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**COMPRESSIVE FLOW BEHAVIOR OF Mg₅₄Cu₂₈Ag₇Y₁₁
IN THE SUPERCOOLED LIQUID REGION (PREPRINT)**

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Compressive flow behavior of Mg₅₄Cu₂₈Ag₇Y₁₁ in the supercooled liquid region

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Uniaxial compression tests of Mg₅₄Cu₂₈Ag₇Y₁₁ metallic glass were performed in the supercooled liquid region (468 K) at a strain rate range of 5×10^{-4} – 2×10^{-4} s⁻¹. In the course of testing, shear thickening behavior was observed. The deformation behavior of the glassy metal is discussed with special emphasis on the stress overshoot commonly reported in the metallic glass literature, relaxation behavior, and the previously unreported shear thickening behavior observed. Two potential mechanisms are presented to explain the deformation behavior of the glassy metal.

Keywords: Metallic glasses; Crystallization; Deformation; Supercooled liquid; Mg alloy

Metallic glasses have been the subject of intensive research following their discovery 50 years ago. The rapid crystallization kinetics of these early metallic glass ribbons prevented the study of the material above the glass transition. In the 1980s and 1990s, glass forming alloys with slower crystallization kinetics were discovered, these materials are referred to as bulk metallic glasses (BMGs) [1]. These new alloy systems allowed the formation metallic glasses with ever increasing critical casting diameters, and they also permitted researchers to probe the behavior of amorphous metal systems in the supercooled liquid region (SCLR) above the glass transition temperature but below the crystallization temperature. Of particular interest is the near Newtonian flow behavior of BMGs in the SCLR. Strain rate sensitivity values (*m*-values) between 0.8 and 1 are typically reported in strain rate ranges between 10^{-5} and 10^{-2} s⁻¹ [2].

As a result of the Newtonian behavior, BMGs exhibit excellent superplastic properties. Tensile elongations above the glass transition vary widely depending on testing and material parameters, but elongations in excess of 1,000% have been observed in multiple alloy systems with some elongations exceeding 10,000% [2-4]. Furthermore, the strength of a BMG in the supercooled region is nearly an order of magnitude lower than the strength of the same material below the glass transition temperature [5,6]. An excellent example of the low flow stresses in the SCLR is the superplastic blow forming performed on a Zr-based BMG. Parts with excellent surface finish and feature replication were formed with gas pressures as low as 0.2 MPa [6]. Due to the exceptional formability and superplasticity exhibited by BMGs in the SCLR and their exceptional room temperature strengths [7], BMGs show a great deal of promise in MEMS devices and other small scale, mechanically demanding applications.

At present, the most successful commercial metallic glasses, Zr-based glasses being the most widely studied, have been the focus of the bulk of research in the field. Unfortunately, these BMGs contain elements that result in high densities. Lower density BMG systems, such as Mg- and Ca-based, have shown lower room temperature fracture toughness than the more studied glass forming systems [8]. The poor performance at room temperature has limited the amount of work being done on monolithic samples from these systems in the supercooled liquid region. The present study highlights material behavior discovered during compressive deformation in the

SCLR of one Mg-based glass alloy. Uniaxial compression testing on cylindrical samples of Mg₅₄Cu₂₈Ag₇Y₁₁ revealed that this alloy exhibits a strain rate sensitivity of approximately 1.5 when deformed in a narrow temperature range and at relatively low strain rates.

Compression samples used in this study were prepared from cylindrical Mg₅₄Cu₂₈Ag₇Y₁₁ rods obtained from the Air Force Research Lab at Wright-Patterson Air Force Base. Cylinders 6mm in height were cut from the as quenched rods, and the ends of the cylinders were polished to obtain parallel faces. Compression tests were performed on an MTS hydraulic test frame equipped with an MTS environmental chamber for elevated temperature testing. Initial strain rates ranging from 5×10^{-4} to $2 \times 10^{-3} \text{ s}^{-1}$ were used in the study, and all compression tests were performed at 468 K ($T_g + 45 \text{ K}$). The environmental chamber was raised to temperature and held until the compression platens reached the desired temperature. Platen temperatures were measured using thermocouples on the contact face of each platen. Samples were placed on the lower platen and the top platen was lowered until light contact was obtained. The system was held in this state for 300 seconds to ensure that the core of the sample reached the desired temperature. Unfortunately, the long hold time and high temperature limited the minimum strain rates that could be tested as crystallization would occur before significant deformation was induced into the glassy sample at strain rates below $5 \times 10^{-4} \text{ s}^{-1}$. X-ray diffraction was used to determine the degree of crystallinity following deformation in the SCLR.

