_{15}\text{Cu}_{30})_{99}\text{Y}_1$ BMG sample with $2.5 \text{ mm} \times 2.5 \text{ mm} \times 25 \text{ mm}$ was tested at a stress of 450 MPa until the failing cycle number reached 10^7 . A $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BMG sample with $2.3 \text{ mm} \times 2.3 \text{ mm} \times 25 \text{ mm}$ was tested at a stress of 900 MPa until the failing cycle number reached 464. Here, failure is considered when the displacement of the specimen is greater than the set-up maximum value, which will lead to the shutdown of the machine if it is overwhelmed. After fatigue treatments, the samples for compression tests were cut from two different sections of the fatigue specimens, including a section “a” within the inner pins and section “b” outside the outer pins, which denoted as inside-pin and outside-pin samples, respectively.

Elastostatic Compression Treatments

Uniaxial compression stress-strain curves of as-cast $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ in the paper [157] shows that the yield stress is around 1,500 MPa. Then, $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ specimens were treated with elastostatic compression for holding different times (12, 24, and 40 h) under percent levels of yield stress (90%) of 1,500 MPa. Sheet specimens ($2 \times 4 \text{ mm}^2$ in cross section and 0.7 mm in thickness) will be cut from these treated bulk metallic glass specimens along loading direction plane for ex-situ PDF measurements.

RUS Tests

The elastic moduli of the samples were measured with the resonant ultrasonic spectroscopy (RUS).

Ex-Situ High Energy Synchrotron X-Ray Diffraction

Structures of samples were examined by high-energy synchrotron X-ray diffraction at 11-ID-C beam line of the Advanced Photon Source at the Argonne National Laboratory. The measurements were performed in transmission geometry using an incident X-ray beam energy, E_i , of 115 keV ($\lambda = 0.1078 \text{ \AA}$) and a sample to detector (Mar-345 area detector) distance of 254 mm for $(\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30})_{99}\text{Y}_1$ and 311 mm for $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$, respectively. The schematic view of the setup is shown in Figure 29. The x-ray beam cross-section was $0.5 \text{ mm} \times 0.5 \text{ mm}$. The detector calibration was done using CeO₂ NIST powder standards. The two-dimensional scattering data sets were integrated about the azimuth to obtain the elastic scattering-intensity, $I(Q)$, where Q is the scattering vector magnitude by using *FIT2D* [109] to correct data for detector-geometrical errors due to small angular misalignments, obliqueness, x-ray beam polarization, background intensity, and for 2D image generation and file format conversion. Total structure function, $S(q)$, of the resultant data were conducted with a *PDFgetX2* package [145].

Anisotropy in the atomic structure was characterized by a difference in the Q -positions of the scattering maxima for the longitudinal and transverse directions, $S(Q)_{\text{long}}$ and $S(Q)_{\text{trans}}$, respectively. The difference in the scattering intensity, $\Delta S(Q)$, is shown in the equation:

$$\Delta S(Q) = \Delta S(Q)_{\text{pre}} - \Delta S(Q)_{\text{ref}} = [S_{\text{long}}(Q) - S_{\text{trans}}(Q)]_{\text{pre}} - [S_{\text{long}}(Q) - S_{\text{trans}}(Q)]_{\text{ref}} \quad (26)$$

The subscript “*pre*” and “*ref*” stand for a preload (elastostatic compression) sample and the reference (as-cast) sample, respectively. Since the reference sample was as-cast sample, its atomic structure should be isotropic, and thus, any differences in the

average bond length for the longitudinal and transverse directions should be representative of anisotropy in the beam line optics or detector. The contribution of these experimental artifacts can be separated from the structural anisotropy by subtracting the $\Delta S(Q)$ for the reference sample from that of the deformed sample according to Equation (26). After the measurement was made in the first geometry the sample was rotated by 90 degrees with respect to the original position, and the measurement was repeated.

In-Situ High Energy Synchrotron X-Ray Diffraction

In-situ HESXRD was performed in the same beamline under compression using a motorized screw-driven load cell on rectangular/cylindrical specimens with an aspect ratio (length/diameter) of 2:1. The load was stepwise increased up to 1200 MPa for $(\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30})_{99}\text{Y}_1$, in steps of 300 MPa. While the load was stepwise increased up to 1400 MPa for $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$, and until yield for $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$, respectively, in steps of 200 MPa. The schematic view of the setup is shown in Figure 21. For in-situ measurements, the x-ray beam cross-section was 0.5 mm $\times$ 0.5 mm for $(\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30})_{99}\text{Y}_1$ and 0.3 mm $\times$ 0.3 mm for $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ and $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$, respectively. The distances between the samples to the detector were 457 mm for $(\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30})_{99}\text{Y}_1$ and 311 mm for $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ and $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$, respectively. The two-dimensional scattering patterns under different stress levels were extracted by azimuthally averaging the ring pattern over an arc of approximately 5° centered on the vertical (loading) direction using the *FIT2D* software [109] to obtain $I(Q)$. A pseudo-Voigt function was used to fit the first peak of $I(Q)$. The resulting strains at each different

stress level can be calculated with the equation of $\varepsilon = \frac{Q_0}{Q_\sigma} - 1$ (where Q_σ and Q_0 are the positions of the first peak in $I(Q)$ under stress σ and zero stress, respectively).

The information for local atomic responses to stress was also deduced from reduced pair distribution function, $G(r)$ data for $(\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30})_{99}\text{Y}_1$. The strain, ε , is defined as $\varepsilon = (r_\sigma - r_0)/r_0$, where r_0 and r_σ denote the positions of peak in $G(r)$ under zero stress and stress σ , respectively. Since the peaks at low r are asymmetric while those at larger r are rather broad, we focused not on the tops of the peaks, but on the crossing points where $G(r) = 0$, which are less sensitive to the effects of asymmetry and can be accurately determined even for peaks at large r .

SEM

The shear-band morphology on the side surfaces of specimens was examined to study deformation mechanisms, using a Leo 1526 SEM.

5.3 Results and Discussions

$(\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30})_{99}\text{Y}_1$: plastic deformation introduced by four-point-bend fatigue

Figures 36(a) and (b) show the optical microscope image for the compressive and tensile-side surfaces of section a, respectively, after a maximum fatigue stress of 450 MPa, which is much lower than the compressive yield strength. Straight and wavy shear bands can be observed in section a, suggesting that the critical stress for the shear bands to form under cyclic loading is lower than that under static loading, which could be related to the fatigue softening. However, no shear band is observed in section b. the change in the shear-band morphology on the side surfaces could be explained by the stress distribution due

to the four-point-bend fatigue set-up. Section a was subjected to the stress, however, section b bore almost zero stress. After a long fatigue life under fatigue stress, stress lead to plastic deformation, which explain the different shear-band morphology between section a and b.

Figure 37 indicates the evolution of strains in loading and transverse directions with the applied stress for inside-pin and outside-pin samples, respectively. It can be seen that there is a linear relationship between the measured strain and applied stress for both samples. The strain tensors for both the alloys have been calculated in the linear-elastic region in loading direction to estimate the Young's modulus (E), 103.2 GPa for outside-pin sample and 78.2 GPa for inside-pin sample, respectively. It is surprising that there is a huge difference of E between them, which indicates a corresponding structure difference. Then we deduce the information for local atomic responses to stress during compression from $G(r)$ data by using the equation, $\varepsilon = (r_{\sigma} - r_0)/r_0$. The strain results are shown in Figure 38. It indicates that the local strain of two samples under each stress is roughly consistent with the microscopic strain (shown by short dashed line) obtained from $I(Q)$ data. Again, the difference of local atomic responses to stress for two samples is very obvious. For example, under the stress of 300 MPa, the local strains of outside-pin sample and inside-pin are around 0.3% and 0.45%, respectively. Thus the stiffness of outside-pin sample should be higher than that of inside-pin sample, which indicates there are weaker atomic bonds or more structure defect (free volume) in inside-pin samples. RUS was used to double check the difference of E since it is more accurate. For the first time without polishing the samples, it turns out that E of the outside-pin sample is 84.4 GPa. However, no result came out for inside-pin sample. One of the most common reasons for failing RUS measurement is the microcracks in the sample. After polishing all six side surfaces,

the samples were measured with RUS again. The results indicate the same E , 84.4 GPa, for both samples. The diffraction patterns of $S(Q)$ and $G(r)$ confirmed that there is no obvious structure change for both samples. It looks likely that after a long fatigue life under a fatigue stress, microcracks, which were associated with the formation and propagation of shear bands, formed near the surface. Those defects of microcracks act as open areas, which are across the cross-section perpendicular to the loading direction during compression, and lead to a decrease of an actual cross section and an increase of actual applied stress on the sample. Under a higher actual stress, the inside-pin sample appeared to respond with a greater strain. The peak width change in $I(Q)$ data is sensitive to the stress as well. The larger the stress, the larger the change of peak width. The FWHM of the first peak of $I(Q)$ for both outside-pin and inside-pin samples are shown in Figure 39. The difference of the change of FWHM could be explained since the inside-pin sample experienced larger actual stress.

Zr₅₀Cu₄₀Al₁₀: plastic deformation introduced by four-point-bend fatigue

We performed similar four-point-bend fatigue treatments on Zr₅₀Cu₄₀Al₁₀ BMG sample. However, the tested stress was changed to 900 MPa and the sample failed when the cycle reached 464. Similarly like (Zr₅₅Al₁₀Ni₅Cu₃₀)₉₉Y₁, shear bands can be observed on section “a” of the compressive and tensile-side side surfaces. However, none was observed on section “b”. The shear band morphology for tensile-side surface of section a is shown in the Figure 40.

Figure 41 indicates the evolution of strains in loading and transverse directions with the applied stress for inside-pin and outside-pin Zr₅₀Cu₄₀Al₁₀ samples, respectively. It can be seen that there is a linear relationship between the measured strain and applied

stress for both samples as well. However, unlike $(\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30})_{99}\text{Y}_1$ samples, there is almost no difference of the stress-strain behaviors between them. The results of elastic constants from RUS measurements indicate no change for them as well. E is 89 GPa for both of them.

Qiao et al. [158] investigated the fatigue softening on a Zr-based BMG. They did observe that shear bands form in the area inside the pins and those pre-existing shear bands could decrease the compressive strength of the material. In their case, the space between shear bands is less than 10 μm , which indicates the high shear-band density. If the deformed glass is treated as a composite of hard amorphous “grains” surrounded by soft shear-band “boundaries”, the higher the shear-band density, the softer the composite sample. Bei et al. [155] achieved a very large strain of 80% in a Zr-based BMG by controlling the specimen aspect ratio. The space between shear bands is less than 10 μm as well. As a result, the material became softer due to those profuse shear banding. Compared to our case, the space between shear bands is at least larger than 80 μm , which indicate that the soft areas of shear band is not abundant enough to induce the structure or property change of the materials, or at least the change can not be detected with the limit of synchrotron x-ray diffraction. There is almost no difference of the change of FWHM for the outside-pin and inside-pin samples shown in Figure 42.

Zr₇₀Cu₆Ni₁₆Al₈: plastic deformation introduced by Elastostatic Compression

Figure 43 shows the evolution of strains in loading direction with the applied stress for as-cast and preloaded Zr₇₀Cu₆Ni₁₆Al₈ for 12, 24, and 40 h, respectively. It can be seen that there is a linear relationship between the measured strain and applied stress for all samples until they reached yielding. Here, when the in-situ synchrotron

compression tests were performed, the samples were loaded under a displacement control until the load could not be increased, which means the yield has been accessed. Interestingly, the yield points of the preload samples becomes less than the as-cast sample, especially the preloaded sample with 40 h has a yield strength obviously about 100 MPa lower than of the as-cast one. It is know that the mechanical and physical properties of amorphous alloys are closely related to their structural stability, which is determined by their atomic packing density of free volume. With preloading time increasing, more extra free volume is induced by elastostatic compression. The abundant free volume facilitates the shear deformation of STZ. Thus, the shear resistance of STZ against the applied stress decreases. As a result, shear bands can be initiated at a lower stress, leading to lower yield strength of the preloaded sample. The Young's moduli were determined by calculating the slopes of the stress-strain relationship in the linear-elastic region along loading directions. The results indicated that the Young's moduli for as-cast and preloaded $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ for 12, 24, and 40 h were 86, 85.1, 80.2, and 76.7 GPa, respectively. The variations in the Young' modulus after the elastostatic compression revealed a tendency similar to that observed from the yield strengths of the samples. The decrease of the yield strengths of the preloaded samples is thought to be due to the increased disorder, i.e., free volume, generated during the elastostatic compression. This increased disorder is associated with an increase in the average interatomic spacing, resulting in a lowering of the atomic bonding force. The reduced Young's moduli of the preloaded samples occur due to this increase in interatomic spacing.

Figure 44(a) and (b) reveal the difference in the scattering intensity, $\Delta S(Q)$, for the preload samples of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ in the plane parallel to the loading direction for

two measurement geometries, respectively. In first measurement geometry the z axis of the sample along which external stress was applied was in the vertical direction of the detector. In the second measurement the samples were rotated 90° in the plane orthogonal to the beam and parallel to the image plate so that the scattered intensities from the longitudinal and transverse directions swapped orientations on the area detector, i.e., the z axis of the sample was along the horizontal direction. The difference plots for all preload samples exhibit a sigmoidal shape in the Q-range around the first scattering maximum, and, to a lesser extent, around the second scattering maximum. The data are noisy due to the small magnitude of changes being examined. The maximum magnitude of the change of $\Delta S(Q)$ is less than 2% of that of $S(Q)$, which is reasonable considering the applied stress was smaller than the yield strength and the compression was conducted at room temperature. Despite this small magnitude of changes, the shape of the different plots is consistent with the peak position of the first scattering maxima in the longitudinal direction being shifted to a higher Q-position relative to the peak position of the first scattering maxima for the transverse direction. Therefore, the average bond length along the loading axis is smaller than the average bond length normal to the loading axis. Similar results can be observed in the second geometry, which confirms that the difference plots are indeed representative of structural anisotropy and not experimental artifacts. It is revealed from Figure 44 that the structural anisotropy of the preload sample become more obvious as the preload time increases except the preload sample with 40 h.

The elastostatic compression can be considered as a “room-temperature creep”. For normal creep at elevated temperature, the anisotropy was explained to be a result of bond reorientation. [111] During the creep experiment, the external elastic stress induces

anisotropy but a material tries to recover isotropy by bond reorientation. Microscopically, the bond orientation is produced by cutting old bonds in the direction stress and forming new bonds in the perpendicular direction. This anisotropy is preserved when the external stress is removed because sample is cooled down with the stress. [110] The anisotropy in the samples elastostatically compressed should experience in the similar way despite much smaller magnitude of the change. In other word, with the treatment time increasing the structural anisotropy should increase. However, we must point out the anisotropy of the samples was measured after two steps of treatments. The first step is that the samples were elastostatically compressed and then the second step is that the preloaded samples were uniaxial loaded until yielding. Actually both steps will induce anisotropy by “creep” and plastic deformation, respectively. The anisotropy of another group of samples only treated with elastostatic compression was measured, which allow us to know the effect of preloading time on structural anisotropy. Figure 45 indicates that with the treatment time increasing, the structural anisotropy in deed increases. Then the decrease of anisotropy for the preloaded sample with 40 h in the first group may due to the plastic deformation during yielding. When the in-situ compression tests were performed, it was under displacement control. The increase of the applied load is proportional to the increase of the displacement. The increases of the displacement for the preloaded samples with 12, 24, 40 h when yielding are 0.0135, 0.0092, 0.0248 mm, respectively. Considering that the preloaded sample with 40 h has a yield strength around 100 MPa smaller than the other two preloaded samples, the difference of the increase of the applied load is more effective to induce larger plastic deformation in the preloaded sample with 40 h. The anisotropy introduced by this plastic deformation may partially cancel out the anisotropy by

elastostatic compression. As a result, the anisotropy of the preloaded sample with 40 h decreases.

5.4 Summary

We introduced inhomogeneous plastic deformation in $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BMG samples by four-point-bend fatigue. There is almost no difference of the stress-strain behaviors between the deformed and undeformed samples. It may be due to the small shear-band density in the deformed sample, which means that the soft areas of shear bands is not abundant enough to induce the structure or property change of the materials, or at least the change can not be detected with the limit of synchrotron x-ray diffraction. Elastostatic compression was used to introduce homogeneous deformation in $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ BMG samples. The preloaded samples are softer with the decreases of yield strength and Young's moduli. Anisotropy was observed in the preloaded samples despite their small magnitudes, which even occurred at a relatively low temperature and a low applied stress level.

CHAPTER 6: STRUCTURAL EVOLUTION OF A $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ BMG UNDER COMPRESSION

In the previous three Chapters, we more focused on the analysis of the data in reciprocal space. In this Chapter, the anisotropy PDF will be used to analyze the structural evolution of the $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ BMG in the elastic region. A new approach to extract the microscopic strain is present here with PDF analysis. The structural evolution in the plastic region of the $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ BMG is investigated as well by discussing the changes of the shift and FWHM of the first maximum in the elastic scattering intensity. The excess free volume is measured in the plastic region.

6.1 Introduction

There are two ways to investigate the structural evolution in BMGs using in-situ high-energy synchrotron x-ray diffraction. One is by analyzing the data, $I(Q)$ or $S(Q)$ in the reciprocal space. The other is to analyze the data, PDF in real space. The most important information from $I(Q)$ or $S(Q)$ is the shift and FWHM of the first maximum. From the shift of first maximum, the “lattice strain” can be extracted. Most early works [19, 20, 22-25] with in-situ synchrotron x-ray diffraction are in an effort to obtain the strain by which the Young’s modulus can be calculated to compare with the measurements from resonant ultrasonic spectroscopy. Most of the results in the literatures show the differences between those two approaches. In real space, the strain can be also gotten by the shift of the PDF, which is achieved either by fitting the peaks with multi-

Gauss functions or using the cross point when $G(r) = 0$ or $g(r) = 1$. The same again, the calculated Young's moduli do not match the RUS measurement well. It is well known that when the load is applied, the structure of the sample becomes anisotropic, which means the isotropic PDF analyses no longer work for it. However, there are very few studies that investigate the structural evolution in the elastic region with anisotropic PDF. Using this analysis method of anisotropy pair density function, Mattern et al. [25] measured amorphous ribbons with the compositions, $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{65}\text{Zr}_{35}$, under tensile loading. The authors determined the positions of the maxima of $\rho(r)$ using a Gaussian function fitting. The direction-dependent strain values behave quite similarly for the maxima at $r > 0.4$ nm. By deconvoluting the first RDF peak which corresponds to the first coordination shell, two partials Cu-(Zr,Cu) and Zr-Zr atomic pairs are resolved to estimate the variation of the coordination numbers of them. For the Cu-(Zr,Cu) pairs, the coordination number decreases in the loading direction but increases in the transverse direction and an opposite behavior occurs for the Zr-Zr pairs. The coordination number changes reflect the topological rearrangements within the atomic nearest-neighbor environment in the elastic region. However, the total coordination numbers of the Cu-(Zr,Cu) and the Zr-Zr atomic pairs remain almost constant respectively. It means that, for Zr-Zr pairs, the bond reorientation is processed by breaking the bonds in the transverse direction and reforming new bonds in the loading direction, and the opposite behavior occurs for Cu-(Zr,Cu) pairs. This bond reorientation leads to direction-dependent changes in chemical short-range order, which is associated with the structural change in the nearest-neighbor in BMGs. Wang et al. [26] observed the similar results in $\text{Cu}_{64.5}\text{Zr}_{35.5}$ in the case of compressive stresses.

It is very difficult to study the structural evolution of BMGs in the plastic region at room temperature with in-situ high-energy synchrotron x-ray diffraction since the BMG has very limited plastic strain. To our knowledge, there is no report on this issue so far.

In this Chapter, we investigate the structure evolution in elastic and plastic region for the $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ BMG with in-situ high-energy synchrotron x-ray diffraction.

6.2 Experimental Procedure

Sample Preparation

$\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ (in at.%) BMGs were prepared by arc-melting mixtures of pure Zr, Ni, Cu, and Al metals in an argon atmosphere. To avoid oxygen contamination, a special crystal Zr rod (< 100 mass ppm oxygen) was used. The master alloy was completely remelted and cast into a rod shape (3.5 mm in diameter and 30 mm in length) by the arc-tilt-casting method. After casting, the rods were reduced to a uniform diameter of ~ 2 mm by centerless grinding and cut to the length: diameter ratio of approximately 2:1. The bar ends were polished in a specially-designed fixture to ensure parallelism for the following compression tests. One sample is used to investigate the structural evolution in the elastic region (denoted as sample 1). The other one is used to focus on the structural evolution when the sample starts yielding (denoted as sample 2).

In-Situ High Energy Synchrotron X-Ray Diffraction

In-situ HESXRD was performed in the same beamline under compression using a motorized screw-driven load cell on cylindrical specimens with an aspect ratio

(length/diameter) of 2:1. The load was stepwise increased up to 1200 MPa for the sample 1, in steps of 200 MPa. However, the load was stepwise increased up to the yielding point for the sample 2, in steps of 200 MPa. The schematic view of the setup is shown in Figure 21. For in-situ measurements, the x-ray beam cross-section was 0.3 mm $\times$ 0.3 mm for both samples. The distances between the samples to the detector were 338 mm for the sample 1 and 310 mm for the sample 2, respectively. The two-dimensional scattering patterns under different stress levels were extracted by azimuthally averaging the ring pattern over an arc of approximately 18° centered on the vertical (loading) direction using the *FIT2D* software [109] to obtain $I(Q)$. A pseudo-Voigt function was used to fit the first peak of $I(Q)$. The resulting strains at each different stress level can be calculated with the equation of $\varepsilon = \frac{Q_0}{Q_\sigma} - 1$ (where Q_σ and Q_0 are the positions of the first peak in $I(Q)$ under stress σ and zero stress, respectively).

6.3 Results and Discussions

Structural evolution in the elastic region

Figure 46 shows the structure factor $S(Q, \varphi=90^\circ)$ of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass measured along the loading direction. The position of the first maximum Q_I at about 2.54 $\text{\AA}^{-1}$ is shifted to high Q -values whereas, along the perpendicular direction, Q_I moves to lower Q -values as expected. Using equation, $\varepsilon = \frac{Q_0}{Q_\sigma} - 1$, where Q_σ and Q_0 are the positions of the first peak in $S(q)$ under stress σ and zero stress, respectively, the

calculated strain values of the $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass along loading and transverse directions at different loads are shown in Figure 47. The strain tensors for both the alloys have been calculated in the linear-elastic region and diagonalized in order to estimate the elastic constants, including the Young's modulus (E) and Poisson' ratio (ν). The results indicated that the E and ν are 83.6 and 0.33, respectively. According to the paper [157], the E and ν of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass are 73 and 0.39, respectively. There are the differences around 10 GPa for E and 0.6 for ν between these two measurement methods. The reasons have been discussed in Chapter 4.

In real space, for isotropic amorphous materials the atomic density function, $\rho(r)$, can be calculated by the sine-Fourier transform of the structure factor:

$$\rho(r) = \rho_0 + \frac{1}{2r\pi^2} \int (S(Q) - 1) \cdot Q \cdot \sin(Q \cdot r) \cdot dQ \quad (27)$$

Where ρ_0 is the average atomic density.

However, in the presence of stress the sample becomes anisotropic. In such a case, the direction dependence of the $S(\vec{Q})$ can be described by the expansion into spherical harmonics [110-112]:

$$S(\vec{Q}) = \sum_{l,m} S_l(Q) Y_l(\vec{Q}/Q) \quad (28)$$

For the uniaxial cylinder symmetry, the spherical harmonics Y can be reduced to the Legendre polynomials:

$$Y_l(\varphi) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos \varphi) \quad (29)$$

Since the higher-order terms $l > 2$ contribute much less than the term $l = 2$ does, the higher-order terms $l > 2$ can be neglected. Then the structure factor of any direction φ is given by:

$$S(Q, \varphi) = S_0(Q) \sqrt{\frac{1}{4\pi}} + S_2(Q) \sqrt{\frac{5}{16\pi}} (3 \sin^2 \varphi - 1) \quad (30)$$

The components of the structure factor $S_0(Q)$ and $S_2(Q)$ can be calculated from the two measurements parallel ($\varphi = 90^\circ$) and perpendicular ($\varphi = 0^\circ$) to the compressive directions:

$$S_0(Q) = \frac{\sqrt{4\pi}}{3} [S(Q, \varphi = 90^\circ) + 2S(Q, \varphi = 0^\circ)] \quad (31)$$

$$S_2(Q) = \sqrt{\frac{16\pi}{45}} [S(Q, \varphi = 90^\circ) - S(Q, \varphi = 0^\circ)] \quad (32)$$

Analogous to the structure factor, the atomic density function $\rho(\vec{r})$ can be given by:

$$\rho(\vec{r}) = \sum_l \rho_l(r) Y_l(\vec{r}/r) \quad (33)$$

The components of the anisotropic PDF and the corresponding components of anisotropic structure factor are related by a transformation [110-112]:

$$\rho_l(r) = \frac{(i)^l}{2\pi^2} \int S_l J_l(Qr) Q^2 dQ \quad (34)$$

where $J_l(Qr)$ is the l th order of the spherical Bessel function with $J_0(Qr) = \sin(Qr)/Qr$, and $J_2(Qr) = [3/(Qr)^3 - 1/Qr] \sin(Qr) - 3/(Qr)^2 \cos(Qr)$.

