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Cooling – As a “Heat Treatment” for the Mechanical Behavior of the Bulk Metallic Glass Alloys

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1. Introduction

Metals play a significant role in human life since the Bronze Age. Metals' important advantages include higher toughness and predictable fracture behavior in all directions, which are fundamentally essential for engineering applications. In coarse-grain polycrystalline alloys, the plastic deformation is mediated by dislocations within the grains. Micromechanisms of dislocation-based plasticity have been well investigated. Taylor, Polanyi, and Orowan's speculative models and Hirsch and Whelan's experimental results clearly demonstrate that the existence of dislocations in the metals, like a double-edged sword, enhances the ductility, while reducing the theoretical strengths of most of the metallic crystalline systems [1]. However, the toughness depends on the integration of both strength and ductility. Hence, designing of advanced metallic materials to answer the challenging strength-ductility dilemma become an urgent call. There is natural limitation on the conventional polycrystalline metallic alloys. In practical uses, there are always some inherent defects in the crystalline phases, which degrade the alloys properties. Recently, the limitation of the crystalline-material strength was passed when the metallic alloys with amorphous structures were successfully synthesized in many material systems through advanced manufacturing methods[2]. Although most of the metallic elements existing in the nature are present with crystalline structures which are the most stable structures with the lowest energy state, sometimes they can be made by various ways into metastable amorphous solid forms, such as rapid quenching techniques [3-5], mechanical alloying [6-8], accumulative roll bonding [9-12], and vapor condensation [13]. The characteristics of the mechanical, thermodynamic properties of such category of metallic materials are very similar to ceramic glasses, and thus they are also called as metallic glasses. Moreover, by introducing specific crystalline phases, such as crystalline dendrites, in an amorphous matrix, bulk metallic glass-

composite materials demonstrate the improved plasticity and toughness, compared with monolithic amorphous materials [14]. These metallic systems have the capacity of revolutionizing current metal-forming technologies and manufacturing industries.

2. The development of metallic glasses

In 1960, Klement *et al.* [15] developed the first metallic glasses of $\text{Au}_{75}\text{Si}_{25}$ by the rapid quenching techniques for cooling the metallic liquids at very fast rates of 10^5 - 10^6 K/s. Their work quickly initiated broad interest among the scientists and engineers because they showed a new "heat treatment" without nucleation and growth of crystalline phase when it cooled fast enough to frozen the liquefied configuration. Later on, the ternary amorphous alloys of Pd-Si-X (X = Ag, Cu or Au) were discovered successfully by Chen and Turnbull [16], and the Pd-T-Si (T = Ni, Co or Fe) ternary amorphous alloys which included the magnetic atoms were also developed in the same period [17]. The maximum size of these metallic glasses could be as large as 1 mm in diameter by using the die casting and roller-quenching method. The effects of the alloy systems, compositions and the existence of a glass transition was demonstrated, it led to the first systematic studies in the formation, structure and property investigations of amorphous alloys. Because of their fundamental science interests and engineering application potential, the metallic glasses have attracted great attention since then. The geometry of metallic glasses, however, is limited to thin foils or lines since the formation of glass states needs super-fast cooling rates, which are not easy for industrial mass production. How to determine the glass forming ability (GFA) of amorphous alloys and increase the diameter of specimens becomes the important topic in that time. Turnbull and Fisher [18] advanced a criterion to predict the glass forming ability of an alloy. According to their criterion, the reduced glass transition temperature T_{rg} , equal to the glass transition temperature T_g over liquids temperature T_l , or $T_{rg} = T_g/T_l$ is the primary factor. If T_g is larger and T_l smaller, the value of T_{rg} will be higher so that such a liquid can be easily undercooled into a glassy state at a lower cooling rate. Although there are several new criteria proposed following them [19-20], the T_{rg} has been proved to be useful to reflect the GFA of metallic glasses including BMGs.

In 1974, the rods of Pd-Cu-Si alloy about 1~3 mm in diameter, the first bulk metallic glasses were prepared by Chen [17] using simple suction-casting methods. In 1982, Turnbull's group [21-22] pushed the diameter of critical casting thickness of the Pd-Ni-P alloys up to 10 mm by processing the Pd-Ni-P melt in a boron oxide flux and eliminated the heterogeneous nucleation. A series of solid state amorphization techniques that are completely different from the mechanism of rapid quenching had been developed during that time. For example, mechanical alloying, strain-induced amorphization in multilayers, ion beam mixing, hydrogen absorption, and inverse melting [23]. The thin films or powders of metallic glasses can be acquired as well as by interdiffusion and interfacial reaction of the temperature just below the glass transition temperature.

