UNIVERSITY OF CINCINNATI

Date: 12/01/2006

I, Ling Yang, hereby submit this work as part of the requirements for the degree of:

Doctor of Philosophy

in:

Material Science

It is entitled:

Devitrification of Bulk Metallic Glasses Studied by Neutron and X-Ray Scattering

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DEVITRIFICATION OF BULK METALLIC GLASSES
STUDIED BY NEUTRON AND X-RAY SCATTERING

A dissertation Submitted to the Division of Research
and Advance Studies of the University of Cincinnati

in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

In the Department of Chemicals and Materials
Engineering of the College of Engineering

November 2006

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ABSTRACT

The structural evolutions during the devitrification of three bulk metallic glasses, including Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_{5} (BAM-11), Zr_{50}Cu_{40}Al_{10} and Mg_{65}Cu_{25}Tb_{10}, have been studied in-situ by neutron and synchrotron X-ray scattering. By measuring simultaneously the wide-angle X-ray scattering (WAXS) patterns and the small-angle X-ray scattering (SAXS) patterns, a good comparison of the structural evolutions at the atomic scale and nano scales during the different transformation stages are achieved. Also the evolutions of pair distribution functions (PDFs) in real space have been measured by neutron and X-ray total scattering. These results are further complemented by ex-situ experiments including DSC, conventional XRD, TEM and SEM. The results show all three samples are amorphous in the as-cast state, and that phase separation precedes crystallization for Zr-based BMGs. BAM-11 devitrifies in two stages; the first stage is related to topological changes within a 2 nm range, and a metastable fcc NiZr_{2} phase is formed, which transforms to the tetragonal NiZr_{2} phase in the second stage. Above 690 K, Zr_{50}Cu_{40}Al_{10} decomposes to form the Cu_{10}Zr_{7} phase and CuZr_{2} phase, which transform to the CuZr phase eutectoidly at higher temperature. Mg_{65}Cu_{25}Tb_{10} devitrifies in three stages, the first stage is related to the formation of icosahedral clusters, the second and third stages are the formation of quasicrystalline phase and further decomposition. Kinetic model and SAXS model are proposed and applied to refine the patterns. The topologies of conventional oxide glasses and BMGs are compared and summarized. The nonperiodic order plays an important role in nanometer scale for BMGs.
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Preface

I declare that, except where otherwise stated, this dissertation is the result of my own work and includes nothing that is the outcome of others. No part of this dissertation has submitted at University of Cincinnati or any other University for a degree or diploma or other qualifications.

Ling Yang
November 2006
Acknowledgements

My great sincere thanks go to all people who had spiritually supported and encouraged me, and aided me in the process of pursuing the PhD degree, and helped and contributed to this project. Without these, it is impossible for me to reach this academic summit.

Foremost, I would like to thank Prof. Donglu Shi, from the Department of Chemical and Materials Engineering, University of Cincinnati, for his supervision, guidance, patience, and support throughout the years. Also, it is my luck and honor to have Dr. Xun-Li Wang, from Spallation Neutron Source, Oak Ridge National Laboratory, to be my associate advisor, who supports and guides me during my second phase of research at Oak Ridge National Laboratory. It is my fortune to work in their research groups, during which I not only gained knowledge and experiences, but also become more professional and get prepared for developing a successful career in the future. I appreciate their guidance, tutoring, and their enduring efforts in helping their students to be a better researcher and a mature scholar.

My gratitude goes to all the committee members, Dr. Relva C. Buchanan, Dr. Ray Y. Lin, Dr. Rodney Roseman and Dr. Donglu shi, for their time, efforts to read this dissertation and give me useful advices, encouragement, and opportunity for me to present this thesis.

I would like to thank our group members, Dr. Xun-Li Wang, Dr. Alexander D. Stoica, Dr. Dong Ma and Dr. Sheng Cheng, for their continuous support in helping me with experimental design and data analysis, as well as their keen viewpoints throughout
the whole project. I learned a lot from many insightful discussions and their advices on academic writing.

Special thanks must be given to Dr. C. T. Liu and Dr. Zaoping Lu, from the Materials Science and Technology Division of ORNL, for preparing the samples for us. A lot of work including samples processing and rudimental tests was done in their laboratory.

I would like to thank Dr. Wallace D. Porter, from High Temperature Materials Laboratory in ORNL, in helping me with the DSC experiment. Credit must also be given to Dr. Andrew Payzant and Dr. Thomas R. Watkins from the same division, who helped me finishing the conventional XRD tests and helping me using the software.

I would like to give special appreciations to Dr. M. K. Miller, from the Materials Science and Technology Division of ORNL, in helping us with the Atom Probe tests. Dr. J. A. Horton from the same division helped me with the TEM and SEM tests.

I also like to thank Dr. Dean Haffner and Dr. Jon Almer, scientists of Advanced Photon Source, Argonne National Laboratory, for helping us design and finish the very important experiment using synchrotron scattering, on instrument 1-ID. A lot of thanks must be given for their patience and technical support, as well as their support on data analysis.

I must thank Dr. James W. Richardson, Evan Maxey and Ashfia Huq, from Intense Pulse Neutron Source, Argonne National Laboratory, in giving us tremendous help using their instrument to do a lot of experiments. From them I learn a lot about instrumentation in neutron scattering, and the experience of interactions between instrument scientist and users is precious for my careers.
Acknowledgements

Dr. Thomas Proffen, from Los Alamos Neutron Science Center in Los Alamos National Laboratory, helped us with the neutron total scattering tests, and gave us a lot of advices for the afterwards data analysis through many discussions.

I also like to thank Dr. Matthew Kramer, from Department of Materials Science and Engineering, Iowa State University, in helping us with the synchrotron X-ray total scattering tests. Through many emails and phone calls, Dr. Kramer is very patient and instructive in helping me processing data.

I feel very obliged to Dr. J. Neuefeind, from Spallation Neutron Source in ORNL, for his help in data analysis; and Dr. T. Egami, from the Materials Science and Technology Division of ORNL, for his profound thinking in the area of bulk metallic glasses.

I sincerely appreciate Dr. K. Crawford, the leader of facilities group in SNS, ORNL, Dr. Thom Mason, the SNS director, as well as the SURA program. Without their support this work could not be performed in ORNL. My thanks also extend to many people who have contributed to this research both directly and indirectly, many of them are not included here.

Great thanks must be given to Dr. Yongli Xu and Dr. Peng He from Dr. Shi’s group, who helped me both academically and in life routines. Special thanks to Dr. Xu for his continuous encouragement. I appreciate the help from professors and staff in the Department of Materials science and engineering, University of Cincinnati, and secretaries in Spallation Neutron Source, Oak Ridge National Laboratory.

Gratitude must be given to my family back in China. I cannot make any progress without their love and support both spiritually and financially.
Acknowledgements

This research was sponsored by Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy under Contract DE-AC05-00OR22725 with UT-Battelle, LLC. Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38. Part of this work was sponsored by the U.S. Department of Energy (USDOE), Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, as part of the High Temperature Materials Laboratory User Program, under contract number DE-AC05-00OR22725 with UT-Battelle, LLC.
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Chapter 1  Introduction

Perhaps, liquid and amorphous materials (glasses) are the least understood areas in material science. Research in this area has become more and more intense and exciting, with the hope that our understanding of material science will be expanded to a new level. This chapter is a brief introduction about the development of the research area of bulk metallic glasses (BMGs), including the history, main research interest and problems. Based on this, the objective of this thesis work is given.

1.1 History and development of bulk metallic glasses

Bulk metallic glasses (BMGs), namely, are metals in the form of glasses. Being quite different from the conventional silicate glasses, BMGs have many interesting and novel properties, which have stimulated intensive research for more than two decades. Details about the history and research interest in BMGs can be found in many reviews [1-13]. Here, only a brief introduction is given.

Metallic alloys, due to the strong metallic bonding, usually assume a highly-ordered crystalline phases at low temperature. However, some ‘bad’ metals can be significantly supercooled [4]; in this supercooled liquid state, crystallization is suppressed and the liquid structure is arrested when the viscosity increases to around $10^{15}$ poise [10], forming metallic glasses (MGs). The history of the development of MGs is schematically drawn in Figure 1-1. The first recognized MG is the Au$_{75}$Si$_{25}$ alloy developed by Duwez et al in 1960 [14]. The early MGs usually belong to the metal-metalloid type, containing
a noble metal (Au, Ag, Pd) and metalloids like Si and P [14, 15]. In order to obtain large cooling-rate, these MGs were made by spin-casting, and the products were very thin.

During the 1980s, Turnbull’s group made the first BMG on Pd-Ni-P by flux casting, and obtained a critical thickness of 1 cm, which could be considered as the first BMG [16]. This system was later improved by Inoue’s group. By partially replacing Ni with Cu, the produced Pd$_{40}$Ni$_{30}$Cu$_{10}$P$_{20}$ achieved a critical casting thickness of 72 mm; highest to date [17]. Inoue’s group also developed the La-Al-based, Zr-based and Mg-based BMGs. By using both the heavy rare-earth elements and the light elements like Al and Mg, it was expected that these alloys will have a very high strength/weight ratio. Mg$_{65}$Cu$_{25}$Y$_{10}$ is one of the typical good glass formers which they found [18]. In the 1990s, Johnson’s group worked intensively on the Zr-based system and developed a series of Zr-based good glass formers which exhibit high thermal stability and super properties. The most famous BMG they found is Zr$_{41.2}$Ti$_{13.8}$Cu$_{12.5}$Ni$_{10}$Be$_{22.5}$ (Vitreloy1), which can be cast several centimeters thick, with a critical quenching rate of less than 1 K/sec [19]. Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_{5}$ (Vitreloy 105, named BAM-11 in this report) is another good glass former developed by Johnson’s group [20]. The high glass forming ability (GFA) and good processibility of these BMGs enable them to be considered as potential engineering materials and have been applied in industry. Recently Fe-based and Cu-based amorphous steel have also been reported [21]. These materials are expected to exhibit properties comparable to steels while maintaining the superb properties of BMGs, i.e., high strength, good corrosion resistance and non-magnetism.

A recent trend in the field of BMGs is the study of binary BMGs such as CaAl [22], PdSi [23], CuZr [24] and CuHf [25, 26]. Although containing only two elements, these binary alloys are quite different from the early MGs made by spin casting, they
have large supercooled liquid region and can be cast with a critical thickness of about 2 mm. It has also been found that the partially crystallized CuZr alloys have good ductility while maintaining high strength [24]. This observation stimulated new interest in the study of BMGs, with the hope that partially crystallized BMGs, or composites, which have good ductility without sacrificing too much strength, can be found and successfully produced. Another reason for the interest in these alloys is that the structure of the binary systems is comparably much simpler than multi-component systems, enabling the theoretic studies of structure evolution of the amorphous alloys by applicable experimental methods.

![Critical casting thickness for glasses produced over the last four decades](image)

Figure 1-1 Critical casting thickness for glasses produced over the last four decades [8].

### 1.2 Research interest and questions

Researches for BMGs are mainly carried out in the following areas:
1.2.1 Processing

Early researchers focused on improving fabrication methods and locating the best glass formers, and the continuous discovery of large BMGs promotes interest in this area. Turnbull [10] in 1969 suggested that the reduced glass temperature $T_{rg}$, which is the ratio of the glass transition temperature to the melt point, should be bigger than $2/3$ for good GFA. Inoue proposed three empirical rules for designing of BMG alloys, i. e., (i) the alloy should contain more than three components, (ii) atomic size difference among the main three constituent elements should be bigger than 12%, and (iii) the heat of mixing between the main elements should be negative [27, 28]. Similarly, Johnson suggested the “confusion principle”, which states that the best glass formers should be located around the deep eutectics zone on the binary diagram, then adding other atoms will “confuse” the alloy and increase their GFA [7]. Liu and Lu proposed another parameter $T_x/(T_g+T_l)$, with $T_g$, $T_x$ and $T_l$ being the glass transition, on-set of crystallization and melting temperature respectively [29], which they claimed is a precise assessment of GFA. The above criteria are basically empirical, i. e., parameters like $T_g$, $T_x$ and heat of mixing must be measured before assessment. Many researchers are working on more ‘theoretic’ methods to locate glass formers by various modeling methods, but their work is not summarized here.

Melt-spinning is the main technique to produce early MGs. Other techniques which can provide large cooling rates ($>10^5$ K/s) include atomization, pulsed laser quenching, evaporation and sputtering, et al. In order to provide clean conditions to prevent heterogeneous nucleation, the liquid may be cooled by encapsulating in another liquid (the emulsion or fluxing technique), e. g., Pd-Ni-P is produced by fluxing in Boron oxide. Solid state techniques like ion implanting, mechanical alloying have also been
reported. For BMGs, since the critical cooling-rate is largely reduced, various casting methods can be applied to produce BMGs in the form of rod or plate. Drop-casting is a common method used in the laboratory, with a cooling-rate around 10-100 K/s [30]. The as-cast BMGs have a mirror-like, appealing appearance.

Figure 1-2(a) is a schematic plot of the critical cooling rate and reduced glass transition temperature for three types of glasses, including early MGs made by super cooling, BMGs by casting, and the silicate glasses. Apparently BMGs have good GFA compared to conventional MGs, also comparable to conventional silicate glasses. The similarity between BMGs and silicate glasses explains some properties characteristic for BMGs, e.g., the sluggish kinetics during devitrification, and the high strength but poor ductility.

Much work on the mechanical properties of BMGs has been carried out by Busch and Johnson et al. Figure 1-2(b) is an example of the time-temperature-transformation diagram for Vitreloy1 [31], with the solid and dashed lines being the calculated results for crystalline volume fraction of $10^{-4}$ using different diffusion parameters. The C-shape curve is a result of the competition of thermodynamic driving force and the kinetic diffusion of atoms. Apparently for Vitreloy1, a critical cooling rate of 1 K/s will create a glass. For other BMG systems, the critical cooling rates are higher.
Chapter 1 Introduction

1.2.2 Structure and devitrification

The availability of bulk specimens has enabled measurements of various physical properties and offer opportunities for basic research of the nature of the glassy and supercooled liquid states for metals. One of the focused area is the study of thermodynamics and kinetics during vitrification or devitrification. The question remains open whether the structure of the solid glass is the same as in liquid, or, as stated by Greer [5], whether metals form true glasses or are microcrystalline; even the structures of liquid and the glassy state remain a mystery. The establishment of TTT diagram, measurement of thermophysical properties, shear viscosity and atomic diffusion, are all subjects in this area. The roles of atomic packing and free volume during vitrification are also being studied intensively.

When BMGs are heated, structural relaxation first occurs, during which the atoms resettle to the more stable positions and the strains produced during cooling are relieved.
It has long been observed that annealing at low temperature for a long time makes BMGs more brittle, and some researchers have tried to explain this phenomenon as the intrinsic properties of BMGs [32-34]. Similar to silicate glasses, glass transition happens as the temperature increases, followed by crystallization, resulting in very homogeneous nucleation with a high density (usually $10^{23}$ m$^{-3}$, but as high as $10^{24}$ m$^{-3}$ have been reported [35]).

There have long been debates about the mechanisms for devitrification. Johnson’s group found the appearance of interference peak on the small-angle scattering patterns and suggested that phase separation happens prior to crystallization, the mechanism is similar to spinodal decomposition [8, 9, 36]. Hono et al, using TEM, small-angle scattering and atom probe (AP), claimed that for Zr-based BMGs, there is no evidence of decomposition in the amorphous state; rather, decomposition happens after the appearance of an icosahedral phase [37, 38]. Similar results have been reported early by Revesz et al [35]. They argued that for good glass formers which have negative heat of mixing, phase separation is unlikely to happen thermodynamically; instead, if a system has the mixed compositions of two amorphous alloys, phase separation has been observed, due to a positive heat of mixing between the two main components [39]. These contradictions is a sign that the structure evolution during the early stage of devitrification is still unclear, which is important for applications.

Many have attempted to model the structure of BMGs. The early models based on microcrystalline aggregates have been proved to have significant problems. The most successful models are based on dense random packing [40], but had to be modified in order to comply with the observed local chemical order. A lot of evidence pointed to the short range orders (SROs) in supercooled liquids, while MGs have the icosahedral
configuration. Nelson et al provided a model of a disordered network of icosahedral clusters separated by disclination lines [41, 42]. Recently, Miracle provided a competing structure model for BMGs, based on dense packing of atomic clusters (fcc configuration with icosahedra and interstitial polyhedra) [43]. Despite these facts, a precise and reasonable model still remains to be solved for most BMGs. Successful modeling must be based on experimental results, which, combined with simulation, is expected to reveal the true structure of BMGs.

1.2.3 Mechanical properties and applications

Besides their excellent mechanical properties such as high strength and elasticity, BMGs also have high electric resistivity, good corrosion resistance and wear resistance, compared to many of the alloy counterparts. These excellent properties and the appealing appearance make them potential for applications where small products with complex shapes are needed. For example, protective coatings can be produced using such techniques as “laser glazing” and “flash annealing”. Before 1980’s, the most widely applied property of MGs is their soft magnetism. By devitrification of amorphous glass, nano-composites have been maturely synthesized for soft-magnetic Fe-Si-B (FINEMET) alloys [44] and for hard-magnetic Fe-Nd-B alloys [45].

The most advantageous property of BMGs is their high yield strength up to above 2 GPa. Figure 1-3 is a summary of the yield strength and Young’s modulus for all structural materials [46]. BMGs belong to a class that has near theoretical strength, but has poor plasticity. This makes BMGs ideal for applications where plastic deformation is not desired. Commercially, many sports goods have been produced by Zr-based BMGs [47]. On the other hand, due to the absence of dislocation strengthening mechanisms,
deformations are concentrated in very narrow slip band; once initiated, the failure is catastrophic, limiting the application of this material [48]. Study of the failure mechanisms, as well as deriving the intrinsic relations between the parameters like viscosity, fragility, Poisson ratio and elastic modulus, is another hot area in the field of BMGs. Some pioneering work has been given by Egami [49], Johnson [50] and Busch [51].

Figure 1-3 Elastic limit $\sigma_y$ plotted against modulus $E$ for 1507 metals, alloys, metal matrix composites and metallic glasses. The contours show the yield strain $\sigma_y/E$ and the resilience $\sigma_y^2/E$ [46].

Recently there are some reports on increasing the plasticity of BMGs by introducing nano particles inside the amorphous matrix, either by slightly changing the composition, or by partial crystallization using heat treatment. These particles act as concatenates enabling the propagation of multi slip bands, thus the alloys show the combination of work-hardening and high toughness [24, 52-54]. As a promising direction for applications of BMGs, these nanocrystal/amorphous composite materials also require that the devitrification of BMGs be fully understood.
1.3 Objectives and aim

As a summary of the reviews above, study of the devitrification process will not only have academic significance in understanding the structure of amorphous alloys, as well as the thermodynamic and kinetic mechanisms during crystallization of BMGs, but also will provide the bases for locating good glass formers and synthesizing nanocrystal/glass composites with optimum properties. Since the transformations of BMGs mainly involve structural evolution at the atomic scale, and the time-scale can be very short, conventional experimental methods are insufficient in studying such problems for these materials. Instead, by using the modern high-intensity high-resolution characterization tools such as neutron and synchrotron scattering instruments, the time-resolved structural evolutions during devitrification can be acquired by measuring the scattering patterns while thermally annealing the BMGs in a certain temperature window. Using this technique, both the long-range structural decompositions and the atomic-range topological changes can be identified.

Three BMGs, Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_{5}$ (BAM-11), Mg$_{65}$Cu$_{25}$Tb$_{10}$ (MgBMG), and Zr$_{50}$Cu$_{40}$Al$_{10}$ (ZrBMG) have been chosen for this purpose. These samples stand for three typical types BMGs. BAM-11 stands for the multi-component Zr-based BMGs that have very good GFA but do not contain poisonous Beryllium. Fully amorphous BAM-11 around 7 mm can be made by drop-casting in a copper mode. The alloy is very stable below the glass transition temperature, which is around 670 K, considerably higher than many other BMGs. Although extensive studies have been carried out on Zr-based BMGs, there is debate about their devitrification mechanisms and the structures for the glassy state as well as at different transformation stages. MgBMG stands for the Mg-based
BMGs, which is also a good glass former. Since large rare-earth (RE) atoms are usually contained in this type of BMGs, it is expected that their structure and properties would be different from those of Zr-based BMGs. ZrBMG stands for a large categories of marginal BMGs, i.e., their GFA is not as good as the other two, and it is more difficult to cast the sample into purely amorphous glass, but it is important to study their devitrification process since nanocrystalline composite is a potential direction to produce applicable tough BMGs.

The goal of this thesis includes:

1. Dynamic characterization of the structure evolution of each alloy during devitrification, using mainly the neutron and X-ray scattering method, with complementary tools like DSC, TEM, XRD, AP, etc.

2. On the basis of data analysis, provide reasonable explanations with a focus on local atomic ordering, particle growth and crystallography for different states. This part also requires modeling and kinetic analysis for large scale evolution.

3. Compare the behaviors of different BMGs; summarize the role of clusters in BMGs; proposing new processing methods for applications.

1.4 Overview of this thesis

After a brief introduction about the history, application and research interest for this project in Chapter 1, Chapter 2 will give an abbreviated introduction about scattering theories. In Chapter 3 details of experimental methods are included. The experimental results are accompanied with analysis in each chapter.
As stated above, we focus on the analysis for BAM-11, which is spread from Chapter 4 to Chapter 7. The results for ex-situ experiments are given in Chapter 4. In Chapter 5 a model for small angle scattering during devitrification is deduced for the structural evolution in large scale. The structural evolution in atomic scale is analyzed in Chapter 6, where the details for different transformation stages are given. Chapter 7 shows the results and analysis for total scattering, the structural changes are viewed in real space.

Chapter 8 focuses on the results and analysis for MgBMG.

Chapter 9 is the results for ZrBMG.

In Chapter 10, a comparison is given for the topology between conventional silicate glasses and BMGs, and some conclusions about the characteristics of BMGs structures are drawn.
Chapter 2  
Fundamentals of Scattering Theory

For structure analysis, especially in different length scales from the atomic scale to micron scale, a proper ruler should be selected. Neutron and synchrotron X-ray are such rulers since their wavelengths are in the angstrom scale. Also due to the neutrality of neutron and the high energy of synchrotron X-ray, the particles can transmit through bulky materials, so that the properties measured are not just from surface. For more theoretical and detailed discussions about neutron and X-ray scattering theory, the following books are good references: Warren [55], Marshall and Lovesey [56], Squires [57], and Roe [58], et al. Here a much abbreviated introduction is given, with a focus on some main equations that will be used in this dissertation.

2.1 Scattering cross-sections

Both neutron and X-ray generated from a source can be characterized with a wavelength $\lambda$. The wavevector $k$ is defined to have a magnitude of

$$k = \frac{2\pi}{\lambda} \quad (2-1)$$

The momentum of the particle is defined as

$$\vec{p} = \hbar \vec{k} \quad (2-2)$$

The energy of the wave is defined as

$$E = \frac{1}{2} mv^2 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

$$E = h\nu = \hbar c / \lambda \quad (X - Ray) \quad (2-3)$$

$$E = k_b T \quad (neutron)$$
Where $k_B$ is the Boltzmann constant, $m$ is the mass of particles. Thus, the thermal neutrons generated at room temperature (293 K) have a wavelength of 1.798 Å, with energy of 25.3 meV. Comparably, X-ray with the same wavelength will have much higher energy of 6.9 KeV. This indicates that the energy of neutron is comparable to that of phasons and magnetons for the lattice, thus it is more effective for inelastic scattering to investigate the motions of atoms in materials. X-ray generally is only applied for elastic scattering.

Figure 2-1 is a schematic plot of how the instrument is arranged for scattering experiment. The incident particles are generated from a source. The incident particles are parallel, and coherent for some instruments. After hitting the sample, the particles are scattered in all directions and are detected by a detector located somewhere along a scattering angle of $2\theta$. $\Delta \Omega$ is the solid angle in 3-d space covered by the detector.

![Figure 2-1 A schematic diagram of neutron/X-ray scattering instrument](image)

When a neutron or photon with a wave vector $K_0$ hits an atom, it is scattered in all directions. The incident neutron or X-ray can be represented by a plane wavefunction

$$\psi_{\text{inc}} = \exp(i\vec{k}_0 \cdot \vec{r})$$

(2-4)
When this wave is scattered by a single atom, the behavior of neutron and X-ray is different, because the neutron is scattered by the much smaller nuclei, thus the scattering wavefunction is spherical (isotropic)

\[ \psi_{sc} = \frac{b}{r} \exp(i k r) \]  \hspace{1cm} (2-5)

where \( b \) is the atomic scattering length, which is constant for certain type of atom, but could be quite different for isotopes.

On the other hand, X-ray is scattered by the electrons outside the nuclei. The radii of these electrons to the center are much larger than the nuclei, and the interaction of photons with electrons is more complicated. Consequently the scattering amplitude is not only related with the electron distribution, but also related with scattering angle and wavelength.

\[ f(\vec{Q}) = \int \bar{n}(\vec{r}) \exp(-i \vec{Q} \cdot \vec{r}) d\vec{r} \]  \hspace{1cm} (2-6)

Where \( n(r) \) is the distribution of electrons in the element, and \( Q \) is transferred momentum, which is related with the scattering angle of \( 2\theta \)

\[ \vec{Q} = \vec{k}_1 - \vec{k}_0 \]

\[ |Q| = 4\pi \sin \theta / \lambda \hspace{0.5cm} (elastic) \] \hspace{1cm} (2-7)

Empirically the atomic scattering function for X-ray is calculated with the function given in the International Tables for Crstallography [59].

The differential cross-section is given by the ratio of measured flux and the incident flux

\[ \frac{d\sigma}{d\Omega} = \frac{C}{\Phi d\Omega} \] \hspace{1cm} (2-8)
Chapter 2 Fundamentals of Scattering Theory

Where flux \( C \) is monitor count rate, \( \Phi \) is the incident flux, \( d\Omega \) is the 3-dimensional solid angle for the monitor. The total cross-section for an element is

\[
\sigma = \int_0^\pi \int_0^{2\pi} \frac{d\sigma}{d\Omega} \sin \theta \, d\phi \, d\theta
\]  
(2-9)

If only elastic scattering is considered, the cross-section of an atom is the effective collision spherical area, for neutron this area is given by

\[
\sigma = \frac{\pi}{2}
\]  
(2-10)

The cross-section is what is actually measured in experiments. The intensity detected by the detector is the sum up of the square of the amplitude of scattering wavefunction generated by each atom. Mathematically this is a Fourier transformation of the scattering length distribution from real space to Q-space

\[
I(Q) = |A(Q)|^2 = \left| \int_V \rho(r) \exp(-iQr) \, dr \right|^2
\]  
(2-11)

where \( \rho(r) \) is the scattering length density distribution.

The square operation causes the loss of phase information, and consequently the structural information can not be retrieved by reverse Fourier transformation directly. It also contains a correlation term between different atoms. A basic equation for differential cross-section for nuclear scattering is given in Squires’ book [57]:

\[
\frac{d^2\sigma}{d\Omega dE} = \frac{k_i}{k_o} \frac{1}{2\pi\hbar} \sum_y b_y b_j \int_{-\infty}^{\infty} \exp(-i\vec{k}_o \cdot \vec{R}_j(0)) \exp(i\vec{k} \cdot \vec{R}_j(t)) \exp(-i\omega t) \, dt
\]  
(2-12)

This is a complex equation involving the dynamic movement of both the sample and the scattering particle. For neutron, the intensity for elastic scattering (no energy change) is simplified as
where $R_i$ and $R_j$ are the positions of atoms, which indicate how correlation between atoms could result in different scattering patterns.

Two concepts need to be clarified: coherent and incoherent scattering, elastic and inelastic scattering. These concepts may be simply differentiated by stating that elastic/inelastic scattering is related with energy of the scattering particle (unchanged/change), while coherent/incoherent scattering for neutron is caused by the fact that the individual atoms for the same element can have different scattering lengths. The incoherent scattering is only important for neutron scattering.

$$b_{inc} = (\langle b^2 \rangle - \langle b \rangle^2)^{1/2}$$

The Compton-modified scattering for X-ray is also incoherent because the phase coherence is lost. Incoherent scattering contains no structural information and thus can be considered to be only contributed to the background.

### 2.2 Wide-angle scattering

The scattering patterns for most crystalline materials are measured in the high-Q range, where the correlation in atomic scale is important. Since the phase information is lost in intensity, modeling is necessary to match the scattering patterns. Namely, this is called the Rietveld refinement. The crystals are modeled as the replication of a unit cell in real space.

$$\rho(r) = \rho_u(r) \otimes z(r)$$

Where $\rho_u(r)$ is the scattering length density of the unit cell, and $z(r)$ is lattice points expressed as 3-d $\delta$-function.
Chapter 2 Fundamentals of Scattering Theory

\[ z(r) = \sum_{uvw} \sum_{uvw} \sum_{uvw} \delta(r - r_{uvw}) \]  

(2-16)

The amplitude of the scattered wave is the Fourier transform of \( \rho(r) \), thus

\[ I(Q) \propto |F(Q)Z(Q)|^2 \]  

(2-17)

Where \( F(Q) \) and \( Z(Q) \) are the structure factors of the unit cell and the lattice, respectively. \( Z(Q) \) is a lattice in reciprocal space. Due to the relationship of real space and reciprocal space, Bragg law must be satisfied for a diffraction peak, as illustrated in Figure 2-2(a).

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

(2-18)

In reciprocal space, only those \( <hkl> \) located on the Ewald sphere will have a diffraction peak, as demonstrated in Figure 2-2(b). For synchrotron X-ray, the wavelength is constant, but the image plate can detect the scattering pattern in a range of scattering angles. For neutron scattering, the wavelength is continuous, while the scattering angle is usually fixed. The time of flight technique is applied to bin the scattering patterns from several angles in order to increase statistics.

Figure 2-2 schematic plot for (a) Bragg law, and (b) Ewald sphere [60]
Since the atoms are oscillating around their equilibrium positions, which is basically a temperature effect, Debye-Waller factor is induced to modify the structure factor

\[
D = \exp(-2W_d) = \frac{1}{3} Q^2 \langle u \rangle^2 \\
F_{hkl}' = F_{hkl} \exp(-W_d)
\]  

(2-19)

where \( \langle u \rangle \) is the root-mean-square displacement of the atom.