The anisotropic part of the atomic pair correlations $\rho_2(r)$ is obtained from the anisotropic part of the structure factor $S_2(Q)$ by:

$$\rho_2(r) = -\frac{1}{2\pi^2} \cdot \sqrt{\frac{45}{16\pi}} \int S_2(Q) \cdot J_2(Qr) \cdot Q^2 dQ \quad (35)$$

The atomic density of any direction, φ , is then given by

$$\rho(r, \varphi) = \rho_0(r) \sqrt{\frac{1}{4\pi}} + \rho_2(r) \sqrt{\frac{5}{16\pi}} (3 \sin^2 \varphi - 1) \quad (36)$$

Figure 48 compares the calculated isotropic structure factors $S_0(Q)$ of the $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass for the highest load (1200 MPa) and the zero load (0 MPa). The difference curve $S_0(1200 \text{ MPa}) - S_0(0 \text{ MPa})$ exhibits small changes of about 1.8% of the isotropic structure factor $S_0(Q)$ occurring at the first maximum. The anisotropic part of the structure factor $S_2(Q)$ is shown in Figure 48 as well. The amplitude of $S_2(Q)$ increases gradually as function of the applied stress and reaches values up to 18 % at the first maximum when the applied load is 1200 MPa.

The anisotropic part of the PDF is shown in Figure 49. The amplitude of $\rho_2(r)$ increases gradually with stress, which is similar to the anisotropic structure factor $S_2(Q)$. It should be noted that in the case of pure elastic deformation the anisotropic PDF part should be proportional to the first deviate of the isotropic PDF as discussed by Suzuki et al. [111] The relationship between the anisotropic part, $\rho_2(r)$ and the first deviate of the isotropic PDF, $\rho_0(r)$ can be written as:

$$\rho_2(r) = -\sqrt{\frac{4\pi}{5}} \cdot \frac{2}{3} \cdot (1 + \nu) \cdot \varepsilon_3 \cdot r \cdot \frac{d\rho_0}{dr} \quad (37)$$

Where ν is the Poisson' ratio of the material (it equal 0.39 in this case) and ε_3 is the strain along the loading direction. It should be noted that the sign of ε_3 is negative since the sample is compressed. The corresponding curves of $\rho_2(r)$ at the stress level of

1200 MPa and $-\sqrt{\frac{4\pi}{5}} \cdot \frac{2}{3} \cdot (1+\nu) \cdot \varepsilon_3 \cdot r \cdot \frac{d\rho_0}{dr}$ at a strain of $\varepsilon_3 = -0.01675$ are given in

Figure 50. It indicates that there is a good match beyond 4 Å between them. Suzuki et al. [111] pointed out that the anisotropy in the medium- to long range (beyond 4 Å) atomic correlation is characterized by the uniform shear strain. Thus by fitting each other between the anisotropic part, $\rho_2(r)$ and the first deviate of the isotropic PDF, $\rho_0(r)$ with the equation, the compressive strain along the loading direction can be obtained for each loading level. The fitting results are shown in Figure 51. Amazingly, the slope of the curve, indicating the Young's modulus, is around 72.1 GPa, which matches perfectly the result of 73 GPa in the literature.

Figures 52(a) and (b) compare the direction dependences of first maximum of the PDF of the $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass for the loading and transverse directions as a function of the load. The $\rho(r)$ curves represent the weighted sum the partial atomic pair correlation functions. Considering the small content of Al as well as its comparatively weak scattering powers, the partials of Al-Al, Al-Zr, Al-Cu can be neglected. Also, Cu and Ni can be treated equivalently since their atomic radii are almost identical ($R_{\text{Cu}}^0 = 1.27 \text{ Å}$ and $R_{\text{Ni}}^0 = 1.28 \text{ Å}$). Thus, the visible two components of the PDF can be attributed to the partial (Cu,Ni)-Zr and Zr-Zr pair correlations. It can be seen from Figure 52(a) that the PDFs of two directions at zero load are almost the same, which indicates an isotropic structure of the sample before load. The small difference is caused by either the cylindrical sample set-up or the anisotropy of the detector. Figure 52(b) shows obvious differences in position and height of the two components. The values of the position, r_i and the area, N_i of the two components were determined by a fit of two Gaussian

functions. The results are summarized in Table 5. The positions of the two maxima corresponding to the nearest neighbor distances (Cu,Ni)-Zr and Zr-Zr decrease along the compressive direction and increase in the transverse direction. The N_i is coordination number. From the analysis of the first maximum it indicates that the number of (Cu,Ni)-Zr neighbors increases in the loading direction but decrease in the transverse direction and an opposite behavior occurs for the Zr-Zr pairs. The coordination number changes reflect the topological rearrangements within the atomic nearest-neighbor environment in the elastic region. The total area of the (Cu,Ni)-Zr pair and the Zr-Zr pair remain almost constant, respectively, which indicate that for the Zr-Zr pair, the bond reorientation is processed by breaking the bonds in the loading direction and reforming new bonds in the transverse direction, and the opposite behavior is present for (Cu,Ni)-Zr pair.

Structural evolution in the plastic region

Figure 53 shows the evolution of strains in loading and transverse directions with the applied stress for the sample 2. It can be seen that there is a linear relationship between the measured strain and applied stress in the elastic region. However, the increment of strains slightly deviates from linearity around 1,500 MPa, which is the macroscopic yielding point of the $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass. Figure 54 gives the evolution of stress and the change of FWHM in the loading direction with the displacement. If we focus on the region that the sample started yielding shown in an enlarged insert, the stress-displacement curves become serrated in this region. In general, the serration is a result of shear-banding [159-161]. Actually, the patterns were recorded after each obvious load drop when the compression tests were performed. It is known that each load drop is associated with a shear band event (note that one single shear band event could

include one or many shear bands) [162]. The change of FWHM becomes highly fluctuant since the yielding starts. Interestingly, the change of FWHM is associated with the serration of the stress-displacement curve. We can plot the rate of change of FWHM on the change of stress as function of the displacement shown in the Figure 55. It can be seen that the rate of change of FWHM on the change of stress maintain a small value in the elastic region. Then, it dramatically increases when the yielding starts and drops back to a small value which is still larger than that in elastic region. In order to investigate the evolution of “lattice strain” vs. stress, we plot the curve of stress vs. strain in the loading direction shown in Figure 56. At very beginning of the yielding, the strain exhibits a right shift. However the strain starts a left shift at the point A which is exactly the point at which the rate of change of FWHM on the change of stress drops.

When the load was applied on the sample to yielding, STZs become activated. According to the model suggested by Schuh et al. [163], a STZ causes other STZs to form in the vicinity. Once a sufficient number of STZs is formed, the shear-bands will start propagating, and accelerates theoretically to infinite speed. This unstable process momentarily relieves a large amount of stress and results in the load drops. At point A, there may a lot of shear-band events occurring, which soft the sample by inducing excess free volume in the sample. This is also why BMG samples would not exhibit working hard as the crystalline materials have. Figure 57(a) and (b) show the fitted peak positions in the loading and transverse direction, respectively, as function of the displacement for the sample after the point A. The measured Q-position of the first scattering peak in the loading direction is greater than that in the transverse direction, which is consistent with a smaller average atomic bond length in the loading direction. To measure the excess free

volume present in the sample after plastic deformation, we followed a similar approach that used by Ott and coworkers [164] who calculated the free volume in crept samples as followings:

$$\Delta V_f = \frac{\left(\frac{1}{Q_{creep}}\right)^3 - \left(\frac{1}{Q_{comp}}\right)^3}{\left(\frac{1}{Q_{comp}}\right)^3} \quad (38)$$

where Q_{comp} and Q_{creep} are the peak positions of the first scattering maxima for the companion and creep samples, respectively. For calculating the excess free volume, they assume that the average bond lengths in the two transverse directions of the samples are equivalent, and thus

$$\left(\frac{1}{Q}\right)_{comp, creep}^3 = \left(\frac{1}{Q_{long}}\right)\left(\frac{1}{Q_{trans}}\right)^2 \quad (39)$$

where Q_{long} and Q_{trans} are the peak positions of the first scattering maxima for the longitudinal (loading) and transverse samples, respectively.

In our case, the equation will be rewritten as:

$$\Delta V_f = \frac{\left(\frac{1}{Q_{deform}}\right)^3 - \left(\frac{1}{Q_{comp}}\right)^3}{\left(\frac{1}{Q_{comp}}\right)^3} \quad (40)$$

where Q_{comp} and Q_{deform} are the peak positions of the first scattering maxima for the companion and deformation cases, respectively. Here, we use the point A as the companion case.

Figure 58 gives the calculated excess free volume in the plastic region of $Zr_{70}Cu_6Ni_{16}Al_8$ sample as a function of macroscopic plastic strain. The excess free

volume increases with increasing plastic strain. The magnitude of the excess free volume is consistent with reported values for inhomogeneously deformed metallic glasses measured by in situ X-ray scattering.

6.4 Summary

We analyzed the structural evolution of the $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ BMG in the elastic region with anisotropic PDF. The amplitude of the anisotropic parts of total structure factor, $S_2(Q)$, and the PDF, $\rho_2(r)$ increase gradually as function of the applied stress. The $\rho_2(r)$ is proportional to the first deviate of the isotropic PDF, $\rho_0(r)$. By fitting these two functions beyond the 4 Å, a Young's modulus of 72.1 GPa is estimated, which matches perfectly the result of 73 GPa in the literature. The analysis of the first shell of the $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass confirms the structural changes in the elastic region. The bond reorientation leads to direction dependent changes in the chemical short-range order. The number of (Cu,Ni)-Zr neighbors increases in the loading direction but decrease in the transverse direction with applied stress and an opposite behavior occurs for the Zr-Zr pairs. The structural evolution in the plastic region of the $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ BMG is investigated as well. The serrations were observed for both the stress-displacement and the FWHM-displacement curves. The rate of change of FWHM on the change of stress dramatically increases when the yielding starts. The excess free volume was measured, which increases with increasing plastic strain.

CHAPTER 7: CONCLUSIONS

This dissertation investigated the effect of composition, fabrication method, and pretreatment of plastic deformation on the mechanical properties and structure of BMGs and the mechanical response and structural evolution of BMGs in the elastic and plastic regions with the technique of high-energy synchrotron x-ray diffraction. Pertinent findings are summarized as follows:

- $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ amorphous alloys were used to study the effect of the composition on mechanical properties and structures of BMGs. An obvious mechanical-behavior difference was observed from both the in-situ high-energy synchrotron x-ray diffraction characterization and macroscopic-compression tests. The Poisson's ratio does not vary much for the different measurements but the Young's modulus becomes greater between 9.6 and 9.3 GPA measured from synchrotron x-ray scattering than those measured from RUS for $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ alloys, respectively. Despite the difference of these two measured results, $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ exhibits a lower Young's modulus and larger Poisson's ratio than $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$. The macroscopic compression tests shows that the $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ alloy has a lower yield stress and better plasticity ability than $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$. DSC results indicates that $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ has a better thermal stability than $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$. MD simulations show that with increasing the Al content, local structure orders of full icosahedra with the dense-packing density increase. More importantly,

covalent bonds form due to the addition of Al. Both the topological (dense packing) and chemical (stable bonding) effects of Al addition account for the differences of mechanical and physical properties between $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$.

- The $\text{Zr}_{55}\text{Ni}_5\text{Al}_{10}\text{Cu}_{30}$ glass-forming alloys with injection casting (controlling the melt temperatures at 1,550 K and 1,250 K, respectively) and with suction casting were fabricated, respectively. The x-ray diffraction results reveal that the injection-cast sample (the melting temperature is 1,550 K) and the suction-cast sample remain an amorphous structure. However, there is a quenched-in CuZr-B2 crystalline phase present in the amorphous matrix of injection-casting samples (the melting temperature is 1,250 K). It is a high-temperature stable phase and does not impair the thermal and mechanical properties of the injection-cast samples (the melting temperature is 1,250 K). Despite their amorphous structure, the suction-cast samples exhibit a lower yield stress, lower Young's modulus, and larger plastic strain than the injection-cast samples (the melting temperature is 1,550 K). The structural relaxation exothermic heat (ΔH_0) for the injection-cast sample (the melting temperature is 1,550 K) and the suction-casting sample are 2.3 and 2.8 J/g, respectively, which indicates that the suction-cast sample may possess a larger amount of quenched-in free volumes than the injection-cast samples (the melting temperature is 1,550 K). This difference of quenched-in free volumes in the injection-cast samples (the melting temperature is 1,550 K) and the suction-cast

sample is leaded by the higher cooling rate provided by suction casting than injection casting.

- The inhomogeneous plastic deformation in $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ BMG samples by four-point-bend fatigue was introduced. There is almost no difference of the stress-strain behaviors between the deformed and undeformed samples. It may be due to the small shear-band density in the deformed sample, which means that the soft areas of shear bands is not abundant enough to induce the structure or property change of the materials, or at least the change can not be detected with the limit of synchrotron x-ray diffraction. Elastostatic compression was used to introduce the homogeneous deformation in $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ BMG samples. After the pretreatment, the yield strength of the preloaded samples for 12, 24, and 40 h decreases compared to the as-cast sample. The Young's moduli of the as-cast and preloaded $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ for 12, 24, and 40 h were 86, 85.1, 80.2, and 76.7 GPa, respectively, which indicates that the preloaded samples become softer. Anisotropy was observed in the preloaded samples despite their small magnitudes, which even occurred at a relatively low temperature and applied stress level.
- The structural evolution of the $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ BMG in the elastic region was analyzed with the anisotropic PDF. The amplitude of the anisotropic parts of the total structure factor, $S_2(Q)$, and the PDF, $\rho_2(r)$, increase gradually as function of the applied stress. The $\rho_2(r)$ is proportional to the first derivative of the isotropic PDF, $\rho_0(r)$. By fitting these two functions beyond the 4 Å, a Young's modulus of 72.1 GPa is estimated, which matches perfectly the result

of 73 GPa in the literature. The analysis of the first shell of the $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass confirms the structural changes in the elastic region. The bond reorientation leads to direction-dependent changes in the chemical short-range order. The number of (Cu,Ni)-Zr neighbors increases in the loading direction but decreases in the transverse direction with the applied stress and an opposite behavior occurs for the Zr-Zr pairs. The structural evolution in the plastic region of the $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ BMG is investigated as well. The serrations were observed for both the stress-displacement and the FWHM-displacement curves. Dependence of rate of change of FWHM on stress dramatically increases when yielding starts, which indicates a structural change in the BMG sample. Shear bands could form and propagate, which is associated with the increase of free volume present in the sample. The measured Q position of the first scattering peak in the loading direction is greater than that in the transverse direction, which is consistent with a smaller average atomic-bond length in the loading direction. Also, with increasing the plastic strain, the Q position of the first scattering peak in the loading direction decreases obviously, and the value in the transverse direction decreases slightly. The excess free volume was measured, based on the change of these Q position values, which increases with increasing the plastic strain.

CHAPTER 8: FUTURE WORKS

The technique of high-energy synchrotron x-ray diffraction is a powerful tool for studying the mechanical response and structure of amorphous materials, especially with the in-situ load capability. Based on this dissertation, the following future work could be proposed:

In Chapter 6, inhomogeneous plastic deformation was introduced by four-point-bend fatigue. Unfortunately, the shear-band density was not high enough to address the difference between the deformed and undeformed samples. Thus, new pretreatment methods should be considered to introduce more heavily inhomogeneous deformation for BMG samples. For example, a precompression treatment on the sample with tapered ends or constraining the sample with reducing the ratio of length/diameter are possible to introduce profuse shear bands, which may be suitable for the study of the effect of the plastic-deformation history on the mechanical properties and structure of BMGs.

Elastostatic compression is a very interesting topic too. A more systemic study should be conducted on the effect of the preload stress level and time on the mechanical properties and structure of BMGs. It is believed that elastostatic compression leads to homogeneous deformation even at room temperature and low stress levels close to the yield strength of the materials. However, why this homogeneous deformation can happen is not clear yet. Our results show that the anisotropy is present although the magnitude of anisotropy is pretty small. Three directions of the structural anisotropy should be emphasized in the future study. They are the loading direction, transverse direction, and

45° direction between the loading and transverse direction. Moreover, the structural evolution of elastostatic compression may be characterized with the in-situ high-energy synchrotron diffraction. It is feasible since the major structural evolution occurring in the first 24 h, when the sample is elastostatically compressed.

Recently, the newly-developed in-situ bulk-metallic-glass-matrix composite demonstrates significantly-improved ductility, even in the tensile case. Macroscopically, the plastic-deformation mechanism of in-situ BMGMGs is characterized by the multiplication of shear bands, caused by the impediment of crystalline phases to the operation of shear bands. The possible micromechanism of the plastic deformation could be the severe lattice distortion and local amorphization in the dendrites, as well as pile-ups of dislocations close to the interface between the dendrites and the glass matrix. Therefore, the detailed structure information can be in-situ characterized with high-energy synchrotron x-ray diffraction.

REFERENCES

1. Inoue A. *Acta Mater* 2000; 48: 279.
2. Loffler JF. *Intermetallics* 2003; 11: 529.
3. Jonson WL. *MRS Bulletin* 1999; 24: 42.
4. Wang WH, Dong C, Shek CH. *Mater Sci Eng A* 2004; 44: 45.
5. Greer AL, Ma E. *MRS Bulletin* 2007; 32: 611.
6. Nishiyama N, Amiya K, Inoue A. *Mater Trans JIM* 2004; 45: 1245.
7. <http://www.liquidmetal.com>.
8. Schuh CA, Hufnagel TC, Ramamurty R. *Acta Mater* 2007; 55: 4067.
9. Spaepen F. *Metall Trans.* 1977; 25: 407.
10. Schroers J, Johnson WL. *Phys Rev Lett* 2004; 93: 255506.
11. Park KW, Lee CM, Lee JH, Lee HG, Lee JC. *Scripta Mater* 2008; 59: 1174.
12. Park KW, Lee CM, Wakeda M, Shibutani Y, Falk ML, Lee JC. *Acta Mater* 2008; 56: 5440.
13. Lee SC, Lee CM, Yang JW, Lee JC. *Scripta Mater* 2008; 58: 591.
14. Lee CM, Park KW, Lee BJ, Shibutani Y, Lee JC. *Scripta Mater* 2009; 61: 911.
15. Lee SC, Lee CM, Lee JC, Kim HJ, Shibutani Y, Fleury E, Falk ML. *Appl Phys Lett* 2008; 92: 151906.
16. Park KW, Lee CM, Kim HJ, Lee JH, Lee JC. *Mater Sci Eng A* 2009; 499: 529.
17. Argon AS. *Acta Mater* 1979; 27: 47.
18. Srolovitz D, Egami T, Vitek V. *Phys Rev B* 1981; 24: 6936.
19. Poulsen HF, Wert JA, Neuefeind J, Honkimaki V, Daymond M. *Nat Mater* 2005; 4: 33.

20. Stoica M, Das J, Bednarcik J, Wang G, Vaughan G, Wang WH, Eckert J. JOM 2010; 62: 76.
21. Wang XD, Bednarcik J, Franz H, Lou HB, He ZH, Cao QP, Jiang JZ. Appl Phys Lett 2009; 94: 011911.
22. Hufnagel TC, Ott RT, Almer J. Phys Rev B 2006; 73: 064204.
23. Wang XD, Bednarcik J, Saksli K, Franz H, Cao QP, Jiang JZ. Appl Phys Lett 2007; 91: 081913.
24. Das J, Boström M, Mattern N, Kvick A, Yavari AR, Greer AL, Eckert J. Phys Rev B 2007; 76: 092203.
25. Mattern N, Bednarcik J, Pauly S, Wang G, Das J, Eckert J. Acta Mater. 2009; 57: 4133.
26. Wang G, Mattern N, Pauly S, Bednarcik J, Eckert J. Appl Phys Lett 2009; 95: 251906.
27. <http://en.wikipedia.org/wiki/Glass>.
28. [http:// en.wikipedia.org/wiki/Amorphous_metal](http://en.wikipedia.org/wiki/Amorphous_metal).
29. Klement W, Willens RH, Duwez P. Nature 1960; 187: 869.
30. Chen HS, Turnbull D. J Chem Phys 1968; 48: 2560.
31. Chen HS, Turnbull D. Acta Metall 1969; 17: 1021.
32. Chen HS. Acta Metall 1974; 22: 1505.
33. Drehman AJ, Greer AL, Turnbull D. Appl Phys Lett 1982; 41: 716.
34. Kui HW, Greer AL, Turnbull D. Appl Phys Lett 1984; 45: 615.
35. Inoue A, Zhang T, Masumoto T. Mater Trans JIM 1989; 30: 965.
36. Inoue A. Acta Mater 2000; 48: 279.

37. Inoue A, Nakamura T, Nishiyama N, Masumoto T. Mater Trans JIM 1992; 33: 937.
38. Inoue A. Mater Trans JIM 1995; 36: 866.
39. Inoue A, Zhang T, Nishiyama N, Ohba K, Masumoto T. Mater Trans JIM 1993; 34: 1234.
40. Peker A, Johnson WL. Appl Phys Lett 1993; 63: 2342.
41. Inoue A, Zhang W. Mater Trans JIM 2004; 45: 1210.
42. Zhang QS, Zhang HF, Deng YF, Ding BZ, Hu ZQ. Scripta Mater 2003; 49: 273.
43. Yi S, Park TG, Kim DH. J Mater Res 2000; 15: 2425.
44. Choi-Yim H, Xu DH, Johnson WL. Appl Phys Lett 2003; 82: 1030.
45. Lin XH, Johnson WL. J Appl Phys 1995; 78: 6514.
46. He G, Eckert J, Hagiwara M. J of Appl Phys 2004; 95: 1816.
47. Inoue A, Nakamura T, Nishiyama N, Masumoto T. Mater Trans JIM 1992; 33: 937.
48. Inoue A, Masumoto T. Mater Sci Eng A 1993; 173: 1.
49. Zhang T, Inoue A. Mater Trans JIM 2002; 43: 708.
50. Louzguine DV, Inoue A. J of Mater Res 2002; 17: 2112.
51. He Y, Dougherty GM, Shiflet GJ, Poon SJ. Acta Metall 1993; 41: 337.
52. Inoue A, Sobu S, Louzguine DV, Kimura H, Sasamori K. J of Mater Res 2004; 19: 1539.
53. Ponnambalam V, Poon SJ, Shiflet GJ. J of Mater Res 2004; 19: 1320.
54. Lu ZP, Liu CT, Thompson JR, Porter WD. Phys Rev Lett 2004; 92: 245503.
55. Inoue A, Nishiyama N, Matsuda T. Mater Trans JIM 1996; 37: 181.

56. He Y, Schwarz RB, Archuleta JJ. Appl Phys Lett 1996; 69: 1861.
57. Cohen MH, Turnbull D. J Chem Phys. 1959; 31: 1164.
58. Polk DE, Turnbull D. Acta Metall 1972; 20: 493.
59. Shi FG, Nieh TG, Chou YT. Scripta Mater 2000; 43: 265.
60. Egami T. JOM 2010; 62: 70.
61. Kittel C, '*Introduction to solid state physics*', 7th edition, 1996.
62. Kunzi HU. Top Appl Phys 1983; 53: 169.
63. Courtney TH. Mechanical behavior of materials. Boston, MA: McGraw-Hill; 2000.
64. Jovanovic S, Smith CS. J Appl Phys 1961; 32: 161.
65. Ashby MF, Nelson AN, Centamore RMA. Scripta Metall 1970; 4: 715.
66. Masumoto T, Maddin R. Acta Metall 1971; 19: 725.
67. Golding B, Bagley BG, Hsu FSL. Phys Rev Lett 1972; 29: 68.
68. Chen HS. J Appl Phys 1978; 49: 3289.
69. Weaire D, Ashby MF, Logan J, Weins MJ. Acta Metall 1971; 19: 779.
70. Suzuki Y, Egami T. J Non-Cryst Solids 1985; 75: 361.
71. Lu J, Ravichandran G, Johnson WL. Acta Mater 2003; 51: 3429.
72. Lewandowski JJ, Greer AL. Nat Mater 2006; 5: 15.
73. Leamy HJ, Chen HS, Wang TT. Metall. Trans. 1972; 3: 699.
74. Pampillo CA. J Mater Sci 1975; 10: 1194.
75. Wright WJ, Saha R, Nix WD. Mater Trans JIM 2001; 42: 642.
76. Masumoto T, Maddin R. Mater Sci Eng 1975; 19: 1.
77. Waseda Y, Aust KT, Masumoto T. Scr Metall 1979; 13: 187.