In the late 1980s, Inoue's group [24-25] in the Tohoku University, Japan, developed new groups of multicomponent metallic glass systems with lower cooling rates in Mg-, Ln-, Zr-,

Fe-, Pd-, Cu-, Ti- and Ni- based systems. The Inoue group found exceptional glass forming ability in La-Al-Ni and La-Al-Cu ternary alloys system [24]. By casting the alloy melt in water-cooling Cu molds, the cylindrical samples with diameters up to 5 mm or sheets with similar thicknesses were made fully glassy in the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ alloy. Similarly, the $\text{La}_{55}\text{Al}_{25}\text{Ni}_{10}\text{Cu}_{10}$ alloy, fabricated by the same method, was even bigger with a diameter up to 9 mm.

In the 1990s, the Inoue group further developed a series of multicomponent Zr-based bulk metallic glasses, such as Zr-Cu-Ni, Zr-Cu-Ni-Al, etc., along with Mg-based, e. g. Mg-Cu-Y and Mg-Ni-Y alloys, all exhibiting a high Glass Forming Ability (GFA) and thermal stability [26-29]. For one of the Zr-based BMGs, $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$, the critical casting thickness was up to 15 mm, and the largest critical casting thickness was 72 mm in the Pd-Cu-Ni-P family [30]. With Inoue's advancement of the aforementioned bulk metallic glass alloys, the BMGs were no longer laboratory curiosity. The possibility of promising engineering applications became reality. One of the examples was that the Zr-based bulk metallic glasses were applied in the industries just three years after it was invented [31]. Subsequently, a set of the very famous empirical rules in order to direct the selection of alloying elements and composition of glass forming alloys have been summarized by Inoue and Johnson as follows [32-33]: (1) Multicomponent alloys with three or more elements; (2) More than 12% atomic radius difference among them; (3) Negative heat of mixing between constituent elements; (4) The deep eutectic rule based on the T_{rg} criterion. These rules concluded critical criteria for the design of the BMGs until 1999. However, the exception was found in the binary systems, such as the Ni-Nb [34], the Ca-Al [35] the Zr-Ni [36], and the Cu-Zr [37-38] alloys. The above systems can also produce BMGs with the size up to several millimeters without the limitations of the eutectics. In summary, the formation mechanism and criteria for the binary BMGs might not follow the traditional multi-component systems. These results suggest that there are many other potential forming systems of the metallic glasses to be discovered.

3. How to describe the mechanical behavior of the bulk metallic glasses

Over the past four decades, considerable research efforts have been made on the BMGs due to their potential opportunity based on the high yield strength, relatively high fracture toughness, low internal friction, high fatigue resistance, as well as better wear and corrosion resistance [31-32, 39]. Although the bulk metallic glasses (BMGs) are one of such species of materials which are considered for future industrial applications, the insufficient plastic deformation at room temperature is still the Achilles' heel for the industrial applications regardless of its highly scientific value. In general, metallic glasses (MGs) are disordered materials which lack the periodicity of long range ordering in the atom packing, but the atomic arrangement in amorphous alloys is not completely random as liquid. In fact, many scholars believe that amorphous structures are composed of short range ordering, such as icosahedra clusters or other packing forms related to the intermetallic compounds that would form in the corresponding equilibrium phase diagram [40-41]. The short range order is identified as a structure consisting of an atom and its nearest neighbors perhaps two or

