Toward damage-tolerant bulk metallic glasses: Fracture behavior and brittle–ductile transition

Wook Ha Ryu, Ji Young Kim, and Eun Soo Park*

In order to replace the conventional alloys with bulk metallic glasses (BMGs), studies have been actively conducted to investigate the mechanical characteristics of BMGs in various aspects. One of the major ongoing issues is process-related variations in key properties such as fracture toughness. Although there is still a lack of knowledge on how to prevent catastrophic failure in most BMGs, Griffith's theory, modified by Irwin and Orowan, allows us to understand that the dissipation of plastic energy by atomic rearrangement within the shear band is a key factor in designing damage-tolerant BMGs by preventing crack opening. In this article, we discuss the fracture behavior of BMGs in relation to Griffith's theory and review studies that examined how intrinsic and extrinsic factors, such as alloy composition, temperature, sample size, and strain rate affect the brittle–ductile transitions in BMGs. As several BMGs recently reported excellent fracture toughness similar to that of ductile alloys such as conventional low-carbon steels, damage-tolerant BMGs will be a new class of high-performance structural engineering materials with significant technological strengths.

Introduction

Amorphous alloys are multicomponent metallic materials that have been extensively studied since the late 1980s and exhibit excellent strength and elastic properties, opening up new possibilities for a wide range of engineering applications.[1–4] However, there have been difficulties in the commercialization of amorphous alloys due to brittle fracture phenomena and manufacturing difficulties such as size restriction. In particular, in the early stages, it was difficult to produce a standard sample due to the limitations of glass-forming ability (GFA), making it difficult to investigate the fracture behavior. Accordingly, until the 2000s, the majority of research on amorphous alloys has focused on developing bulk metallic glasses (BMGs) with excellent GFA (low critical cooling rate below 10^3 K/s and large maximum diameter for glass formation over 1 mm).[5–9] As a result, we have a sufficiently long list of BMGs for which we can measure mechanical stability, such as fracture toughness, and the focus in the literature has shifted to the development of damage-tolerant BMGs.

Because of the disordered atomic structure, BMGs do not exhibit dislocations unlike their crystalline counterparts, and have almost zero tensile ductility. Therefore, one might incorrectly infer that there is no plastic deformation mechanism and brittle fracture inherently occurs in BMGs, especially in unconstrained loading geometries. However, unlike oxide glass, BMGs can dissipate energy plastically and shield crack openings by atomic rearrangement in the shear bands.[10–17] This unique fracture behavior[12,14,18] can be interpreted based on Griffith's theory,[19] which was subsequently modified by Irwin[20] and Orowan.[21] Griffith's remarkable insight was initially given simply to explain the brittle fracture of oxide glass, but now it is the basis for analyzing fracture behavior and designing damage-tolerant materials in a variety of modern high-performance engineering materials such as superalloys, graphene, and amorphous alloys. In this article, first we try to focus on understanding the fracture behavior of BMGs in relation to Griffith's theory, which can provide meaningful insight into what causes embrittlement and how to reduce its extent in BMGs.

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Furthermore, in recent years, researchers' interest has expanded to various applications of BMGs in high-value-added industries such as precision gear and aerospace parts that can significantly benefit from unique advantages of BMGs such as high strength, large elastic limit, and high thermoplastic processability.[22–30] In terms of mechanical reliability, fracture toughness is an important characteristic that must be guaranteed for commercialization in all of these applications. BMGs in a wide variety of compositions may be utilized at various temperatures and in various sizes from millimeters to nanometers, so their fracture toughness should be carefully evaluated under various conditions. Although there are still significant gaps in our knowledge, several studies have recently reported that the fracture behavior of BMGs has variable characteristics representing brittle–ductile transition under various conditions.[17,31–34] In this regard, the second part of this article will focus on reviewing studies on the criteria for the brittle–ductile transitions in BMGs depending on intrinsic and extrinsic factors such as alloy composition, temperature, sample size, and strain rate, which can provide a guideline on how to control the brittle–ductile transitions in BMGs, a key to their successful commercialization.