78. Calvayrac Y, Harmelin M, Quivy A, Chevalier JP, Bigot J. *Scr Metall* 1980; 14: 895.
79. Koba ES, Milman YV, Rachek AP. *Acta Metall Mater* 1994; 42: 1383.
80. Pekarskaya E, Kim CP, Johnson WL. *J Mater Res* 2001; 16: 2513.
81. Li J, Spaepen F, Hufnagel TC. *Philos Mag A* 2002; 82: 2623.
82. Jiang WH, Atzmon M. *Acta Mater* 2003; 51: 4095.
83. Wright TW. *The physics and mathematics of adiabatic shear bands*. Cambridge: Cambridge University Press; 2002.
84. Deng DG, Lu BH. *Scripta Metall* 1983; 17: 515.
85. Cahn RW, Pratten NA, Scott MG, Sinning HR, Leonardsson L. *Mater Res Soc Proc* 1984; 28: 241.
86. Bever MB, Holt DL, Titchene AI. *Prog Mater Sci* 1972; 17: 5.
87. Chen HS. *Appl Phys Lett* 1976; 29: 328.
88. Vandenbeukel A, Sietsma J. *Acta Metall Mater* 1990; 38: 383.
89. Puska MJ, Nieminen RM. *Rev Mod Phys* 1994; 66: 841.
90. Nasu T, Nagaoka K, Itoh F, Suzuki K. *J Phys Soc Japan* 1989; 58: 894.
91. Donovan PE, Stobbs WM. *Acta Metall* 1981; 29: 1419.
92. Demetriou MD, Johnson WL. *Acta Mater* 2004; 52: 3403.
93. Chaudhari P and Turnbull D. *Science* 1978; 199: 4324.
94. Zachariasen WH. *J Am Chem Soc* 1932; 58: 3841.
95. Cargill GS, *J Appl Phys* 1970; 41: 2248.
96. Sadoc JF, Dixmier J, Guinier A. *J Non-Cryst Solids* 1973; 12: 46.
97. Frank FC. *Proc R Soc London Ser A* 1952; 215: 43.

98. Egami T, Srolovitz D. J Phys F 1982; 12: 2141.
99. Cahn RW. Nature 1978; 274: 848.
100. Nagel SR, Tauc J Phys Rev Lett 1975; 35: 380.
101. Yavari AR. Nature 2006; 439: 405.
102. Miracle DB. Nat Mater 2004; 3: 697.
103. Sheng HW, Luo WK, Alamgir FM, Bai JM, Ma E. Nature 2006; 439: 419.
104. McGreevy RL. J Phys Condens Matter 2001; 13: R877.
105. Payne MC, Teter MP, Allan DC, Arias TA, Joannopoulos JD. Rev Mod Phys 1992; 64: 1045.
106. Finney JL. Nature 1977; 266: 309.
107. Bernal JD. Nature 1960; 185: 68.
108. Greer AL. Science 1995; 267: 1947.
109. Hammersley AP, Svensson SO, Hanfland M, Fitch AN, Häusermann D. High Pressure Res 1996; 14: 235.
110. Dmowski W, Egami T. J Mater Res 2007; 22: 412.
111. Suzuki Y, Haimovich J, Egami T. Phys Rev B 1987; 35: 2162.
112. Egami T, Dmowski W, Kosmetatos P, Boord M, Tomida T, Oikawa E, Inoue A. J Non-Crys Solids 1995; 193: 591.
113. Egami T, Maeda K, Vitek V. Philos Mag A 1980; 41: 883.
114. Ott RT, Mendelev MI, Besser MF, Kramer MJ, Almer J, Sordet DJ. Phys Rev B 2009; 80: 064101.
115. Mendelev MI, Ott RT, Kramer MJ, Sordet DJ. J Appl Phys 2009; 105: 023509.
116. Kumar G, Ohkubo T, Mukai T, Hono K. Scripta Mater 2007; 57: 173.

117. Kim KB, Das J, Baier F, Tang MB, Wang WH, Eckert J. Appl Phys Lett 2006; 88: 051911.
118. Zhu ZW, Zheng SJ, Zhang HF, Ding BZ, Hu ZQ, Liaw PK, Wang YD, Ren Y. J Mater Res 2008; 23: 941.
119. Cheng YQ, Cao AJ, Sheng HW, Ma E. Acta Mater 2008; 56: 5263.
120. Yu P, Bai HY, Tang MB, Wang WL. J Non-Cryst Solids 2005; 351: 1328.
121. Yu P, Bai HY. Mater Sci Eng A 2008; 485: 1.
122. Migliori A, Sarrao JL. Resonant Ultrasound Spectroscopy: Applications to Physics, Materials Measurements and Nondestructive Evaluation, Wiley, New York, 1997.
123. Cheng YQ, Ma E, Sheng HW. Phys Rev Lett 2009; 102: 245501.
124. Luo WK, Sheng HW, Alamgir FM, Bai JM, He JH, Ma E. Phys Rev Lett 2004; 92: 145502.
125. Kelton KF, Lee GW, Gangopadhyay AK, Hyers RW, Rathz TJ, Rogers JR, Robinson MB, Robinson DS. Phys Rev Lett 2003; 90: 195504.
126. Johnson WL, Samwer K. Phys Rev Lett 2005; 95: 195501.
127. Demetriou MD, Harmon JS, Tao M, Duan G, Samwer K, Johnson WL. Phys Rev Lett 2006; 97: 065502.
128. Johnson WL, Demetriou MD, Harmon JS, Lind ML, Samwer K. MRS Bulletin 2007; 32: 644.
129. Cheng YQ, Cao AJ, Ma E. Acta Mater 2009; 57: 3253.
130. Stief PS, Spaepen F, Hutchinson JW. Acta Metall 1982; 30: 447.
131. Chen H, He Y, Shiflet GJ, Poon SJ. Nature 1994; 367: 541.

132. Choi-Yim H, Johnson WL. Appl Phys Lett 1997; 71: 3808.
133. Kato H, Inoue A. Mater Trans JIM 1997; 38: 793.
134. Hays CC, Kim CP, Johnson WL. Phys Rev Lett 2000; 84: 2901.
135. Fan C, Ott RT, Hufnagel TC. Appl Phys Lett 2002; 81: 1020.
136. Lee ML, Li Y, Schuh CA. Acta Mater 2004; 52: 4121.
137. Fan C, Inoue A. Appl Phys Lett 2000; 77: 46.
138. Das J, Tang MB, Kim KB, Theissmann R, Baier F, Wang WH, Eckert J. Phys Rev Lett 2005; 94: 205501.
139. Kim KB, Das J, Baier F, Tang MB, Wang WH, Eckert J. Appl Phys Lett 2006; 88: 051911.
140. Kim KB, Das J, Venkataraman S, Yi S, Eckert J. Appl Phys Lett 2006; 89: 071908.
141. Mao J, Zhang HF, Fu HM, Wang AM, Li H, Hu ZQ. Adv Eng Mater 2010; 12: 170.
142. Mao J, Zhang HF, Fu HM, Wang AM, Li H, Hu ZQ. Mater Sci Eng A 2010; 527: 981.
143. Kumar G, Ohkubo T, Hono K. J Mater Res 2009; 24: 2353.
144. Chen LY, Setyawan AD, Kato H, Inoue A, Zhang GQ, Saida J, Wang XD, Cao QP, Jiang JZ. Scripta Mater 2008; 59: 75.
145. Qiu X, Thompson JW, Billinge SJL. J Appl Cryst 2004; 37: 678.
146. Zeng K, Hamalainen M, Lukas HL. J Phase Equilib 1994; 15: 577.
147. Slipenyuk A, Eckert J. Scripta Mater 2004; 50: 39.
148. Kanungo BP, Glade SC, Kumar PA, Flores KM. Intermetallics 2004; 12: 1073.

149. Bhowmick R, Raghavan R, Chattopadhyay K, Ramamurty U. *Acta Mater* 2006; 54: 4221.
150. Santos FS, Franco IP, Miyamoto MI, Bolfarini C, Botta WJ, Kiminami CS. (11th Intl. Conf. on Advanced Mater. Symp. Proc.).
151. Jiang WH, Liu FX, Wang YD, Zhang HF, Choo H, Liaw PK. *Mater Sci Eng A* 2006; 430: 350.
152. Huang YJ, Shen J, Sun JF. *Appl Phys Lett* 2007; 90: 081919.
153. Yan X, Hirscher M, Egami T, Marinero EE. *Phys Rev B* 1991; 43: 9300.
154. Yan X, Egami T, Marinero EE. *J Appl Phys* 1991; 69: 5448.
155. Bei H, Xie S, George EP. *Phys Rev Lett* 2006; 96: 105503.
156. Shi Y, Katz B, Li H, Falk ML. *Phys Rev Lett* 2007; 98: 185505.
157. Yokoyama Y, Fujita K, Yavari AR, Inoue A. *Philos Mag Lett* 2009; 89: 322.
158. Qiao DC, Huang L, Jiang WH, Fan C, Liaw PK. *Metall Mater Trans A* 2010; 41A: 1787.
159. Jiang WH, Liu FX, Qiao DC, Choo H, Liaw PK. *J Mater Res* 2006; 21: 1570.
160. Jiang WH, Fan GJ, Liu FX, Wang GY, Choo H, Liaw PK. *J Mater Res* 2006; 21: 2164.
161. Jiang WH, Jiang F, Liu FX, Choo H, Liaw PK, Qiu KQ. *Appl Phys Lett* 2006; 89: 261909.
162. Kimura H, Masumoto T. *Acta Metall* 1983; 31: 231.
163. Schuh CA, Lund AC, Nieh TG. *Acta Mater.* 2004; 52(20): 5879.
164. Ott RT, Kramer MJ, Besser MF, Sordellet DJ. *Acta Mater* 2006; 54: 2463.

APPENDIX

Table 1. The values for Young's Modulus E and Poisson's ratio ν for the metallic glasses in the literatures [20].

Composition	Experiment	E(GPa)	ν
$Zr_{64.13}Cu_{15.75}Ni_{10.12}Al_{10}$	Tensile, synchrotron[20]	94	0.325
	Ultrasound[20]	78	0.377
$Zr_{62}Al_8Ni_{13}Cu_{17}$	Tensile, synchrotron[23]	83	0.37
	Ultrasound[23]	80	0.38
$La_{62}Al_{14}(Cu_{5/6}Ag_{1/6})_{14}Co_5Ni_5$	Tensile, synchrotron[23]	34	0.36
	Ultrasound[23]	35	0.36
$Cu_{50}Zr_{50}$	Tensile, synchrotron[25]	63	0.31
	Ultrasound[20]	83	0.384
$Cu_{65}Zr_{35}$	Tensile, synchrotron[25]	97	0.33
	Ultrasound[20]	92	0.352
$Mg_{60}Cu_{30}Y_{10}$	Compression, synchrotron[19]	64.1	0.373
	Ultrasound[20]	51.5	N/A
$Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$	Compression, synchrotron[22]	87	0.34
	Macroscopic compression[20]	82	0.362
$Cu_{47.5}Zr_{47.5}Al_5$	Compression, synchrotron[24]	99.2	0.34
	Ultrasound[24]	90.1	0.365
$Zr_{55}Cu_{20}Ni_{10}Al_{10}Ti_5$	Compression, synchrotron[24]	91.1	0.38
	Ultrasound[24]	85.5	0.378

Table 2. Elastic constants measured from the x-ray (XR) and resonant ultrasonic spectroscopy (RUS) measurements: Young's modulus, E and Poisson's ratio, ν .

Alloy composition	E_{XR} (GPa)	ν_{XR}	E_{RUS} (GPa)	ν_{RUS}
Cu ₄₇ Zr ₄₇ Al ₆	99.8	0.393	90.2	0.3785
Cu ₄₆ Zr ₄₆ Al ₈	102.1	0.372	92.8	0.3634

Table 3. The glass transition temperature (T_g), the onset crystallization temperature (T_x), the supercooled region (ΔT), and the structural relaxation exothermic heat (ΔH_0) for the IC (1550), IC (1250), and SC glass-forming alloys.

Alloy composition		T_g (K)	T_x (K)	ΔT	ΔH_0
Zr ₅₅ Ni ₅ Al ₁₀ Cu ₃₀	IC(1550K)	672.8	745.8	73	2.3
	IC(1250K)	671.5	755.3	83.8	0.8
	SC	670.2	758.2	88	2.8

Table 4. Plastic strain, yield stress, Young's modulus (E), and Poisson's ratio (ν) of the IC (1550), IC (1250), and SC glass-forming alloys.

Alloy composition		Plastic strain (%)	Yield stress (MPa)	E (GPa)	ν
Zr ₅₅ Ni ₅ Al ₁₀ Cu ₃₀	IC (1550 K)	0.52	1925	88.7	0.374
	IC (1250 K)	0.7	1906	–	–
	SC	1.7	1816	85.4	0.375

Table 5. Direction-dependent r_i and coordination numbers N_i of nearest neighbourhood in $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass under compressive stress.

	$\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$		
	$\sigma = 0 \text{ MPa}$	$\sigma = 1200 \text{ MPa}$	$\sigma = 1200 \text{ MPa}$
	$\rho(r)$	$\rho(r, \varphi = 90^\circ)$	$\rho(r, \varphi = 0^\circ)$
$r_1 (\text{\AA})$	2.6631	2.6464	2.6689
$r_2 (\text{\AA})$	3.1827	3.1445	3.1949
N_1	2.34	2.43	2.3
N_2	9.94	9.4	10.16
$N_1 + N_2$	12.28	11.83	12.46

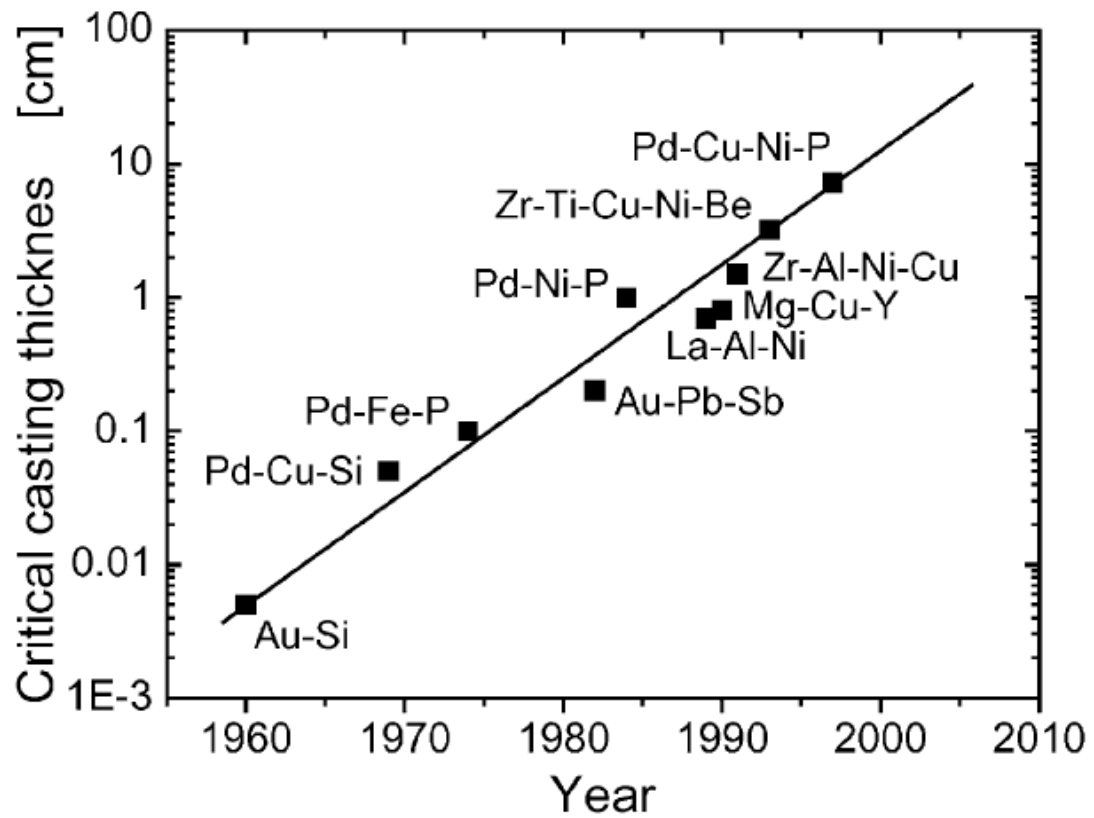


Figure 1. Critical casting thickness for glass formation as a function of the year the corresponding alloy was discovered [2].

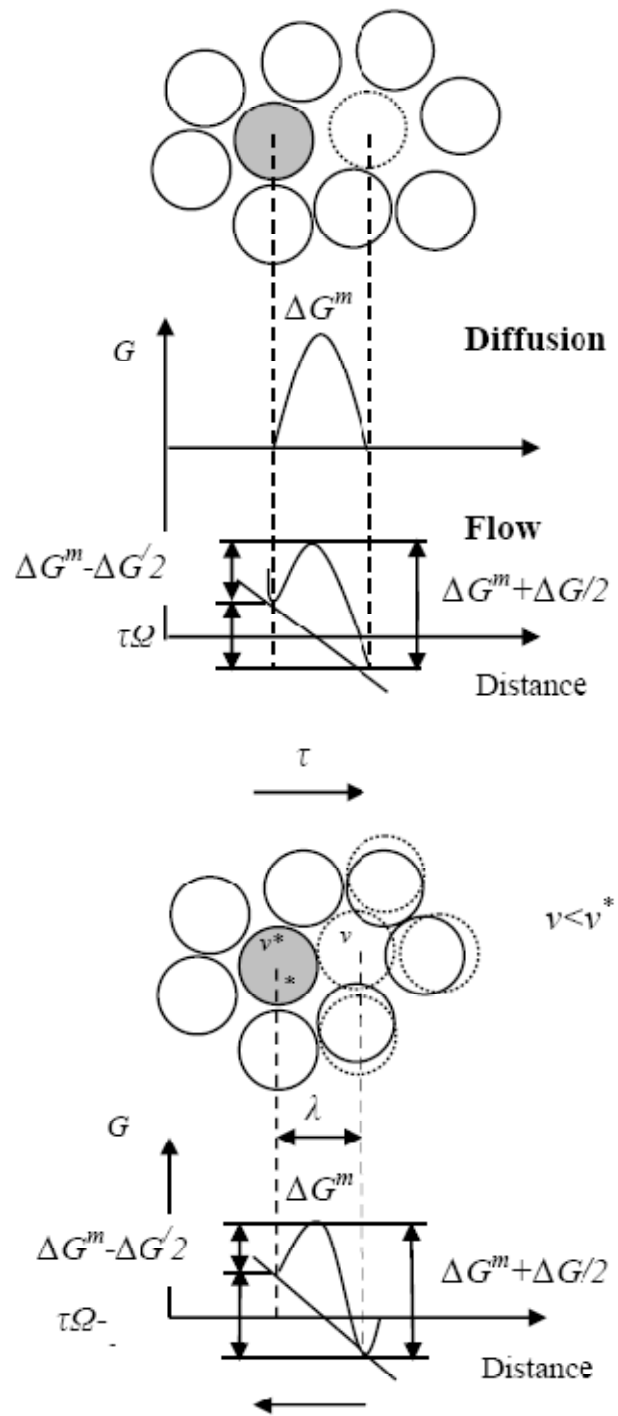


Figure 2. Free-volume model. Top: Plastic flow; Bottom: Free-volume evolution. [9]

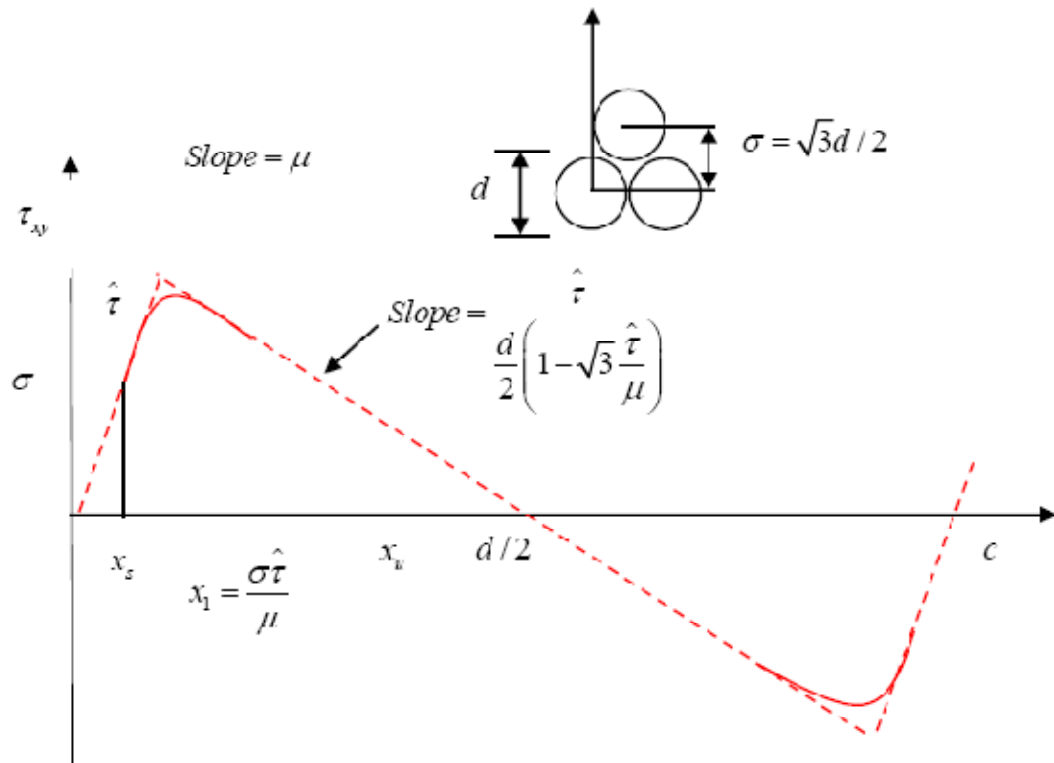


Figure 3. Shape of the assumed interlayer shear resistance of a metallic glass: solid curve after Foreman and dotted curve actually using a linear approximation. [17]

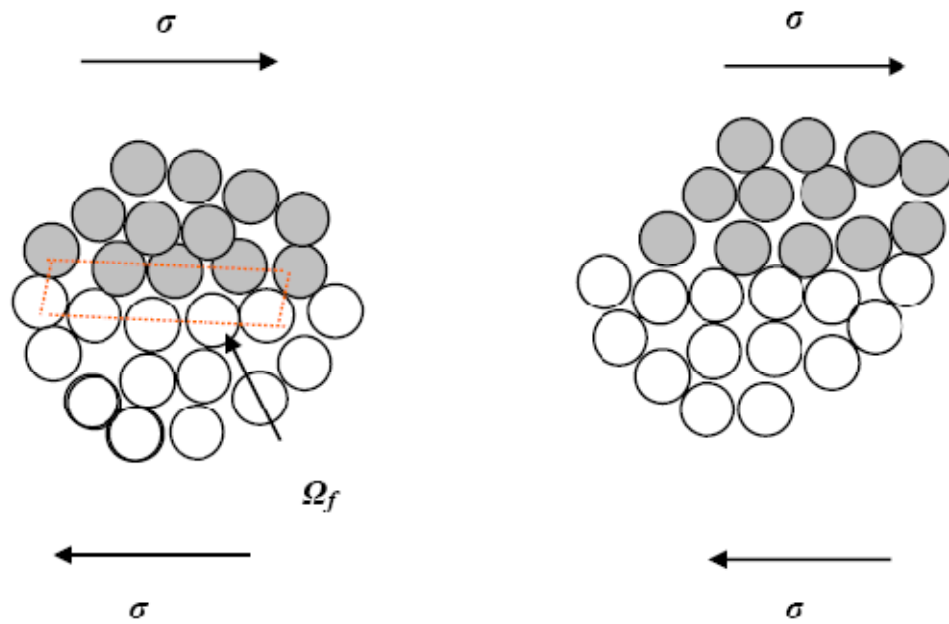


Figure 5. A more intense shear transformation in a disk-shaped volume element, which is favored at low temperature. [17]

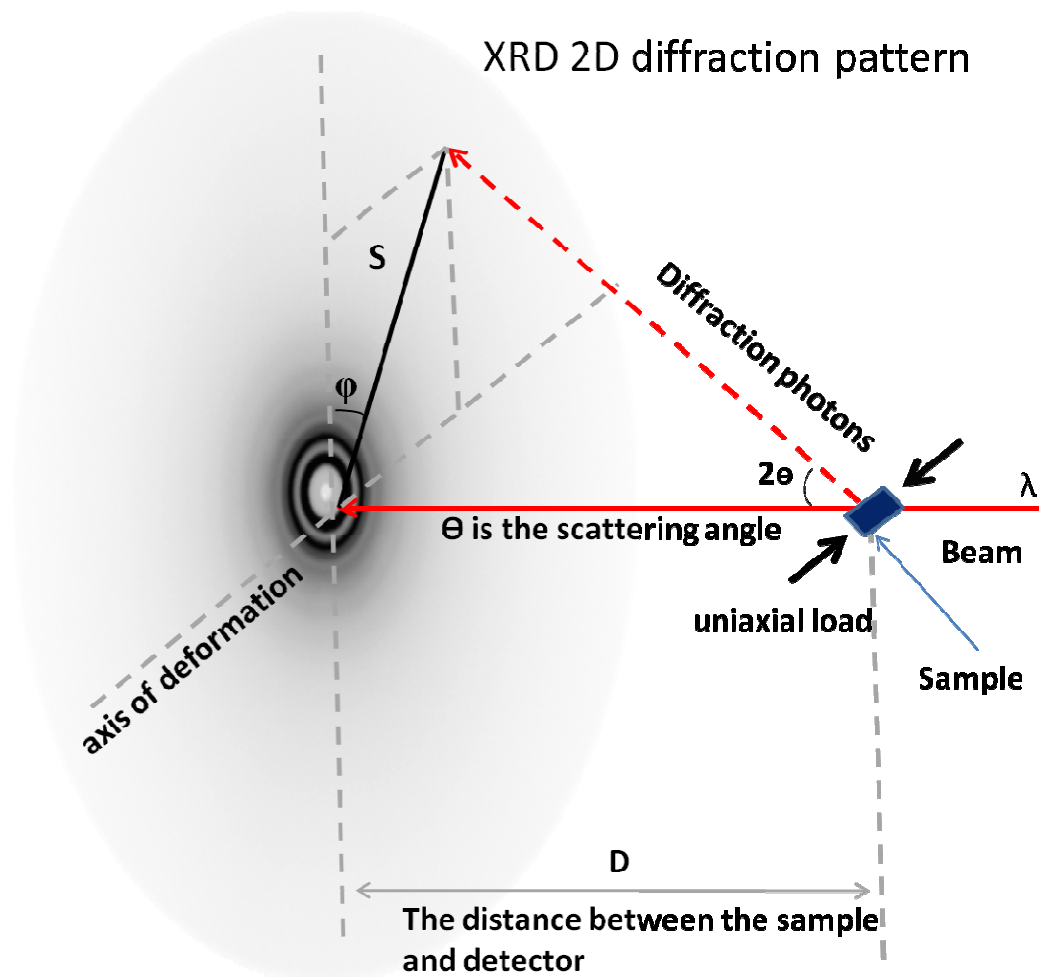


Figure 6. A sketch of a typical in-situ high-energy synchrotron x-ray diffraction experiment. [20]