In Rietveld refinement, the measured scattering intensity is compared with a calculated intensity according to [61]

\[
I_c = I_b + I_d + S_h \sum_p S_{ph} Y_{ph} \\
Y_{ph} = F_{ph}^2 H K_{ph} = F_{ph}^2 H E_{ph} A_h O_{ph} M_p L / V_p
\]

(2-20)

Where \( I_b \) is the background, \( I_d \) is the diffuse scattering, \( S_h \) and \( S_{ph} \) is the scale factor for the histogram and for each phase, \( Y_{ph} \) is the Bragg intensity of the phase, \( H \) is the peak profile, \( K_{ph} \) is the intensity correction factor, which contains extinction correction (\( E_{ph} \)), absorption (\( A_h \)), preferred orientation correction (\( O_{ph} \)), multiplicity (\( M_p \)), angle dependent correction (\( L \)), and \( V_p \) is the unit cell volume of the phase.

### 2.3 Small-angle scattering (SAS)

According to the reciprocal relation of \( Q \) and \( r \), scattering patterns must be measured in small \( Q \)-range in order to detect the structure in large scale (10 Å or larger). Small scattering angle (below 2°) and long distance between sample and detector are required for this purpose. SAS is a collective name for small angle neutron scattering (SANS), small angle X-ray scattering (SAXS) and light scattering (LS). The types of samples can be studied, sample environment can be applied, length scale can be probed.
and information can be obtained, are largely related with the nature of radiation. For SANS and SAXS, the probable length scale is from several nm to about 1 μm. Examples in the area of SAS include the particle shape in dilute solute, nonparticulate two-phase system, blends, phase boundary, etc.

The intensity of small angle scattering (SAS) is expressed by [62]

\[ I(Q) = SN_p V_p^2 (\Delta \rho)^2 P(Q)S(Q) + B_{inc} \]  \tag{2-21} \]

Where S is a scale factor determined by instrument, \( N_p \) is the number density of particles, \( V_p \) is the volume of particles, \( \Delta \delta \) is the difference of scattering length density (contrast) between particle and solvent, \( P(Q) \) is the form factor of the particle, \( S(Q) \) is the interparticle structure factor, and \( B \) is the background.

The scattering length density is given by

\[ \rho = \sum_i b_i \frac{DN_A}{M_w} \]  \tag{2-22} \]

where \( b \) is the scattering length for each atom, \( D \) is the mass density, \( N_A \) is the Avogadro's constant, and \( M_w \) is the molecule weight.

Equation 2-21 shows that the scattering intensity can be separated into two contributions, one is the intraparticle form factor \( P(Q) \), namely, from the interference of radiations from different parts inside the particle, which is important for studying the interference peak appears on SAS patterns for BMGs. The general form of \( P(Q) \) is [63]

\[ P(Q) = \left| \int_0^{V_p} \exp(i f(Qa)) dV_p \right|^2 / V_p^2 \]  \tag{2-23} \]

where \( a \) is a shape factor related with particle size, usually radius of gyration. \( P(Q) \) for most common shapes is available in literatures [62, 63].

The structure factor describes the interparticle correlations.
\[ S(Q) = 1 + \frac{4\pi N_p}{QV} \int_0^\infty [g(r) - 1] r \sin(Qr) dr \]  

(2-24)

which has the similar meaning of the total structure factor that will be described in the next section, except that the pair distribution function (PDF) \( g(r) \) is the distribution of particles, not atoms. For dilute particulate system, \( S(Q) \) can simply be assumed to be 1.

Details about the modeling for small angle scattering will be given in the part of analyzing SAXS patterns in this thesis.

### 2.4 Pair distribution function

In crystallography, besides the method of modeling the diffraction patterns of crystalline materials by Rietveld refinement of the intensity and positions of Bragg peaks, another method called “total scattering” has become important for noncrystalline materials. By measuring the scattering patterns in large Q-range, the PDFs can be obtained by Fourier transformation, thus structural information in real space can be retrieved. By definition, the PDF is the probability of finding any two atoms at a given interatomic distance [55]. Although this technique has long been developed ever since the early days of neutron and X-ray scattering, it has been further benefited by the improvement in instrumentation, making it an ideal tool for studying the atomic and medium range order of complex materials, especially glass and liquids [64]. It has also been applied to study the defects of crystalline materials that contain structural information underneath the Bragg peaks [65].

The interatomic positional correlations can be described by a set of interatomic distances
Chapter 2 Fundamentals of Scattering Theory

\[ \rho(r) = \rho_0 g(r) = \frac{1}{4\pi N r^2} \sum_u \sum_v \delta(r - r_{uv}) \]

\[ \rho_0 = d \frac{N_A}{M_W} \]

where \( \rho_0 \) is the number density of atoms, \( N \) is the total number of atoms, \( d \) is the mass density, \( N_A \) is the Avogadro constant and \( M_W \) is the molecular weight. The function \( \rho(r) \) is called the atomic pair density function (PDF), and \( g(r) \) is called the atomic pair distribution function (also PDF). This equation indicates that PDF is an averaging of the 3-dimensional positional information into 1-dimension. For multi-component system, generally it is hard to get the partial PDFs for each pair of atoms; instead, a total PDF is obtained, which is the average of all partial PDFs, weighted by their relative scattering length

\[ g(r) = \sum_{a \beta} \frac{c_a c_\beta b_a b_\beta}{\langle b \rangle^2} g_{a\beta}(r) = \frac{1}{4\pi \rho_0 r^2} \sum_{i,j} \frac{b_i b_j}{\langle b \rangle^2} \delta(r - |r_i - r_j|) \]

Experimentally, the average/total structure factor \( S(Q) \) is obtained by removing the incoherent scattering and normalizing the equivalent scattering intensity to the average scattering factor [66]

\[ S_a(Q) = \frac{I(Q) / N - \langle b_i a_i b_i a_i \rangle}{\langle b_i b_i \rangle} \exp \left( -\frac{BQ^2}{8\pi} \right) \]

\[ \langle b_i b_i \rangle = \sum_i a_i b_i \]

where \( N \) is the sum of scattering atoms, \( B \) is the Debye parameter, \( a_i \) is the atomic concentration, \( b \) is the atomic scattering factor, which is a constant for neutron, but is a function of \( Q \) for X-ray.

Empirically, \( S(Q) \) is obtained using the criterion that the asymptote of \( S(Q) \) should equal to 1 at high-\( Q \), after corrections for contributions from absorption, polarization, multi-scattering, background etc.
Chapter 2 Fundamentals of Scattering Theory

\[ I(Q) = \frac{(S - S_B) - \alpha(C - C_B)}{V - V_B} \]  

(2-28)

\( S(Q) \) contains the information for both local and long range structure. The reduced pair distribution function \( G(R) \) is widely used to describe the correlation in real space, since it is a direct Fourier transformation of \( S(Q) \)

\[ G(r) = \frac{2}{\pi} \int_0^\infty S(Q) \sin(Qr) dQ = 4\pi r [\rho(r) - \rho_0] \]  

(2-29)

accordingly \( G(r) \) will be around 0 in the limit of larger \( R \), and at small \( R \) this function has a slope of \(-4\pi\rho_0\). The advantage of using \( G(r) \) instead of \( g(r) \) is that the random uncertainties of \( G(r) \) are constant in all \( r \)-ranges [64].

Another widely used function is the radial distribution function (RDF)

\[ R(r) = 4\pi r^2 \rho_0 g(r) \]  

(2-30)

which has the useful property that \( R(r)dr \) gives the number of atoms in a spherical shell of \( dr \) in thickness at distance \( r \) from another atom. Numerically, the RDF has the physical meaning of

\[ R(r) = \sum_i \sum_j \frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij}) \]  

(2-31)

which has the meaning that the peaks come from well-defined atom-atom pairs and the RDF reflects the precise shape of the pair-probability distribution.

The coordination number \( (N(r)) \) is then calculated by

\[ N(r) = \int_{r_1}^{r_2} R(r)dr = \int_{r_1}^{r_2} 4\pi r^2 \rho(r)dr \]  

(2-32)
2.5 Comparison of neutron and X-ray scattering

Due to the fact that neutron is scattered by nuclei while X-ray is scattered by electrons, neutron and X-ray have different advantages as tools for structure characterization, thus complement each other.

First, since the atomic scattering factor for X-ray is proportional to atomic number, it is hard for X-ray to detect the light elements like hydrogen. While for neutron, the atomic scattering factor can be quite different for different isotopes of the same element, for example, there is a large difference between the scattering factors of deuterium (b=6.67 fm) and hydrogen (b=-3.74 fm), which is why neutron scattering is especially important for studying organic materials.

Second, the atomic scattering factor of X-ray decreases with Q, while for neutron the scattering factor is constant. This limits the application of X-ray in the area where scattering from high-Q is important. For example, for total scattering experiment, the Q-range of neutron instrument can reach up to 40 Å⁻¹, while the Q-range of X-ray can only reach up around 20 Å⁻¹, using the image plate as detector [67]. Also because of this, the correction for X-ray scattering is more complicated in order to retrieve structure factors, which will be described in later chapters.

Neutron is uncharged and can penetrate deeply into the target. Laboratory (conventional) X-ray can only be scattered by the surface in micron range, because of the strong interaction between photons and electrons. Synchrotron X-ray can penetrate into the sample much deeper and scattering can be measured in transmission mode. Yet the transmission thickness is still much smaller than neutron. For example, as calculated by Withers, the penetration depth of neutron on Ni plate is 15 mm, while the 60 keV...
synchrotron X-ray can only transmit 5 mm through Ni [68]. Experimental depth is even smaller than these numbers, usually samples for neutron scattering can reach cm, while for X-ray the depth should be in mm scale. In this sense it is safe to say neutron characterizes the structure of bulky materials.

The energy of thermal neutrons is in the range of several tens or hundredth of mW, in the same order as that of many excitations in condensed materials, making neutron extremely suitable for inelastic scattering, which provides information on the energies of excitations while providing structural information. X-ray, on the other hand, has much higher energy, and usually is not scattered inelastically. Yet, the anomalous X-ray scattering can detect the position of certain element by tuning the wavelength to the absorption edge of that element, which is especially advantageous for measurement of partial PDFs.

Another advantage of neutron is that neutron has a magnetic moment, which can be applied to give information on the arrangement of electron spins and the density distribution of unpaired electrons. Inelastic scattering can give the energies of magnetic excitations or be applied to study spin correlations.

Due to their specific properties, neutron and X-ray scattering are two characterization methods which often complement each other. Since the scattering factors of the same material can be quite different, the scattering patterns, especial the PDFs, could be quite different for neutron and X-ray scattering. This feature is very useful in solving the structure, especially local structure, of glasses or materials having local disorder.
Chapter 3  Experimental Methods

In this chapter, a detailed description of all the experiments involved for this thesis work is given.

3.1 Sample systems studied

Three BMG alloys have been studied, including Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_{5}$ (BAM-11), Zr$_{50}$Cu$_{40}$Al$_{10}$ (ZrBMG) and Mg$_{65}$Cu$_{25}$Tb$_{10}$ (MgBMG). The quinary BAM-11 stands for multi-component Zr-based good glass former, which was first developed at Caltech, with a trade name of Vitreloy105, while the sample developed in Oak Ridge National Laboratory has the name of BAM-11. The ternary ZrBMG stands for the marginal glass former, the GFA of which is not so good as BAM-11, but is still quite good. The MgBMG stands for the Mg-RE-based BMG with quite good GFA, which is a derivative of the Mg-Cu-Y system first developed by Inoue group.

Samples for BAM-11 are prepared by drop-casting at Oak Ridge National Laboratory. The stoichiometric pure elements with high purity (>99.9%) are arc-melted in a purified argon atmosphere using Zr-getter. The ingots are flipped and remelted for five times before drop-casting into a copper mold with 6.4 mm in diameter and 76.2 mm in length. The cooling rate is around 10-100 K/sec. Due to the high purity of Zr (< 500 ppm), the oxygen concentration of the as-cast sample is very low (concentration of impurities <590 ppm), and microscopy test show total glassy phase [30].
The MgBMG was prepared by arc melting Cu and Tb (purity ~99.9 at%) first, then induction melting the Cu-Tb alloy with Mg (purity 99.99 at%) in a quartz tube under vacuum. The homogeneously melted liquid was injected into a copper mold to get a rod of 5 mm in diameter and 50 mm in length. Details about sample preparation is described in [69]. The oxygen content for samples made under vacuum is around 0.1 at%.

The ladle-hearth type arc-melt tilt-casting technique was employed to manufacture the ternary ZrBMG. Similar to BAM-11 a high purity Zr getter was also applied to reduce the oxygen contamination. The cast rod sample of 8 mm in diameter and 60 mm in length was fabricated by the tilt-casting method in an arc furnace via a pseudo-floating-melt state before casting to obtain a completely melted state [70].

The composition, sample sizes, density, molecular weight and number densities of all three samples are given in Table 3-1. A lot of work of this dissertation will be focused on BAM-11, since this alloy has very good GFA and its properties are typical for multi-component BMGs, which are quite different from the early MGs manufactured by fast cooling. And, an important part of this dissertation is allocated to the comparison between different BMG systems, based on the experimental results for all samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Diameter (mm)</th>
<th>Oxygen (ppm)</th>
<th>Density (g/cm³)</th>
<th>Mw (g/mol)</th>
<th>ρ₀ (Å⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAM-11</td>
<td>Zr₅₂.₅Cu₁₇.₉Ni₁₄.₆Al₁₀Ti₅</td>
<td>6.4</td>
<td>590</td>
<td>6.50</td>
<td>72.9</td>
<td>0.05365</td>
</tr>
<tr>
<td>MgBMG</td>
<td>Mg₆₅Cu₂₅Tb₁₀</td>
<td>5</td>
<td>1000</td>
<td>3.79</td>
<td>47.6</td>
<td>0.04796</td>
</tr>
<tr>
<td>ZrBMG</td>
<td>Zr₅₀Cu₄₀Al₁₀</td>
<td>5</td>
<td>~590</td>
<td>6.60</td>
<td>73.7</td>
<td>0.05389</td>
</tr>
</tbody>
</table>
3.2 In-situ experiments

In order to characterize the inside structure of bulky samples, scattering particles must be able to transmit the sample that has a large thickness and the scattered particles should be detected and collected for certain time interval to ensure good statistics. With the development of new generation neutron and synchrotron instruments that have high intensity and high resolution, in-situ characterization of structure evolution is possible under conventional and extreme conditions. Presently, the brightness of neutron source can reach $10^{15} \text{s}^{-1}\text{m}^{-2}\text{ster}^{-1}$ for the Spallation Neutron Source [71]—which will be available very soon, and about $10^{33} \text{s}^{-1}\text{m}^{-2}\text{ster}^{-1}$ for Synchrotron using an undulator at Advanced Photon Source in Argonne National Laboratory [72]. Unlike the conventional X-ray Diffraction (XRD), synchrotron X-ray can transmit through bulk samples of several minimeters in thickness and the scattering patterns contain the structural information of the bulky material [68]. The penetration depth of neutron and X-ray has been calculated and shown in Table 3-2 for some known instruments. The actual sample thickness should be smaller than these values. It is obvious from this table that the penetration depth of neutron is much bigger than that of synchrotron, while laboratory X-rays can detect only a thin layer near the surface (micron range).

With the high-flux neutron instruments, a scattering pattern with good statistics can be obtained in minutes, while only several seconds are needed by synchrotron scattering. This means that neutrons and high-energy synchrotron X-ray are extremely advantageous for dynamic structure studies. Two kinds of neutron/X-ray scattering experiments have been carried out in this work. Both are in-situ dynamic study.
Chapter 3 Experimental Methods

Table 3-2 Calculated penetration depth of neutron and X-ray in minimeters [68]

<table>
<thead>
<tr>
<th>Source</th>
<th>$2\theta$ °</th>
<th>Al</th>
<th>Ti</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutrons</td>
<td>45</td>
<td>115</td>
<td>55</td>
<td>15</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>ID31 (60 keV)</td>
<td>45</td>
<td>115</td>
<td>55</td>
<td>15</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>ID11 (50 keV)</td>
<td>55</td>
<td>3.2</td>
<td>16</td>
<td>1.1</td>
<td>9</td>
<td>0.6</td>
</tr>
<tr>
<td>BM16 (40 keV)</td>
<td>55</td>
<td>3.2</td>
<td>13</td>
<td>0.9</td>
<td>6</td>
<td>0.4</td>
</tr>
<tr>
<td>16.3 SRS (30 keV)</td>
<td>10</td>
<td>17</td>
<td>1.5</td>
<td>3.2</td>
<td>1.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Lab. Cu X-ray</td>
<td>65</td>
<td>0.034</td>
<td>0.005</td>
<td>0.002</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

* $D_t$ -- the depth for transmission scattering
** $D_r$ -- the depth for reflective scattering

3.2.1 Synchrotron scattering with WAXS and SAXS simultaneously

The in-situ experiment was carried out on sector 1-ID at Advanced Photon Source (APS), Argonne National Laboratory. Samples were cut from the rods into disks of 1 mm in thickness. After removing the surface contaminates by grinding, samples were placed in a copper holder inside a vacuum furnace. As shown in Figure 3-1(b), the copper holder is composed of two pieces of copper disks which have a hole of 2 mm in diameter at the center. The 80 keV X-ray photon beam with a focus size of 1 mm$^2$ transmitted through the Boron window, illuminated the sample through the hole, then the photons were scattered by the sample and detected simultaneously by two CCD cameras, one for SAXS ($Q \sim 0$-0.0065 Å$^{-1}$, $Q = 4\pi \sin \theta / \lambda$), the other for WAXS ($Q = 1.96$-8.5 Å$^{-1}$), as shown in Figure 3-1. Using silicon double crystal, the resolution ($\Delta d/d$) of this beamline can reach 0.15%. The flux is around $10^{12}$ photons/sec, thus only about 4 seconds are needed for excellent statistics. Including the data processing time, the scattering patterns were recorded every 20 or 30 seconds.
Figure 3-1 (a) Schematic diagram of the arrangement of instrument; (b) sample standing inside the furnace, the upper part is a rectangular copper holder, the hole is where X-ray transmit through the sample.

The heat-treatment histories for all samples are shown in Table 3-3. A focus has been made on BAM-11, which has been isochronally annealed at different heating rate and isothermally annealed at several temperatures separately around its glass transition temperature. MgBMG samples were isochronally annealed with a rate of 5 K/min, and two samples were measured at the same heating rate to exam the reproducibility. ZrBMG was isochronally annealed at a relatively high rate (10 K/min), and it was also isothermally annealed at 690 K and 700 K. For all isothermal annealing, the samples were heated quickly (30 K/min) before reaching the setting temperature.

<table>
<thead>
<tr>
<th>Table 3-3 Heat treatment for all sample during synchrotron scattering</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Isochronal</strong></td>
</tr>
<tr>
<td><strong>Heating-rate (K/min)</strong></td>
</tr>
<tr>
<td><strong>Isothermal</strong></td>
</tr>
<tr>
<td><strong>Temperature (K)</strong></td>
</tr>
<tr>
<td>BAM-11</td>
</tr>
<tr>
<td>MgBMG</td>
</tr>
<tr>
<td>ZrBMG</td>
</tr>
</tbody>
</table>
Data recorded by the CCD cameras were first corrected for detector efficiency; the 2-dimensional data were then binned in Q-space using the software Fit2D. Finally the intensities were normalized according to monitor counts.

### 3.2.2 Neutron and synchrotron total scattering

The neutron total scattering experiments were carried out on the instrument of Neutron Powder Diffractometer (NPDF) in Los Alamos National Laboratory (LANL). For BAM-11, samples of $\phi 6.4\text{mm}*4.5\text{cm}$ cut directly from the as-cast rods were put inside the vanadium container and mounted in a vacuum furnace. After collecting data at room temperature for one hour, temperature was increased with a rate of 5 K/min to the setting isothermal temperature (one at 663 K, the other at 678 K), and kept there until the samples were fully crystallized. Data were recorded every 20 min.

For ZrBMG, the sample size is smaller ($\phi 5\text{mm}*4.5\text{cm}$). One sample was annealed at 663 K for 10 hours, and because of the slow evolution at this temperature, the temperature was increased to 673 K and stayed there for 2 hours, then increased to 683 K for 2 hours, and again up to 693 K for 5 hours until the Bragg peaks appeared. Another sample of ZrBMG was measured at room temperature for 1 hour, then the temperature was increased 5 K/min to 685 K and isothermally annealed for 8 hours.

Total scattering patterns for BAM-11 were also obtained by X-ray scattering. Experiments were carried out at APS, sector 6-ID. The scattering patterns were detected by a CCD camera, with a Q-range of 0.01-20 Å$^{-1}$. Samples with a size of $2\text{mm}*3\text{mm}*0.5\text{mm}$ were placed inside a vacuum furnace, and temperatures were calibrated and well-controlled. The scattering patterns for three samples were obtained,
one isochronally annealed with a rate of 10 K/min, the other two isothermally annealed at 678 K and 708 K. The interval between each scan is 30 seconds.

Some parameters of the two instruments are listed in Table 3-4. Obviously the synchrotron instrument has much better resolution, but the neutron instrument has larger Q-range, and the sample is much bigger, that means, the scattering factor measured is more reliable because it comes from a large gauge volume. Although the flux of the neutron source in LANL is high, data still need to be collected for longer time on the neutron instrument to ensure good statistics. *Egami rule* states that one need to accumulate $10^6$ neutrons / Å$^{-1}$ in the high Q region [66]. For BAM-11, results show that combining datasets within one hour is good enough; for ZrBMG, the time should be increased to around two hours, because of the smaller sample size. The statistics of synchrotron scattering is always very good.

<table>
<thead>
<tr>
<th>Table 3-4 Instrument parameters for total scattering tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>$NPDF$ (Neutron)</td>
</tr>
<tr>
<td>Bank</td>
</tr>
<tr>
<td>D-spacing (Å)</td>
</tr>
<tr>
<td>Q (Å$^{-1}$)</td>
</tr>
<tr>
<td>$\Delta d/d$ (%)</td>
</tr>
</tbody>
</table>

### 3.3 Ex-situ experiments

In this work, the main role of ex-situ experiments is to complement the in-situ experiments. As a demonstration BAM-11 has been carefully studied. The first widely applied experiment is the differential scanning calorimetric (DSC) test. In a quick scanning mode, DSC can provide such parameters as glass transition temperature (Tg),
crystallization temperature (Tx), and melting temperature (Tm), which are not only important to evaluate the GFA of BMGs, but also help design the scattering tests by providing suitable temperature and time window. Another important application of DSC is the kinetic studies, in a high resolution mode. Experiments were carried out at High Temperature Materials Laboratory in Oak Ridge National Laboratory. The high temperature Netzsch DSC404C was used for DSC tests.

Laboratory X-ray diffraction (XRD) tests were performed on a Scintag PAD V room temperature diffractometer, using Cu-Kα source. Patterns were obtained by scanning from 10 to 90 (2θ) with a speed of 1 degree/min. The samples were prepared by isothermal or isochronal annealing in the DSC chamber for different time followed by quenching in the chamber.

Transmission electronic microscopy (TEM) tests were performed on Philips CM200 in the Metals and Ceramics Division of ORNL. Similarly the samples were prepared by annealing in the DSC chamber, then the oxides on the surface were mechanically grinded, and the TEM samples were prepared by electropolishing thinning.
Chapter 4  BAM-11 Ex-situ Experimental

Results

This chapter is a summary of all the ex-situ experiments carried out for BAM-11, including DSC, XRD and TEM. The DSC traces are refined with a Johnson-Mehl-Avrami (JMA) model.

4.1 Thermokinetic study by DSC

4.1.1 Experimental

The high temperature Netzsch DSC404C was used for DSC tests. The calorimeter was carefully calibrated before each set of tests. Argon was used as purging and protecting gas. Sample disks of 5 mm in diameter and about 1 mm in thickness were cut from a drop-cast rod. The sample mass was around 180 mg for isochronal tests. Five tests were performed with a heating rate of 1, 2, 5, 10 and 20 K/min. A 63 mg sapphire was used as reference.

For isothermal tests, the samples were considerably larger (~250mg), Pt-Rh pans were used, with a sapphire reference around 90 mg. From room temperature to 573 K, the samples were heated with a rate of 30 K/min; from 573 K to set point, the heating rate was 10 K/min. For stability the furnace temperature was controlled, which is about 4 degree higher than that of the sample temperature, in the experimental temperature range. Figure 4-1 shows the recorded heating curve for isothermal annealing at 665 K. The
temperature difference between sample and furnace was quickly reduced after reaching the set temperature (669 K), in about 5 minutes the sample temperature became very stable around 665.6±0.02 K. The samples were isothermally annealed at 655, 665, 670 and 675 K until almost fully crystallized. Due to the high resolution of the calorimeter, very weak signals can still be detected when the isothermal temperature is rather low.

Figure 4-1 Heating curve for isothermal annealing at 665 K; in the stable state, the difference between set point and sample temperature is in the range of ±0.02 K.

4.1.2 Results

Figure 4-2(a) is the isochronal results for 5 heating rates. All these patterns show glass transition and two continuous exothermal peaks for the devitrification process, which become more overlapped at higher heating rates. At 20 K/min, a common heating-rate in literature, the two peaks collapse into a single asymmetric peak. This indicates that the heating-rate must be very low to study the structure evolutions by neutron or X-ray scattering. Two more separate peaks are also observed at higher temperature, but the peak areas are rather small.

Table 4-1 shows several parameters obtained from DSC, including Tg (by different definitions), Tx, and the peak areas. These parameters are obtained using a
Chapter 4 BAM-11 Ex-situ Experimental Results

tangential baseline in the software associated with the instrument. It is clear from theses results that the transformation fraction is closely related with heating rate. At lower heating rate (< 5 K/min), the fraction of the first peak among the two devitrification peaks is almost constant (39%); but at higher heating rate, the first peak shrinks to less than 20%. These facts prove that in order to study the early devitrification stages, it is essential to study the transformation at lower heating rates.

Figure 4-2 DSC traces for (a) isochronal annealing with a rate of 1, 2, 5, 10 and 20 K/min, and (b) Isothermal annealing at 675, 670, 665 and 655 K

Table 4-1 Glass transition temperature, crystallization critical temperature and peak areas obtained from isochronal scans

<table>
<thead>
<tr>
<th>Heating rate (K/min)</th>
<th>Tg (K)</th>
<th>Tx (K)</th>
<th>Area (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>onset</td>
<td>mid</td>
<td>inflection</td>
</tr>
<tr>
<td></td>
<td>Tx1</td>
<td>Tx2</td>
<td>peak1</td>
</tr>
<tr>
<td>1</td>
<td>654.5</td>
<td>667.5</td>
<td>664.5</td>
</tr>
<tr>
<td>2</td>
<td>657.4</td>
<td>668.4</td>
<td>672</td>
</tr>
<tr>
<td>5</td>
<td>660.4</td>
<td>674.6</td>
<td>678.3</td>
</tr>
<tr>
<td>10</td>
<td>666.2</td>
<td>681.3</td>
<td>686.1</td>
</tr>
<tr>
<td>20</td>
<td>672</td>
<td>688.4</td>
<td>692.4</td>
</tr>
</tbody>
</table>

Figure 4-2(b) shows the isothermal DSC traces. Two exothermal peaks develop not long after the sample reaches the set temperature. These two peaks correspond to the
two main peaks on isochronal patterns. As stated in Chen’s paper [73], it is possible that nanocrystalline materials can show a peak on isochronal DSC test, but will show only constant growing on isothermal traces. Thus our results prove that the original sample is truly amorphous instead of being microcrystalline. This means that the material must undergo a nucleation and growth process. The peaks become broad as the temperature decreases; at 655 K the two peaks are so broad and overlapped that it is hard to separate them. It takes long time for the second peak to reach the base line, which can be explained by the fact that the 3rd and 4th crystallization peaks, as observed on isochronal traces, are buried underneath. It is clear from these DSC traces that isochronal scans can provide quick information about important parameters, while isothermal tests provide the appropriate temperature window for precise kinetic study and controllable processing, as well as for designing of the in-situ scattering tests.

4.1.3 Kinetic model

Crystallization of BMG belongs to the first-order phase transition during which the crystalline phase is formed by nucleation and growth. The Kolmogorov-Johnson-Mehl-Avrami (KJMA) theory is widely applied to model this transformation, which depicts the evolution of crystalline phase as [74, 75]

\[ x(t) = 1 - \exp(-K(t - t_0)^n) \]  

(4-1)

where \( x \) is the transformed volume fraction, \( K \) is the rate constant, \( n \) is the Avrami exponent and \( t_0 \) the incubation time. The value of \( K \) is related to activation energy following Arrhenius law

\[ K = K_0 \exp(-E / RT) \]  

(4-2)
Chapter 4 BAM-11 Ex-situ Experimental Results

For isochronal tests, the activation energy is obtained from Kissinger equation [76]:

\[
\ln(T_p^2 / b) = E / RT_p + \text{const}
\]

(4-3)

where \(b\) is the heating-rate, and \(T_p\) is the temperature for the same peak on different DSC traces.

For isothermal tests, the activation energy is obtained by the Arrhenius law

\[
t_x = A \exp(E / RT)
\]

(4-4)

where \(t_x\) is the time needed for reaching certain reaction ratio \(x\).

The Avrami exponent \(n\) can be obtained from the slope of the JMA plot with \(\ln[-\ln(1-x)]\) vs. \(\ln(t-t_0)\). This parameter reflects the transformation/reaction mechanisms. Basically, for 3-d system, the meaning of \(n\) is as follows [77]:

- \(n=4\): the transformation is characterized by constant nucleation rate
- \(n=3\): there exist latent germ nuclei;
- \(n=2.5\): particles grow by 3-d long-range diffusion;
- \(n<2.5\): particles grow by long-range diffusion at lower dimensions.

