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TRIBOLOGICAL CHARACTERISTICS
OF METALLIC GLASS IN SLIDING CONTACT
EXPEDIMENT INVESTIGATIONS
AND MOLECULAR DYNAMICS SIMULATIONS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the
Graduate School of The Ohio State University

By
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The Ohio State University
2001

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ABSTRACT

The unlubricated sliding characteristics of zirconium-based bulk metallic glass disks have been examined in vacuum and in air using sliders made from the same material or from a hard bearing steel (52100). The pin-on-disk test system allowed collection of debris, monitoring of the friction force and, using a Kelvin probe, in situ detection of changes in the structure and chemical composition of the disk surface. Friction coefficient and wear rate of metallic glass were found to vary with normal load, sliding velocity and test environment. Post-test characterization included microhardness testing, X-ray diffraction, SEM and EDS. Examination of worn surfaces, cross-sections and debris confirmed the importance of plastic deformation, material transfer and environmental interactions. When devitrified material was tested, sliding processes caused the near-surface material to re-amorphize. Results from sliding of bulk metallic glass specimens were compared with those from related experiments involving crystalline metals and alloys. Although bulk metallic glasses are reported to have only limited ductility in tensile tests, the friction coefficients and worn surfaces of these materials are typical of ductile materials.

Molecular dynamics (MD) calculations were used to simulate the sliding of a 2D 2-component amorphous system interacting via Lennard-Jones potentials. The friction
coefficient showed a transient before reaching an average steady state value. The steady state friction coefficient was observed to decrease with an increasing sliding velocity. Mixing was observed at the sliding interface. The mixed layer grew at a rate that scaled with the square root of time. A density decrease was recorded in the region adjacent to the sliding interface. This spatially corresponded to the softer layer detected experimentally near the worn surface in a Zr$_{41.2}$Ti$_{13.8}$Cu$_{12.5}$Ni$_{10.0}$Be$_{22.5}$ bulk metallic glass alloy after sliding. Subsurface displacement profiles produced in these simulations were similar to those observed in other material systems. The Navier-Stokes equation was used to analyze the material flow pattern, with results in agreement with data obtained from simulations. This suggests that the observed subsurface displacement profile may be a generic material flow pattern under combined compression and shear.
Dedicated to my wife and my parents
VITA

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Major Field: Materials Science and Engineering
ACKNOWLEDGMENTS

I would like to acknowledge my advisor, Professor David Rigney, for his advisory and mentorship in the past three years. Professor Rigney provided me with two things that are most needed for a career in research: guidance in science and in how to do science. The first part is best illustrated by my thesis work; whereas the second part will show up more pronouncedly as my career develops. Working with Professor Rigney has been a true pleasure for me, and the experience will always be cherished.

Professor Michael Falk at the University of Michigan spent tremendous amount of time teaching me the technique of molecular dynamics simulation. With the kind assistance of Dr. Sharon Glotzer (then NIST, now University of Michigan), Michael came to NIST (National Institute of Standards and Technology) campus spent two weeks there with me, trying to get me started on MD simulation. Help from a collaborator rarely comes bigger than this.

I am also grateful for a lot of good suggestions given by Professor Michael Mills and Professor Prabhat Gupta, both are on my advisory committee. For example, the high resolution TEM work (Fig. 3-3) was suggested by Professor Mills; the work described in
Section 6.4 has its root in a piece of advice offered by Professor Gupta. Dr. James Hammerberg (Los Alamos National Laboratory) and I had numerous exchanges with regard to simulation techniques. In fact, the boundary condition used in my work is a modified version of what Dr. Hammerberg used for his research. Campus Electron Optics Facility staffs Mr. Hendrik Colijn and Mr. Cameron Begg offered invaluable help with various material characterization techniques.

It would be much more difficult to finish this work if there weren't helps from my colleagues. Mr. Toshikazu Kasai always has the talent to make sure that the Kelvin probe is in reliable working condition; Mr. Kenneth Lepper stood by my side when I used the sliding equipment for the first time; Mr. Robert Woodruff and Mr. Frederick Meisenkothen reviewed my candidacy exam documents for grammatical errors; Mr. Jianhui Wu, Mr. Tim Frech and Mr. Mahavir Sanghavi showed lot of interest in my work and raised many good questions.

My most sincere thank goes to my families. My parents live in a city thousands of miles away, but I can feel their support every day. Their love and encouragement have been there with me every step of my life and will forever be treasured. Finally, let me thank my wife, Hanyan. She is often the first reviewer of my paper, the first audience of my presentation, and above all, she is the one waiting for me when I leave the lab late in the night.
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CHAPTER 1

INTRODUCTION

The development of bulk metallic glass (BMG) [1, 2, 3] has renewed interest in research on glassy metals. The amorphous structures of metallic glass (MG) materials lead to new combinations of properties for various engineering applications. For example, it has been reported that Fe-P based MG has a high tensile strength of about 4000 MPa; Fe-B based MG has a Vickers hardness of more than HV1200; in composite form with nanocrystalline particles, Zr-Al-Ni-Cu alloy exhibits a fracture toughness (K_{IC}) of 160 MPa\sqrt{m}; Zr-Ti-Cu-Ni-Be MG shows a high elastic strain limit of 2.0%; particularly relevant to this study, several MG systems were reported to have low friction coefficient and high wear resistance [1, 4, 5, 6, 7]. The recent availability of BMG systems allow experimental evaluation of the tribology of these interesting materials.

Before the development of BMG, a limited number of studies were conducted on the tribological properties of thin ribbons of metallic glass materials. Morris studied the wear of Metglas 2826® (Fe_{40}Ni_{40}P_{14}B_{6}) and found that its wear rate increased when either the normal load or the sliding velocity increased [6]. Miyoshi and Buckley conducted a series
of studies on iron-based metallic glass [4, 8]. They reported sliding-induced crystallization and differences in behavior in air and vacuum. Lee and Evetts proposed a theory based on the kinetics of structure relaxation to rationalize the velocity dependence of friction of Metglas 2826® [7]. The theory and their data apparently correlated well. Kishore et al. suggested an alternative model involving dynamic crystallization in a transfer layer to explain the low wear rates of metal-metalloid based metallic glasses [9]. Boswell reported that the wear rate of a Pd$_{78}$Cu$_{55}$Si$_{17}$ metallic glass was a function of microstructure [10]. The lowest wear rate was recorded when the structure was a composite consisting of amorphous and crystalline phases.

However, relatively little work has been done to investigate the tribological behavior of BMGs. Blau investigated a Zr-Cu-Ni-Ti-Al BMG with and without lubrication [11], reporting friction coefficients similar to conventional engineering materials.

In this work, the friction and wear properties of one of the representative BMG materials, Zr$_{41.2}$Ti$_{13.8}$Cu$_{12.5}$Ni$_{10}$Be$_{22.5}$, were studied experimentally using a pin/disk geometry without lubrication. The friction coefficient and wear rate were measured. Morphology, composition and microstructure of the worn surface, debris and plastically deformed subsurface region were examined using SEM, EDS, TEM, XRD, XPS and DSC. Complementary to the experimental studies, molecular dynamics (MD) simulations of the sliding of amorphous solids were conducted. The combined results from experimental investigations and the MD simulations provide useful insights not only into the sliding behavior of metallic glass material but also the generic responses of solids under sliding contact.
CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Metallic material with a nearly random atomic structure is called metallic glass (MG) or amorphous alloy. The discovery of MG material was largely due to the pioneering work of P. Duwez [12] who, by using a splat cooling method, successfully prepared an amorphous Au-Si alloy. A large number of MG systems have been discovered ever since. However, because of the extremely high cooling rate required to achieve an amorphous structure, most of the conventional MG materials were prepared in the form of thin ribbons, which severely hampered research efforts as well as application of MG’s.

In the late 1980s and the early 1990s, W.L. Johnson [3] and A. Inoue [13] reported that certain complicated alloy systems can be quenched to glassy structures at moderate cooling rates. The relaxation of the cooling rate requirement allowed the preparation of BMG materials. The availability of BMG has important implications in scientific research. For example, unlike most of the conventional MG materials, BMG tend to be a strong glass former [14]. The slower kinetics found in BMG allows one to study the properties of
supercooled liquid which are inaccessible using conventional MG. Some BMG systems were reported to have very good mechanical properties [1]. While some other BMG alloys achieve high strength and hardness in composite form with nanocrystalline particles [15]. Compared with conventional ribbon-shaped metallic glasses, BMG also has a better chance for engineering applications. When deformed in the supercooled liquid region, BMG flows almost like a Newtonian liquid which makes it a good candidate for MEMS components [16]. Since its discovery in early 1990s BMG has been studied extensively and it may have potential for some industrial applications.

In the following literature review, a brief description of the preparation methods for MG will be presented. Atomic structures of MG will be discussed afterwards. Mechanical properties, in particular, the plastic deformation behavior, will then be reviewed. Finally a summation of previous work on the tribological characteristics of MG will be given, covering both experimental research and computational simulations.

2.2 Preparation of Metallic Glasses

J. Kramer first reported successful preparation of amorphous Sb by means of metallic vapor condensation [17]. Since then, many alloy systems have been made amorphous. Major experimental approaches of MG preparation include

Vapor-quenching

By vapor-quenching, metallic glass is prepared by quenching the vapor onto a supercooled substrate. A record quench rate of $>10^{10}$ K/s has been achieved with this method, but to produce samples large enough for further studies has been difficult.
Melt-quenching

Melt-quenching is by far the most widely used method in making MG. It was first introduced by P. Duwez and his colleagues in 1950s. The idea was to “bring a thin layer of liquid rapidly into contact with a cold solid chill-block.” This idea can be realized by various experimental setups, including piston and anvil, melt-spinning, pendant-drop-melt extraction and twin roller, etc. Schematic representations of these methods can be found in Fig.2-1. Typical quench rate of these methods ranges from $10^4$ to $10^8$ K/s \[18\].

Ion implantation

Some wear-resistant amorphous layers were prepared by implanting high-energy solute ions \[19\].

Irradiation

Irradiation with high-energy electrons or heavy ions has been proven effective in amorphizing some intermetallic compounds \[20\]. It is believed that both ion implantation and irradiation amorphize by knocking the atoms off their equilibrium positions. Low temperature, high doses and high dose rate were generally found necessary \[21\].

Interdiffusion

An interesting phenomenon was discovered by Schwarz and Johnson in 1983. An amorphous alloy can be formed by interdiffusion of two pure polycrystalline metals (Au and La) in a multilayer \[22\]. The thermodynamic paradox that two stable phases generate a metastable phase incurred much discussion \[23, 24\]. Two hypotheses were made in the analyses: 1) The amorphous phase has a lower free energy than the initial
multilayer mixture of elements; 2) The formation of the more stable intermetallic compound is prevented by the sluggish diffusion of one of the constituents.

**Mechanical alloying**

Metallic glasses can also be made by rolling, milling, sliding or extrusion. Schwarz and Koch prepared Ni-Ti and Ni-Nb amorphous powders by ball milling [25]. Schultz achieved mechanically induced amorphization by co-deforming a layered composite structure of Ni and Zr [26]. It has been established that in the case of mechanical alloying, an amorphization reaction takes place at the interface between the initial elements mechanically brought into contact [27]. When grinding an intermetallic compound, disordering is mechanically induced, much the same as in irradiation induced amorphization [28].

Besides all of the above, there are many other methods that have been used to prepare amorphous materials, including electrolytic deposition [29], high pressure reactions [30] and ultrasonic-chemical synthesis [31]. With more and more alloy systems being prepared in amorphous form, it was suggested by W.L. Johnson that MG may not be a material as abnormal and rare as we had believed [2].

### 2.3 Glass Forming Ability

#### 2.3.1 Composition ranges of glass formation

There has been continuous interest in the range of composition over which amorphous alloy can be prepared. It turns out that the composition range is closely related to the chosen method. Fig.2-2 is an example of such composition ranges for different glass-
making methods. As a crude generalization, melt-spinning favors amorphous phases near
deep eutectics while mechanical alloying favors amorphous phase formation around the
compositions at which compounds form. Many researchers have reported that, given the
same composition, glasses prepared by different methods are almost identical in properties;
for example, the same glass transition temperature ($T_g$) and crystallization temperature ($T_c$)
have been reported [32]. Similarity has also been found in their structures. Radial
distribution functions (the probability of finding a neighboring atom plotted against the
distance) measured for Ni$_{40}$Ti$_{60}$ prepared by melt quenching and mechanical alloying can
almost be superimposed on each other (Fig.2-3).

It is also clear that for a give method, glass forming composition ranges can vary with
experimental conditions. In the case of rapid cooling, the composition range is a strong
function of cooling rate; for mechanical alloying, the range reflects the ball milling energy
[33], amount of deformation [34] and conditions of the initial materials [35].

2.3.2 Criteria for glass forming

Most studies concerning the glass forming ability (GFA) have been focused on glasses
made by rapid quenching from the melt. For these glasses, GFA is usually measured by the
critical cooling rate ($R_c$), which is defined as the lowest cooling rate demanded to avoid
crystallization.

Atomic size is considered to be the most important factor determining the GFA of an
alloy system [19]. A study conducted by Mader et al. [36] led to the recognition that the
atomic sizes of constituents in a melt must differ enough to allow amorphization. A critical
radius mismatch of about 15% was proposed and, thus, called the anti-Hume Rothery
criterion. This value was supported by a 2D simulation carried out by Simpson and Hodkinson [37] using rafts of soap bubbles. It is very interesting to notice how soap bubbles have been very helpful in understanding the deformation behavior of both crystalline and amorphous materials.

Another approach to examine GFA was to consider the strain energy of a system. Egami and Vitek [38] adopted an atomic site stress tensor defined by Born and Huang to calculate the equilibrated forces acting on individual atoms. Further development of this approach resulted in the conclusion that in glass, the local stress level does not vary too much with the solute concentration, and the same is true for the local strain energy [39]. In contrast, in the crystalline phase, the strain energy rises steadily with solute content [40]. Thus, glass may be favored, from the strain energy point of view, beyond a certain critical composition.

Thermodynamic analyses conducted by Yavari [41] concluded that a zero or negative change of specific volume on melting of a crystalline species favors glass forming. This idea, in effect, was developed using the concept of excess free volume. GFA can also be estimated by simply considering the requirement to prevent crystallization upon cooling. Development of this approach led to a widely accepted index of GFA, $T_g/T_m$, where $T_g$ is the glass transition temperature and $T_m$ is the thermodynamic melting temperature [42, 43]. The higher the ratio, the higher the GFA (Fig.2-4) [44]. This criterion can be reiterated in another way: glass forming is favored around the composition where the phase diagram shows a deep eutectic [12]. A deep eutectic means the system is stable in the liquid state down to a lower temperature, which allows the system to increase its viscosity further before crystallization. Guided by these criteria, researchers have been able to find alloy
systems that have high GFA and therefore low critical cooling rates. For these high GFA alloy systems, formation of BMG becomes possible [3, 13]. Representative BMG systems include Zr-Ti-Cu-Ni-Be, Zr-Ti-Cu-Ni, Pd-Ni-Cu-P, etc.

2.4 **Atomic Structure of Metallic Glasses**

2.4.1 *Radial distribution function (RDF)*

Compared to that of crystalline materials, the current understanding of atomic structures of metallic glasses is far from complete. This is primarily due to the lack of experimental methods capable of directly recording the atomic structures in glasses. In addition, an accurate and efficient way of describing a random structure is yet to be discovered.

The most widely used description of glass structure is the Radial Distribution Function (RDF) where the average atomic density, \( \rho(r) \), is plotted against the inter-atomic distance, \( r \). It is usually plotted in the reduced form: \( G(r) = 4\pi r [\rho(r) - \rho_o] \), where \( \rho(r) \) is the actual atomic density at distance \( r \) and \( \rho_o \) is the average density at distance \( r \). RDF can be derived from X-Ray or other diffraction patterns. Two RDF traces are plotted in Fig.2-5 [45]. One is measured from a Ni\textsubscript{76}P\textsubscript{24} alloy, the other was calculated based on the densely packed hard sphere model. It is important to realize that the RDF is not a complete description of the structure; instead, it is a value averaged over all directions. It tells us the probability and is only a description of a statistical nature. By averaging over a sphere at a certain distance, the RDF does not reveal any information about inhomogeneities on the atomic level. As we will see, atomic level inhomogeneities play a vital role in many
properties of glass including inelastic deformation. Because of the limitations of the RDF, it is desirable to have a description for the distributive properties of glass.

2.4.2 Material property distributions in metallic glasses

One of the most important contributions in glass science was the analysis of a random packed hard ball model proposed by Bernal in 1964 [46]. The model was initially intended to understand the atomic structure of liquid but soon it was adopted to analyses of amorphous solids. Bernal suggested that disordered structures can be conceived as an assembly of five different polyhedrons with an atom at each polyhedral corner. An alternative way of doing the same thing is to make a polyhedron around each atom instead of an interstitial site where the volume of each polyhedron would be equal to the volume of the atom at the center. Finney [47] gave the distribution of volume per atom in a densely random packed structure (Fig.2-6). It turns out that the average atomic volume in glass is 9% larger than that of a reference crystal. More importantly, it showed that there exist some atomic sites that are 10% larger than the average. The distributive nature of the structure makes the properties of glass also distributive, for example, one would expect the activation energy during deformation to be distributive. Egami et al. calculated the local strain distribution in a computer-generated glass [38]. Their results showed that the mean normal stress is about 6% of the bulk modulus and the shear stress is 18% of the shear modulus (Fig.2-7) [48, 49, 50]. These are substantial values. Egami proceeded further to suggest that this elastic strain energy stored in glass might account for the excess entropy associated with the glassy state. Actual measurement of distribution of activation energies
for anelastic response was conducted by Argon and Kuo (Fig.2-8) [50] and Ocelik et al. [51].