Fracture behavior of bulk metallic glasses

BMGs lack macroscopic tensile elongation, resulting in near-zero tensile ductility.[12,34] The apparent lack of ductility of BMGs is due to a shear localization phenomenon. The shear localization is related to a strain-softening behavior. The shear deformation-induced dilation promotes structure disordering with more free volumes.[35–37] Plastic deformation of BMGs at temperatures below the glass-transition temperature (T_g) is inhomogeneous with highly localized strain into narrow shear bands with 10–20 nm in thickness.[38–40] Because of the deformation-induced softening with local rearrangement of atomic clusters,[36] the shear bands propagate rapidly, easily leading to catastrophic failure.[41,42] However, BMGs reject the traditional concept that large tensile ductility is a requirement for high toughness. BMGs whose fracture toughness is similar to those of the toughest engineering alloys such as low-carbon steel and Ti alloys have been reported in Zr-based and Pd-based alloy systems.[12,13] BMGs have been reported to exhibit fracture toughness in the range of 1–230 MPa $m^{1/2}$ depending on the alloy composition, which is a wide range covering brittle ceramics and tough crystalline alloys.[10–17]

In Griffith's theory modified by Irwin and Orowan, fracture stress is determined by the surface energy and plastically dissipated energy involved in crack propagation. When stress is applied to a sharp crack tip, ductile materials such as crystalline alloys undergo plastic deformation at the crack tip by the movement of defects, relieving local stress concentrations, which promotes high fracture toughness. In contrast, brittle materials with no structural defects such as oxide glass have limited plasticity near the crack tip, resulting in low fracture toughness. This concept also can be utilized to predict the fracture strength and to interpret the fracture behavior of the BMGs. They possess a plastic deformation mechanism in which the shear band plastically shields an opening crack. While tough BMGs can delay crack propagation and exhibit high fracture toughness through multiple shear band formations around the crack tip, brittle BMGs have a large shear band formation activation barrier, which easily causes catastrophic failure. The atomic structure of BMGs is not completely homogeneous, and the local liquid-like regions that exhibit low atomic density and high energy states act as viscous flow units for deformation.[43–49] When the liquid-like flow unit activated by shear stress exceeds the percolation limit, a deformation band (i.e., a shear band), is formed in the direction with the maximum shear stress. When a shear band is formed, a large amount of atomic rearrangement is instantaneously accompanied and plastic energy dissipation occurs.[38–40] Therefore, the stress applied to the surrounding area can be relieved and crack opening delayed. The evidence for the plastic energy dissipation can be found in studies that reported that, based on experimental and calculation results, the temperature can rise up to 900 K when a shear band is formed.[35,37,50–52] Therefore, a low activation barrier for additional shear band formation may result in high fracture toughness in the BMGs by dissipating the accumulated elastic energy into thermal energy by atomic rearrangement within the shear band and delaying crack propagation. **Figure 1** shows that multiple shear bands are formed around a pre-crack in $Pd_{79}Ag_{3.5}P_6Si_{9.5}Ge_2$, one of the toughest BMGs.[12] A crack-tip opening displacement (CTOD) method can be utilized to determine the fracture toughness of BMGs with a critical size less than the thickness required for direct measurement of J-integral toughness (Figure 1a). Figure 1b shows the results for the back-calculated stress intensity K_J. Shear bands are formed along the fan-shaped slip line (Figure 1c–e), and the shear offset is gradually concentrated (indicated by arrows) in specific shear bands (Figure 1f–g). When an extensive shear strain that exceeds the critical value is applied, the shear band opens and develops into a crack (Figure 1g–k). On the other hand, in the case of brittle BMGs mainly found in Ca-based, Mg-based, and rare-earth-based alloy systems, multiple shear bands are not formed during fracture measurement, and the initially formed shear bands easily develop into cracks. These results can provide meaningful insight into what causes embrittlement and how to reduce its extent in BMGs.