Figure 4-3 illustrates the calculation of activation energies for different stages. (a) is the Kissinger plots for isochronal tests, and (b) presents the isothermal tests. It is assumed that the isoconversion assumption is valid in the range of isochronal heating-rates or isothermal temperatures. The values of activation energies are determined by the slopes of linear fitting according to equation (4-3) and (4-4), respectively. For isochronal tests, 5 nominal values are obtained for the glass transition and the four crystallization peaks; for isothermal tests, the activation energies for the beginning of crystallization and 3 exothermal peaks (the 3rd peak is barely distinguishable but shows as a plateau on the
tail of the second peak) are obtained. The results are shown in Table 4-2. Both the isochronal and the isothermal tests show similar trend for activation energies at different stages. For isochronal tests, the activation energy for the first peak is much smaller than that from the isothermal tests (304.3 vs 396.3KJ/mol). And the activation energies for both stages are higher for isothermal test.

![Figure 4-3 Activation energy decided by a) Kissinger plot for isochronal DSC traces, and b) Arrhenius law for isothermal DSC traces.](image)

**Table 4-2 Activation energies obtained from Kissinger plot and Arrhenius plot**

<table>
<thead>
<tr>
<th></th>
<th>Start</th>
<th>Peak1</th>
<th>Peak2</th>
<th>Peak3</th>
<th>Peak4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isochronal</td>
<td>354.1</td>
<td>304.2</td>
<td>377.4</td>
<td>335.1</td>
<td>243.3</td>
</tr>
<tr>
<td>Isothermal</td>
<td>326.6</td>
<td>396.3</td>
<td>407.8</td>
<td>370.1</td>
<td>-</td>
</tr>
</tbody>
</table>

The thermokinetic analysis is performed by refining the DSC traces using the accompany software developed by Netzsch. The modeling starts with a general reaction equation [78]

\[ \frac{dE}{dt} = -A \exp\left(-\frac{E}{RT}\right) f(e, p) \] (4-5)
where e and p are the concentration of the educt and product respectively. For a one step unary transformation A->B, the n-dimensional nucleation/nucleus growth model according to Avrami/Erofeev gives [74, 75]

\[
dx/dt = A \exp(-E / RT) \cdot n \cdot (1 - x) \cdot (\ln(1 - x))^{(n-1)/n}
\]

which can be directly derived from equation (4-1) and (4-2).

The single DSC pattern may be well fitted with different models, but for multiple curves, only one model will fit all the curves, assuming the reaction model does not change during the range of temperature or heating-rates applied. This is the bases for multivariate fitting [78].

Figure 4-4 shows the refining result with a three-step consecutive reaction model A->B->C->D for both isochronal and isothermal traces. The two exothermal peaks are modeled with two continuous unary reaction A->B and B->C of nth-order Avrami-Erofeev reaction type. In order to refine the tails, a reaction of C->D is added, which belongs to 3-dimentional diffusion (Jander’s type, \(f(e, p) = 1.5e^{l/3}(e^{l/3} - 1)\)). The linear type baselines are applied for all curves to remove the difference of specific heat between different phases, which cannot be decided even by scanning the transformed samples a second time. For isothermal refinement, the curve for 655 K is not included, because the peaks on that pattern are so broad and overlapped, and the baseline is quite difficult to determine. The refinement parameters are shown in Table 4-3.

There are some possible reasons for the errors. First the change of specific heat during the devitrification is complicated and the background may not be linear. Second it is hard to decide where the devitrification starts, because the glass transition and the first stage of crystallization are consecutive. It is also possible that the parameters for thermal
resistance of the furnace is not well adjusted, which results in larger error at higher temperature. Thus considered, the fitting results are quite good.

Figure 4-4 Fitting of the (a) isochronal and (b) isothermal DSC curves with a three-step consecutive model. Symbols—experimental data; solid lines—calculation. The first two steps are the nth-order Avrami type, and the third step is the 3-d diffusion model (Jander’s type). The refined parameters are shown in Table 4-3.

Table 4-3 Parameters obtained by refining the DSC curves

<table>
<thead>
<tr>
<th>Stages</th>
<th>Isochronal</th>
<th></th>
<th>Isothermal</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>lgA</td>
<td>E(KJ/mol)</td>
<td>n</td>
<td>Fraction (%)</td>
</tr>
<tr>
<td>A-&gt;B (An)</td>
<td>21.9</td>
<td>331</td>
<td>2.83</td>
<td>40.4</td>
</tr>
<tr>
<td>B-&gt;C (An)</td>
<td>31.1</td>
<td>455.6</td>
<td>4.15</td>
<td>28.1</td>
</tr>
<tr>
<td>C-&gt;D (D3)</td>
<td>25.5</td>
<td>392.4</td>
<td>-</td>
<td>31.5</td>
</tr>
</tbody>
</table>

As shown in Table 4-2 and Table 4-3, the values of activation energies of the two peaks obtained from multivariate fitting and those from Kissinger or Arrhenius methods are different; the values from the former method are larger than that of the latter. This may come from data correction and baseline selection during refinement. And it should be considered that the value obtained from Kissinger or Arrhenius method is the
activation energies at the peak point, while that from the curve fitting is the average 
activation energy for each reaction step. But all of the results show the first 
transformation has lower activation energy than the second, especially for isochronal tests. 
This indicates the transformation of the first stage is more kinetic-driven.

The Avrami exponent $n$ shows more features of the reaction mechanisms. Both 
isochronal and isothermal refinement show that $n$ is bigger than 4 for the second stage 
(4.15 and 4.4 respectively), which proves that transformation of this stage is 
characterized by 3-d constant nucleation and growth. The Avrami exponent for the first 
stage is 2.38 for isothermal and 2.83 for isochronal, indicating that the transformation for 
the first stage is diffusion controlled, and isothermal annealing is more diffusion-limited 
because of the slower kinetics. Possibly this suggests the first transformation is related 
with the growth of latent nuclei [74, 75]. The meaning of Avrami exponent will be 
discussed further combining the results from microscopy and in-situ scattering in later 
chapters.

Previously some authors pointed out the limit of JMA model in describing the 
crystallization of BMG [79]. As we examine carefully about the DSC traces for BMGs 
from literature, we find that most previous DSC traces are measured with high heating 
rates, and the glass transition and different crystallization stages are not well separated. 
Some of the crystallization peaks are overlapped and should be modeled with two 
reactions; also as stated before, it is hard to decide the baseline since the specific heat is 
different for different phases. It has been stated that the appearance of metastable phases 
is common for the crystallization of BMG [80], which would be the first exothermal peak 
for our sample, and for other BMGs it would show as a shoulder or asymmetric profile of 
the exothermal peak. The question comes whether there is always a transformation to
metastable phase before crystallization in BMGs. The multivariate fitting results above indicate if the DSC traces are measured at low heating rate so that different transformation stages are separated, and if baselines are well selected, JMA model is applicable to most peaks.

4.2 XRD

The XRD samples were prepared by annealing at 665 K for different time in the DSC chamber and then quickly cooled with a cooling rate of about 20 K/min. After removing the surface contamination, XRD measurements were performed on a Scintag PAD V room temperature diffractometer, using Cu-Kα source. Patterns were obtained by scanning from 10 to 90° (2θ) range at 1°/min.

Figure 4-5 shows the XRD patterns for different samples annealed at 665 K; the annealing time intervals are shown as red crosses on the DSC pattern. The as-cast sample has broad peaks, which is typical for amorphous alloys. All the patterns for as-cast, 21 min, 141 min and 431 min samples show only broad diffuse peaks. For the samples annealed for 41 min and 431 min, which belong to the first stage, the main peaks are slightly sharpened. The sample annealed for 656 min shows very small fraction of crystalline phase only after measuring with high statistics. The sample annealed for 930 min is almost at the end of the second exothermal peak, and its pattern shows the combination of tetragonal NiZr₂ and amorphous phase. The pattern after annealing for 25 hours still contains amorphous phase. It is possible that during cooling some crystalline particles become amorphous again.
Figure 4-5 (a) the XRD patterns for samples annealing at 665 K, and (b) the corresponding time. The patterns for 656 and 930 min were obtained with higher statistics (0.2°/min); others all at 1°/min.

Our XRD results are quite different from those of Pekarskaya et al.’s [81]. Their DSC curve for isothermal annealing at 400 C show two broad exothermal peaks, and XRD patterns at the end of first DSC peak show very prominent diffraction peaks, which they attributed to the big cubic fcc NiTi2-type nanoclusters for the first stage and quasicrystal for the second stage. All of our experiments do not show the same results. Both the in-situ synchrotron scattering experiment and the ex-situ XRD indicate that during the first stage, no diffraction peaks appears, the only effect is the slight sharpening of main diffusive peaks; for the second stage, only the tetragonal NiZr2 crystalline peaks gradually develop. Details of the structure of the phases will be given in later chapters from the analysis of in-situ experiments. However, these results indicate that the ex-situ XRD must be carried out with extreme care for sample preparation to eliminate artifacts,
and even when the experiments have been well controlled, it is still very hard to obtain quantified structural evolution.

### 4.3 TEM

Samples for TEM tests were also prepared in the DSC chamber by isothermally annealing at 665 K for certain time followed by rapid cooling. Figure 4-6 shows the TEM images for samples annealed for 430 min, 650 min and 950 min, corresponding to the stage right after the first transformation, the early stage of the second transformation and the quite late stage of the second transformation.

Possibly due to the fact that the TEM samples were prepared by electropolishing instead of ion milling, the structure after the first transformation is hard to be distinguished from that of the as-cast sample. In the sample annealed for 650 min, high-density tiny crystalline particles of around 12 nm appear homogeneously inside the amorphous matrix. These particles, after being annealed for long time, grow into big well-ordered single crystals (Figure 4-6(c)), which have been identified to be the tetragonal NiZr$_2$ phase.
4.4 Summary for ex-situ experiments

To conclude, several ex-situ experiments have been carried out for BAM-11. These experiments are supposed to provide quick and direct information about the kinetics and structure of the materials, and also act as guides for the in-situ experiments.

Figure 4-6 TEM images for BAM-11 isothermally annealed at 665 K for (a) 430 min; (b) 650 min; (c) 950 min. The corresponding time on DSC trace is shown in (d).
All tests identify that the as-cast alloy is truly amorphous. Both isochronal and isothermal DSC traces show two continuous exothermal peaks, indicating the crystallization of this alloy belongs to a two-stage transformation. Multivariate refinement has been achieved for isochronal and isothermal DSC curves respectively, using a three-step consecutive reaction model. The activation energy of the first stage is smaller than that of the second. The Avrami exponent is a bit lower than 3 for the first stage, and around 4 for the second stage, suggesting the first stage is diffusion-controlled and possibly there are pre-exist germs in the as-cast BAM-11, and the second stage follows the rule for constant nucleation and growth of the crystalline particles. It is proposed that JMA model is viable for the devitrification of most BMGs, as long as the different stages can be separated.

The XRD patterns of samples annealed for different time show only a slight sharpening of the main peaks during the first stage, while during the second stage tetragonal NiZr$_2$ phase are formed.

TEM tests can not identify the structure of the product of the first transformation. During the early stage of the second transformation, very tiny particles with a tetragonal NiZr$_2$ structure appear with a high density. Those particles grow into larger single crystals after long-time annealing, yet the amorphous phase still has a good volume fraction.

Summarily the ex-situ experiments can give quick information about the dynamic parameters, as well as provide guides for the designing of in-situ experiments; XRD and TEM give qualitative information about structure information. But XRD and TEM can not identify the structure of the product of the first transformation. Thus they can not be used to characterize the dynamic evolution of structures during devitrification.
The most prominent deficiency of ex-situ experiments is that long time is needed for sample preparation, as every sample needs to be annealed in the DSC chamber, so that the history of heat-treatment can be monitored, and each sample should be processed before each characterization. Also, the testing time is very long, due to the low intensity of laboratory XRD. Another deficiency is that, since the experiments are carried out ex-situ, the structure measured may not be the exact structure at certain stages as intended, even when careful control has been applied. This not only requires the controlling of time should be good, but also introduces unpredictable artifacts. For example, the XRD may detect only the structure of the surface contamination, and TEM may give artifacts due to bad electropolishing process or due to the high energy beam, or just simply shows the structure for processing-induced devitrification. And since during the ex-situ experiments, samples are exposed in the ambient atmosphere, the nucleation mechanisms could be quite different from that of the bulk materials, because of the contamination from air.

All thus said, it is especially important to do in-situ experiment, especially for the characterization of BMGs and other materials which have local disorders.
Chapter 5  SAXS Model

Before looking into the details of results from in-situ experiments, a SAXS model is given here, as an attempt to explain the common fact that interference peak often appears on the SAS patterns during devitrification.

5.1 Previous study of BMGs by SAS

When a BMG devitrifies, an interference peak often appears on the small angle scattering profile, as a consequence of correlations between areas which have different scattering length density. This have been observed for the multicomponent systems such as Zr-Ti-Cu-Ni-Be [82], Mg-Cu-Y-Li [83], and Fe-Si-B-Cu-Nb [84]. Several authors explained the interference peak as consequence of phase separation followed by polymorphous crystallization, within the mechanism of spinodal decomposition [85, 86].

Previously phase decomposition of various systems have been studied by SAS, for example, the spinodal decomposition of Au-Pt [87] and porous Vycor glass [88] have been studied by SANS, and SAXS has been applied for the studies of phase formation of conventional silica [89] or sodium borate [90] glasses. These materials show interference peak, which has been explained as a consequence of spinodal decomposition. Yet a satisfactory model of scaling structure factor that could fit both early and late stages of the evolution of structure function is still not available.

In the field of BMGs, there is no consensus on the origin of the interference peak on SAS profiles. The devitrification of BMGs often involves the appearance of metastable phases and the nucleation density is very high (~ \(10^{23-24} \text{ m}^{-3}\)), indicating that
the devitrification mechanism for BMGs can be quite different from that of conventional glass. The model of spinodal decomposition may not be applicable for BMGs, because our results show that ever since the beginning of devitrification in BMGs, crystalline particles are formed, which have constant scattering length density, instead of the ever changing scattering length density depicted by spinodal decomposition. Heinemann et al [84] proposed a model of polydisperse particles with diffusion zones, which is used to fit the magnetic SANS profile of the partial crystallized FINEMET. This model is rather complicated, and a precise estimation of many parameters based on other experiments or calculations is important for good refinement.

As stated in Chapter 3, the three types of BMGs we studied stand for different BMG systems with different GFAs and mechanical properties. During the synchrotron scattering, it is found that although the evolution of SAXS profiles are different, interference peak appears for all three samples. Here a cluster model based on simple core-shell model is proposed. It is demonstrated that the SAXS profiles of all three samples are well captured by this model.

5.2 Cluster model

SAS is a suitable tool for the study of inhomogeneities on a length scale from several nanometers to about 1 \( \mu \)m [91]. Some of the theoretic equations are given in Chapter 2, but here more details are given. The SAS intensity is proportional to the differential cross-section of the whole sample

\[
\frac{\partial \Sigma}{\partial \Omega}(Q) = N_p P(Q) \epsilon(Q) + \text{bkg}
\]  

(5-1)
Where $N_p$ is the total number of particles, $S(Q)$ is the interparticle structure factor, $P(Q)$ is the differential cross-section for each particle, which is defined as

$$P(Q) = \frac{d\sigma}{d\Omega} (Q) = \frac{\langle b^2 \rangle}{V_p} p(Q)$$  \hspace{1cm} (5-2)

where $b$ is the atomic scattering length, $V_p$ is the volume of the particle, and $p(Q)$ is a unitless form factor decided by the shape of the particle (intraparticle form factor).

For particulate system, the interference peak may come from the intraparticle correlation for particles that have a diffusion zone, or from interparticle correlation for dense-packed particles. Similar to the statement of Lembke et al [89], we rule out the dense packing model, at least for the early stages, because that model predicts the peak position would shift to larger $Q$ values for the nucleation stage, when the volume fraction of the particles with constant size increases. It was also illustrated by Guinier that “it is improbable that the packing of particles will lead to large changes in the scattering cures” [92]. Thus in our model only the intraparticle correlation is considered.

For spherical particles, $P(Q)$ is calculated as the squared Fourier-Bessel transform of the contrast [62]

$$P(Q) = \frac{1}{V_p} \left[ \int_0^\infty 4\pi r^2 (\rho_p - \rho_m) \frac{\sin(Qr)}{Qr} dr \right]^2$$  \hspace{1cm} (5-3)

where $(\rho_p - \rho_m)$ the contrast between the particle and the matrix. By multiplying with a scale factor, which is related to the number density of particles and the instrument, the SAS intensity can be expressed as (Rayleigh equation)
This function will produce a strong peak at Q=0, and a small peak at QR=5.76, which is smeared out for poly-disperse particles and can not contribute to the interference peak appeared on SAXS.

For particles that have a diffusion zone, the scattering intensity comes from both the core and the shell

\[
P(Q) = \frac{1}{V_s} \left[ \int_0^{r_C} 4\pi r^2 (\rho_c - \rho_m) \frac{\sin(Qr)}{Qr} dr + \int_{r_C}^{r_S} 4\pi r^2 (\rho_s - \rho_m) \frac{\sin(Qr)}{Qr} dr \right]^2 (5-5)
\]

Here the subscripts C, S and M stand for the core, shell and matrix respectively. This results into

\[
P(Q) = \left[ 3V_c (\rho_c - \rho_m) \Phi(QR_c) + \rho_s - \rho_m \right] \Phi(QR_s) - V_c \Phi(QR_c) \right] / V_s (5-6)
\]

By separating the core and shell contributions, and multiplying a scale factor, the intensity is derived as [62]

\[
I(Q) = \frac{S}{V_s} \left[ 3V_c (\rho_c - \rho_s) (\rho_c - \rho_m) \Phi(QR_c) + 3V_s (\rho_s - \rho_m) \Phi(QR_s) \right] + bkg (5-7)
\]

If it is considered that net contrast between core and shell compensates each other, i.e., \(V_c (\rho_c - \rho_s) + V_s (\rho_s - \rho_m) = 0\), which is reasonable since the original phase is amorphous, then the essential part of Equation 5-7 becomes

\[
I(Q) = SV_s (\rho_s - \rho_m)^2 [\Phi(QR_c) - \Phi(QR_s)]^2 + bkg (5-8)
\]

Because the square operation is over contributions from both core and shell, the interference peak would appear at lower Q, as shown in Figure 5-1(a). Figure 5-1(b) demonstrates how the peak profile evolves when a monosphere particle gradually
develops a shell of thicker diffusion zone. The form factors are calculated according to Equation 5-4 and 5-8, without considering the difference of contrast and volume. Apparently the interference peak is caused by diffusion zone, and the intensity increases with the thickness of diffusion zone. It is also important to note that if hard-spheres and core/shell particles coexist, and if they have the same size, the interference peak is buried inside the high intensity from hard spheres. Thus, for the case where interference peak is prominent and the intensity at low-Q is also high, two groups of particles with different size should be considered.

Figure 5-1 (a) Demonstration of the origin of interference peak: contributions from core and shell result in a interference peak, according to Equation 5-8; (b) Form factors for hard spheres (solid line, according to Equation 5-4), and core-shell particles (dashed lines, according to Equation 5-8).

Equation 5-8 may be over-simplified. Since the crystalline particles usually have constant density, it is necessary to introduce two parameters: \( t \) — the ratio of radii between the core and shell, and \( b \) — the ratio of contrast between core and shell, thus Equation 5-7 is modified as

\[
[\Phi(Q, R_\text{c}) - \Phi(Q, R_\text{s})]^2
\]
Chapter 5 SAXS Model

\[ I(Q) = SV_s (\rho_M - \rho_S)^2 [bt^3 \Phi(QR_s t) - \Phi(QR_s)]^2 + bkg \]
\[ t = R_c / R_s \]
\[ b = (\rho_c - \rho_s)/(\rho_M - \rho_S) \]

(5-9)

In practice nucleation can be inhomogeneous locally; if phase separation happens first, particles may nucleate with a higher density in some areas, as has been proved by the TEM images for half crystallized BAM-11. We call this the cluster model, as schematically plotted in Figure 5-2. In this case, the whole cluster is viewed as a solid sphere inside the amorphous matrix, while the particles/domains inside the cluster follow the core-shell model. Generally the size of particles formed by nucleation and growth follows a lognormal distribution. Assuming the two ratios introduced in Equation 5-9 are the same for all particles, and assuming the absolute value of the contrast is constant, the scattering intensity from contributions of both core-shell particles and large particles (monospheres) will have 7 parameters:

\[ w(r,[R_a,\sigma]) = \frac{1}{(2\pi)^{1/2} r \ln \sigma} \exp[-0.5(\ln(r/R_a))^2] \]
\[ I(Q,[R_a,\sigma,t,b,R_b,c,S]) = S \left\{ r^3 \int_0^\infty w(r)[bt^3 \Phi(Qr t) - \Phi(Qr)]^2 dr + c \times R_b^3 \Phi(QR_b)^2 \right\} + bkg \]

(5-10)

where \( R_a \) is the center of \( R_s \), \( \ln \sigma \) is the size distribution, \( c \) is the contribution from clusters. \( R_b \) is the cluster radius, which could also have a distribution, but for our data, the low-Q part is not complete, so \( R_b \) is assumed to be monodisperse to simplify the equation. \( S \) is proportional to the number of the particles times the contrast between core and shell. Indeed, this model is a combination of sphere model and core-shell model, and it would not be different if the larger particles are formed by different mechanisms.
For log-normal distribution, the average particle size (of the shell) is given by
\[ 2R_a \exp(0.5\ln^2 \sigma) \] [93]. For the core, the average particle size is therefore

\[ D_1 = 2R_a \cdot t \cdot \exp(0.5\ln^2 \sigma). \] (5-11)

![Schematic view of core-shell particles aggregating to form larger cluster, the right figure is the scattering length density distribution in space. Rc, Rs and Rb stand for the radius of core, shell and cluster, respectively.](image)

A good estimate of the initial parameters is important for good fitting. Amongst these parameters, the radii are most important. The size of the core-shell particles is estimated according to the relation that QR_a should be around 3 at the interference peak center (Equation 5-9); the size of the large sphere is estimated according to QR_b=4.49 at the position of the first minimum (Equation 5-4). The scattering intensity is refined directly without considering Q-dependence of atomic scattering factor, because this effect is very small in the low-Q range.

All the SAXS patterns with a interference peak have been refined. The evolution of the SAXS patterns and the refined parameters will be discussed in the following chapters. Here we only show the results for typical SAXS patterns.
5.3 Refinement results

5.3.1 Mg$_{65}$Cu$_{25}$Tb$_{10}$

The Mg$_{65}$Cu$_{25}$Tb$_{10}$ alloy was heated with a rate of 5 K/min. SAXS patterns show a prominent interference peak from 450 K to about 550 K, all of which can be described with this model. Figure 5-3 shows one example for the pattern measured at 530 K. The fitted parameters (for all samples) are listed in Table 5-1. The errors within 95% confidence band are given in brackets. The small residual (4%) indicates the excellent quality of the fit. The average core size (diameter) at this temperature is 26 nm, according to Equation 5-11. The shell thickness is around 6 nm.

To demonstrate the contributions from the core-shell particles and the large solid spheres, the intensities from the two parts were calculated according to Equation 5-10 and plotted separately in the same figure as dashed curves. Obviously the larger solid spheres only contribute for the low-Q intensity and do not affect the fitting of the interference peak. The mismatch in the vicinity of 0.007 Å$^{-1}$ mainly comes from the small ripples of intensities from the solid spheres.

![Figure 5-3 SAXS profile for Mg$_{65}$Cu$_{25}$Tb$_{10}$ (collected at 530 K during isochronal heating with a rate of 5 K/min) along with the fit by the SAXS model. The contributions from core-shell particles and the large mono-disperse solid spheres are plotted as dashed lines.](image)
5.3.2 Zr<sub>52.5</sub>Cu<sub>17.9</sub>Ni<sub>14.6</sub>Al<sub>10</sub>Ti<sub>5</sub>

BAM-11 was isothermally annealed at 670 K. Compared to Mg<sub>65</sub>Cu<sub>25</sub>Tb<sub>10</sub>, the SAXS pattern shows a relatively weak interference peak, while the intensity at low-Q is much higher. The core-shell model was applied to fit the SAXS patterns measured after annealing for 2 hours, and the result is shown in Figure 5-4(a). An attempt was made to examine how the size distribution of solid spheres can affect the fitting, by introducing a log-normal distribution for R<sub>b</sub>. The result is not shown here, but the fitted size distribution is very small (lnσ=0.026) and only the intermediate part around Q~0.01 Å<sup>-1</sup> was improved slightly, which justifies the mono-disperse size distribution for R<sub>b</sub>. The average size of the core (D<sub>1</sub>, according to Equation 5-11) was calculated to be around 19 nm and the shell thickness around 2.5 nm, which agrees well with the previous TEM results by others [38], also agrees with our TEM results.

The separate contributions from core-shell particles and the mono-disperse solid spheres were also plotted on the same figure as dashed curves. Similar to the case of Mg<sub>65</sub>Cu<sub>25</sub>Tb<sub>10</sub>, a core-shell model describes the interference peak very well; the contribution of the large solid spheres is seen at only very low-Q.

As a comparison, we also attempted to fit the SANS patterns for Vit105 alloy (same composition, but processed differently) with the same model. The SANS data were obtained from the paper by [36]. Since SANS data is not available below 0.015 Å<sup>-1</sup>, the patterns were fitted with the core-shell model only. Figure 5-4(b) is a representative plot showing the fitting result along with the data measured after annealing at 686 K for 576 min. The average core size was calculated to be around 14.5 nm, somewhat larger than what the authors obtained from Guinier analysis (11 nm). The parameters in Table 5-1 indicate that for both types of measurements, the core-shell ratios are quite similar, which
validates our assumption that the core/shell ratio is constant for all particles for a given alloy. Compared with the SAXS results, the particle size obtained from the SANS data is more concentrated, and the average particle size is also smaller. This is presumably due to the differences in sample preparation and the annealing temperatures.

Figure 5-4 (a) SAXS profile of Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_{8} (BAM-11, isothermally annealed at 670 K for 2 hours) along with the fit by our model. The contributions from core-shell particles and mono-disperse hard spheres are plotted as dashed lines. (b) SANS profile of Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_{8} (Vit105, isothermally annealed at 686 K for 576 min) [36] along with the fit by a core-shell model.

5.3.3 Zr_{50}Cu_{40}Al_{10}

Zr_{50}Cu_{40}Al_{10} was isothermally annealed at 690 K. The interference peak appears only for a short period of time as the center moves to low-Q. The contribution from the large solid spheres could not be measured within the experimental Q-range, thus the data were fitted with the core-shell model only.

The SAXS pattern measured at 20 minutes is shown in Figure 5-5, along with the best fit using the core-shell model. The calculated average core size is around 55 nm, and the shell thickness is about 4.5 nm. Comparably, the scale factor is much smaller than that of MgBMG and BAM-11, indicating the number density of these core-shell particles could be much lower, or the contrast between core and shell is much smaller.
Figure 5-5 SAXS profile for Zr$_{50}$Cu$_{40}$Al$_{10}$ (isothermally annealed at 690K for 20 min) along with the fit by a core-shell model.

Figure 5-6 Size distribution of the core for Zr$_{52.5}$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$Ti$_{5}$, Zr$_{50}$Cu$_{40}$Al$_{10}$, Mg$_{65}$Cu$_{25}$Tb$_{10}$ and Vit105, calculated from fitted parameters in Table 5-1.

Table 5-1 The refined parameters for the SAXS patterns of three BMGs

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Mg$<em>{65}$Cu$</em>{25}$Tb$_{10}$</th>
<th>BAM-11</th>
<th>Vit105</th>
<th>Zr$<em>{50}$Cu$</em>{40}$Al$_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R$_a$ (nm)</td>
<td>18.5(1)</td>
<td>11.3(1)</td>
<td>9.42(2)</td>
<td>30.1(4)</td>
</tr>
<tr>
<td>lnσ</td>
<td>0.271(4)</td>
<td>0.428(8)</td>
<td>0.256(1)</td>
<td>0.40(1)</td>
</tr>
<tr>
<td>t</td>
<td>0.68(2)</td>
<td>0.78(4)</td>
<td>0.748(2)</td>
<td>0.856(7)</td>
</tr>
<tr>
<td>b</td>
<td>3.5(2)</td>
<td>1.6(3)</td>
<td>2.63(3)</td>
<td>1.35(2)</td>
</tr>
<tr>
<td>R$_b$ (nm)</td>
<td>56(2)</td>
<td>59.2(5)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>c</td>
<td>7.5(8)E-3</td>
<td>1.1(5)E-3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>6.6(8)E-3</td>
<td>6.9(7)E-2</td>
<td>3.8(1)E-4</td>
<td>9.9(9)E-3</td>
</tr>
<tr>
<td>R (%)</td>
<td>4.1</td>
<td>4.2</td>
<td>1.9</td>
<td>4.7</td>
</tr>
</tbody>
</table>

R$_a$, lnσ — center and width of the log-normal distribution of the shell radius
t, b — ratio of the radius and scattering length density between the core and the shell
R$_b$ — radius of the monodisperse large solid spheres
c, S — contribution of solid spheres, and the total scale factor
R — normalized residual ($R = \sqrt{\sum (I_o - I_c)^2 / I_o^2}$)

$^a$ Mg$_{65}$Cu$_{25}$Tb$_{10}$ was annealed at 5 K/min, SAXS pattern is taken at 530 K
$^b$ BAM-11 was annealed at 670 K, SAXS pattern is taken after 2 hours
$^c$ Vit-105 was annealed at 686 K for 576 min, data obtained from Figure 2 in [36]
$^d$ Zr$_{50}$Cu$_{40}$Al$_{10}$ was annealed at 690 K, SAXS pattern was taken after 20 minutes
5.4 Discussions

Despite the differences in compositions, all three samples show an interference peak on their SAXS patterns during devitrification. More importantly, a simple core-shell model with poly-disperse particle size distribution provides a stable fit to the SAXS data for all three samples, and also for the SANS data of alloy Vit105. As shown in Table 5-1, the standard deviations for the fitted parameters are small, on the order of 10% or less. It is true that large, mono-disperse solid particles were also included in the model, in order to account for the rise of SAXS intensity at low Q for some of the samples. However, as can be seen from Figure 3-5, the large particles only contributed to the intensities for $Q \leq 0.01 \text{ Å}^{-1}$ and do not affect the fit in the higher Q region. The core-shell particle size obtained for BAM-11 and Vit105 also agrees well with previous studies by TEM and atom probe tomography [38].