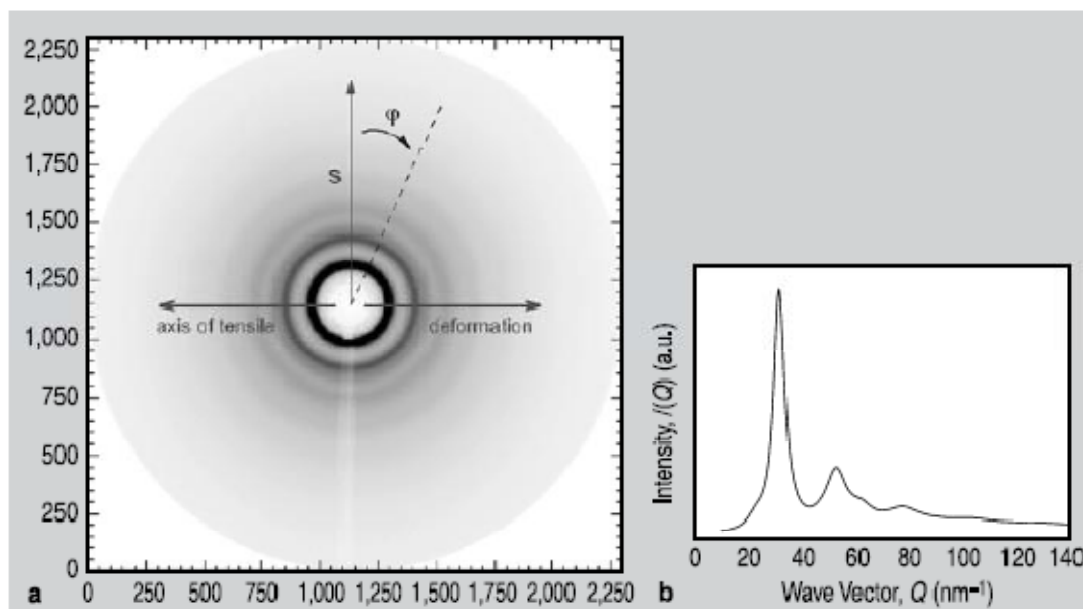


Figure 7. (a) Diffraction image as recorded by the MAR 345 2D image plate detector for $\text{Zr}_{64.13}\text{Cu}_{15.75}\text{Ni}_{10.12}\text{Al}_{10}$ BMG. The polar coordinates (s , ϕ) and the axis of tensile deformation are depicted. (b) X-ray diffraction pattern resulting from integration among the polar coordinates (s , ϕ) of the image presented in (a). [20]

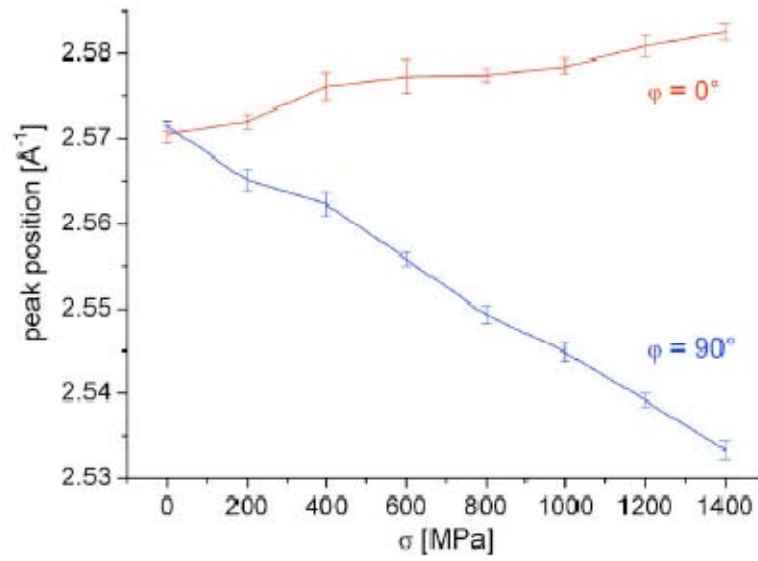


Figure 8. Change in the first peak position with applied tensile stress observed in the tensile ($\varphi = 90^\circ$) and transversal ($\varphi = 0^\circ$) direction. [20]

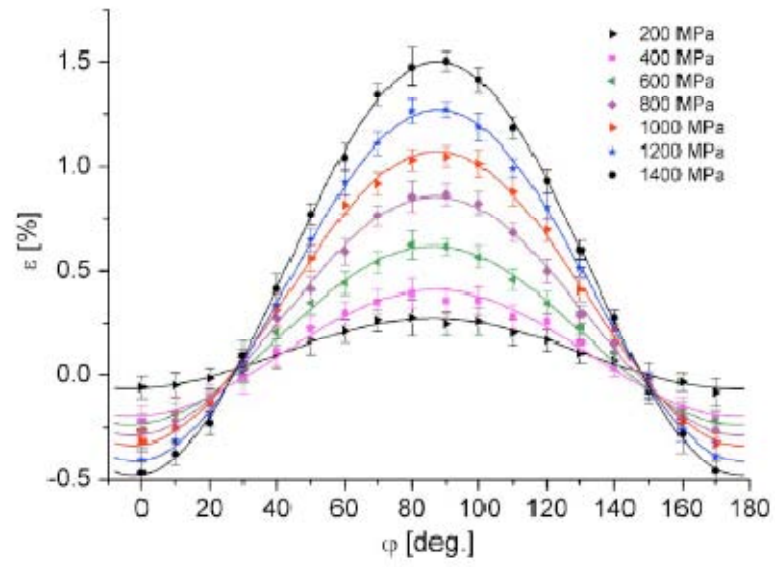


Figure 9. Angular dependence of the strain determined at various stages of tensile deformation. The full line denotes fits of the experimental data to equation. [20]

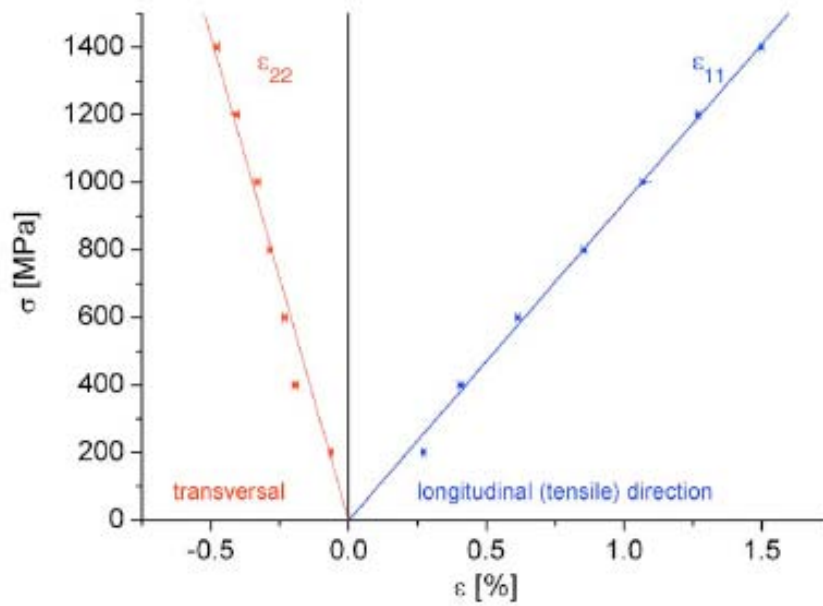


Figure 10. Stress-strain curves for different strain tensor components. The lines correspond to the fit of the data to a linear function starting from the origin of the coordinate system. [20]

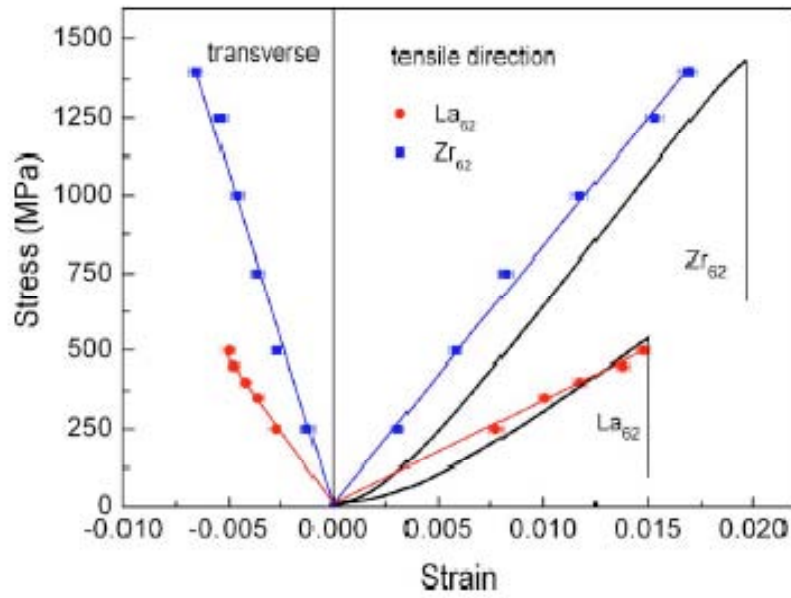


Figure 11. Strains determined from the diffraction data of tensile/transverse directions. In addition, the tensile stress-strain curves of Zr₆₂Al₈Ni₁₃Cu₁₇ and La₆₂Al₁₄(Cu_{5/6}Ag_{1/6})₁₄Co₅Ni₅ BMGs are also included for comparison. [23]

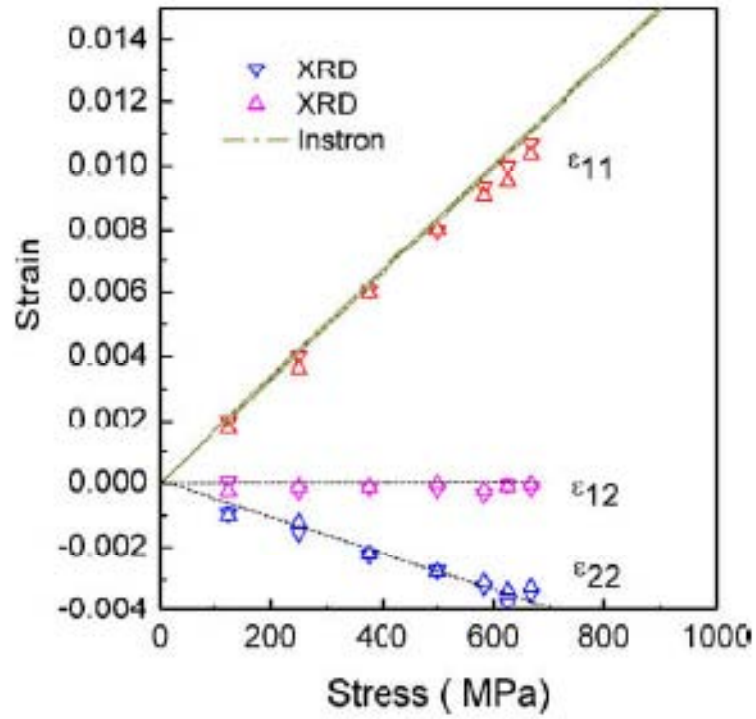


Figure 12. Strain vs. applied stress of $\text{Cu}_{50}\text{Zr}_{50}$ glass measured by XRD and mechanical testing. [25]

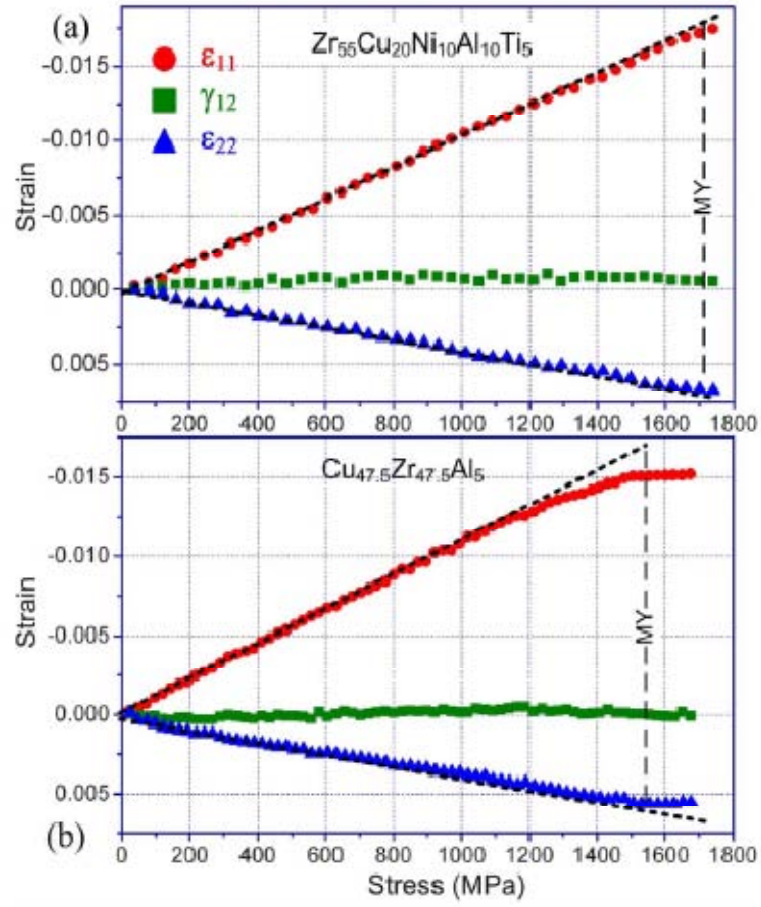


Figure 13. Evolution of elastic strain components of (a) $\text{Zr}_{55}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}\text{Ti}_5$ and (b) $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ during loading. The increment of ϵ_{11} and ϵ_{22} strains deviates from linearity on atomic scale before the onset of macroscopic yielding. [24]

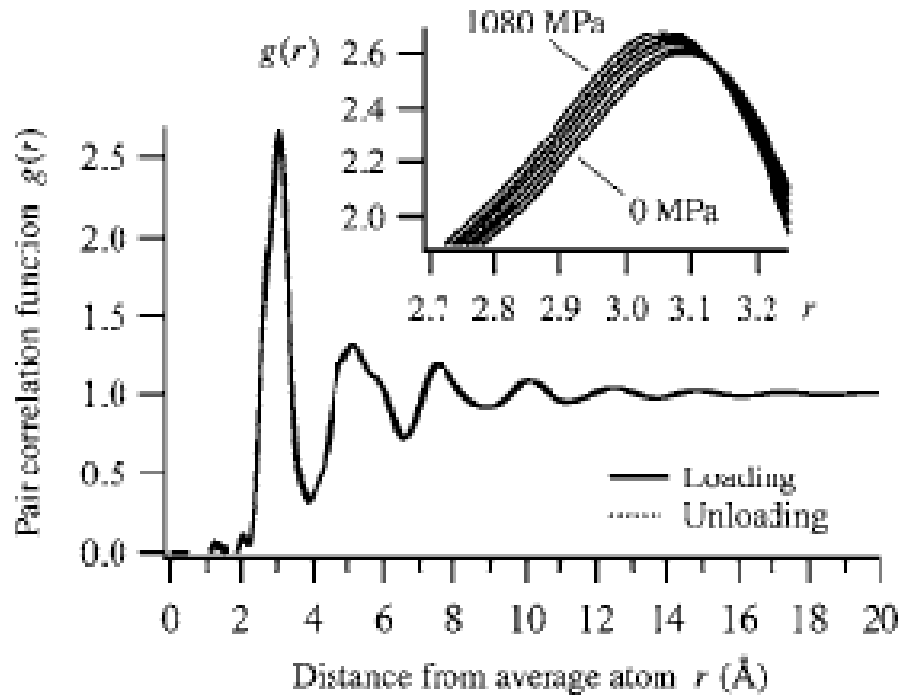


Figure 14. Pair correlation function $g(r)$ calculated from the $S(Q)$. Inset: shift in the first peak in $g(r)$ to smaller r with increasing compressive stress. [22]

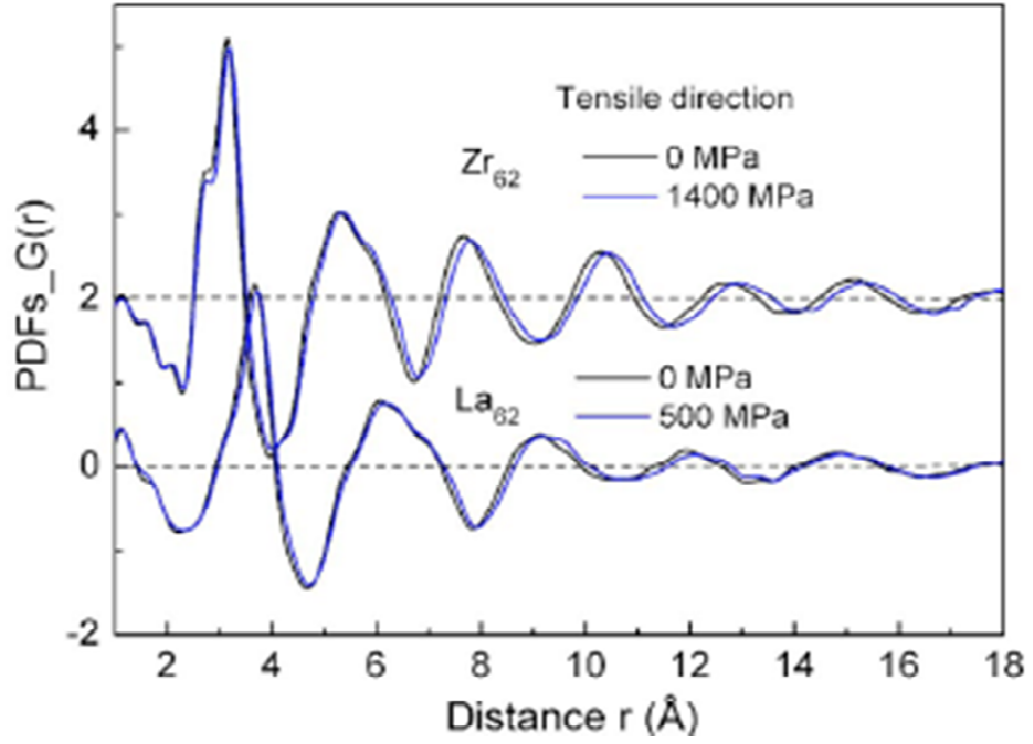


Figure 15. Pair distribution function $G(r)$ of as-cast and tensioned samples for $\text{Zr}_{62}\text{Al}_8\text{Ni}_{13}\text{Cu}_{17}$ and $\text{La}_{62}\text{Al}_{14}(\text{Cu}_{5/6}\text{Ag}_{1/6})_{14}\text{Co}_5\text{Ni}_5$ BMGs. [21]

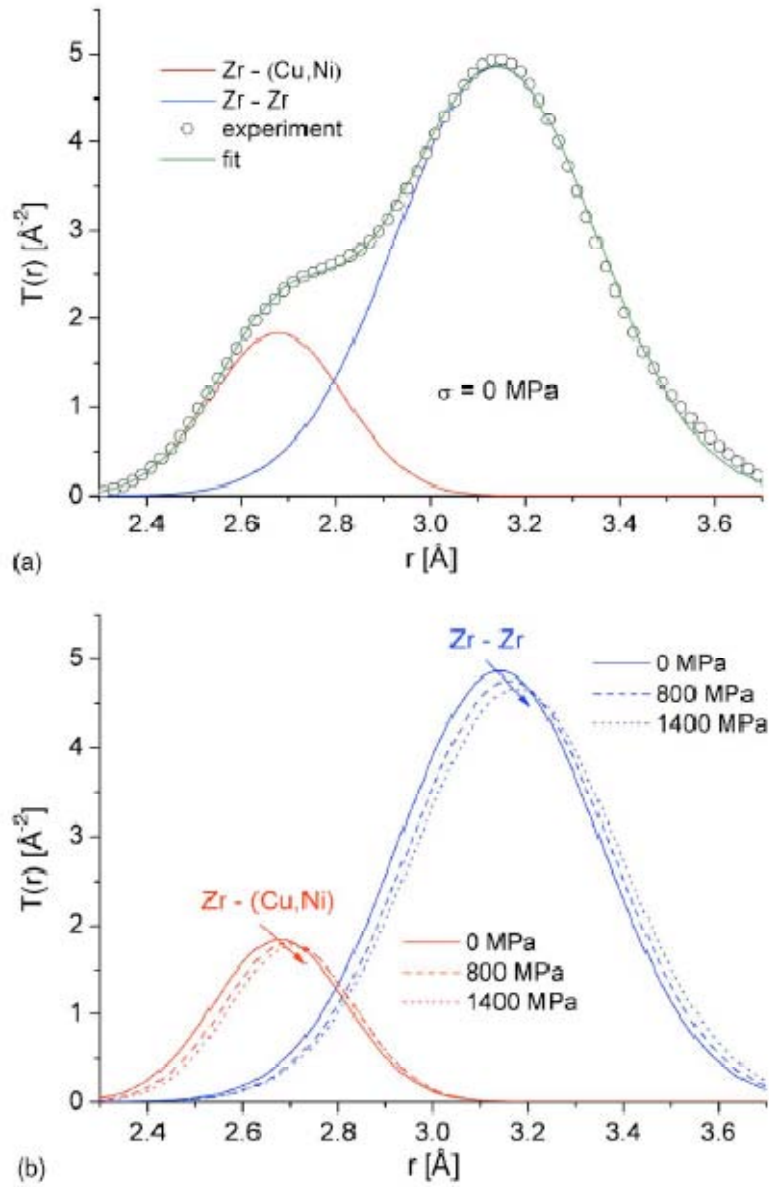


Figure 16. (a) Deconvolution of the first coordination shell into two Gaussians for an unloaded sample and (b) at different stages of deformation. [20]

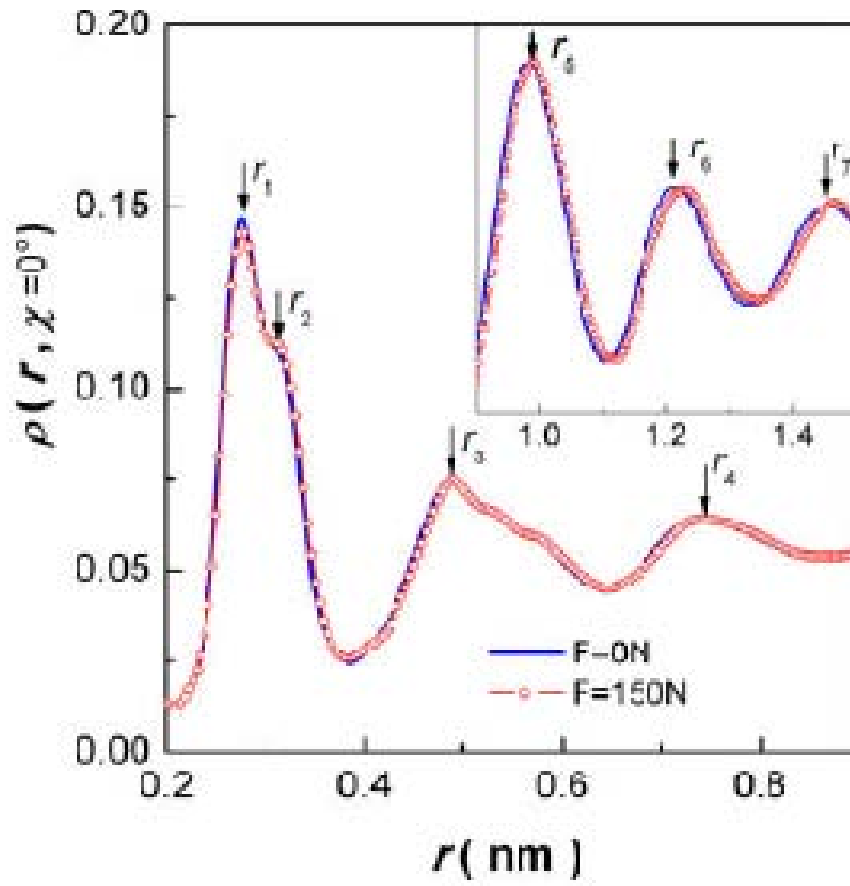


Figure 17. Atomic density $\rho(r, \chi = 0)$ of $\text{Cu}_{50}\text{Zr}_{50}$ glass in the tensile direction vs. load. [25]