Dependence of the brittle–ductile transition on intrinsic factors

The nucleation barrier of shear band is an intrinsic property that depends on the alloy composition. Although there is a notable difference among alloy systems, it can vary greatly depending on the composition in the same alloy system. When comparing mechanical properties of BMGs in various alloy systems, it is reported that the ratio of the shear modulus (μ) over bulk modulus (B), or equivalently the Poisson's ratio (ν), has a clear

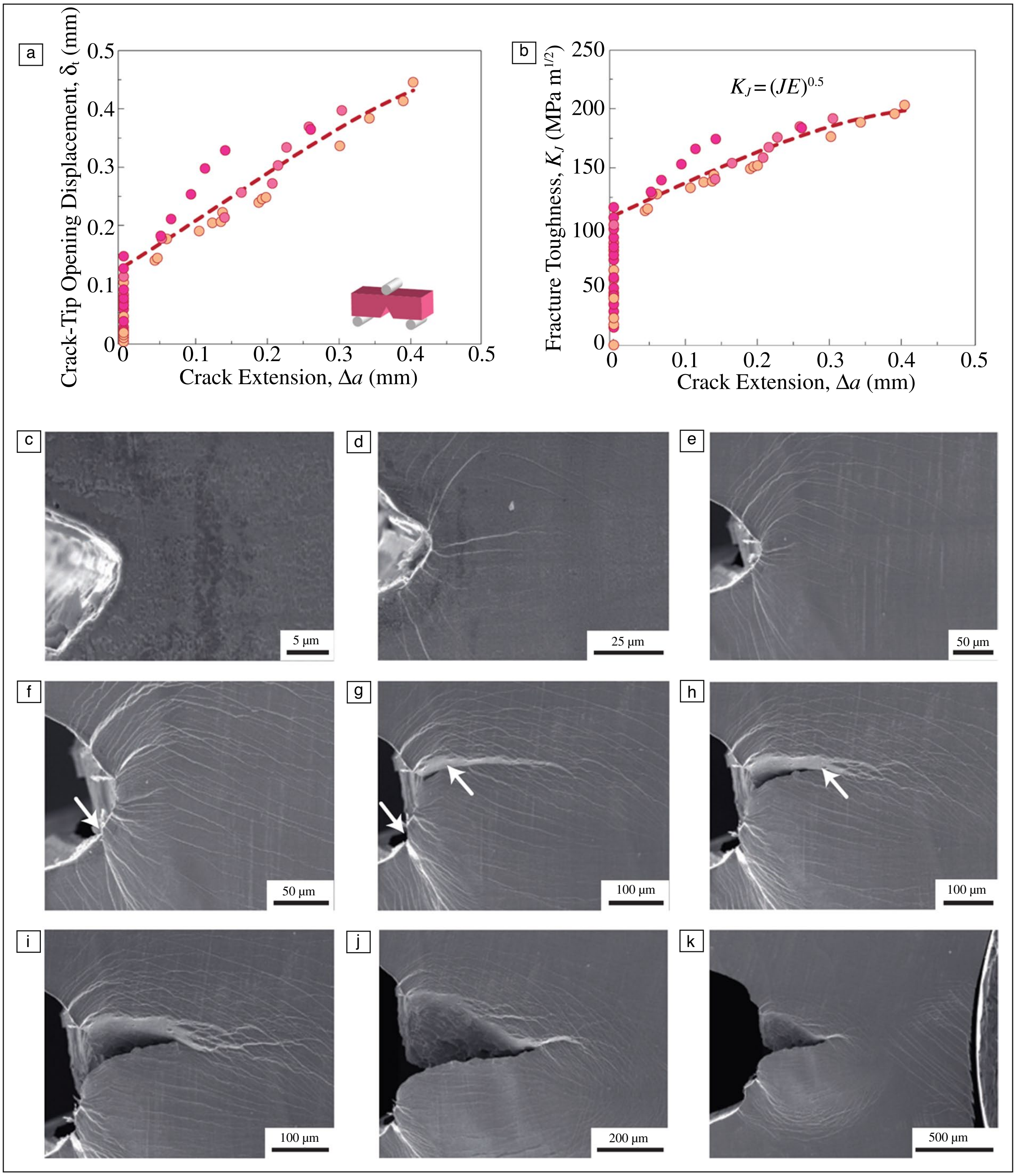

Figure 1. Fracture toughness measurement results and the scanning electron microscope (SEM) images near the crack tip of the $Pd_{79}Ag_{3.5}P_6Si_{9.5}Ge_2$ bulk metallic glass. (a) The crack-tip opening displacement plotted against the crack extension, (b) fracture toughness, K_J, plotted against the crack extension, (c–k), *in