The good agreement between the fits and experimental data demonstrate the robustness and universality of our model in describing the morphology of the nanoscale structure in BMG materials during devitrification. Nanoscale core-shell structures have been reported in many alloy systems, most recently by [94] in Al-Zr-Sc alloys.

Our model supports the view of cluster formation during the initial stage of devitrification of BMGs [95]. Apparently, as the BMG materials undergo amorphous-crystalline phase transition, some elements are drawn to the center, leaving behind a depleted zone. As a consequence, nano-scale clusters are formed, whose structure, to first degree of approximation, is adequately described by a core-shell model as shown by the fitting results. It is not clear what caused the initial congregation of some of these elements. One possible reason is the local composition fluctuation, although small,
resulting from the rapid cooling from the liquid phase. As the BMG is heated to above the glass transition, composition fluctuation intensifies and neighboring atoms exchange their positions in order to minimize the total energy. When the composition of the cluster reaches a critical stage, the BMG crystallizes into the lower energy state.

We note that Zr$_{50}$Cu$_{40}$Al$_{10}$ is a marginal glass former, Mg$_{65}$Cu$_{25}$Tb$_{10}$ a good glass former, while BAM-11 and Vit105 have excellent glass forming ability. Figure 5-6 shows the core-shell particle size distributions for all samples (calculated according to Equation 5-11). It is found that the particle sizes for BAM-11 and Vit105 are the smallest, and the size distributions are also more concentrated. The Zr$_{50}$Cu$_{40}$Al$_{10}$ has the largest average particle size and broadest size distribution, which is evident from the long tail in the SAXS pattern. Although a fair comparison should be based on similar experimental conditions, the size distributions in Figure 5-6 suggest that BAM-11 and Vit105, which are of identical composition but prepared differently, have relatively finer and more uniform crystalline particles, which is consistent with the high degree of stability against crystallization observed for both alloys.

The scale factor of large particles shown in Table 5-1 is very small, indicating that our assumption (Figure 5-2) that core-shell particles may enrich in some area to form large scale contrast could be quite valid, because even a slight difference in scattering length density would create such an increase of intensity at low-Q. This also suggests that at the beginning of devitrification, the idea of phase separation could be true.

5.5 Summary for SAXS modeling

As a summary, we studied the devitrification of three types of BMGs by measuring the SAXS patterns in-situ. It is found that interference peak appears for all
three samples, and the peak intensity and existing time interval are quite different.

Assuming that interference peak is a consequence of diffusion zone, a cluster model is
developed to refine the SAXS patterns successfully. The refinement results show that the
good glass former (BAM-11) has finer particle size, and there is a contribution from
contrast of large-area. The MgBMG shows strong interference peak, which can be refined
with a core-shell model. Even the marginal ZrBMG shows a weak interference peak for
short interval, and the grain size is much larger than the other two. Using this model, the
evolution of particle size, size distribution and diffusion zone thickness, can all be
obtained. Combined with results from other experiments, these results will give more
insightful information on the devitrification mechanisms of BMGs, as will be discussed
in following chapters.
Chapter 6  Synchrotron Scattering for BAM-11

In this chapter, the results from the first in-situ experiment using synchrotron X-ray scattering for BAM-11 are presented. The structures for different transformation products are analyzed. The kinetics of particle growth is also analyzed from the results of SAXS.

6.1 Experimental results

As described in Chapter 3, data recorded by the CCD cameras were corrected for detector efficiency and binned in Q-space. The intensities are then normalized according to monitor counts, so that the evolution of scattering patterns reflects the real structural changes. The results are displayed as 3-d plot on the Q-T/t plane. Figure 6-1 shows the results for isochronal tests with a heating-rate of 1 K/min and 10 K/min. The results for 2 K/min and 5 K/min are not shown, since they are quite similar. Figure 6-2 is the result for isothermal annealing at 670 K. There are several samples isothermally annealed at lower and higher temperatures, but since the SAXS and WAXS behavior for these conditions are quite similar, those results are not shown. The brighter and hotter colors represent higher intensity. All data shown here are original without extra processing. The smooth development of the patterns indicates the resolution and statistics are very good.

Similar to the laboratory XRD test, before the start of devitrification, the WAXS patterns show only broad diffuse peaks, one from 2 to 3.5 Å⁻¹, the other from 3.5 to 6Å⁻¹, with a shoulder at 5.2 Å⁻¹. These features are characteristic for BMGs. Yet quite different from laboratory XRD, a prominent sharpening effect of the main peaks is observed.
before the appearance of Bragg peaks, as is shown on the plots for isochronal annealing with low heating-rates (Figure 6-1(b)) and isothermally annealing (Figure 6-2(b)). The interval for this sharpening effect is relatively very short, compared with the time needed for Bragg peaks to fully develop. At higher heating-rates the first stage is not observed and the diffuse peaks split directly. Interference peak appears on SAXS patterns, almost simultaneously with the start of devitrification. The timing of the evolution of SAXS and WAXS, as well as further analysis about their indications, will be discussed below.

Figure 6-1 3-d plot of (a) SAXS and (b) WAXS patterns for BAM-11 isochronally annealed with a rate of 1 K/min; and (c) SAXS and (d) WAXS patterns for BAM-11 annealed with a rate of 10 K/min.
In order to show the details during the early devitrification process, results from two typical samples are chosen for analysis here, one is isochronally annealed with a rate of 1 K/min, and the other is isothermally annealed at 670 K.

### 6.2 Two-stage devitrification

Although it is observed from the 3-d plot that two transformation stages are involved in devitrification, it is necessary to calculate the integrated intensity to show this trend as well as the subtle changes at the early stages. For SAXS, several patterns measured before devitrification are averaged and subtracted from the later patterns, in order to remove the background and calculate the net contribution from structure evolution. For WAXS, the integrated intensity is calculated, which is the summing up of the absolute difference between current pattern and reference pattern (also the average of several early scans).
Chapter 6 Synchrotron Scattering for BAM-11

\[
I_{I_{\text{SAXS}}}(t) = \int_0^\infty (I(Q, t) - I(Q, t_0))dQ \\
I_{I_{\text{WAXS}}}(t) = \int_0^\infty [I(Q, t) - I(Q, t_0)]dQ \\
DI_{I_{\text{WAXS}}}(t) = \int_0^\infty [I(Q, t) - I(Q, t - \Delta t)]dQ
\]

(6-1)

Here the first two equations are for the integrated intensity of SAXS and WAXS, the third equation is for the differential integrated intensity for WAXS. The integrating range can be varied to cover certain peaks. Since the statistics and resolution of the data are very good, here the values are obtained by simply integrating over the whole range. The result is shown in Figure 6-3.

![Figure 6-3 Two-stage transformation for BAM-11 illustrated by the integrated intensity of WAXS (black curves) and SAXS (blue curves), and by the differential integrated intensity of WAXS (red curves), for (a) isochronal annealing at 1 K/min, and (b) isothermal annealing at 670 K, calculated according to Equation 6-1.](image)

The integrated intensity of both SAXS and WAXS show the two transformation stages clearly. For comparison, the DSC trace for isochronal annealing with a heating rate of 1 K/min is shown at the bottom of Figure 6-3(a). The differential integrated intensity of WAXS is also plotted on the same figure (the red curves), which has a similar profile.
as DSC traces. We propose that the integrated intensity is proportional to the volume fraction of transformation product,

$$II(t) \propto V_c F_c^2$$  \hspace{1cm} (6-2)

Where \(V_c\) and \(F_c\) are the volume fraction and form factor of crystalline phase. Since DSC measures the heat flow rate, the integration of which is proportional to the volume fraction of transformation product, thus theoretically the differential integrated intensity should have similar profile as DSC.

As a comparison with isochronal and isothermal DSC traces, it is found that there is a temperature difference of more than 20 K between the in-situ scattering experiments and the DSC experiments, as shown in Figure 6-3(a). Three reasons could be attributed to this big difference. First, the calibration of our furnace is not as good as that of the DSC, which is well calibrated. The temperature error due to calibration could be in the range of 5 K. Second, the high-energy X-ray could heat the sample illuminated by the beam and increase the temperature in this area, while the bulk temperature detected by the thermal couple may not show this difference. The third reason is the same as has been explained by Lu [96], i.e., the heat released at the early transformation stage can be largely canceled by the energy needed for forming interface between the particle and the matrix, thus the thermal peaks on DSC traces are actually much delayed. On the other hand, the scattering method measures the density changes as soon as the structure is changed, thus it is more sensitive to phase transformations.

A relaxation phenomenon is observed during both isochronal and isothermal annealing, as indicated by the slight yet prominent increase on the WAXS integrated intensity before the first transformation. Almost simultaneously with the relaxation, the intensity of SAXS increases, which precedes the increase of WAXS. This has been used
as a proof that phase separation happens before crystallization in the paper of Wang et al [95]. Since relaxation is mainly related with the relief of strain stress caused by the atoms occupying the unstable positions, it is expected that this effect would be reflected by some changes of the peak profile on WAXS patterns. Yet the simultaneous increase of SAXS intensity indicates that possibly ever since the atoms have been reset to more stable positions, contrast between large areas is created. This contrast, although small at the beginning, increases with time, as evidenced by the continuous increase of SAXS intensity at low-Q. The increase of SAXS intensity may also come from the formation of a small fraction of crystalline particles in certain areas, i. e., the nucleation may be inhomogeneous in the nano level. The first assumption is stated in the SAXS model in Chapter 5. The second assumption has not been confirmed yet, but is basically supposed to be not true, because as shown in Chapter 5, the length scale for this contrast is quite large and it is hard to imagine that such large crystalline particles are not detected by WAXS, which can detect even 1% volume fraction of crystalline phase. The mechanism for this separation is still not clear. We are not sure whether this is due to some kind of modulations similar to the origin of spinodal decomposition. The relaxation behavior will be subjected to further experiments.

6.3 Structural evolution at atomic scale

6.3.1 As-cast

The WAXS patterns for the as-cast state and before the first transformation show similar profile; there is no observable difference before and after relaxation. A typical pattern is shown in Figure 6-4, which was measured when the temperature just reached
the isothermal set point (670 K). Broad diffuse peaks are observed around 2.7 Å⁻¹ and 4.5 Å⁻¹, and a shoulder is shown around 5.1 Å⁻¹ at the right side of the second peak.

![WAXS pattern for BAM-11 isothermally annealed at 670 K for 0 minute. The red lines and labels are peaks positions for icosahedral SRO by Ginzburg-Landau theory [97].](image)

Figure 6-4 WAXS pattern for BAM-11 isothermally annealed at 670 K for 0 minute. The red lines and labels are peaks positions for icosahedral SRO by Ginzburg-Landau theory [97].

It has been suggested by many researchers that the SROs in supercooled liquids and MGs have icosahedral configuration [4]. Sachdev et al [97] calculated the density correlation functions using Ginzburg-Landau free energy to describe the icosahedral order. With a single indexing number, the peak positions can be estimated according to

\[ Q_n^2 = \kappa^2 n (n + 2) \] (6-3)

Where \( \kappa \) is related with the near-neighbor distance by \( \kappa d = \pi / 5 \). Assuming \( d \) equals 3.0 for BAM-11, which is justified by the result from PDF experiments, the peak positions are plotted in Figure 6-4 as red lines for \( n=12, 20, 24, 30 \) and 32. It is evident that the peak positions are well matched with the peak center and shoulder of the broad diffuse peak on WAXS patterns. Although intensity is not calculated here, qualitatively the model of icosahedral SRO is reliable for BAM-11, suggesting that in the as-cast BAM-11, a large number of icosahedral SRO may exist, which may be separated by the “frustration” wedge disclination lines [97].

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6.3.2 First transformation

In order to show the contrast between the two transformations, three WAXS patterns measured at 0, 8 and 13 min during isothermal annealing at 670 K are plotted in Figure 6-5. These three patterns stand for the structure before transformation, during the first transformation and at the early stage of the second transformation, respectively. During the first transformation, a sharpening and shifting of the first diffuse peak around 2.7 Å⁻¹ is observed, accompanying by the prominent sharpening of the peak around 4.4 Å⁻¹ and the shoulder being more obvious. The peak positions and intensities match well with the theory given by Sachdev et al [98], by showing that when the icosahedral SROs condense out of the undercooled liquid and develop into icosahedral crystals, second generation peaks appear, and the peak positions satisfy the relation that the ratios of peak centers (q/q₀) equal to 1.05, 1.7 and 2. The first and the second generation peaks are plotted as black and red arrows respectively in Figure 6-5. The domain size can be roughly estimated from the Scherrer equation [55, 93]

\[
< L >_{vol} = \frac{K \lambda}{B \cos \theta}
\]  

(6-4)

where \(<L>\) is the volume-weight size, \(K\) is a geometry dependent constant which is usually between 0.85 and 0.99, \(B\) is the full-width-half-max of the peak in radian. If we assume that the sharpened peak at 4.4 Å⁻¹ is responsible for a Bragg peak for the first phase, the estimated domain size is about 2 nm.
Previously the sharpening effect has been reported, which is attributed to relaxation [99]. The results from our time-resolved in-situ experiment prove that this sharpening effect indeed belongs to a transformation. Figure 6-6 displays the simultaneous evolution of WAXS and SAXS more precisely. The WAXS patterns are plotted as projection in the time-intensity plane. For the SAXS patterns background has been removed by subtracting the averages of several scans measured at the beginning of isothermal annealing, thus the scattering intensity is only attributed to structural changes.

Figure 6-6 shows that the first transformation happens in very short interval (4-10 min for isothermal annealing at 670 K, and around 10 K for isochronal annealing with a rate of 1 K/min). The sharpening of the main peak is shown as a maximum increase of intensity of around 7%. As soon as crystalline peaks start to develop, the intensities of the main peaks draw back. This is evidence that the first transformation may be a precursor for the second. Simultaneous on SAXS patterns, a continuous increase of intensity at low-Q is observed ever since the beginning of annealing. Yet, there is no interference peak below 10 min; it is after the appearance of Bragg peaks on WAXS, that interference peak starts to develop on SAXS patterns. According to the analysis for SAXS model, it is
obvious that it is only during the second stage, when the particles start to grow, that the intraparticle correlation creates the interference peak. Another fact should be noted is that for isochronal annealing, the increase of intensity during the first stage is not so prominent as during isothermal annealing, although a continuous increase of intensity at low-Q is also observed. This is mainly because of the diffusion-controlling nature of the first stage, as will be discussed later. The temperature effect is negligible for SAXS.

![Figure 6-6](image)

Figure 6-6 (a) Projection of 3-d WAXS patterns along time axis; (b) Simultaneous SAXS patterns, for isothermal annealing at 670 K, and (c) Projection of WAXS patterns along temperature axis; (d) Simultaneous SAXS patterns for isochronal annealing with a rate of 1 K/min.
6.3.3 Second transformation

The Bragg peaks developed during the second transformation can be well indexed with the tetragonal (C16) NiZr\(_2\) phase, with the lattice parameter of \(a=6.477\), \(c=5.241\), and Ni atoms occupy the 4a sites, Zr at the 8h sites. This phase is stable in a large temperature range during isochronal annealing, and is the only stable phase for isothermal annealing in long time (>20 hours at 670 K). Figure 6-7 shows that at 710 K most peaks can be indexed with NiZr\(_2\) phase. At 823 K, which is the highest temperature for our in-situ test, the remaining matrix further decomposed and only a small fraction peaks are identified as AlZr and Ni\(_{10}\)Zr\(_7\), and some amorphous phase still remain undevitrified even at this high temperature. The final structure decided from XRD
patterns of a DSC sample heated to 1045 K (not shown here) is mainly tetragonal CuZr2, together with other phases like Ni10Zr7, AlZr and NiZr2.

6.4 Kinetics for particle growth

Small angle scattering is a tool to characterize the dynamic evolution of structure in the range of several nanometers to 1 micron. The growth of crystalline particles is reflected by the evolution of SAXS profiles. For the devitrification mechanisms, phase separation has long been observed in various isotropic systems, including inorganic glasses, polymers with high or low molecular weight, and it has also been attributed to metallic glasses. This theory depicts that the amorphous phase first separate into two amorphous phases with different compositions, one of them crystallize polymorphously later. Power law is widely applied for the phase separation dynamics, in which the time-dependent average concentration correlation length is given by [100]

\[ d_m \propto t^\phi \quad \text{or} \quad Q_m \propto t^{-\phi} \quad (6-5) \]

And the corresponding maximum scattering intensity is given by

\[ I_m \propto t^\gamma \quad (6-6) \]

Apparently power law relationships will not hold true for the entire phase separation process. Cahn [101] provided a linear model for spinodal decomposition. The evolution of structure in isotropic systems is described by a superpositioning of sinusoidal composition modulations of a fixed wavelength, but random in amplitude, orientation and phases. In this linear model \( \phi = 0 \) and \( I_m \) does not obey a power law but grows exponentially. The ratio of peak center to the position of crossover (where
intensity is zero) is fixed, i.e., $Q_c / Q_m = \sqrt{2}$, where $Q = 4\pi \sin \theta / \lambda$. The composition is given by

$$c(x) = A \cos(Qx)$$

(6-7)

It is derived that

$$c(t) - c(0) = \exp[R(\beta)t] \cos(\beta \cdot r)$$

(6-8)

where $\beta$ is the wave vector, synonym of $Q$. The scattering intensity is given by

$$S(Q, t) = S(Q, 0) \exp[2R(Q)t]$$

(6-9)

Thus $R(Q_m)$ is determined from the slope of $\ln S(Q_m, t)$ vs $t$, and the effective diffusion constant is related to $R(Q_m)$ by

$$D(Q_m) = -2R(Q_m) / Q_m^2$$

(6-10)

Further optimization of power law has been proposed by many authors. Langer [102] found that $\phi = 0.212$ and $\Upsilon = 0.81$ for the stages when concentration gradients are small. Some empirical equations were also given to describe the relationship between correlation length and time [100].

In order to show how the particles grow, parameters about correlation length and scattering intensities are obtained from refining SAXS patterns. These parameters are applied to verify the power law, and hopefully, will give more information about the mechanisms for the devitrification of BMGs.

For this purpose, two approaches have been applied. In the first one (called the “Direct method”), the peak center and intensity are directly obtained from SAXS patterns. These values are used to verify the power law. In the second method, a SAS model described in Chapter 5 is applied to refine the SAXS patterns. The obtained parameters are discussed and compared with the power law. As stated in the above
section, the SAXS patterns do not show interference peak for the first transformation, thus all the discussions about kinetics are for the second transformation.

6.4.1 First method

Interference peak is observed to appear on SAXS patterns as soon as the crystalline phase is formed. However, it could be hard to obtain the precise value for the peak center, especially for the case of BAM-11 where the intensity at low-Q also increases and the interference peak is usually broad and superimposed on background. For consistency, an empirical function is applied to fit the SAXS patterns

$$I(Q,t) = a_1 \exp(b/(Q^{1.5})) + a_2 \exp[-\exp(-(Q - Q_c)/w) - (Q - Q_c)/w + 1] + I_b$$  \hspace{1cm} (6-11)

In this equation, the first part is used to describe the increase of intensity at low-Q, which should be similar to Gaussian function theoretically, but empirically it is found this form is better. The second part is an extreme-value function, with $a_2$, $Q_c$ and $w$ as the amplitude, center and width respectively for the interference peak. Before fitting, the same background is removed from all the SAXS patterns by subtracting the average of several earliest scans (before devitrification). The quality of refinement is very good, especially for the part of interference peak.

6.4.1.1 Isothermal

Figure 6-8 shows a set of SAXS patterns for BAM-11 annealed at 670 K. The red curve is the fitting of one pattern. From this figure it is clear that in the time scale of about four hours, the center of the interference peak does not change much. Both the intensity at low-Q and that of the interference peak increase with time. It is hard to decide
a position for the cross-over point, but the relation of \( \frac{Q_c}{Q_m} = \sqrt{2} \) for Cahn’s linear theory of spinodal decomposition apparently is not satisfied.

Corresponding to the evolution of WAXS patterns, as shown in Figure 6-6, the behavior of SAXS patterns shows two transformation stages. For the first stage, as viewed by the first four patterns in Figure 6-8, the intensity increases without apparent appearance of interference peak. During the second stage, the crystalline particles are formed, and the interference peak appears. Within about 4 hours at 670 K, the peak center does not move much, the intensity increases. In addition, there is a prominent increase of intensity below 0.015 Å⁻¹.

Figure 6-8 SAXS patterns for BAM-11 isothermally annealed at 670 K. Background has been removed. The red curve is the refinement according to Equation 6-11.

The refinement results for isothermally annealing at two temperatures, 670 K and 683 K, are shown in Figure 6-9. Since the glass transition temperature for BAM-11 is around 670 K, the sample annealed at 683 K show sudden appearance of interference peak after a short incubation time. Instead, the one annealed at 670 K show more details for the early stage.
Figure 6-9 The refinement parameters for interference peak on SAXS patterns of BAM-11, including (a) peak center, (b) amplitude, (c) width and (d) calculated area (Area = amplitude × width), for isothermal annealing at 670 K and 683 K, according to the first method described in Equation 6-11.

The evolution of interference peak center is shown in Figure 6-9(a). Within 4 hours, the peak center decreases only slightly (4% for 670 K and 10% for 683 K). Except for the very early stage at 670 K, both curves show almost a linear decrease, thus the power law for correlation length described by Equation 6-5 is not satisfied. For the very early stage (< 30 min) of isothermal annealing at 670 K, an increase of peak center is obtained from fitting, which seems is not a fitting artifact, as can be observed from the
SAXS patterns below the red curve in Figure 6-8. This suggests that because of the very slow kinetics, possibly there is a stage of contraction before the highly ordered crystalline particles are formed. The mechanism for this phenomenon is still not clear.

The evolution of amplitude, i.e., the intensity of the interference peak at peak center, is shown in Figure 6-9(b). The two curves are refined with power functions. The results are quite similar,

\begin{align*}
    a_2 &= 21.6 \times (t - 9.11)^{0.32} \quad (670 \text{K}) \\
    a_2 &= 23.1 \times (t + 48.56)^{0.33} \quad (683 \text{K})
\end{align*}

(6-12)

Thus the power law in Equation 6-6 is satisfied, with \( \gamma = 1/3 \). This value does not agree with the value of 0.81 for the case of small concentration gradient [102]. Neither does it follow the exponential relation given by Equation 6-9. Apparently, the coefficient (21.6 and 23.1) is temperature-related, reflecting the growing speed of particles. The parameter for reference time (9.11 and -48.56) indicates that at 670 K particles grow starting at 9.11 min after reaching 670 K, whereas at 683 K particles have been formed before reaching the isothermal temperature.

Although the intensity at the peak center does not follow the exponential relation given by Equation 6-9, the effective diffusion constant is estimated according to Equation 6-9 and 6-10, choosing two points on Figure 6-9(b) and using the average peak center on Figure 6-9(a). The result is around 4.1 Å²/s for 670 K and 4.9 Å²/s for 683 K. As a comparison, Loffler et al [36] obtained the value of 2.2 Å²/s at 686 K for Vit105.

The interference peak width is shown in Figure 6-9(c). Very similar trend is observed for the two temperatures. The width for 683 K is refined with a power function

\[ w = 0.011 \times (t + 1.19)^{0.055} \].

The decrease of peak width with time is a sign that the particles become more uniform. The area under that interference peak is calculated by
multiplying amplitude by width. The result is shown in Figure 6-9(d). The curve for 670 K is refined with a logarithm function

\[ A = -0.24 + 0.59 \ln(t-5.98) \]  \hspace{1cm} (6-13)

The area for 683 K is almost linear with time, which is very similar to the later stage of 670 K. If we assume that the area is proportionally to the volume fraction of crystalline phase, it seems at the early stage the volume increases logarithmically.

Overall, a long steady growth stage has been observed for isothermal annealing, which does not satisfy the equations proposed for spinodal decomposition. During annealing near the glass transition temperature, the origin of particle growth is observed, and there seems to be a very short period of “shrinking”, during which the correlation length decreases.

\textbf{6.4.1.2 Isochronal}

During isochronal annealing the crystallization process advances to a higher degree, and the results show a more complete range. Figure 6-10 is the refined parameters for BAM-11 isochronally annealed with a rate of 5 K/min by the first method. Compared with the results for isothermal annealing in Figure 6-9, these parameters show quite different behavior. The peak center in Figure 6-10(a) shows a continuous decrease, with a parabolic relation to time

\[ Q_c = 0.244 - 5.743t^{2.287} \]  \hspace{1cm} (6-14)

Both the amplitude and area follow the exponential law given by Equation 6-9, and the coefficients are similar. According to Equation 6-10, the effective diffusion coefficient is estimated to be around 5.8 Å²/s at the beginning and increases almost
exponentially with temperature. This value is compatible with the results from isothermal annealing.

Nevertheless, the peak width shows a strange behavior at higher temperature. Below 750 K the peak width decreases almost linearly, similar to the results from isothermal annealing. Yet there is an anomalous increase of peak width between 760 K...
and 780 K, and it decreases sharply above 780 K. Whether this is a sign of hidden transformation is a subject remains to be discussed. This probably suggests that before Ostwald ripening, some particles are aggregated, thus the size distribution of the particles become anomalous.

### 6.4.2 Second method

In Chapter 5 a simple model has been applied to refine the SAXS patterns, in which the interference peak is described by the spherical core-shell model with log-normal size distribution, and the high intensity at low-Q is described by the hard sphere model. The evolution of parameters is shown below. The meanings of the parameters are the same as described in Chapter 5.

#### 6.4.2.1 Isothermal

The results for isothermal annealing at 670 K and 683 K are shown in Figure 6-11. For comparison, the SANS patterns from Figure 2 in the paper of Loffler et al [36] are also fitted with this model and the particle size and distribution are shown as insets in Figure 6-11(a) and (b). The quality of fitting is very good, and the results are consistent in showing the same trends, indicating that this core-shell model is effective and applicable for possibly all BMGs that show interference peak. The low residues assure that the parameters are comparable.
Figure 6-11 Parameters obtained by fitting SAXS patterns for BAM-11 with core-shell model: (a) center of shell radius, (b) width for the log-normal distribution of particles, (c) ratio of radius, (c) ratio of scattering length density (contrast), and (e) ratio of volume multiply scattering length density (bt³), between core and shell, for isothermal annealing at 670 K and 683 K.
Among all the parameters, the accuracy of the center of shell radius ($R_0$, as shown in Figure 6-11(a)) and the width of the log-normal distribution should be quite good, because they are preliminarily determined by the interference peak center and the peak width. On the other hand, it is found that the core/shell size ratio and the contrast ratio are related in some unknown way. The calculated $b t^3$, which can be viewed as the portion of the core that can be detected by X-ray, is plotted in Figure 6-11(e). The continuous increase of this parameter indicates that the core becomes more important with annealing time.

Both the results from fitting of SAXS patterns at low temperature (670 K) and SANS patterns show particles grow exponentially with time, as stated in Loffler et al’s paper [36], with a relation of

$$R(t) - R_0 = (R_{\text{max}} - R_0) \times (1 - \exp(-((t - t_0) / \tau)^d))$$

(6-15)

The gray curve in Figure 6-11(a) is the refinement of particle size for 670 K with this equation. By forcing R0 and t0 to be zero, the fitted results are $R_{\text{max}} = 12.9$ nm, $\tau = 3.2$ min, $d = 0.214$. According to Loffler et al, the diffusion constant is obtained by

$$D = (2\pi / Q_{\text{max}} - \Phi_{\text{max}})^2 / (4\tau)$$

(6-16)

Where $\Phi_{\text{max}}$ is the maximum particle size corresponding to $R_{\text{max}}$, which is calculated to be 221Å using the number-average particle size. Thus the diffusion constant is calculated to be around 2.1 Å²/s, which is quite similar to the result given by Loffler et al (2.21 Å²/s) for their sample, and is also comparable to the value of 4.1 Å²/s obtained by the first method. For annealing at higher temperature, this exponential trend is not prominent; the particles grow almost linearly.
Figure 6-11(c)-(e) show that for both temperatures, the width of the log-normal distribution decreases with time, indicating the particles become more uniform with time. The ratio of core/shell radii increases and the contrast decreases with time. The value of $bt^3$, which is proportional to the ratio of volume multiply contrast, increases with time, and has larger values for isothermal annealing at low temperature. These parameters indicate that growth of particles may involve the assimilation of shell to the core, which is very similar to the linked-flux model proposed by Kelton [103]. Compared to the results from the first method in Figure 6-9, the size distribution (ln$\sigma$) shows similar behavior to the peak width, while other parameters can not find counterparts. Evidently the second method resolves more details about the structure of the particles.

It also should be noted that although the sample compositions are the same for both experiments (SAXS and SANS), the results of SANS show finer particle size and more concentrated size distribution. This may be attributed to the different sample preparation conditions, mainly, the cooling rates.

6.4.2.2 Isochronal

In order to view the more complete evolution of crystalline particles, the SAXS patterns obtained by isochronally annealing with a heating rate of 5 K/min are refined with this model. The results are shown in Figure 6-12. The particle sizes obtained from both methods are plotted in Figure 6-12 (a). The black dots are the log-normal distribution center of shell radius. The red dots are the estimated particle radius by $3/Q_C$, where $Q_C$ is obtained by the first method. The results agree well at the later stage, proving...
that QR=3 is a reasonable estimation of the particle size. There is a difference about 2 nm for the early stage (<760 K).

