Using Simulated Selected Area Electron Diffraction Patterns to Validate Molecular Dynamics Models of Metallic Glasses

by

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Abstract

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Metallic glasses are a class of material with many potential applications. However, they are difficult to produce, placing emphasis on simulations. There are difficulties in validating the simulated structures of these complex materials, so the application of virtual diffraction patterns to validate molecular dynamics samples of metallic glasses is explored and compared to traditional radial distribution functions. These patterns are tested with several types of CuZr samples: a true metallic glass sample formed by quenching, two tiles of different sizes, a larger sample created by repeating the true sample, and two mechanical alloying samples. The resulting stress-strain curves show a link between strain hardening behaviour and intense points further from the centre of the diffraction patterns. These diffraction patterns offer additional insights into the structures of metallic glasses compared to radial distribution functions and are a valuable tool for validation of molecular dynamics samples of metallic glasses.

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List of Abbreviations

BMG	B ulk M etallic G lasses
MG	M etallic G lasses
MD	M olecular D ynmaics
DFT	D ensity F unctional T heory
LAMMPS	L arge-scale A tomc/ M olecular M assively P arallel S imulator
EAM	E mbdedd A tom M odel
RDF	R adial D istribution F unction
SAED	S electd A rea E lectron D iffraction
TEM	T ransmission E lectron M icrosocopy
BCC	B ody C entered C ubic
FCC	F ace C entered C ubic
HCP	H exagonal C lose- P acked

List of Symbols

d	distance between diffraction planes	$\text{\AA}$
$g(r)$	radial distribution function	N/A
r	distance	$\text{\AA}$
K	reciprocal vector	$\text{\AA}^{-1}$
n	any integer	N/A
θ_B	angle between diffracted and incident beams	$^\circ$
λ	wavelength of electron beam	$\text{\AA}$
$\text{\AA}$	Angstrom	$1 \times 10^{-10} \text{ m}$

Chapter 1

Introduction

Materials research is driven by the continual desire for better properties. More efficient engines, lighter and stronger structures, longer lasting tools, and more are all limited by available materials. The desire for better jet engines drives research into many types of coatings and higher temperature alloys to permit higher combustion chamber temperatures, which is important to achieve better efficiency. Space missions are limited by the weight of the delivery vehicles, which are limited by material's strength-to-weight ratio. Aircraft are limited in range and payload by structure weight, and in life-cycle and maintenance costs by the fatigue behaviour of the materials that make up the major components. Because of this, almost all fields of engineering benefit from new materials with better properties.

One promising class of materials are bulk metallic glasses (BMGs), which have been intensely studied since their discovery [1]. BMGs come in many compositions, leading to different combinations of high strength, high hardness, low damping, corrosion resistance, and good magnetic properties. This leads to many possible applications, including: corrosion resistant coatings, hard coatings, high strength alloys, metallic foams, high speed springs, components in micro-electro-mechanical systems, and magnetic inductor cores [1], [2]. However, these materials

are difficult to manufacture and have other limitations. They require cooling rates typically on the order of hundreds or thousands of degrees Celsius per second, and have poor crack growth behaviour, due to the particularly small region of plastic deformation at the crack tip, meaning pieces larger than the plastic region will fail in a brittle fashion [2]–[4]. This has limited their use so far to a coating for golf clubs and inductor cores in transformers [1]. In order to learn more about them such that they may be used for more applications, simulations are appealing. One common method is molecular dynamics (MD) simulations, which are a type of atomistic simulation [5]–[7]. One of the limitations in MD is the gap between real world observations, such as electron microscope imaging, x-ray diffraction, selected area electron diffraction (SAED), and mechanical property testing (which requires fairly large samples to measure using traditional methods). Whereas MD simulations typically characterize samples with different methods, including Voronoi polyhedron analysis, radial distribution functions, and mechanical testing (of small samples with diameters of tens of nanometers).

This research project investigates the use of simulated selected area electron diffraction (SAED) patterns for validation of MD models of metallic glasses and their comparison to real systems. The main goals of the report are to determine if there is information available in the SAED that is not available through more traditional MD tools, such as radial distribution functions (RDF) in the following scenarios: 1. Amorphous samples; 2. Periodic amorphous samples; 3. Structure development during mechanical alloying; and 4. Rearranged samples similar to application in a tiling. Tilings are one method of efficiently creating a larger sample, where the original sample has pieces extracted and rearranged into tiles, which are

then assembled together algorithmically to appear aperiodic [8].

This thesis is organized into the following chapters; 2 Background, which provides relevant information on metallic glasses and their properties, molecular dynamics simulations, and diffraction patterns; 3 Methodology, where the simulation and analysis methods will be described along with reasoning; 4 Results and Discussion, where the results of the simulations will be presented and analyzed; and 5 Conclusion, where the results and simulations will be summarized and important conclusion emphasized.

Chapter 2

Background

This section will provide sufficient background on metallic glasses, their history, properties, structure, applications, some common compositions, manufacturing methods and differences with traditional metals; molecular dynamics, its principles, capabilities, limitations, and characterization techniques; and diffraction patterns and their application.

2.1 Metallic Glasses

Metallic glasses are a classification of metals for which there is no atomic-scale repeating structure with a consistent orientation, much like a liquid, as illustrated in figure 2.1. This could also be described as having no long-range order (>1 nm). This apparent lack of order is the reason they are also called amorphous alloys. While there can still be short to medium range (<1 nm) order, which exhibits itself as certain structural shapes (such as icosahedrons), this structure has stark contrast to traditional metals which have a repeating crystal structure with the same orientation forming each grain [3], [7], [9]–[11]. The distinctive structure of metallic

glasses leads to their unique properties and will be discussed further in the following sections. These properties include differences in deformation behaviour, magnetic properties, mechanical properties, and more.

The first sample of a metallic glass was made in 1960 by Klement et al. [12] in California. It was theorized that this structure could be obtained with fast enough quenching from any composition [12]. This first composition of Gold and Silicon required an extreme quench rate and was unstable at room temperature, tending to recrystallize. BMGs, with high glass forming ability leading to stable room temperature structure and the ability to create larger samples (such as rods with diameters greater than 1 cm) were discovered accidentally in the 1980s during relaxation studies on amorphous alloys, and had until then been believed to be impossible to form [2], [4]. Since then, many new compositions have been formed, with much of the work attempting to increase glass forming ability (and by extension the maximum sample diameters), understand the structures of metallic glasses by investigating binary alloys, micro-alloy additions to obtain better properties, and to select alloys with high potential engineering value [13], [14].

While the current engineering value of metallic glasses is limited due to the small maximum sizes achieved, the largest samples created so far are CuZr rods with 1.5 cm diameters [15]. There is still great potential for glassy alloys in engineering applications, due to their extremely high strength, with some compositions exceeding 5 GPa fracture strength, high hardness, and excellent magnetic properties [2], [16]. Current samples are large enough to acquire good data on structural properties, such as in the studies summarized in the review by Ashby and Greer [2], but are still too small for most applications [1].

(a) Crystalline Sample

(b) Amorphous Sample

FIGURE 2.1: Closeup showing the comparison between crystalline and amorphous structures

2.1.1 Properties

Metallic glasses generally have very good mechanical properties with many exceeding 1 GPa yield stress, and some even exceeding 5 GPa, as can be seen in figure 2.2, which plots the yield stress and Young's modulus of common metal families as well as many metallic glasses (in shaded circles) [16]. Metallic glasses also have high hardness as a class, 10-20% greater than electroplated chrome, low mechanical damping, and fracture toughness comparable to that of steel, all at a lower density. In addition to their mechanical properties, metallic glasses tend to have good corrosion resistance and good soft and hard magnetic properties, depending on composition [1], [2]. These properties make metallic glasses a desirable class of materials. However, they are currently ill-suited for large structural members due to limited region of plastic deformation at the crack, making crack detection before brittle failure impossible, and low maximum plastic strain (typically <2%)

[2], [17]. They are also ill-suited to high temperature applications (where the application temperature exceeds the crystallization temperature) due to the risk of crystallization with an uncontrolled cooling rate. Fe-, Co-, Ni- and ZrCu-based alloys so far stand out in the class for engineering applications due to high stability, glass forming ability and strength [1], [2].

In addition to mechanical properties, the local deformation behaviour must also be discussed. For elastic strain in a crystalline sample, the behaviour is extremely easy to understand. Elastic deformation happens as long as the positions of atoms stay within their lattice position and they will move back to their previous location without issue. In metallic glasses, the phenomenon is much more complex, as, for reasons related to the heterogeneous structure that will be discussed in more detail in the next section, there tends to be non-linear, microplastic, and anelastic behaviour occurring even at small strains, as well as elastic behaviour that depends on the measurement scale. That is to say, within local regions there is atomic rearrangement in some regions even at very small strain, but on a large enough scale the behaviour may appear elastic due to rearrangement in other regions [18]. This leads to a dependence on the sample size for the elastic behaviour. This bulk elasticity may even result in a 2% elastic limit for Zr based alloys [17]. When it comes to plastic deformation, behaviour also varies from crystalline materials. There is no strain hardening as there are no dislocations to pile up and restrict further plastic flow, and as a result shear banding occurs as regions with high local stress do not harden and simply continue to deform. This shear banding leads to a low amount of plastic deformation to failure, as little as 0.2% strain past the maximum elastic strain [19].