2.4.3 Models of glass structure

The dense randomly packed hard sphere (DRPHS) is the first and is still one of the most widely used models for MG structure. As a modification, soft spheres were introduced instead of hard spheres, giving rise to the dense randomly packed soft sphere model (DRPSS) [52]. Amorphous structure has also been modeled by introducing a network of dislocations into a perfect crystal [53]. The validity of each model is to be checked against the measured properties, e.g. the density and RDF.

Binary metallic glasses have been divided into two broad groups, transition metal-transition metal (TM-TM) and transition metal-metalloid (TM-Met). For TM-TM glasses, the structure was conceived as substitutional, whereas for TM-Met glasses, the structure was rationalized as metalloid atoms sitting at the interstitial sites among hard spheres of transition metal atoms. Such a crude model works well with many binary glasses [19].

Structural models were also generated by means of computer simulation. 2D and 3D simulations using either a molecular dynamics or Monte Carlo method have produced encouraging results with regard to atomic structure of glasses [54, 55, 56, 57].

Despite the enormous amount of research and much progress, it may still be fair to say that there is a long way to go before we can conceive the structure of any MG as clearly as we are able to think of a cube of crystalline sodium chloride.
2.5 **Plastic Deformation of Metallic Glasses**

2.5.1 *Experimental observations*

In metallic glass the bonds between atoms are mostly metallic with some covalent component if a fair amount of metalloid is present as solute. It is therefore expected that metallic glasses may be able to withstand some degree of plasticity before fracture.

Inspections of the fracture surfaces of MG samples after tests showed that there are two basic modes of plastic deformation: inhomogeneous plastic flow and homogeneous plastic flow. Depending on the experimental conditions, either one of these modes can be the dominant mechanism.

2.5.2 *Inhomogeneous plastic flow*

Fig.2-9 is a MG wire after drawing down to an area reduction ratio of 23% at room temperature [58]. The sample wire showed clear deformation marks called shear bands. These bands came in two orientations with respect to the wire axis: nearly perpendicular and slanted at about 45°. The number of bands in each orientation increased with the area reduction ratio, i.e., with the total plastic strain. Locally, large plastic strain was observed across these bands. All shear bands were very sharp or, in other words, shear was highly localized. At the same time, it seemed that shear took place exclusively within shear bands, i.e., there was no observable shear in the regions between two neighboring bands. If the whole process of plastic deformation were put in motion, it was reported that these shear bands appear rather suddenly, on the order of millisecond [59]. Shear bands appeared regardless of whether the stress state is compressive or tensile. If a glass deforms by means
of localized shear bands, at room temperature with strain rate typically no less than 10^{-4} \, s^{-1}, the behavior is described as inhomogeneous plastic flow.

2.5.3 Homogeneous plastic flow

If the deformation temperature is high, i.e., \( 0.7T_g < T < T_g \), the number of shear bands appearing on the surface will be very limited and the material will deform in a more homogeneous manner. In this temperature range, each volume element within the material contributes to the strain. This behavior is close to Newtonian flow where approximately we have \( \dot{\gamma} \propto \tau \). Deformation of glass in this temperature range is described as homogeneous plastic flow.

If the temperature is higher than \( T_g \) but lower than the melting temperature \( (T_m) \), the material is in the overcooled liquid state. By the definition of \( T_g \), the material has a viscosity \( \eta \) between \( 10^{12} \) to \( 10^{14} \, \text{Nm}^{-2} \cdot \text{s} \). No shear bands are present in this temperature range and the material deforms by means of Newtonian viscous flow.

The dependence of deformation mode on temperature suggests that homogeneous flow is more thermally assisted, whereas inhomogeneous flow is more stress activated. However, the actual mode of deformation can not be predicted by temperature alone, as material composition, strain rate and thermal history all have their roles. Fig.2-10 shows the changes in the maximum or yield tensile stress and the deformation mode of \( Zr_{65}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{15} \) MG as a function of temperature and strain rate [60]. It is clear from the data that at a given temperature, low strain rate favors homogeneous flow whereas high strain rate promotes inhomogeneous flow. The yield stress displays a maximum with respect to strain rate at a given temperature.
2.6 MECHANISMS OF INELASTIC RESPONSES OF METALLIC GLASS

Two models have been proposed to rationalize the inelastic responses of MG below the glass transition temperature $T_g$. One is the generalized dislocation model, which is generalization of the dislocation model developed for crystalline materials. Another school of thought emphasizes the role of excess free volume. It proposes that macroscopic plasticity is produced by local shear transformations nucleated under the applied stress and assisted by thermal fluctuations in regions around excess free volume sites.

2.6.1 Generalized dislocation model

The striking similarity between the shear bands observed in crystalline materials and those in metallic glasses led to the idea that plastic deformation of MG is also a result of dislocation motion. But the term “dislocation” has to be re-defined in a more general sense so that it can be extended to the structure of glass. Li and Morris proposed that the disordered structure of metallic glasses can be achieved by putting a network of closely spaced dislocations into a perfect crystalline material (Fig. 2-11) [53, 61, 62]. Ninomiya et al. introduced $10^{14}$-$10^{15}$ cm/cm$^3$ dislocations into a FCC lattice in a computer. The calculated RDF for the generated material agrees with experiment [63].

A generalized dislocation is defined as the linear region where the atomic configuration deviates from the structure of an ideal “dislocation lattice”. A dislocation defined in such a way can move around in the “perfectly” disordered structure, while maintaining separation between the slipped and unslipped zones. The Burgers vector would have to be redefined as a displacement vector, $\vec{S}$, which reflects the amount of local deviation from the original atomic sites. $\vec{S}$ still equals the closure failure accumulated along
a circuit around the linear defect, i.e., \( \bar{\delta} = \int (\partial \bar{u} / \partial l) dl \), where \( \bar{u} \) is the local displacement and \( dl \) is an incremental distance along the circuit. Unlike dislocations in crystals, \( \bar{\delta} \) is not required to be conservative along the generalized dislocation line. It may vary in magnitude or invert its sign along the way. As a consequence, generalized dislocations can end inside the glass material, which is consistent with the reported observation of terminated shear bands inside the material [64, 65]. It has been demonstrated that at a stress about 1/20 that of the homogeneous deformation stress, material constructed by a dislocation network can deform inhomogeneously by means of dislocation motion (Fig.2-11) [61, 66]. J. Gilman has proposed that at low enough temperatures, the viscous relaxation time becomes much longer than the time for plastic flow, adjacent shear events will be correlated, and, hence, flow may be described by the motion of dislocations [67]. These statements apparently fit a picture of low temperature deformation be means of shear bands. At high temperatures, on the other hand, Gilman has also estimated that lower viscosity at higher temperatures makes local relaxation more effective, shear events become uncorrelated and flow becomes homogeneous.

Although the generalized dislocation model explains many of observations, it is far from perfect. M. Ashby et al. questioned the stability of an existing dislocation in an amorphous material [68]. Why shouldn’t the dislocation be relaxed by displacements of atoms? This kind of “dissipation” is not possible in crystals where the positions of atoms are fixed, but it is possible in a disordered structure. The stability of dislocations in glass has been further studied by computer simulations. One such study suggests that a minimum critical displacement is required to make the dislocation stable [69]. But there has been no
report of actual observation of generalized dislocations. In addition, the force that keeps the segments of defects together to form a generalized dislocation, or in J. Gilman’s words the “correlation between shear events”, would be expected to cause interaction between different dislocations and give rise to strain hardening. But, strain hardening has been established to be in-significant in metallic glasses. Deng et al. used molecular dynamics to simulate the plastic deformation of a 2D glass system [70]. It was reported in ref. [69] that the volume of the material tends to increase upon plastic deformation. This trend of volume increase appears as a pressure increase on the rigid simulation cell (Fig.2-12). Direct measurement shows that a substantial density reduction takes place in the shear bands in Pd$_{77.5}$Cu$_{6}$Si$_{16.5}$ MG [71]. But the generalized dislocation model, which incorporates only shear events, does not predict volume dilatation to accompany deformation.

2.6.2 Local shear model

Based mostly on the work of D. Turnbull, F. Spaepen [72, 73] and A. Argon [74], another mechanism of inelastic deformation in metallic glasses was proposed. In this model, plastic strain in MG is produced by local shear transformation nucleated under the applied stress and assisted by thermal fluctuations in regions around excess free volume sites.

2.6.2.1 Excess free volume

As it is for most materials, the mechanism of inelastic deformation in metallic glasses is closely related to the structure. In the local shear model, the glass structure is modeled as randomly close packed hard spheres. The concept of excess free volume is established
based on such a structural model. Excess free volume, $\Omega_f$, is defined for a one-component system as

$$\Omega_f = \frac{1}{n} \sum_{i=1}^{n} (V_i - V_0)$$ (2.1)

where $\Omega_f$ is the average excess volume per atom in a local cluster of $n$ atoms, $V_i$ is the volume of the $i^{th}$ atom in the cluster and $V_0$ is the average volume per atom over the whole material [70]. Regions with positive excess free volume would have a lower atomic coordination number or a longer bonding length compared with that of a reference material having a dense randomly packed structure with the same composition. It is in these regions of positive excess free volume that the local bonding is weaker than the average and inelastic relaxation becomes possible by local rearrangement of neighboring atoms. Local shear at excess free volume sites is the single most important event in the local shear model.

It was discussed in section 2.4.2 that the properties of a glass may not be homogeneously distributed throughout the whole material. The same is true for the excess free volume and hence the activation energy of local relaxation. It is important to keep in mind that those larger excess free volume sites, though limited in number, have the lowest activation barrier for local shear. Because of the distribution of activation barriers, different volume elements will be activated at different levels of external stress. Since the initial packing of atoms is random, the sheared structure is also assumed to be random; therefore, the original structure is repeatedly reconstructed during the shear process and the distribution of excess free volume is kept unchanged, as is the capability for further shearing [49, 74].
2.6.2.2 High temperature deformation mechanism

It was proposed that shear of metallic glasses at high temperatures \( T > 0.7T_g \) happens in a way best described as diffusive shear transformation \([74]\). When the material is under external stress, local shear happens at activated sites. This is represented in Fig.2-13, where a cluster of atoms rearrange their positions collectively leaving the cluster sheared for a magnitude of \( \gamma_0 \). To accommodate the shear, the immediate matrix deforms elastically. If the external stress is small and the activated shear sites are isolated from each other, the elastic energy stored in the matrix will encourage the sheared regions to shear back when the external stress is released, which describes the “elastic” region of the stress strain curve. When the stress is large, sheared regions start to relax their associated elastic energy by plastically shearing the neighboring regions, the material loses its “memory” and deformation become inelastic.

When the temperature is high, elastic energy can also be relaxed by diffusion. This contribution is described as a “back flow” of strain \([75]\). Combining the external stress induced strain and the “back flow” strain, the following strain rate \( \dot{\gamma} \) expression is derived for the high temperature flow mechanism \([74]\),

\[
\dot{\gamma} = \alpha \cdot \gamma_0 \cdot \nu_o \exp\left(-\frac{\Delta \varepsilon + \gamma_0 \cdot \dot{\varepsilon} \cdot \Omega_f}{kT}\right) \sinh\left(\frac{\sigma \cdot \gamma_0 \cdot \Omega_f}{kT}\right)
\]  

(2.2)

where \( \alpha \) is the volume fraction of flow units contributing to shear, \( \nu_o \) is the attempt frequency of each volume unit, \( \gamma_0 \) is the local strain (as illustrated in Fig.2-13), \( \Delta \varepsilon \) is the elastic energy associated with the local shear and \( \dot{\varepsilon} \) and \( \sigma \) are material properties based on the assumption of the shear resistance curve shown in Fig.2-14.
If diffusive shear was indeed occurring in metallic glass, we would expect the shear resistance \( (\sigma) \) to be sensitive to shear rate, \( \dot{\gamma} \). Diffusive relaxation has a characteristic relaxation time at a given temperature, which puts a limit on the amount of elastic energy that can be relaxed per unit time. So, when strain rate is high, deformation can only continue at the price of raising the total elastic energy until a new balance is achieved between shear and relaxation. Therefore, we would expect a strong dependence of shear resistance on shear rate. To better study the effect of shear rate, the strain rate sensitivity exponent \( m \) is defined by Megusar et al. [76] as,

\[
m = \left( \frac{\partial \ln \dot{\gamma}}{\partial \ln \sigma} \right)_T
\]

which is computable based on equation (2.2).

On the other hand, \( m \) can be obtained based on the measured relationship of flow stress and strain rate like the one shown in Fig.2-15. Megusar et al. compared the value of \( m \) obtained from measurement and from calculation using Pd_{80}Si_{20} MG (Fig.2-16) [76]. The agreement is apparently satisfactory. It is noted that the value of \( m \) decreases as the temperature approaches \( T_g \), which means the system become more sensitive to strain rate as expected.

2.6.2.3 Low temperature deformation mechanism

Computer simulation of shearing based on a hard sphere model demonstrates that shear transformation under high stress becomes more intense and narrow to a region between two short rows of a few atoms around a free volume site [77]. Simpson and Hodkinson simulated on another scale using a raft of floating bubbles where deformation by slipping between two atomic layers was also observed [37]. Another bubble raft
simulation carried out by Argon and Kuo also confirms the existence of local planar shear at high strain rate [74]. This kind of atomic motion can be represented as in Fig.2-17. Although these observations may not be very convincing, Argon assumed that at low temperatures, a shear transformation happens in shape of a thin disk containing only a few atoms and with the shear transformation direction in its plane (Fig.2-17). This configuration, in a sense, is analogous to a dislocation loop in crystalline materials. Because the temperature is relatively low (viscosity is high), diffusion processes will not be as effective; therefore the local shear, once completed, will not relax very fast, and the “back flow” contribution can be safely neglected. Deformation continues by successive local shears taking place at different places in the material. Each sheared region retains its local configuration without propagating across the material. At low temperature, the local shear model distinguishes itself from the generalized dislocation model by considering collective local shear events instead of a few active propagating shear systems.

The rate of shear is then determined by calculating the rate of activation of the flow units (or, in analogy to the dislocation loop idea, the nucleation rate), which is given by an Arrhenius type of expression.

\[
\dot{\gamma} = \dot{\gamma}_G \exp\left(-\frac{\Delta G^*}{kT}\right)
\]  

\[ (2.4) \]

where \( \dot{\gamma}_G = \alpha \gamma_0 \nu_G \) and \( \Delta G^* \) is the average activation free energy of a local shear event under an external shear stress \( \sigma \). The definitions of \( \alpha, \gamma_0 \) and \( \nu_G \) have been given in earlier section on the high temperature mechanism. \( \Delta G^* \) can be calculated from first principles by considering the associated Helmholz free energy and elastic energy. For a detailed
discussion of $\Delta G^*$, readers are referred to the paper by Argon in 1979 [74]. Alternatively, $\Delta G^*$ can also be phenomenologically expressed as,

$$\Delta G^* = \Delta G_0 \cdot (1 - \frac{\sigma}{\tau})$$  \hspace{1cm} (2.5)$$

where $\Delta G_0$ is the barrier height under zero external stress. With applied external stress, the barrier for local shear reduces to $\Delta G^*$, which is to be overcome by thermal fluctuation, as is the case in equation (2.4). The physical picture presented in [74] involves a stress induced thermally assisted local shear mechanism.

Using the $\Delta G^*$ expression derived from first principles, one could calculate the dependence of flow stress on temperature. A similar dependence can also be derived for a high temperature model using equation (2.2). Calculated results were compared with experimental data with the results shown in Fig.2-18. The data for the high temperature range was measured for Pd$_{80}$Si$_{20}$ [76], while the low temperature data were obtained from Pd$_{77.5}$Cu$_6$Si$_{16.5}$ [64]. As can be seen, the high temperature and low temperature curves intersects at approximately $0.68T_T/T_g$. Because the mechanisms proposed for the high and low temperature regimes utilize the same structural defect, i.e., the excess free volume site, the system must choose the easier one, resulting in the solid curve. Data in the whole temperature range fit the calculated curves reasonably well.

2.6.2.4 Shear localization

As we have discussed in previous sections, the phenomenon of shear localization is a common observation in metallic glasses. Localization of plastic flow requires structural change within the bands so that they deform differently from the rest of the bulk. Fracture
in a tensile specimen is most likely to occur along a shear band, which makes a 45° angle with the tensile axis. It was thus speculated that shear planes are weakened by some shear-related structural change [73]. The typical vein pattern observed on the fracture surfaces indicates lower viscosity within the shear bands, which is consistent with the assumptions of structural change. Differential etching of shear bands after deformation indicates that there indeed exist structural changes associated with localized flow [78].

It has been established for crystalline materials, where strain hardening is possible, that shear localization is due to a plastic shear strain induced reduction of deformation resistance [79]. For metallic glasses, where strain hardening is insignificant, local softening was proposed as the responsible mechanism [73, 80]. It was proposed that during local shear transformations at free volume sites, the surrounding atoms might be pushed apart, producing a local dilation (Fig.2-19). It was assumed that the local dilatation was not totally elastic and would not relax immediately afterwards, provided the temperature was low enough. Consider a piece of material under external stress and deforming at an overall shear rate of \( \gamma_0 \). If there is an initial perturbation in the region that is to become a band, the strain rate will continue to accelerate in the band due to dilation and decelerate in the surroundings, which gives rise to shear localization. Based on the idea outlined here, shear strain within a shear band, \( \gamma_b \), and that of the matrix, \( \gamma_m \), can be calculated. The result is plotted in Fig.2-20, where \( \Delta \gamma_0 \) is the overall shear strain. We can tell from Fig.2-20 that shear localization starts out slowly, then accelerates soon after, leaving the shear concentrated within the shear bands. The ratio of shear taking place in the bands to that in the matrix almost reaches infinity at the final steady state. This is consistent with the
observation mentioned earlier in 2.5.1 Experimental observations that low temperature shear happens mostly by shear bands, and regions between the bands are essentially unsheared.