All of the parameters show that there exist two stages with different kinetics, with 760 K as the dividing temperature. Compared to the isothermal results in Figure 6-11, it is evident that all the isothermal SAXS patterns belong to the first stage, which may be called the “steady growth” stage, during which the particles grow very slowly with an exponential relation with time, the particle size distribution becomes narrower, core/shell ratio increases, and contrast decreases. Yet during the second stage, the particles grow much faster (almost linear with time), the size distribution becomes wider, there is a constant decrease of core/shell ratio and an increase of contrast ratio. And the value of \( b t^3 \) decreases steadily, indicating that particles are composed of a thick shell and a more condensed core. The number-averaged core size is calculated and plotted in Figure 6-12(e), which shows a shrink at the beginning of the second stage. This shrinkage is coincident to the increase of particle size distribution width from the first method in Figure 6-10(c). We are still not sure about how to explain this phenomenon. An assumption as stated in the session 6.4.1.2 is that this is related with the aggregation of particles before the ripening stage, i.e., the crystalline particles become contacted with each other during this time and try to form a new core-shell structure, as a consequence the parameters vary anomalously. The absolute values of these parameters may not be accurate, but the evolution of them is a good evaluation of the transformation kinetics for different stages.
Figure 6-12 The parameters obtained by refining SAXS patterns (measured while isochronal annealing BAM-11 at a rate of 5 K/min) with the SAXS model. (a) Particle size (the log-normal distribution center of shell radius), as a comparison the red symbols show the estimated particle size obtained by 3/QC, where QC is obtained by the first method; (b) Size distribution width; (c) Core/shell ratio; (d) Contrast ratio between core and shell; (e) Number-averaged particle size (diameter of the core); and (f) Calculated bt^3.


6.5 Conclusions

Summarily, we have carried out the experiment of in-situ synchrotron scattering with simultaneous SAXS and WAXS for BAM-11. As expected, the experiment is proficient in characterizing the structure evolution at both atomic scale and sub-micron scale, which gives us more specified view about the structural evolution in local and large scale. The WAXS and SAXS patterns are carefully analyzed, and some conclusions are drawn here:

1. BAM-11 is very homogeneous and show good resistance to devitrification. The GFA of this alloy is very good.

2. A two-stage transformation has been characterized during the devitrification of BAM-11. Before devitrification, a stage of relaxation has also been observed. The first transformation happens in short interval and is characterized by the sharpening of the main diffuse peaks on WAXS. The second transformation takes long time to complete, and is characterized by the interference peak on SAXS patterns.

3. The WAXS patterns show that the as-cast sample contains icosahedral SROs, which further develop to form tiny quasicrystal-like nanoclusters (~2 nm) during the first transformation. During the second transformation the tetragonal NiZr₂ phase (C16) is formed.

4. The intensity of SAXS increases ever since relaxation and the intensity at low-Q increases continuous during devitrification, indicating that possibly phase separation happens before crystallization. During the first transformation, SAXS intensity at low-Q increases without interference peak; interference peak is developed once the
crystalline NiZr$_2$ phase is formed. A SAXS model based on the core-shell model has been proposed and the SAXS patterns are well refined with this model.

5. Two methods have been applied for kinetic study. By the direct method, the interference peak position, amplitude and width are measured. The results show they do not follow the rules for spinodal decomposition. For the second method, the particle size, size distribution, core/shell ratio and contrast ratio, are obtained by refining the SAXS patterns with our model. It is found that there are two stages during the particle growth (the second transformation from WAXS). The first is the independent growth stage with very slow kinetics, during which the particles become more uniform with a swelling core. The second stage is more temperature-driven and has faster kinetics. During this stage the particle size becomes more diverse, and the particles are composed of a condensed core and a thick shell. An anomalous period has been found at the beginning of the second stage.
Chapter 7  Total Scattering for BAM-11

In this chapter, first the necessary procedures to obtain pair distribution functions (PDFs) are discussed, then the details of PDFs for BAM-11 are analyzed for the as-cast state, after relaxation and during each transformation, with the intention to separate the partial contributions of each group of bonds and identify the respective structures.

7.1 Retrieving PDFs

7.1.1 Corrections

As introduced in Chapter 2, the structure factor is obtained by normalizing the total scattering intensity to the averaged scattering form factor. Many corrections should be considered before the precise PDF can be obtained, including multiple scattering, incoherent scattering, absorption, polarization, etc. For neutron scattering, since the energy level of neutrons is comparable to the excitation energy for atoms, the static approximation cannot be applied directly and the Placzek correction should be considered to correct inelastic scattering [104]. For X-ray there are more corrections, mainly due to the fact that the atomic form factor is not constant for different momentum transfer (Q), and more corrections should be applied to detector efficiency for different energy scale.

Figure 7-1(a) shows the structure factor S(Q) for as-cast BAM-11 obtained from both neutron and X-ray scattering. The results are obtained using the software PDFGetN [105] for neutron scattering and PDFGetX [106] for X-ray scattering. Due to the difference of atomic form factor by neutron and X-ray scattering, the profiles of S(Q) are
quite different. Basically, the structure factor from X-ray scattering has sharper and higher peaks in the low-Q range. The figure also shows that data in the high-Q range becomes noisy. For X-ray this is because the form factor is very small in this range, and more corrections are applied in this range. Thus, the maximum effective Q for neutron scattering is generally larger. For neutron the statistics error increases with scattering angle, according to the relation that

\[ Q = 4\pi \frac{\sin \theta}{\lambda} \]

\[ \frac{\delta Q}{Q} = \frac{\delta \lambda}{\lambda} + \cot \theta \delta \theta \]  

(7-1)

The above equation indicates resolution deteriorate with Q, and for X-ray, statistics also decreases with Q. Figure 7-1(a) shows that the statistics of X-ray scattering is much better than neutron scattering, due to the high intensity of synchrotron source. The “Egami rule” states that in order to ensure good statistics, one wants to accumulate 10^6 neutrons / Å^-1 in the high Q region [66], which is barely satisfied if we combine the data collected within one hour for neutron scattering. One the other hand, the structure factor S(Q) must be truncated before Fourier transforming to obtain PDF. Due to the reverse relationship between Q and R, the high-Q part of S(Q) will result in tiny local waves on G(R), which is called the “truncation error”. As demonstrated in Figure 7-1(b), G(R) becomes very noisy if Qmax is too large.

Thus there is a tradeoff between including more information within a large Q-range and excluding the part that has small signal/noise ratio. In our case, it is found that truncating S(Q) from neutron scattering at Qmax=25 Å^-1 will give very reasonable results. Thus all the discussions below is based on Qmax=25 Å^-1 for neutron scattering. For X-ray scattering, the whole range of S(Q) is used, with Qmax=20 Å^-1.
7.1.2 Optimization

As stated by Egami and Billinge [64], the structure factor $S(Q)$ is very robust and the PDFs will not be affected much in the large range by corrections. Still, some optimizing method should be considered, especially when we want to get the precise PDFs for the first few atomic shells. The most efficient optimization, as proposed by Peterson et al [67], is the $\Delta G_{\text{low}}$ method. The main idea is canceling the asymptote of $S(Q)$ at high $Q$ using a linear function

$$S'(Q) = aS(Q) + bQ + c$$ (7-2)

So that $S(Q)$ has the average value of 1 in the large $Q$-range, and the obtained $G(R)$ has smallest sum below the first shell. Practically more complicated functions could be used if the unprocessed $S(Q)$ has complex asymptote at the high-$Q$ range. In this paper only the linear function is applied for optimization.
7.1.3 Peak profile

The PDF for multiple component system obtained from the measured structure factor is actually the average of many partial PDFs, weighted by their scattering cross-sections [64]:

\[
G(r) = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dQ = 4\pi r [\rho(r) - \rho_0]
\]

\[
g(r) = \rho(r) / \rho_0 = \sum_y W_{ij} g_y(r)
\]

\[
g_y(r) = \frac{1}{4\pi N \rho_0 r^2} \sum_i c_i b_i \sum_{\mu \nu} \delta(r - r_{\mu \nu})
\]

Where \(i\) and \(j\) are the element types, \(G(r)\) is the reduced PDF, \(g(r)\) is the actual PDF, and \(W_{ij}\) is the weight for each partial PDF \(g_{ij}(r)\), calculated by

\[
W_{ij} = \begin{cases} 
\frac{2 c_i c_j b_i b_j}{<b^2>} & (i \neq j) \\
\frac{c_i^2 b_i^2}{<b^2>} & (i = j)
\end{cases}
\]

where \(c_i\) and \(b_i\) are the atomic concentration and scattering length of element \(i\), respectively.

Previously the PDF is simply interpreted by the sum of 1-d Gaussian distributions centered at the average atomic pair distance as determined from Rietveld analysis. However the total PDF is heavily averaged. Both thermal average (average over time) and powder average (average over Azimuth angle) are applied before the total PDF is obtained. Regarding to the peak profiles of different expression of PDFs, it has been deduced by Dimitrov et al [107] that for anisotropic crystals the peak positions and profiles of \(g(r)\) will deviate from the Gaussian approximation. Yet for isotropic materials the peak profile of \(r \rho(r)\) is theoretically Gaussian. Thus in this paper, all refinement of
PDFs are expressed in the form of \( r g(r) \) and the Gaussian peaks are applied for each partials.

\[
T(r) = r g(r) = \sum_i W_i T_i(r) \tag{7-5}
\]

The coordination number is calculated by the equation

\[
N(r) = \int_{r_1}^{r_2} 4\pi r^2 \rho(r) dr = \int_{r_1}^{r_2} 4\pi r \rho_0 T(r) dr \tag{7-6}
\]

### 7.2 Results

Figure 7-2 shows the 3-dimensional plots of S(Q) and G(R) for BAM-11, measured by neutron scattering during isothermal annealing at 663 K. Figure 7-3 shows similar results measured by X-ray scattering while isothermal annealing the sample at 708 K. By comparing with the time scale of DSC measurements, it is apparent that the temperature calibration of these two experiments is better than the first synchrotron experiment. Similar to the results of the previous synchrotron experiment, the two-stage transformation is prominent on S(Q). The first stage is characterized by the sharpening and swelling of the main diffuse peak. The two stages are smeared and overlapped with each other on the neutron scattering patterns, because 663 K is a rather low temperature (around the onset of glass transition), and the sample used for neutron scattering is much larger.

The reduced PDFs from both neutron and X-ray scattering show that only SROs below 2 nm exist in BAM-11 for the as-cast state and during the first transformation stage. LRO develops during the second transformation. Details are discussed below. We focus on the PDFs obtained by neutron scattering, since the results from neutron scattering is more reliable due to the less corrections applied.
Figure 7-2 Evolution of (a) structure factor and (b) reduced pair distribution function for BAM-11 measured by neutron total scattering during isothermal annealing at 663 K. The first curve on G(R) is measured at room temperature.

Figure 7-3 Evolution of (a) structure factor and (b) reduced pair distribution function for BAM-11 measured by synchrotron total scattering during isothermal annealing at 708 K.
7.3 Analysis

In this section, the PDFs at each stage, first at the as-cast state, then during relaxation, finally during each transformation of the devitrification process, are analyzed.

7.3.1 Atomic scale decoding for as-cast BAM-11

The reduced PDFs for the as-cast BAM-11 from both neutron and X-ray scattering are plotted in Figure 7-4. As a comparison, the reduced PDF for fused silica, which is pure nonmetallic glass, is also plotted. Despite the difference of peak profiles of the first shells, both neutron and X-ray scattering show similar SRO within the scale of 2 nm for the as-cast BAM-11. The sharp peaks for fused silica come from the tetrahedra, which are the basic units for this material. Since the slight orientation variation between these tetrahedrons can break the LRO and make the silica amorphous, it is quite possible that BMGs may be composed of SROs which are separated by defects, like the disclination lines proposed by Frank [4] and Sachdev et al [97]. This will be discussed further in later sections.

For the quinary BAM-11, the total PDF is composed of 15 partial PDFs, making it hard (almost impossible) to render each partial PDF quantitatively. Yet with the result from both neutron and X-ray scattering, and with some previous knowledge like atom size, concentration, weights for each partial PDF, etc, it is still possible to obtain insightful information from the PDFs, especially for the first atomic shell. This is important because although previously there are many models about the configurations of SROs inside BMGs, like the solute cluster model given by Miracle [43], a precise experimental result has not been given to verify these models.
Some parameters for each element in BAM-11 are given in Table 7-1. The atom radii are obtained from Pearson’s handbook [108]. The weight ratios of each element as viewed by neutron and X-ray are also calculated, according to their atomic scattering factor ($W_i = c_i b_i / \langle b \rangle$). The results indicate that X-ray sees a larger fraction of Zr than neutron, while neutron is more sensitive for Ni. If just seeing from the viewpoint of atom size, the quinary BAM-11 can be classified as a pseudo-ternary alloy Zr-(Al, Ti)-(Cu,Ni), with Zr being the large solvent atom, Al and Ti the solute atom with intermediate size, and Cu and Ni the smallest solute atom. This ternary BMG has been discussed in Miracle’s model [43], in which the large solvent atoms tend to form random icosahedral clusters with intermediate atoms at the center, and the smallest atoms occupy the interstitial positions. Within this scenario, many BMGs can be classified in this pseudo-ternary system, and it seems that the topology of BMGs is only related with atom sizes. In order to verify this assumption, we calculate the weight for each partial PDFs for both neutron and X-ray scattering. The results are listed in Table 7-2. The bond lengths are
also calculated simply by adding the atomic radii. Accordingly, there are only four
groups of bonds which are most important: Zr-Zr, Zr-(Al,Ti), Zr-(Cu,Ni), and (Cu,Ni)-
(Cu,Ni), with the bond lengths decrease sequentially. The total weights from other types
of bonds sum up to below 5%. Thus we can ignore these bonds and calculate the
contributions from the four main bonds, and compare with the results from theoretic estimation.

Table 7-1 Parameters of elements in BAM-11 and their weights as viewed by neutron and X-Ray

<table>
<thead>
<tr>
<th>Element</th>
<th>Atom%</th>
<th>Radius(Å)</th>
<th>b (fm)</th>
<th>WN%</th>
<th>WX%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>52.5</td>
<td>1.5863</td>
<td>7.16</td>
<td>55.1</td>
<td>64.3</td>
</tr>
<tr>
<td>Al</td>
<td>10</td>
<td>1.4286</td>
<td>3.449</td>
<td>5.1</td>
<td>4.0</td>
</tr>
<tr>
<td>Ti</td>
<td>5</td>
<td>1.4449</td>
<td>-3.37</td>
<td>-2.5</td>
<td>3.4</td>
</tr>
<tr>
<td>Cu</td>
<td>17.9</td>
<td>1.2754</td>
<td>7.718</td>
<td>20.3</td>
<td>15.9</td>
</tr>
<tr>
<td>Ni</td>
<td>14.6</td>
<td>1.2433</td>
<td>10.3</td>
<td>22.0</td>
<td>12.5</td>
</tr>
</tbody>
</table>

Table 7-2 The possible nearest bonds, bond-lengths and their partial weights as viewed by neutron and X-Ray scattering

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length</th>
<th>$W_N^{ij}$</th>
<th>$W_X^{ij}$</th>
<th>$\sum W_N^{ij}$</th>
<th>$\sum W_X^{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-Zr</td>
<td>3.1726</td>
<td>0.304</td>
<td>0.413</td>
<td>0.304</td>
<td>0.413</td>
</tr>
<tr>
<td>Zr-Ti</td>
<td>3.0312</td>
<td>-0.028</td>
<td>0.043</td>
<td>0.028</td>
<td>0.094</td>
</tr>
<tr>
<td>Zr-Al</td>
<td>3.0149</td>
<td>0.056</td>
<td>0.051</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr-Ni</td>
<td>2.8296</td>
<td>0.243</td>
<td>0.161</td>
<td>0.466</td>
<td>0.365</td>
</tr>
<tr>
<td>Zr-Cu</td>
<td>2.8617</td>
<td>0.223</td>
<td>0.204</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-Cu</td>
<td>2.5508</td>
<td>0.041</td>
<td>0.025</td>
<td>0.179</td>
<td>0.081</td>
</tr>
<tr>
<td>Cu-Ni</td>
<td>2.5187</td>
<td>0.089</td>
<td>0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Ni</td>
<td>2.4866</td>
<td>0.049</td>
<td>0.016</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-Ti</td>
<td>2.8735</td>
<td>-0.003</td>
<td>0.003</td>
<td>0.023</td>
<td>0.048</td>
</tr>
<tr>
<td>Al-Al</td>
<td>2.8572</td>
<td>0.003</td>
<td>0.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-Cu</td>
<td>2.704</td>
<td>0.021</td>
<td>0.013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-Cu</td>
<td>2.7203</td>
<td>-0.01</td>
<td>0.011</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-Ni</td>
<td>2.6719</td>
<td>0.022</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-Ni</td>
<td>2.6882</td>
<td>-0.011</td>
<td>0.008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-Ti</td>
<td>2.8898</td>
<td>0.001</td>
<td>0.001</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 7-5 shows the results of the total PDF for the first atom shell refined with four groups of partials for the as-cast BAM-11 measured by both neutron and X-ray scattering. It is noted that the peak profiles from neutron and X-ray scattering are quite different. For neutron scattering, the obtained g(r) is not zero below 2.2 Å, which is assumed to be the limit for nearest atomic bonds. This fact is not an artifact of Fourier transform because the PDF in the range of 1-2 Å is nonzero even after careful optimization. Consequently the coordination number calculated is not zero below 2 Å, as shown in Figure 7-6. The reason is still not clear. Possibly this is due to the fact that neutron scattering is more sensitive to inelastic scattering, which is enhanced by the large sample. The CN at 3.76 Å is exactly 12, indicating that the alloy is dense-packed. There is a small peak at around 3.7 Å, which is not so prominent on g(r) from X-ray scattering. A small fraction of interstitial bonds are observed between the first and second shell, which is more evident from the results of neutron scattering. Possibly these bonds can be attributed to the existence of “free volume”. In the refinement, these parts are simply ignored.

The four Gaussian peaks are refined by fixing the peak center for both neutron and X-ray PDFs. The refined peak center and FWHM are given in Table 7-3. The coordination numbers for each peak are also calculated and their ratios in the first shell are given. For comparison, the estimated peak center and weights in Table 7-2 are listed beside. Compared with the theoretic values calculated under the random distribution assumption, the measured bond lengths of Zr-Zr and Zr-(Al,Ti) about 2.2% longer. If we assume that the large Zr atoms form homogeneous solvent overwrapping all other atoms, the “free volume” can be attributed solely to the enlargement of the effective size of all the Zr atoms. Previously the specific volume of Vit1 was measured by Johnson’s group.
It was found that Vit1 is about 2-3% denser than the ideal liquid that follows the dense random packing model, and there is about 1% excessive volume in the glass compared with the fully crystallized counterpart. We think the specific volume of BAM-11 would show the same behavior as Vit1, since the compositions of these two alloys are very similar. This implies there are attractions between dissimilar elements in the glass, yet the attraction is not as strong as in the crystalline phase. Indeed, the CN of Zr-Zr takes a much higher percentage than calculated, and the FWHM of this peak is very broad, suggesting that the Zr atoms have a larger chance to bond with each other than expected.

![Figure 7-5 The refinement of total PDF with 4 groups of partial PDFs for the as-cast BAM-11 measured by (a) neutron scattering and (b) synchrotron scattering.](image)

On the other hand, the (Cu,Ni)-(Cu,Ni) bond takes a much smaller fraction (only a few percent) than expected, suggesting that the smallest atoms do not have the chance to see each other. The bond length of Zr-(Cu,Ni) is about 4% shorter than expected, as have been pointed out by many previous experiments [111-113]. This implies stronger interaction between Zr and Cu, Ni atoms. The CN fraction of Zr-(Cu,Ni) bonds is the same as expected. The Zr-(Al,Ti) bond has a larger length than expected, yet the fraction
is similar (the larger fraction detected by X-ray can be attributed to Zr-Zr bond since the two peaks mix with each other).

Figure 7-6 Coordination number calculated from PDF measured by neutron scattering for as-cast BAM-11.

These results indicate that BAM-11 is not homogeneous at the atomic level. Clusters are formed around the solute atoms. The clusters centered at (Cu,Ni) are dense-packed, while the cluster centered at (Al,Ti) are loose-packed. This seems to comply with Miracle’s cluster model, in which he proposed that Zr-(Al,Ti)-(Cu,Ni) will form <12-10> type clusters [43]. Yet we are still not sure about the configurations of the icosahedral clusters, because it is hard to separate the partial PDFs for the second shell.

Table 7-3 The Gaussian peak parameters refined for the partial PDFs of the first atomic shell for as-cast BAM-11

<table>
<thead>
<tr>
<th>Peak</th>
<th>Center (Å)</th>
<th>Neutron</th>
<th>X-ray</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Expect</td>
<td>FWHM (Å⁻¹)</td>
</tr>
<tr>
<td>Zr-Zr</td>
<td>3.24</td>
<td>3.17</td>
<td>0.56</td>
</tr>
<tr>
<td>Zr-(Al,Ti)</td>
<td>3.09</td>
<td>3.02</td>
<td>0.19</td>
</tr>
<tr>
<td>Zr-(Cu,Ni)</td>
<td>2.73</td>
<td>2.85</td>
<td>0.45</td>
</tr>
<tr>
<td>(Cu,Ni)-(Cu, Ni)</td>
<td>2.62</td>
<td>2.54</td>
<td>0.23</td>
</tr>
</tbody>
</table>
7.3.2 Relaxation

A prominent change is observed on the PDF profile after relaxation, as shown in Figure 7-7(a). The PDF obtained during the first hour of annealing at 663 K is before devitrification. There is a sharp decrease of the peak for the first shell, and a slight decrease of the sharp peaks for the second and third shell, indicating that the peaks are more smeared and the atomic topology becomes more homogeneous. This change is too big to be simply attributed to temperature effect. Similarly, we use four Gaussian peaks to refine the T(r) for the first shell, with the confinement that the peak positions are not changing except for that of the Zr-(Al,Ti) bond. The results are listed in Table 7-4.

Compared with the parameters for as-cast state, the fraction of Zr-(Cu,Ni) bonds decreases significantly, and the fraction of (Cu,Ni)-(Cu,Ni) bonds increases. Overall, the total fraction of Zr-(Cu,Ni) and (Cu,Ni)-(Cu,Ni) bonds decreases. The bond length of Zr-(Al,Ti) decreases slightly, and there is a slight increase of the fraction of Zr-Zr bonds with broader distribution. These results indicate that some atoms occupy the metastable positions for the as-cast state, which settle to more stable positions after relaxation. Since the as-cast sample is actually the quench-in state of the liquid, it may be proposed that Zr and (Cu,Ni) atoms have stronger interaction at higher temperature, and they tend to separate at low temperature. The increase of the peak at 2.62 Å may not be attributed to (Cu,Ni)-(Cu,Ni) bonds, more probably, it is due to the shortened Zr-(Cu,Ni) bonds. Since the annealing temperature is just around the onset of glass transition temperature, when the kinetics is very slow, the separation of these bonds happen at only atomic scale, benefited by the existence of free volume.
Figure 7-7 (a) Reduced PDFs of as-cast state and after relaxation; and refinement of total PDF after relaxation with 4 groups of partials for (b) neutron scattering measured during the first hour at 663 K, and (c) X-ray scattering measured at 0 min at 708 K.

Table 7-4 The fraction of each of the four bonds within the first shell, obtained by calculating the coordination number from the refinement of $T(r)$, for three states: I—as-cast, II—after relaxation, III—the first transformation.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Bond assumed</th>
<th>Center (Å)</th>
<th>Neutron $W_{ij}^N$</th>
<th>Neutron I</th>
<th>Neutron II</th>
<th>Neutron III</th>
<th>X-ray $W_{ij}^X$</th>
<th>X-ray I</th>
<th>X-ray II</th>
<th>X-ray III</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zr-Zr</td>
<td>3.24</td>
<td>0.30</td>
<td>0.52</td>
<td>0.62</td>
<td>0.56</td>
<td>0.41</td>
<td>0.50</td>
<td>0.55</td>
<td>0.50</td>
</tr>
<tr>
<td>2</td>
<td>Zr-(Al,Ti)</td>
<td>3.09 *</td>
<td>0.03</td>
<td>0.03</td>
<td>0.04</td>
<td>0.12</td>
<td>0.09</td>
<td>0.20</td>
<td>0.23</td>
<td>0.29</td>
</tr>
<tr>
<td>3</td>
<td>Zr-(Cu,Ni)</td>
<td>2.73</td>
<td>0.47</td>
<td>0.44</td>
<td>0.19</td>
<td>0.16</td>
<td>0.37</td>
<td>0.26</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>4</td>
<td>(Cu,Ni)-(Cu,Ni)</td>
<td>2.62</td>
<td>0.18</td>
<td>0.02</td>
<td>0.14</td>
<td>0.16</td>
<td>0.08</td>
<td>0.04</td>
<td>0.11</td>
<td>0.10</td>
</tr>
</tbody>
</table>

* The peak center for II (after relaxation) is 3.07 Å.
7.3.3 Two-stage transformation

The two-stage transformation is further demonstrated by the integrated intensity of $S(Q)$ from 2 to 4 Å$^{-1}$ measured by neutron scattering, as shown in Figure 7-8(a). The calculation method is the same as shown in Equation 6-1. Due to the large sample volume and the low temperature, the two peaks are broadened and smeared, yet the peak profile and time scale are quite similar to the results of DSC.

![Image of Figure 7-8](image.png)

Figure 7-8 Two-stage devitrification as viewed from (a) Integrated intensity (black) and differential integrated intensity (red) of $S(Q)$ within the Q-range of 2-4 Å$^{-1}$, measured by neutron scattering while annealing at 663 K, and (b) $\delta G(r)$, Fourier transformation of $\delta S(Q)$, measured by synchrotron scattering while annealing at 708 K.

The two-stage transformation is also shown in real space by continuous development of $\delta G(r)$, which is the Fourier transformation of $\delta S(Q)$

$$\delta G(r,t) = 2/\pi \int_0^\infty Q[S(Q,t) - S(Q,0)]\sin(Qr) \, dQ \tag{7-7}$$

Where $S(Q,0)$ is the structure factor for amorphous phase. This method is only applicable to the data from synchrotron scattering, because its resolution and statistics are better than neutron scattering, thus the $\delta S(Q)$ reflects the structural evolution instead of being buried in noise. The result measured by synchrotron scattering while annealing at 708 K is
shown in Figure 7-8(b). Due to the high quality of the data, the trend is very prominent after some smoothing has been applied. It is clear that at 708 K, the first transformation starts around 200 seconds, and the second transformation starts at 700 seconds. The first stage is characterized by the development of MROs within the range of 2 nm (the figure shows only up to 15 Å). The second transformation is characterized by development of LRO and the changes of MRO, as evidenced by the new peak at 8 Å and the shifting of the peaks around 10 Å and 12 Å.

Details about the PDFs for each stage are discussed below.

7.3.3.1 First transformation

We use the same four groups of Gaussian peaks to refine the PDF profile of the first shell, measured from fifth to sixth hour during annealing at 663 K. This is assumed to be valid because at this stage the structural changes are still at the atomic level (in fact it is within the 2 nm range). As shown in Figure 7-8, the time is almost at the end of the first transformation. The refinement result is shown in Figure 7-9, and the parameters are given in Table 7-4. Compared to the parameters obtained after relaxation, it is clear that the sum of the peaks centered at 2.62 Å and 2.73 Å remains unchanged, while there is a quite big shift of the peak centered at 3.24 Å to the peak at 3.09 Å. If the four Gaussian peaks can still be attributed to the four different groups of bonds as assumed in section 7.3.1, it seems that there is a rising of the Zr-(Al,Ti) bonds. More possibilities are given below.
Although only very slight changes have been observed on the diffraction patterns during the first transformation, it is believed that a new phase is formed during this stage. As shown in Figure 7-2 and Figure 7-3, the structural evolution during this stage only happens within 2 nm’s range. The new phase is in the form of very tiny clusters. In fact, previously there are several reports about the metastable phase in the Zr-Ni alloys, especially near the composition of NiZr₂ [113-116]. These studies pointed out that there is an fcc phase forming before the more stable tetragonal NiZr₂ appears. The fcc phase is similar to the NiTi₂ phase, which has a large unit cell (cF96, a=11.32 Å), and if stabilized by oxygen, the saturated phase has the composition of Ni₂Ti₄O with E₉₃ structure [115]. The oxygen concentration for our BAM-11 sample is very low (< 500 ppm), thus if the fcc NiZr₂ phase is formed, it may be distorted and the particle size is very tiny.

In order to resolve the structure of the first transformation product, ΔG(r) is plotted in Figure 7-10, which is the difference of G(r) obtained during the 6th hour and that of the 1st hour during annealing at 663 K. If we consider the PDF during the first
transformation is a linear combination of PDFs of two phases, the amorphous phase and the first transformation product:

\[ G(r,t) = f G_t(r,t) + (1 - f)G_a(r) \]  

(7-8)

where \( f \) is the volume fraction of the transformed phase. If the PDF for the amorphous is assumed not changing with temperature, then the difference is obtained by

\[ \Delta G(r,t) = G(r,t) - G_a(r) = f[G_t(r,t) - G_a(r)] \]  

(7-9)

This means that the \( \Delta G(r) \) is actually the difference of PDFs between the new phase and the amorphous phase, scaled by the volume fraction. In our analysis, we assume that the structure during the first hour is still amorphous.

For comparison, the PDF for fcc NiZr\(_2\) is simulated using the software PDFFit [117]. The structure is the same as the cF96 NiTi\(_2\) [118], with Zr taking the positions of Ti. The lattice parameter is scaled to 12.27 Å, as given by Altounian et al for NiZr\(_2\) [115]. The atoms occupy three positions: Ni (32e), Zr\(_1\) (48f), and Zr\(_2\) (16c), as shown in Table 7-5. The bonds between different atoms are labeled beside.

It is found that besides the Ni-Zr and Ni-Ni bonds, most bonds match well with the peak positions in \( \Delta G(r) \). Since Equation 7-9 indicates \( \Delta G(r) \) is actually the difference of PDFs between the new phase and the amorphous phase, if we assume that the Ni-Zr bonds do not move during the transformation, while Zr atoms move, then \( \Delta G(r) \) can be explained by the fcc NiZr\(_2\) model successfully up to the third atomic shell. The most prominent movement of the Zr atoms is to the Zr\(_2\) sites, which contains only 16 atoms in the 96-atom unit cell, as evidenced by the strong peaks for all the first three layers, which match well with the Zr\(_1\)-Zr\(_2\) bonds in NiZr\(_2\). This indicates that the increase of the peak at 3.09 Å in Figure 7-9 is actually due to the Zr-Zr bond, the fraction of Zr-(Al,Ti) bond
possibly does not change. There is no evidence that the first phase is Ti-enriched, because Ti has negative scattering length, and if it is enriched in the first phase, a large difference will be observed on the amplitude of the first peak around 3 Å. In fact, the amplitudes for $\Delta G(r)$ from both neutron and X-ray scattering are in the same scale, and the difference is largely caused by the difference of scattering length. For the third shell, contributions from all bonds are smeared together, yet $\Delta G(r)$ from X-ray scattering shows a prominent separation, which is mainly because X-ray is more sensitive to Zr atoms, and the separation of Zr atoms is obvious up to the third shell.