FIGURE 2.2: Groupings of materials with strength and Young's modulus data reproduced from [2].

CuZr is a bialloy metallic glass, whose relative simplicity and high stability have made it the subject of lots of recent research, including the simulations in this work [20], [21]. In addition to the simplicity of binary CuZr, CuZr-based alloys have been identified as one of the more important groups engineering materials within the class of BMGs due to their high glass forming ability. This makes production more feasible and gives them excellent mechanical properties. An example of this high glass forming ability is the early formation of CuZrAlAg samples with diameters greater than a centimeter [1].

2.1.2 Structure

Metallic glasses as a class have a disordered structure, with no long-range order. However, they are not completely amorphous, with distinct ordered structures on the Å scale, and some medium range structures [22]. While in general metallic glasses can be single- or mixed-phase, with possible phases in a mixed-phase system including nanocrystalline, nanoquasicrystalline and dendritic phases embedded in the disordered glassy matrix, the most commonly referred to form is a single-phase glassy alloy. Mixed-phase samples can gain improvements in certain properties, with crystalline phases introducing greater maximum strain [1], but typically decreasing strength and glass forming ability [13]. For this work, we will focus on single-phase glasses. In specific, this work uses a CuZr bimetal alloy, as bimetal metallic glasses have been the subject of extensive study due to the relative simplicity of their production, with fewer materials and preparation steps required, and more simple structures in comparison to three or more component alloys [7]. CuZr is a desirable BMG due to its very good mechanical and thermal properties, with a high glass transition temperature, high glass forming ability and stable behaviour [6], [7], [23], [24].

BMGs' unique combination of properties is due primarily to their heterogeneous structure [14]. While a crystalline material is composed of a repeating unit cell, with consistent orientation, such that the same structure is found anywhere within the grain of the material, metallic glasses have an aperiodic structure. It has been theorized that the structure is composed of perfect icosahedra [25], however, newer research has found that the structures within metallic glasses vary [10], [14],

[18], [22]. Almost all of the icosahedrons are deformed, and have a mixture of face-centered cubic and icosahedral order. Some perfect icosahedrons may be present, but it seems that most of the structure is composed of five fold symmetry of tetrahedral clusters, which has icosahedral symmetry but are not icosahedraons, as displayed in figure 2.3. These clusters then share atoms, creating networks of clusters as seen in figure 2.4. The heterogeneous structure comes from the inability of either icosahedrons or tetrahedral clusters to fill 3D space which leads to geometric frustration [10]. These clusters and heterogeneous structures are responsible for the unique mechanical behaviours of metallic glass, which include no true elastic strain, as the irregular structure will cause some atoms to relocate with any strain, and plastic strain primarily coming from shear banding, not dislocation movement as in crystalline materials [26]. This shear banding is also due to the lack of strain hardening, due to the lack of both dislocations and grain boundaries [18]. This mechanism also limits the amount of plastic deformation possible before failure and helps to explain the low maximum strain achieved.

As for the relationship between structure and corrosion, the lack of permeable grain boundaries provides this resistance by preventing corrosive material from penetrating into the material [2], [14], [17]. This same characteristic also allows for extremely high polish finishes and sharp edges as the only inherent limiting factor is the atomic radius of the components.

While the structures become more complex, it is also possible to achieve both improved mechanical properties and increased glass forming ability by adding other elements to metallic glasses, primarily in very small quantities [7], [13]. These

FIGURE 2.3: A five fold tetrahedral cluster illustrating the geometric frustration, used under the creative commons attribution license from [18].

minor alloying additions need to be carefully controlled in amount, as larger fractions can cause the formation and growth of other phases, reducing glass forming ability and diminishing mechanical properties, as the local ordered structures, as described above, are important for achieving the high strength and hardness BMGs are known for [6].

2.1.3 Formation

Metallic glasses are difficult to manufacture, requiring sufficiently fast cooling rates or other mechanisms in order to prevent crystals from forming [4], [6]. While there are a few techniques available, they each have their own limitations. Methods which will be discussed are casting, quenching, deposition, and mechanical alloying [1], [27], [28].

FIGURE 2.4: Snapshot of icosahedral clusters in $\text{Zr}_{50}\text{Cu}_{50}$, blue and red represent Zr and Cu respectively. Zoom in is with smaller atoms than reality to showcase the links within clusters.

Quenching and casting techniques are the most popular, both for creating physical samples and accurate simulated samples [1], [5], [23], [29]. They involve cooling a suitable alloy from a liquid state, which is highly disordered, to a solid rapidly enough to prevent crystal formation. This solid can also be referred to as a supercooled liquid. In the first generation of metallic glasses, this was on the order of millions Celsius per second [4], [12]. Since then, newer BMG alloys have a much slower cooling rate of only hundreds of Celsius per second. This still limits the size of pieces to only a few cm in diameter, but allows for reasonable samples for conventional mechanical testing, as well as some applications such as inductor cores and face plates in golf clubs.

For coatings, deposition can be an excellent method for forming and applying metallic glasses, as vapor deposition techniques allow co-deposition, which readily creates the characteristic amorphous structures of metallic glasses [30]. Given the

cost and low thickness typically associated with vapor deposition, however, there are some limitations to its use. This method is primarily reserved for high value coating applications, which take advantage of the combination of hardness and high corrosion resistance typical of metallic glasses [2], [14].

Another method for forming metallic glasses is mechanical alloying. This method is focused on transitioning a solid sample from crystalline to amorphous without melting. This is primarily done in two ways, one of which involves layering sheets of the desired alloying components together, pressing them together, stretching and folding until the materials have completely mixed and no layers remain. This method requires fairly fine plate thickness to begin with. The other process involves repeated striking of smaller particles against each-other until the phase transformation has occurred [27], [28]. This process only works in certain materials, such as CuZr, which have a high tendency to create amorphous structures that do not re-crystallize. This is due to the tendencies of the stable clusters formed to halt crystal growth [31].

2.2 Molecular Dynamics (MD)

Classical MD is a classification of atomistic simulations that generally relies on semi-empirical potentials for forces and solves Newtonian equations of motion for each atom. The use of semi-empirical potentials allows for much greater time scales and system sizes (i.e. number of atoms) than first principles ab-initio simulation using density functional theory (DFT) [23]. DFT is a computational quantum mechanical model, which accurately accounts for quantum mechanical effects. In

comparison, the semi-empirical and simplified nature of MD potentials reduces the range of conditions for which the simulation is accurate, as not every electronic and quantum interaction is accurately modeled leaving only the interactions and effects from the temperature and interaction types in the data used to fit the potential. The potentials are limited by the style and amount of fitting parameters, as well as by the accuracy and scope of the data-set used for fitting. This can result in trade-offs in melting temperature, density, mechanical properties, thermal properties or phase transformation characteristics [23]. In general, the pairwise function which model interactions pair by pair has been popular, but fails to accurately reflect many real behaviours, which is why many-body potentials which account for the density of atoms, and not just single neighbor forces are becoming more popular. They also have minimal performance trade-offs compared to a pairwise potential. These many-body potentials come in several types, but the one used in this work is of the embedded atom model (EAM) type, derived by Mendelev et al. [23]. The EAM potential takes the form of equation 2.1 from the pioneering work by Daw and Baskes [32].

$$E_i = F_\alpha \left(\sum_{j \neq i} \rho_\beta(r_{ij}) \right) + \frac{1}{2} \sum_{j \neq i} \phi_{\alpha\beta}(r_{ij}) \quad (2.1)$$

Where i and j are each an atom, α is the atom type of i and β is the atom type of j , $\phi_{\alpha\beta}$ is a pair potential interaction between the two atoms, F is the embedding energy, and ρ is the atomic electron density. This equation includes the standard pair potential as the second term, as well as an approximation of electron density interactions. As these are semi-empirical parameters, the embedding force and atomic electron density are both fit to data, and not true physical values from

within the simulation, as electrons are not tracked in classical MD.

In order to get accurate results for amorphous samples with MD, randomly seeded liquid samples are typically generated, and then quenched to room temperature and relaxed. This process allows for diffusion during the liquid phase, as well as some dispersion of residual stresses [5], [23], [29]. The high rate of cooling required for some types of metallic glasses is easily satisfied with these calculations, as typical timescales of entire simulations are on the order of hundreds of picoseconds, and the relaxation phase is important for getting to realistic lower energy atomic positions [23].