Based on Fig. 2-20, the rate of shear band development can also be determined. If we ignore the amount of shear in the matrix, the total shear, $\Delta \gamma_0$, can be expressed as

$$\Delta \gamma_0 = \int \left( \frac{\partial \gamma_b}{\partial t} \right) dt = \gamma_b \cdot \Delta t$$

where $\gamma_b$ is the average shear rate of the band, which is typically about $10^3$ times the overall rate, $\gamma_o \cdot \gamma_0$ is typically $10^{-4} - 10^{-3} \text{s}^{-1}$. Total shear $\Delta \gamma_0$ equals $10^2$. Substituting these values into equation (2.6), the time to generate one shear band, $\Delta t$, is estimated to be on the order of $10^{-2} - 10^{-1} \text{s}$. This is close to the value reported by Neuhauser [59].

The comparison between experimental data and theoretical predictions has been satisfactory so far. The local shear model is currently accepted by many researchers [81] [82]. However, due to the uncertainty with respect to the structure of amorphous metals and the lack of systematic direct observations, the validity of many of the assumptions made for the local shear model is still to be verified. Among others, the following assumptions are the most important and the most needing verification: the scale of local shear events, whether it indeed involves only a few atoms, the existence of dilation and the way dilation is accomplished.

2.6.3 Computer Simulation results

Because there is no tool allowing one to observe directly the atomic movements in metallic glasses during plastic deformation, computer simulation becomes an effective
alternative. Some simulations have been very fruitful in providing a better understanding of
the inelastic deformation of amorphous metals. Pioneer work includes that of Maeda and
Takeuchi [77] and that of Srolovitz [49]. One of the most comprehensive simulations
conducted thus far is the one done by Deng et al. in 1989 [70]. In their study, Deng et al.
constructed a 2D 2-component glass by filling the simulation cell with polygons of
different sizes and shapes. The Radial distribution function (RDF) was calculated for a
constructed cell, and it closely resembles the actual RDF of metallic glass (Fig.2-21).
Molecular dynamics simulation was carried out assuming Lennard-Jones potentials (A-A,
A-B and B-B) up to fourth nearest neighbors. For detailed description of the simulation,
readers are referred to the paper by Deng et al. [54, 70]. A short summary of the results is
listed below.

• Simulated 2D glass could be sheared up to a strain of 0.27. The corresponding
  stress-strain curve was similar to actual observations (Fig.2-22).

• Inelastic deformation occurred as shear transformation involving only a few
  “atoms” locally. Such localized shear events were observed in the initial stage of
deformation when the material was still in the elastic range of the stress-strain
curve. (For further discussion, please refer to the section “2.6.2.2 High temperature
def ormation mechanism” for the roles of local shear and of elastic energy stored in
the neighboring matrix.)

• An elastic-plastic transition on the stress-strain curve was observed when the shear
  became continuous within the material.

• Shear induced dilatation was suggested by the build up of pressure on the rigid
  simulation cell (Fig.2-11).
• Shear localization was observed at high strain regime. Fig.2-23 shows the evolution of shear localization as the strain increased. The local shear strain was represented by the sizes of the squares at the sheared sites.

• Local dilatation was also recorded and demonstrates a strong spatial correlation with local shear events (Fig.2-24).

One should use these 2-D results with caution when considering 3-D phenomena. Nevertheless, these results provide a consistent picture of plastic deformation in MG. As listed on page 24, a number of these simulation results are consistent with actual experimental observations. Other results also support some of the important assumptions made in the local shear model.

2.7 Friction and Wear Properties of Metallic Glass

There is only a limited number of studies in the literature focusing on the friction and wear properties of MG.

Amuzu [83] measured the friction coefficient of 5 different metallic glasses, and found very low friction coefficients for all 5 materials, i.e., 0.01 – 0.02. Moreton and Lancaster [84], however, found fairly high friction coefficients in 17 metallic glasses, i.e., 0.4 – 0.9. Based on their experiences, Moreton and Lancaster suggested that the low friction coefficients reported by Amuzu could be the result of surface contamination. Very low static and kinetic friction coefficients of an Fe_{78}Bi_{13}Si_{9} alloy were reported by Imura et al. [5]: the kinetic friction coefficient was measured to be 0.04. However, no information on load sliding velocity and sliding distance was reported; therefore the reported low friction coefficient would be difficult to confirm. Miyoshi and Buckley [4] compared the friction
coefficients of amorphous Fe$_{67}$Co$_{18}$B$_{14}$Si$_1$ and that of 304 stainless steel. Although each material showed a transient in the early part of the friction trace, the MG sample gave a lower steady state value (0.2 for MG and 0.45 for stainless steel). The phenomenon of an early stage transient in friction coefficient has been observed in many sliding systems, including Fe$_{40}$Ni$_{40}$B$_{20}$, Metglas 2826 (Fe$_{40}$Ni$_{40}$P$_{14}$B$_6$), Metglas 2826MG (Fe$_{40}$Ni$_{38}$Mo$_{14}$B$_8$) [7], Fe$_{81}$B$_{13.5}$Si$_{3.5}$C$_2$ and Fe$_{67}$Co$_{18}$B$_{14}$Si$_1$ [9]. The origin of the transient was associated with the subsurface microstructure evolution during sliding.

Boswell and Street [10] studied the wear resistance of Pd$_{78.1}$Cu$_{5.5}$Si$_{16.4}$ MG alloy. They reported that the wear resistance was a function of material microstructure, the highest wear resistance being achieved when the material was a composite of crystalline precipitates and amorphous matrix. Wong and Li [85] found that the wear mechanism of Fe$_{81}$B$_{13.5}$Si$_{3.5}$C$_2$ varied with the roughness of the slider, and the amount of wear depended linearly on the sliding distance and the normal load. In the same study, the effect of annealing and crystallization on the wear properties were studied. The wear resistance decreased in the order of amorphous, annealed (still amorphous) then crystallized. Morris [6] recorded an early stage transient in the wear rate in compacted MetGlas 2826 (Fe$_{40}$Ni$_{40}$P$_{14}$B$_6$). For Fe$_{78}$Bi$_{13}$Si$_9$ amorphous alloy, the wear rate was found to vary with sliding speed in a rather complicated way [5]. In one study, MG Fe$_{67}$Co$_{18}$B$_{14}$Si$_1$ was described to have "superior wear resistance", because "there was a complete absence of any visible wear track on the amorphous alloy foil" [4]. However, the load was low (2.5 N) and an oxide layer was formed on the surface of the MG sample; therefore the high wear resistance may well be the property of the oxide rather than the property of the MG. In fact, one would expect a high wear resistance for any sample that was covered by a layer of hard oxide, provided
that the loading condition was mild enough so that the oxide layer did not break during sliding.

Crystalline products were found in wear debris after sliding for many MG’s [4, 7, 9, 85]. Many MG materials were found to be ductile in sliding although they may be very brittle under tension. For some MG systems, sliding induced surface oxidation [4, 84], which in turn affected the sliding behavior. This is true even when the sliding velocity is not high enough to raise the temperature significantly. Attempts had been made to rationalize the sliding behavior of MG based on its microstructure. Lee and Evetts suggested that relaxation of the sheared surface material may be responsible for the observed dependence of friction coefficient on sliding velocity [7]. Kishore et al. proposed that dynamical recrystallization, i.e., during deformation, may be the mechanism responsible for the observed shear localization. However, due to the difficulty of structure characterization for glass, there has been little success in efforts trying to correlate tribological behavior directly with material microstructure. In addition, most studies were conducted using ribbon-shape MG samples. Therefore the processes taking place underneath the sliding interface have been inaccessible.

In addition to experimental investigations, computational simulation has been proven effective in studying sliding behavior. Its effectiveness lies in the fact that simulation provides a third way to do research in addition to analytical modeling and experimental investigation. Strict analytical modeling often looks for a set of partial differential equations that completely describe the evolution of the system; however, most of the time, successful discovery and solution of these equations only become possible when one makes assumptions that grossly simplify the system. On the other hand, experimental studies can
produce large amounts of data, but interpreting the data can be difficult due to the complexity of the real system. In other words, analytical modeling often suffers from over simplification, whereas experimental investigations can be hampered by over complication. Computational simulation provides a valuable compromise in between. With the capability of hardware growing at an astonishing rate, so does the capability of computational simulation.

One of the most important simulation techniques is molecular dynamics (MD) simulation. In a typical MD simulation, the motion of each constituent molecule is assumed to be governed by the classical Newton's law, and the evolution of system is thereby numerically solved as an N-body problem. Systems far from equilibrium are in general quite difficult for analytical approaches, but MD simulation has been shown to be very effective.

For the above reasons, there is growing interest in the applications of molecular dynamics simulation in tribology [86, 87]. Comparisons between experiments and simulation results have shed light on some of the most fundamental questions in this field. Robbins and Krim [88] considered the origin of frictional force from the energy dissipation point of view. They experimentally investigated the frictional energy dissipation of thin films using a quartz crystal microbalance (QCM) and compared the experimental results with observations from MD simulations. It was suggested that the kinetic frictional force is due to energy dissipation via phonon generation and electronic excitation. The energy dissipated by phonon generation can be compared favorably with the QCM data. The electronic excitation mode is evident in that the friction force exhibits a sudden drop when the temperature goes below the critical temperature for superconductivity of the substrate.

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material. On the other hand, Robbins and Krim suggested that the static frictional force is a result of atomic level spatial registry across the interface, i.e., commensurate or incommensurate. Such atomic level registry produces a local energy minimum which has to be overcome before any sliding is possible. Such atom position registry is missing in incommensurate interfaces and therefore near-zero static friction was predicted by MD simulation [89]. At the macroscopic level, most interfaces are incommensurate but static friction is almost always present. A surface absorbent layer was suggested to be the key to understand this paradox. Flexible surface absorbent molecules deform upon contact of solids to accommodate surface potential corrugations on both surfaces, effectively establishing an atomic level registry. Harrison and Perry [90] studied the effect of absorbent layer in more detail. They reported that the chain length of the absorbed molecules exerts an observable effect on the friction force and argued that the chain structure determines the availability of certain paths for energy dissipation. In addition to the "physical" aspects of sliding, empirical potentials have been proposed to account for "chemical" bonding in small hydrocarbon molecules [91]. When there is enough material present at the interface, it becomes a layer of lubricant. Gao et al. studied the behavior of a multi-layer lubricant using MD [92]. It was found that when two asperities approach, lubricant molecules tend to line up in between.

These studies are mostly focused on surface phenomena during sliding. Given the very low load used, the surface approach was valid and effective. But in the majority of cases, sliding involves more than what is on the surface. When plastic deformation becomes the dominant means of energy dissipation, friction and wear properties are also determined by what is happening under the sliding interface. Hammerberg [93, 94] and Holian [95] et al
studied subsurface microstructure evolution during the sliding of pure copper using 2D molecular dynamics. A layer of nanocrystals was generated at the interface during sliding. The size of the nanocrystals evolves dynamically as sliding goes on but the typical size decreases with sliding velocity. The results seem to suggest that the typical size of the microstructure is determined at least partially by the strain rate. The role of strain gradient was not addressed in this study. Rigney and Hammerberg [96] compared the simulation results and experimental data. They suggested that the generation of nanocrystals is associated with mechanical mixing; dislocation generation and evolution of dislocation structures are important in understand the sliding behavior of crystalline materials.

Wear has been a more difficult subject to simulate on an atomic level, mainly because the manageable size of the system in a MD simulation is typically very small. Therefore loss of material is not affordable. However, some studies looked at deformation processes associated with wear. Landman et al. [97] looked at the nanoscale indentation process of a Ni (001) tip on Au (001). Upon close approach, the tip jumped to contact with the substrate. During separation, atomic scale necking was observed in the simulation, and after separation, transfer of Au atoms onto the Ni tip was observed. Very similar observations were reported for simulated indentation of Cu (111) on Cu (111) [98]. The sequence of events observed in the simulations was very similar to those observed in experiments on a larger length scale, i.e., indentation, plastic deformation and transfer [99]. However, it is not clear yet whether macroscopic transfer happens as a collection of atomic events or due to some other instability processes taking place on a different length scale.
2.8 Summation

Because of the random atomic structure, some MG materials provide desirable mechanical properties. For example, it has been reported that Fe-P based MG has a high tensile strength of about 4000 MPa; Fe-B based MG has a Vickers hardness of more than HV1200; in composite form with nanocrystalline particles a Zr-Al-Ni-Cu alloy exhibits a fracture toughness (K_{IC}) of 160 MPa\text{\textperiodcentered}m; Zr-Ti-Cu-Ni-Be MG shows a high elastic strain limit of 2.0%.

Unlike the case with crystalline materials, the mechanism of plastic deformation has not been determined for MG. This severely limits our capability to further strengthen MG alloys by manipulating their microstructures. Two mechanisms have been proposed for plastic deformation in MG. Both have their merits and limitations. The generalized dislocation model allows a much simpler picture in that it is closely analogous to our knowledge and intuition about deformation in crystalline materials. But the existence and stability of generalized dislocations in amorphous structure have to be properly addressed before this model can regain the acceptance it had in the early 1970s. The local shear model works well so far and has support from both observations and simulations. However, some of its assumptions were based on either bubble raft or 2D computer simulations and the existence of shear induced local dilation is still controversial.

A limited number of studies on the friction and wear properties of MG suggested that MG's tribological properties depend strongly on material microstructure as well as on the sliding conditions, including load, environment and sliding speed. Some MG systems might have low friction coefficients and others might have high wear resistance, but so far there have not enough data to support any generic claim about the merit of the tribological
characteristics of MG. Computational simulations provide important insights into the basics of friction and sliding motion. More fundamental understanding of tribology is expected from comprehensive simulations and, more importantly, from the combination and comparison of experimental observations and simulation results.
Fig. 2-1 Principle methods of liquid quenching: a) Piston-anvil b) Melt spinning c) Pendant drop melt extraction d) Twin roller quenching [19].
Fig. 2-2 The observed concentration ranges in the Co-Zr system for melt-spinning (m.s.), ion-mixing (i.m.), co-condensation (c.c.), mechanical alloying (m.a.) [19].
Fig. 2-3 Total reduced atomic pair radial distribution of amorphous Ni$_{40}$Ti$_{60}$ prepared by mechanical alloying (solid curve) and rapid solidification (dashed curve) [19].
Fig. 2-4 Critical cooling rate and maximum glass thickness (melt mold casting) vs. $T_g/T_m$. The alloy used for the present work was alloy 22. 1) Ni, 2) Fe$_{91}$B$_9$, 3) Fe$_{89}$B$_{11}$, 4) Te, 5) Au$_{78}$Ge$_{14}$Si$_8$, 6) Fe$_{83}$P$_{12}$C$_7$, 7) Fe$_{41.5}$Ni$_{41.5}$B$_{17}$, 8) Co$_{75}$Si$_{15}$B$_{10}$, 9) Ge, 10) Fe$_{79}$Si$_{10}$B$_{11}$, 11) Ni$_{75}$B$_9$Si$_{17}$, 12) Fe$_{80}$P$_{13}$C$_7$, 13) Pt$_{60}$Ni$_{15}$P$_{25}$, 14) Pd$_{82}$Si$_{18}$, 15) Ni$_{62}$Nb$_{28}$, 17) Pd$_{50}$Ni$_{40}$Si$_{20}$, 18) Au$_{55}$Pb$_{22.5}$Sb$_{22.5}$, 19) La$_{35}$Al$_{25}$Ni$_{10}$Cu$_{10}$, 20) Mg$_{65}$Cu$_{25}$Y$_{10}$, 21) Zr$_{65}$Cu$_{17.5}$Ni$_{10}$Al$_{17.5}$, 22) Zr$_{41}$Ti$_{14}$Cu$_{12.5}$Ni$_{10}$Be$_{22.5}$, 23) Ti$_{34}$Zr$_{11}$Cu$_{47}$Ni$_{8}$ [44].
Fig. 2-5 The Radial distribution functions for DRPHS model (solid line) and the experimental data of Ni\textsubscript{76}P\textsubscript{24} glass (dotted line). Both data set are plotted in unit of $\rho(r)/\rho_0$ [45].
Fig. 2-6 Distribution of volume per atom in an atomic packing model [47].
Fig. 2-7 Distribution of atomic site stresses  
a) negative stress  b) shear stress [48,49]
Fig. 2-8 Distribution of activation energies for anelastic response in Pd$_{80}$Si$_{20}$ glass [50].
Fig. 2-9 SEM of two families of deformation bands on Pd$_{77.5}$Cu$_6$Si$_{16.5}$ metallic glass after drawing down to area reduction ratio of 23% [58].
Fig. 2-10 Changes in the maximum stress and deformation mode of Zr$_{65}$Al$_{10}$Ni$_{10}$Cu$_{15}$ metallic glass as a function of temperature and strain rate. The open and solid symbols represent the homogeneous and inhomogeneous deformation modes respectively [60].
Fig. 2-11 Generalized dislocation model for an amorphous metal [66].

a) Homogeneous deformation

b) Localized deformation
Fig. 2.12 Increase in pressure on the 2D simulation cell due to the deformation induced volume increase [70].
Fig. 2-13 Idealization of local shear in high temperature mechanism [73].
Fig. 2-14 Shape of assumed interlayer shear resistance of a metallic glass [74].
Fig. 2-15 Tensile stress-strain curves at three average strain rates at three different temperatures [76].
Fig. 2-16 Temperature dependence of strain rate sensitivity for Pd$_{80}$Si$_{20}$ glass [76].
Fig. 2-17 Idealization of local shear in low temperature mechanism [74].
Fig. 2-18 Dependence of the flow stress on the temperature for Pd$_{80}$Si$_{20}$ glass and for Pd$_{77.5}$Cu$_6$Si$_{16.5}$. Solid curve is the fit obtained with the low and high temperature models [74].
Fig. 2-19 Illustration of creation of free volume by squeezing an atom of volume $V^*$ into a neighboring hole of a smaller volume $V$ [73].
Fig. 2-20 Computed plastic flow in shear band region and matrix region for Pd$_{80}$Si$_{20}$ undergoing shear dilation. Upper part of the figure is the reduced remote shear resistance [74].
Fig. 2.21 Arrangements of polygons of atomic sites of a 2-D model glass. Positions of 5-sided and 7-sided polygons are noted on the upper figure. Lower figure shows the calculated RDF [70].
Fig. 2-22 The shear stress-shear strain curve of the model atomic glass [70].
Fig.2-23 Sequence of development of shear localization in the simulation cell due to the accumulated effect of deformation induced dilatations.

a) $\gamma = 0.05$  b) $\gamma = 0.10$  c) $\gamma = 0.15$  d) $\gamma = 0.20$ [70]
Fig. 2-24 Distribution of total accumulated local dilatations at atom sites at total strains of
a) $\gamma = 0.05$  b) $\gamma = 0.10$  c) $\gamma = 0.15$  d) $\gamma = 0.20$ [70]
CHAPTER 3

EXPERIMENTAL SETUP

3.1 THE TEST EQUIPMENT

A pin/disk geometry was used for experimental investigations. The disk was mounted on a shaft that rotated around a horizontal axis. The pin was brought into contact through a pulley and lever system. Frictional force was monitored by a full bridge arrangement of four strain gauges mounted on the pin holder arm (Fig.3-1). The average disk wear rate was determined by measuring disk weight before and after each test. Several in situ monitoring devices were built into the system. These included a Kelvin probe and a CCD camera. A Kelvin probe (KP) is a non-contact device capable of detecting the difference in contact potential of the probe material and the probed material. In a high vacuum environment, the Kelvin probe signal (KPS) is proportional to the difference of the electronic work function of the probe and the sample. In air, however, the KPS is still sensitive to changes in the surface condition of the sample. A. Zhariin applied the KP technique to sliding tests [100]. During tests, the KP monitors the disk surface and the variations observed in KPS are recorded. Zhariin proposed that the KPS variations are due to the accumulation of defects
underneath the sliding interface [100]. Kasai et al. suggested an alternative explanation which emphasized changes in the sample surface chemical composition during sliding. In the latter study, a good correlation was found between the KPS and the oxygen concentration on the sample surface. A detailed description of the principle of KP and examples of KP applications in tribology can be found in reference [101].