Figure 1 shows three typical stress strain curves obtained during compression testing. The strain rate of the test had a large impact on the peak stress of the material, but steady state stresses were not significantly affected by the initial strain rate of the test. Initial strain rate also impacted the amount of strain performed within the stress overshoot portion of the curve, where there was no stress overshoot at $5 \times 10^{-4} \text{ s}^{-1}$, 0.1 strain at $1 \times 10^{-3} \text{ s}^{-1}$, and 0.2 strain at $2 \times 10^{-3} \text{ s}^{-1}$. Similar behavior is seen in some tensile experiments on Zr-based glasses [9].

It has, at times, been put forward that the relaxation behavior is a result of changing true strain rate, formation of nanocrystal aggregates, altering glass transition temperature, or some combination of the three [9]. These explanations for relaxation behavior are suspect for a variety of reasons. The claim that a continuously decreasing true strain rate significantly impacts stress relaxation is not probable because the behavior is observed in both tensile and compressive loadings. In fact, because it is present in the constant displacement rate compression tests conducted in this study, the relaxation behavior will occur despite a constantly increasing true strain rate. The work conducted by Kawamura et al. [10] on stress overshoots and undershoots in Zr₆₅Al₁₀Ni₁₀Cu₁₅ glassy ribbons indicate that there is a reversible and strain-rate dependent viscoelastic softening mechanism similar to that seen in polymer melts. Assuming similar behavior occurs in bulk glasses, it is unlikely that crystallization plays a major role in relaxation, similarly a shift in glass transformation temperature does not adequately explain the reversible strain-rate dependent overshoot and undershoot behavior.

The steady state flow region of the stress-strain curve is a non-equilibrium state in which the BMG is able to accommodate the strain being introduced into the material without any significant changes. In the case of constant displacement tensile tests, this steady state flow behavior occurs in spite of the continually decreasing true strain rate. Kim et al. [9] present the calculated decrease of stress with decreasing strain-rate depending on the m-value of the material being loaded. Similarly, an apparent hardening type behavior should be seen in the constant

displacement compression testing performed in this study. Despite the expected response, a stress plateau is present in many samples. It is important to note that the apparent strain hardening at the end of the stress-strain curves is an artifact of crystallization introduced to the sample from time at temperature and mechanically induced devitrification [1,9]. Figure 2 shows DTA data on the Mg-based glass before and after compression that supports this claim.

The most interesting observation from the compression tests was the strain-rate sensitivity of the material under the testing conditions. Figure 3 shows the strain rate sensitivity exponent calculated from the peak stresses of each compression test. The m -value for the BMG tested is ~ 1.35 . This indicates non-Newtonian shear thickening behavior. This trend differs significantly from behavior reported in the literature, but in a Ca-based BMG analysis of two stress vs strain curves from low strain-rate tests also show an m -value greater than one [11].

Shear thickening behavior has previously been observed in solid materials, most notably silicon nitride based ceramics and polymer gels [12-14]. The shear thickening behavior in silicon nitride is attributed to layers of liquid, or glass, which surround the grains of the material and directly impact the interaction between grains [12]. This behavior occurs at strain rates greater than $1 \times 10^4 \text{ s}^{-1}$ in many liquid phase sintered silicon nitride-based ceramics, but has not been observed in silicon nitride-based ceramics with only small amounts of glassy phase in the intergranular regions [13]. Shear thickening behavior is also observed in polymer melts and gels. In polymer systems, shear thickening is attributed to non-linear high tension along middle chains, intramolecular associations being transformed into intermolecular associations, and floating chain interactions [14].