2.2.1 Characterization

MD simulations can be used to characterize samples in a number of ways. Engineering stress-strain properties can be calculated using fixed strain rate simulations but are limited by the very high minimum strain rates necessitated by the short time scale of MD simulations, which typically leads to strain rates greater than 10^9 . Thermodynamic properties can be analyzed, but are highly dependent on the potential files, as the way they are fit can drastically effect melting point, how atomic volume changes with temperature, free energy and more [23]. Other properties such as diffusion and chemical reactions cannot be easily modeled in MD, as they are heavily dependent on the potential file being modeled after these behaviours [32].

While there are many ways to evaluate structures in molecular dynamics simulations; radial distribution functions, common neighbor analysis, cluster analysis, structure factor, Voronoi polyhedron analysis and 3D views; diffraction patterns

are not historically a tool available within them, but is a process that has been possible using advanced techniques [33]. More recently, however, an extension for the Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) has been created by Coleman et al. [34] allowing for this to be done much more easily. It does not seem to be used in many papers on amorphous structures so far, but allows for another type of direct comparison to real results. This work will investigate the application of these patterns (which will be introduced in more detail in the next section) for evaluating samples of metallic glasses prepared in a few ways.

One technique for characterizing the MD outputs is Voronoi polyhedron analysis. It is a way to determine what neighboring atom arrangements occur within a sample, based on the number of faces with a certain edge count surrounding an atom [7]. These polyhedrons are valuable in determining what types of local structures occur and how often, but are limited by deformation, with deformed icosahedrons having 8 different possible configurations [29]. Another limitation is that they do not readily provide information about orientation, or the overall state on the order disorder continuum, merely that certain local configurations exist, and these local arrangements may be possible in multiple crystal types (Such as BCC and HCP which share a Voronoi polyhedron). As such, they will not be used going forwards in this work, but an example of an FCC unit cell and Vornoi faces is provided in figure 2.5.

RDFs are also very useful, they give the probability that a neighbor is at each distance from a statistically average atom. This is useful for determining how much variation there is in atomic position and can be used to calculate strain, predict

average structures, and identify crystal types. Some important examples are perfect crystals, lightly deformed crystals, typical amorphous structures (such as in metallic glasses), and a completely random sample (such as an ideal gas) which are provided in figure 2.6. It is important to note that a metallic glass, despite being known as an amorphous metal, is not a randomly structured system with no order; the atomic spacing is relatively consistent, and the previously described short and medium range structures exist. However, RDFs do not give information about cluster orientation or whether the structure is disordered. These will be the other primary characterization method examined in this paper alongside the diffraction patterns. Some of the advantages of additionally using diffraction patterns may include more obvious changes compared to distribution functions, as well as direct comparison to real results. This should allow for a typical sample to be readily identified with confidence.

2.3 Diffraction Patterns

Diffraction is the process of beam bending that occurs as a wave encounters an obstacle. Within materials science, this obstacle is going to be a sample. In general, the new vector of diffracted beams is reciprocal to the original vector as described by Bragg's law, equation 2.2. Where K is the reciprocal lattice vector with units $\text{\AA}^{-1}$, θ is the angle between incident and diffracted beams, and λ is the wavelength of the beam in $\text{\AA}$, n is any integer, and d is the distance between reflecting planes, also in $\text{\AA}$. Due to this, we can see the vector is reciprocal to both λ and d . This means that for a sample with a periodic structure, such as a crystal, this diffraction

FIGURE 2.5: a) Unit cell and b) Voronoi structure for an FCC arrangement. The Voronoi index is 0, 12, 0, 0, indicating 12 4 sided faces as each index corresponds to the number of faces with that many sides. 1 or 2 sided faces are impossible, so the index starts with 3 sides. Reproduced from [35] © 2009 IEEE.

(a) Crystalline RDFs

(b) Amorphous and Random RDFs

FIGURE 2.6: Examples of RDFs for different structures. A perfect FCC crystal of Cu, a slightly deformed FCC crystal (at temperature), the RDF for our quenched metallic glass sample, and a random CuZr sample. The noise in the random curve is due to atom count, as an RDF curve for a perfectly random specimen should be flat.

will result in the generation of a Fourier or reciprocal space version of the original pattern of atoms, figure 2.8 is provided to help understand this relationship. This resulting pattern is typically referred to as a diffraction pattern in crystallography [36].

$$|K| = \frac{2 \sin \theta_B}{\lambda} = \frac{n}{d} \quad (2.2)$$

The two simplest cases of crystal structures are face centered cubic (FCC) and body centered cubic (BCC). For an FCC arrangement the reciprocal lattice would be a BCC lattice, and for a BCC arrangement the reciprocal lattice is an FCC lattice as seen in figure 2.9. Hexagonal close-packed (HCP) structures however have a more complex reciprocal, which can resemble those of FCC or BCC depending on the plane of diffraction. For all these types of crystals however, spacing, variations in point brightness and superposition of other lattices can be used to understand composition, local structure, variations in crystal types or orientations, identify defects or dislocations and more. An example of the diffraction pattern for an FCC crystal can be found in figure 2.10. However, in disordered structures these patterns are less able to provide insight, due to the lack of periodicity resulting in broad diffuse points with typical beam sizes [36]. In the case of a randomly arranged sample, the diffraction pattern will feature a plain disk with decaying intensity. In the case of a metallic glass however, the diffraction pattern will be broad uniform rings as seen in figure 2.10, these broad rings are related to the average spacing of the atoms in the material, and can still provide some insight, despite lacking detailed information about local structures, however there are some techniques to improve the information with diffraction, which will be discussed later in this section [18], [36].

The diffraction patterns in materials science are typically an outcome from either x-ray scattering, or electron scattering in transmission electron microscopy (TEM). In this work TEM-style selected area electron diffraction patterns will be the focus. For this case the output is viewed as a 2D pattern projected onto a screen placed at the back focal plane of the objective lens as depicted in figure 2.7. This diffraction pattern is a result of the arrangement of atoms in the sample, and is taken closer to the sample than an image, where parallel rays leaving the specimen are concentrated into one spot, which allows ordered arrangements within the sample to be identified. The diffraction add-on for LAMMPS is built around computing the intensities at the points on the reciprocal lattices from the structure factor. The structure factor is a way of mathematically describing the scattering caused by a particular structure, and in this case is found on a per atom basis. This allows for even complex structures to have their diffraction patterns determined accurately, but is computationally expensive.

Diffraction patterns are a very important tool for investigating structure and understanding materials. Offering insight directly into the 3D atomic arrangements of real samples, they are also the only method of truly determining if a material is crystalline since the discovery of quasicrystals has caused the definition of a crystal to be changed to "any solid having an essentially discrete diffraction diagram" [37]. Nanocrystalline materials, which are those with many small crystals with different orientations, will appear similar to an amorphous structure, such as in a metallic glass. Nanocrystals can be differentiated from amorphous structures by the variation in intensity along the rings with some distinct peaks rather than complete uniformity, due to the finite number of crystals as can be seen in figure 2.10. Despite

this, A large x-ray beam for a sufficiently large number of grains, such as in a powder sample, may no longer have this point arrangement. In this case, the rings will be sharper than the broad rings of a metallic glass, which will allow them to be differentiated. However it may be hard to gain any useful information from patterns such as those of nanocrystalline samples and metallic glasses compared to those of a crystal [36]. This leads to the importance of correctly sizing the electron beam for the sample and features being investigated, with too large obscuring information about local structures, and too small leading to the conclusion that the material is more structured than the whole, so knowledge of the length scale across which the order being investigated should appear is important. One example of using an extremely small beam is the 4 Å beam used in [10] to investigate single icosahedra clusters, an example of which is provided in figure 2.11, and examples of larger beams can be found across several papers and in figure 2.10 [9], [30]. The average spacing and any crystalline regions can be identified through the diffraction patterns however, and differences in the patterns can be used to measure elastic strain [18], [38], [39].

The use of extremely small beams to investigate the local structure of metallic glasses has allowed for an understanding of the icosahedra that make up the amorphous structures that was impossible with conventional TEM techniques due to the extremely small size of these structures [10]. The use of larger beam diffraction to characterize the general order such as in [9], [23] lead to accurate RDFs, but have a tendency to incite greater amounts of perfect icosahedra to be expected than can be found in real samples [7], [9], [10]. This is consistent with the issues that arise from geometric frustration as discussed previously.

FIGURE 2.7: Simple depiction of the electron beam path in a transmission electron microscope, reproduced from [40] under Creative Commons BY-SA 3.0.

FIGURE 2.8: Illustration of the relationship between the direct and reciprocal lattices.

(a) BCC Lattice or FCC Reciprocal Lattice (b) FCC Lattice or BCC Reciprocal Lattice

FIGURE 2.9: FCC and BCC lattices and reciprocal lattices unit cells. Reproduced from [41].

(a) FCC diffraction pattern. Note that this is a 2D circular slice of the periodic reciprocal lattice. Reproduced from [42].