situ* SEM images taken under R-curve measurement. The corresponding K_J values are (c) 0, (d) 25, (e) 44, (f) 63, (g) 115, (h) 133, (i) 144, (j) 196, and (k) 203 MPa $m^{1/2}$.[12]

correlation with fracture toughness,[17] which is also the law identified in isotropic crystalline alloys.[33] This correlation can be understood by considering that a low μ decreases the resistance of a shear band propagation, and a high B increases the resistance of a shear band to open a crack.[53,54] **Figure 2** shows the correlation between the ratio μ/B and the fracture energy G. Higher μ/B favors the improvement of the toughness of BMGs.[17] The critical value of μ/B, which separates brittle

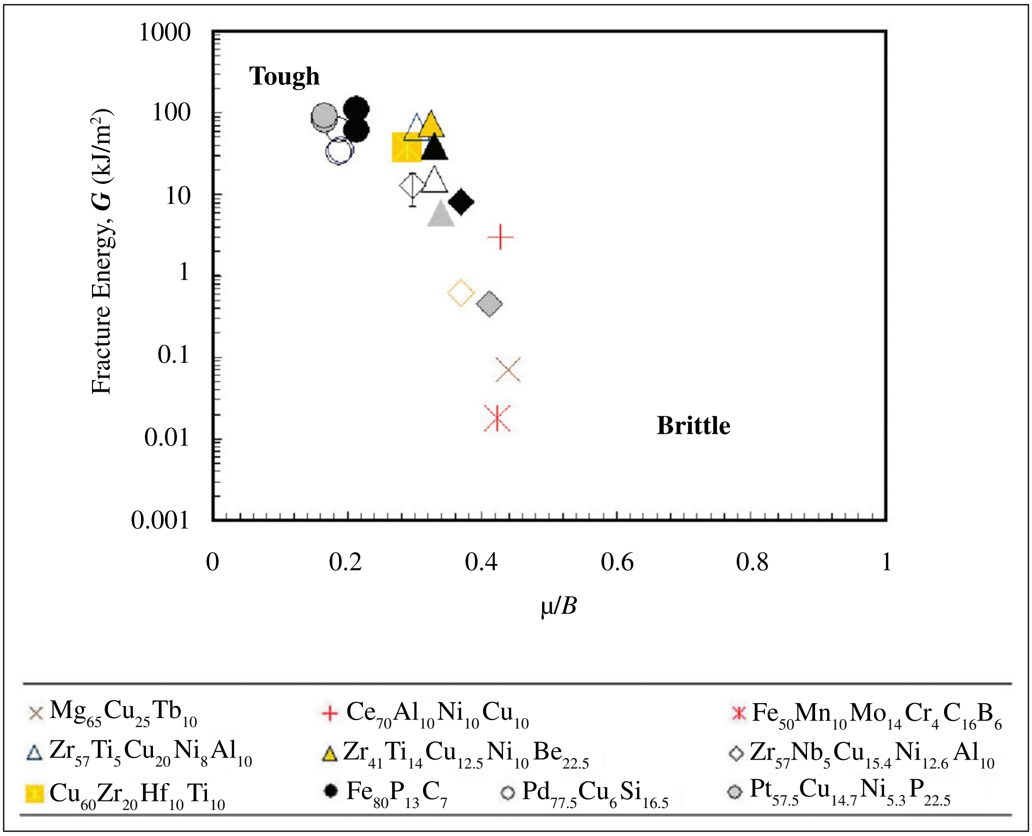

Figure 2. The relationship between fracture energy *G* and μ/*B* for bulk metallic glasses of various alloy systems and oxide glasses.[17]