3.2 THE MATERIAL

Two kinds of material were used in the study, i.e., Zr\textsubscript{41.2}Ti\textsubscript{13.8}Cu\textsubscript{12.5}Ni\textsubscript{10.0}Be\textsubscript{22.5} bulk metallic glass alloy (concentration in at.%) and 52100 stainless bearing steel. BMG alloy was produced by direct casting at Howmet Corp. The 52100 bearing steel was provided by Jorgenson Steel. Disks were 31mm in diameter and 3mm in thickness. They were cut from either bulk metallic glass alloy or 52100 steel. Pins were either BMG square rods (3mm×3mm×12mm) or 52100 bearing steel balls with 6mm diameter.

The structure of the as received Zr\textsubscript{41.2}Ti\textsubscript{13.8}Cu\textsubscript{12.5}Ni\textsubscript{10.0}Be\textsubscript{22.5} alloy was examined by X-ray diffraction and high resolution TEM. Both technique confirms its amorphous structure (Fig.3-2 and Fig.3-3).

3.3 THE TEST CONDITIONS

Normal loads were 0.1 – 1.2 kgf, and sliding speeds were typically 0.05 m/s. To determine the sliding behavior under higher sliding speeds, sliding speeds up to 1.16 m/s were used. Disk surfaces were prepared by standard metallographic procedures, with the final polish using 1.0 μm diamond paste. The test apparatus was contained within a bell-jar system equipped with a two stage pumping system consisting of a mechanical pump and a turbomolecular pump. The vacuum level during a vacuum test was typically 3.0×10\textsuperscript{-5} Torr.
or $4.0 \times 10^{-3}$ Pa. X-ray diffraction (XRD) confirmed that the polished surface remained amorphous. Disks and pins were ultrasonically cleaned in acetone, methanol and distilled water before tests.

### 3.4 Post-test Characterization Methods

Worn surfaces and debris were characterized by optical microscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), XRD, transmission electron microscopy (TEM), differential scanning calorimetry (DSC), X-ray photoelectron spectroscopy (XPS) and microhardness. SEM and EDS were done with a Philips XL30-FEG instrument. XRD was done with a Scintag PAD-V system using Cu K$_\alpha$ radiation, DSC was done with a Seiko DSC320, XPS used a VG ESCALABII with a Mg K$_\alpha$ source and TEM was performed with Philips CM-200 and CM-300 FEG (high resolution) instruments.
Fig. 3.1 Experimental set-up for pin/disk tests. Shows the pulley system, CCD camera and the Kelvin Probe.
Fig. 3-2 XRD pattern of the as received Zr$_{41.2}$Ti$_{13.8}$Cu$_{12.5}$Ni$_{10.0}$Be$_{22.5}$ metallic glass sample.
Fig. 3-3 High resolution TEM image of the as received $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10.0}\text{Be}_{22.5}$ metallic glass sample.
CHAPTER 4

MOLECULAR DYNAMICS (MD) SIMULATION

Complementary to the experimental studies, a molecular dynamics (MD) simulation was conducted to study the sliding behavior of amorphous metal. In this chapter, the setup of the MD simulation will be discussed.

4.1 POTENTIAL AND COMPOSITION

Ideally, one uses potentials and compositions closest to those of the alloy system investigated experimentally. However, for the bulk metallic glass alloy system Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}, the precise forms of the interatomic potentials are unavailable for many of the atomic pairs involved. In addition, a large scale 3D simulation of a five component system would involve excessive computational time and resources. Therefore, a two-component 2D model amorphous system was used in the simulation. Despite these simplifications, it was anticipated that the simulation results from this simplified model system would be useful in interpreting experimental observations and might stimulate new ideas about sliding phenomenon.
The system used for these simulations was a two-component system interacting via Lennard-Jones potentials. Of course, other potentials for MD simulation, for example the embedded atom potential, could be used. However, the Lennard-Jones potential accounts for the major features of metallic interactions in a concise form albeit neglecting many-body interactions [102]. Therefore, although it does not simulate a specific metallic glass system, simulations with a Lennard-Jones potential are likely to exhibit phenomena relevant to sliding behavior. A typical Lennard-Jones potential can be expressed as,

\[ U_{ij}(r) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} \right] \]  

(4.1)

where \( i \) and \( j \) denote the species of the particles involved, either \( L \) (for large) or \( S \) (for small) and \( \sigma \) is the distance at which the interatomic potential \( (U) \) is zero; \( \varepsilon \) is the bond strength and \( N \) is the particle number. In this study, the values of the parameters \( \sigma, \varepsilon \) and \( N \) were the same as those used by Lancon et al. [103]. The values are shown in equations 4.2 - equation 4.4.

\[ \sigma_{LL} = 2\sin\left(\frac{\pi}{3}\right) = 1.1756; \quad \sigma_{SS} = 2\sin\left(\frac{\pi}{10}\right) = 0.6180; \quad \sigma_{LS} = \sigma_{SL} = 1.0 \]  

(4.2)

\[ \varepsilon_{LL} = \varepsilon_{SS} = \frac{1}{2}; \quad \varepsilon_{LS} = 1.0 \]  

(4.3)

The composition of the system was such that the ratio between the number of particles of species \( L \) to the number of particles of species \( S \) satisfied

\[ \frac{N_L}{N_S} = \frac{1 + \sqrt{5}}{4} \approx 0.80902 \]  

(4.4)

This system was studied earlier by other researchers [103] and was found to have a quasicrystalline ground state. It was chosen for this study primarily because it is easily
quenched into a metastable glassy state. The glass transition temperature was reported to be 0.3 in rescaled units. The calculation proceeds in a standard sequence, beginning with specifying initial conditions. Pair-wise interactions via the chosen potential yield local forces, these give accelerations, and these in turn give new positions. The simulation continues by repetition of this basic cycle. A more detailed description of the simulation process is given in the Appendix, with an emphasis on computational implementation.

All quantities in the simulation are expressed in dimensionless units by rescaling using the atomic mass $m$ and parameters in the pair potential ($\sigma$ and $\varepsilon$). Details of the rescaling are given in the Appendix.

4.2 Sample preparation

A system with 10,000 atoms, i.e., 5528 atoms of species $S$ and 4472 atoms of species $L$, was generated in a square simulation cell with periodic boundary conditions defined at all four boundaries. During sample preparation, a Nosé-Hoover thermostat and a Parinello-Rahman barostat were implemented in the algorithm for temperature and pressure control [104]. The system was equilibrated at high temperature and pressure, then quickly quenched (from $T = 2.3$ ) to a low temperature of $T = 0.1$, i.e., about 30% of the glass transition temperature, $T_g$. During the quench, a positive pressure was imposed on the system to suppress the formation of voids. Pressure was released to zero after reaching $T = 0.1$. Finally the sample was cooled further to $T = 0.01$. After the full quench sequence, the sample was "equilibrated" at $T = 0.01$ and $P = 0$ for 100-rescaled time units. The prepared sample material is shown in Fig.4-1 together with the calculated radial distribution function (RDF).
Next the mechanical properties of the prepared sample were determined. Fig.4-2 is the stress-strain relationship measured by a simple uniaxial tensile test at a strain rate of 0.001 (rescaled). It is obvious from the plot that the material responded in an elastic-perfectly-plastic manner with very little observable work hardening. Elastic-perfectly-plastic response is expected to be the generic mechanical response for materials lacking the microstructure necessary to produce work hardening. This was experimentally observed some 25 years ago in the Pd-Cu-Si system [64] and more recently in Zr based BMG systems [105, 106] and in La-based BMG systems [107]. The rescaled Young's modulus was measured from the plot to be about 28.4 and the Poisson's ratio was about 0.55 (Note: The Poisson's ratio has a maximum value of 1.0 in 2D). These values agreed with those reported in an earlier independent study [108].

4.3 SET-UP OF THE SLIDING PAIR

In order to form the sliding pair, the periodic boundary condition in the Y direction was relaxed. Then, a duplicate of the prepared sample was made and translated along the X direction for 1/2 the width of the simulation cell. Because the periodic boundary condition still exists in the X direction, those atoms that moved out of the cell on the right hand side would enter the system at the left hand side. The sliding pair was formed by putting the translated duplicate on top of the original sample (Fig.4-3). Sliding tests were conducted using this 20,000-atom 2D amorphous system.

To simulate the normal load in experiments, an initial pressure was applied to the sliding pair in the Y direction. The pressured sample was equilibrated before the onset of
sliding. For the simulation results described in this paper, the initial rescaled normal load was chosen to be 1.0.

In experiments, heat diffuses away from the sliding interface. To simulate this effect, two reservoir regions were defined at the upper and lower ends of the sliding pair (Fig.4-3). During the simulation, a Nosé-Hoover thermostat algorithm was implemented in the reservoirs. In experiments, the external forces needed to maintain the sliding motion are usually applied some distance away from the interface. Similarly, in the simulation, forces were applied only to the atoms in the reservoirs. Except for the temperature control and force application, the atoms in the reservoirs were treated exactly the same as those in the rest of the system, and atoms were free to enter or leave the reservoir regions.

In the corresponding experiments, the initial pin/disk contact was made when the disk was rotating; i.e., there was a relative speed between the pin and the disk. The simulations were initiated in a similar fashion. At $t = 0$, all of the atoms in the upper block were given a velocity in the positive $X$ direction with the magnitude equal to $V_s/2$, while all the atoms in the lower block were given a velocity in the negative $X$ direction with exactly the same magnitude, $V_s/2$. Therefore, at $t = 0$ the relative sliding velocity of the system was $V_s$, the desired sliding velocity. At time $t > 0$, the temperature and frictional force controls started to operate in the reservoirs. Temperature in the reservoirs was kept low at 0.01 (rescaled). The difference between the actual sliding velocity and the desired sliding velocity was used as the input to a feedback loop in sliding force control such that the average sliding velocity over long time is $V_s$. Experience suggested that the choice of the barostat time constant (see Appendix, equation A.8) directly affects the stability of the system, thus introducing

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unnecessary complexity into the system. Therefore, the volume of the simulation cell was kept constant throughout the simulation for this study.

Some features of the system used in this study were like those used by J.E. Hammerberg et al. [93, 94, 95]. In particular, these procedures include the initiation of the sliding motion, the definition of two reservoirs, and the periodic boundary condition in the X direction. The simulation procedures used for this study differ from those of Hammerberg et al. in the system composition, interatomic potentials, constraint during sliding (i.e., constant pressure vs. constant volume), and shear force application.
Fig. 4-1 The prepared sample for MD simulation and its RDF.
Fig. 4-2 Stress-Strain relationship measured from uniaxial tensile test conducted at a rescaled temperature of 0.01 (about 3% of the glass transition temperature, $T_g$). Note: the maximum possible value of $v$ is 1.0.
Fig. 4-3 The set-up of the sliding simulation cell.
5.1 **Friction Coefficient and Wear Rate**

5.1.1 *Friction coefficient and wear rate vs. load and environment*

Friction coefficient showed an early transient when tested in air (Fig. 5-1). Wear rates tended to be higher during early stages of sliding, then decreased to lower steady-state values (Fig. 5-2).

The steady state friction coefficient depended on the normal load and test environment. (Fig. 5-3) In general, a higher normal load leads to a lower friction coefficient. For a given load, sliding in air gave a lower friction coefficient and lower fluctuation amplitude compared with sliding in vacuum. Steady state wear rate (in $10^{-10}$ kg/m) increased with normal load (Fig. 5-4). For a given load, wear rate was lower in vacuum compared to that in air.

Surprisingly, a different counterface material did not alter either the friction coefficient or the wear rate significantly. Insensitivity to the choice of counterface material was associated with transfer of BMG onto the counterface material (52100), which generated a
self-mated system. The friction coefficient and wear rate of 52100 steel vs. 52100 steel obtained using the same test equipment are also plotted on Fig.5-3 and Fig.5-4 for comparison. Both the friction coefficient and the wear rate of BMG are comparable to those of 52100 steel.

The widely held belief that metallic glass in general has better tribological properties is mostly based on the test results on thin ribbon-shaped iron-based MG samples [1, 4, 5, 6, 7]. However, Fig.5-3 and Fig.5-4 clearly show different results for the BMG used for the current investigation. Blau in his recent research on a Zr-Cu-Ni-Ti-Al BMG also reported that friction coefficient and wear rate are comparable to those in typical crystalline engineering materials [11]. Based on these results, there is no indication of exceptional tribological properties for the BMG alloy $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10.0}\text{Be}_{22.5}$ when tested with a pin/disk geometry without lubrication. This conclusion does not exclude the possibility that other BMG systems might have very good friction and wear properties, but it is clear that one should not simply assume that all BMG’s have exceptional tribological properties.

5.1.2 Wear rate and friction coefficient vs. sliding speed

Most of the tests used a sliding speed of about 0.05 m/s to keep thermal effects low. However, since metallic glass is thermodynamically metastable, thermal effects at high sliding speeds could be important in potential applications; other effects, like the high strain rate accompanying a high sliding speed, may also be important in applications. Therefore, the relationship among wear rate, friction coefficient and sliding speed was investigated.
During this series of tests, both the pin and the disk were MG; test environment was air and the normal load was set to be 0.5 kgf. Sliding speed ranged from 0.05 m/s up to 1.16 m/s.

Fig.5-5 is the measured relation between wear rate and sliding speed. It is shown on the figure that sliding speed does have a noticeable effect on wear rate for both the pin and the disk. The effect was more pronounced for the pin. Starting from a low sliding speed of about 0.1 m/s, the pin showed a drop in wear rate as the sliding speed increased up to about 0.5 m/s, after which there was an increase. The increase was dramatic when the sliding speed exceeded 1.0 m/s. The wear rate of the disk showed a moderate decrease as the sliding speed went from 0.05 m/s to about 0.5 m/s. The measured disk wear rate at 1.0 m/s is slightly higher than that at 0.5 m/s. However, as the sliding speed increased further, the disk wear rate dropped, in contrast to the drastic increase in wear rate for the pin.

To rationalize the observed behavior we consider two main effects, namely the strain rate effect and the temperature effect. We assume the strain rate to be approximately proportional to the sliding speed, at least for the near surface region. We also assume that significant temperature rise will not occur until the sliding speed is beyond 1.0 m/s. Following the analysis of kinetics of plastic deformation, we would expect that the strain rate would correspond to a modification of test temperature, a higher strain rate corresponding to a lower test temperature. An example of tensile yield strength at different strain rates and temperatures can be found in the paper by Megusa and Argon [76]. A plot of their data is shown in Fig.2-15. The hardness of the material usually goes up as the temperature goes down; therefore, the initial decrease in the wear rate for both pin and disk could be rationalized as a result of a shear strain rate effect. When the sliding speed
increased further up to about 1.0 m/s, the local heating became significant. In fact, after a test at 1.16 m/s, the disk was warm to the hand. We have to consider contributions from both temperature and strain rate terms. Temperature rises much more rapidly than strain rate as the sliding speed increases. So, beyond a certain critical sliding speed, the temperature effect will be the dominant one. Also considering the fact that the pin/disk geometry is not a symmetric setup, it is expected that the pin (which is in constant contact) experiences high local heating earlier than the disk. Based on the above considerations, it is reasonable to expect that when the sliding speed exceeds 1.0 m/s, local heating becomes significant for the pin but remains moderate for the disk. This asymmetric heating results in a softer pin riding on a harder disk, resulting in a much higher wear rate for the pin and a drop in the wear rate for the disk, which was rubbing against a softer pin.

Similar considerations also apply to the observed friction coefficient evolution with respect to the sliding speed, as shown in Fig.5-6.

At higher sliding speed, crystalline peaks in XRD patterns of wear debris were found more frequently. This is considered to be a result of higher local heating at higher sliding speeds. However, the peak positions and peak heights could not be correlated with sliding speed and/or sliding environment in a simple manner (Fig.5-7). This might be a result of the complexity of the crystallized phases and statistical sampling of the crystalline particles.