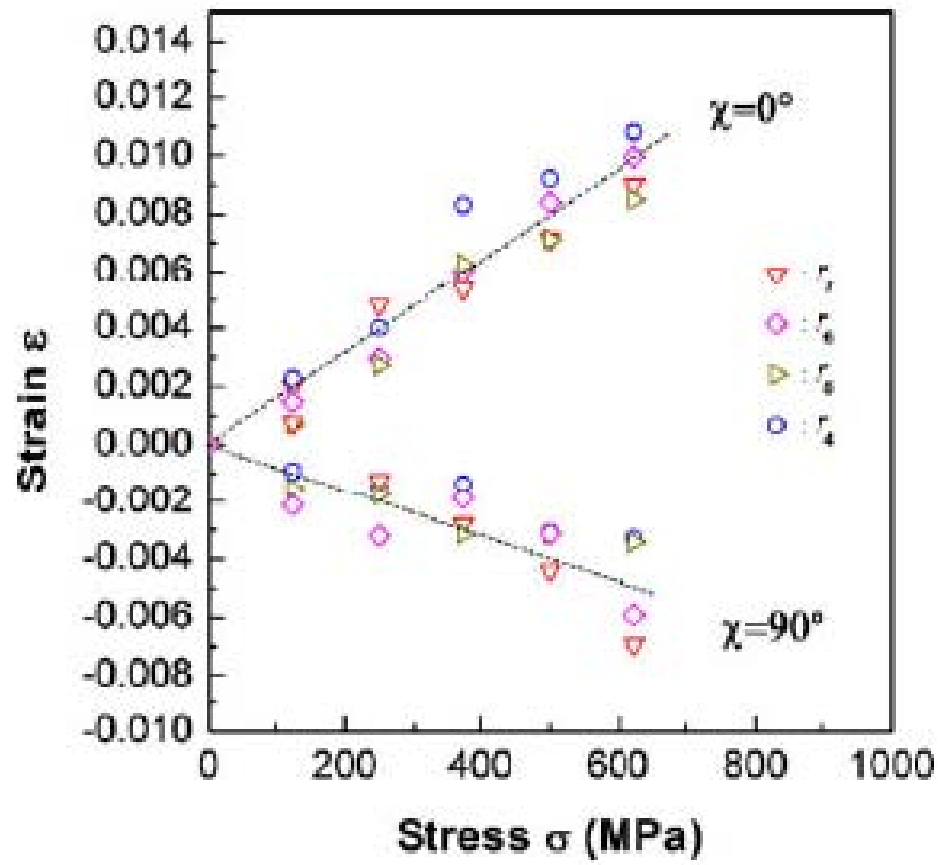


Figure 18. Strain vs. applied load of $\text{Cu}_{50}\text{Zr}_{50}$ glass determined from the shift of maxima positions r_i of $\rho(r, \chi)$. [25]

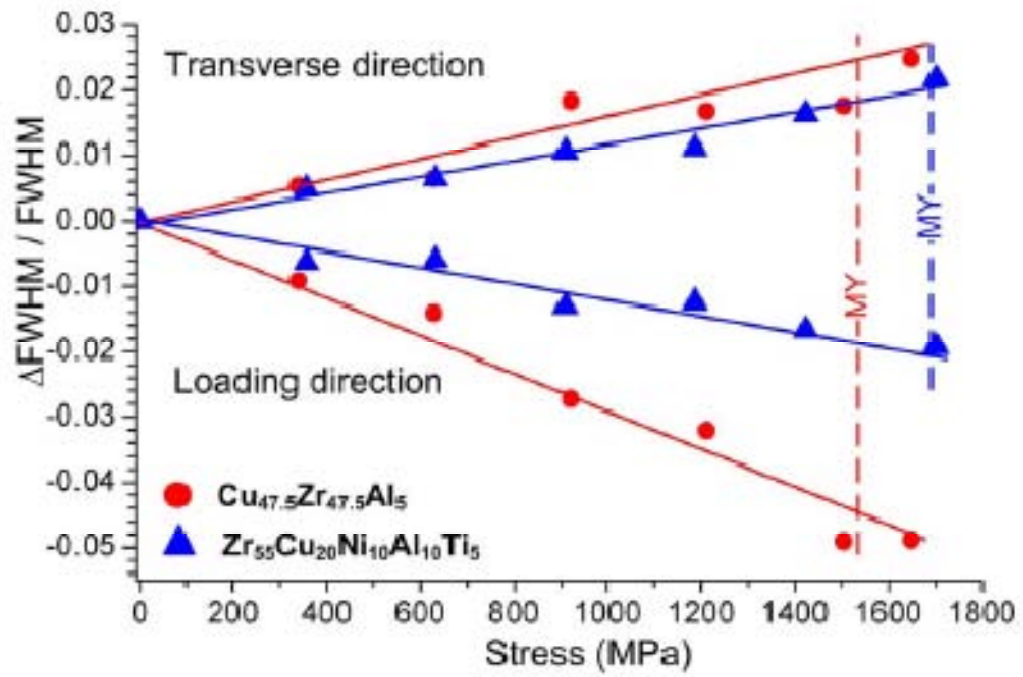


Figure 19. The change of width [full width at half maximum (FWHM)] with applied stress for the “plastic” $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ is higher than for the macroscopically “brittle” $\text{Zr}_{55}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}\text{Ti}_5$. [24]

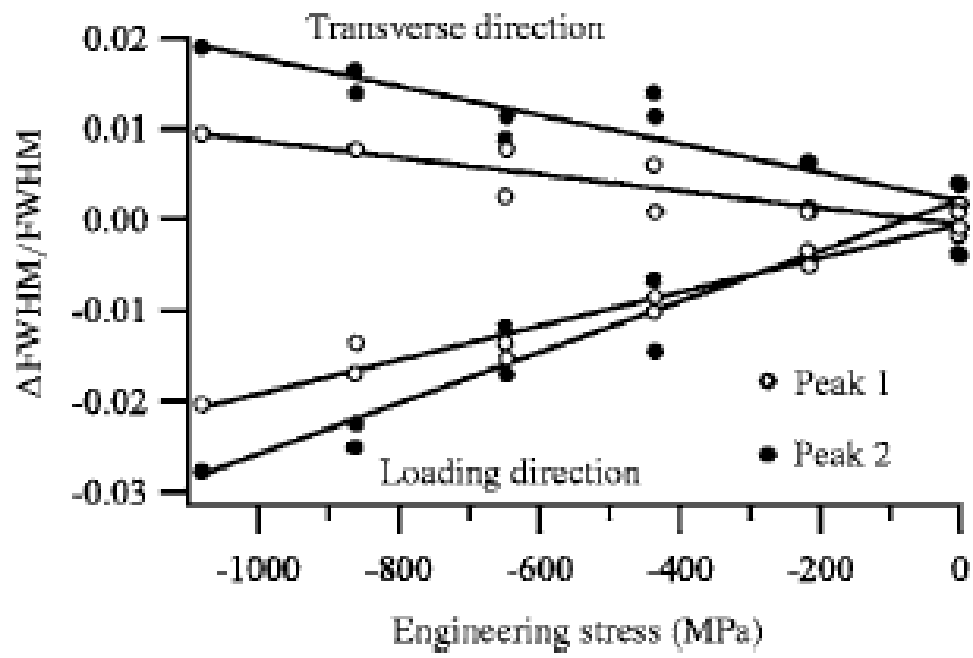


Figure 20. Change in the widths (FWHM) of the two overlapping peaks in the RDF. [22]

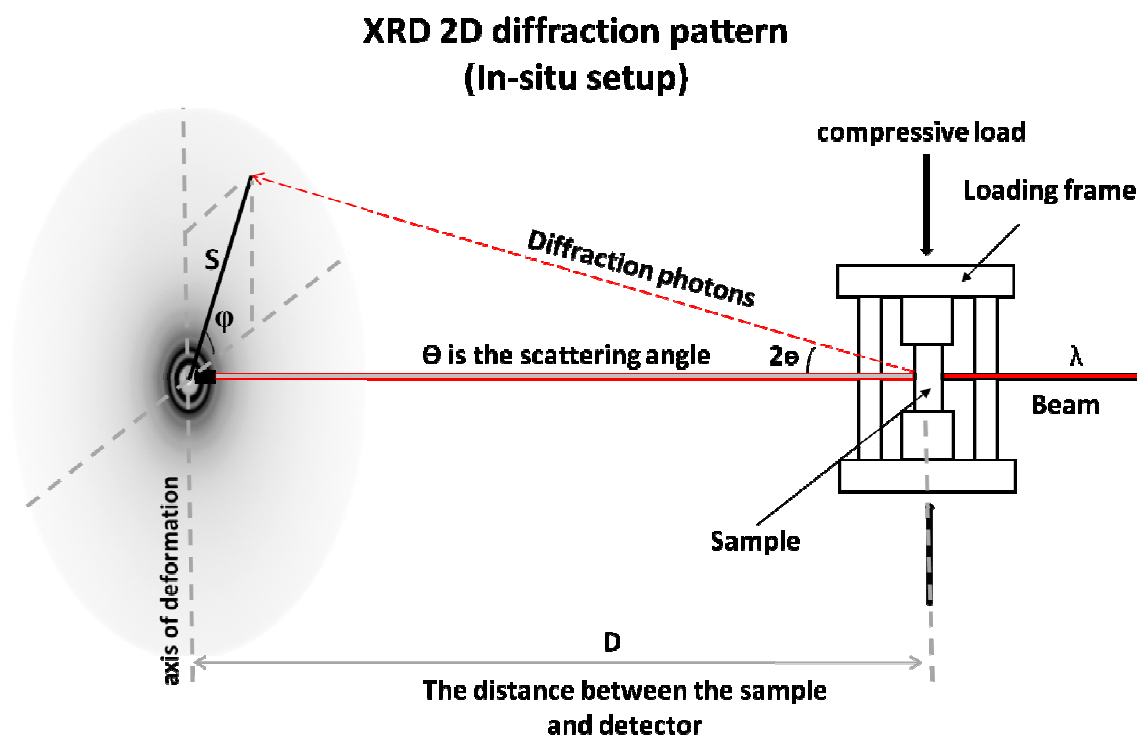


Figure 21. Schematic view of the scattering setup for in-situ compression tests.

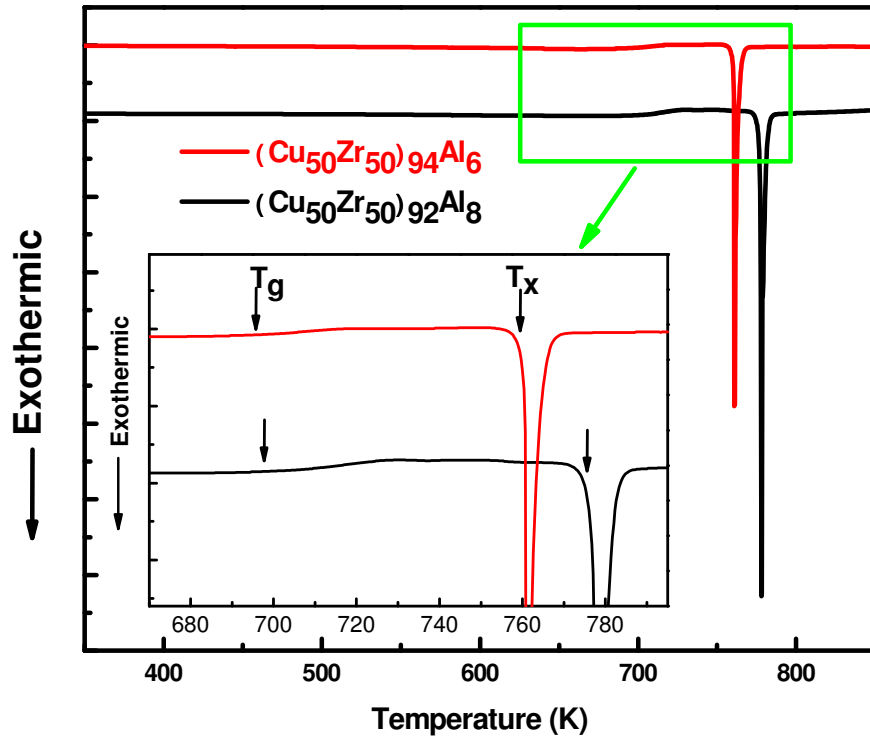


Figure 22. DSC traces of $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ glass-forming alloys at a heating rate of 20 K/min.

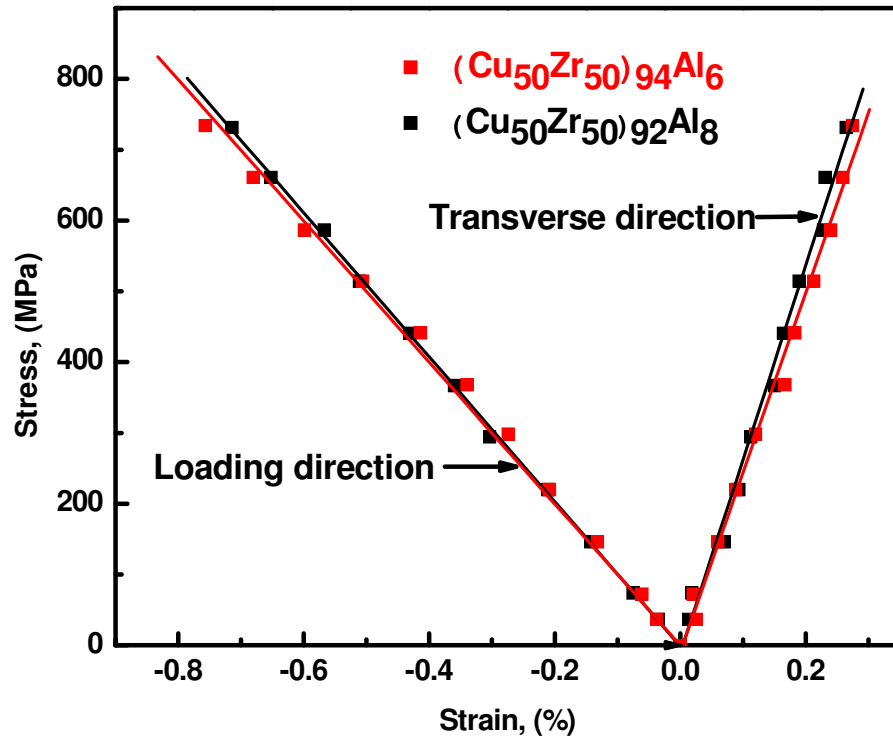


Figure 23. Evolution of elastic strain components of $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ glass-forming alloys during loading in the elastic region.

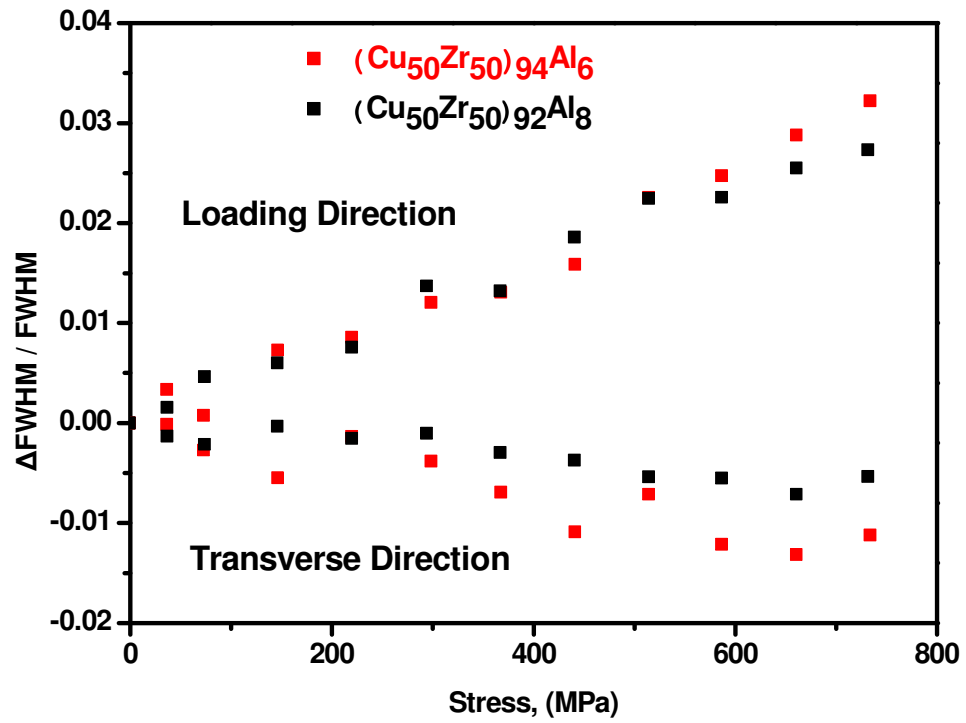


Figure 24. The change of width [full width at half maximum (FWHM)] with the applied stress for $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ glass-forming alloys.

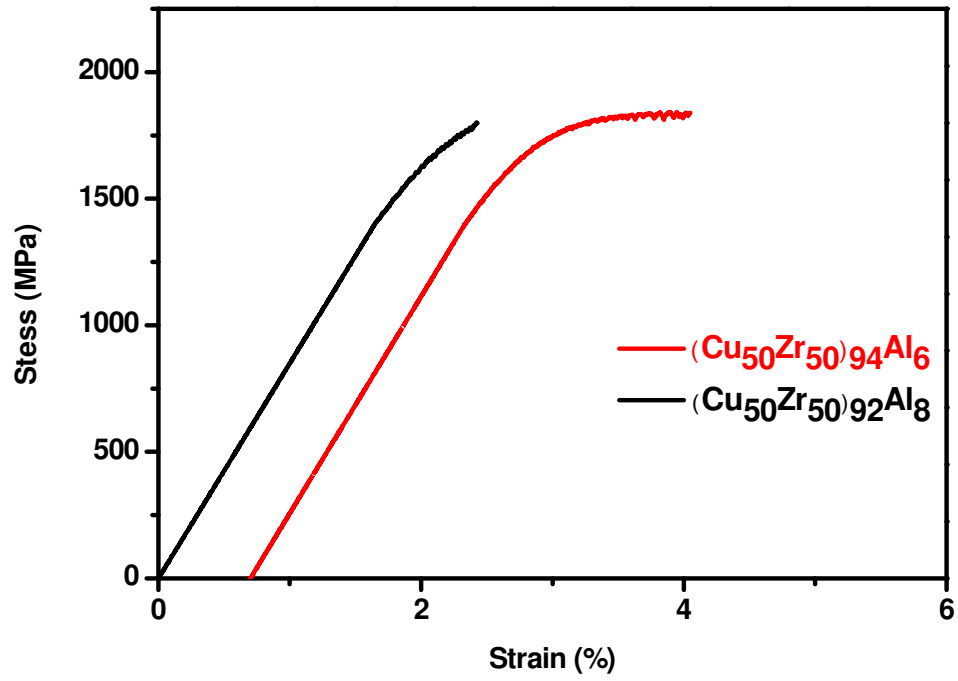


Figure 25. Uniaxial compression stress-strain curves of $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ glass-forming alloys at a strain rate of $8 \times 10^{-4} \text{ s}^{-1}$.

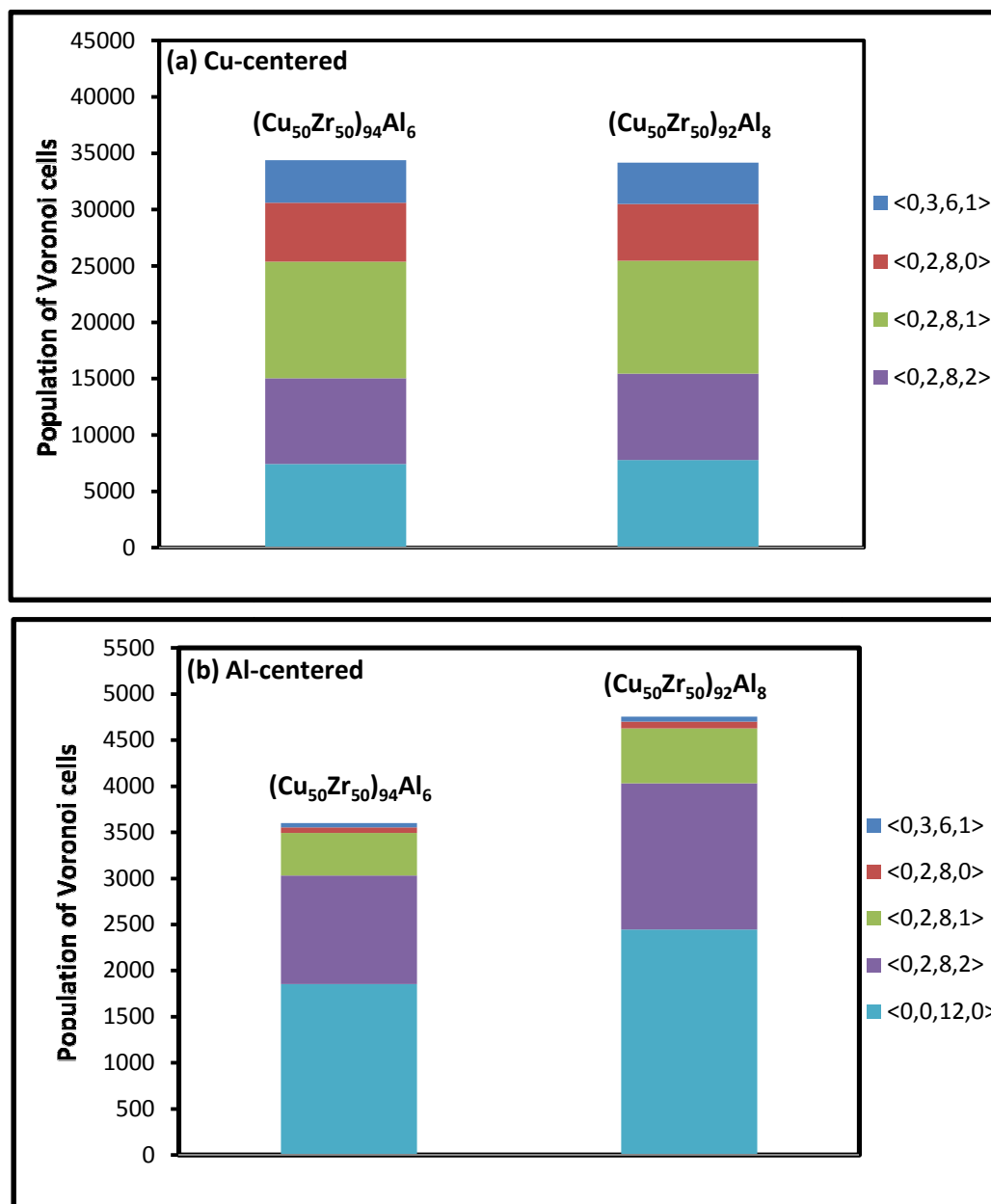


Figure 26. Histogram showing the polyhedral fractions with various Voronoi indices for Cu-centered and Al-centered polyhedral.