and ductile fractures in BMGs, is in the range of 0.41–0.43. The correlation between *G* and elasticity can also be expressed as ν. The higher the ν value, the higher the *G*, and the critical ν value for the brittle–ductile transition is in the range of 0.31–0.32. However, recently reported conflicting studies have shown that μ/*B* or ν is insufficient to universally predict fracture toughness within different alloy systems.[32,55,56] When the alloy system is different, the yield strain, surface energy, and atomic structures such as short-range ordering or medium-range ordering can be different, and these variables greatly influence the fracture toughness.[57–60] Fracture toughness of BMGs can vary significantly for a very small compositional change and such difference is reported to be non-monotonic,[32] but the correlation has not been fully investigated yet. Therefore, the value of μ/*B* (0.41–0.43) or ν (0.31–0.32) can be used as a factor to predict the brittle–ductile transition, but it is difficult to use it as an absolute criterion, especially when comparing BMGs with different alloy systems. In order to identify the correlation between alloy composition and global fracture toughness, it is imperative to conduct follow-up studies on the relationship between the atomic structure of BMGs and fracture toughness.

Temperature dependence of the brittle–ductile transition

In BMGs, a decrease in fracture toughness is commonly observed when the temperature decreases. In this section, the effect of temperature on fracture behavior is discussed separately for three different regions of temperature: a low-temperature region below room temperature (RT), an intermediate region between RT and 0.8 T_g, and a high-temperature region above 0.8 T_g.

Recent studies clearly demonstrate that BMGs are susceptible to a brittle–ductile transition in the low-temperature region near or below RT.[34,61–64] The brittle–ductile transition temperature is sensitive to the energy state and packing density of the local liquid-like flow unit in the BMGs.[34,62,64] As shown in **Figure 3**a, when the temperature decreases down to 20 K, the failure strength of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ (at.%) BMG starts to decrease. When BMG is cooled to 4.2 K, the breaking strength is further reduced and widely dispersed. The discrete distribution of failure strengths at a certain temperature could imply the brittle fracture behavior.[65] Figure 3b represents the