three atom distance. Recently, the study of medium range order is highlighted as a new ordering range between the short range order and the long range order in the amorphous structure [42]. When an amorphous structure is achieved by quenching, it may be composed of icosahedral local short-range ordering, network-forming clusters medium-range ordering, and other unidentified-random local structures [42-43], that is, a complex association in their topology. How to build the atomic structural model in BMGs and how to fill three dimension spaces with these local structural units are still important issues although only limited research has been done so far [44-47]. Due to the difference in the structural systems between metallic glasses and crystalline alloys, it has an unusual performance on the mechanical properties [48-51]. For example, most metallic glasses exhibit evident brittle fracture under an uniaxial tensile loading, but sometimes give very limited plasticity before failure by means of shear-band propagation. Also, BMGs can perform a large global plasticity through the generation of multiple shear bands during unconfined or confined compression test. Activities of shear band are viewed as the main factor on the plastic deformation of BMGs. The more shear bands on the lateral surface of deformed samples, the larger plasticity is obtained. Liu *et al.* [52] show profuse shear bands on a lateral surface of a Zr-based BMG sample after failure. It can be seen the high-density shear bands are distributed corresponding to large plasticity. Despite a wealth of investigations, many questions about shear bands and their microstructures are still unclear so far. For instance, how does a shear band initiate in the MG and develop in to a mature shear band from its embryo, how do shear bands interact with each other, and how would the shear band develop in a composite surroundings such as interactions with embedding crystals? These issues not only depend on the effect of temperature but are also related to the strain rate and other else. The width of a typical shear band is around 10^1 nm[53], and the size scale used to define the structures of metallic glasses is within 1-3 nm.

The studies in the microstructures of metallic glasses in this shortest length scale by laboratory X-Ray, scanning electron microscope (SEM), and Transmission electron microscopy (TEM) are usually excellent and interesting, but they are relatively less in the theoretic models either in the statistic or continuum simulation computing than those in experiments. Through the studies of simulation methods to compare with experimental data, such as electron scattering data and pair distribution functions, it is expected to be able to investigate the shear-band mechanisms and the microstructures of BMGs in depth. Also, a completely theoretic model could be built up due to the combination of computing model and experiments, not only to explain the current experimental phenomena but also to predict the probative behavior in the future.

Molecular dynamics (MD) simulation is one of important simulation methods provided significant insight into material properties under the atomic level. The major advantage of MD simulations is to see a detailed picture of the model under available investigation, and so they have been very instrumental in explaining the connection of macroscopic properties to atomic scale [54]. For instances, MD simulation has been carried out successfully in the studies of various metallic systems such as point defect movement [55], dislocation mechanisms [56-57], and grain-boundary structures in polycrystalline materials [58-61] in

recent years. However, a number of limitations in the simulations will also be confronted, while simulations are treated as key insights in the study. Generally, there are three limitations in the current MD simulation, namely the availability of MD potential, time-scale limitations, and the limit on the system size. Two of the later can be alleviated in the promotion of computer efficiency and by adding the parallelization techniques in program, but the former is still challenged on the accuracy of material specificity and on the development for the multicomponent system, especially for the BMGs. Hence, some pioneering attempts [42, 62-64] have shown the possibility of the MD to resolve the mysterious of the BMGs.

4. Microstructures in metallic glasses

In 1959, a structural model of dense random packing of hard spheres is first suggested by Bernal [65] to be a simple model for metal liquids, and subsequently indicated by Cohen and Turnbull [66] that this simple model can be also applied to describe the metallic glasses. In 1979, Wang [67] supposed that the amorphous metal alloys may be a special class of the glassy state whose short-range structure is random Kasper polyhedral close packing of soft atoms similar to those in the crystalline counterparts. This short-range structure is described based on a new type of glassy structure with a high degree of dense randomly packed atomic configurations. The density measurements show that the density difference is in the range 0.3~1.0% between bulk metallic glasses and fully crystallized state [68-69]. There is neither splitting of the second peak nor pre-peak at the lower wave vector as seen in the reduced density function curve of the BMGs [68, 70-71]. These results confirm that the multicomponent BMGs has a homogeneously mixed atomic configuration corresponding to a high dense randomly packing. One of the most important topological short range structures developed among glasses and supercooled liquids are the local icosahedral clusters, which are revealed by many simulation studies [72-76]. An icosahedron is the central atom which forms a fivefold symmetry arrangements with each of its 12 neighbors. In contrast is a regular fragment of an FCC order, and the same pair will become an HCP order if the bottom close-packed plane is shifted as the same as the top plane. This fivefold symmetry and icosahedral clusters is also detected from the experiments of liquids and metallic glasses [77-78], even though in an immiscible binary system with positive heat of mixing [74-76]. The binding energy of an icosahedral cluster of 13 Lennard-Jones (LJ) atoms is 8.4% lower than an FCC or HCP arrangement [79]. The critical size for a transition from icosahedral cluster to icosahedral phase is about 8 nm [25]. Icosahedral packing is a basic structural unit in extended amorphous systems, and the existence of icosahedral clusters offer seeds for the precipitation of the icosahedral phase. The icosahedral quasicrystalline phase will precipitate in the primary crystallization process and then transforms to stable crystalline phases when the amorphous alloys is annealing at higher temperatures [80-82].