Using the efficient cluster packing model (ECPM) as the assumed structure [15], two simple, structurally-oriented mechanisms for the shear thickening behavior are proposed here. Drawing on the current understating of shear thickening in silicon nitride, it is possible that sliding interactions between conglomerations of FCC clusters are responsible for the shear thickening behavior. In this case, the FCC-type clusters are treated as rigid structures that are bonded into a series of groups of clusters (cluster-groups). Under stress, these tightly connected cluster-groups slide over one another to accommodate the induced deformation at elevated temperatures. As there is no long range order, a collection of atoms without structure surround the cluster-groups. These atoms affect the flow of the rigid clusters similar to the intergranular glassy phase in silicon-nitride based ceramics. Under low strain-rates, the amorphous regions permit the cluster-groups to slide past each other without direct contact, resulting in low flow stresses. As strain-rates are increased, the amorphous regions thin in between sliding cluster-groups and the irregular shaped cluster-groups become entangled and significantly increase the flow stress of the material. A schematic of this behavior is shown in Figure 4. Although the ECPM was assumed, this behavior would be possible in any similar interconnected, rigid cluster model.

The second possible mechanism is based on the overshoot behavior at the onset of testing. In the ECPM, the atomic clusters that make up the medium range order of a BMG can meet at faces, edges, or vertices [15]. It is assumed that, on loading, no structural reconfiguration is required to accommodate introduced strain up to a certain rate. The results obtained in this study suggest that this rate is approximately $5 \times 10^4 \text{ s}^{-1}$ at the testing temperature, but the results of other studies indicate that the rate limit is both material and temperature dependent [16]. As the strain rate is increased, changes in the configuration of the clusters are required to accommodate the rate of

deformation being introduced into the system. During the overshoot period, bonds between neighbor clusters are broken such that more rigid cluster bonds (such as face to face bonds) are transformed into more flexible bonds (edge-edge or vertex-vertex) or broken completely. Schematic drawings of the bond transitions are shown in Figure 5. By decreasing the rigidity of cluster groups, the ability of the material to flow is increased and a lower stress is required to accommodate the strain being put into the glassy material. The magnitude of, and strain incorporated in, the stress overshoot is related to the total number of bond transitions required and the relative frequency of each type of transition. Because the structural alteration occurs during the stress overshoot, the steady state flow stress does not show the same dependence on strain-rate. However, in the case of a rapid increase in strain-rate, a second peak stress, such as those shown in the literature [10], would be expected as additional reordering is required to accommodate the suddenly higher deformation rate. Additionally, the restructuring assumed in this model would explain the steady state stress plateau mentioned previously. Assuming that constant, minor alterations in structure occur as the true strain-rate increases, the absence of the expected hardening behavior due to increasing strain-rate is explained.

The work by Harmon et al. [15] discusses the change in configuration and the associated change in shear modulus during deformation. While this work does not directly support the above described structural model, it does indicate that some structural changes occur which are linked to the temperature and strain-rate of deformation.

In conclusion, elevated temperature compression testing was performed on a Mg-based bulk metallic glass to determine the uniaxial compression behavior of the material. During this testing, the shear thickening response of the metallic glass was observed, and two simple structural based models were developed in the attempt to explain the observed behavior.

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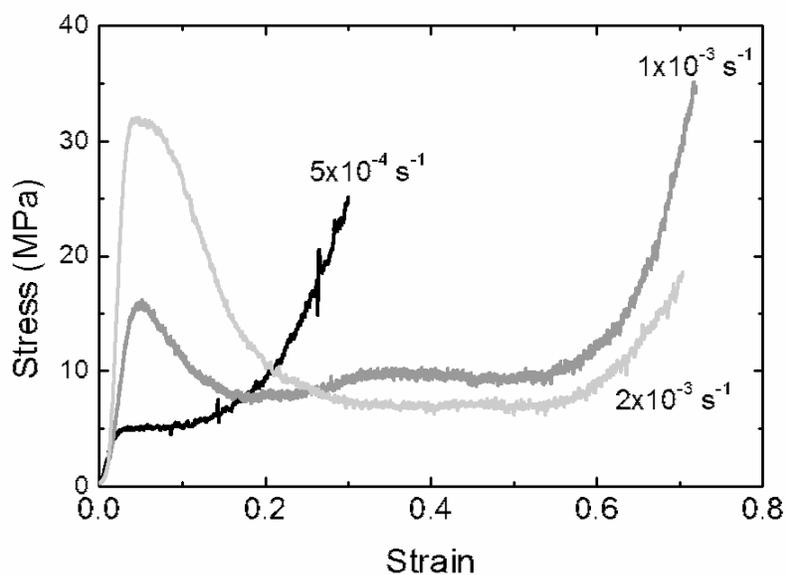


Figure 1: Stress-strain curves from one set of compression tests. Tests were performed at 468 K.