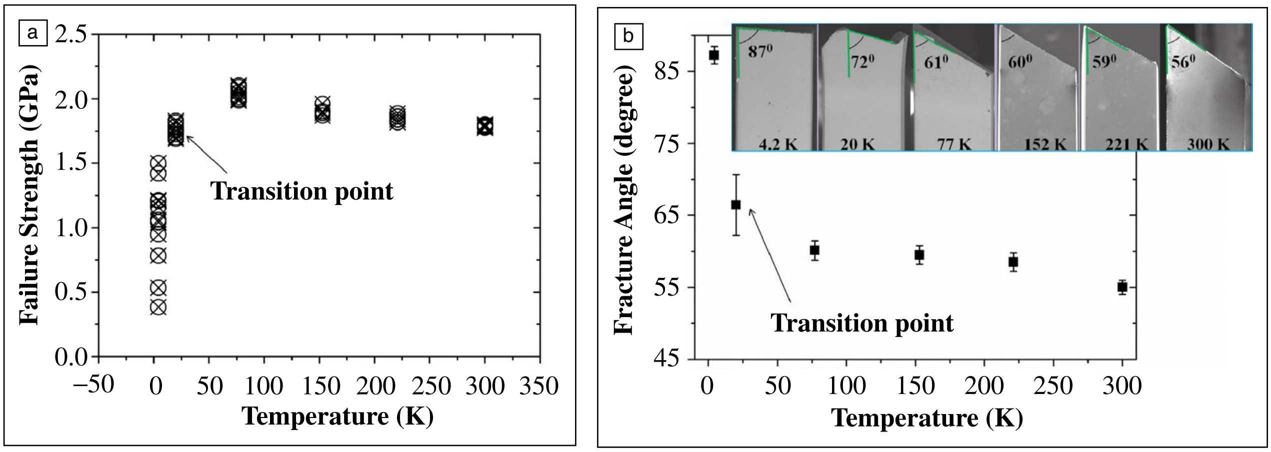

Figure 3. (a) Tensile fracture strength and (b) fracture angle versus temperature from room temperature (300 K) to liquid helium temperature (4.2 K) of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ (at.%) bulk metallic glass. The inset images in (b) show the representative failure angle at each temperature.[62]

measured fracture angle between the loading axis and the fractured planes. When the fracture angle is close to 45°, which is the maximum shear direction, the fracture is dominated by shear stress. As the fracture angle increases and approaches 90°, the effect of normal stress increases, and the fracture mode is converted from ductile fracture to brittle fracture.[34,62] For this BMG, a temperature of about 20 K can be identified as the critical brittle–ductile transition point. In another recent study, a more detailed mechanism was elucidated through the suppressed shear deformation and enhanced cavitation effect at low temperature,[61] but conventional fracture theory cannot satisfactorily interpret these experimental findings.

It is well-known that inhomogeneous plastic deformation by shear localization occurs at temperatures of 0.8 T_g or less.[40] Although there are not many studies dealing with the correlation between temperature and fracture toughness in the range of RT and 0.8 T_g, the temperature dependence of mode I fracture has been systematically identified by Raut et al.[66] The plastic strain of BMGs exhibits a minimum in the bending ductility at about 0.65 T_g. The intermediate temperature ductility minimum (ITDM) in BMGs is the result of a large amount of shear band-mediated plasticity in a few shear bands, followed by conversion to a homogeneous plastic deformation at higher temperatures.[67] The trends in fracture toughness are similar to that in ductility, and the fracture toughness has the lowest value at around 0.67 T_g.[66] At a temperature between RT and 0.67 T_g, the higher the temperature, the lower the fracture toughness, and the fracture toughness tends to increase again at 0.67 T_g or higher.

At temperatures of approximately 0.8 T_g or higher, the strain rate sensitivity is increased by the homogeneous viscous flow, and thus the brittle fracture (mode I fracture) can be induced by the fast strain rate. However, at relatively slow strain rates, a ductile fracture mode with necking instability and subsequent final rupture is generally observed.[40] In this case, a crack is not formed and a fracture occurs with a large amount of energy dissipated into the plastic deformation while forming a necking through the surface.

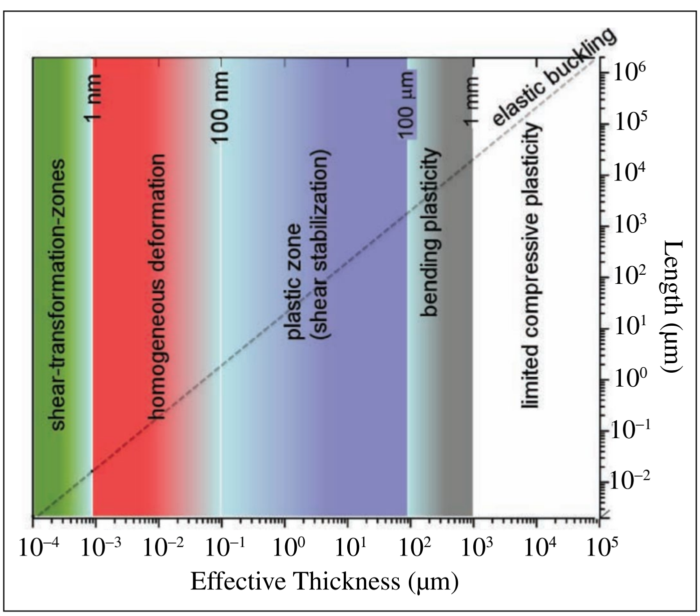

Figure 4. Size-dependent deformation features in metallic glasses estimated for $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass.[25]