In recent years, an order effect, called the medium range order, existing over length scale larger than the short range order but not extends to the long range order as crystalline state, has been detected in the some amorphous alloys [83-85]. Although the icosahedral type

model gives a sound description on the structure in the short range order of metallic glasses but fails beyond the nearest-neighbor shell. For instance, how can the medium range order be defined with the local structural unit, and how would the local structural units be connected to full three-dimensional space? Miracle [86] suggested a compelling structural model for metallic glasses based on the dense packing of atomic clusters. An FCC packing of overlapping clusters is taken as the building scheme for medium range order in metallic glasses. Figure 1 illustrate his promoted model of medium range order. A reality check for these previous structural concepts was proposed by Sheng *et al.* [42] with experiments and simulations. They indicate the icosahedral ordering of single-solute-centered quasi-equivalent clusters is an efficient packing scheme, but is not the only type of medium range order. For each one of the metallic glasses, the several types of local coordination polyhedra units are geometrically different, and not identical in their topology and coordination number. They can be considered quasi-equivalent, or cluster-like units for a given glass, supporting the framework of cluster packing. The cluster connection diagrams for the several metallic glasses maybe represents the important question of how the clusters are connected and packed to fill the three-dimensional space, giving rise to the medium range order. It is short range for the packing of clusters but already medium range from the standpoint of atomic correlation beyond one cluster.

A new insight, imperfect ordered packing, which is closely related to the cooling rate, is exposed on the medium range order embedded in the disordered atomic matrix by selected simulation of high-resolution electron microscopy image [87]. It points out that the packing character of medium range ordering structures can be of two types, i. e. icosahedron-like and lattice-like, and indicates that the solidification from melts or crystallization of metallic glasses is controlled by preferential growth of the most stable imperfect ordered packing. On the other hand, Fan *et al.* [88-89] proposed a structural model for bulk amorphous alloys based on the pair distribution functions measured using neutron scattering and reverse Monte Carlo simulations. There are many clusters of imperfect icosahedral and cubic forms. These clusters are randomly distributed, strongly connected, and result in the space between the clusters. The space between the clusters forms free volume, which provides a degree of freedom for the rotation of the clusters under applied load. This cooperative rotation of clusters forms a layer motion (i. e. shear bands), and plastically deforms the amorphous alloys. This model implies that the mechanical properties, e. g. strength and ductility, are dominated by the combination of the bonding characteristics inside and between these clusters. Since the microstructure of the bulk metallic glass decides the properties, it is important to characterize why and how the microstructure changes subjected to fabrication and deformation. The transmission-electron-microscopy (TEM) technique has offered direct observations of local structural characteristics for materials optimization [14]. However, due to the finite sampling space, special care is required to extract the ensemble-average information from the taken image. On the other hand, the neutrons and the high-energy synchrotron x-ray can penetrate the bulk materials, which can give complimentary statistically-sufficient averaged results [14,90-91]. Recently, with the advance of the synchrotron x-ray and neutron facilities, the neutron and synchrotron x-ray diffractometers are equipped with furnaces and other instruments. Hence, the scattering/diffraction

measurements become real-time *in-situ* observations. The application of the small-angle neutron scattering (SANS) is one of the complementary approaches to gauge a greater volume without destructive sampling. Prof. William Johnson has shown how to combine the aforementioned TEM and SANS to investigate the microstructure evolution of the bulk amorphous metallic glasses [92]. Dr. Xun-Li Wang demonstrates the *in-situ* synchrotron x-ray study of phase transformation behaviors in the bulk metallic glass by simultaneous synchrotron x-ray diffraction and small angle scattering [93]. The special features of the neutron and synchrotron diffractometers bridges the traditional bulk stress-strain measurements with the microscopic-level understanding [94].