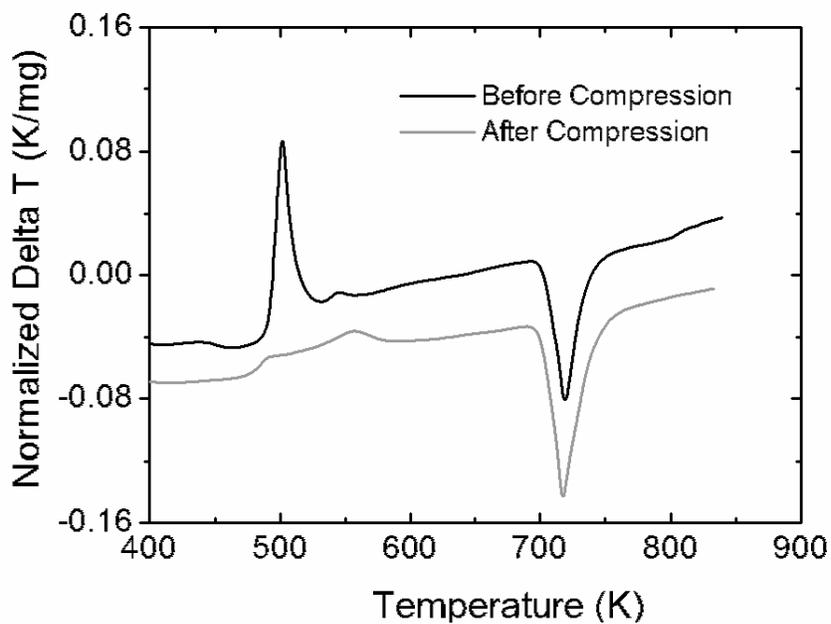


Figure 2: DTA data for glassy material before and after compression.

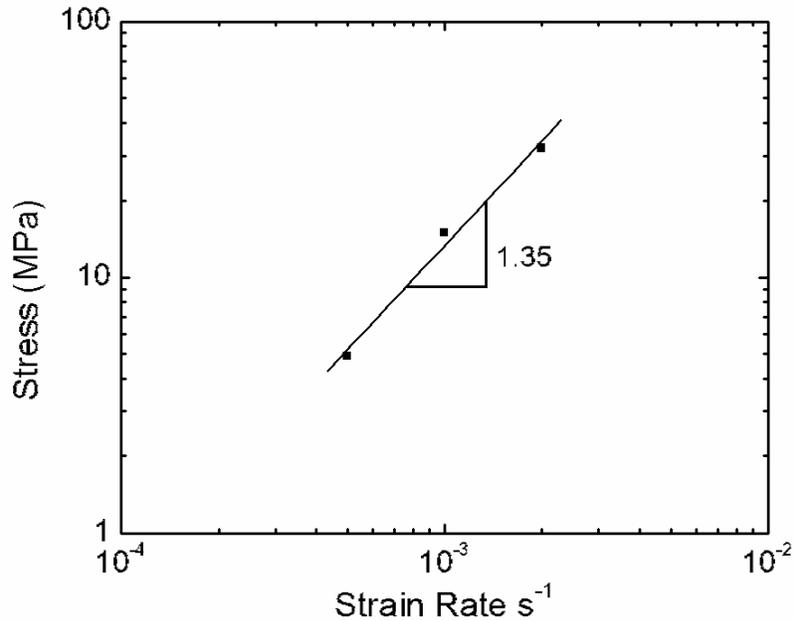


Figure 3: Variation of stress with strain-rate at 468 K.