This is an experimental proof that there is topology rearrangement at the atomic scale during devitrification of BMGs. Beyond the first three layers, the peak positions do not match well, mainly because the concatenations between the transformed SROs are not the same as in the highly ordered NiTi$_2$ phase. A comparison of the scale of G(r) and $\Delta G(r)$ shows the volume fraction of this phase is roughly 10% according to Equation 7-9.

**Table 7-5 Description of the two structures for NiZr$_2$**

<table>
<thead>
<tr>
<th>NiZr$_2$ fcc: Fd-3m (227), [cF96] a=12.27</th>
<th>NiZr$_2$ tI12: I4/mcm (140), [C16] a=6.477, c=5.241</th>
</tr>
</thead>
<tbody>
<tr>
<td>atom site position</td>
<td>atom site position</td>
</tr>
<tr>
<td>Zr1 48f (0.311 0 0)</td>
<td>Zr 8h (0.167 0.667 0)</td>
</tr>
<tr>
<td>Zr2 16c (1/8 1/8 1/8)</td>
<td>Ni 4c (0 0 0)</td>
</tr>
<tr>
<td>Ni 32e (0.912 0.912 0.912)</td>
<td></td>
</tr>
</tbody>
</table>
Figure 7-10 PDF for the first transformation expressed as the difference between $G(r)$ for (a) the 6th hour and the 1st hour for neutron scattering at 663 K, and (b) the 8th min and 0 min for X-ray scattering at 708 K. The red curve is the simulated $G(r)$ for the large fcc NiZr$_2$ [118].
The structure of the first stage product is further demonstrated by the difference of WAXS intensity, as illustrated in Figure 7-11. According to Equation 7-9, the WAXS intensity is a combination from both the amorphous phase and the first transformation product. The fraction of the latter is estimated by absolute value of the intensity difference, the result is around 8%. In Figure 7-11 only the net intensity for the crystalline phase is plotted. The red curve is the simulated XRD pattern for the NiZr$_2$ fcc structure. Considering that the sizes of the crystallites are very small, thus the intensity at high-Q should be largely decreased, it is obvious that most of the peak positions (even some small peaks) and heights are well matched. The slight deviation of some peak positions indicates there may be some distortions of the unit cell, or probably the site positions are not exactly as in the NiTi$_2$ structure. Nevertheless, this figure is a sound proof for our estimation of the structure of the first phase.

![Figure 7-11](image-url)  
**Figure 7-11** The diffraction pattern for the first stage product illustrated by the difference of WAXS intensity measured at 8 min minus that of the 0 min times 0.92, when BAM-11 was isothermal annealed at 670 K. The red curve is the simulated diffraction pattern for fcc NiZr$_2$ structure.
7.3.3.2 Second transformation

As shown in Figure 7-2 and Figure 7-3, LROs are developed during the second transformation. In this stage the assumption that the PDF for the first shell can be separated to four groups is no longer valid, since the crystalline phase has been separated from the amorphous matrix. The diffraction peaks are well indexed with the tetragonal NiZr$_2$ phase [113], the structure of which is given in Table 7-5. This phase is highly ordered, with only 12 atoms in the unit cell. Similarly, we use $\Delta G(r)$ to characterize the structural changes in real space. A lot of facts support the claim that the first transformation is a precursor for the second transformation, thus Equation 7-9 is still valid, i.e., $\Delta G(r)$ shows the difference of PDFs between the crystalline phase and the amorphous phase. Even if there are remains of the first phase, the fraction would be very small and can be ignored (as proved by the WAXS patterns the maximum volume fraction of the first phase is less than 7%).

$\Delta G(r)$ between the last hour and the first hour during isothermal annealing at 663 K is plotted in Figure 7-12. For comparison, the PDF for the tetragonal NiZr$_2$ phase is simulated and plotted in the same figure, and the peaks are labeled with their corresponding bonds. Due to the large cross-section of Ni atoms, the sharp peaks are all related with Ni-(Ni,Zr) bonds. As shown in this figure, the amplitude of $\Delta G(r)$ for the first shell is much smaller than those of the second to fourth shells. This is mainly because the bonds for the first shell have already existed in the amorphous phase (or first phase, if we consider the idea of precursor). Most prominently, the Ni-Zr bond at 2.74 Å is canceled in $\Delta G(r)$, just the same as for the first transformation in Figure 7-10.
indicates that the Ni-Zr bonds are very strong and they remain unchanged during crystallization. Instead, the sharp peak at 3 Å on $\Delta G(r)$ is attributed to the development of Zr-Zr bond in the tetragonal NiZr$_2$ phase. Comparing with the first transformation in Figure 7-10, it is found the bond length of Zr-Zr is decreasing continuously. This is a proof that the “free volume” in the as-cast BAM-11 is taken by the Zr atoms, and it is cancelled during crystallization. A careful examination found similar results for the second to fourth shell, i. e., the sharp peaks for Ni-Zr bonds in the NiZr$_2$ phase are missing (or not so strong) on $\Delta G(r)$, while the main peaks can largely be attributed to the development of Zr-Zr bonds. The development of the peak at 8 Å and the shifting of the peak at 10 Å and 12 Å as shown in Figure 7-8(b) indicate that in the LRO NiZr$_2$ phase, some Zr atoms move to new positions to link the SRO clusters, while the topology of these SROs clusters are changed simultaneously.

These facts prove that the solute atoms do not distribute homogeneously in the as-cast BAM-11, and the devitrification first happens in the areas where Ni atoms are enriched; during the transformation, these Ni atoms seldom move; instead, the solvent Zr atoms move to new positions. Even when the solute atoms are distributed randomly, energy fluctuations would cause aggregations of these atoms in local area (< 2 nm), it is those areas where nucleation initiates. This explains why the nucleation density is so high.
Figure 7-12 PDF for the second transformation expressed as the difference between $G(r)$ for (a) 938 min and 60 min for isothermal annealing at 663 K by neutron scattering, and (b) 48 min and 0 min for isothermal annealing at 708 K by X-ray scattering; the red curve is the simulated $G(r)$ for the tetragonal NiZr$_2$ phase [113].
7.4 Summary

The results from total scattering experiments have been discussed in details by examining each PDF patterns measured during isothermal annealing, with a focus on those measured by neutron scattering. Below are some facts we found.

1. By combining the results from both neutron and X-ray scattering, it is found that the PDF of the as-cast BAM-11 for the first shell can be separated into four groups. The refinement results support the cluster model, i.e., BAM-11 is composed of tiny clusters with one solute atom at the center, surrounded by Zr atoms.

2. After relaxation, a sharp decrease of the fraction of Zr-(Cu,Ni) bond is observed, indicating that Zr and (Cu, Ni) have stronger interaction in the high temperature liquid state.

3. Two consecutive transformations are involved during devitrification. During the first transformation only sharpening of the main peaks on S(Q) is observed, consequently on G(r) MRO is developed, which is confined within 2 nm range. Careful examination of the PDF peaks found that the structure of the first transformation product matches with the fcc NiZr₂ phase. A topological rearrangement is characterized by the movement of Zr atoms to the Zr2 sites, while the Ni-Zr bonds remain unchanged.

4. The second transformation is related with the development of tetragonal NiZr₂ phase. Only slight changes are observed for the first shell, while LROs are developed by the movement of Zr atoms. The Zr-Ni bonds remain almost unchanged.

As discussed in Chapter 6, the diffraction profile of the as-cast BAM-11 matches well with the icosahedral SRO model, and the variation of scattering patterns during the
first transformation agree with the theory of development of long-range icosahedral order. Also, from the kinetic study of DSC traces, it is found that the first transformation is diffusion-controlled. And, microscopy measurements showed that the nucleation density is very high (~$10^{23}$ m$^{-3}$). As described by Wang et al [119], the fcc NiZr$_2$ phase is composed of tetrahedrally packed icosahedra, and the local structures are similar to the first two shells of the dense-packed Bergman-type clusters.

Bearing all these facts in mind, we may conclude that there are a lot of icosahedral SROs in the as-cast BAM-11, with solute atoms at the center and Zr as the solvent. It seems that the two-stage transformation is intrinsic for Ni-Zr alloys; the presence of other elements only retards the transformation and improves the GFA. Devitrification initiates at the areas where Ni atoms are enriched, which is favorable to form the low-energy metastable fcc NiZr$_2$ phase, because the Ni-Zr bonds are very stable and the topology changes are realized by the slight movement of Zr atoms. This also explains why the first transformation is diffusion-controlled. These metastable nanoclusters are nuclei (precursor) for the crystalline phase, because it is easier for them to transform to periodic order once the large cell metastable phase is formed. It is more difficult for the remaining amorphous areas to crystallize, since the size difference between Zr and (Al,Ti) atoms is around 10% and they tend to form the icosahedra with CN=12, which are nonperiodic and need extra energy to transform to periodic crystalline phase [43, 120].

Thus, it seems the actual situation is quite contrary to previous predictions that quasicrystalline phases form during crystallization because they have lower energy than the crystalline phase, at least for the Zr-based BAM-11 alloy. Instead, we found this theory may be more reasonable. That is, the BMGs are composed of icosahedral SROs,
which is a configuration basically determined by the size of components, and
devitrification initiates at those “weaker” areas which are easier to transform to periodic
order. These areas could be the interstitial tetrahedron or octahedrons in Miracle’s model
[43]. Indeed, the metastable phase shows the characteristics of quasicrystals because the
transformation of these areas link the icosahedral SROs together and possibly make them
ordered to form approximate-like structure, as in the case of the fcc NiZr₂ phase [119].
Thus the rearranged structure shows the property similar to large cell intermetallics; due
to the large unit cell, the diffraction peaks show the characteristics of quasicrystals. The
structure of BAM-11 will be further discussed in later chapters.
Chapter 8  \( \text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10} \)

This chapter focuses on all the experimental results for \( \text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10} \). The structural evolution has been discussed from the result of both WAXS and SAXS. The phases for different stages are identified, and kinetics for grain growth is analyzed.

8.1 Introduction

Besides the Zr-based and Pd-based bulk metallic glasses, Mg-based BMGs have attracted a lot of interest because of their high strength/weight ratio [18]. Among the Mg-Ln-TM (Ln=lanthanide metal, TM=Ni, Cu or Zn) alloys, \( \text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10} \) has been reported to have very good GFA with a critical casting thickness around 5 mm and a temperature interval \( \Delta T_x \) of 69 K [121]. GFA could be further improved by replacing Cu partially with noble atoms [122] or Zn [123], or replacing Y with Rare-earth (RE) atoms [69, 124]. The best Mg-based glass formers have the general composition of Mg65-TM25-Ln10.

Although the Mg-Cu-Y BMG has high tensile strength of more than 600 MPa [121], it has poor ductility and the mechanical properties deteriorate after annealing at low-temperature [125]. Nanoparticles-toughening is one potential direction to improve the mechanical properties of BMGs, as reported by Kim et al on the Mg-Zn-Ce alloy [126]. Understanding the structure evolution during devitrification is of essential significance for this purpose. However, most of previous studies on structures were based on the melt-spun alloys and ex-situ characterization methods. In our study, the high energy synchrotron X-ray makes it possible to characterize the structure of BMGs in-situ.
Mg$_{65}$Cu$_{25}$Tb$_{10}$ (MgBMG) is studied, which is reported recently to have good GFA and ignition resistance [127].

### 8.2 Results

As described in Chapter 3, the time-resolved WAXS and SAXS patterns were obtained simultaneously while the sample was annealed with a heating rate of 5 K/min. Data recorded by the CCD cameras were corrected for detector efficiency and binned in Q-space. The intensities are then normalized according to monitor counts and displayed as a function of temperature and Q. The result is shown as projections on the Q-T plane in Figure 8-1. The brighter colors represent higher intensity. All data shown here are original without extra processing. The smooth development of the patterns indicates the resolution and statistics are very good. We tested two samples, and the results are reproducible.

Figure 8-1(a) shows the WAXS patterns. The Q-range is truncated to the range of 2-6 Å$^{-1}$, which contains basically all main features. From room temperature to 450 K, the patterns show only two broad peaks, one from 2 to 3.5 Å$^{-1}$, the other from 3.5 to 6 Å$^{-1}$, with a shoulder at 5.2 Å$^{-1}$. These features quite similar to BAM-11 and are characteristic for BMGs. It should be noticed that two weak peaks are observed at 4.46 and 4.67 Å$^{-1}$ at the beginning, which probably come from oxides on the surface. From 450 K to 500 K, strong peaks develop at 2.72 and 4.39 Å$^{-1}$, above the two main diffusive peaks respectively. From 500 K to 575 K, the peaks further split and three peaks develop at the place of the first broad peak. Above 575 K strong crystalline peaks show up. Thus the WAXS patterns identify two main transformations during devitrification, one from 450 K to 500 K, the other from 500 K to 575 K.
Simultaneously, the SAXS patterns in Figure 8-1(b) show complex behavior. Observable interference peak starts to develop at 450 K. Below 480 K the interference peak swells a bit, as evidenced by broader full-width half maximum (FWHM) and almost constant peak center. Different to BAM-11, there is almost no increase of intensity at low-Q during the first stage. Then the interference peak center starts to move to lower Q, while the FWHM decreases. There is a period from 540 K to around 560 K when both the peak center and FWHM do not change much while the amplitude increases. Above 560 K, the interference peak cannot be identified.

![Figure 8-1](image)

**Figure 8-1** (a) Projections of WAXS and (b) contour plot of SAXS patterns on the Q/T plane, measured for Mg_{65}Cu_{25}Tb_{10} while annealing with a rate of 5 K/min.

### 8.3 Discussions

#### 8.3.1 Transformation stages

In order to characterize the transformation stages, the integrated intensities are calculated, as shown in Figure 8-2(a). The calculation method is the same as described in
Chapter 6, Equation 6-1. Although the integrated intensities of SAXS do not show prominent features (mainly because of the large contributions from low-Q part), the integrated intensity of WAXS shows clearly all the transformation stages. This is even clearer by plotting the differential integrated intensity (red curve). A short period of relaxation is observed before 440 K, similar to the results of BAM-11. This indicates that relaxation is an intrinsic character for BMGs. Shortly after relaxation there is a main transformation starting at 450 K, and at higher temperature, possibly there are two transformations, one around 500 K, the other starts at 520 K.

![Figure 8-2](image)

(a) Integrated intensity for WAXS (black) and SAXS (blue) patterns for Mg$_{65}$Cu$_{25}$Tb$_{10}$, calculated according to Equation 6-1; the red curve is the differential integrated intensity for WAXS; (b) DSC traces for as-cast MgBMG with a heating rate of 20 K/min [127].

For comparison the DSC traces obtained by Xi et al [127] are shown in Figure 8-2(b). Similar to what has been found for BAM-11 in Chapter 6, there is a temperature difference of around 30 K between the two experiments, indicating that this difference is largely come from bad temperature calibration of our experiment. Yet it is amazing how
good the in-situ synchrotron X-ray scattering can characterize the different
transformation stages. The second and third stages were hardly observable by isochronal
[127] and isothermal DSC [124]. Probably this indicates that the energy difference
between the products of the later stages is not large, while the structural difference is
prominent.

8.3.2 Structural evolution at the atomic scale

8.3.2.1 Structure identification

WAXS patterns show the structure evolution in the atomic scale. Typical patterns
at 330 K, 470 K, 519 K, 540 K and 581 K, standing for patterns for the as-cast state and
those right after the three transformation stages, as well as the one after fully
crystallization, are plotted in Figure 8-3. Diffraction peaks from several known structures
are show underneath the WAXS patterns.

The as-cast sample has broad diffuse peaks, typical for BMGs; the prickles
around 4.5 Å⁻¹ come from the surface contamination, which disappear as the bulk sample
starts to crystallize. The pattern at 470 K is just after the first transformation. Bragg peaks
at 2.7 and 4.38 Å⁻¹ are observed overlapping with the diffuse peaks. Previous studies of
Murty and Hono [128] on the melt-spun Mg-Cu-Y alloys shows this phase has the
CuMg₂ structure. A careful examination shows that the pattern does not match perfect
with the well-ordered CuMg₂ phase; instead, the peak position and intensity match well
with that of Mg₁₀₂.₀₈Zn₃₉.₆ (Mg₇Zn₃, for short) [129]. Mg₇Zn₃ is a 1/1 approximant that
contains a lot of icosahedra. This indicates that the first transformation is related with the
formation of icosahedral SROs, and these icosahedra may only be collected in a short
length scale without forming LROs.
A prominent peak appears at 2.43 Å\(^{-1}\) during the second transformation. Most probably this is the TbMg\(_3\) phase (fcc, a=7.324) [130], but not so highly ordered. On the other hand, the peaks from icosahedral order are further developed, as shown by the patterns for 519 K and 540 K. For the Mg-Cu-RE system, it is more favorable for Mg (1.6 Å) and Tb (1.78 Å) atoms to form complex icosahedra other than Mg and Cu (1.28 Å) atoms, in order to satisfy the requirement that the length between center and vertex should be 5% shorter than the rhombohedra edge length for ideal icosahedron [120]. Except for the first peak at 2.43 Å\(^{-1}\), all the peak positions can be indexed with an icosahedral quasicrystal, as shown by the 6-d labels [131]. Also shown in the figure, the peak intensity and positions match quite well with the Zn-Mg-Ho quasicrystal, which has perfect 3-d Penrose tiling with the large Ho atoms on the body diagonal of the prolate rhombohedra [132]. In fact, the peak positions and intensity also match well with the binary Cd\(_{5.7}\)Yb quasicrystal [133], which has a complex 4-layer icosahedral cluster with the large Yb atoms at the center. This is justified by the fact that the size and concentration of Mg and Tb match with those of Cd and Yb. Thus it seems intrinsic for Mg and RE atoms to form quasicrystals.

In fact, if we consider that quasicrystals/approximants are also formed in Cd\(_{85}\)Ca\(_{15}\) [133] and Cd\(_6\)Y [134], we may draw the conclusion that the icosahedral configuration is largely determined by atomic size. Calculated from the peak positions, the lattice parameter of this quasicrystal (the rhombohedral length) is 5.13 Å. The lattice parameter of the unit cell is determined by shifting that of the Cd\(_6\)Y approximant to match the main peak positions. The result is 14.13 Å, this will give the ratio of a/a\(_R\) around 2.754, proving the second phase is a 1/1 approximant [135]. Thus, the second transformation is
the decomposition and separation around Tb atoms, forming TbMg₃ and a quasicrystalline phase which is stabilized by Tb atoms.

![WAXS patterns](image)

Figure 8-3 WAXS patterns for as-cast state (330 K) and for different transformation stages for Mg₆₅Cu₂₅Tb₁₀. The red lines are reference patterns from known alloys. The labels index the peak positions for icosahedral quasicrystal.

The pattern at 540 K (third stage) is quite similar to that at 519 K (second stage), except that the Bragg peaks are sharper. Some small peaks start to develop, indicating further decomposition. The phase is hard to identify due to the small fraction. It is around 575 K that more sharp crystalline peaks start to appear. At 581 K the phases include several types of oxides, CuMg₂ and TbMg₃. This proves that the icosahedral phase is quite stable in a large temperature range (from 450 to 575 K).
8.3.2.2 Atom packing configurations

Several types of polyhedra in known phases are drawn in Figure 8-4. The first one is the icosahedron center around Zn in the orthorhombic Mg₇Zn₃ phase, which is basically the same as the MI-type 1/1 approximants like a-(Al-Mn-Si) [136]. Figure 8-4(b) show a polyhedron around Cu in the orthorhombic CuMg₂ intermetallic phase [137]. Since Cu atoms are smaller than Zn (Cu 1.28Å, Zn 1.4Å, Mg 1.6Å, Tb 1.78Å) [108], icosahedra are not formed in CuMg₂ phase. Yet, the diffraction pattern of this phase [138] is quite similar to that of Mg₇Zn₃. This is mainly because most atoms have the “555-type nearest neighbors” (i.e., icosahedral configurations [139]), as shown in Figure 8-4(b). Figure 8-4(c) shows a 4-layer icosahedral cluster in Cd₆Y [134], which have been observed in several rare-earth contained binary alloys [133, 140].

![Figure 8-4](image-url) Some polyhedra in three phases: (a) Icosahedron in Mg₇Zn₃; (b) A Cu-centered polyhedron in CuMg₂; (c) 4-layer icosahedron in Cd₆Y, first shell is tetrahedron formed by 4 Cd, second shell is 20-Cd-formed dodecahedron (atoms are not drawn), third shell is 12 Y icosahedron, fourth layer is 30 Cd icosidodecahedron (not shown).
Since diffraction patterns for these phases show similar features, it is concluded that WAXS shows the feature of mainly the local packing configurations, instead of the different type of large unit cells. It may also be deduced that, the good glass forming ability of Mg-Cu-RE alloys comes from the fact that two kinds of atom packing themes, one between Mg and RE, the other between Mg and Cu, can mingle with each other and form a more stable structure.

### 8.3.2.3 Pair distribution functions

Although we did not carry out the total scattering measurement for MgBMG, the PDFs can still be calculated from WAXS patterns, using the PDFGetX software [106]. The Q-range for our measurement is not large enough, but most of the features are shown in the Q-range from 2 to 8 Å\(^{-1}\) on the WAXS patterns. The high-Q part is flat, while the low-Q part may cause some error because literatures show there could be a prepeak around 1.5 Å\(^{-1}\) in the case of chemical order. Yet this effect is expected to be very small for X-ray scattering [141]. Similarly, the contribution from container is ignored because Boron is almost transparent to the high energy X-ray. Thus said, the PDFs obtained from WAXS should show the main structural features qualitatively in real space.

The result is shown in Figure 8-5. For comparison the PDFs for TbMg\(_3\) and TbMg\(_6\) are simulated using the software PDFFit [117]. The TbMg\(_6\) is assumed to be isostructure of YCd\(_6\) [134], with lattice parameter reduced to 14.13 Å to match the peak positions.
Figure 8-5 Pair distribution functions calculated from WAXS patterns for Mg65Cu25Tb10. For comparison PDFs for TbMg3 and TbMg6 are simulated by PDFFit [117].

The as-cast sample shows SROs below 20 Å, typical for BMGs, indicating the pre-existence of clusters. The PDF at 470 K stands for the first stage. Little change can be observed for the first four shells, yet, the intensity of peaks above 10 Å increases, and another set of peaks appear around 20 Å (not shown), suggesting that the clusters start to concatenate and correlate. This agrees with the estimation of domain size of around 45 Å by Scherrer equation. At higher temperature (519 K), subtle changes are observed for the first three shells, basically due to the formation of second phase (TbMg3), as the shoulders of the first and second shells match well with the positions of Tb-Mg bonds at 3.64 Å and 6.05 Å in the TbMg3 phase; and, the detectable order is increased to up to 30 Å, above 30 Å another set of peaks appear, suggesting that the second transformation involves the interpenetrating of clusters to form larger domains. The PDF for the third
Chapter 8 \( \text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10} \)

Stage is quite similar to that of the second stage below 30 Å; above 30 Å the peaks become stronger, proving the formation of LROs. It is found that the peak positions for the first four layers match well with PDF of \( \text{TbMg}_6 \); the decomposition at higher temperature produce only a little difference around the second shell. The overall PDF at 540 K matches quite well with that of \( \text{TbMg}_6 \), proving the development of approximant from the icosahedral clusters. The mismatch in the intermediate range (12 to 25 Å) indicates different linkage between the icosahedral clusters, mainly due to the presence of Cu atoms.

A precise resolving of the structure depends on more special experiments. However, it can be deduced from the above analysis that the high GFA of this system is due to the fact that both Mg-Cu and Mg-Tb can form nonperiodic polyhedra, and these two kinds of polyhedra tend to complement each other to form a dense stable packing in the supercooled liquid phase.

Although it is believed that all Mg-Cu-RE BMGs would have similar structure, our results are quite different from those of Liu et al’s on \( \text{Mg}_{62}\text{Li}_3\text{Cu}_{25}\text{Y}_{10} \) [83] and Murty et al’s on Mg-Cu-Y [128], in which the Mg-Li or Mg-Cu phases start to appear at quite early stage. In our case, the quasicrystal phase is quite stable even at 575 K (could be higher if we consider the temperature error of around 30 K for our experiment). Possibly this is because of the difference of sample processing and experimental environment; they used super-quenched foils and tested the structure by ex-situ XRD.
8.3.3 Structure evolution in large scale (SAXS)

Similar to the kinetic study for BAM-11, we study the structural evolution in large scale by two methods, one is the direct method, and the other is the refinement of SAXS patterns with a model. Details about the modeling are described in Chapter 5, and the two methods are described in Chapter 6.

8.3.3.1 First method

In order to remove the parasitic scattering, the first few scans are averaged as background and subtracted from later patterns. Using an empirical function to fit the SAXS patterns, the parameters for interference peak are obtained and plotted in Figure 8-6. The peak center in Figure 8-6(a) reflects the different transformation stages remarkably, as marked by the segments. The first stage (<500 K) shows a smooth exponential decrease of peak center, while during the second and third stages the peak center decreases much quicker. This is a proof for our assumption that the later transformations are related with the formation of different icosahedral approximants. Both the amplitude and area plotted in Figure 8-6(b) and (c) show similar trend, i.e., the first stage shows a steady growth, which is modified by the later transformations. The amplitude has an exponential relationship with time at both low and high temperature. The effective diffusion coefficients calculated according to Cahn's theory [101] is 4.4 Å²/s below 500 K, and around 65 Å²/s above 540 K. The peak width is almost constant for the first stage, and decreases continuous during the second and third stages.
8.3.3.2 Second method

Individual SAXS patterns for different transformation stages are plotted in Figure 8-7. It is found that before transformation (450 K), there is almost no increase of intensities; during the first stage, the most important fact is the development of interference peak with almost constant peak center, while the intensities at low-Q remain constant. This demonstrates that there is no phase separation before devitrification, and
the first stage is related with the formation of small clusters that do not correlate. It is during the second stage that these clusters are concatenated to form LRO. Demonstrated on the SAXS patterns is the steady moving of interference peak center, with large increase of amplitude, and the peak becomes more asymmetric. Above 540 K the particles are too big, and the interference peak is buried underneath the scattering pattern from large particles.

The SAXS patterns are refined with a model described in Chapter 5. The fitting quality is very good, as demonstrated by the red curves in Figure 8-7.

![Figure 8-7 Typical SAXS patterns for Mg₆₅Cu₂₅Tb₁₀ refined with core-shell model.](image)

The results from fitting the SAXS patterns with core-shell model are shown in Figure 8-8. Similar to the results for BAM-11 in Chapter 6, the center of the shell radius matches extremely well with the results obtained by 3/Qc, where Qc is determined by the first method. On the first hand, this proves that 3/Qc is a good estimation of particle size; on the other hand, this indicates the SAXS model is consistent in obtaining accurate parameters for the particles. The development of particle size shows clearly there are
about three transformation stages, corresponding to the integrated intensity shown in Figure 8-2. The slopes in Figure 8-8(a) are the exponential coefficients before time, calculated according to Equation $S(Q,t) = S(Q,0)\exp[2R(Q)t]$, given by Cahn [101], which may not be applied for isochronal conditions. The value of 0.15 indicates the later stage is related with *asymptotic ripening*. The slopes are steeper than those for BAM-11 (with the same annealing heat-rate), indicating BAM-11 is more resistant to devitrification.

Similar to the isochronal results for BAM-11 during isochronal annealing, the parameters for MgBMG show very distinct stages for particle growth. The first stage is characterized by a steady slow growth of particle size, with the size distribution decreases slightly, and the core/shell ratio increases slightly, and contrast decreases a little bit. During the later stages, particles grow much faster, and the size distribution is wider, the core/shell ratio has a sharp decrease and the contrast increases, indicating the particles are composed of a more condensed core and a thick shell. The difference between the second and third transformation is evident from R0, while for other parameters it is not so prominent. Also similar to BAM-11, the number-averaged particle size (diameter of core) [93] shows a shrink at the beginning of the second stage, suggesting that this may be common for BMGs.
Figure 8-8 The parameters obtained by refining SAXS patterns of MgBMG (annealed with a rate of 5 K/min) with the SAXS model. (a) Particle size (the log-normal distribution center of shell radius), for comparison the red symbols show the estimated particle size by $3/Q_C$, where $Q_C$ is obtained by the first method; (b) Size distribution width; (c) Core/shell ratio; (d) Contrast ratio between core and shell; (e) Number-averaged particle size (diameter of the core); and (f) Calculated $b_1^3$. 

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On the other hand, domain size can be estimated from FWHM of the Bragg peaks on the WAXS patterns, following the Scherrer equation (Equation 6-4). The instrument broadening is estimated from the peak width of large CeO₂ powders, K is assumed to be 1. The result shows that the domain size \( \langle D \rangle_{\text{vol}} \) is 60 Å at 505 K and 52 Å at 530 K. Assuming the size distribution \( \ln \sigma \) is 0.3, the number-averaged domain size \( D_1 \) is around 45 Å below 530 K, and around 100 Å at 556 K. The above results indicate that, although the particles grow with temperature, the domain size does not change below 530 K. This proves that the particles are made of clusters, more precisely, icosahedral clusters, as described in section 8.3.2.

Combing the results from both WAXS and SAXS, the following conclusions can be made. First, there is no large scale phase separation before crystallization. Second, the first stage transformation is related with establishing of icosahedral clusters, while the correlations between these clusters are very weak (the nucleation stage). During the second stage, the structure is further decomposed and the clusters are linked to form large quasicrystalline approximants (the concatenate stage). The later transformation stages involve the ripening of the particles, while decomposition inside the particles happens.

### 8.4 Summaries

The time-resolved synchrotron scattering patterns with simultaneous SAXS and WAXS have been analyzed in detail for Mg₆₅Cu₂₅Tb₁₀. These are some facts we found.
1. MgBMG is not as homogeneous and stable as BAM-11, as demonstrated by the surface contaminates and the features of WAXS patterns for the as-cast state. Nevertheless, the WAXS patterns show typical features for BMGs.