(b) Nanocrystalline diffraction pattern. Note the variation in intensity along the rings. Reprinted by permission from Springer Nature GmbH [43].

(c) Real diffraction pattern of a metallic glass. Note the smooth broad rings. Reproduced from [9].

FIGURE 2.10: Example diffraction patterns.

FIGURE 2.11: Real and simulated angstrom scale diffraction patterns for deformed icosahedra from [10]. Reprinted with permission from AAAS.

Chapter 3

Methodology

This thesis makes use of the EAM potential for glassy CuZr created and validated by Mendelev et al. [23]. This is due to the ability of many body potentials to accurately reflect melting behaviour such that a quench from high temperature approach creates an accurate sample. All atomic images are generated with the Ovito visualization software [44].

3.1 True Metallic Glass Samples

The true metallic glass samples were generated using the popular method of high temperature melt and quench as it is well validated to create accurate samples in literature [5], [23], [26], [29]. The material was allowed to relax at 1600 K and then quenched to 300 K over 100,000 time-steps for a cooling rate of $7.617\text{E}12$ K/s. While this is slightly faster than the commonly cited process in Mendelev et al. [5], however the results are consistent with another work by Mendelev et al. [23]. After this the sample was allowed to equilibrate at 300 K for 20,000 time-steps before having the diffraction pattern calculated. One difficulty encountered during the quenching was formation of voids in the samples as seen in figure 3.1. This was

FIGURE 3.1: Void in a low density amorphous sample.

addressed by increasing the initial density of the simulation to $0.052 \text{ Atoms}/\text{\AA}^3$ which eliminated the void formation. This approach is consistent with the typical research approach to creating MD samples of metallic glasses.

3.2 Rearranged Specimens

The next set of samples are similar to tiles that would be used in a tiling, which were produced by taking sections of a true sample and rearranging them. Two

FIGURE 3.2: Labelled atomic groups before and after rearranging.

sizes of tiles were created, one matching the original size of the metallic glass sample ($120 \text{ \AA} \times 120 \text{ \AA} \times 40 \text{ \AA}$ with 30,000 atoms), the other much smaller, using subsections of the true sample. The small tile has dimensions of $60 \text{ \AA} \times 60 \text{ \AA}$ by $40 \text{ \AA}$ with 7,656 atoms. The large tile was rearranged such that none of the same sides were in contact, either directly or due to periodicity, as during the original simulation as shown in figure 3.2. This is intended to allow the effect of butting pieces together at low temperature on the diffraction pattern to be shown. For the small tile the same rearrangement is performed with the same objectives, but with all the sections needing to be relocated closer to the center of the simulation such that all edges are in contact with each other, the simulation box is then re-sized. After being rearranged, the tiles are minimized so that a lower energy state is reached to allow the simulation to be stable. The tiles are then equilibrated in a 0 Pa 300 K NPT simulation for 20,000 time-steps to allow the atoms to rearrange and relax. After this the SAED pattern, atomic image, and RDF are created.

3.3 Mechanical Alloying

The mechanical alloying specimens were created using a stretch and layer method that mimics the folding/rolling approach to mechanical alloying. The specimens were stretched to twice their original length, then one side was moved on top of the other and the sample was re-centered as shown in figure 3.3. This deformation process was carried out with NVT conditions and a deform command. While this is unlikely to be a perfect representation of real mechanical alloying, where the strain will not be uniaxial with constant volume, this is similar to a 3D version of the mechanical alloying work by Lund and Schuh [28]. The strain rate was high, at $1.96\text{E}6/\text{s}$. These high strain rates are typical for MD simulations which operate on typical timescales of hundreds of picoseconds for 3D simulations. This strain rate was selected after running simulations over a few different strain rates from $1\text{E}6$ to $4\text{E}6$ as being the most computationally efficient while having results matching that of the lower strain rate. After each layering step the system is minimized, then allowed to relax with a 0 Pa pressure 300 K NPT simulation for 20,000 time-steps to release some residual stress and allow the atoms to settle into their natural arrangements, such that the simulation is accurate. After this, a diffraction pattern, atomic image, and RDF are created before the system is stretched again, and allowed to relax until which is repeated until the desired number of folds is accomplished. Mechanical alloying is a disadvantageous method for creating MG samples in MD, as the computation and coding times required are much greater, and sample uniformity tends to be worse. However, this approach still has some distinct advantages, in being representative of one real method of formation, as well as allowing characteristics of the order-disorder transition to be observed and

FIGURE 3.3: Mechanical alloying process.

characterized, which cannot be done during a melt and quench procedure.

3.4 Diffraction Patterns

The diffraction patterns were generated using the user:diffraction module for LAMMPS developed by Coleman et al.[34]. Due to the unpredictable orientation of atomic clusters in the metallic glass sample it was determined that a diffraction pattern orientation of $[0\ 0\ 0]$, which is complete 3D diffraction pattern (not a slice through a particular lattice plane) would be most informative. In order to save computational time, as well as due to memory issues, an increased reciprocal lattice spacing of twice the default was used for the mechanical alloying simulations and the repeated metallic glass sample due to the large number of atoms. This has some impact on the results due to the decreased density, which is consistent with the decrease in lattice density as seen in figures 3.6 and 3.7, note the relative sparsity of the double-spaced lattice. However the major features remain, with clear rings of close to uniform density, and so there is a relatively small impact on the insight provided. The number of lattice points is also related to the total number of atoms,

so as this is used in the larger simulations the detail lost by increasing spacing is somewhat compensated for. Uniform spacing on all vectors was used as there is no direction where increased density is likely to yield greater insights.

For viewing the SAED patterns and generating the figures presented, the VisIt parallel visualization software was used [45]. A contour map mode was used with logarithmic colour intensity relation, along with set upper and lower intensity bounds. These choices are supported by the difference in detail and clarity shown the additional clarity in the log scaled plots with fixed maximum and minimum intensity in figure 3.4, and detail for the contour plot, figure 3.5 when both have logarithmic mappings. Another benefit of the contour plots is the ability to slice the contour plot, such that 2D slices can be provided to allow for additional clarity due to the difficulty in understanding 3D structures presented in 2D images. The volume plots cannot be sliced.

As an additional method to characterize the diffraction patterns, the difference was taken between the other samples and what is considered to be the true metallic glass plot (the quenched sample). These difference plots are presented as a volume style plot, as the continuous nature allows these differences to be presented in a smoother manner. An appropriate range was found to be -200 to 200 arbitrary units with a Gaussian curve for opacity and a blue to red difference colour map, with blue representing where the good metallic glass sample has higher intensity and red where the current sample's pattern has higher intensity.

FIGURE 3.4: Comparison of 2D slices with different colour scales. Note the improvements in detail in (d) compared to the others. This lead to the choice of colour-scaling for the rest of the diffraction images, where legends will be excluded in favor of simplicity.

FIGURE 3.5: Volume and Contour plots for the 50 thick sample at fold 9. Note the difficulty in interpreting (a) and seeing through the center.

FIGURE 3.6: 3D contour plots comparing single and double reciprocal lattice spacing. Note the decrease in density with the doubled reciprocal lattice spacing, but the similar features.

FIGURE 3.7: 2D contour plots comparing single and double spacing. Again note the decrease in density.

Chapter 4

Results

The results from the simulations will be presented and discussed for each generation method in turn. An amorphous sample of a metallic glass, created with the quenching method (broadly considered the gold standard for generating MD samples of metallic glasses), which can be considered the "gold standard" to compare the others to. Followed by the other samples that use the good sample as a seed (small and large tiles, and repeated amorphous), then the mechanical alloying results. These results are important, as without an effective means to validate samples, a poor representation of metallic glasses may appear similar to certain methods of characterizing samples. Complex periodic structures of atoms and inadequately relaxed samples can both present misleading results, seeming similar to an amorphous structure to a visual estimation or RDFs, without sharing the behaviour. This leads to the investigation of virtual SAED patterns to validate samples.

4.1 True Metallic Glass Results

These results are taken to be an accurate representation of an amorphous metallic glass sample (and will also be referred to as the "amorphous" sample), and is presented first to give a reference point of a good amorphous samples' diffraction patterns, RDF, and atomic arrangement against which to compare the other systems when presented. This sample is made with quenching, as quenching is well validated to create accurate samples. Important features to note are the event mixing in figure 4.1a, the broad peaks in figure 4.1b, and the uniform rings in figure 4.2 with a low intensity region between them. The RDF shows the expected broad peaks, and a small double peak between 5-6 Å. While grouped peaks are more typical in structured samples, which tend to have a greater number of narrow peaks, in this case the double peak is consistent with the expected distribution of the potential file used. This adds confidence to the simulation for having created an accurate sample as it is consistent with established literature [23]. The broad rings in the diffraction pattern are typical and expected features of amorphous metals as introduced in section 2, and they reflect the lack of translational order that would be found in a traditional crystalline metal, as crystalline materials have many discrete points, as shown in chapter 2 [9], [28], [30], [36]. The diffraction pattern allows a generalized verification of the sample being accurate, as the broad rings, with no sharp points is universal to metallic glasses with larger beam sizes. While a sub-nanometer electron beam may generate a diffraction pattern that shows short range order, the diffraction pattern is taken across the entire sample, which is large enough that this does not occur [9], [10]. Looking at the stress-strain curve in figure 4.3 the amorphous sample exhibits reasonable attributes. The stress rises to

FIGURE 4.1: Amorphous sample RDF and atomic arrangement.

a nearly 2 GPa peak, then falls, without rising again consistently for the rest of the deformation, despite some noise likely due to high strain rate and lower atom amount. There is no strain hardening (referring specifically to increases in strength after the peak and dip) exhibited, as expected. The maximum stress exhibited is higher than realistic, as it is similar to the fracture strength in compression of a CuZr based alloy [15]. This is likely due to the extremely high strain rate, as high strain rate behaviour is not typically representative of quasi-static.