Since the experiments were carried out in air, we ought to consider the effect of oxidation on both wear rate and friction coefficient. On both the pin and the disk, patchy areas of high oxygen concentration were found at all tested sliding speeds. So it is unlikely that oxidation would contribute to the minimum in wear rate and friction coefficient.
However, more work is needed to understand the relation between oxidation and the sliding speed.

5.2 **Morphology of Wear Track, Pin and Debris**

5.2.1 *Wear track*

Fig. 5-8 is a secondary electron SEM image of a wear track generated during sliding of BMG against BMG in air with a sliding speed of 0.05 m/s and a normal load of 1.0 kgf. The morphology of the track indicates that the material experienced plastic deformation. The bright particles on the track have a higher oxygen content according to EDS analysis. The distribution of these particles was not uniform along the track; they were distributed as "patches" on the worn surface. The distribution and evolution of oxygen-rich patches were monitored in situ by a Kelvin probe. Results obtained from the Kelvin probe correlated well with visual observations and EDS analyses, indicating that the patches are important in the sliding behavior of the BMG alloys [101]. The oxygen-rich patches were found only after tests in air. Similar morphologies were observed for tracks generated by sliding of a 52100 steel pin against a BMG disk. After tests in air, the hardness along the track typically increased to about HV580. The oxygen-rich patches were somewhat harder, with an average hardness of HV640. Hardness tests on cross-sections provided similar readings.

Fig. 5-9 shows a typical wear track after testing in vacuum. Grooves and lateral flow were visible but the bright regions found after air tests were absent. The average track hardness after tests in vacuum remains approximately the same as in the original BMG material.
5.2.2 Pin

When the pin was BMG, its morphology was very similar to that of the track; i.e., grooves and bright patches were evident for tests in air. When the pin was a spherical 52100 steel pin, transfer material was found on the pin as shown in Fig.5-10. Chemical analysis suggested that transfer material was mainly from the disk, so the test became essentially self-mated. The amount of transfer was higher for tests with higher load or for tests in vacuum.

5.2.3 Debris

Flake and plate like debris were the most common type of debris observed in both air and vacuum tests. On the surfaces of debris collected from air tests, bright particles similar to those on the wear track were found (Fig.5-11). These particles are absent on the debris collected during testing in vacuum. The number of these oxygen-rich particles decreased as the sliding speed increased. Cutting-chip debris showing serrations indicative of shear instability were also collected, mostly from tests in air. A debris particle with such features can be seen in Fig.5-11. XRD analysis showed that most of the debris particles were amorphous. However, a very small amount of crystalline material was detected in debris by using TEM. The amount of crystalline material produced by sliding was found to increase as the sliding speed increased, which suggests either partial crystallization or increased formation of oxide products. Although most of the wear debris and the original BMG material were amorphous according to XRD, thermal analysis suggested that the structure may have changed during sliding. More discussion on sliding induced structure changes can be found in section 5.3.
Although the Zr$_{41.2}$Ti$_{13.8}$Cu$_{12.5}$Ni$_{10.6}$Be$_{22.5}$ BMG has limited tensile ductility, it is ductile under sliding conditions. Chemical analysis showed that most of the debris collected in air tests had a composition similar to that of the bright patches on the wear track. These observations, combined with hardness data, suggest mechanisms for the formation of both kinds of debris observed in Fig.5-11. Plastic deformation exposes fresh surface to the ambient environment. Because of the chemically active elements contained in the BMG (Zr and Ti), a thin oxide layer forms quickly. Surface passivation was confirmed by X-ray photoelectron spectroscopy (XPS) analysis (Fig.5-12). During continuing plastic deformation, the thin layer of oxide is broken and mixed with unoxidized BMG. As the amount of oxygen increases the hardness of the patches increases. Typical debris particles are derived from patches of mixed material. If the mixed material on the pin becomes at least 20% harder than the BMG and has a suitable geometry, it can cut the BMG [109]. The hardness of the mixed layer generated after an air test was about HV700 based on measurements made on cross-sections. The near-surface material had a hardness of HV450 due to work softening (Fig.5-20). Therefore, the hardness difference is sufficient to allow occasional production of cutting chips, as observed in Fig.5-11, for BMG sliding on BMG in air.

5.3 **Sliding Induced Structure Changes**

5.3.1 *Sliding induced crystallization*

When sliding involves crystalline material, structure modification often takes place in the regions close to the sliding interface. Such structure changes may involve an increase in dislocation density, generation and evolution of dislocation cell structure, mechanical
mixing, mechanical alloying, material displacement along the sliding direction and sometimes recrystallization in the heavily deformed regions.

It is reasonable to expect that structure changes also take place when sliding involves MG alloys. Fig.5-13 shows a dark field TEM micrograph with corresponding electron diffraction pattern of wear debris collected from a sliding test of MG vs. MG, in air under 1.0 kgf normal load at 0.05 m/s sliding speed. It is obvious from the images that crystalline material was generated during the sliding of two pieces of amorphous material. Three of the rings on an electron diffraction pattern matched the strongest peaks expected for ZrO\textsubscript{2} (either cubic or tetragonal baddelyite). However, a complete identification of the crystalline phases could not be achieved due to the complexity of the diffraction pattern and also the lack of information about the equilibrium phase diagram of the alloy system. The presence of an oxide phase in wear debris collected during testing in air was expected given the presence of active elements like Zr and Ti in the alloy, and it is consistent with the XPS data shown in Fig.5-12. There may be non-oxide crystalline phases generated during sliding as well, since crystalline peaks were observed on XRD of debris collected during a test in vacuum (the bottom trace on Fig.5-7). The amount of crystalline material generated during sliding is very small; the majority of the debris collected was still amorphous.

5.3.2 Structure changes in the amorphous material

The majority of the debris collected during sliding tests were amorphous as evident in the debris’ XRD patterns (Fig.5-14). But debris differs from the as-received amorphous MG in that it experienced extensive amounts of deformation; if the test is in air, it can also have different chemical composition. These differences showed up in the DSC traces of
debris collected under different test conditions (Fig.5-15). Compared with the DSC trace of the as-received BMG, none of the four traces of the debris show the two lower temperature peaks around 410°C. The shape and position of the higher temperature peak (the one around 700°C on the trace of the as-received BMG) also change in a consistent way reflecting the differences in test conditions, i.e., load and environment. The simplest explanation would be that sliding causes more thorough homogenization of the alloy via mechanical mixing processes, thus eliminating prime sites for nucleation of new phases. The tendency for more thorough mixing during sliding is supported by the observation of sliding induced re-amorphization which is described in section 5.3.3. Alternatively, changes in the distribution of oxygen may be responsible. Microhardness measurements on the surface of the wear track suggested a hardness increase for the oxygen-rich patches generated in air tests. These later broke off to become part of the debris. The oxygen-rich patches are shown in Fig.5-8; data and discussion of the corresponding hardness profile obtained on a longitudinal cross-section can be found in section 5.4.2.

5.3.3 Sliding induced re-amorphization

Compared to the crystalline state, the metallic glass structure is thermodynamically metastable. Therefore, for industrial applications, it is important to know how BMG materials would behave if devitrification occurs in service. To address this, the sliding of BMG in its annealed (devitrified) form was investigated.

Annealing was carried out at 500°C for 2 hours. The hardness of the annealed BMG increased from HV530 to HV720. The diffraction pattern of the annealed BMG, shown in
Fig. 5-16a, clearly shows that the BMG crystallized during annealing. There is no detectable change in the average composition measured by EDS before and after annealing.

Sliding tests were conducted using annealed BMG vs. annealed BMG, in air and in vacuum. XRD patterns from the collected debris showed broad peaks (trace b on Fig. 5-16), which suggests that the annealed BMG was re-amorphized during sliding. Steady-state friction coefficients were found to be 0.6 for the test in air and 0.8 for the test in vacuum, values comparable with those obtained for as-received BMG (fully amorphous) under similar conditions. Wear rates for the annealed BMG were also found to be comparable to the values for the amorphous BMG. Wear tracks generated on the annealed BMG look very different from those on the as-received BMG. On the track generated in air, parallel grooves were found with oxygen-rich particles on the track (Fig. 5-16c). The composition of debris after an air test was found to be similar to that of the particles found on the track. On the tracks generated after vacuum tests, grooves were irregular, flow of material was evident, and oxygen-rich particles were absent (Fig. 5-16d).

It is interesting to find very similar friction coefficients and wear rates for the annealed and the as-received BMG. The material structures and properties were very different before and after annealing. However, these differences only persisted near the surface for a short time after the start of sliding. The softer re-amorphized material allowed shear to be localized at the sliding interface, giving sliding behavior similar to that of the as-received amorphous BMG.

The re-amorphizing found in these tests is not surprising since the BMG alloy Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5} is a strong glass former [14] which means it does not take much energy to go from the crystalline structure to the amorphous structure. Perepezoko [34] and
his colleagues reported amorphizing of layers of thin pure metal sheets subject to repeated rolling. Ball milling of pure metallic powders can also lead to amorphizing [110]. The common factor involved in these amorphizing processes is plastic deformation which provides the energy needed for the transformation from crystalline to amorphous. Continuous deformation increases the density of defects in crystalline materials and therefore increases the free energy. Hence, if recrystallization does not intervene, there will be a point where the free energy of the deformed crystalline material becomes higher than that of an amorphous material with the same composition. For strong glass formers, the critical density of defects is low enough so that only a moderate amount of deformation is sufficient to trigger the crystalline to amorphous transformation.

The idea outlined in the previous paragraph may seem contradictory to the observation of sliding induced crystallization (section 5.3.1), i.e., which product is thermodynamically more stable, crystalline or amorphous? Considering the fact that the majority of the debris collected was amorphous, it may not be far-fetched to say that the amorphous phase is the preferred product during sliding. The small amount of crystalline material could be products of local heating near asperity contacts.

If an amorphous structure is preferred for some applications involving sliding contact, then BMG materials would have the desired ability to self-heal any crystallization caused by local heating. This would tend to stabilize the desired amorphous structure.

5.4 CHARACTERISTICS OF CROSS-SECTIONS

Observations of the wear tracks showed that the near-surface portion of the BMG specimens plastically deformed in all cases. Thus the tribological properties of BMG
depend not only on the surface but also on processes taking place beneath the surface. Studies of cross-sections provide useful information on this deformed region.

5.4.1 Transverse cross-sections (normal to the sliding direction)

Fig.5-17a is a back-scattered electron image of a transverse cross-section of a wear track generated in vacuum during sliding of BMG against BMG with 0.2 kgf normal load at 0.05 m/s sliding speed.

The worn surface was rough with typical grooves and ridges. Careful examination revealed that some of the ridges were not produced by a plowing process alone. The feature marked as "A" contains cracks and voids in it while feature "B" is similar to the substrate material structurally. Features like "A" could have been produced by transfer of heavily deformed material, while "B" would probably be a result of deformation alone. Chemical analysis showed that features "A" and "B" had essentially the same composition as the substrate material, which is expected for a self-mated test in vacuum.

The transverse cross-sections after tests in air looked very different from those generated in vacuum. Fig.5-17b is a back-scattered electron image of a cross-section of a wear track generated in air for BMG vs. BMG under 1.1 kgf normal load at 0.05 m/s sliding speed. The interface appeared smoother compared to that of a typical vacuum test. A layer with defects similar to those at "A" in Fig.5-17a, was also observed. According to EDS analysis, oxygen content was at least 1.5 times higher in this layer compared to the substrate material. The enhancement of oxygen content is consistent with the observed atomic number contrast in the BSE image.
5.4.2 Longitudinal cross-sections (parallel to the sliding direction)

Shown in Fig.5-18 is a longitudinal cross-section of a wear track after a test in vacuum involving BMG vs. BMG with 0.2 kgf normal load and 0.05 m/s sliding speed. It is well known from profilometer measurements that traces across a wear track are typically "rougher" than those parallel to the same wear track. This difference is evident in the cross-sections of the BMG system also. Cracks running parallel to the interface were found on the cross-section and they appeared at two equally spaced depths. Similar equally spaced cracks were found on the same cross section 400 \( \mu \)m away from the region shown in Fig.5-18. These cracks divided the material into three regions, i.e., the surface layer, the intermediate layer and the substrate. The composition of each of these regions was examined using EDS. Except for a slight increase of oxygen content toward the surface, all three regions had essentially the same composition, as expected for a self-mated test in vacuum.

Fig.5-19a shows a longitudinal wear track cross-section after a test in air with 1.1 kgf normal load and 0.05 m/s sliding speed. Of particular interest is the appearance of a slightly darker layer at the surface. Because Fig.5-19a is a back-scattered electron image, this darker layer probably had a lower average atomic number, as confirmed by the EDS analysis shown in Fig.5-19b. The composition of this darker layer differed from the substrate material only in the oxygen content, which is about 3.6 times higher in the darker layer compared to the substrate material.

A simple calculation is consistent with the results from chemical analysis. Earlier XPS studies of the wear track indicate that at room temperature a few atomic layers of BMG at the surface are oxidized. Therefore, if sliding did not continue, the surface would become
passivated quickly. Assume that 50 Langmuirs (1 Langmuir exposure equals $10^{-5}$ Torr·sec.) exposure to air is necessary for passivation. This takes account of the probability that not every incoming oxygen molecule successfully reacts with the BMG. The average vacuum level during a test is about $3 \times 10^{-5}$ Torr and the disk rotation is at a frequency of 2 Hz. Therefore, the sample surface experiences about 15 Langmuirs of exposure during each rotation. During the air test there will be more than enough oxygen available to passivate the fresh surface for every rotation. Using these numbers, one can estimate the oxygen content in the mixed layer for an air test to be about $50/15 = 3.3$ times the amount for a vacuum test. This is close to the value found from actual measurements (Fig.5-19b).

Mechanical mixing is suggested as the responsible mechanism for the formation of the slightly darker layer in Fig.5-19a. During sliding, the near interface region often experiences large strain and strain rate. Therefore instability is likely to take place. The flow patterns caused by instability associated with high strain rate shear were observed by Li et al. in an Al alloy under friction-stir welding conditions [111]. The instability thus established is expected to cause material flow normal to the sliding direction near the sliding interface (see also discussions in section 6.2). For rough surfaces, plowing of asperities is also expected to increase the degree of mechanical mixing.

Multiple cracks can be seen on this cross-section, but unlike the case of the vacuum test, where they run parallel to the surface, cracks in the air test run through a range of depth.

It is difficult to unambiguously identify the origin of the cracks observed on cross-sections. They could have initiated subsurface and then made their way to the surface. Rosenfield [112] has calculated the driving force for a locally weak region below the
surface to undergo shear instability in ductile material. He concluded that the driving force, $K_{II}$, peaks at some depth below the surface. When it exceeds $K_{IC}$ a crack will grow. In a separate investigation, Gilbert et al. [113] showed that crack initiation in BMG is less sensitive to stress level compared with conventional crystalline materials. Both studies suggest that crack initiation, even at low stresses is possible in the subsurface material near a sliding interface. Deng and Argon [70] reported based on MD simulations that free volume regions tend to line up under shear (Fig.2-24), giving rise to planes of weakness and localized shear bands. In sliding, they would tend to line up parallel to the sliding direction, suggesting a possible mechanism for crack propagation parallel to the interface. However, other calculations, assuming low ductility, indicate that even if a subsurface crack under compression and shear is initially parallel to the sliding surface, it should eventually turn toward the surface [114]. Another possibility is that the observed cracks originated at the surface and then propagated in the subsurface region for some distance before they emerged again on the surface. This would be consistent with the high values of the measured friction coefficients, indicating that the maximum shear stress would appear at the surface rather than below it [115].

Another prediction made by Rosenfield states that the crack deflection angle should increase as the ratio of the compression to shear increases [112]. In a sliding test, this would mean that the deflection angle should increase when the friction coefficient decreases. The friction coefficient for a vacuum test with 0.2 kgf normal load was measured to be higher than that of an air test under 1.1 kgf normal load. Therefore a more irregular crack pattern is expected for an air test with 1.1 kgf normal load. Perhaps this is at least partially responsible for the differences in the crack patterns observed in Fig.5-18 and
Fig. 5-19a. The cracks in vacuum with 0.2 kgf load were longer than those in air with 1.1 kgf load.

5.5 HARDNESS PROFILES IN CROSS-SECTIONS

In crystalline materials, grain or phase boundaries serve as displacement markers as microstructure evolves during sliding. However, no such features are available for amorphous materials. Therefore, microhardness measurements on the cross-sections were used to check for changes in structure near the surface.

Fig. 5-20 shows the Knoop hardness profiles collected for cross-sections, including tests in air and vacuum. One interesting feature is the existence of a softer layer adjacent to the contacting interface. This appeared on all three hardness profiles. The thickness of the soft layer was between 30 μm and 70 μm. This is a real effect, not an artifact related to taking measurements too close to the surface [116]. Similar measurements on crystalline material usually show increased hardness near the surface because of work hardening. However, metallic glass materials tend to work soften during plastic deformation, producing the softer layer observed near the sliding interface of the BMG.

A second interesting feature was the high hardness measured for the dark layer (or the mixed layer) present on cross-sections after tests in air. The thickness of this layer was not uniform along the track and hardness measurements were only possible for regions where the layer was sufficiently thick. The relatively large spread of the data for the three measurements made in this layer was probably due to the cracks present. Despite these factors, it is fair to say that the oxygen-rich layer generated after testing in air was harder than the base material, probably because oxygen atoms fill some of the excess free volume.
5.6 APPLICATIONS OF THE KELVIN PROBE

In this part of the thesis, several observations of the Kelvin probe signal (KPS) during sliding tests involving the metallic glass alloy will be described. Then, a correlation between the KPS and the local oxygen concentration along the wear track will be established. Finally, a macroscopic model for the KPS evolution during an Al vs. Bronze test will be developed.