Size dependence of the brittle–ductile transition

According to Griffith's theory, in oxide glass, the smaller the sample size, the larger the toughness tends to be because the population of defects depends on the sample size, which is a factor that significantly lowers the actual strength compared to the theoretical strength. Although the mechanism is different, even in BMGs, the smaller the size, the higher the deformation stability. The size-dependent deformation features in a BMG at temperatures below T_g are summarized in **Figure 4**.[25] BMGs with thickness larger than 1 mm exhibit compressive plasticity, but are brittle under bending and tension. Bending plasticity can be improved at a thickness of less than 1 mm. The shear bands become further stabilized when the sample thickness becomes smaller than the size of plastic zone (~100 μm for $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$). Below 100 nm, the deformation mechanism is converted from shear localization to homogeneous deformation. Below the size of shear transformation zone (STZ) of 1 nm, plastic deformation might no longer be effectively carried out by STZ motion. Therefore, a further increase in deformation resistance can be expected on a thickness near 1 nm. Size dependence has also been investigated for fracture toughness. Gludovatz et al. carefully investigated the effect of sample size and geometry on fracture toughness of BMGs, and clearly indicated that the sample geometry has a significant effect on the fracture toughness values, even if the BMG samples meet the size requirements according to ASTM standards.[68] The sample size and geometry have a much more significant effect on the fracture toughness in BMGs than in crystalline alloys. According to their more sophisticated follow-up studies recently,[31] ASTM alternative samples with smaller sizes exhibit significantly higher fracture toughness values compared to the larger-sized ASTM standard samples but less scatter in the toughness values as a result of ductile fracture characteristics. At a ligament width (the distance between the crack tip and the opposite surface) larger than the critical bending thickness, BMGs generally exhibit fracture in a brittle manner. When the ligament width is similar to the critical bending thickness, the fracture toughness values are dependent on the sample size and geometry. If the ligament width is smaller than the critical bending thickness, fracture occurs in a fully ductile manner with less deviation in the toughness values. These works suggest that BMGs represent a brittle–ductile transition during deformation that is closely related to the sample size. Samples with ligament widths larger than the critical thickness show brittle fracture characteristics and low toughness values, whereas samples whose ligament widths are below the critical thickness show fully ductile and non-catastrophic fracture characteristics. In general, BMG samples are often tested with a ligament width that is close to or less than the critical bending thickness, and it should be considered that these results reflect the influence of sample size and geometry.

Overall, BMGs exhibit a wide range of fracture behavior, including the brittle–ductile transition depending on intrinsic factors such as Poisson's ratio as well as extrinsic factors such as temperature, sample size, and geometry. This concept can also be applied to other deformation modes such as compression, tension, and bending. Recently, we constructed a plastic deformation sequence map using the compression test data in various BMGs. **Figure 5** schematically shows how the deformation behavior is determined according to the contact friction, aspect ratio, and Poisson's ratio in the uniaxial compression mode.[69] It can be shown that the conditions for superplastic behavior in BMGs, as those in their crystalline counterparts, can be specified by appropriately optimizing each variable even under unconstrained loading geometries. Contact friction induces brittle fracture by concentrating shear stress on the sample corners. As the aspect ratio is small, the interaction probability between major shear bands increases, and as Poisson's ratio increases, the nucleation activation barrier decreases, which promotes shear band nucleation during compressive deformation. This prevents catastrophic failure and induces a stable plastic deformation mechanism (steady-state serrated flow). In particular, if the steady-state serrated flow is maintained until an aspect ratio