4.1.1 Repeated Amorphous Sample

One technique for creating larger glassy MD samples is to create a moderately sized true sample (typically by rapid cooling) and then repeating those atomic arrangements in multiple times in each direction to create a larger sample as seen in the work by Chen et al. [29]. This saves on computational time but it is unclear if these

FIGURE 4.2: Diffraction patterns for amorphous samples.

results are a perfect representation, as heterogeneity in metallic glasses is important for their properties [14]. The atomic image in 4.4a shows a well mixed structure and the RDF in figure 4.4b shows no differences from the true amorphous. However, this repeating technique results in significant changes to the diffraction pattern compared to the true amorphous sample as in figures 4.5 and 4.2. The diffraction pattern in 2D, figure 4.5b, is much higher intensity throughout, with the inner ring having more than doubled in intensity. The general shape is the same, but the changes in intensity are due to the repeating features [36]. These repeating features were not diffused by a low temperature equilibration, and indicate that the sample may not be a perfect representation of the metallic glasses they are meant to simulate. The difference plot in figure 4.6 shows the same information, with the entire plot at a much higher intensity. This is not close to the goal of zero differences, or small differences without a clear arrangement that would indicate a close

FIGURE 4.3: Stress-strain curves for the amorphous, repeated amorphous, and tile specimens. Note that the high maximum strain is due to the periodic boundary conditions preventing failure.

FIGURE 4.4: Repeated amorphous sample RDF and atomic arrangement.

match between the diffraction patterns. Looking at the mechanical behaviour in figure 4.3, it is clear the behaviour matches the original amorphous sample almost perfectly, just with moderate smoothing due to increased atom count. There is a deviance between 0.2 and 0.25 strain, where the original samples has increased stress. However, this may just be due to the noise in the smaller sample. In this case, the changes in the SAED pattern do not accurately reflect a change in behaviour, as the pattern changes with no change in behaviour. However, the concern here is that a repeated sample may reduce heterogeneity across the sample, and fail to reflect some local effects that are expected in metallic glasses [14]. It may be that for these cases an adjustment of the SAED pattern intensity range would provide better understanding of the characteristics of the new sample, or this may be a case SAED is ill-suited to. While these samples do a good job reflecting behaviour [29], care should be taken due to the differences between the repeating structure and the heterogeneity that is typically expected of an amorphous sample.

FIGURE 4.5: Diffraction patterns for the repeated amorphous sample.

4.2 Tiled Samples

For the tiled samples each size will be looked at independently. The diffraction patterns will be analyzed and compared to the radial distribution functions of the tile and both will be compared back to the amorphous sample.

4.2.1 Large Tile

In the larger tile we can see that the RDF, atomic arrangement and diffraction patterns in figures 4.7a, 4.7b, and 4.8 are all quite similar to that of the true amorphous sample above. The difference plots presented in figure 4.9 however show the slight differences between the diffraction patterns. These differences appear to be arranged in 6 clusters, with 2 low value sections, 2 higher value sections and two that are unclear. These differences are relatively small but indicate some changes

FIGURE 4.6: Diffraction difference pattern for repeated amorphous structure.

FIGURE 4.7: Large tile sample RDF and atomic arrangement

in structure. The deviation from the behaviour of the amorphous sample is not yet clear from this plot. When the stress and strain shown in figure 4.3 is considered we can see that this structural difference causes differences in the mechanical behaviour. This shows the capability of the SAED pattern to present changes reflective of a change in mechanical properties. The maximum stress is slightly higher, but the rest of the behaviour is similar, with nearly identical elastic regions, and similar noise after the maximum stress. This cannot be treated as an exact sample, as the structural changes impact the behaviour, despite identical RDFs. This case may provide a good reference point for what magnitude of deviation in diffraction patterns causes changes in mechanical behaviour.

FIGURE 4.8: Diffraction patterns for the large tile.

FIGURE 4.9: Diffraction difference patterns for the large tile.

4.2.2 Small Tile

In this smaller tile sample the atomic images in figure 4.10a, RDF in figure 4.10b, and diffraction patterns in 4.11 are similar to both the large tile and the true amorphous samples. However, we see much larger differences in the diffraction difference pattern in figure 4.12, with stronger red and blue spots. These points do not form a complete shell, implying that these intensity differences are not due to a difference in average intensity related to sample size, but due to differences in order and structure. These differences are however unnoticeable on the RDF and could simply be attributed to noise related to the reduction in atom count. The dim points on the XY plane imply that there is an orientation along which the spacing is more consistently narrow than in the true amorphous sample, and the bright points implying the opposite, that is, an orientation with consistently wider spacing. The small tile also shows fairly severe changes from the original stress-strain curve in figure 4.3. While some of this is due to being a smaller sample, which causes variations due to heterogeneity to occur, some of the difference is due to the different structure of the diffraction pattern captured. The maximum stress is higher, and maintained for longer. It is possible that this is due to the same strain value being a smaller absolute distance leading to atoms changing positions only after a greater amount of strain, but it seems likely this is a result of the change in structure. This adds further evidence that the diffraction patterns add important information in the analysis of these samples, as these types of observations could be used to tune both singular tiles, and tiling patterns to more accurately represent amorphous samples, due to the ability to detect order where it is not easily observed directly. The methods of tuning could include relaxation times, length

FIGURE 4.10: Small tile sample RDF and atomic arrangement.

scales of tile components (as shown by the difference between the small and large tiles), compare tiling algorithms and more. These adjustments should help prevent issues like those encountered in Singh's [46] application of tilings to 2D metallic glasses.

4.3 Mechanical Alloying

The mechanical alloying process was performed 10 times on each of two samples. These samples will be referred to as "50-thick" and "33-thick" based on the number of atom layers in the initial Cu portion. The 50-thick sample contains a total of 658,584 atoms of CuZr (atomic per cent 55.7 and 44.2 respectively) in a $218 \text{ \AA} \times 218 \text{ \AA} \times 238 \text{ \AA}$ box and the 33-thick sample is a $218 \text{ \AA} \times 218 \text{ \AA} \times 160 \text{ \AA}$ box with 448,011 atoms of CuZr (atomic per cent 56.3 and 43.7 respectively). These compositions are within 0.5% of each other, and are reasonable compositions for a CuZr metallic glass so the variation is considered acceptable [7]. The results will be presented as

FIGURE 4.11: Diffraction patterns for the small tile.

FIGURE 4.12: Diffraction difference patterns for the small tile.

images of the atomic arrangements, radial distribution functions, and selected area electron diffraction patterns interspersed with discussion. The two thicknesses will be presented separately, with the 33-thick sample first. This is a good opportunity to remind the reader that the prediction for number of folds until layers are completely destroyed is 6 folds from the work by Lund and Schuh [28].

4.3.1 33-thick Sample

For the 33-thick sample we can see a clear evolution in the diffraction patterns, the RDFs, and the atomic positions in figures 4.13, 4.14, 4.15 and 4.16. The first fold takes it from two discrete layers to four layers with mixing at the boundaries. The effect of this on the 2D diffraction patterns, figures 4.16a and 4.16b, is a transition from the extremely high intensity discrete points of the undisturbed (0 fold) state to slightly diffuse points, many of which have blended together into a somewhat diamond shaped pattern. The locations remain similar, reflecting a superimposed combination of BCC (the reciprocal lattice of the Cu's crystal structure FCC) and the additional points related to the reciprocal lattice of the HCP crystal structure of Zr, with some disorder introduced. In the 3D pattern figure 4.15b it can be seen that a tilt has been introduced, which explains the points that have disappeared in 2D. Those points no longer intersect with this slice due to the change in orientation, so the change in the diffraction pattern is smaller than figure 4.16b would indicate. A figure showing this tilt is shown in figure 4.17 as a comparison with the 50-thick sample. The continued existence of both the concentrated points in the diffraction pattern and the sharp peaks in the RDF show that the sample is still quite ordered and primarily crystalline after the first fold.