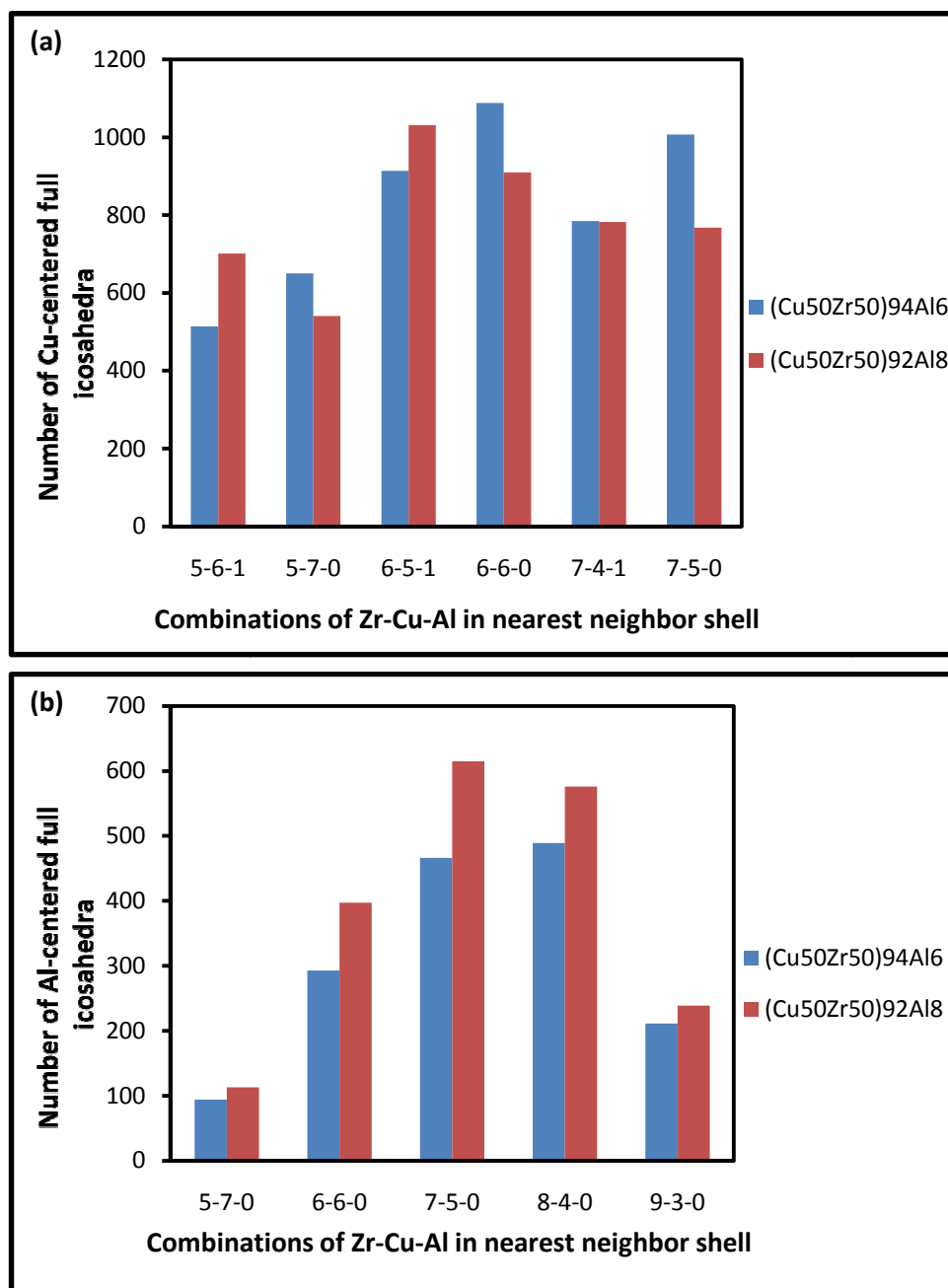
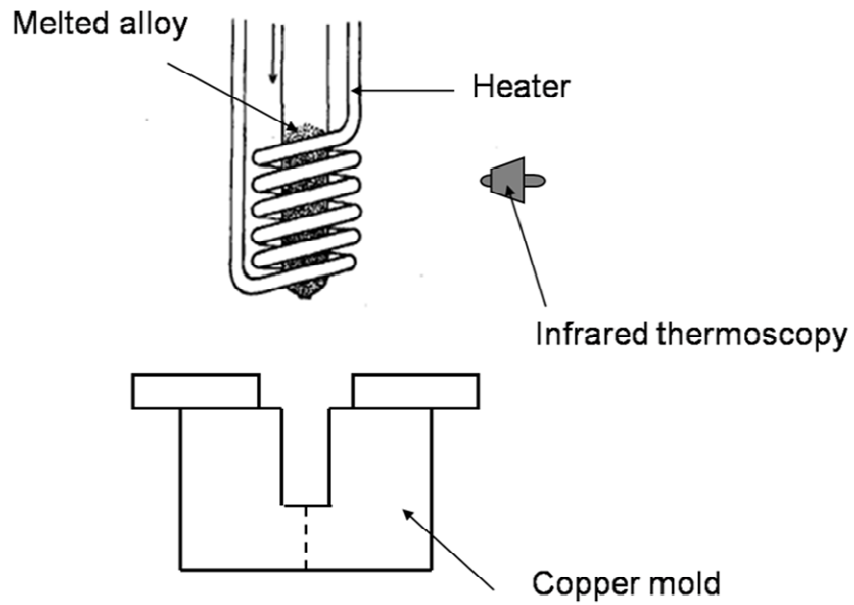


Figure 27. Zr-Cu-Al combinations in the shell of (a) Cu-centered FI and (b) Al-centered FI in $(\text{Cu}_{50}\text{Zr}_{50})_{94}\text{Al}_6$ and $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$, respectively.

(a) Injection casting



(b) In-situ suction casting

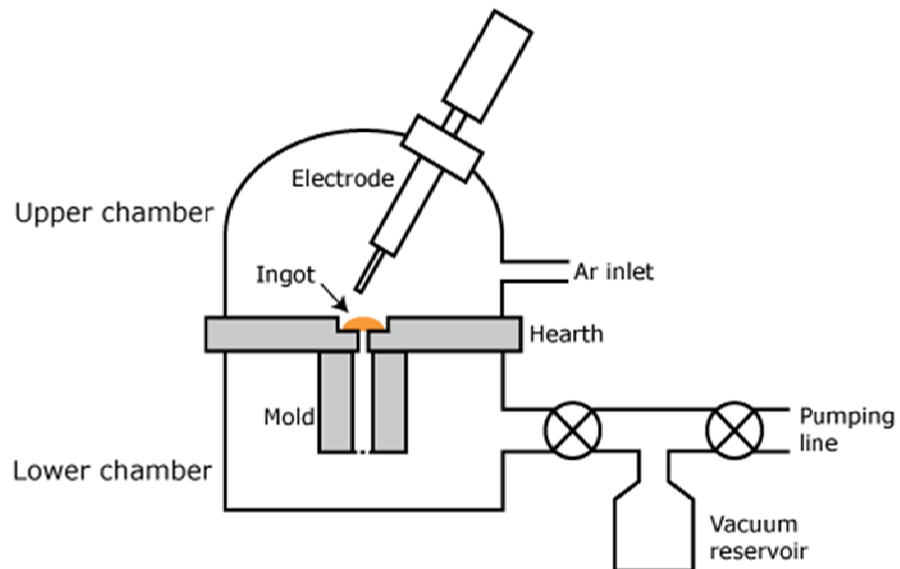


Figure 28. The schematic view of (a) injection casting and (b) in-situ suction casting.

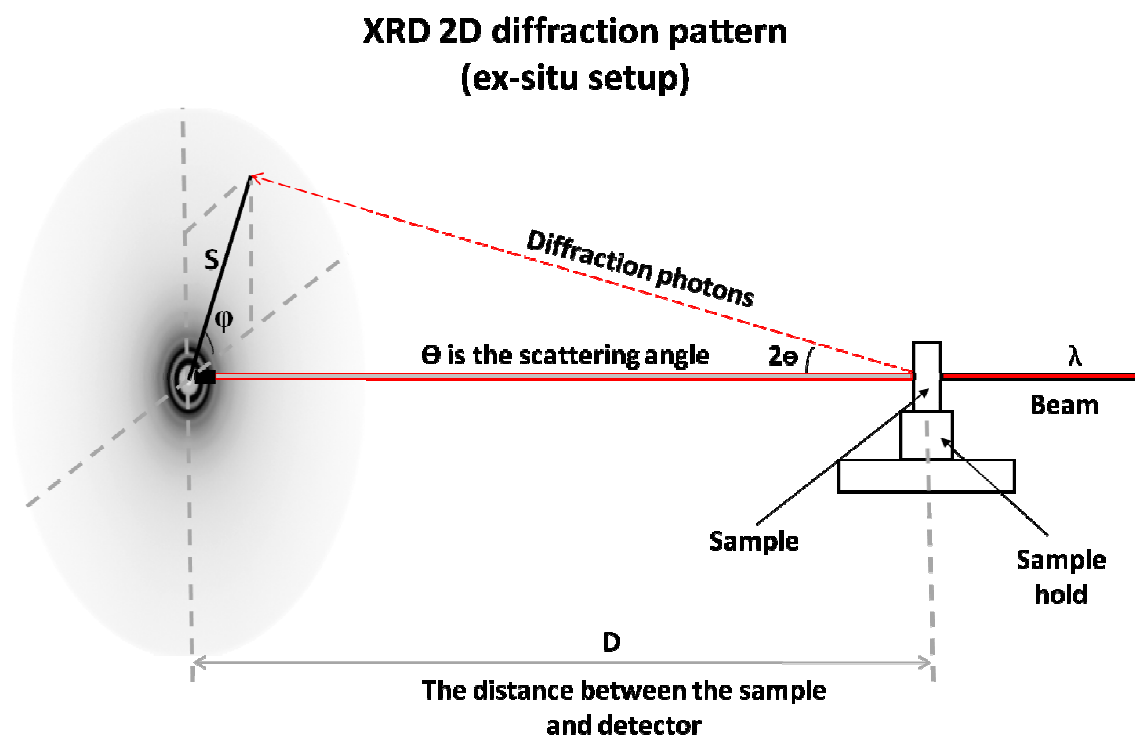


Figure 29. Schematic view of the scattering setup for ex-situ measurement.

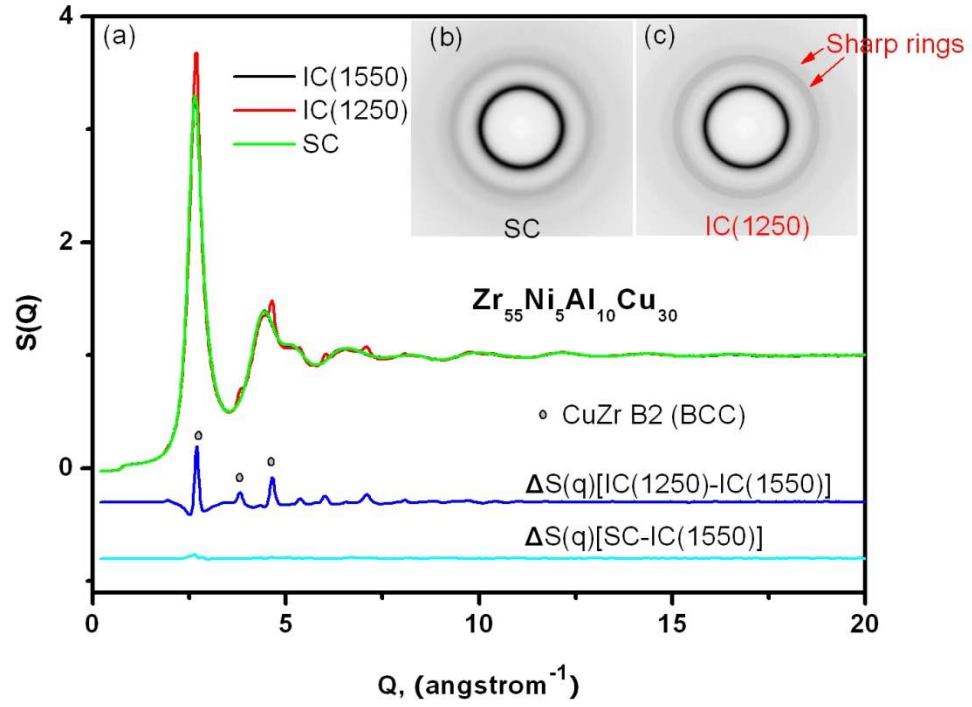


Figure 30. The high-energy synchrotron x-ray results of the IC (1550), IC (1250), and SC samples, and the corresponding diffraction patterns shown in the inset of (b) SC sample and (c) IC (1250) sample.

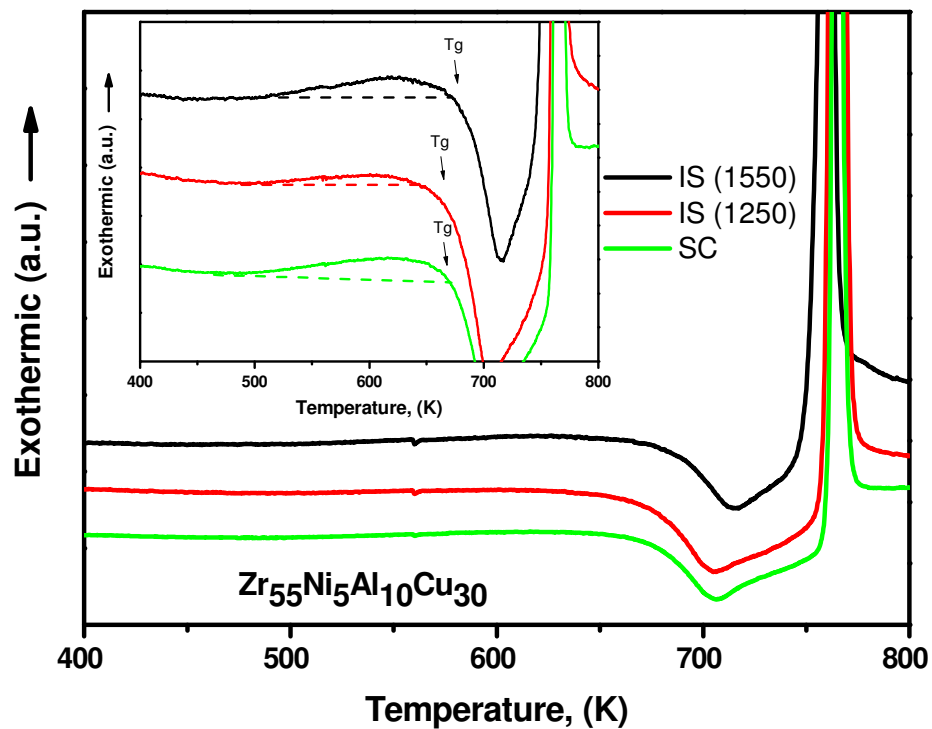


Figure 31. DSC traces of the IC (1550), IC (1250), and SC samples tested under a continuous argon flow at a heating rate of $20 \text{ K}\cdot\text{min}^{-1}$. The inset is an enlargement in the temperature range around the glass transition temperature.

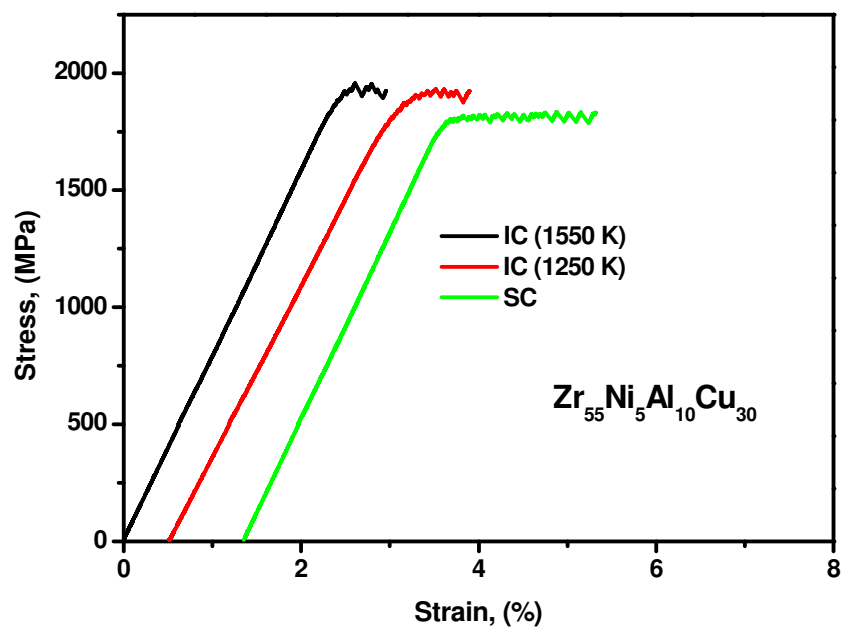


Figure 32. Uniaxial compression stress-strain curves of the IC (1550), IC (1250), and SC samples at a strain rate of $4 \times 10^{-4} \text{ s}^{-1}$ at room temperature.

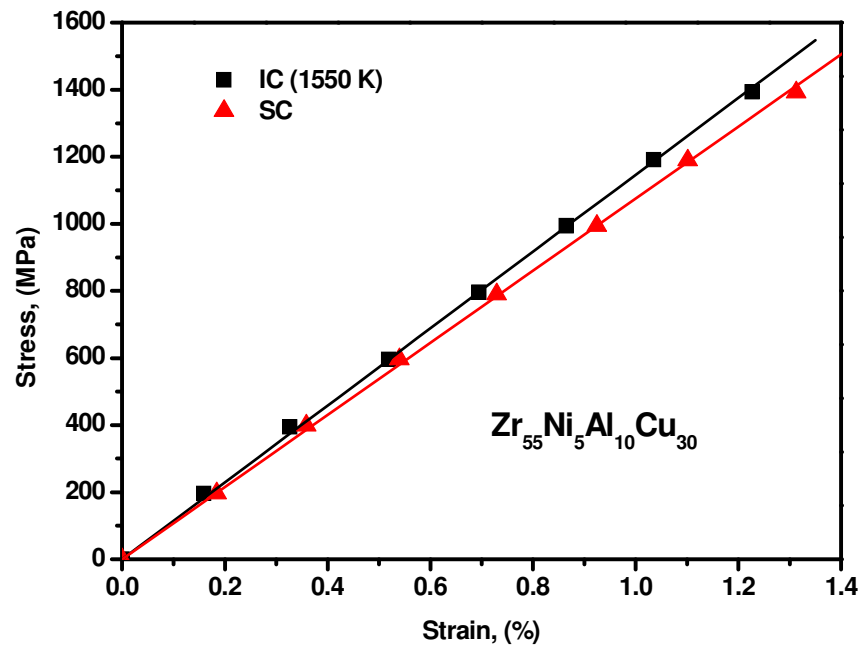


Figure 33. Evolution of elastic strain components of the IC (1550) and SC samples during compressive loading in loading direction.

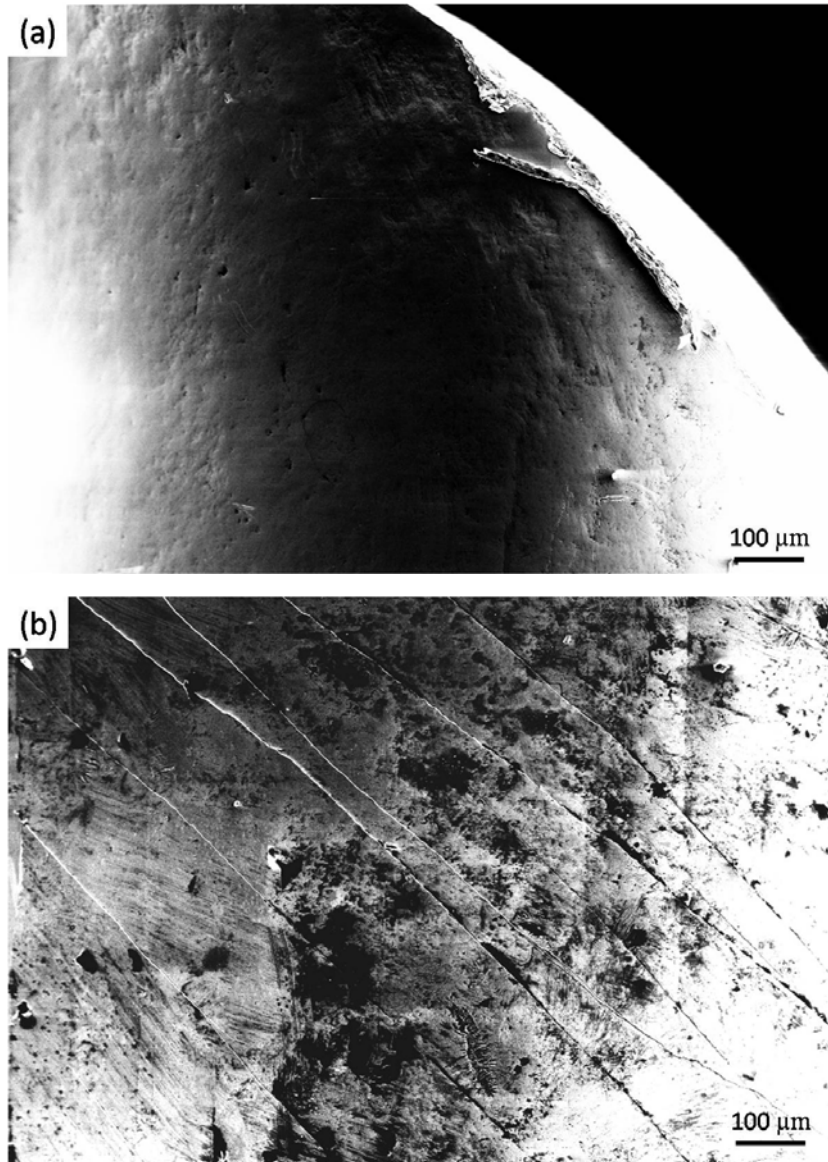
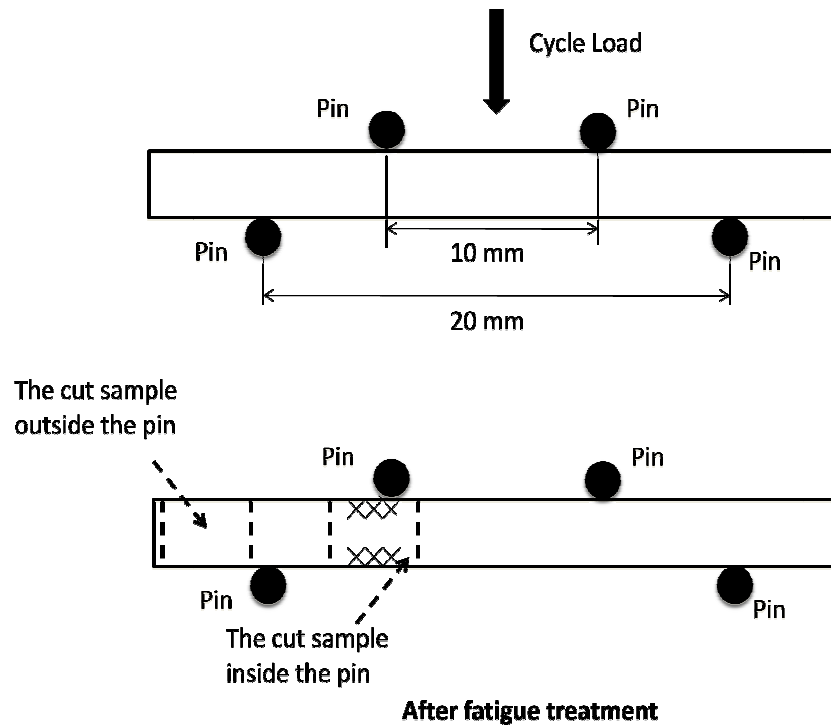


Figure 34. The shear-band morphology on side surfaces of fractured rods of (a) IC (1550) and (b) SC.



Four point bend fatigue: $R (= \sigma_{\min} / \sigma_{\max})$ ratio of 0.1, 10 HZ

Figure 35. The schematic view of the fatigue treatment.

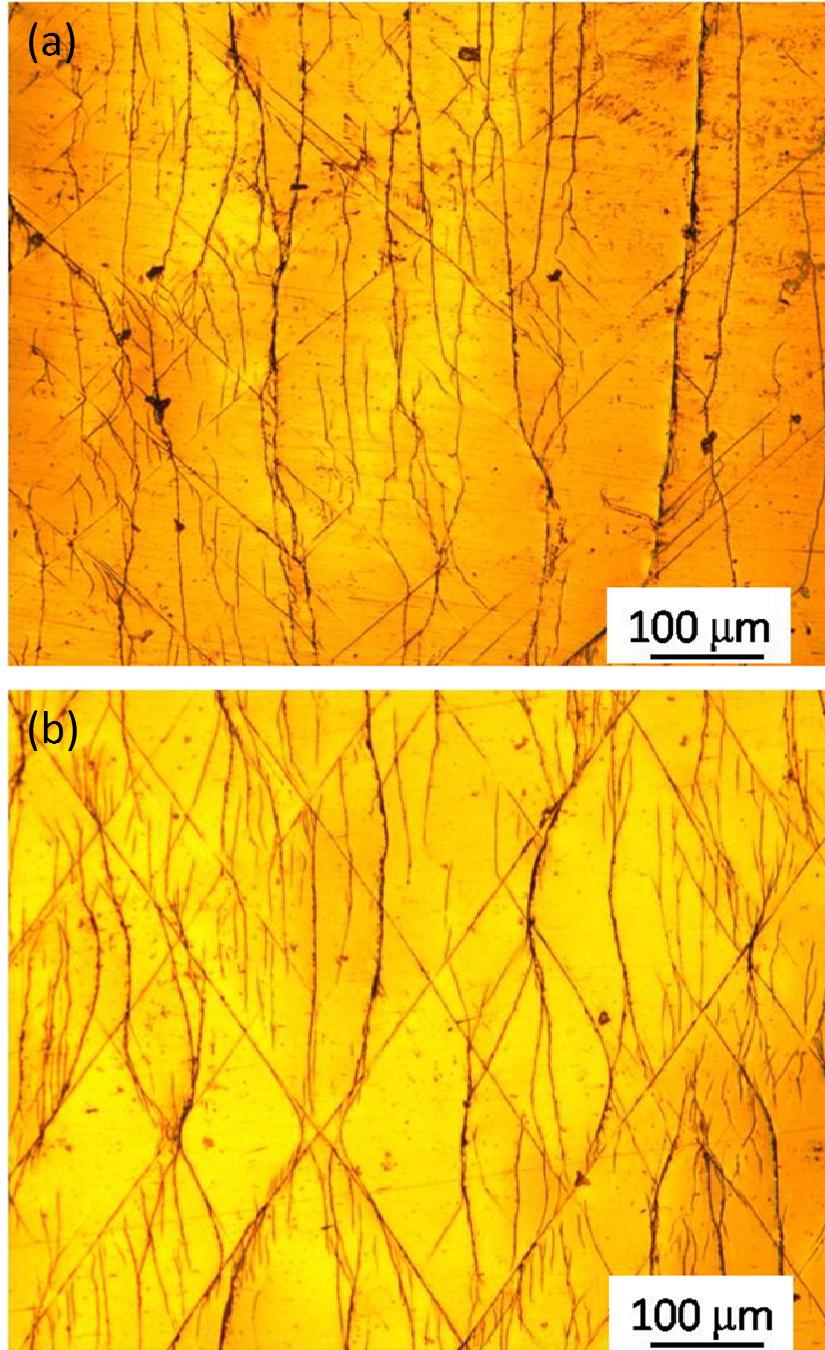


Figure 36. Shear band morphology for (a) the compressive and (b) tensile-side surfaces of section a in $(\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30})_{99}\text{Y}_1$, respectively.