5.6.1 KPS during sliding involving BMG

Application of the Kelvin probe (KP) technique to sliding tests involving BMG material is interesting for two reasons. First, the KP can be used as a supplementary tool to study the sliding behavior of BMG material; secondly, the results obtained from tests involving BMG could be useful in helping to clarify the mechanism responsible for the observed variations of the KPS during sliding tests.

The test environment was observed to have a strong influence on KPS evolution, which suggested a strong contribution of chemical effects. An example is the case of a metallic glass disk sliding against a 52100 steel pin. Fig.5-21 shows the results for a test conducted with 60% relative humidity. After the initial break-in period, the friction coefficient remained near 0.75 except for occasional sudden drops to 0.5. These were associated with sharp drops in the KPS and a dark surface coating containing oxygen. Fig.5-22 shows the results when the relative humidity was increased to 75%. The KPS decreased smoothly, with much smaller departures from typical values, and the surface remained covered with dark material containing oxygen. The steady-state friction coefficient was about 0.5. SEM images for these two cases are shown in Fig.5-23. While
both wear tracks had regions that were similar, and both contained areas of granular material containing oxygen and iron (from the pin), the area fraction of patches of material with oxygen and iron was larger when the relative humidity was increased (Fig. 5-23b).

The results for BMG vs. 52100 tested in vacuum are shown in Fig. 5-24. In this case the friction coefficient fluctuated around 0.75, the KPS was steady and the wear track remained metallic. Together, the results from tests of BMG vs. 52100 in vacuum and in air with different humidity levels are consistent with friction coefficients near 0.75 when the pin contacts the BMG surface and with friction coefficients near 0.5 when contact is with a layer of at least partially oxidized material.

The observed variation of KPS can be understood assuming KPS mainly responds to the changes in the average surface chemical composition which in turn varies as a result of two competing processes, namely the generation and removal of the surface tribolayer. This idea is further developed in section 5.6.3. The observations discussed so far can be summarized as follows. When the humidity is low, the generation of an oxygen-rich tribolayer is less efficient, leaving the surface mostly metallic, which corresponds to the friction coefficient of 0.75. Occasionally the coverage of the oxygen-rich tribolayer increased over a short period of time so the surface coverage increased, therefore lowering the friction coefficient to about 0.5. When the relative humidity was high at 75%, the generation of a tribolayer was effective, leaving the wear track covered with the tribolayer almost all the time. The friction coefficient then stays at about 0.5.
5.6.2 Correlation between KPS and local oxygen concentration

Most of the reported results of KPS have been obtained while using a time constant of 30 sec. Therefore the KPS reflected the average condition, not only over the track, but also over several rotational cycles of the disk. In some cases, e.g., BMG/BMG in air, it was clear that the surface condition of the track varied with position in the sliding direction. This phenomenon was examined more carefully by increasing the time for one revolution to 30 sec. and reducing the time constant to ~3 sec.. While still large enough to eliminate some of the short-term fluctuations in the KPS, this time constant was small enough for the chosen sliding speed (2 mm/s) to detect changes in surface condition extending for millimeters. A plot of the KPS along the sliding direction is shown in Fig.5-25a as a function of rotation angle. Data are shown for just over one rotational cycle so small changes and general reproducibility can be observed. A marker at the side of the track allowed subsequent correlation of the KPS data with the appearance of SEM images and with chemical differences detected by EDS. Fig.5-25b is a plot of the oxygen concentration, but inverted (i.e., 1.0 - O at%) to allow convenient comparison with the KPS. Fig.5-26a is a secondary electron image of a portion of the wear track corresponding to one of the minima in Fig.5-25. This is a region with elevated oxygen concentration compared with the smoother area shown in Fig.5-26b, as indicated by the EDS results shown in Fig.5-26c.

To be sure that these results with metallic glass were not influenced by the formation of crystalline phases, either through devitrification or reaction to form crystalline oxides, the wear track and the debris were examined by XRD. The results showed that most of the
material remained amorphous. Therefore, the variations shown in Fig.5-24 and Fig.5-26 are related to the effects of oxygen.

All of these examples point to the importance of the environment in modifying the disk surface during sliding. A common feature for tests in air was the development of surface material having elevated oxygen concentration. This in itself is not surprising. However, there was a wide range of behavior related to the rate of accumulation of this modified material, the area fraction covered at any given time, and the nature of the removal of this material. It is tempting to analyze the results in terms of the kinetics of formation of surface layers and the processes responsible for removal. With this approach one could rationalize the different behaviors in terms of differing rates of formation, accumulation and removal.

5.6.3 Macroscopic model for KPS evolution in Al vs. Bronze test

In this section, a model for the combined processes of transfer, oxidation, mixing and local removal of a tribolayer is described. The case chosen is one like that shown in Fig.5-27 for 1100Al vs. bronze in air [101]. That is, the model should account for the increasing amount of copper transferred to the disk, resulting in a decreasing KPS, and the random spikes due to sudden local removal of surface material.

It is assumed that the KPS depends linearly on the surface coverage of the tribolayer, which in this case contains copper. At a given time, \( t \), the local surface is either covered by an effective tribolayer or it is clean metal, free from any coating. Therefore, if \( L \) and \( M \) are the fractional coverage of the tribolayer and metallic material, respectively, \( L+M=1 \) (5.1)
The generation rate of the tribolayer is assumed to depend on the fractional coverage, \( M \), of the metallic material, with a proportionality constant given by \( k_i \). At the same time, the tribolayer is subject to wear, with a removal rate assumed to be proportional to the fractional coverage, \( L \), of the tribolayer, with a proportional coefficient of \( k_p \). Given these assumptions, the system’s evolution can be expressed by the following equations,

\[
\begin{align*}
\dot{L} &= -k_0 L + k_i M \\
\dot{M} &= k_0 L - k_i M
\end{align*}
\]  

(5.2)

The relative magnitudes of \( k_0 \) and \( k_i \) determine the steady state coverage of the tribolayer. In this model, their values were chosen to be \( k_0 = 0.01 \) and \( k_i = 0.003 \). Linear stability analysis shows that such a system will approach a steady state [117], which corresponds to the observed long-time-scale decay of the KPS. Since each experiment began with metallographically polished specimen surfaces, the initial conditions were chosen to be

\[
\begin{align*}
M(t = 0) &= M_0 = 1.0 \\
L(t = 0) &= L_0 = 0.0
\end{align*}
\]  

(5.3)

Equations 5.2 were then solved with the initial conditions expressed by equations 5.3. The resulting simulated KPS is shown by the dashed curve in Fig.5-28. It closely resembles the general trend of the KPS resulting from progressive transfer of copper from the pin to the aluminum disk.

The sudden appearance of a bright streak on the wear track is interpreted as a cutting event during which the tribolayer is quickly removed. This observation is incorporated in the model by using a delta function in the removal rate. The cutting events intervene at apparently random intervals. Therefore the modified removal rate, with the cutting process
included, would have a constant value for most of the time but would instantaneously jump to a much larger value at random intervals. The modified removal rate of the tribolayer could then be expressed as,

\[
k'_0 = k_0 \cdot \left[ 1 + \alpha \cdot \delta(t - t_i) \right]
\]  

(5.4)

where \(\delta(t-t_i)\) is the Dirac delta function, \(t_i\) is a series of randomly chosen times, and \(\alpha\) is a large number representing the sudden increase in the removal rate at \(t = t_i\). In this simulation, \(\alpha\) is chosen to be 99 and \(k_0\) is the wear rate of the tribolayer at times when there are no cutting events. A typical form of the \(k'_0\) thus defined is shown in the lower part of Fig.5-28. A typical simulated KPS, including the modified \(k'_0\), is plotted in Fig.5-28 as the solid curve punctuated by spikes.

The solid curve in Fig.5-28 qualitatively reproduces all features of the measured KPS for tests involving 1100Al vs. bronze in air (Fig.5-27). Despite the simplifying assumptions made in the model, the results suggest that the basic processes modeled are similar to what actually happens on the wear track.

The model provides further insight into the evolution of tribolayers in general. Equations 5.2 predict that all tribolayers generated by competing accumulation and removal processes will eventually reach a steady state in terms of surface coverage, so one would also expect that both friction and wear would approach steady state conditions, as commonly assumed in the literature. However, in the work of Kasai et al. [101], several systems that do not achieve steady state conditions are described. In those cases, it may be that the fractional coverage of the tribolayer does not become constant because the coefficient of the removal rate and/or the accumulation rate are/is not constant over time.
A proper simulation would then require the use of more complicated function than the one used in equation 5.4.
Fig. 5-1 Friction coefficient as a function of time, showing a transient in the early stage of sliding. MG vs. MG, 1.2 kgf, 0.05 m/s in air.
Fig. 5-2 Change of wear rate with sliding distance MG vs. MG, air, 0.5 kgf
Fig. 5-3 Friction coefficient as a function of normal load.
Fig. 5-4 Wear rate as a function of normal load.
Fig. 5-5 Wear rate as a function of sliding speed for BMG vs. BMG, 0.5 kgf normal load in air.
Fig. 5-6 Friction coefficient as a function of sliding speed with 0.5 kgf normal load, in air.
Fig. 5-7 XRD patterns of debris collected under different sliding speeds.
Fig. 5-8 Wear track generated in air on the disk by sliding BMG vs. BMG, 1.0 kgf, 0.05 m/s. Regions with bright contrast have higher oxygen content, SE image.
Fig. 5-9 Wear track on BMG disk generated in vacuum by a 52100 steel pin, 1.2 kgf, 0.05 m/s, SE image.
Fig. 5-10 Contact region of a spherical 52100 steel pin after sliding vs. BMG in air, 1.2 kgf, 0.05 m/s. A piece of transfer material has developed on the pin, SE image.
Fig. 5-11 Debris collected from test of BMG vs. BMG, 1.0 kgf, 0.05 m/s, in air. One cutting-type particle is visible in this SE image.
Fig. 5-12 Zr XPS signals of a sample generated in air, with BMG vs. BMG, 1.0 kgf, 0.05 m/s. Only pure Zr peaks remain after 4 min. ion beam sputtering.
Fig.5-13 Dark field TEM image of the debris generated in MG vs. MG, air test, 1.0 kgf.
Fig. 5-14 XRD of the debris collected from MG vs. MG, air, 1.0 kgf.
Fig. 5-15 DSC traces for as received MG and debris generated with 0.05 m/s sliding speed, in vacuum and air with different loads. All peaks are exothermic. Heating rate was 5°C/min. with argon flow of 100 ml/min. W. Johnson et al. also reported the low temperature peaks for the alloy [2,3]. Below these two peaks the material is amorphous; above these two peaks the material is nanocrystalline.
MG annealed at 500°C for 120min.

Annealed MG/annealed MG, air, 200gf

Fig. 5-16a. XRD patterns of the annealed BMG. Typical grain size after annealing was 50 – 100 nm; some large grains were as large as 200 nm in diameter. b. XRD patterns of the debris collected after sliding annealed BMG vs. annealed BMG in air.

Fig. 5-16 continues on the next page.
Fig.5-16 c-d Secondary electron images of wear tracks generated by sliding annealed BMG vs. annealed BMG, 0.2 kfg, 0.05 m/s. Image c was a track generated in air; image d was one generated in vacuum.
Fig. 5-17 Back-scattered electron images of transverse cross-sections of wear tracks.

a. BMG vs. BMG, 0.2 kgf, 0.05 m/s in vacuum
b. BMG vs. BMG, 1.1 kgf, 0.05 m/s in air
Fig. 5-18 Secondary electron image of a longitudinal cross-section of a wear track generated by sliding of BMG vs. BMG, 0.2 kgf, 0.05 m/s in vacuum.
Fig. 5-19a Back-scattered electron image of a longitudinal cross-section of a wear track generated by sliding BMG vs. BMG, 1.1 kgf, 0.05 m/s in air.
Fig. 5-19 b Chemical compositions of the surface layer generated after sliding and of the substrate BMG material. BMG vs. BMG, 1.1 kgf, 0.05 m/s, in air.
Fig. 5-20 Hardness profiles on cross-sections. Each shows a similar region of work-softening. The softer region has the same chemical composition as the base material.
Fig. 5-21 Friction coefficient and KPS vs. time for MG disk sliding against 52100 steel ball (diameter 6.35 mm) in air with relative humidity of 60%. Normal load 0.2 kgf, sliding speed 0.05 m/s.
Fig. 5-22 Friction coefficient and KPS vs. time for MG disk sliding against S2100 steel ball (diameter 6.35 mm) in air with relative humidity of 75%. Normal load 0.2 kgf, sliding speed 0.05 m/s.
Fig. 5-23 Secondary electron images for the two cases illustrated in Figs. 5-21 and 5-22 (MG vs. 52100 steel system, different humidity). a. 60% relative humidity, as in Fig. 5-21; b. 75% relative humidity as in Fig. 5-22.
Fig. 5-24 Friction coefficient and KPS vs. time for MG vs. 52100 stainless steel sliding in vacuum. 1.31 kgf, 0.05 m/s.
Fig. 5-25 Results from test of MG vs. MG sliding in air. **a.** KPS vs. position along the wear track in sliding direction. **b.** EDS results plotted as (1-at.%O) for the same path used in **a.**, allowing direct comparison of the two patterns.
Fig. 5-26  

a. SEM image of the wear track where KPS is at one of its minima. 

b. SEM image of the wear track where KPS is at one of its maxima.
Fig. 5-26 c. EDS analysis on regions shown in Fig. 5-25a&b. Region corresponding to a minimum of KPS. The patch area has higher oxygen concentration.
Fig. 5-27 KPS and friction coefficient as functions of sliding time for an 1100Al disk and bronze pin in air [101].
Fig. 5-28 Simulation of KPS using a model based on accumulation and removal of a tribolayer. This correlated well with actual KPS behavior observed for an 1100Al disk and bronze pin in air (Fig. 5-27).
Chapter 6

Results and Discussion -- MD Simulations

In the preceding chapter, the results of experimental studies on the tribological properties of Zr$_{41.2}$Ti$_{13.8}$Cu$_{12.5}$Ni$_{10.0}$Be$_{22.5}$ bulk metallic glass alloy were described. These included the morphology of the wear track, pin and debris, the effects of devitrification on friction and wear, re-amorphization after sliding of devitrified BMG, the generation of a mixed layer at the interface and the evolution of subsurface microstructure. However, because of the amorphous structure of the BMG system, certain experimental techniques proven effective for crystalline materials are not available for a BMG system. For example, for crystalline materials, useful information on microstructure evolution can be obtained by examining cross-sections of worn specimens by SEM or TEM. However, the structural inhomogeneities that give rise to the contrast in various electron microscopies do not exist in BMG alloys. An alternative approach involves computer simulation. Molecular dynamics (MD) simulation provides a powerful tool to complement experimental studies.

In some cases, simulations can provide information that is difficult to obtain
experimentally. The sliding behavior of BMG materials provides a good example for the complementary applications of experimental and simulation techniques.

The setup of the MD simulation was described in Chapter 4. In this chapter, the application of MD simulation to an amorphous solid in sliding contact is described. Connections between the experimental observations described in chapter 5 and the simulation results will also be presented.

6.1 **Friction Coefficient**

The friction coefficient $\mu$ at any time $t$ was calculated using

$$\mu(t) = \frac{F(t)}{W(t)}$$

(6.1)

where $F$ is the frictional force and $W$ is the normal load.

Fig.6-1 is a typical plot of friction coefficient evolution observed in the simulation. The friction coefficient exhibits a transient overshoot before it settles down to an average steady state value. The maximum friction coefficient reached during overshoot is about 0.5 for all sliding speeds tested. However, the steady state value is observed to decrease as the sliding speed increases, as shown in Fig.6-2. Similar dependence of friction coefficient on the sliding velocity was reported by J.E. Hammerberg et al. in [93, 94].

Transient behavior in friction is commonly observed in experiments although details may differ from system to system. Similar transients have been observed in experimental studies and the simulations. It is believed that changes in subsurface microstructure develop during the transient period. For crystalline materials, many studies have been conducted on microstructure development during the early stages of sliding [118, 119, 120, 121]. In the experimental studies (Chapter 5) on BMG alloy $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ti}_{10.0}\text{Be}_{22.5}$, it was found
that DSC patterns of debris had different features compared to those of the original material, which indicated that sliding-induced structure changes also took place in the BMG material.

6.2 SLIDING INDUCED MIXING AT THE INTERFACE

It is commonly observed that when two pieces of material are brought into sliding contact, in addition to the tangential shear motion, there is a component of flow perpendicular to the sliding interface. This can lead to the generation of a layer of mixed material which can play a vital role in determining the friction and wear characteristics of a sliding system. The existence of the mixed layer is relatively easy to identify experimentally if the structure and the composition of the layer are different from those of either component. However, for a self-mated test in a non-reactive environment, identifying the mixed layer is more difficult.

In the experimental studies on sliding of the BMG alloy (Chapter 5), a layer of material that was slightly darker on back scattered electron images was found on the wear track after tests in air (Fig.5-I9a). Except for a higher oxygen content, the composition of the layer was essentially the same as that of the substrate material (Fig.5-19b). Finer structures inside the layer indicated material flow. It was concluded that the layer was produced by transfer and mixing processes. Detailed discussion of this layer was presented in section 5.4.2. Visual observation of the track indicated that the thickness of the mixed layer varied with the test conditions. Under a given test condition the average thickness of the mixed layer reached a steady state value after an initial transient. It was found that the mixed layer affected the friction and wear properties of BMG in several ways: it affected
the morphology of the wear track, it played a central role in the debris generation process, thereby directly affecting the wear rate, and it determined the friction coefficient and wear rate of the devitrified BMG. The development of the mixed layer contributes to the sliding behavior during the early transient stages of sliding, and the well-developed mixed layer is responsible for steady state behavior. Therefore, mixing phenomena are important at all stages of sliding.