Moving to the second fold diffraction patterns, figures 4.14c, 4.15c and 4.16c, a further decrease in intensity of existing peaks, additional blurring between nearby points, and the beginnings of a ring near the centre shows that the crystalline phases are becoming smaller, with more variation in orientation between layers. The pattern does not yet resemble that of the amorphous sample figure 4.2, as the ring is not circular, indicating a relatively small number of crystals and there are long range points reflecting the large amount of crystal structure remaining. The RDF figure 4.14c also shows the high amount of crystallinity through many narrow peaks, that have nonetheless shrunk since the first fold. This is further supported by the amount of crystallinity apparent in figure 4.13c.

In the third fold there can be seen a much greater diffusion in the points that lie directly on the x and y axes in figure 4.16d. The inner ring is becoming more defined, and while it is currently hexagonal we can see it is transitioning from square in figure 4.16b towards the expected circular rings of an amorphous structure. These changes show a further increase in the variation of orientations. However, the large peaks visible just inside the inner ring in figure 4.15d shows that there are repeating structures within the sample. In the RDF figure 4.14d we can note that the dips between nearby peaks are starting to become more level, showing blending of pair separation distances and not uniform spacing as in a crystalline structure. The atomic positions in figure 4.13d show that the layers of crystal structure are being broken into chunks, with mixed phases on the edges.

The fourth fold continues this trend, with further reduction in in all points on the diffraction pattern figures 4.15e and 4.16e. In the 3D pattern figure 4.15e we can see more high intensity points than in the 2D pattern, figure 4.16e. This is due to the

orientation change of the reciprocal lattice that occurs as the layers have mixed. We can see that the mixing is incomplete still from both the regular structure of intense points in both 2D and 3D patterns and the atomic image. In the RDF figure 4.14e we can observe that the peaks have continued to broaden and the curve is starting to have a similar value to the amorphous. The atomic structure has also started to break down the crystal pieces more, with figure 4.13e showing one of the larger Cu crystals (in red) having almost disappeared.

As of the fifth fold the changes are fairly subtle in 3D figure 4.18a. The most notable change is the reduction in the size of the high intensity points, as they appear to shorten from this perspective. In 2D, figure 4.18b, the changes are more obvious, with high intensity points on the inner ring having been partly relocated. There are still some located directly on the Y axis and 6 high intensity points. Another important change is the dramatic softening of the points between the inner and outer rings. These points do not exist at all in an amorphous sample, so this representative of a change towards amorphization. In the RDF, figure 4.14f, the curve is closely matching the amorphous for most of its length. There is some separation near in the second set of peaks, and on the first half of the third set, positions consistent with peaks in the pure crystal at 0 folds. This suggests that there is some residual stress. The structure as a whole is still not amorphous, which is consistent with the large volume of pockets seen in the atomic arrangement figure 4.13f, but the progression towards amorphization is apparent in the largest Zr crystal (in blue) having shrunk significantly since the fourth fold.

Looking at the sixth fold's RDF, figure 4.14g, the distant pair peak around 9 Å has decreased further, and the first in the double near 4 Å has as well. Moving on to

the diffraction patterns, and starting with the 2D pattern in figure 4.19b we can see further softening in the points on the outer ring, and the 6 distinct points appear to have almost completely removed. In 3D figure 4.19a the existing structure is more clear. The rows of points clearly show translational symmetry continues to exist. This leads us to determine the layers and crystal structures have not been eliminated as predicted in [28]. This can be confirmed by also looking at the atomic structure in figure 4.13g, which shows a number of pockets of crystals thicker than atom diameters.

With seven folds completed the RDF in figure 4.14h has hardly changed since fold six. This shows a limitation in using RDFs, they do not contain information about crystal orientation or translational symmetry, merely spacing which is correlated with crystal type. When the diffraction patterns in figure 4.19 are considered it can be seen that the 3D pattern in figure 4.20a has the same general pattern of intense points arranged in angled rows as previously. The points near the center have become more diffuse and have smaller radii. The 2D pattern, figure 4.20b, has 2 clear high intensity points that have reemerged since fold 5. These points existed in the previous folds, but have only now returned to intersecting with the plane of the 2D patterns. Other than those points, we can see the furthest out points have softened or disappeared, and the point on the right side, just inside the inner ring, has disappeared. These changes indicate a further reduction in the amount of translational symmetry related to crystallinity and transition towards an amorphous state. The atomic image figure 4.13h shows that this is likely due to improved mixing of the mixed phase, as the larger crystal pieces have not changed much in size this fold.

After the eighth fold the diffraction patterns figure 4.21 are showing further progress along the path to amorphization. Looking at the 3D pattern in figure 4.21a it seems largely unchanged from the seventh fold, despite softening of the outermost points. The 2D pattern figure 4.21b on the other hand shows several changes. The two intense points on the inner ring in the 7th fold have disappeared, and the points between the rings have become more diffuse, and appear stretched. The atomic image shows that the Cu crystals have been nearly completely eliminated, with only 3 very small pieces remaining, and the largest Zr crystal has shrunk significantly.

In the ninth fold differences in the 3D diffraction pattern figure 4.22a are more apparent. The inner most points have shrunk, leaving a visible gap. In the 2D pattern figure 4.22b it can be noted that the outermost points are smearing further, becoming low intensity. The points between the rings have moved slightly outwards, towards the outer ring and separated. On the inner ring itself the high intensity points closest to the x axis have softened and the dark point just inside the inner ring has disappeared. As a whole these changes indicate further changes toward amorphization, but the lines of intense points in 3D and high number of distinct points in 2D show the transformation is far from complete, even though the equations developed in [28] would predict this change to have occurred 3 folds ago. This likely speaks to the differences in strain behaviour and mixing in 2D and 3D. With a 2D simulation atoms cannot move freely due to their restriction to one plane, which may prevent preferential strain around the crystals. In addition, the use of a real potential likely has contributed as well, if the crystalline structures are

more stiff that would lead to more preferential strain, in a way that was not considered with the simplified potential used by Lund and Schuh. When we examine the RDF in figure 4.14j it appears to have stopped changing shape. The atomic image in figure 4.13j shows only 2 large pockets of Zr with some smaller regions of other crystals helping support both the ideas that the sample is not completely amorphous, and that there has been further mixing.

When the 10th fold is completed we can see in the 2D pattern, figure 4.23b, there are 2 points which disappear, from the lower left and upper right, just inside the ring. These points have become tilted off axis, as the series of points which intersects there can still be seen in figure 4.23a but are much smaller. The other intense points on the 2D pattern have all softened and relocated slightly, changes that indicate more crystalline regions are either in new orientations or destroyed. The points between the inner and outer ring have also reduced again, which indicates the spacings expected of the broad peaks shown in figure 4.14k are becoming more dominant, despite no changes in the RDF. These changes together indicate it is likely that the crystal grains are changing orientation relative to each other rather than changing in spacing and mixing in. The atomic image seems to indicate some breakdown of one Zr crystal, and a splitting of the other, which supports the idea that there are no major changes in crystallinity, despite some mixing and changes in orientation. This further confirms that the RDF alone is insufficient for understanding the structure and highlights the value of a diffraction pattern for some applications.

Looking at the difference plots we can see at the 9th fold, figure 4.24, that there are substantial differences from an amorphous sample in both the inner ring, and

the outer edges. There are 2 intense spots further out, as well as a line along the X-axis across the center. In the difference plot for the 10th fold, figure 4.25, we immediately see 4 points outside of ring, further highlighting the long range order. Sections of the ring are in cool tones, showing the lack of uniform intensity in the locations of the amorphous ring, and 2 dark red points in the ring itself which highlights the more concentrated nature of the 9th fold's diffraction pattern. These plots do not reveal anything new compared to the standard diffraction patterns for the 33-thick sample, as it was already clear the structure had far too many regular structures to be an accurate model of the amorphous state of a metallic glass. Despite this, it is important to give a point of reference for the other difference plots to come.

With the stress-strain curves provided in figure 4.26 we can see how the specimen changes in terms of mechanical behaviour. The general trend is lower maximum stress and less strain hardening in these early folds. This reduction in maximum stress is due to transitioning from an unrealistic perfect (defect free) crystals with extreme resistance to plastic strain, to a disordered structure. Once the amorphization is complete additional folds should not cause further changes in strength. The residual stresses appear to be playing a meaningful role, causing the maximum stresses to be significantly higher than that of the true amorphous sample, even after several folds. After the 10th fold we can see there is still some strain hardening, which confirms that the structure does not behave in a way consistent with an amorphous sample. In addition, we can see that there are still meaningful changes in the peaks of the curves from folds 6-10, further confirming the structure is not completely disordered, as we will see the 50-thick specimen become.

FIGURE 4.13: Progression of atom arrangement in the 33-thick sample.

FIGURE 4.14: Progression of the Radial Distribution Function on the 33-thick sample.