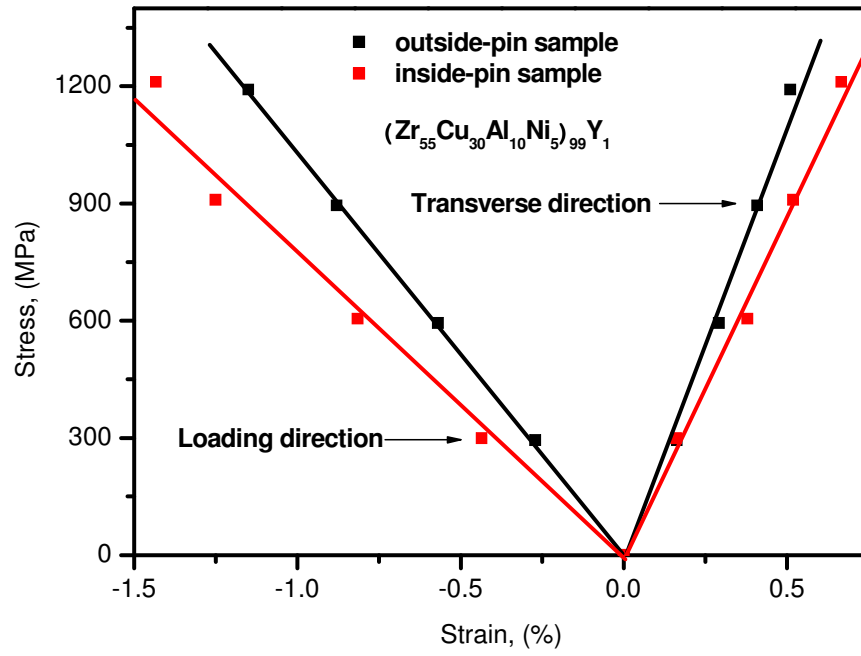


Figure 37. The evolution of strains in loading and transverse directions with the applied stress for inside-pin and outside-pin samples in $(\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30})_{99}\text{Y}_1$, respectively.

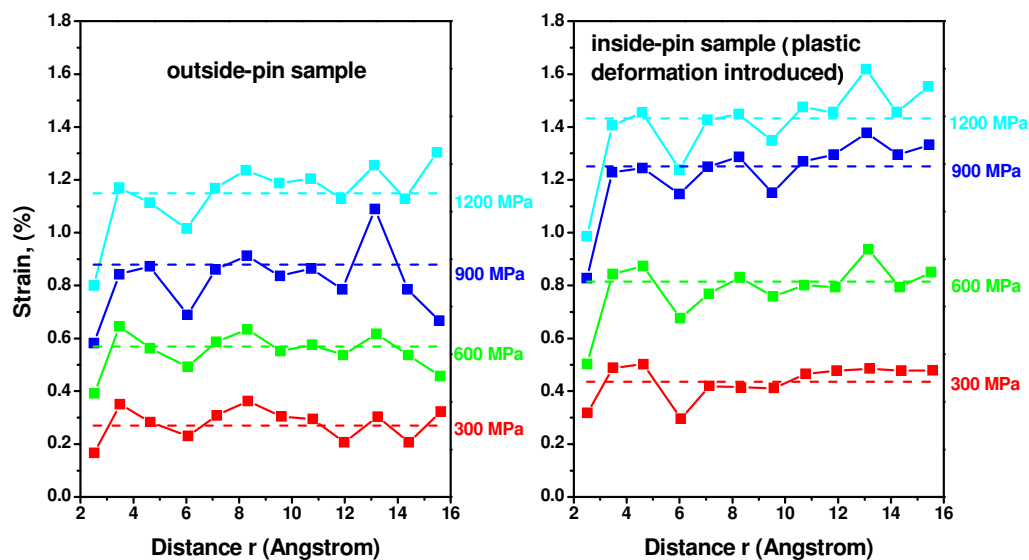


Figure 38. Strain determined from $G(r)$ at several stresses for inside-pin and outside-pin samples in $(\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30})_{99}\text{Y}_1$, respectively.

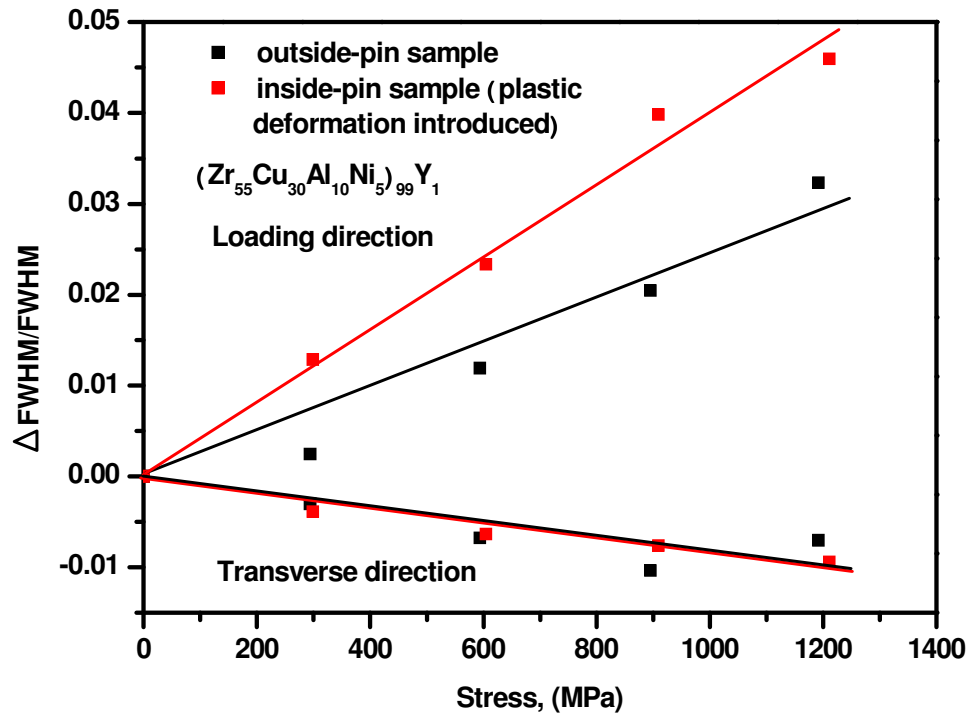


Figure 39. The change of width [full width at half maximum (FWHM)] with the applied stress for inside-pin and outside-pin samples in $(\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30})_{99}\text{Y}_1$, respectively.

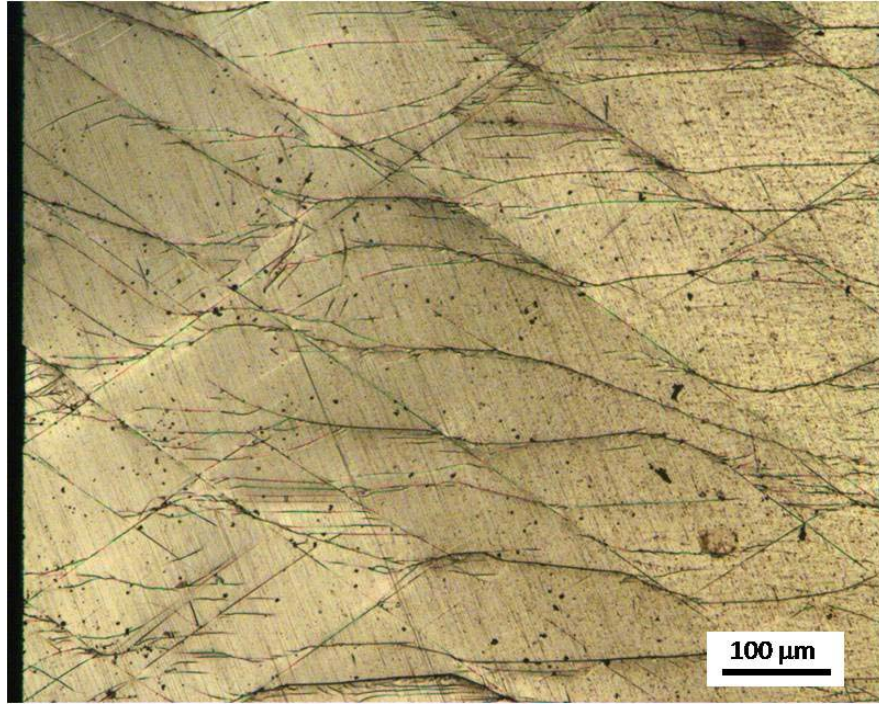


Figure 40. Shear band morphology for tensile-side surface of section a in **Zr₅₀Cu₄₀Al₁₀**.

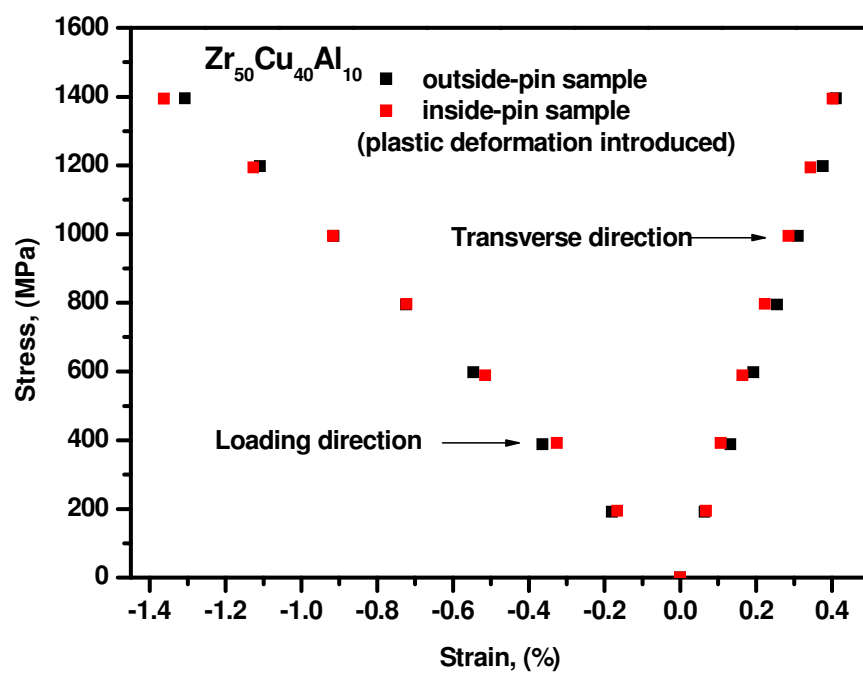


Figure 41. The evolution of strains in loading and transverse directions with the applied stress for inside-pin and outside-pin samples in $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$, respectively.

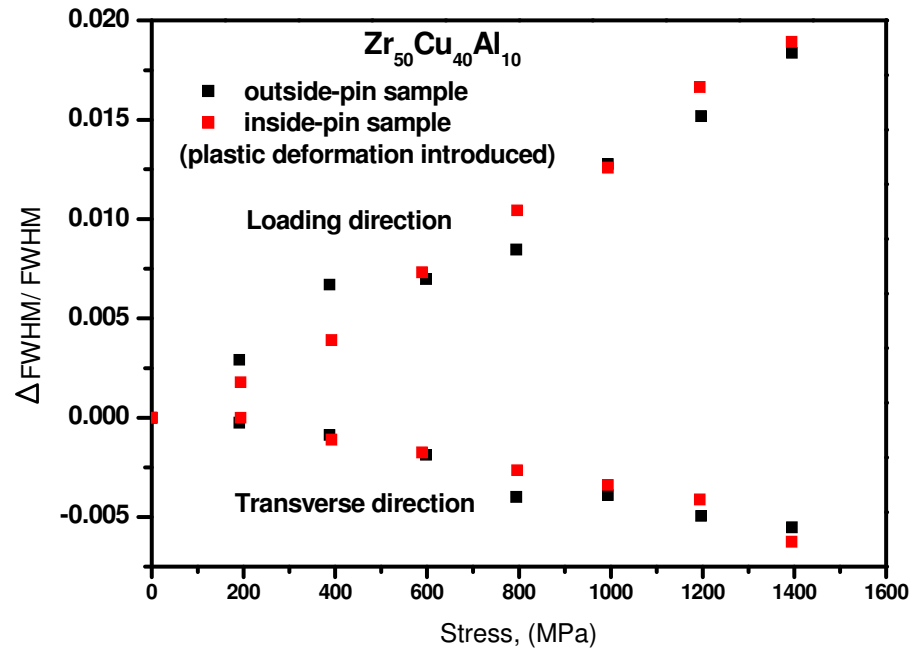


Figure 42. The change of width [full width at half maximum (FWHM)] with the applied stress for inside-pin and outside-pin samples in $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$, respectively.

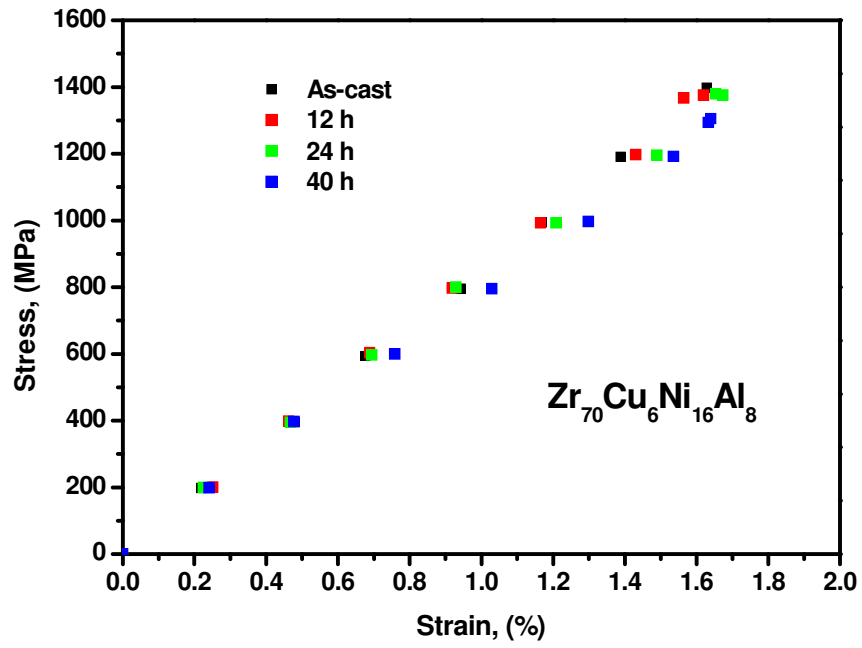


Figure 43. The evolution of strains in loading directions with the applied stress for inside-pin and outside-pin samples in $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$, respectively.

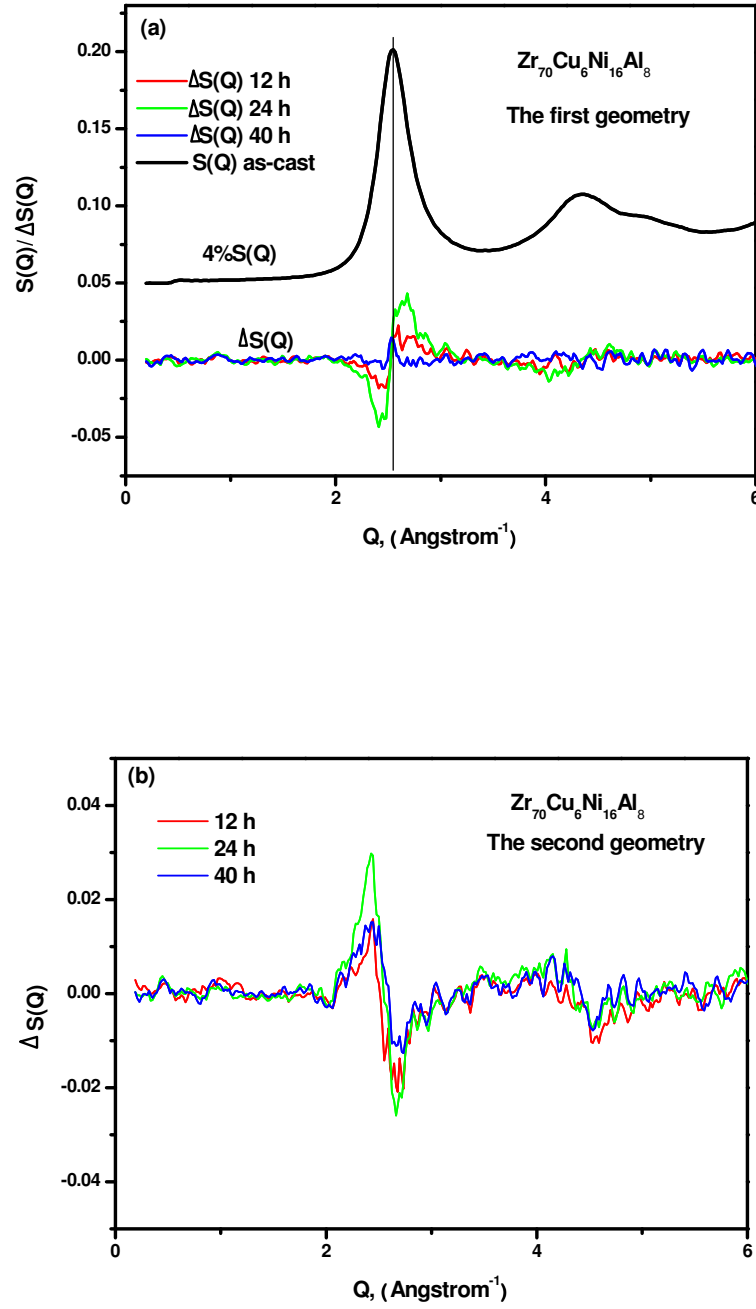


Figure 44. The difference in scattering intensity, $\Delta S(Q)$, for the preload samples of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ in loading direction plane for two measurement geometries, respectively, in the first group.

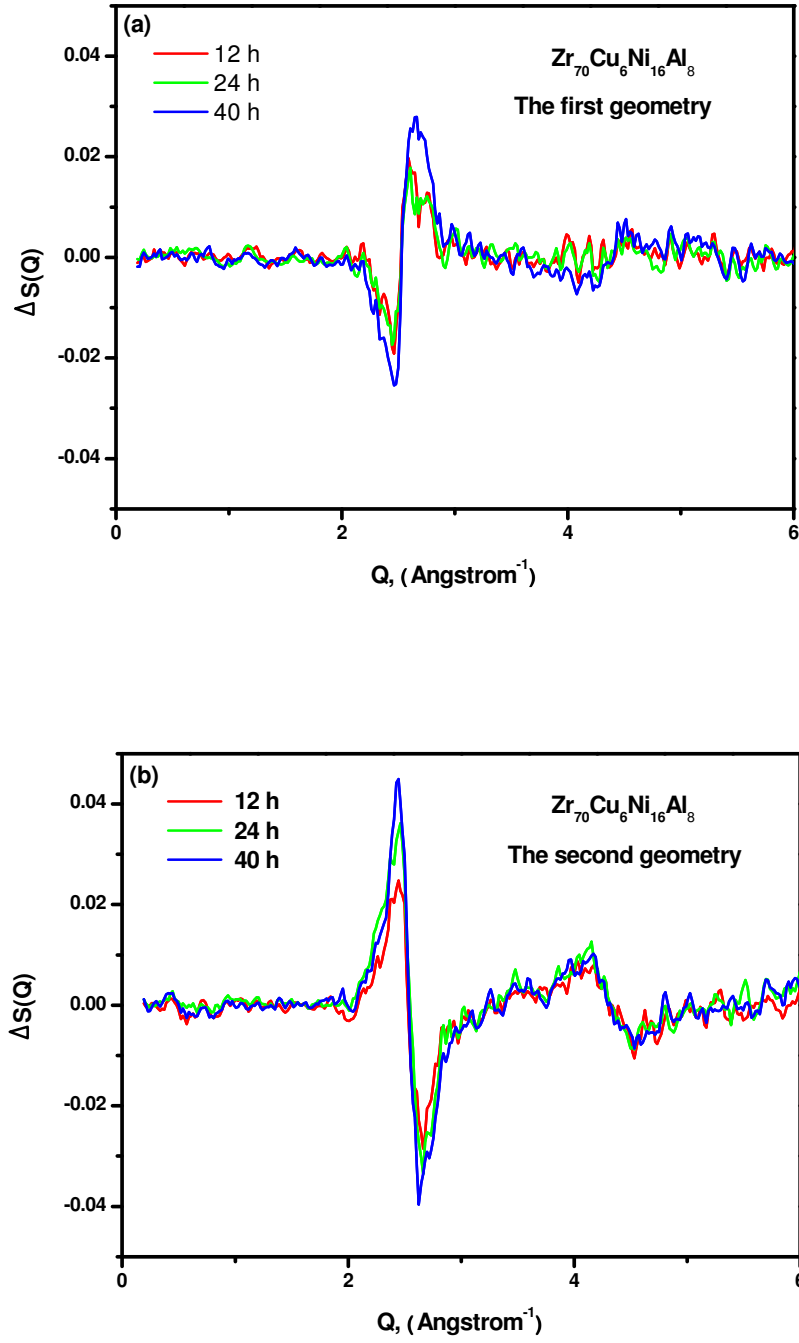


Figure 45. The difference in scattering intensity, $\Delta S(Q)$, for the preload samples of $Zr_{70}Cu_6Ni_{16}Al_8$ in loading direction plane for two measurement geometries, respectively, in the second group.

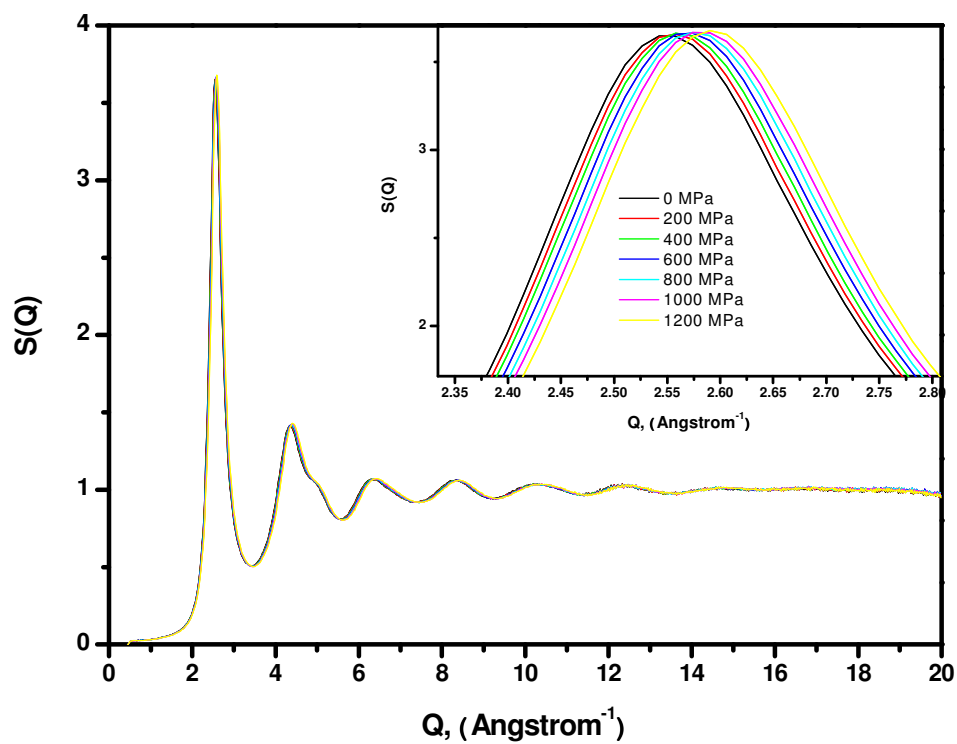


Figure 46. Structure factor $S(Q, \phi=90^\circ)$ of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass as a function of load.

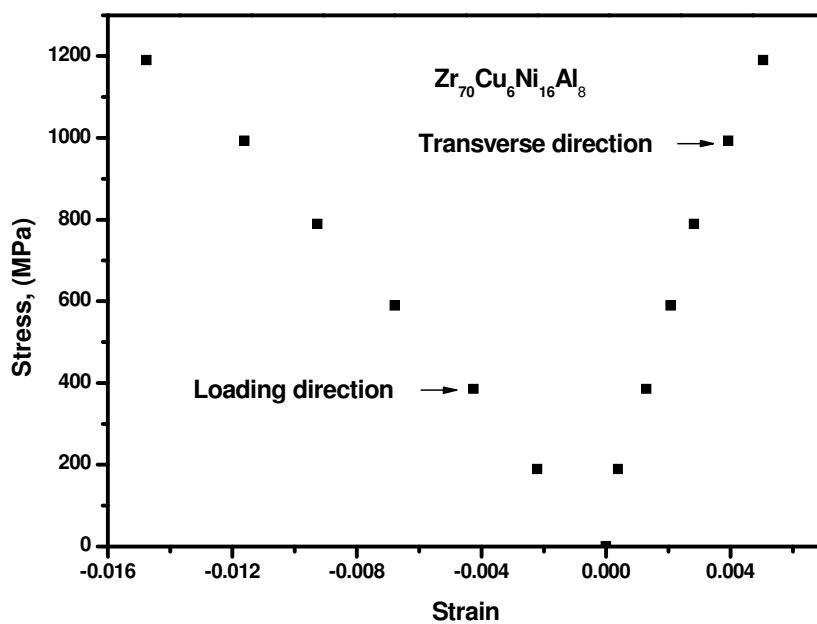


Figure 47. Strain vs. applied stress of Zr₇₀Cu₆Ni₁₆Al₈ glass along loading and transverse directions.