The detailed structure of the mixed layer is experimentally accessible on a cross-section. Therefore, to study the growth of such a layer, one prepares multiple cross-sections generated from well controlled tests stopped at different stages of layer formation. In addition, the early stages of mixing would occur at the tips of local contacting asperities, and these may not show up on a given cross-section. Therefore, experimental study of the evolution of the mixed layer generated at the sliding interface is difficult and time-consuming. MD simulations offer a complementary way to study mixing and other processes involved in sliding systems.

In the simulations, mixing was observed and the mixed layer was found to grow as sliding continued. Fig.6-3 shows the sequence of mixing found in the vicinity of the sliding interface. The upper block and the lower block are color-coded differently to provide a simple way to observe the mixing process. Chemically, the upper and the lower blocks are identical; therefore, the mixing is not an effect of diffusion driven by a chemical potential difference. Self diffusion could also give rise to mixing. However, it is expected that in order to achieve the observed amount of mixing, a much longer time or a much higher temperature would be required. Although the details of kinetics may differ, Fig.6-3
represents the typical generic sequence of interfacial mixing observed in simulations for different sliding speeds. The mixing is quite thorough, taking place on an atomic scale.

In the experimental studies, the annealed BMG was re-amorphized upon sliding. XRD patterns of the collected debris showed little indication of crystallinity (XRD pattern b in Fig.4-16). Considering the fact that XRD is capable of resolving structural periodicity at the nanometer scale, it is reasonable to assume that atomic scale mixing is necessary for the sliding-induced re-amorphizing. In other words, the mixing process at and near the sliding interface is responsible for sliding-induced re-amorphizing.

It is clear from Fig.6-3 that the mixing process is a dynamic process and the thickness of the mixed layer is a function of time. Therefore, it is interesting to examine the growth kinetics of the layer. For this analysis, a parameter $\delta$ was defined to describe the mixing process quantitatively, with

$$\delta(y,t) = \frac{\sum_{i=1}^{n_t} |y_i^t - y_0^t|}{n_t} - \frac{\sum_{i=1}^{n_t} (y_i^t - y_0^t)}{n_t}$$  \hspace{1cm} (6.2)

where $y_i^t$ is the y coordinate of the $i^{th}$ atom at time $t$, $y_0^t$ is the y coordinate of the $i^{th}$ atom at $t = 0$, i.e., the initial y coordinate, and $n_t$ the number of atoms originally having y coordinates between $y$ and $y + dy$. The first term represents the average distance traveled by atoms originally located between $y$ and $y + dy$, and the second term represents the absolute value of displacement of those atoms. Physically, the first term would represent the total amount of displacement occurring within the layer of thickness $dy$; the second term would represent the part of the movement that is due to the shift of the center of mass of the layer. The difference between them, $\delta$, therefore represents the amount of relative
displacement with respect to the center of mass. The higher the \( \delta \) value, the further those atoms move away from their original positions, i.e., the higher the value of \( \delta \) the higher the degree of mixing. \( \delta \) is a function of both the \( y \) coordinate and the time, \( t \), which are the two relevant variables in discussions of mixing.

Intuitively, mixing would be the most effective at the sliding interface. A plot of \( \delta \) at a given time, in this case \( V_s = 1.0 \) and \( t = 25 \), clearly shows such a feature (Fig.6-4). The \( \delta \) value is highest at the interface and decreases on both sides. Quantitatively, the distribution of \( \delta \) at a given time fits well to a Gaussian function with its center at the sliding interface. The general form is

\[
\delta(y, t) = \frac{A(t)}{w(t)\sqrt{\pi}} e^{-\left(\frac{y - y_0}{w(t)}\right)^2} \tag{6.3}
\]

where \( A \) and \( w \) are fitting parameters related to the height and width of the Gaussian function and \( y_0 \) is the center position of the Gaussian. Both \( A \) and \( w \) are functions of time. The height of \( \delta \) at the interface, i.e., \( \delta(y_0, t) \) would be used to describe the thickness of the mixed layer quantitatively at any time \( t \).

Next, the kinetics of the growth of the mixed layer can be studied by investigating the evolution of \( \delta(y_0, t) \) as a function of \( t \), as shown in Fig.6-5 for the case \( V_s = 1.0 \). At this sliding speed, the square of \( \delta(y_0, t) \) exhibits a linear relationship with \( t \). Therefore, we can say that the growth kinetics of the mixed layer scales linearly with the square root of \( t \), which can be expressed as

\[
\Delta^2 = k_m \cdot t \tag{6.4}
\]
where $\Delta$ is the thickness of the mixed layer and $k_m$ is a constant describing the growth rate. This is a very interesting observation. The development of the mixed layer scales in the same way as the kinetics of thermal diffusion, which suggests that the underlying mechanism also involves a kind of random process. In sliding experiments, a mixed layer seems to be generated even with very low sliding speeds where thermal effects are negligible. Our MD simulation results obtained at lower sliding speeds also showed that a mixed layer is generated at the interface. Therefore, the driving force for the generation of the mixed layer seems to involve more than thermal energy. Further work is needed to understand the transport processes associated with mixing.

The growth kinetics observed in MD simulations can be used to predict the thickness of the mixed layer in experiments. In real systems, the mixed layer will not grow indefinitely because of wear. If we assume that the mixed layer wears at a rate proportional to its thickness (similar to a result reported in [122]), then

$$\text{steady state wear rate} = -k_w \cdot \Delta$$

(6.5)

where $k_w$ is a constant describing the wear rate. In fact, a near constant or steady state wear rate has been reported by many researchers when sliding continues for an extended time. The mixed layer is then subject to two competing processes, i.e., generation by flow of material and removal by wear. The net growth rate of the mixed layer can be expressed as

$$\frac{d\Delta}{dt} = \frac{k_m}{2 \cdot \Delta} - k_w \cdot \Delta$$

(6.6)

An obvious steady state solution for Eq.6.6 would be
\[ \Delta^* = \sqrt{\frac{k_m}{2 \cdot k_w}} \]  

(6.7)

where \( \Delta^* \) is the steady state thickness of the mixed layer. Experimentally, it is expected that for systems that achieve steady state sliding conditions the average thickness of the mixed layer typically reaches a steady value. Equation 6.7 predicts that the steady state thickness of the mixed layer is higher if the growth rate is high and lower if the wear rate is high. The parameters \( k_m \) and \( k_w \) would be determined by the materials involved in the pair and the details of the test conditions.

### 6.3 Subsurface Density Profile

In the previous chapter, a near-surface soft layer detected on cross-sections of worn BMG was described. It was suggested that the softer layer resulted from shear-induced accumulation of excess free volume. The concept of excess free volume has been discussed by Spaepen and Turnbull [72] and Argon [74]. Several constitutive relations based on the concept of excess free volume have been proposed. Many of these worked well with available data [74, 80, 108]. Recently, de Hey et al., measured the strain-induced excess free volume as a function of strain rate, temperature and pre-test annealing history of a Pd\(_{40}\)Ni\(_{40}\)P\(_{20}\) alloy [123].

In this section, MD simulation results that indicate the generation of a low-density region near the sliding interface are reported.

The average density, \( \rho(y) \) (in units of atoms per rescaled area) of the thin layer between \( y \) and \( y + dy \) was calculated for the initial time \( t = 0 \) and some later time \( t > 0 \) for
simulation with a sliding velocity of 1.0. The difference between the two density profiles was then calculated:

\[ \Delta \rho_r(y) = \rho_r(y) - \rho_0(y) \]  

This density difference is plotted in Fig.6-6 for \( t = 25 \). A negative density difference on the plot, which represents a decrease in density between \( t = 0 \) and \( t = 25 \), is observed for the region near the sliding interface. Because the volume of the simulation cell was kept constant during the simulation, regions away from the interface necessarily experienced a density increase. The density decrease appeared soon after the start of sliding; therefore it is likely that the density decrease was shear-induced. A similar strain induced accumulation of free volume was measured experimentally on a \( \text{Pd}_{40}\text{Ni}_{40}\text{P}_{20} \) alloy [123].

An increase in the local kinetic energy was also recorded in the present simulation. To study the contribution of the thermal expansion on the density profile, a separate test was conducted. In this test, there was no sliding between the upper and lower blocks. But the center part of the sliding cell was heated such that the system repeated the thermal history of the sliding test. The density change during heating was measured and the result is also plotted on Fig.6-6. It is clear on the plot that at the same temperature, the density was lower when there was sliding. The extra density decrease, or equivalently, the excess volume accompanying the sliding motion is very likely a result of shear induced excess free volume.

It has been reported from experiments that higher free volume leads to lower flow stress [124]. Therefore, it is expected that the density decrease observed near the sliding interface in the simulation would result in a decrease in hardness. In the experimental studies described in the preceding chapter, a near-surface softer region was indeed detected.
after sliding tests. The correlation between the simulation and the experiments suggests that shear-induced accumulation of excess free volume may be the mechanism responsible for the generation of the soft layer during sliding.

6.4 **Subsurface displacement profile**

One measurement that has been found particularly interesting and meaningful in tribology is the strain field, or equivalently, the subsurface displacement profile. This has been widely studied for crystalline materials using various microstructure features as markers. However, such experimental measurements in amorphous material are difficult because there is no microstructure features that can be used as markers. In an MD simulation, markers can be put in digitally which means one can easily keep track of displacements of all atoms and keep a complete record of the displacement field evolution for later analysis. Marker atoms were chemically identical to other atoms in the system but were given different colors to show the profile.

Fig. 6-7 shows an originally straight marker that bends over during sliding. Preliminary quantitative analysis suggests that the displacement profile at any given time can be fit to an exponential function. The way it bends over is very similar to what had been reported in crystalline materials. For comparison, careful measurements made on TEM pictures of cross-sections of crystalline copper also suggested an exponential decay of displacement from the interface into the substrate material [121]. In an independent study conducted at Los Alamos National Laboratory, MD simulation was used to study pure Cu sliding on pure Cu using embedded atom potentials [125]. In that study very similar subsurface displacement profiles were obtained. Similar profiles have appeared in experiments on
different materials despite differences in microstructure, composition, test condition, etc. They have also been observed in simulations of sliding involving crystalline and amorphous materials, despite the differences in interatomic potential and atomic microstructure. The robust reappearance of such a pattern suggests that something very basic is responsible for its occurrence.

The observance of the same pattern in systems of very different microstructures seems to indicate that the pattern is not sensitive to details of the microstructure, i.e., crystalline or amorphous, one phase or multiphase, etc. This suggests a generic material flow pattern under typical sliding conditions involving compression plus shear.

The Navier-Stokes equation can be used to describe the flow behavior of a material. In most cases, the dominant material flow takes place along the sliding direction. This allows one to model the problem as a 1D viscous flow problem.

Consider a material with viscosity $\eta$ bounded by a large plate with no initial relative motion (Fig. 6-8). At $t = 0$, the plate begins to move in the $X$ direction with a constant velocity $V$. It should be noted that this situation exactly mimics the start of the MD simulation described earlier. Therefore, one expects the observed subsurface displacement profile in the simulation to correspond to the unsteady viscous flow pattern generated near the bottom plate.

If one ignores the pressure gradient and the gravitational force and assumes that the velocity perpendicular to the shear direction, $v_y$, is very small compared to the shearing velocity in the $X$ direction, $v_x$, then the Navier-Stokes equation in 1D has the form

$$\rho \frac{dv_x}{dt} = \eta \frac{d^2v_x}{dy^2}$$

(6.9)
where $\rho$ is the density of the material and $\eta$ is the viscosity. Eq.6.9 can be re-written in the form

$$\frac{d\nu_x}{dt} = \lambda \frac{d^2\nu_x}{dy^2}$$

(6.10)

where $\lambda = \eta/\rho$, the kinematic viscosity. The boundary and initial conditions of the problem were

$$\begin{cases}
t = 0, y > 0, \nu_x = 0; \\
t \geq 0, y = 0, \nu_x = V; \\
t \geq 0, y \to \infty, \nu_x = 0; \\
\end{cases}$$

(6.11)

Under these boundary and initial conditions, Eq.6.10 has a complementary error function solution

$$\frac{\nu_x}{V} = 1 - \frac{2}{\pi} \int_0^\infty e^{-t^2} dt = 1 - erf(\xi)$$

(6.12)

where $\xi = \frac{y}{2\sqrt{\lambda t}}$. The mathematical treatment is the same as for the case of 1D diffusion except that in this case the "species" that actually diffuses is the momentum and the diffusivity is replaced by the kinematic viscosity.

The ratio of sliding velocities in Eq.6.12 is the same as the ratio of displacements. Therefore, Eq.6.12 can be used to fit the simulation data of displacements. The only fitting parameter here is $\lambda$. Equation 6.12 describes only the plastic or viscous part of the deformation. Therefore the elastic part of the displacement profile obtained from simulations needs to be subtracted before a comparison can be made between Eq.6.12 and the simulation data. Subtraction of the elastic strain was carried out based on the fact that the elastic strain will saturate after some time but the plastic strain will not. Fig.6-9 shows...
four displacement profiles for sliding in the lower block at different times in simulations with sliding speed of $V_s = 1.0$. Two observations can be made from Fig.6-9. First, the plastically deformed zone extends to about 50 length units below the sliding interface and it does not continue to grow beyond that depth. Second, the elastic strain saturates at a time in the range between $t = 25$ and $t = 150$. It is clear from Fig.6-9 that the strain profile in the elastically deformed region is not linear. It can be fitted well to a second order polynomial function as shown in Fig.6-10. It is assumed that the same function can describe the elastic displacement profile for the entire sample, i.e., the total strain is a simple combination of elastic and plastic strains, and the occurrence of plastic deformation does not change the elastic portion. Given the local increase in free volume, this is not realistic, but this assumption simplifies the calculation. Under such an assumption, a second order polynomial elastic displacement is assumed for the entire sample, including the regions where deformation is dominantly plastic. The elastic displacement profile is subtracted from the measured total displacement profile. The corrected displacement data were fitted to Eq.6.12 and the results are shown in Fig.6-11. The solid line on the right hand side of Fig.6-11 shows a satisfactory fit to the simulation data represented by open circles. As a by-product of the fitting, one obtains the $\lambda$ value, which should only be a function of the system. That is, for a given system $\lambda$ is a constant over time. Knowing the value of $\lambda$, one can predict the subsurface displacement profile at any given time $t > 0$ using Eq.6.12. The left hand curve on Fig.6-11 is such a prediction made for $t = 550$ using the $\lambda$ value obtained in the first fit. Simulation data at $t = 550$ are shown on the plot as triangles for comparison. The prediction is again satisfactory.
In the derivation of Eq.6.12, there was no assumption of any particular microstructure. The material was assumed to have a finite viscosity value so that \( \lambda \) is neither zero nor infinite. It should be noted that with a sliding velocity of 1.0, regions near the interface experienced steady state temperatures higher than the glass transition temperature. Further analysis is needed to focus on data obtained from tests with low sliding velocities, for which no portion of the system has a temperature higher than the glass transition temperature. If the lower temperature results can also be described by Equation 6.12, then this equation would provide a generic description for the flow of material during sliding.

Of course, there are times when microstructure must be considered. In crystalline materials that work harden, the viscosity value is no longer a constant. Instead, to a first approximation the viscosity will become a function of local strain or local displacement. Thermal effects would also cause the viscosity to vary with \( y \). In such cases, the governing equation Eq.6.9 would become

\[
\rho \frac{dv_\perp}{dt} = \frac{d}{dy} \left[ \eta(y) \frac{dv_\perp}{dy} \right]
\]  

(6.13)

If the functional form of \( \eta(y) \) is complicated, then Eq.6.13 may not have a simple solution in closed form. But if \( \eta(y) \) is not a strong function of \( y \), then Eq.6.12 should be a reasonable approximation.
Fig. 6-1 Evolution of friction coefficient with the sliding velocity $V_s = 0.1$. 

Average $\mu = 0.31$. 

Friction coefficient vs. Rescaled time.
Fig. 6-2 The steady state friction coefficient as a function of sliding speed.
Fig. 6-3 Sequence of mixing, $V_s = 1.0$, showing initial configuration and configurations at two later times.
Fig. 6-4 Distribution of $\delta$ at $t = 25$. 
Fig. 6-5 Observed growth kinetics of the mixed layer.
Fig. 6-6 Density variation profile at $t = 25$. Calculated for sliding and for interface heating only (not sliding).
Fig. 6-7 Evolution of a straight marker during sliding.
starts to move at $t = 0$ with a velocity of $V$

Fig. 6-8 The set-up for Navier-Stokes analysis.
Fig. 6-9 Displacement profiles at 4 different times, showing the saturation of elastic displacement.
Fig. 6-10 The elastic displacement data and the 2nd order polynomial fitting.
Fig. 6-11 Curve fitting using Eq. 6.12 for $t = 1050$ and the comparison between the predicted curves and the simulation data at $t = 550$. 
CONCLUSIONS

Experimental Investigations:

1. A Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5} bulk metallic glass is ductile under sliding conditions. Extensive material flow takes place during dry sliding in both air and vacuum.

2. Both the friction coefficient and the wear rate show early stage transients during sliding before reaching steady state values.

3. The friction coefficient decreases with an increasing normal load in air and vacuum; at a given load, the friction coefficient is higher in vacuum compared to that in air.

4. The wear rate increases with an increasing normal load in air and in vacuum; at a given load, the wear rate is higher in air compared to that in vacuum.

5. The friction coefficient and wear rate for self-mated Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5} bulk metallic glass are comparable to those for 52100 steel.

6. Sliding velocity affects both friction coefficient and wear rate via strain rate and thermal effects.
7. Flake-like and plate-like debris are the dominant types of debris observed; some cutting-chip debris are generated during tests in air.

8. Sliding generates a small amount of crystalline material; sliding alters the atomic structure of BMG and this shows up in the DSC traces of debris.

9. The sliding of annealed BMG re-amorphizes the devitrified material, resulting in friction coefficient and wear rate values that are comparable to those of the as-received BMG.

10. A mixed layer generated by transfer and plastic deformation processes is observed. The mixed layer generated during sliding influences the tribological properties of BMG alloys.