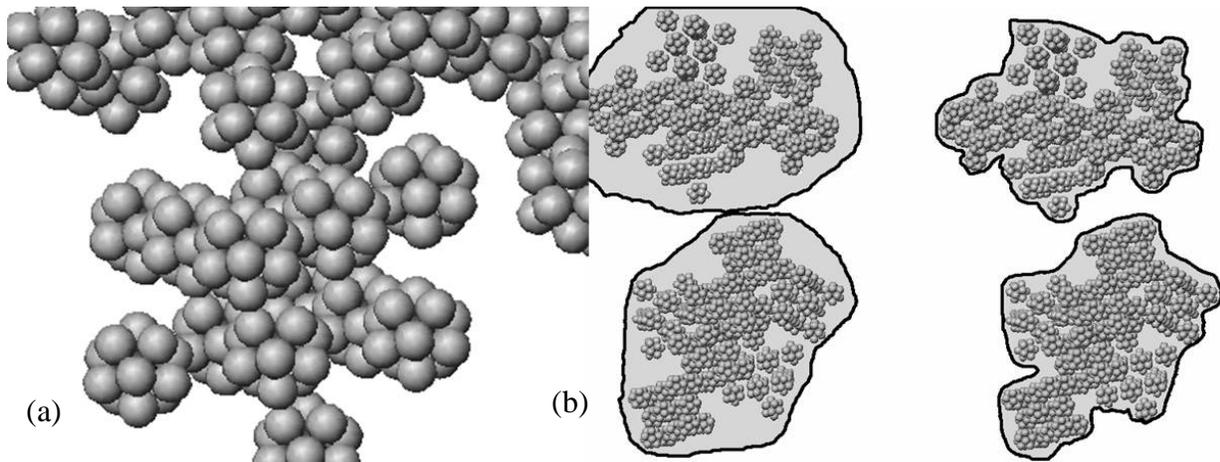
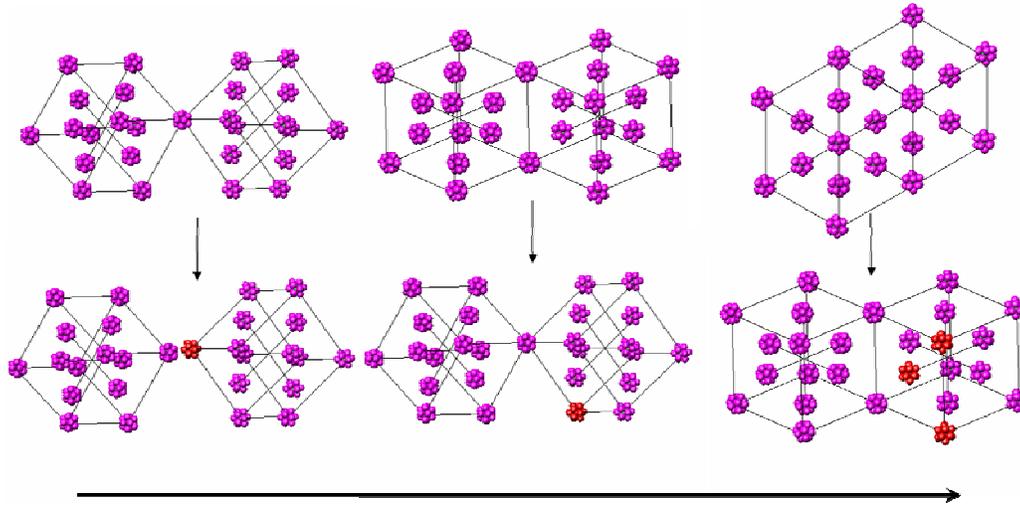


Figure 4: (a) View of simplified FCC cluster from ECPM. Open space is used to improve visibility of the structure. (b) Illustration of cluster-group sliding at low strain rates (left) and high strain rates (right). The outlined gray regions surrounding the cluster-groups are amorphous atoms surrounding, and loosely associated with, the more ordered cluster groups. This region thins under increasing strain rate, a concept based on the thinning of the glass regions during shear thickening in silicon nitride based ceramics.



Increasing stress required to force transition and strain associated with transition

Figure 5: Schematic showing cluster bond types and deformation associated with altering the bond type. Red atomic groups indicate groups required to complete the clusters after the transition. The higher strength of the face-face to edge-edge transition is believed to be the primary cause of the large stress overshoots and shear thickening behavior seen in this study.