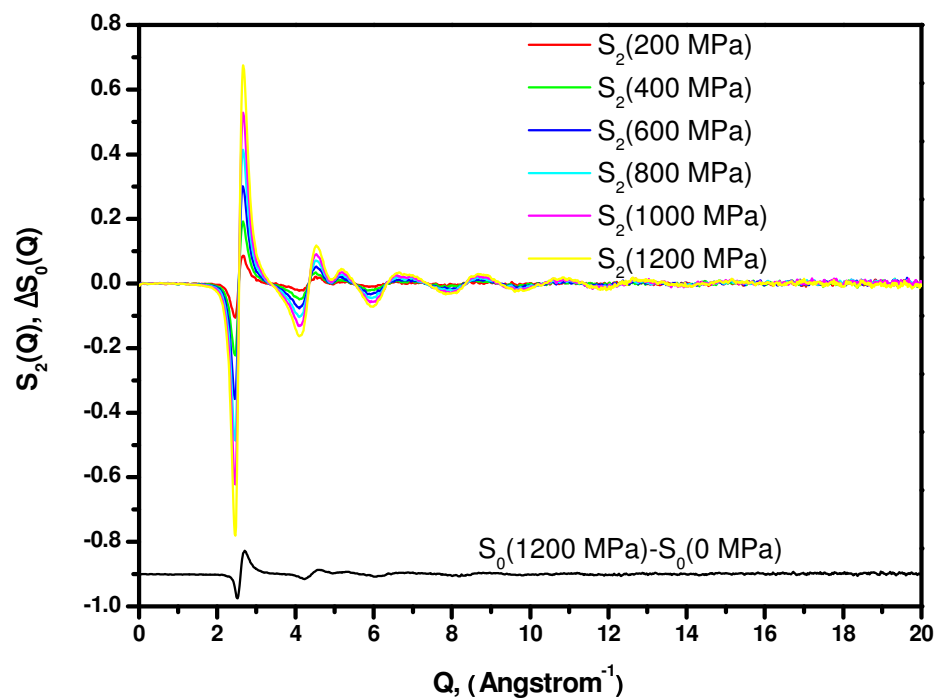


Figure 48. Change of isotropic structure factor S_0 vs. load and anisotropic structure factor S_2 of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass.

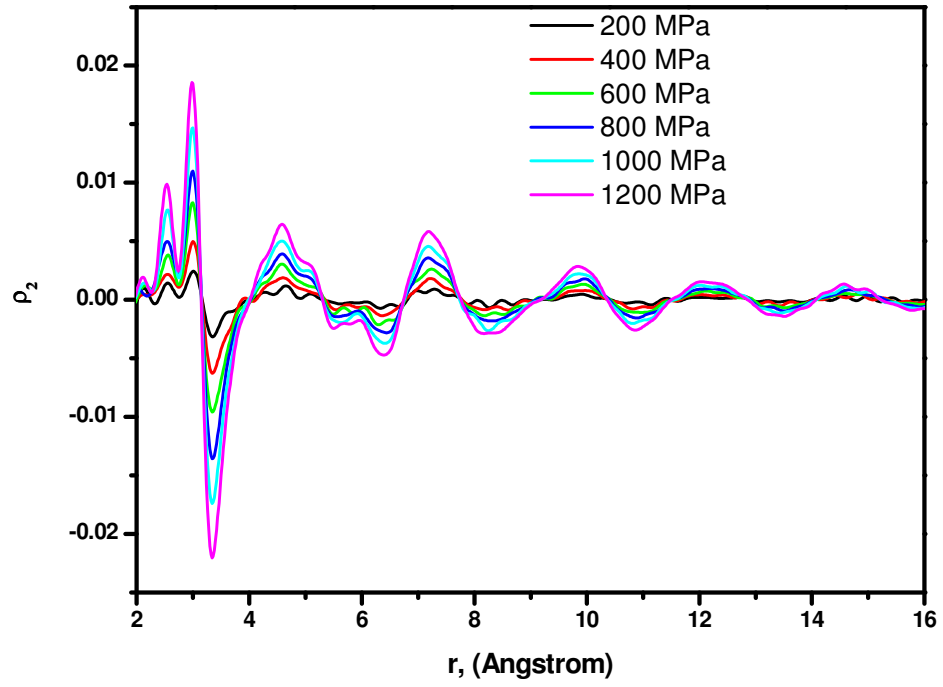


Figure 49. Anisotropic pair density functions (PDFs) $\rho_2(r)$ of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass under different loads.

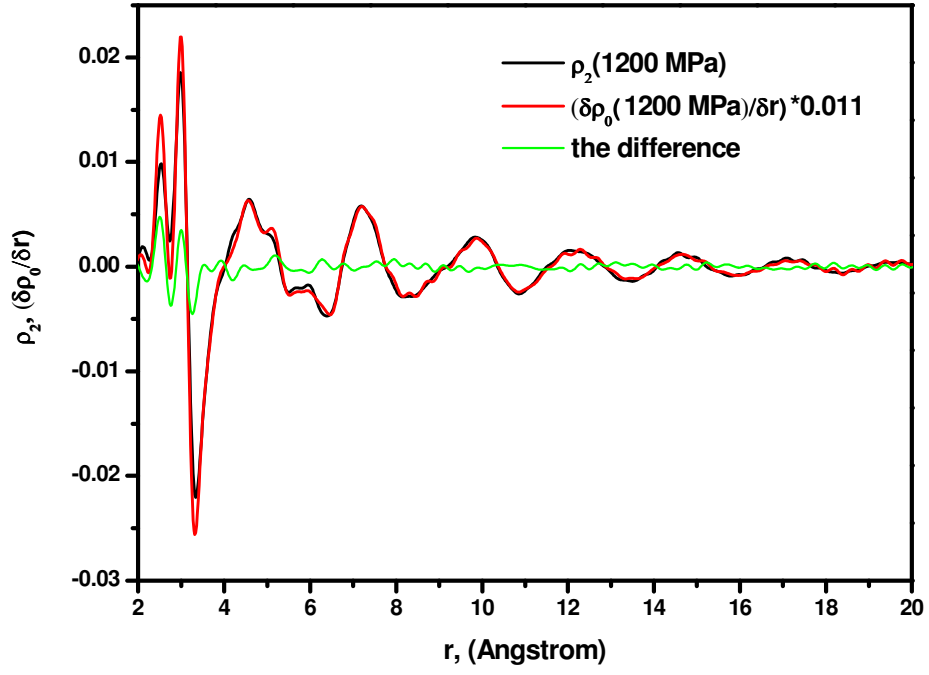


Figure 50. Anisotropic PDFs $\rho_2(r)$ and first derivative of $\rho_0(r)$ of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass at 1200 MPa.

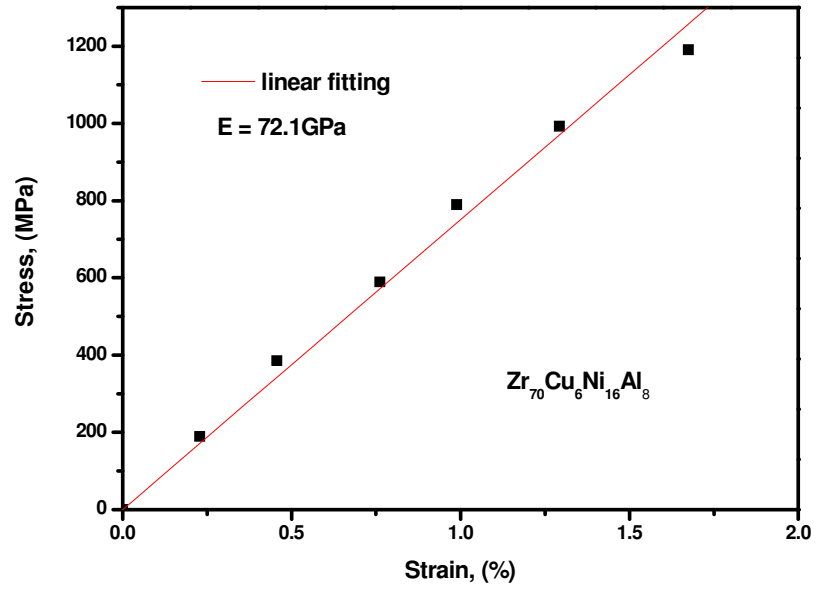


Figure 51. The strains obtained by fitting the anisotropic part, $\rho_2(r)$ and the first derivative of the isotropic PDF, $\rho_0(r)$ with the equation (37) at different stress levels for $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass.

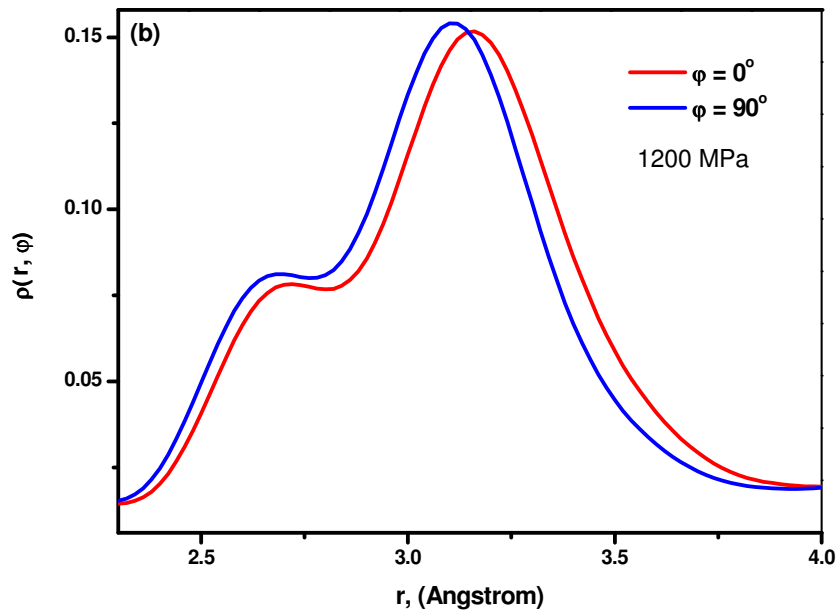
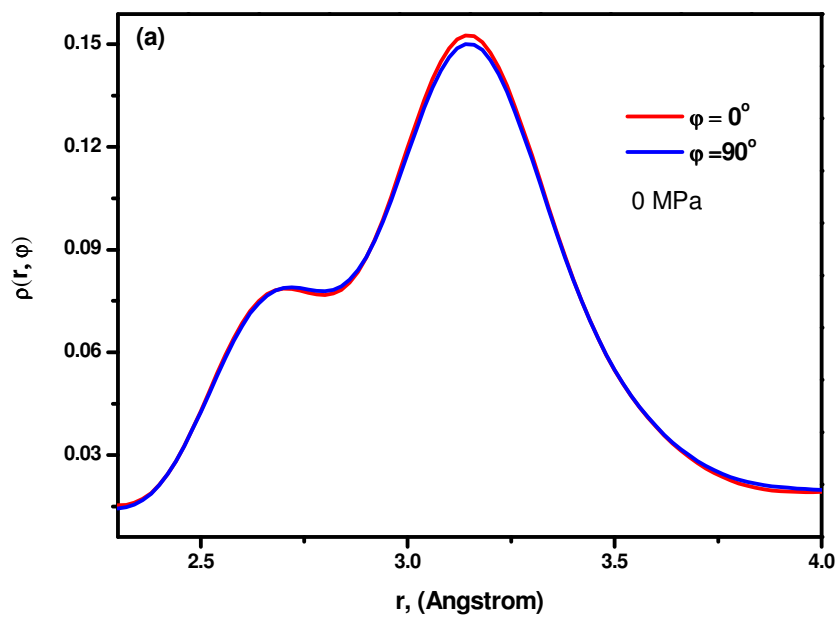


Figure 52. Direction dependence of nearest neighbourhood of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass; (a) 0 MPa, (b) 1200 MPa.

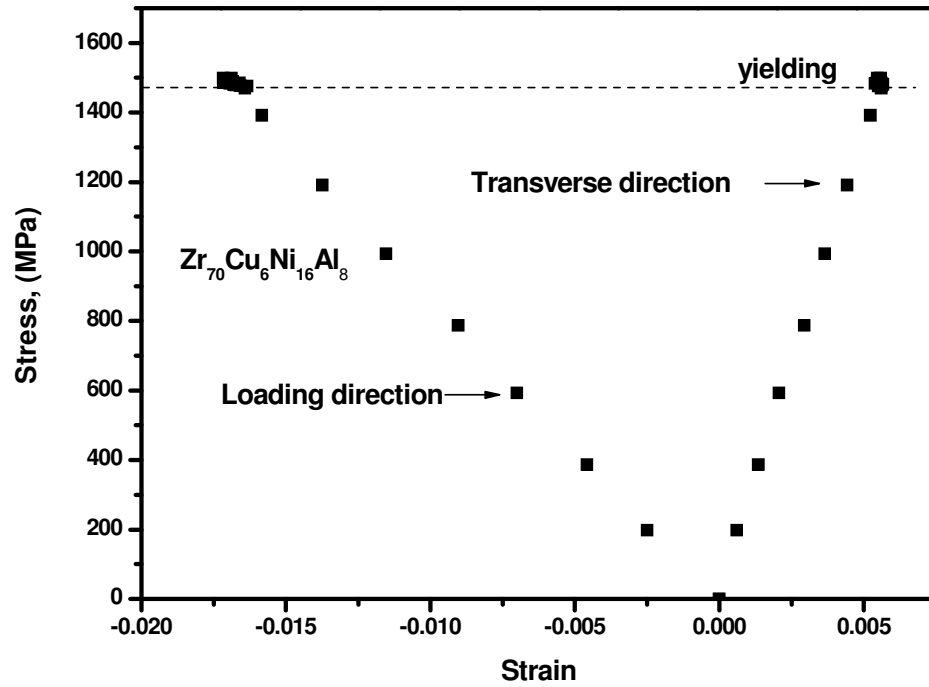


Figure 53. The evolution of strains in loading and transverse directions with the applied stress to plastic region for the sample 2 of $Zr_{70}Cu_6Ni_{16}Al_8$ glass.

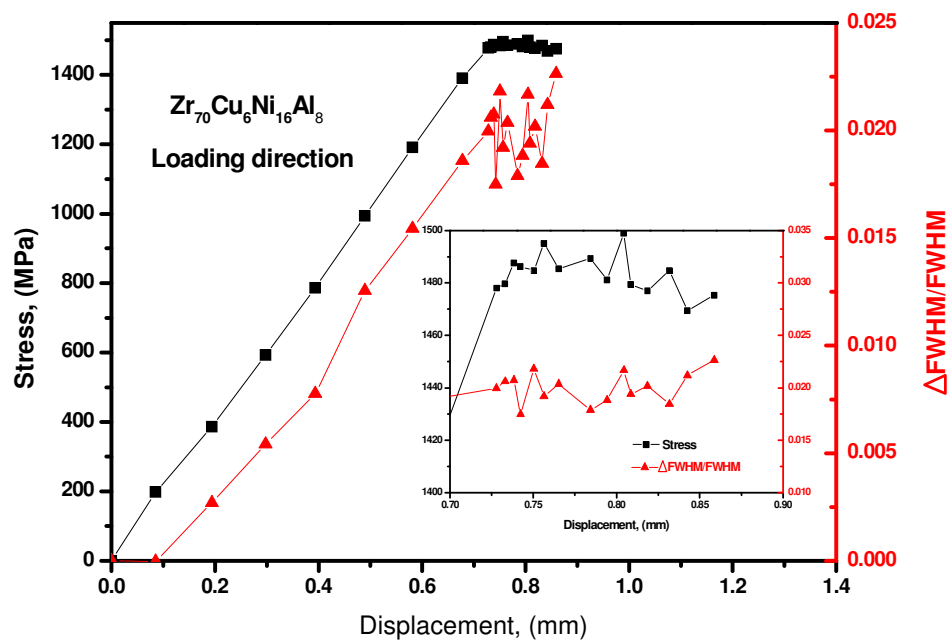


Figure 54. The evolution of stress and the change of FWHM in the loading direction with the displacement for the sample 2 of $Zr_{70}Cu_6Ni_{16}Al_8$ glass.

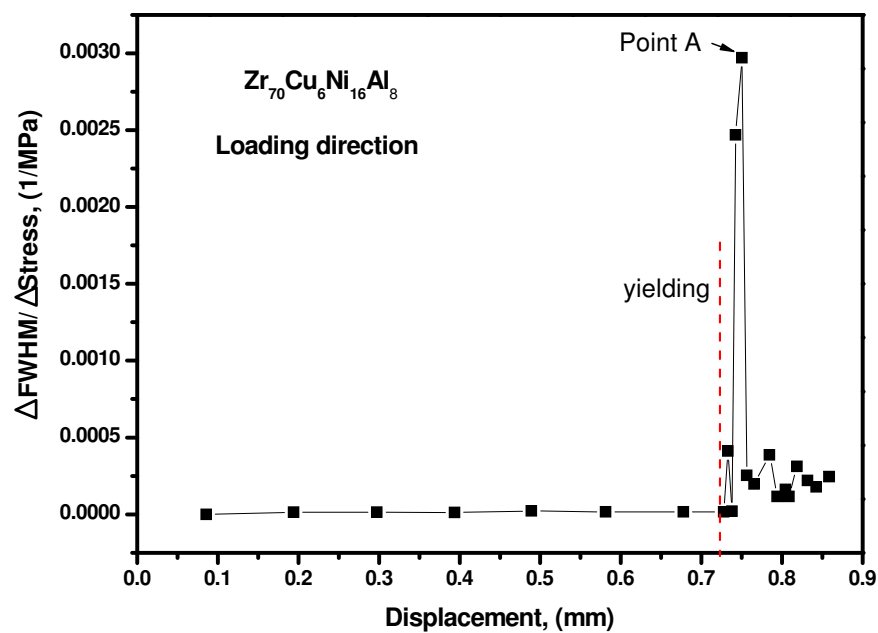


Figure 55. The rate of change of FWHM on the change of stress as function of the displacement in the loading direction for the sample 2 of Zr₇₀Cu₆Ni₁₆Al₈ glass.

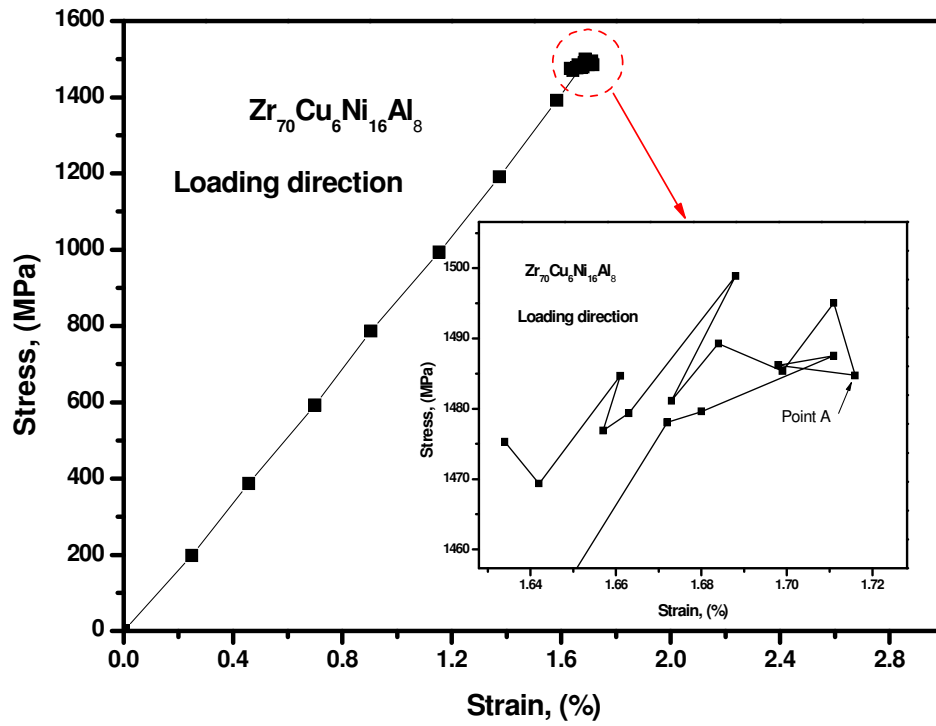


Figure 56. The curve of stress vs. strain in the loading direction for the sample 2 of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass.

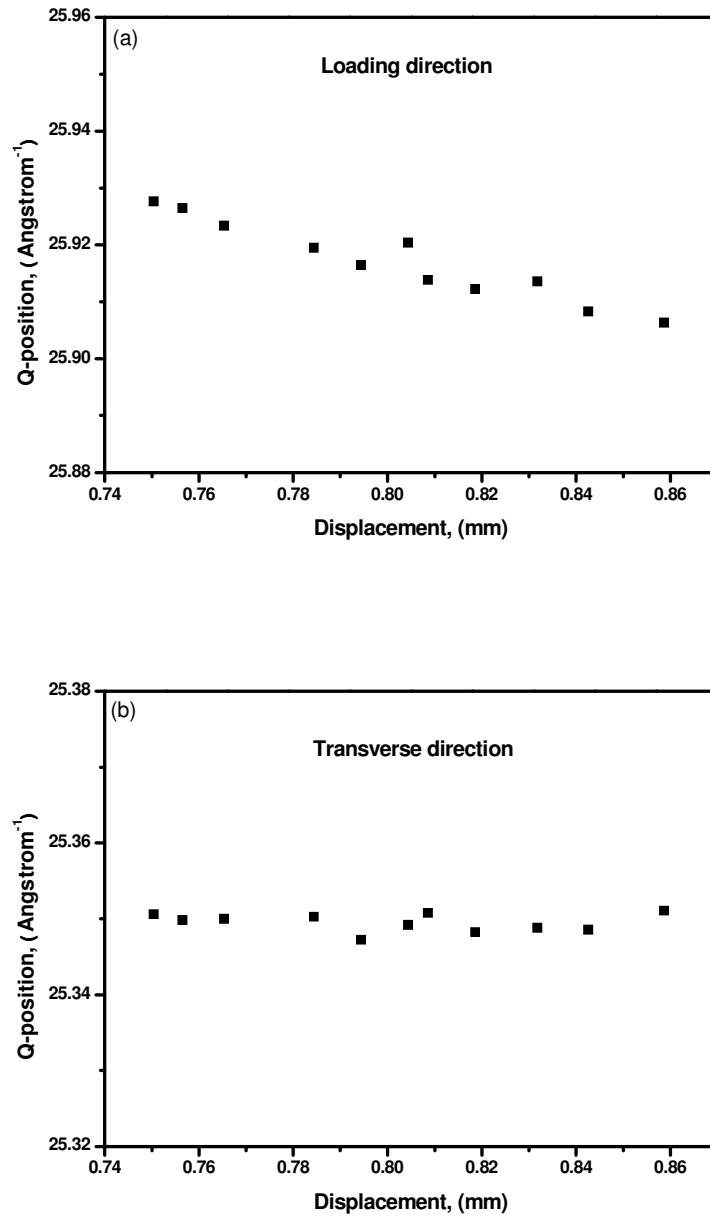


Figure 57. Measured peak position of the first scattering maxima in (a) the loading and (b) transverse directions as a function of the displacement for the sample 2 of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass.

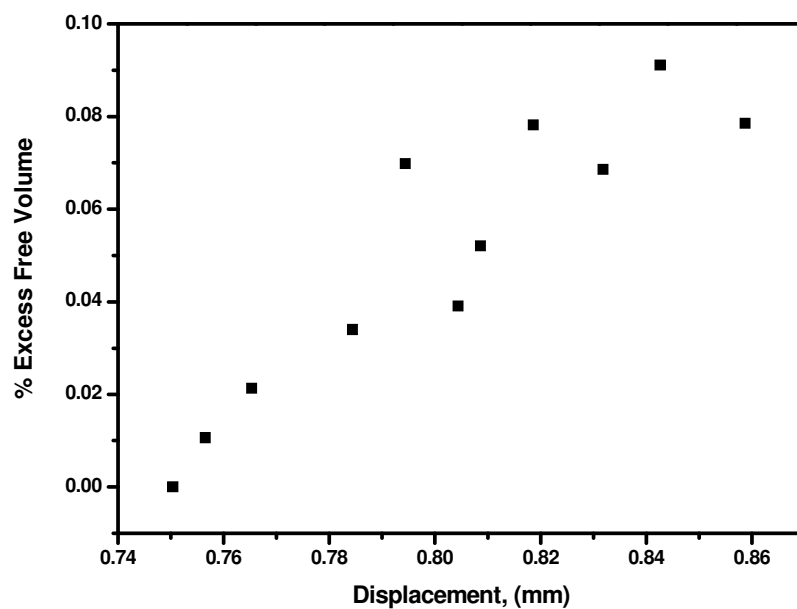


Figure 58. Measured excess free volume in the sample 2 of $\text{Zr}_{70}\text{Cu}_6\text{Ni}_{16}\text{Al}_8$ glass as a function of the displacement.

VITA

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