2. WAXS patterns show a short period of relaxation before devitrification. Crystallization happens in three transformation stages. Icosahedral clusters are formed in the first stage. During the second stage the alloy decomposes to form TbMg3 phase, while a 1/1 quasicrystal approximant is formed. The third stage sees the growth of the quasicrystal phase and further decomposition. It is at quite higher temperature that the CuMg2 phase forms.

3. PDFs calculated from WAXS patterns indicate the icosahedral clusters have a configuration very similar to the 4-layer icosahedron in TbMg6, isostructure of YCd6. The formation of TbMg3 is also confirmed.

4. The 3-stage transformation has also been identified by SAXS patterns. There is no phase separation before crystallization. Kinetic studies have been carried out by the direct method and by fitting with a model. The refined parameters show that at low temperature the particles grow steadily and independently, similar to BAM-11; yet the kinetics for MgBMG is much faster than for BAM-11, and the parameters are affected by the later transformations, indicating the transformation happens within the particles. Similar to BAM-11, a ripening stage is observed, in which the particles are consisted of a dense core and a thick shell.

According to these results, we may conclude that the as-cast MgBMG contains a lot of icosahedral SROs; the reason that MgBMG is more inhomogeneous than BAM-11 is not only because Mg and Tb atoms are more active, but also because the icosahedral SROs in MgBMG have different configurations as in BAM-11. The Mg and Tb atoms
have a tendency to form complex 4-layer icosahedra, with a composition of TbMg6, which is isostructure of several other RE-based quasicrystal/approximants. The large GFA of this BMG comes from the fact that both Mg-Tb and Mg-Cu pairs can form nonperiodic polyhedra which complement each other and stabilize the whole structure.

Further experiments are needed to resolve the structure. Yet it is clear that during the first transformation, these clusters are linked to form a 1/1 approximant, and during the second transformation, decomposition happens and TbMg3 phase starts to precipitate.

Here is a comparison of BAM-11 and MgBMG. First, it is found that icosahedral SROs preexist in both alloys, with different configurations. These icosahedral SROs are stabilized by the presence of other polyhedra, which also have the nonperiodic feature. Second, they show similar behavior during the first transformation stage, i.e., the diffraction patterns show the feature of icosahedral quasicrystal, although the order range is confined within around 2 nm. Commonly this is due to the fact that the icosahedra are linked together due to the ordering of the interstitial bonds. For BAM-11, this is mainly because the Ni-Zr bonds have strong interaction and they tend to transform first in the Ni-rich area; for MgBMG, this is realized by the decomposition of local bonds, such as Mg-Tb and Mg-Cu, as demonstrated by the formation of the TbMg3 phase in later stage. The difference is that, in BAM-11 these interstitial ordering becomes strong and transformation is based on these areas during the later stage, and the diffraction patterns show mainly the feature of this phase, while in MgBMG the icosahedral orders are more stable because of the large Tb atoms, thus the later stages are characterized by the growth of quasicrystals. These facts should be helpful in the design of ductile BMGs, because the quasicrystals are very brittle.
Chapter 9  \( Zr_{50}Cu_{40}Al_{10} \)

This chapter focuses on all the experimental results for \( Zr_{50}Cu_{40}Al_{10} \). The structural evolution has been discussed from the result of both WAXS and SAXS. The results from total scattering tests have also been analyzed.

9.1 Introduction

Besides the quinary Zr-based BMGs, ternary Zr-based alloys containing Zr, TM (TM = Co, Ni, Cu, Ti etc) and Al can also be cast into bulk amorphous alloy within a quite large composition range, and the supercooling liquid region can exceed 100 K [142]. Among these alloys, the Zr-Cu-Al BMGs have been studied a lot, because of their cheap cost (compare with those containing noble metals) and good glass forming ability (a 90 K \( \Delta T_x \) has been reported by Inoue et al [143] for \( Zr_{65}Cu_{27.5}Al_{7.5} \)). Systematic studies about structural analysis, thermal stability and crystallization kinetics of \( Zr_{65}Cu_{27.5}Al_{7.5} \) have been reported by Inoue’s group, and the large supercooled liquid region has been attributed to the difficulty of precipitation of crystalline phases because of the large solid-liquid interfacial energy and the energy needed for long-range diffusion of Al [144]. Saida et al studied the devitrification behavior of both \( Zr_{65}Cu_{27.5}Al_{7.5} \) and \( Zr_{65}Cu_{35} \) [145], and found that the presence of Al will largely suppress the growth of CuZr\(_2\) phase, due to the strong chemical affinity between Al and Zr. Murty et al [146, 147] reported that the concentration of oxygen is especially important in determining the crystallization behavior; with high oxygen concentration, the alloys first crystallize into an oxygen-stabilized icosahedral phase.
Beside $\text{Zr}_{65}\text{Cu}_{27.5}\text{Al}_{7.5}$, another Zr-Cu-Al ternary BMG has the composition near $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ is also a good glass former, which is what we studied. The atomic bonding in the ternary BMG is much simpler than that of the quinary BAM-11. Thus, by measuring the pair distribution functions (PDFs), the evolution of atomic bonds may be resolved. In this chapter, the devitrification of $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ has been studied by various methods including differential calorimeter scanning (DSC), synchrotron scattering and neutron total scattering. The results will be compared with those of the quinary BAM-11, and also those of $\text{Zr}_{65}\text{Cu}_{27.5}\text{Al}_{7.5}$, as well as the PDF results of $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ reported by Fan et al [148]. In this sense, the mystery of as-cast BMGs, and the evolution of topological configurations in forming orders during devitrification, is expected to be revealed.

### 9.2 Experiments

The experimental procedures have been described in Chapter 3. For ex-situ experiments, DSC traces were measured to obtain the characteristic temperature, which is important for setting the isothermal temperature for the in-situ experiments; the microstructure of the crystallized alloy was measured by scanning electron microscopy (SEM).

The DSC traces measured at two heating rates, 1 K/min and 10 K/min, are plotted in Figure 9-1. Both traces show similar behavior, except that there is a temperature lag of around 30 K between the two curves, indicating that the devitrification process is very sensitive to heating rate. The glass transition temperature ($T_g$) for 10 K/min is 697 K, and the onset of crystallization temperature ($T_x$) at the same heating-rate is 761 K, resulting in a $\Delta T_x$ of 64 K. Compared with the value of 90 K for $\text{Zr}_{65}\text{Cu}_{27.5}\text{Al}_{7.5}$ [143], this is a sign
that the GFA of Zr_{50}Cu_{40}Al_{10} may not be so good as Zr_{65}Cu_{27.5}Al_{7.5}, although the
difference of processing may have some influence. There is only one main peak appears
on DSC traces for the principle devitrification around 761 K, indicating that there may
not be any metastable phases formed, as observed in BAM-11. Around 848 K, a small
endothermal peak is observed, indicating that energy much be provided for further
transformation. Another exothermal peak appears around 890 K. The transformation
products for each stage will be analyzed below.

![DSC traces for Zr_{50}Cu_{40}Al_{10}, measured at 1 K/min and 10 K/min.](image)

Figure 9-1 DSC traces for Zr_{50}Cu_{40}Al_{10}, measured at 1 K/min and 10 K/min.

Figure 9-2 shows a scanning electron microscopy image for Zr_{50}Cu_{40}Al_{10} after
heating to 820 K. Crystalline particles with an average size of 320 nm distribute
homogeneously in the matrix. The particle number density estimated from the image is
roughly 5.2*10^{12} m^{-2}, giving a volume fraction of around 40%. These values indicate that
crystallization has proceeded to a quite advanced stage. Consider the heating rate is 10
K/min, and there is a lag of about 30 K between the measured and the actual temperature
for the furnace (as described in Chapter 6), the devitrification of this sample is estimated
to advance to the second stage as viewed by the endothermal peak on the DSC trace in
Figure 9-1.
9.3 Synchrotron scattering

9.3.1 Overview of devitrification stages

Two samples were measured by synchrotron scattering. One was isochronally annealed with a heating rate of 10 K/min. The other isothermally annealed at 690 K, and the temperature was increased to 700 K after 80 minutes, in order to quicken the crystallization process. Figure 9-3 show the WAXS and SAXS patterns as projections on the Q-t plane. The isothermal SAXS patterns are plotted as contours in order to identify the interference peak.

The isochronal WAXS patterns show that before the transformation (740 K), almost no changes can be observed. The SAXS patterns show no increase of intensity before 690 K, but from 690 K to 740 K, a continuous increase of intensity is observed. This indicates that there are almost no structural changes below the glass transition temperature (~690 K), once above Tg long range contrast of scattering length density is first developed, while there is no change for local structure. Similar results have been
found for BAM-11, indicating that decomposition before crystallization may be a common phenomenon for Zr-based BMG. It still remains a question how this long-range contrast has been developed without the occurrence of diffusion; probably this is related with composition modulation, with a similar mechanism of spinodal decomposition.

Around 740 K, crystallization occurs suddenly, and strong Bragg peaks are observed. A second transformation is observed at quite high temperature (805 K). Both transformations are evident on the WAXS and SAXS simultaneously.

Figure 9-3 The projection of (a) WAXS and (b) SAXS patterns on the Q-t plane for Zr50Cu40Al10 isochronally annealed with a heating rate of 10 K/min; (c) projection of WAXS patterns and (d) contour plot of SAXS patterns on the Q-t plane for Zr50Cu40Al10 isothermally annealed at 690 K and 700 K (the temperature is increased within 10 min).
The isothermal WAXS patterns show that at 690 K, there is almost no change during the first hour. The peak profiles show very slight change after one hour, as a sign of onset of local decomposition. Around 70 minutes the temperature is suddenly increased to 700 K and Bragg peaks appears right after. Nevertheless, small interference peak is observed on the SAXS patterns at the early stages, proving that long-range structural evolution precedes that of local structure. The isothermal transformation never reaches the second stage, as observed for the isochronal test.

In order to show the subtle changes of both WAXS and SAXS patterns, the integrated intensities are calculated and plotted in Figure 9-4. The calculation method is the same as described in Chapter 6. Background has been removed by subtracting the average of several original scattering patterns. The integrated intensity curves are plotted in logarithmic scale.

It is clear that the curves for isochronal and isothermal annealing are quite different. The isochronal curves show clearly that there is only one main transformation for devitrification (not including the second transformation at high temperature). There is a slight increase of intensity before transformation on both curves, and the increase of SAXS intensity is very small compared with the sharp increase when crystalline phase appears. Usually this slight increase can be attributed to relaxation, during which the quenched-in strain of local atoms is relieved and the atoms are settled to more stable positions, which will cause some variation in WAXS profile while the intensity of SAXS remains unchanged.

The integrated intensities for isothermal patterns show quite different behavior. Since there is a temperature increase at 70 minutes, the small hump around 70 min on
SAXS integrated intensity can be simply attributed to temperature-induced influence on the speed of particle growth. In this sense, the SAXS patterns show an exponential growth of only one stage during the whole isothermal range. On the other hand, the integrated intensity of WAXS shows an evident relaxation stage before 60 min. From 60 min to 70 min, the increase of intensity shows the onset of crystallization, which was quickened by the sudden increase of temperature. The intensity after 85 min remains almost constant. These facts indicate that the evolutions of local and large-scale structures are not simultaneous. The large-scale structure is constantly changing, while the local structure is relatively stable and transforms at quite later stage, which is driven by thermokinetics.

Figure 9-4 Integrated intensity of WAXS and SAXS patterns for (a) isochronal annealing at 10 K/min, and (b) isothermal annealing at 690 K and 700 K.

9.3.2 Structure analysis from WAXS

Several typical WAXS patterns are plotted in Figure 9-5. For isochronal annealing, the pattern measured at 332 K is for the as-cast state, which shows broad diffuse peaks characteristic for metallic glasses. The pattern remains almost unchanged even at 736 K.
Three neighboring patterns, measured at 736 K, 741 K and 746 K, show drastic change during the short interval. Small peaks appear on the 741 K pattern, yet at 746 K, very strong Bragg peaks appear, and the volume fraction of the crystallized phase is around 30%, estimated from the peak area from 2 to 3.5 Å⁻¹. The pattern at 821 K has sharper peaks and the estimated volume fraction of crystalline phase is around 40%, which confirms the calculation from SEM image. For the isothermal patterns, at the end of 690 K (71 min), only very small peaks are observed. Yet after the temperature has been increased to 700 K (78 min), the crystalline peaks become obvious. The kinetics for isothermal annealing is much slower, and the volume fraction of crystalline phase at 211 min is around 28%. The peak profile is quite different for isothermal and isochronal patterns, indicating different phases may have various volume fractions.

Figure 9-5 Typical WAXS patterns for Zr₅₀Cu₄₀Al₁₀ (a) isochronally annealed with a rate of 10 K/min, and (b) isothermally annealed at 690 K and 700 K, where the 3 traces in (a) labeled as 736 K, 741 K and 746 K are three neighboring critical patterns, and the time in (b) stands as: 0 min—right after reaching 690 K; 71 min—the last scan at 690 K; 78 min—right after reaching 700 K; 211 min—the last scan at 700 K.
The crystalline phases are identified using the MDI Jade 5.0 XRD pattern processing software [149]. Figure 9-6 shows the WAXS patterns for 746 K and 821 K, and the reflection peaks for three phases as nearest match are plotted under the patterns. The space group, lattice parameter and site occupancies are listed in Table 9-1. The pattern of 746 K shows that, at the beginning of devitrification for isochronal annealing, the tetragonal CuZr₂ phase and the orthorhombic Cu₁₀Zr₇ phase are formed, probably simultaneously, as a result of decomposition at the nanoscale. Although not shown in the figure, some peaks match with the diffraction pattern of fcc NiTi₂ isostructure, with a lattice parameter of 11.37 Å, but this phase is not very prominent. This implies that icosahedral clusters also exist during this stage, which may contain Al atoms. At 821 K, the fraction of the highly-ordered cubic CuZr phase is largely increased. Thus, the second transformation, shows as endothermal peak on the DSC traces in Figure 9-1 and the evident changes on WAXS in Figure 9-3(a), is actually a eutectoid reaction of \[ \text{CuZr} + \text{Cu₁₀Zr₇} \rightarrow \text{CuZr}. \]

The isothermal scattering patterns in Figure 9-5(b) shows a high fraction of the Cu₁₀Zr₇ phase, and the fraction of CuZr₂ phase is very small even at 211 min. This indicates that the first product is indeed the Cu₁₀Zr₇ phase, which has a complex structure with large unit cell (Table 9-1). This metastable phase is favored in isothermal annealing because the kinetics is slow enough to enable the movement of atoms to form new topological configurations. The late stage of the first transformation is related with the formation of CuZr₂ phase, at the expense of Cu₁₀Zr₇ phase. The stability of Cu₁₀Zr₇ phase is greatly influenced by temperature, as proved by the isochronal WAXS patterns. The domain size of Cu₁₀Zr₇ is around 2 nm, estimated from the peak width of Cu₁₀Zr₇ according to Sherrer equation [93]. This value remains unchanged even at 211 min. Thus,
the WAXS patterns for isothermal annealing at 690 K and 700 K show only the evolution of SROs within 2 nm range.

The similar reaction at high temperature has been observed in Zr_{54}Cu_{46} binary alloy \[150]\, in which a $\Delta T_x$ of 44 K is reported, 20 K smaller than that of Zr_{50}Cu_{40}Al_{10}. This proves that the addition of Al tends to stabilize the amorphous phase. In Inoue’s reports \[144]\, the first main phase is the b.c.t. Zr_2(Cu,Al), and Zr_2Cu is formed by significant disappearance of ZrAl, which is a proof that Al must be redistributed during crystallization. In our opinion, the stabilization role of Al is due to the fact that Zr and Al atoms have a size difference of around 10\%, thus it is easy for them to form Al-centered icosahedron \[151]. The nonperiodic five-fold order is hard to break, because the interaction between Zr-Al (the enthalpy of mixing $\Delta H_{\text{mix}} = -44$ KJ/mol) is much stronger than that of Zr-Cu ($\Delta H_{\text{mix}} = -23$ KJ/mol \[152]). These icosahedral clusters are responsible to the unidentified peaks on WAXS patterns. This also explains why long time is needed for the formation of Cu_{10}Zr_{7} phase during isothermal annealing.

![Figure 9-6 Phase identification of Zr_{50}Cu_{40}Al_{10} measured at 746 K and 821 K.](image)
Table 9-1 Space, lattice parameter and sites of three Cu-Zr phases

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<thead>
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<th>Phases</th>
<th>Space</th>
<th>Lattice</th>
<th>Sites</th>
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<tbody>
<tr>
<td>CuZr$_2$</td>
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<td>I$_4$/mmm (139)</td>
<td>Cu (0 0 0)</td>
</tr>
<tr>
<td></td>
<td>a=3.22</td>
<td>c=11.18</td>
<td>Zr (0 0 0.34)</td>
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<tr>
<td>CuZr</td>
<td>Cubic</td>
<td>Pm$_3$m (221)</td>
<td>Cu (0 0 0)</td>
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<td></td>
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<td></td>
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<tr>
<td>Cu$_{10}$Zr$_7$</td>
<td>Orthorhombic</td>
<td>Aba$_2$ (41)</td>
<td>Cu$_1$ (0.21 0.0008 0.7582)</td>
</tr>
<tr>
<td></td>
<td>a=9.347</td>
<td>b=9.322</td>
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<tr>
<td></td>
<td>c=12.68</td>
<td></td>
<td>Cu$_2$ (0.2915 0.0082 0.5956)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Zr$_2$ (0 0 0.6434)</td>
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<td>Cu$_3$ (0.0031 0.2919 0.5978)</td>
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<td></td>
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<td>Zr$_3$ (0 0 0.2572)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Cu$_4$ (0.0122 0.2986 0.3082) Zr$_4$ (0.2459 0.2560 0.7018)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cu$_5$ (0.1063 0.1090 0.4501) Zr$_5$ (0.3129 0.3106 0.4529)</td>
</tr>
</tbody>
</table>

9.3.3 SAXS

![SAXS pattern graph](image)

Figure 9-7 SAXS patterns refined with core-shell model, for Zr$_{50}$Cu$_{40}$Al$_{10}$ measured at 10 min and 20 min during isothermal annealing at 690 K.

As shown in Figure 9-3(d), interference peak appears on the SAXS patterns for very short time, and the amplitude is comparably low. Similar to BAM-11 and MgBMG, the SAXS patterns can be well fitted with a core-shell model. The result is shown in Figure 9-7. The average diameter of the core is estimated to be around 40 nm, which does not change much within 10 min. The fact that interference peak can not be observed later...
than 20 min may due to the low contrast between the core and the shell, i.e., the core-shell structure is not very prominent, and since the particles are much larger than observed for BAM-11 and MgBMG, the interference peak moves to lower-Q and can not be measured in the experimental Q-range.

9.4 Total scattering

The PDFs are measured by in-situ total neutron scattering for Zr$_{50.6}$Cu$_{40.4}$Al$_9$, with the compositions slightly deviate from Zr$_{50}$Cu$_{40}$Al$_{10}$. The structure factors for different temperatures are plotted in Figure 9-8. The patterns within two hours are combined for good statistics. Unlike what is shown in Figure 9-5 for Zr$_{50}$Cu$_{40}$Al$_{10}$, the S(Q) for Zr$_{50.6}$Cu$_{40.4}$Al$_9$ in as-cast state shows some small peaks, indicating that there are some nanoparticles inside, with the peaks match that of Cu$_{10}$Zr$_7$ or icosahedral clusters. This is mainly due to the difference of composition and the larger casting size of the Zr$_{50.6}$Cu$_{40.4}$Al$_9$ sample. In order to show how the structure evolves, the sample was annealed in-situ at 663 K for 10 hours. There were no observable changes during this time, and the temperature was increased to 673 K, 683 K and 693 K, staying at each temperature for 2 hours and finally remained at 693 K. Obviously from this figure, the scattering pattern shows almost no difference even during the first two hours at 693 K. It is during the third and fourth hour that Bragg peaks suddenly appear, instead of showing up gradually. This proves our conclusion from synchrotron scattering that the transformation at atomic scale is mainly influenced by temperature, and there is no precursor states.
Chapter 9 Zr_{50.6}Cu_{40.4}Al_{9}

Figure 9-8 Structure factor of Zr_{50.6}Cu_{40.4}Al_{9} measured at different temperatures.

The reduced PDFs for the as-cast state and that after annealing at 693 K for 4 hours are shown in Figure 9-9. Although S(Q) shows some minor peaks, the G(r) shows quite similar feature as that of BAM-11, i.e., the as-cast Zr_{50.6}Cu_{40.4}Al_{9} contains SROs within 2 nm range. Also similar to the results for BAM-11, the first shell show splitting peaks, and there is a more prominent peak with short bond length (2.77 Å). This sharp peak decreases at higher temperature, and LROs are formed.

It is difficult to decode the PDF of the first layer by several groups of bonds, as has been done for BAM-11, because the as-cast sample is not fully amorphous but contains nanoparticles, thus the total PDF is a combination of amorphous phase and ordered (probably distorted) crystalline phase. It is also difficult to identify the parital PDFs after crystallization, because several phases attribute to the total PDF, at least two of which are identified as orthorhombic Cu_{10}Zr_{7} and tetragonal CuZr_{2}, and there is possibly cubic CuZr and another unidentified phase. It will be difficult to weight and
combine the partial PDFs from all these phases to match the measured PDF. Nevertheless, the simulated PDFs for Cu$_{10}$Zr$_7$ and CuZr$_2$ for the first shell are plotted as in-sets in Figure 9-9, in order to compare the contributions from difference structures.

![Figure 9-9](image_url)

**Figure 9-9** The reduced PDF of Zr$_{50.6}$Cu$_{40.4}$Al$_9$ measured at (a) as-cast state, and (b) after partially crystallized.

As shown in Figure 9-9(a), Cu$_{10}$Zr$_7$ has a prominently peak around 2.77 Å, which agrees well with the sharp peak on the measured PDF. This peak comes from both Cu-Cu and Cu-Zr bonds in Cu$_{10}$Zr$_7$ phase. Compared with the idea bond length and partial weights calculated from dense packing model (Table 9-2), the bond length of Cu-Zr is effectively shortened for about 3%. Similar behavior has been found in BAM-11 for Ni-Zr bond. This phenomenon can be explained by the strong interaction between Cu and Zr, evidenced by the large negative enthalpy of mixing of -44 KJ/mol for Cu-Zr, and -49 KJ/mol for Ni-Zr [152]. The peak at 3.15 Å is attributed to Zr-Zr bond in the amorphous phase. Thus it is reasonable to conclude that the as-cast Zr$_{50.6}$Cu$_{40.4}$Al$_9$ consists both amorphous phase and some tiny clusters which have a local configuration similar to Cu$_{10}$Zr$_7$. 

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After crystallization, an evident increase of the bond at 3 Å is observed for the first shell, as shown in Figure 9-9(b). The CuZr$_2$ phase show a major peak around 3 Å, which is a combination of Cu-Zr and Zr-Zr bonds. The bond length of Cu-Zr is larger than that of Cu$_{10}$Zr$_7$ phase. The peak around 2.72 Å is due to the Cu$_{10}$Zr$_7$ phase. Overall, the transformation is a process in which the dense-packed Cu$_{10}$Zr$_7$ transforms to the sparser and more ordered CuZr$_2$ phase. This seems to be contrary to the fact that there are about 1-2% free volume in BMGs compared with their crystalline counterparts. Fan et al [148] studied the PDFs of Zr$_{55}$Cu$_{35}$Al$_{10}$ and found similar results. They explained this by introducing vacancies into the matrix. Based on this assumption, they did Reverse Monte Carlo (RMC) simulation [156] to match the measured PDF, and the refined structure contains many clusters with a large number of vacancies. This, they explained, can explain why the shear bands, by which the BMGs fail under stress, have a thinkness of around 20 nm.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>$W_{ij}^N$</th>
<th>$W_{ij}^X$</th>
<th>$\Delta H_{mix}$ (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-Cu</td>
<td>2.8617</td>
<td>0.429</td>
<td>0.450</td>
<td>-23</td>
</tr>
<tr>
<td>Zr-Zr</td>
<td>3.1726</td>
<td>0.370</td>
<td>0.261</td>
<td></td>
</tr>
<tr>
<td>Cu-Cu</td>
<td>2.5508</td>
<td>0.124</td>
<td>0.194</td>
<td></td>
</tr>
<tr>
<td>Zr-Al</td>
<td>3.0149</td>
<td>0.048</td>
<td>0.050</td>
<td>-44</td>
</tr>
<tr>
<td>Cu-Al</td>
<td>2.704</td>
<td>0.028</td>
<td>0.043</td>
<td>-0.8</td>
</tr>
<tr>
<td>Al-Al</td>
<td>2.8572</td>
<td>0.002</td>
<td>0.002</td>
<td></td>
</tr>
</tbody>
</table>

Although RMC simulation may be good to find a structure that matches well with measured PDF, the method of RMC is limited in that it is an empirical method and does not contain physical meanings, thus the obtained structure could be just one of the
configurations which show the same average PDF. A reasonable simulation must involve more work on providing a reasonable initial structure and applying constraints, and possibly optimization of the method by introducing physical properties, for example, the enthalpy of mixing. Due to the complexity, this part of work is involved in future work.

In order to show the structure evolution in long range, the critical PDFs are calculated in 10 nm range. These PDFs are obtained by combining the scattering data counted within one hour. The PDFs are optimized using the methods described in Chapter 7, with a truncation at $Q_{\text{max}} = 15 \text{ Å}^{-1}$. Three critical PDFs, one measured at 683 K, the other measured at 693 K within the 3rd and 4th hour, are plotted in Figure 9-10. These curves show that at 683 K (even during the first two hours at 693 K), only SROs below 2 nm are observed; during the 3rd hour at 693 K, LROs are developed, and a concatenate area between 6 to 7 nm is observed, which is still observable during the 4th hour when the local structure becomes well ordered. This indicates that ordering first happens in some concentrated domains, which propagate by assimilating the neighboring domains. In this scenario, the core-shell model as described in Chapter 5 is verified. Although in fact the particles calculated by SAXS model have a much larger size (> 40 nm), the model is still valid because the particle may contain many domains.

The PDFs we measured have very high resolution, providing the basis for further study by simulation, using those established methods like RMC and other modified methods. This will be included in future work.
9.5 Summary

As a summary, we studied the devitrification of ZrCuAl BMG by DSC, SEM, in-situ synchrotron scattering with simultaneous SAXS and WAXS, and total scattering. The following results are observed:

1. DSC shows the devitrification happens in one principle step, and $\Delta T_x$ is around 64 K. After crystallization at 820 K the SEM image shows very homogeneous and dense nanoparticles.

2. Synchrotron scattering shows that the structure changes first happen in large scale, as observed by intensity increase of SAXS; ordering of local structure happens quite later, and is mostly propelled by temperature increase.

3. During isochronal annealing the Bragg peaks appear on WAXS with no intermediate state. The products of the first transformation are tetragonal CuZr$_2$ phase.
and the orthorhombic Cu\textsubscript{10}Zr\textsubscript{7} phase, and probably another unidentified phase. At high temperature (around 821 K), a eutectoid reaction \( CuZr_2 + Cu10Zr7 \rightarrow CuZr \) happens and the fraction of cubic CuZr is largely increased.

4. During isothermal annealing the kinetics is much slower. Interface peak appears on the SAXS patterns for a short interval. The core-shell model is applied to fit the SAXS patterns and a particle size of around 40 nm is observed for the early stage. The evolution of local structure starts much later, and the first phase is the metastable Cu\textsubscript{10}Zr\textsubscript{7}, which is diffusion-limited and has a domain size of about 2 nm. The existence period of Cu\textsubscript{10}Zr\textsubscript{7} phase is greatly influenced by temperature.

5. The PDFs indicate that the as-cast sample contains some Cu\textsubscript{10}Zr\textsubscript{7}-like clusters, which have a Cu-Zr bond length of 2.77 Å, shorter than theoretic bond length. The PDFs witness the evolution from Cu\textsubscript{10}Zr\textsubscript{7} to the CuZr\textsubscript{2} phase in local region, and the propagation of ordering in a core-shell mode in longer distance (within 10 nm).

Based on the above results, and comparing with the results for BAM-11, it is surprising that the ternary ZrCuAl BMG is so stable, and it seems the local structure is even more stable than BAM-11, although the nanoparticles grow much larger and faster. The SAXS patterns show large scale changes precede that of local structure for ZrCuAl, while for BAM-11 the interference peak is only observed once the Bragg peaks appear. This is reasonable because in BAM-11, the first crystalline phase is the metastable NiZr\textsubscript{2} phase, which, although forms at much lower temperature, is difficult to grow because the interactions between multiple atoms tend to impede the diffusion of certain atoms. In the ternary ZrCuAl system, Al atoms act as stabilizer, because the formation of highly-ordered Zr-Cu phase must involve the breaking of Zr-Al icosahedra and the movement of some atoms. Nevertheless, this impeding effect is more prominent in the multi-
component system, that is why in ZrCuAl the particle size is much larger and the particles grow more rapidly. The PDF results provide the basis for further structure analysis.
Chapter 10  Topology

The previous chapters show detailed analysis for the structure evolution at local and large scale for all three BMGs separately. In this chapter, some common features will be summed up, and the topology in BMGs are analyzed, finally a comparison between conventional nonmetallic glasses and BMGs is summarized.

10.1 Orders in silica and the proposed models

For comparison, a summary is given here for fused silica, which is the most simple and very important conventional glass from the point of view of both application and scientific study. Although this material has been studied for more than one hundred years, uncertainties still exist about its local and intermediate structure. This is mainly because, as stated in Wright’s review [157], there are very few structural formalisms that can be used to completely define the structure of glasses quantitatively, and the regeneration of 3-d structure can never be unique based on the 1-d correlation function measured by scattering experiments. This makes modeling especially important, and the comparison between model and experiment is important for quantitative study.