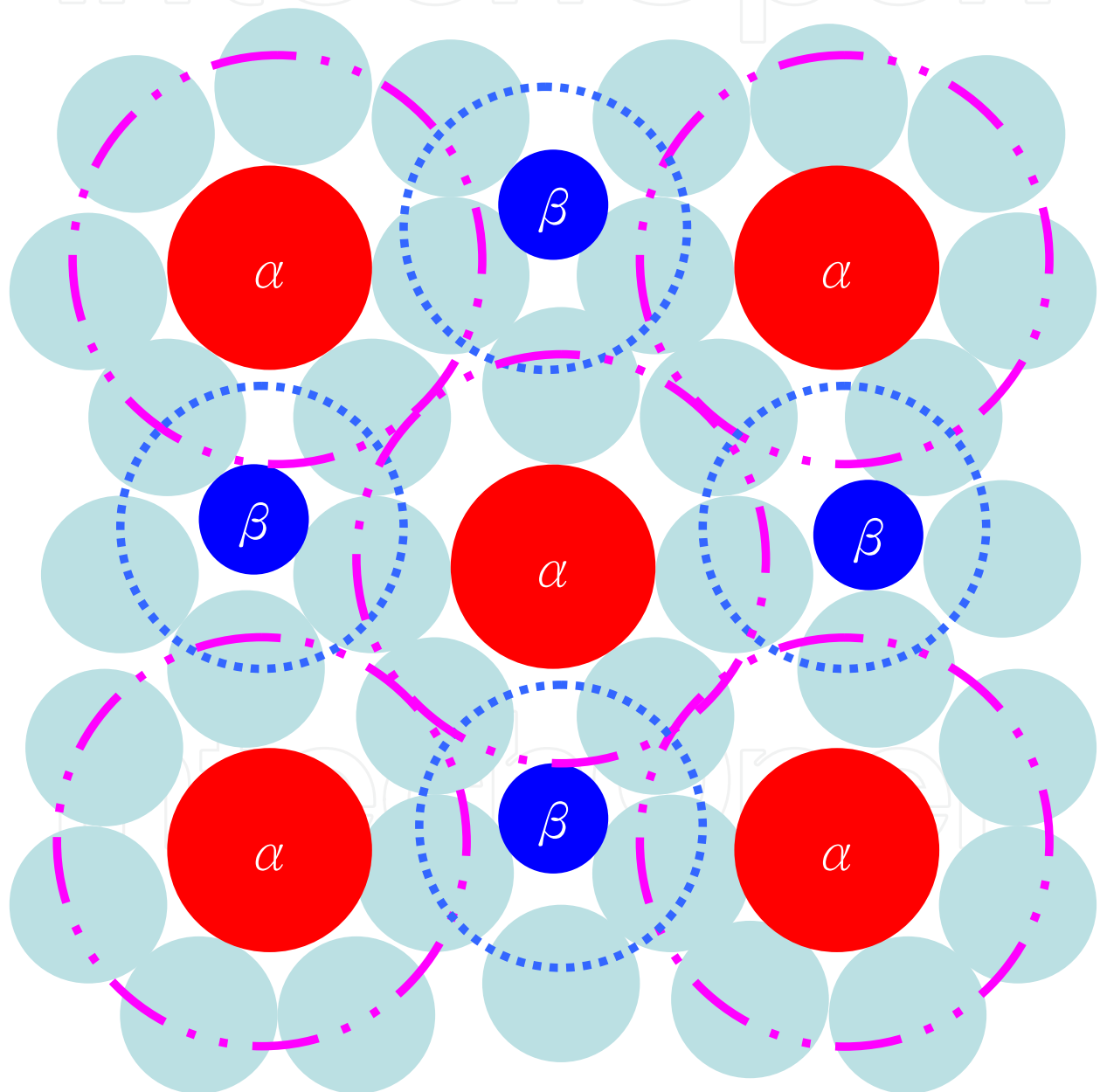


Figure 1. Medium range order model: A two-dimensional representation of a dense cluster-packing structure illustrating the interpenetrating clusters of their efficient atomic packing around each solute α and β .