11. Sliding generates a softer region adjacent to the sliding interface. The decreased hardness may be a result of shear-induced accumulation of excess free volume.

12. The Kelvin probe signal is sensitive to the changes in the surface chemical composition during sliding.

13. The observed Kelvin probe signal in tests involving metallic glass alloys can be explained by considering competing processes of generation and removal of a surface tribolayer during sliding.

14. A model based on the accumulation and local removal of a tribolayer has been proposed. The features predicted by a simulation of the KPS agree well with experimental KPS data.
Molecular Dynamics Simulations:

1. The friction coefficient in the simulation has an initial transient before reaching an apparent steady state value.

2. The steady state friction coefficient decreases as the sliding speed increases.

3. Atomic scale mixing takes place at the sliding interface. The growth of the mixed layer scales with the square root of time for a sliding speed of $V_s = 1.0$.

4. The density near the sliding interface decreases after the start of sliding, probably due to the accumulation of shear-induced excess free volume. This observation suggests that the same mechanism may be responsible for the softer region observed near the surface in experiments.

5. The evolution of the subsurface displacement profile in simulations can be described by equation 6.12. The shape of the displacement profile may be a generic material flow pattern under combined compression and shear.
FUTURE WORK

1. Investigate the origin of high temperature DSC peak of the as-received BMG sample and the relationship among test conditions and the features on the DSC traces of debris.

2. Separate the effect of thermal diffusion from the effect of mechanical mixing in the MD simulation.

3. Look into the phenomenon of sliding induced re-amorphization using MD simulation.

4. Study the propagation of preexisting cracks underneath the sliding interface.

5. Expand the MD simulation to incorporate more atoms or use a full 3D model with more realistic potentials.
A1. Notes on C++ Code for MD Simulation

A1.1 Code for sample preparation

The sample was prepared by the procedures shown in Fig.A-1:

Start: start the program. The program looked for a “setup file” for running parameters.

Setup file: The “setup file” was a separate file containing parameters used to control the simulations. A list of the parameters specified in a typical setup file is tabulated in Table A-1.

$t = 0$ check: This judgment was made after the program had read in from the setup file. If $t = 0$, then this run would be a new run therefore requiring initialization of a new system. If $t > 0$, this run was going to be a continuation of a previous run so it involved reading in system information from a previously generated continue file.

Initialize a system: If $t = 0$, the initialization routine was called. At the beginning of initialization, the program asked for composition information, based on which it would generate a 2D array of atoms that had the desired composition.

Read in system configuration: If $t > 0$, the program looked for a previously generated “continue file”, then read in the system configurations specified there.
<table>
<thead>
<tr>
<th>N</th>
<th>Total number of particles in the system</th>
<th>DIMN</th>
<th>Dimension of the system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Number of species in the system</td>
<td>Time</td>
<td>The starting time</td>
</tr>
<tr>
<td>DeltaT</td>
<td>Time step size</td>
<td>CutOff</td>
<td>Cutoff distance</td>
</tr>
<tr>
<td>Minimum Bin Length</td>
<td>The minimum bin length used in binning process</td>
<td>TotStep</td>
<td>Total number of steps set to run</td>
</tr>
<tr>
<td>M</td>
<td>Mass of the particles</td>
<td>Output interval</td>
<td>Set the number of steps between two consecutive output sessions</td>
</tr>
<tr>
<td>T0</td>
<td>Initial system temperature</td>
<td>L</td>
<td>Lengths of the simulation cell (expects two input numbers)</td>
</tr>
<tr>
<td>Thermostat time scale</td>
<td>The constant used in thermostat algorithm, indicating the degree of coupling of the system and the thermal bath. When it is negative the thermostat is turned off.</td>
<td>Tf</td>
<td>Final system temperature</td>
</tr>
<tr>
<td>Initial Stress/Strain Rate</td>
<td>Three inputs expected. When barostat is on, these inputs give the initial stress in x, y and shear directions. When barostat is off (negative) these inputs specify the value of constant strain rate in these directions.</td>
<td>Barostat time scale</td>
<td>Three inputs expected. The constants used for barostat algorithm. Expect three inputs, the first one for the x-direction, the second one for the y-direction and the third one for shear in the xy plane. If any one of these is negative, the barostat in that direction is turned off.</td>
</tr>
<tr>
<td>Pulling force time scale</td>
<td>The constant working with shear force application. When negative, no shear force is applied.</td>
<td>Final stress</td>
<td>Three inputs expected. The final stress in x, y and shear directions</td>
</tr>
<tr>
<td>Eps</td>
<td>A 2x2 matrix specifying the bond strength</td>
<td>Sigma</td>
<td>A 2x2 matrix specifying the bond lengths</td>
</tr>
<tr>
<td>Vs</td>
<td>The chosen sliding velocity</td>
<td>I/O Tag</td>
<td>A tag used to identify a certain run</td>
</tr>
</tbody>
</table>

Table A-1 Typical parameters contained in a setup file.

**Force calculation:** The program calculated the forces on each atom. Measures were taken to improve the calculation efficiency. A cutoff distance was used so that atoms beyond this cutoff distance were assumed to have negligible influence on the behavior of the atom under consideration. In addition, the simulation cell was binned into many sub...
cells (Fig. A-2). The dimensions of the sub cells (i.e., $X$ and $Y$) were slightly greater or equal to the cutoff distance. Therefore, in a force calculation, only atoms in adjacent sub cells needed to be considered. For example, if the force on an atom in sub cell A was to be calculated, only those atoms in sub cells labeled B deserved consideration. Because all atoms beyond type B sub cells were located more than the cutoff distance away from any atom in sub cell A. The symmetry of forces (i.e., forces of atom #1 on atom #2 is the same as atom #2 on atom #1, only opposite in direction) allows us to further increase the efficiency by considering only those atoms in shaded sub cells. A more detailed description of binning can be found in references [126, 127]. The force was calculated using

$$F_{ij} = -\left(\frac{\partial U_{ij}(r)}{\partial x} \hat{i} + \frac{\partial U_{ij}(r)}{\partial y} \hat{j}\right)$$ \hspace{1cm} A.1$$

where $U_{ij}$ is the potential energy of the atom pair. $i$ and $j$ denote the species of the particles involved, either $L$ (for large) or $S$ (for small). $\bar{r}$ is the vector connecting the two atoms involved. In this simulation the potential was assumed to be of Lennard-Jones type,

$$U_{ij}(r) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right]$$ \hspace{1cm} 4.1$$

$\sigma$ is the distance at which the interatomic potential ($U$) is zero; $\varepsilon$ is the bond strength.

The boundary conditions should be considered in determining the distance between any atom $m (x_m, y_m)$ and $n (x_n, y_n)$, i.e., $r_{mn}$,

$$r_{mn} = (x_m^2 + y_m^2)^{1/2}$$ \hspace{1cm} A.2$$

where $x_{mn}$ and $y_{mn}$ are resolved distances in $X$ and $Y$ directions. Assuming that a periodic boundary condition is imposed in the $X$ direction, then $x_{mn}$ can be calculated as,
\[
\begin{cases}
    x_{mn} = x_m - x_n & \text{when } -\frac{L_x}{2} < (x_m - x_n) < \frac{L_x}{2} \\
    x_{mn} = x_m - x_n - L_x & \text{when } (x_m - x_n) > \frac{L_x}{2} \\
    x_{mn} = x_m - x_n + L_x & \text{when } (x_m - x_n) < -\frac{L_x}{2}
\end{cases}
\]  

where \( L_x \) is the \( X \) dimension of the simulation cell. Without the periodical boundary condition, \( x_{mn} \) is simply

\[ x_{mn} = x_m - x_n \]

A.4

Similar procedures were followed in determining \( y_{mn} \).

**Temperature and pressure modifications:** Both temperature and pressure modifications were made in this step. Control of temperature and pressure was accomplished by modifying the forces on each atom. The complete set of equations of motion is

\[
\ddot{\mathbf{v}} = \mathbf{v} + \left[ \mathbf{\dot{e}} \right] \cdot \mathbf{\ddot{r}} 
\]

A.5

\[
\ddot{a} = \mathbf{\ddot{r}} - \left( \left[ \mathbf{\dot{e}} \right] + \xi [I] \right) \mathbf{\ddot{v}}
\]

A.6

\[
\dot{\xi} = \frac{1}{\tau_r^2} \left( \frac{T_{\text{kin}}}{T} - 1 \right)
\]

A.7

\[
\left[ \mathbf{\dot{e}} \right] = \frac{1}{\tau_p^2} \frac{V}{Nk_B T} \left( \left[ \mathbf{\sigma}_{\text{av}} \right] - \left[ \mathbf{\sigma} \right] \right)
\]

A.8

\[
\dot{L} = \left[ \mathbf{\dot{e}} \right] \cdot \mathbf{\ddot{L}}
\]

A.9

where \( \mathbf{\ddot{r}} \) is the position of an atom; \( \mathbf{\ddot{a}} \) is the acceleration of an atom; \( \mathbf{\ddot{r}} \) is the force; \( \left[ \mathbf{\dot{e}} \right] \) is the strain rate matrix; \([I]\) is the unit matrix; \( \xi \) is the thermostat parameter; \( \tau_r \) is the thermostat time scale constant; \( T_{\text{kin}} \) is the instantaneous temperature of the system; \( T \) is the
desired temperature; $\tau_p$ is the barostat time constant; $V$ is the volume of the simulation cell; $N$ is the total number of particles in the system; $k_b$ is the Boltzmann constant; $[\sigma_n]$ is the instantaneous stress tensor of the system; $[\sigma]$ is the desired stress state tensor; $L$ is the dimension of the simulation cell expressed as a column matrix. The system described by equations A.5 – A.9 has been shown to produce average system properties as in an $NPT$ ensemble.

**Update particle positions:** By this time, forces on each atom with temperature and pressure modification were known. In this step, the position of each atom was updated according to the force it experienced.

$$d\vec{r} = \vec{a} \cdot dt$$  \hspace{1cm} A.10

where $dt$ is the size of a time step, typically $1/100$ of the atomic vibration period.

**Apply periodic boundary conditions:** Periodic boundary conditions were applied in this step so that atoms moved out from one side entered the system from the opposite side.

**Calculate system properties:** Based on the particle position and velocity, the system temperature ($\text{Temp}$), pressure ($P$), kinetic energy ($E_k$) and total energy ($E_{\text{total}}$) were calculated.

**Step number checking:** The current number of steps was compared against the preset step number. If the current step number was smaller, the program would proceed to do another step by calculating the force based on the updated system configuration. If the current step number was greater or equal to the preset step number, the current simulation session would come to an end.

*A1.2 Code for sliding test*
Other than some modifications to the boundary conditions, the sliding test was carried out in a way very similar to the sample preparation routine. Several differences are noted here.

**Initial Sliding:** After reading in from the setup file, the program would judge whether the system was newly prepared, i.e., experienced no sliding, or it was a system that already experienced some sliding. For a virgin system, the sliding motion will be initialized. For a previously slid system, only configuration read-in would be performed.

**Force Calculation:** The boundary conditions for a sliding test were different from those used in sample preparation. This affects the calculation of atomic distance, e.g., atoms in sub cell M would be adjacent to those in sub cell N only if there was a periodic boundary condition in Y-direction (Fig.A-4), in which case sub cell N would in fact experience the force of sub cell M through its mirror cell M* produced by the periodic boundary. Without the periodic boundary condition, sub cells N and M would be situated more than the cutoff distance apart and therefore would not “feel” each other at all. Because of these considerations, the implementation of binning and the distance calculation were modified for a sliding test.

**Temperature, P and sliding velocity modifications:** During the sample preparation stage, the thermostat and barostat were implemented throughout the sample. For a sliding test, temperature control was only implemented within the two reservoirs defined in the upper and lower parts of the simulation cell. Because constant volume was required during the sliding test, no pressure modulation was necessary. Shear force was applied to atoms situated within the reservoirs. The magnitude of the shear force was dynamically controlled such that the system would keep an average sliding velocity of $V_s$, which was the pre-
specified sliding velocity, and at the same time the center of mass of the simulation cell remained stationary.

**Update particle positions**: This part was implemented in the same way as the sample preparation routine.

**Apply sliding boundary conditions**: A periodic boundary condition was implemented in the X-direction only. A rigid boundary condition was implemented for the Y-direction.

**Calculate system properties**: The kinetic energy was defined as the energy associated with atomic random motions. Therefore, when there was sliding, only the random part of the atomic motion would be counted toward the kinetic energy and temperature calculations.

**Check step numbers**: Implemented in the same way as the sample preparation routine.
A2. Unit Rescaling in MD Simulations

All simulation results were presented as rescaled values, meaning each value is relative to a certain chosen unit amount. The unit amounts were chosen naturally using parameters specified in potential formulation, i.e., the Lennard-Jones pair potential,

$$U_{ij}(r) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} \right]$$

4.1

with notations defined in chapter 4.

In MD simulation using Lennard-Jones potentials, it is convenient to rescale the units such that all quantities are expressed relative to the scaling factor. After rescaling, the simulation results are not associated with any particular system; different systems would only affect the scaling factors, leaving the rescaled simulation results unchanged. The rescaling of some of the most commonly used quantities are listed below,

Boltzmann's constant and each atomic mass are set equal to 1.0.

Length is rescaled such that

$$\hat{r} = \frac{r}{\sigma}$$

where \( \hat{r} \) is the rescaled length and \( r \) is the actual length.

Energy is rescaled such that

$$\hat{\varepsilon} = \frac{\varepsilon}{\varepsilon}$$

Time is rescaled such that

$$\hat{t} = \frac{t}{\sqrt{(m\sigma^2/\varepsilon)}}$$

Velocity is rescaled such that

$$\hat{v} = \frac{v}{\sqrt{\varepsilon/m}}$$

Pressure, stress and modulus are rescaled such that
\[
\dot{P} = \frac{P}{(\varepsilon/\sigma^3)} \quad \text{for 3D} \quad \text{or} \quad \dot{P} = \frac{P}{(\varepsilon/\sigma^3)} \quad \text{for 2D}
\]

If the system simulated were pure Cu, the relative coefficients would be,

\[\sigma = 2.5172 \, \text{Å}; \quad \varepsilon = 0.35279 \, \text{eV}; \quad m = 1.0551 \times 10^{-25} \, \text{kg}.\]

Based on these values, the following relationship can be calculated,

\[\dot{r} = 1 \quad \Rightarrow 
\begin{align*}
\dot{\sigma} &= 2.5172 \, \text{Å} \\
\dot{\varepsilon} &= 0.35279 \, \text{eV} \\
\dot{\tau} &= 1 \quad \Rightarrow 
3.4423 \times 10^{-13} \, \text{sec.}
\end{align*}
\]

\[\dot{P} = 1 \quad \Rightarrow 
\begin{align*}
3.5392 \, \text{GPa (3D)} & \quad \text{or} \quad \dot{P} = 1 \quad \Rightarrow 
0.89087 \, \text{N/m (2D)} \\
\dot{v} &= 1 \quad \Rightarrow 
731.42 \, \text{m/s}
\end{align*}
\]
A.3 Observation of Local Shear Events in Simulations

In the MD simulation, local shear events were observed during sliding. Fig.A-5 shows two such events. The two upper pictures are snapshots of the system 2.5 rescaled time units apart. Close-up views of an area near the sliding interface are also shown. The local regions within the ellipsoids sheared much more compared to their neighboring regions. Similar local shear events take place during the entire process of sliding. Regions near the sliding interface, where most of the shear takes place, seem to have more local shear events. The features of the local shear events observed in this study are similar to those described by A. Argon and F. Spaepen et al. in their plasticity model for metallic glass (described in more detail in Chapter 2).
A.4 Sequence of Marker Evolution in MD Simulations

Figures A-6 to A-11 show the sequence of marker evolution during a sliding test with $V_s = 0.15$. For $t \geq 900$, more than one simulation cell is plotted side by side on the figures to show the shape of a complete marker. This is valid because of the periodic boundary condition imposed in the X direction.

The bending of the marker illustrates the strain gradient introduced by sliding. Jogs appear on the marker, e.g., on the lower block of Fig.A-9, indicating that the strain gradient is not smooth during sliding. The sudden changes in strain gradient are consistent with the observation of local shear events. Fig.A-12 is a schematic illustration showing how a local shear event can affect the shape of a marker, or effectively the strain gradient.

After sliding for a long distance (i.e., $t \geq 4100$), it becomes difficult to identify a marker near the sliding interface. From the observation of mechanical mixing, it was concluded that there is atomic level transport taking place in the Y direction near the sliding interface. The nature of the transport perpendicular to the sliding direction is unknown. However, it does seem to involve certain random processes as suggested by the square root of $t$ dependence of the growth kinetics of the mixed region. Such random Y direction transport would accumulate during sliding and eventually can destroy the continuity of the marker. It has been observed experimentally that markers in general do not extend into the most extensively deformed regions.
A.5 Appendix Figures

Fig. A-1 Flow chart for sample preparation routine
Fig. A-2 Illustration of the binning process.
Fig.A-3 Flow chart for sliding test routine
Fig. A-4 Distance calculation with imposed periodic boundary conditions.
Fig. A-5 Illustration of local shear events observed in MD simulation.
Fig. A-6 The marker shapes during MD simulation with $V_s = 0.15$ at $t = 100$, 300, and 500.
Fig. A-7 The marker shape during MD simulation with $V_s = 0.15$ at $t = 900$. 
Fig. A-8 The marker shape during MD simulation with $V_s = 0.15$ at $t = 2100$. 
Fig. A-9 The marker shape during MD simulation with $V_s = 0.15$ at $t = 3100$. 

$t = 3100$
Fig.A-10 The marker shape during MD simulation with $V_s = 0.15$ at $t = 4100$. 

$t = 4100$
Fig. A-11 The marker shape during MD simulation with $V_s = 0.15$ at $t = 6100$. 
Fig.A-12 Schematic illustration of how a local shear event can result in changes of marker shape or equivalently the local strain gradient.
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