FIGURE 4.15: Progression of the diffraction pattern with folding on the 33-thick sample.

FIGURE 4.16: Progression of the 2D slice from the diffraction pattern with folding on the 33-thick sample.

(a) 33-thick Sample

(b) 50-thick Sample

FIGURE 4.17: Diffraction pattern for the 1st fold on the 33 and 50-thick samples.

FIGURE 4.18: Diffraction pattern for the 5th fold on the 33-thick sample.

FIGURE 4.19: Diffraction pattern for the 6th fold on the 33-thick sample.

FIGURE 4.20: Diffraction pattern for the 7th fold on the 33-thick sample.

FIGURE 4.21: Diffraction pattern for the 8th fold on the 33-thick sample.

FIGURE 4.22: Diffraction pattern for the 9th fold on the 33-thick sample.

FIGURE 4.23: Diffraction pattern for the 10th fold on the 33-thick sample.

(a) XY View of Difference Volume Plot (b) ZY View of Difference Volume Plot

FIGURE 4.24: Diffraction difference pattern for 9th fold of the 33-thick sample.

(a) XY View of Difference Volume Plot (b) ZY View of Difference Volume Plot

FIGURE 4.25: Diffraction difference pattern for 10th fold of the 33-thick sample.

FIGURE 4.26: Stress-strain curves for the 33-thick sample across all folds. Note that the high initial stress is due to insufficient time for complete relaxation.

4.3.2 50-thick Sample

With the 50-thick sample, when there are no folds both samples (33-thick and 50-thick) have the same crystal structures, effectively the same proportions of Cu and Zr and neither has been disturbed as we can see in the atomic figure 4.27a. The RDFs in figures 4.28a and 4.14a are also identical, sharing the narrow peaks characteristic of crystalline materials. This leads to the diffraction patterns in figures 4.29a and 4.30a having an identical pattern to the 33-thick sample patterns in figures 4.15a and 4.16a, as expected. After the first fold is performed however we see some variations between the 50-thick and 33-thick samples. Atomically, they look very similar, with four layers each in figures 4.27b and 4.13b. In the 2D pattern figure 4.30b we see a similar arrangement of high intensity points to figure 4.16b, with two points along each axis, and some points arranged in rows along the same X value. In the 3D figure 4.29b the results are similar to the 33-thick sample as well, but with the tilt in the opposite direction and a greater amount of diffusion on the points, which appear as wider stripes than the 33-thick sample. The difference in tilt orientation can be seen in figure 4.17. Looking at the RDFs in figures 4.28b and 4.14b the differences are almost unnoticeable, which indicates the samples are quite similar. Similar changes have occurred in each sample in the first fold, which is the expected outcome. The first fold should be the most consistent across different samples, as there has been less of a chance for disorder to occur in the crystals. In the later folds, as disorder and randomness increases more variation between samples would be expected.

At the second fold there is a much larger difference in the two samples' diffraction patterns. The 50-thick sample's 3D pattern has an oval shape with 4 large

intense points visible near the center in figure 4.29c. While the outer points are becoming much more elongated, and beginning to form rings. Something similar is visible in the 2D pattern, figure 4.30c. While the inner ring is starting to becoming circular, it is uneven due to intense points on the X and Y axes. The outer points are clustered into broad curves which do not resemble rings. At this point the 33-thick patterns had rings that were more square, and much less smearing in the outer points. The RDF figure 4.28c is very close to that of the 33-thick sample, despite the differences in the diffraction patterns. This implies that while there is a similar proportion of crystalline and ordered features, leading to similar average spacing, the arrangement of these features is quite different. Looking at the atomic image we can see 8 somewhat even layers in figure 4.27c, compared to the uneven layers of clustered crystal in the 33-thick sample which lends support to that idea. After this point the samples are more different than similar and comparisons will no longer be made beyond comparing folds required to amorphize.

Once the third fold is applied the diffraction plot figures 4.29d and 4.30d no longer resemble that of a crystalline material. The rings have become much more diffuse, and the points no longer form clear structures. The 3D plot figure 4.30d shows that some of the large points near the center remain, and are arranged in a loose X shape. These features are the remnants of the bright points formed by the eight points initially near the center, four from each the FCC reciprocal lattice and the HCP reciprocal lattice. In the 2D figure 4.30d the high intensity clusters on the inner ring, banding between the inner and outer rings, and high intensity points on the outer ring further guide the interpretation from the 3D patterns that the sample is not amorphous at this point. When the RDF is considered we, get

agreement with the diffraction pattern. The double peak at 3 Å, triple peak at 5 Å, and generally poor agreement with the amorphous RDF indicate the sample is not amorphous yet, but has had a large increase in disorder.

With the fourth fold the 3D diffraction pattern figure 4.29e undergoes significant softening of the 4 inner points. In addition, the outer ring becomes much smoother. The 2D pattern figure 4.30e shows some features not seen in 3D, primarily the intense points on the inner ring at the axes. This indicates the crystals are very much out of alignment, but still exist in reasonable quantities. The RDF figure 4.28e is starting to resemble that of the amorphous, with the triple peak at 5 Å having a much smaller amplitude than in previous folds and the trailing peaks from 7-10 Å also shrinking. The atomic image in figure 4.27e has also shifted from layers of atoms in fold 3 to clusters of crystals in an amorphous solution. While this may qualify as a type of multi-phase amorphous material it is not representative of the homogeneous CuZr glassy alloy typically researched [5], [23] or of the near total diffusion used as the endpoint in this work [28].

In the fifth fold the atoms in figure 4.27f still form crystal clusters that represent a large proportion of the sample, which are starting to separate. The RDF, figure 4.28f on the other hand has very small deviations from the amorphous curve, with only 2 small peaks (one at 4.5 Å and the other around 7 Å) differentiating them. This gives a much harder to interpret set of information on the structure of the sample than the diffraction patterns in figures 4.29f and 4.30f. The 2D pattern figure 4.30f shows another shift towards the expected glassy metal pattern of diffuse rings, with the inner ring having the intense points becoming more diffuse. The two dark points between the rings are also no longer visible as points but as a field.

In the 3D diffraction pattern, figure 4.29f, the most notable changes from fold 4 are the further erosion of the four points near the center, with the upper left and lower right having nearly disappeared, and the nearly complete loss of distinct points outside the outer shell. The remaining two points inner points however still indicate the structure is not finished its transition to disorder.

When the sixth fold is completed the changes are similar. Atomic arrangement in figure 4.27g has slightly smaller crystalline pockets with a less layered appearance. The RDF, figure 4.28g, is a very close match, with the same peak locations as the fifth fold, but slightly shrunk. The diffraction patterns in figure 4.31 highlight that the structure as a whole is getting close to fully disordered, but has one sharp point on the lower left in the 3D figure 4.31a and some spotting between the rings in figure 4.31b. This is the point where the equation proposed by Lund and Schuh [28] predicts a completely mixed state, with layers thinner than atom diameters. This however is not the case here, as we can see both residuals of crystals in the diffraction patterns. This likely is due to differences in deformation behaviour between 2 and 3 dimensional atomic simulations.

After seven folds have been completed the diffraction pattern is starting to look almost completely amorphous in the 3D pattern found in figure 4.32a. The rings are clear, smooth and broad, any separate points are smaller and lower intensity, and the general impression is that of two shells. There are still some higher intensity points diffused near the locations of the four intense points in previous folds, but nothing sharp or large. The 2D pattern in figure 4.32b provides some additional information on the rings, letting us see 4 small clusters of higher intensity points. In the RDF figure 4.28h the agreement with the amorphous curve improves slightly

again. However, this tells us very little about the amount of crystalline features or the total amount of disorder. The atomic structure can help us understand that there are 10 distinct clusters of crystal remaining, but does little to tell us how they influence the total structure, as there is no singular endpoint that can be considered amorphous [1], [28], [47].

Once the eighth fold is applied the reduction in sparse points in the diffraction patterns, figure 4.33, are the most noticeable changes. In the 3D figure 4.33a we see a much smoother overall image due to how the points outside the outer shell have faded, along with the points between rings. The regions of higher intensity points across the center have also faded compared to the seventh fold. The 2D pattern in figure 4.33b has a new moderate intensity feature emerge on the X axis, which is likely due to a change in crystal orientation bringing it back onto the XY plane, along with some softening of the high intensity points that lay directly on the inner ring. The RDF, figure 4.28i, shows nearly imperceptible changes, making it of limited use at this point. The atomic figure 4.27i shows that almost all the pockets of crystals have decayed, matching with the diffraction pattern's implication that the structure is primarily disordered at this point.