5. Deformation mechanisms

Unlike the dislocation mechanisms for plastic deformation in crystalline alloys, the amorphous alloys only allow limited atomic displacements to resist deformation as a result of the glassy structure with a high degree of dense randomly packed atomic configurations, when the applied stress is on the amorphous alloys [25,95]. The BMGs have higher tensile fracture strength σ_f of 0.8-2.5 GPa, Vickers hardness H_v of 200-600, and lower Young's modulus E of 47~102 GPa, than ordinary metallic crystals [25]. It is considered that the significant difference in the mechanical properties is due to the discrepancy in the deformation and fracture mechanisms between bulk metallic glasses and crystalline alloys. It has been widely accepted that shear-band propagation is the major cause affecting the plasticity and toughness of the amorphous alloys. Plastic deformation in metallic glasses is generally associated with inhomogeneous flow in highly localized shear layers with a thickness of about 10 nm. When the shear band went through in the metallic glasses, it is often accompanied with locally rising high temperature to influence the shear flow. From tensile experiments, there was local melting occurs under high strain rate situations such as dynamic loading through unstable fracture [96]. Even under slower loading rates, a veined vein pattern is developed indicating a decrease in the glass viscosity. Due to the highly localized nature of flow and the lack of microstructural features in the metallic glass to distract the flow, shear band propagation typically leads to catastrophic failure. The strain softening and thermal softening mechanisms are closely associated with the localization of shear band [97]. Generally speaking, the metallic glasses have high fracture toughness but brittle as well as negligible plasticity. For instance, the Zr-based bulk metallic glasses present high Charpy impact fracture energies ranging from 110-140 kJ/m² and high fracture toughness limit [98]. Their fatigue limit is close to those of the crystalline alloys. However, standard stress-strain fatigue tests show that the Vitreloy alloy (commercial Zr-based BMG) has an extremely low resistance to crack initiation and a crack propagates rapidly once it is formed. If this alloy does start to yield or fracture, it fails quickly. Geometrical confinement of shear bands can dramatically enhance overall plasticity. Furthermore, the plastic yield point of most bulk metallic glasses is located within a small range around $\sigma_y = 2\%$ at room temperature [99]. Composite approach is used to enhance the ductility and toughness of metallic glasses in recent fabricating efforts[100]. Its behavior is like a typical bulk metallic glasses initially but performs as a perfectly plastic deformation after passing the yielding point of 2%. This Pt-Cu-Ni-P bulk metallic glass has a high Poisson ratio of 0.42, which causes the tip of a shear band to extend rather than to initiate a crack. The above mechanism results in the formation of multiple shear bands and is the origin of the large ductility [101]. Due to the absence of dislocation and grain boundary structures, the plastic deformation mechanism of metallic glasses is well known as shear-band evolution that deeply associates with the mechanical properties and failure behavior in bulk metallic glasses. Nevertheless, the shear band is not the basic defect unit in the deformation mechanisms in the metallic glasses under microscopic scale. In the 1960s, Cohen and Turnbull [102] as well as Spaepen [103] suggested a concept of the free volume which is considered as vacancy-like defect in the metallic glasses, and Argon [104] proposed a theoretical model of plastic flow in

metallic glasses, termed shear transformation zone (STZ), which is the fundamental shear unit consisting of a free volume site and its close adjacent atoms in amorphous metals.

In the conceptual framework of free volume, the mechanical coupling is weak to the surrounding of free volumes, and hence the inelastic relaxation becomes possible by local atom rearrangement, without affecting the surroundings significantly [105]. Thus, free volume regions could be the preferred sites where easy caused the glass structure destabilization by either temperature or applied stresses. The concept of free volume is most frequently used in explaining the deformation behaviors and atomic relaxations in the MGs due to its convenient for a measurement (density or enthalpy change), and easy understanding, that is, a necessary open space allowed for a shear process to operate. For instance, a simple relationship $v_f / v_m = \beta \cdot \Delta H$ assumes that enthalpy ΔH is proportional to the variation of the average free volume per atom v_f / v_m [106]. Thus, based on the enthalpy recovery measurements, the reduction of free volume difference via structural relaxation, v_f / v_m , was determined. Also, a free volume exhaustion mechanism was proposed by Yang *et al.* [107] to explain the interesting fact that propagation of shear bands in metallic glasses can be retarded, with decreasing temperature and shear strains, in the lack of work hardening mechanisms. It is generally thought that the shear bands could form as a result of the movement and accumulation of free volumes (dilatation expansion). Atomic simulations also show that the local free volumes increase in the BMG provides an open space for the movements of atoms and is associated with the localization of shear band, and the shear softening results from the production of excessive free volume in the shear band [108-110]. Despite the successful description on the strain softening, heterogeneous deformation of MGs, and various mechanical properties of experimental observations, the validity of the free volume theory is questionable, and its atomic basis is still being challenged by atomic simulations. One can easily find the ambiguous characteristics that the free-volume sites may initiate plastic deformation and also can be the result of plastic deformation simultaneously, but not the deformation process itself [111]. Besides, the free-volume model has not made clear motion and rearrangement of constituent atoms within shear bands during plastic flow. To clearly identify the “free volumes” is almost impossible either in experiments or simulations that results in the barrier on the building complete physics model so far. Generally, the concept of free volume is successful as a phenomenology but not as a microscopic theory [105].