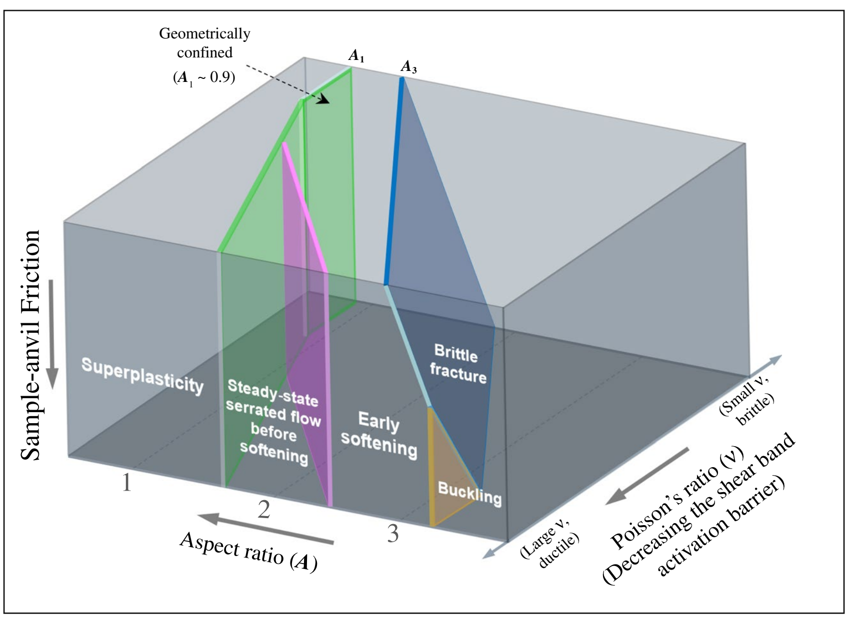

Figure 5. Compressive plastic deformation sequence map for bulk metallic glasses reflecting the three variables of contact friction (stress concentration)—aspect ratio (sample geometry)—Poisson's ratio (shear band activation barrier).[69]

of 0.9 so that the shear band is geometrically confined, fracture can be completely suppressed and superplasticity appears. Through the three-dimensional deformation map, it is possible to specifically understand the change in compressive deformation behavior according to the extrinsic and intrinsic factors. However, compared to the compression test results, sufficient research has not yet been conducted on the fracture toughness of BMGs. It is expected that a methodology for developing various damage-tolerant BMGs can be more clearly proposed when experimental results related to fracture toughness are accumulated in the future.

Concluding remarks

According to Griffith's theory modified by Irwin and Orowan, it could be understood that plastic energy dissipation by dislocations is a key factor in preventing crack opening in crystalline alloys, and thus damage-tolerant structural materials have been successfully designed. This concept can be similarly applied to BMGs, allowing us to design damage-tolerant BMGs by utilizing plastic energy dissipation by atomic rearrangement within the shear band. However, the fracture behavior of BMGs is highly variable depending on composition, temperature, sample size, geometry, etc. Also, in recent years, there is an emerging trend to design alloy compositions and processes to optimize BMGs for high value-added structural applications required under various operating conditions. Therefore, research on an extensive range of fracture behavior of BMGs is required to identify ways to ensure predictable and graceful (non-catastrophic) failure in service.

Recently, in order to overcome the limitations of the fracture toughness measurement method in BMGs, research on an indirect evaluation method using indentation has been conducted.[32,70,71] The studies not only clearly demonstrate the capability of BMGs to actually accommodate plastic deformation through the shear band that controls fracture toughness, but also allow indirect comparison of fracture toughness in a wide range of sizes from millimeters to micrometers through the shear band density occurring at the crack tip and indentation impression. Based on these new measurement methods, it is expected that a comprehensive understanding of the fracture behavior of BMGs will be achieved by more precisely comparing the fracture toughness of BMGs deviating from the ASTM standard and securing more data at low and high temperatures. As mentioned above, we can optimize the mechanical properties of BMGs depending on the combination of intrinsic and extrinsic factors such as alloy composition, temperature, sample size, and strain rate. We hence suggest that securing a systematic database through extensive research on fracture behavior of BMGs can be an effective route for developing damage-tolerant BMGs, a new class of high-performance structural engineering materials with significant technological strengths, to their successful commercialization. It remains to be seen how soon, and to what extent, that potential will be realized.

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Conflict of interest

The authors declare no competing financial interest.

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