The ninth and tenth folds appear much the same as the eighth. The RDFs in figures 4.28j and 4.28k give us little new information and are close to identical, with just the small peak at $4.5 \text{ \AA}$ distinguishing them from the amorphous curve. This peak could be related to the difference in composition between the true amorphous sample and these samples, or the remaining crystals. The diffraction patterns in figures 4.34 and 4.35 show slight changes in the long distance points, with a reduction in amount and intensity with each fold. The 2D patterns in figures 4.34b and 4.35b

have some differences, the 2 points between the inner and outer ring disappear after the ninth fold and return after the tenth reflecting changes in orientation. The atomic images in figures 4.27j and 4.27k show the smaller pockets of crystal structure disappearing due to mixing and the larger ones reducing in size with each fold as the boundary atoms are mixed. All of this is expected, and consistent with the general transformation from order to disorder that occurs with mechanical alloying [28]. These results are interesting however, as the SAED plots provide a clear visual representation of the overall order of the system, and the differences in results between the two thicknesses of samples which are not apparent in the RDFs. The thinner sample failed to become amorphous over the same number of folds as the thicker sample, which defies a simple geometric relationship between the layer thickness and amorphization.

If we look at the difference plots for folds 6-10, what has occurred becomes clearer. The points we see in fold 6, figure 4.36, show the intense points from figure 4.31 are a substantial deviation from the amorphous plot, and are two separate points, one closer along the Z axis and the other further along it. The other details within the ring, which are in line with those points shows that the arrangement has shifted some intensity from close to the XY plane, where the blue points lie, to near the XZ plane where the red points are. This shift is consistent with the gap shown in the 2D patterns taken earlier in the process, such as figures 4.15b. With the difference pattern for the 7th fold, figure 4.37 we see the points have shifted, but the general structure of 2 red and 2 blue larger difference points remain. These appear to be the same points as in the 6th fold with slightly less intensity, showing reliable insight from the difference patterns despite the changing orientations

and alignments of the remaining crystal regions. In the 8th fold, figure 4.38 the concentrated points have diffused substantially, with the red and blue points that were very close to each other and generally combining. These types of changes imply that the pattern is also more similar to the amorphous as the folds are applied due to having less ordered structure in the diffraction. The points are still clustered into two groups, and not randomly distributed, which implies some amount of structure, but it is unclear what the threshold is for these differences to impact behaviour.

Fold 9's difference pattern, figure 4.39, is unexpected, with features that have sharpened considerably and become more organized, in direct contrast to the trends of the earlier folds. This change, while unintuitive, can be explained, as it must be that the crystal fragments within the sample have come into closer alignment with each other, generating sharper diffraction points due to consistent diffraction angles. After this, fold 10 has the most diffuse difference plot in figure 4.40 implying high agreement with the amorphous sample and a nearly complete transition to glassy structure, as expected. The changes to the 9th diffraction plot have little impact on the overall transition to a glassy state, and are transient in nature.

The stress-strain curves in figure 4.41 tell a similar story. With the curves initially showing a peak stress similar to that of the 33-thick specimen, but quickly falling from fold 1-6, with folds-10 lying nearly on top of each other. This agrees quite strongly with the diffraction patterns. The 6th fold is the point where differences became minor enough to use the difference plots for diffraction patterns and the rings were nearly completely uniform. It is also important to notice that there is no strain hardening at the 4th fold, which brings it in line with the expected

behaviour of metallic glasses, but happens earlier than expected. Considering it never occurred in the 33-thick sample, and the sample is not yet adequately amorphous from a diffraction pattern perspective. It seems likely that this strain hardening behaviour is connected to the same residual crystal structures that create the further out points shown in all of the 33-thick samples' patterns but disappear at the 4th fold in this 50-thick sample.

FIGURE 4.27: Progression of atom arrangement in the 50-thick sample.

FIGURE 4.28: Progression of the Radial Distribution Function on the 50-thick sample.

FIGURE 4.29: Progression of the diffraction pattern with folding on the 50-thick sample.

FIGURE 4.30: Progression of the 2D slice from the diffraction pattern with folding on the 50-thick sample.

FIGURE 4.31: Diffraction pattern for the 6th fold on the 50-thick sample.

FIGURE 4.32: Diffraction pattern for the 7th fold on the 50-thick sample.

FIGURE 4.33: Diffraction pattern for the 8th fold on the 50-thick sample.

FIGURE 4.34: Diffraction pattern for the 9th fold on the 50-thick sample.

FIGURE 4.35: Diffraction pattern for the 10th fold on the 50thick sample.

FIGURE 4.36: Diffraction difference patterns for the 6th fold on the 50-thick sample.

(a) XY View of Difference Volume Plot (b) ZY View of Difference Volume Plot

FIGURE 4.37: Diffraction difference patterns for the 7th fold on the 50-thick sample.

(a) XY View of Difference Volume Plot (b) ZY View of Difference Volume Plot

FIGURE 4.38: Diffraction difference patterns for the 8th fold on the 50-thick sample.

(a) XY View of Difference Volume Plot (b) ZY View of Difference Volume Plot

FIGURE 4.39: Diffraction difference patterns for the 9th fold on the 50-thick sample.

(a) XY View of Difference Volume Plot (b) ZY View of Difference Volume Plot

FIGURE 4.40: Diffraction difference patterns for the 10th fold on the 50-thick sample.

FIGURE 4.41: Stress-strain curves for the 50-thick sample across all folds.

Chapter 5

Conclusion

This thesis has provided context for metallic glasses as a desirable class of materials with their unique structure giving them good mechanical properties, electrical properties, and corrosion resistance. CuZr has also been identified as a particularly important material within this class, leading to its selection for this work in Chapters 1 and 2. A deficit in the characterization abilities of traditional methods (e.g. RDFs and Voronoi indices) for validating MD simulations of metallic glasses was identified and a relatively novel approach was proposed using simulated SAED patterns to validate metallic glasses. Simulations to investigate the capabilities of these virtual SAED patterns were performed regarding several different methods of formation for glassy (or amorphous) CuZr alloys. These samples were: a quenched (considered to be most accurate) specimen, two mechanical alloying specimens of different thicknesses (to investigate the order-disorder transition) each rolled/folded 10 times, two tiles of different sizes (a method used in computer graphics to create aperiodic patterns), and a repeated amorphous sample (a common way to efficiently create larger samples). Further details on the samples can be found in chapters 3 and 4. All of these samples had SAED patterns

and RDFs generated, which were presented in Chapter 4. These patterns were displayed as complete 3D patterns, as 2D slices of those patterns, and with plots of the differences between each sample and the "true" sample.

Looking at the tiled samples, the large tile behaved similarly to the true sample, with a slightly higher peak stress as the main deviation. The smaller tile had an increased maximum stress and a wider peak in the stress-strain curve compared to the true sample. The SAED differences show that the large tile is much closer to the true sample than the small tile, while the RDFs of all 3 are the same. This indicates that tile size is an important factor in creating tiled amorphous samples. The repeated amorphous sample is the one case where the diffraction pattern shows unexpected behaviour compared to the mechanical properties. The entire diffraction pattern becomes much more intense, while the mechanical behaviour and RDF is the same as the true sample. Moving on to the mechanical alloying samples, the thinner 33-thick sample did not adequately transition to an amorphous state, while the thicker 50-thick sample did (despite an equation derived by Lund and Schuh [28] expecting both to transition at 6 folds) in both mechanical behaviour and the diffraction pattern. In terms of SAED patterns, the 33-thick sample maintained a regular arrangement of bright spots across all folds, indicating the residual crystal structure, while the larger 50-thick sample created a pattern similar to the true sample with smooth broad rings. The mechanical behaviour was also different, with the 33-thick sample having strain hardening all the way through and the 50-thick losing strain hardening just before the diffraction pattern became representative of a glassy material.

After comparing simulated SAED patterns to RDFs to analyze these samples,

it has been determined that they are a valuable tool for analysis and validation of the MD samples of metallic glasses. This is due to their ability to provide insight into the orientation and amount of order in a way RDFs cannot, leading them to be more sensitive to the order-disorder transition and better correlated with changes to mechanical properties than the RDFs. The SAED results correlate extremely well to mechanical behaviour, with the exception of the repeated amorphous sample, which performed the same as the quenched sample despite having a much greater intensity diffraction pattern. All samples with distinct points further outside of the rings had strain hardening, whereas the RDFs were not distinct between samples with and without these points. The RDFs fail to provide meaningful insight in both of the tiles and the later folds of the 33 thick sample, both for overall changes in structure and for correlations with mechanical properties. These capabilities highlight the value of simulated SAED patterns in validating MD specimens of metallic glasses. Additionally, SAED patterns are a better analogue to real experimental results, where diffraction patterns are a direct result of TEM imaging (which is commonly performed to analyze the structures of real samples). Overall, virtual diffraction patterns are a valuable, if computationally expensive, way to validate MD samples of metallic glasses.

Future work should include investigations into the diffraction patterns of more compositions (such as ternary systems or those with complex minor alloying additions); an analysis of tile sizes using SAED patterns, along with comparisons to repeating the original structure, as well as an investigation to determine the most important features of the diffraction pattern for mechanical properties, in particular the correct absence of strain hardening found in metallic glasses.

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