6. The model of shear transformation zones

According to Argon’s shear transformation zone (STZ) model [112], shear deformation takes place by spontaneous and cooperative reorganization of a small cluster of randomly close-packed atoms [113]. An STZ can supply a small increment of shear strain under the action of an applied shear stress [114], and thus creates a localized distortion of the surroundings to accomplish the shear-band formation. The size of STZ is predicted among the order of 100 atoms from energetic considerations [115-116] and is consistent with the model of molecular dynamics simulation in the investigation of Cu-Ti system [117]. Liu’s [118] schematic view on formation of the first STZs in the year of 2012 suggests that a metallic glass system is assumed

to be sheared under a constant strain rate. Considering the intrinsic heterogeneity and preexisting flaws resulted from casting, the first STZ generates easily under the action of a stress smaller than macro yielding stress. Since the first STZ alters the initial strain field, the surrounding material is subjected to a self-generated dynamic and thermal noise. With the aid of the heterogeneous strain field and thermal noise, the secondary STZ emerges subsequently in the neighborhood of the first STZ. As a consequence, a shear band nucleus or an embryo of avalanche forms, which induces the yielding of the macroscopic material. STZs have equal chances to propagate forward or backward along the shear plane. For simplicity, here, we only report the case that the STZ starts at one edge and propagates in one direction. Compared with abstract free-volume concept, the STZ mechanism is easy to be studied in the atomic models. A number of MD simulation studies by Falk and Langer summarized the crucial features of STZ mechanisms as follows [111, 119]: (a) once a STZ has transformed and relieved a certain amount of shear stress, it cannot transform again in the same direction. Thus, the system saturates and becomes jammed. (b) STZs can be created and destroyed at rates proportional to the rate of irreversible plastic deformation, and plastic flow can take place only when new zones are being created as fast as existing zones are being transformed. (c) The attempt frequency of the transition is tied to the noise in the system, which is driven by the strain rate. The stochastic nature of these fluctuations is assumed to arise from random motions associated with the disorder in the system. (d) The transition rates between jammed and flowing are strongly sensitive to the applied stress. Recently, they also proposed a criterion (effective temperature) that determines which materials exhibit shear bands based on the initial conditions alone, based on their STZ theory [120-122]. The behavior of the effective temperature as a function of time for a system that localizes and a system that does not localize [120]. Their numerical works show that perturbations to the effective temperature grow due to instability in the transient dynamics, but unstable systems do not always develop shear bands. Nonlinear energy dissipation processes interact with perturbation growth to determine whether a material exhibits strain localization [120]. Argon considered the shear deformation of shear-transformation zones (STZs) as a disk of two-layer atoms around a free-volume site, which had a shear strain of $\gamma_0 \approx 1$ [112]. With a shear stress, τ , the plastic work can be expressed as $\tau\gamma_0\Omega$, where Ω is the volume of the STZ. The deformation of a unit STZ is visualized as an adiabatic process, and the instantaneous temperature increase in the STZ is calculated as [123]: $\Delta T = \frac{\alpha\tau\gamma_0\Omega}{\rho C_p \Omega} = \frac{\alpha\tau\gamma_0}{\rho C_p} \approx \frac{\alpha\tau}{\rho C_p}$, where ρ is the density, C_p is the heat capacity, and $\alpha \approx 0.9$ is the ratio of the plastic work converted to heat. Other simulation studies in the nature of STZ model are keeping on publish [124] and become worthy of investigating this crucial issue in depth.