There are basically two models for the structure of silica. The earliest one is the crystallite theory, proposed as early as 1835 [158], which envisages glass as an aggregate of extremely small crystals separated by some kind of boundaries like wedge lines. This is similar to the models for BMGs proposed by Nelson et al [42], which states that BMGs are composed of icosahedral clusters separated by wedge lines. The other is Zachariasen’s famous random network theory [159]. As shown in Figure 10-1(a), the
Chapter 10 Topology

Structural units are connected randomly to form a nonperiodic structure with no LROs. Three regions of orders are indicated in the diagram: I, the structural units (AX₄ tetrahedron); II, the interconnection of adjacent units; III, the network topology. There is an IV region for longer range density fluctuations, which is not shown in the figure. Warren [160] is in favor of the random network theory over the crystallite theory, on the facts that the scattering patterns for these glasses do not exhibit extra peak at low-Q, and the calculated particle size does not match.

Based on the above models, a modern crystallite theory has been proposed [161], as schematically shown in Figure 10-1(b), the crystallites are interconnected by regions with less degree of orders. These crystallites are explained as nuclei for the crystalline phase formed during cooling, but they are very stable and their growth is prohibited. This is because, as stated by Goodman [162] in his “strained mixed-cluster model”, the nuclei for several polymorphous crystalline phases coexist due to their similar free energy, it is this confusion that inhabits their growth, thus crystallites are arrested in the matrix by frustration and interfacial strain. The model predicts chemical heterogeneity in the intermediate scale.

For multicomponent silicate systems, the network-modifying components adapt to their local environment to form polyhedra with more desirable coordination. Two approaches are applied to study the orders in these glasses, structural and chemical, and the details are not covered here. A good reference is Wright’s review [157, 163]. As the characterization methods are improving, further information on larger scale structure quantification is capable, e. g., Gaskell et al [164] reported MRO in silica and proposed the existence of quasi-Bragg planes with a distance about 1 nm inside most oxide glasses, corresponding to the first sharp diffraction peak.
Figure 10-1 (a) Zachariasen’s random network model for a glass of composition A2O3 [159], with structural units shaded to indicated regions of I, II and III order; small atoms, A, large atoms, O. (b) schematic diagram for modern crystallite theory for A2O3 [161], ●, O; ○, A.

10.2 Intermediate orders in BMGs

Despite the fact that the physical and chemical properties of the components for oxide glasses and BMGs are quite different, they must share some common features since both show glass behavior. Due to the complexity of multicomponent systems, it is even more difficult to study the local structures of BMGs quantitatively. Some results are given here, based on previous experimental results and models.

SROs have long been presumed to exist in metallic glasses. Frank [4] first deduced that clusters with icosahedral configurations can be frozen into the matrix during supercooling. Through the later work of many researchers, the presence of icosahedral clusters seems to be accepted by most, which has been assumed to be the basis for the formation of quasicrystalline phase during crystallization. Despite this, only qualitative
information about the local topology has been obtained, quantitative information, such as
the amount of icosahedral clusters and their configurations in forming MROs, remains to
be solved by further work.

10.2.1 BAM-11

10.2.1.1 Orders in as-cast state and during first transformation

As has been analyzed from the results of WAXS (Chapter 6) and PDFs (Chapter 7), the first transformation product for BAM-11 is most probably to be the fcc NiZr₂
phase. The parameters and atomic positions are given in Table 7-5. It is reasonable to
assume that this phase has very similar local configurations to the as-cast amorphous
phase. In order to demonstrate this, the clusters in the unit cell, from the smallest
polyhedra to the larger assembly, are plotted in Figure 10-2. All graphs in this figure are
plotted along the <211> direction.

As shown in Figure 10-2(a) and (b), all Zr atoms at the Zr2 sites are at the centers
of icosahedra, and most of the Ni atoms are at the centers of another type of icosahedra.
The Zr2-centered icosahedron contains 6 Zr₁ atoms and 6 Ni atoms, and the Ni-centered
has 6 Zr₁ atoms, 3 Ni atoms and 3 Zr₂ atoms, indicating that the neighboring Zr₂-
centered icosahedron and Ni-centered icosahedron must interpolate each other. Both
types of icosahedra are distorted, as shown by the ligand and edge lengths in Table 10-1
(M is the multiplicity in the table). The shortest distance is between Ni and Zr₂ (2.69 Å),
which remains constant for the whole cell, and is just coincident to the sharp first peak on
PDFs as shown in Chapter 7. The longest distance is between Zr₁ and Zr₁ atoms (3.245
and 3.28 Å), which probably explains why the measured partial PDF of Zr-Zr bond has
so wide distribution, and the peak center is considerably higher than estimated. The atom
number density of this cell is 0.052 Å⁻³, slightly smaller than the bulk density (0.05365 Å⁻³), which is understandable since if transformation first happens in those areas where the free volume is larger, it will be easier for the polyhedra to move or rotate. Simply, Figure 10-2 (a) and (b) show the basic constructional polyhedra for the cell.

Table 10-1 Ligand and edge distances for the two types of icosahedra in the fcc NiZr₂ phase

<table>
<thead>
<tr>
<th>Icosahedron Center</th>
<th>Ligand length</th>
<th>Edge distance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bond d (Å)</td>
<td>Bond d (Å)</td>
</tr>
<tr>
<td>Zr₂</td>
<td>Zr₂-Ni 2.691</td>
<td>Ni-Ni 3.054</td>
</tr>
<tr>
<td></td>
<td>Zr₂-Zr₁ 3.148</td>
<td>Ni-Zr₁ 2.831</td>
</tr>
<tr>
<td></td>
<td>Zr₂-Zr₁ 3.148</td>
<td>Zr₁-Zr₁ 3.245</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni-Ni 3.054</td>
<td>Ni-Ni 3.054</td>
</tr>
<tr>
<td></td>
<td>Ni-Zr₁ 2.831</td>
<td>Ni-Zr₁ 3.133</td>
</tr>
<tr>
<td></td>
<td>Ni-Zr₂ 2.691</td>
<td>Ni-Zr₂ 2.691</td>
</tr>
<tr>
<td></td>
<td>Zr₁-Zr₁ 3.245</td>
<td>Zr₁-Zr₂ 3.148</td>
</tr>
</tbody>
</table>

Wang et al [119] explained the fcc NiZr₂ structure as Bergan clusters growing layer by layer. We do not apply their method here; instead the assembly of these icosahedral clusters in the whole unit cell is checked. Figure 10-2(c) shows a tetrahedron formed by four Zr₂-centered icosahedra, with each sharing two triangular faces. Figure 10-2(d) is the tetrahedron formed by four Ni-centered icosahedra, with each sharing a vertex. Oxygen has been proposed by many researchers to stabilize this fcc structure [115]. Very slight distortion will be caused by the addition of oxygen atoms, which are located at the octahedral center in Figure 10-2(d), with Zr₁ atoms around. It seems the stabilization effect of oxygen atoms comes from their role in stabilizing Zr atoms and gluing the icosahedra to form tetrahedrons. These two types of tetrahedra are located at the 8 corners and the body-center of the unit cell. As shown in Figure 10-2(e), four Zr₂-centered tetrahedra in Figure 10-2(c) form a large hollow tetrahedron, with the
neighboring icosahedra sharing a face. On the other hand, 5 Ni-centered tetrahedra are located at the other four corners and the body-center of the unit cell (as plotted in Figure 10-2(d), the one at body-center is not plotted, for better view), with the neighboring tetrahedra linked by the interpolating of the boundary icosahedra. The two types of large tetrahedra are inter-locked to fill the unit cell. Oxygen atoms, if exist, tend to occupy the octahedral interstitial positions, thus stabilize the whole structure.

The analysis of the PDFs difference of the first stage and the as-cast state in Chapter 7 found that the first transformation is characterized by that the Zr-Cu bond remains unchanged while Zr atoms move to Zr2 site. Based on Figure 10-2, this seems to be realized by the rotation of certain polyhedra, and the movement of certain Zr atoms to more assembled positions. This is also justified by the DSC result that the first stage is diffusion-controlled. The topological configuration from local to nanoscale is supposed to be this: icosahedra $\rightarrow$ tetrahedra $\rightarrow$ cubic. That is, locally the atoms have icosahedral packing, but the nonperiodic order cannot grow, so the icosahedra must form ordinary orders like tetrahedra or cubic to spread in space. In this sense, the propose of “wedge lines” seems not valid, because only slight rotation and interpolation will assemble the icosahedral clusters, and the five-fold order is lost in the range of several atomic shells.
Figure 10-2  Clusters in fcc NiZr$_2$ phase, showing along the <211> direction. (a) Icosahedron with Zr$_2$ at center; (b) Icosahedron with Ni at center; (c) Four Zr$_2$-centered icosahedra form a tetrahedron, sharing faces; (d) Four Ni-centered icosahedra form a tetrahedron, sharing vertexes. The red symbols are oxygen atoms at the center of octohedra of Zr atoms; (e) In the unit cell, the Zr$_2$-centered icosahedra form a large hollow tetrahedron, with neighboring icosahedra share a triangular face; (f) Ni-centered icosahedra form a complementary large tetrahedron (a tetrahedron as in (d) is located at the center, but not drawn), the neighboring icosahedra interpolate each other.
From these analyses, it may be deduced that the as-cast BAM-11 contains a lot of icosahedral configurations, since the volume fraction of the fcc NiZr₂ has been roughly estimated to be 8%. In fact, from the point view of atomic size, other combinations such as Zr-Al and Zr-Ti, are more capable to form icosahedra similar to those shown in Figure 10-2(a) and (b). Those clusters can be more regular and more stable, yet they are dispersed in the matrix and can not show the features of icosahedral configurations due to their small size. The volume fraction of icosahedra is estimated to be very large, since the fcc NiZr₂ phase is formed only at those areas where the randomly distributed Ni atoms are rich. The icosahedral clusters in fcc NiZr₂ phase are indeed linked together, either by sharing common face or vertex, or interpolating with each other, to form MROs with large unit cell, thus the features of icosahedral configurations can be detected by diffraction. All in all, this is a direct proof that many icosahedral clusters exist in BMGs.

10.2.1.2 Orders during the second transformation

The fcc NiZr₂ phase transforms to the tetragonal NiZr₂ phase during the second stage. As plotted in Figure 10-3, this structure contains polyhedra with Ni at center. It should be noted that there are 16 surfaces and 10 ligand atoms in this polyhedron, 8 Zr and 2 Ni, with all Zr atoms having 5 neighbors and both Ni atoms have 4 neighbors. In the cell, all of the Ni-centered polyhedra are aligned along the [001] direction, and the neighboring polyhedra interpolate with each other by sharing a common Ni atom. As shown in Figure 10-3(b), these lines of clusters develop along the (110) plane, with neighboring polyhedra have different orientation to share a common face.
It is still not clear how the structure evolves from the fcc phase to the tetragonal phase. The number density of the latter is $0.05458 \, \text{Å}^{-3}$, considerably denser than its fcc counterpart. It is also denser than the matrix, proving that diffusion must be involved for the growth of this phase. The bond length of Ni-Ni is effectively shortened from 3.05 Å to 2.62 Å, while the nearest bond length of Ni-Zr is increased a bit from 2.69 Å to 2.74 Å. This indicates there must be some reorientation of the icosahedral clusters and exchange of atoms during the second transformation. This change could be very slight and effective that the environment of most Zr atoms remain unchanged.

![Figure 10-3](image)

(a) A polyhedron with Ni at center, and (b) the assembly of polyhedra along the (110) plane in the unit cell of tetragonal NiZr$_2$ phase.

**10.2.2 MgBMG**

As have been discussed in Chapter 8, icosahedral clusters have been found in many Mg-based BMGs, such as Mg$_7$Zn$_3$ [129], and many Mg-RE-based alloys. It has
also been deduced that the atomic topology is mainly determined by pure size effect, e.g., quasicrystalline configuration has been found in both Cd-Ca [133] and Cd-Y [134] binary alloys, which have very different chemical properties but have similar atomic size ratios. We have concluded that the good GFA of MgBMG comes from the ability of both Mg-Cu and Mg-Tb to form complex clusters. For example, Ishimasa et al [132] studied the structure of Zn$_{59}$Mg$_{31}$Ho$_{10}$ quasicrystal, and found that the three types of elements form a complex but almost perfect Penrose tiling, as shown in Figure 10-4. It is very reasonable to assume that Mg-Cu-Tb will form quite similar but distorted structure.

![Figure 10-4 Penrose rhombohedra for Zn$_{59}$Mg$_{31}$Ho$_{10}$: (a) prolate rhombohedron with Mg and Ho atoms on its body diagonal with the edge length of 5.20 Å; (b) oblate rhombohedron. [132]](image)

After the decomposition of the complex structure at higher temperature, orthorhombic CuMg$_2$ phase is formed. Figure 10-5(a) shows a Cu-centered polyhedron with 16 faces and 10 ligand atoms, 8 Mg and 2 Cu. Comparably, this polyhedron is very similar to the one in tetragonal NiZr$_2$ phase shown in Figure 10-3(a). The whole unit cell of CuMg$_2$ is a face-center configuration of this type of polyhedra, forming a layered
structure along c-axis, with the neighboring polyhedra sharing common vertexes, as shown in Figure 10-3(b). There is an orientation difference of around 60.45° between adjacent layers. The number density of this phase is 0.05488 Å⁻³, much higher than the as-cast alloy (0.04796 Å⁻³), which is also similar to the NiZr₂ phase. The high number density mainly comes from the fact that large Tb atoms are excluded from this phase. In fact, the fraction of CuMg₂ phase is small even at high temperature, and most part of the devitrification products are still belong to an icosahedral phase.

![Figure 10-5](image.png)

**Figure 10-5** (a) A polyhedron with Cu at center, and (b) the assembly of polyhedra in the unit cell for orthorhombic CuMg₂ phase.

Comparably, both NiZr₂ and CuMg₂ have similar polyhedra; yet, the polyhedra in NiZr₂ are interpolated and aligned along one direction, while the polyhedra in CuMg₂ are linked by vertexes. In this sense, the tetragonal NiZr₂ phase has higher order than the CuMg₂ phase.
10.2.3 ZrBMG

As has been analyzed in Chapter 9, the structure of ZrBMG is very stable. It decomposes directly to the orthorhombic $\text{Cu}_{10}\text{Zr}_7$ phase and the bct $\text{CuZr}_2$ phase at high temperature. The as-cast sample is supposed to contain a lot of icosahedral clusters but can not show this feature on WAXS pattern due to their small size. Previous studies of Koster [165] and Murty et al [166] found the formation of an icosahedral $\text{Zr}_2(\text{Cu,Al})$ phase upon crystallization, but the structure was not given. We did not find such phase for $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$; instead, the first phase formed during isothermal annealing is the metastable $\text{Cu}_{10}\text{Zr}_7$ phase.

Two kinds of polyhedra in the $\text{Cu}_{10}\text{Zr}_7$ phase, one Cu-centered, the other Zr-centered, are plotted in Figure 10-6. The Cu-centered polyhedron has 10 ligands and 15 faces, while the Zr-centered polyhedron has 15 ligands and 26 faces. These polyhedra are more distorted than those for NiZr$_2$ and CuMg$_2$, yet, the figure shows that many of the atoms still have the “555-type nearest neighbors” [139]. It is also evident from these polyhedra that some atoms are in the process of moving to more stable positions. The bct CuZr$_2$ phase and the cubic CuZr phase formed at later stages are highly ordered and show no such local configurations. The reason that the metastable phases formed early do not show icosahedral configuration, is mainly because the icosahedra in ZrBMG are tightly bonded, which explains the large $\Delta T_x$; once decomposition happens, it is catastrophic, and there is no intermediate phase like the fcc NiZr$_3$ in BAM-11 formed.
10.3 Comparison of metallic glasses and conventional glasses

Being glasses, the metallic glasses and conventional oxide glasses share some common features. For example, they all show glass transition and crystallization upon heating, and the diffraction patterns show very similar characteristics. Yet, they are quite different in their local structure and structural evolution during devitrification. Here the author tries to explain the difference in multiple length scales. These comparisons are based on the author’s understanding of literatures and the analysis of experimental results, thus may not be necessarily correct.

10.3.1 The structural units (SROs)

The first difference lies in the constitutional units, due to the difference of chemical properties between the two systems. As reviewed in section 10.1, conventional glasses, especially silica, have considerably rigid structural units, usually in the form of tetrahedra formed by M-O (M=Si, alkali metals, alkaline earth metals, etc). These units have only several degrees of freedom, such as the bond angle and torsion angles [157],
which enables the structure of silica to be studied quantitatively under different environment. For multi-component oxide glasses, the structural unit may be more complicated due to the combination of network formers and network modifiers, but the units are still very rigid. This comes from the strong covalent bonding of M-O, which not only requires the composition of the glasses to be stoichiometric, but also limit the geometric shape of the units.

On the other hand, the constructional units in metallic glasses are polyhedra of different coordination number. Although Wang [167] explained tetrahedra can be viewed as unit component which form crystal-like SROs in metallic glass, it is more convenient to consider that MGs are composed of complimentary and dense-packed polyhedra. Especially, the presence of icosahedra has long been recognized. Our results show the presence of distorted icosahedra in the fcc NiZr$_2$ phase for BAM-11, and polyhedra containing “555-type nearest neighbors” coordination for those devitrification products of higher orders, such as the tetragonal NiZr$_2$ phase and the orthorhombic CuMg$_2$ phase. The coordination of these polyhedra is mainly determined by size effect [151]. But due to the complicity of the polyhedra configuration, and due to the much weaker chemical bonding between metals than the M-O bond in oxide glasses, these units are more flexible and can be distorted more readily to satisfy the configuration requirement. In this sense, conventional glasses show more chemical features at atomic level, while MGs show more physical features in this range.

10.3.2 Interconnection between structural units

The second difference lies in the packing of structural units. The collection of structural units in conventional glasses is largely determined by the chemical properties
of oxygen atoms, which can form two bonds with other elements, thus “glue” the adjacent units. The slight change of bond angle between M-O-M makes the formation of network possible. In this sense, conventional glasses are chemically more homogeneous in the intermediate range.

There are no such good gluers as oxygen in metallic glasses. Possibly some elements may have similar roles as oxygen, yet the packing of the polyhedra is mainly realized by the solvents, such as Zr in BAM-11 and ZrBMG, and Mg in MgBMG. The solvent atoms can be arranged in such a way that all polyhedra are dense packed. Still, the packing theme remains a mystery. Whether there are such intermediate range orders as in silica has not been proved experimentally. The cluster model proposed by Miracle [43] is quite similar to the modern crystallite theory for oxide glasses. Even in this model, the overall structure remains somewhat random, because the network made of solvent must assume some randomness in order to maintain dense packing and accommodate free volume.

Probably the orders in different scale can be more clearly demonstrated by the scattering patterns. Figure 10-7 shows the structure factors of both BAM-11 and fuse silica measured by neutron scattering. Since the diffraction peaks are related with periodic density fluctuations [164], the sharper peaks for fuse silica indicate it is more ordered than MGs; since the peaks in the high-Q range comes from planes of high index, it is a proof for the existence of longer range orders in silica. BAM-11 has only one sharp peak and several weak peaks which quickly smear out. This proves that the periodic fluctuations in BMGs are in short range, and also support the above assumption that the packing of structural units in MGs is more geometric. Another point should be noted is that fuse silica has no chemical ordering, as demonstrated by the continuous decrease of
scattering intensity at low-Q [163]. Yet, a small and broad plateau is observed for BAM-11 before the first sharp peak, indicating the presence of chemical ordering in intermediate range, which is inevitable for geometrically random packing of polyhedra, because even random distribution of solute atoms will create some enrich areas at the atomic scale. The metastable phase usually originates in these chemically ordered areas.

![Figure 10-7 Structure factor for BAM-11 and fuse silica measured by neutron scattering.](image)

**Figure 10-7** Structure factor for BAM-11 and fuse silica measured by neutron scattering.

### 10.3.3 Structure evolution during devitrification

The random networks of silicate glasses are quite open, and the density of these glasses are usually low. It is very hard for pure silica to devitrify. Upon heating, the silica can transform into multiple polymorphs, based on the conditions applied. Quartz is only formed under high pressure. Even multi-component silicates glasses need additives to enhance heterogeneous nucleation in these materials. Crystallization is initiated by softening of certain component like Y₂O₃ [168], which sinters the glass and forms
crystalline particles. This technique of controlled-devitrification has long been applied for the fabrication of glass ceramics for multiple applications, e.g., refractories. The nucleation density is very low if no generators are added. For example, the nucleation density for Y$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ system is in the order of $10^{14}$ m$^{-3}$ in the condition of homogeneous nucleation, much lower than the usual $10^{23}$ m$^{-3}$ for BMGs. According to our explanation that there is no geometric MRO in BMGs, it seems the high nucleation density of these materials comes from the spontaneous transformation of chemically aggregated clusters (polyhedra).

During devitrification, the chemical properties of certain atoms become more important. As discussed in section 10.2, transformation happens first in these areas where the energetically more active atoms are enriched; breaking of previous configuration is evidenced by the rotation and interpolating of certain polyhedra. Denser crystalline phases are produced based on this first transformation. In this sense, it is inevitable for multi-component BMGs to show several stages during devitrification, because inevitably the interaction energies between different groups are different. Also in this sense, it seems that the $\Delta T_x$ ($= T_x-T_g$) is not necessarily proportional to GFA, because many good glass formers show a metastable transformation at considerably low temperature. This is proved by the experimental results. Although BAM-11 has a much lower $\Delta T_x$ (around 37 K for $\Delta T_x1$) than ZrBMG (64 K), BAM-11 has better GFA than the ternary ZrBMG.

10.4 Summary

In this chapter we first reviewed the study of the structure of conventional oxide glasses, then studied the structure of several known phases for three kinds of BMGs, the component units and their topological configurations are examined in detail. On the basis
of these studies, the common features and difference for the two different systems are compared. A summary is given in Table 10-2. It must be mentioned that our understanding for BMGs is still very rudimental and some of the conclusions are too abbreviated, probably arbitrary. Nevertheless, these studies are significant for better understanding of BMGs and provide the basis for further study.

Table 10-2 Comparison of conventional glasses and metallic glasses

<table>
<thead>
<tr>
<th>Range/state</th>
<th>Conventional glasses</th>
<th>Metallic glasses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Construction units</td>
<td>Rigid polyhedra (usually tetrahedra)</td>
<td>Polyhedra with different coordination numbers (e.g., icosahedra)</td>
</tr>
<tr>
<td></td>
<td>Geometry determined by chemical properties</td>
<td>Geometry determined basically by size effect</td>
</tr>
<tr>
<td>Intercollection</td>
<td>Networking by oxygen bonds</td>
<td>No medium range geometric order</td>
</tr>
<tr>
<td></td>
<td>Open structure</td>
<td>Dense packed</td>
</tr>
<tr>
<td></td>
<td>No chemical MRO</td>
<td>Chemical MRO</td>
</tr>
<tr>
<td>Devitrification</td>
<td>Softening and soldering of one oxide</td>
<td>Low T: transformation of chemically aggregated cluster</td>
</tr>
<tr>
<td></td>
<td>Low nucleation density (~$10^{14}$ m$^3$)</td>
<td>High T: decomposition of more stable matrix</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High nucleation density (~$10^{23}$ m$^3$)</td>
</tr>
</tbody>
</table>
11.1 Summaries

In this project, we have studied the structural evolution of BMGs during devitrification in-situ, benefited by the advanced modern sources of neutron and X-Ray scattering. Ex-situ experiments were also carried out as complements. Throughout the analysis for the results from all these experiments, some conclusions are drawn as follows:

1. All three types of BMGs, including Zr\textsubscript{52.5}Cu\textsubscript{17.9}Ni\textsubscript{14.6}Al\textsubscript{10}Ti\textsubscript{5} (BAM-11), Zr\textsubscript{50}Cu\textsubscript{40}Al\textsubscript{10} (ZrBMG) and Mg\textsubscript{65}Cu\textsubscript{25}Tb\textsubscript{10} (MgBMG), are good glass formers, enabling them to be made by simple drop casting. Among the three alloys BAM-11 has the best GFA.

2. The DSC tests show that BAM-11 devitrifies in two stages, while both ZrBMG and MgBMG show only one principle stage during devitrification. A JMA model has been applied to refine the DSC traces for BAM-11 and the results are very good. The Avrami exponents indicate that the first transformation is diffusion-controlled, while the second transformation has the feature of principle nucleation and growth.

3. The structures of BAM-11 at different states were tested ex-situ by conventional XRD and TEM. Both of these two experiments identify that the product of the second transformation is tetragonal NiZr\textsubscript{2}, but the phase of the first transformation product and the structural evolution cannot be identified.

4. The in-situ synchrotron scattering with SAXS and WAXS simultaneously is proficient in characterizing the structural evolution of BMGs during devitrification. At
the as-cast state, all three samples show broad diffuse peaks with a shoulder at the right side of the second peak. These features match with the icosahedral cluster model for BMGs.

5. All three samples show an interference peak on the SAXS patterns after devitrification. The interference peak is most prominent for MgBMG and BAM-11, while for ZrBMG the interference peak only exists for a short interval. A core-shell model has been successfully applied to fit all the SAXS patterns, proving that at the early stage of crystallization, particles are grown separately with a core-shell structure.

6. Before crystallization a relaxation stage has been identified for all samples, during which the atoms resettle to more stable positions and strains are relieved. For Zr-based BMGs it seems that right after relaxation phase separation happens to form density fluctuations, as evidenced by the fact that SAXS intensity increases preceding that of WAXS intensity. For MgBMG SAXS and WAXS patterns behave almost simultaneously.

7. The results of synchrotron scattering show that BAM-11 devitrifies in two stages. The first stage is related with the increase of icosahedral clusters, the diffraction pattern matches that of fcc NiZr$_2$ phase. This is a transient stage and the transformation advances to the second stage very soon to form the more stable tetragonal NiZr$_2$ phase. Kinetic parameters have been obtained by fitting SAXS patterns with the model, showing that during isothermal annealing the particles follow the rule for steady growth, and at the very early stage of particle formation, there seems to exist a “shrink” stage, during which the correlation length scale is shortened.

8. The atomic scale structure of BAM-11 has been decoded by analyzing the PDFs measured by both neutron and synchrotron total scattering. The results show that the as-cast BAM-11 has SROs within 2 nm range, and can be viewed as a pseudo-ternary
alloy Zr-(Cu,Ni)-(Al,Ti), which is composed of clusters with Zr atoms as the solvent surrounding the solute atoms. After relaxation a prominent decrease of the Zr-(Cu,Ni) bond is observed, proving that Zr-(Cu,Ni) has stronger interaction at higher temperature. The first transformation stage is characterized by topological changes within the 2 nm range. By comparing $\Delta G(r)$ for both stages with the simulated PDFs for fcc and tetragonal NiZr$_2$, it is found that during transformation, most Zr-Ni bonds remain unchanged, while the Zr atoms move to new positions. It is concluded that the high nucleation density of BAM-11 comes from the fact that transformation happens first in the randomly Ni-enriched areas, as a result of the strong interaction between Zr and Ni, and the first stage is a precursor for the second.

9. The results from synchrotron scattering for MgBMG show that there are three transformation stages during devitrification; the first one is related with the formation of an icosahedral phase, which fully develops into a quasicrystal in the second stage, accompanied by the decomposition and formation of TbMg$_3$ phase; the third state is related with the order transformation of the quasicrystalline phase. PDFs also confirm the above conclusions. The 3-stage transformation has also been identified by SAXS patterns. Kinetic parameters show that similar to BAM-11, the particles in MgBMG grow steadily and independent at low temperature, while at high temperature there is a ripening stage, in which the particles are composed of a denser core and a thicker shell. Overall, MgBMG is not as homogeneous and stable as BAM-11.

10. The ternary ZrBMG has been tested by many methods. The DSC traces show the devitrification happens in one principle step, with a temperature gap of $\Delta T_x$ around 64 K. SEM image shows very homogeneous and dense nanoparticles after fully crystallization. Synchrotron scattering shows that the structure changes first happen in
large scale, and ordering of local structure happens quite later. The products of the first transformation are tetragonal CuZr$_2$ phase and the orthorhombic Cu$_{10}$Zr$_7$ phase, and probably another unidentified phase. At high temperature, a eutectoid reaction

\[ \text{CuZr}_2 + \text{Cu}_{10}\text{Zr}_7 \rightarrow \text{CuZr} \]

happens. PDFs show SROs within 2 nm for the as-cast state, and also witness the evolution from Cu$_{10}$Zr$_7$ to the CuZr$_2$ phase in local region, as well as the propagation of ordering in a core-shell mode in longer distance (within 10 nm).

11. The topologies of the three BMGs have been analyzed by examining the local structure of the known phases. Based on this, the common features and difference between conventional oxide glasses and BMGs are compared. While conventional glasses have rigid polyhedra as units, and open network topology due to the chemical properties of oxygen, BMGs are composed of polyhedra which have different coordination number determined mainly by atomic size, forming a dense-packed structure. BMGs have no geometric MROs, but contain some chemical MROs, which are responsible for the high nucleation density during crystallization. At high temperature the chemical properties become more important, and the multi-component BMGs usually form metastable phases first due to the difference of interaction strength between the atomic bonds.

11.2 Future directories

Based on our previous results, a lot of work can be carried on for better understanding of MGs, as stated below:
1. Continuation of current work to retrieve more quantitative information. We have a lot of excellent data which deserve to be analyzed more deeply and fundamentally.

2. Further study of local structure of BMGs by choosing simpler binary systems. The multi-component systems are too complicated to retrieve the partial PDFs. As is known, some binary systems, like Zr-Cu and Pt-Si, can be cast amorphous, although the requirements are more critical. Quantitative resolving of partial PDFs in these systems can be achieved by applying both neutron and X-ray scattering, or using isotopes or anomalous scattering.

3. Simulation and modeling is another important area for MGs. Due to the complexity of multi-component systems, simulation is indispensable for the study of atomic configurations and orders in BMGs. Our experimental results provide the basis for applying different simulation methods.

4. Study of mechanical properties of BMGs, with the aid of neutron and X-ray scattering. This also includes the study of partially crystallized BMGs, or nano composites.

5. Study of conventional glasses like silica and Germania under severe conditions. Because these systems are simpler, more information can be acquired using the advanced characterization methods. The results can be guidance and comparison for the study of BMGs.

6. Location other good glass formers, optimization of the properties of BMGs, design for empirical applications.
Chapter 12 Bibliography


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Appendix  Publications