7. Theory of shear banding and shear band model

According to the experimental observations, the width of a shear band is about 100 nm, which is the same as its offset shear displacement [125-126], and propagation time of shear bands is about 10^{-5} second [127]. Because shear bands are thin, move fast, and are short-lived, to

observe the dynamic evolution of the shear bands in the metallic glasses is highly difficult. Building the atomic scale model of shear band such as the development of a shear band inside a binary bulk metallic glass model is very beneficial for studying the shear band mechanism [110]. A simple conceptual quantity excess volume, $v_{excess} = v_{voro} - v_{atom}$, is used to investigate the relation between the free volume changes and shear localization. They suggested that shear banding results from the volume-expansion-induced mechanical softening [109-110, 128-129]. A loop of “local volume increase \rightarrow local shear softening \rightarrow large local strain \rightarrow local volume increase” may be the basic mechanism for deformation and shear banding in MGs. Similar results are observed in the shear-band simulation works of the Mg-Cu systems by Bailey et al. [130], the interactions of the shear bands with the free surfaces as well as with each other result in an initial temperature rise, but the rise of temperature are delayed somewhat with respect to the localization of plastic flow itself. Shimizu *et al.* proposed an aged-rejuvenation-glue-liquid (ARGL) model of shear band in BMGs [131]. That is a more complete theoretical model of shear band than that of others so far. They proposed that the critical condition of initiating a mature shear band (MSB) is not the nucleation of embryonic shear band (ESB), but its propagation. The ESB is easy forming in the MGs. However, to propagate an ESB, the far-field shear stress must exceed the quasi-steady-state glue traction stress of shear-alienated glass until the glass transition temperature is approached internally due to frictional heating, at which point ESB matures as a runaway shear crack [131]. In contrast, when applied stress is below the glue traction, the ESB does not propagate, become diffuse, and eventually die. At the same time, an incubation length scale l_{inc} is necessary for this maturation for the BMGs, below which sample size-scale shear localization does not happen. The incubation length $l_{inc} \sim \alpha c_v^2 (T_g - T_{env})^2 / \tau_{glue}^2 c_s$, where α is the thermal diffusivity, c_v is its volumetric specific heat, T_{env} is initial temperature, is the c_s shear wave speed. Through the calculation of this form, the l_{inc} is about 10 nm for Zr-based BMGs [131-132]. Furthermore, it is often questioned whether the shear band mechanisms with regard to metallic glasses is similar to the dislocation mechanisms for crystalline structure, although they are of different definitions. Schuh and Lund [114] found that the plasticity in metallic glasses is consistent with the Mohr-Coulomb criterion by the STZ theory as well as molecular simulation works, and predicted a transition from dislocation-dominated yield processes (following the von Mises criterion) to STZ-dominated yield (following the Mohr-Coulomb criterion) as grain size decreases toward zero for nanocrystalline materials. Ogata et al. [133] simulated the nucleation of local shear transformation zone (STZ) and shear band, under volume-conserving simple shear deformation in molecular dynamics. A significant shear-normal stress coupling which suggests the modified Mohr-Coulomb yield criterion has also been demonstrated. They suggested that the dislocation concept may be applicable to bulk metallic glasses with modifications such as taking into account the structural features of bulk metallic glasses instead of the Burgers vector concept in crystals. The plastic deformation always accompanies the localized heating within shear band that is an important key-point to result in the strain-softening mechanisms and thermal softening on the fracture surface [134]. Understanding the temperature rise in shear bands can also help to improve the ductility and toughness of the metallic glasses. A substantial increase in temperature will correspond with a drop in viscosity

governed by the presence of free volume within the metallic glasses [135]. From the calculation of heat conduction theory and STZ modeling, Yang *et al.* [123] demonstrated that the temperature of shear bands at the fracture strength is strikingly similar to their glass transition temperature for a number of BMG systems. This offered a new guideline for the expansion of ultra-high strength bulk metallic glasses from their glass transition temperature, density, and heat capacity values.

8. Conclusions

In summery, the fabrication techniques of the bulk metallic glasses are reviewed chronically. The fundamental concepts of the unique microstructures of the bulk metallic glasses according to different manufacturing are introduced. Moreover, the proposed, but still under debate, various deformation mechanisms are discussed. We wish to draw more attentions from the readers to explore the exciting potential and underneath mechanisms of the bulk metallic glasses.

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