A mathematical approach to transformation toughening in bulk metallic glasses

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A mathematical framework used to describe transformation toughening in zirconia-based ceramics is adapted to apply to transformation toughening in bulk metallic glass matrix composites. The method is applied to the $Cu_{47.5}Zr_{47.5}Al_5$ bulk metallic glass, showing that the low volume change of transformation in this alloy leads to negligible toughening via the proposed mechanism. An alternative mechanism for toughening is presented, whereby shear bands propagate more easily in the early stages of advance.
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Bulk metallic glasses are a class of material that have attracted attention due to their exceptional strengths [1]; however, poor ductility has limited their industrial applications. Metallic glasses fail by shear localization along a shear band, resulting in catastrophic failure [2]. A leading method for increasing ductility is the formation of a composite containing a volume fraction of crystalline material [2]. This tends to lead to nucleation of multiple shear bands, and the particles inhibit propagation, leading to distribution of shear through multiple shear bands across the material and hence plastic flow.

A series of recent work has focused on alloys in the Cu–Zr–Al shape memory system, which undergo a thermoelastic martensitic transformation. Alloys cast almost entirely glassy but with a small volume fraction of nanocrystals in the B2 austenite structure show unusual ductilities, including plastic strain in compression of 16% [3]. Samples examined after deformation show closely spaced, wavy and diffuse shear bands, and twinned or transformed nanocrystals. The volume fraction of B19′ martensite phase has been shown to increase with deformation.

A mechanism has been proposed by Pauly et al. [4] whereby under applied stress particles nucleate in the matrix and twin or undergo a martensitic transformation.

This transformation has a volume change component and hence exerts a compressive stress on the matrix, inhibiting shear transformation zone activation. This leads to toughening.

We note, however, that the nature of a martensitic transformation in a shape-memory system is such as to produce minimal volume change. Indeed, work by Schryvers et al. [5] shows a volume component of 0.137% in the transformation from B2 to B19′ in equiatomic CuZr. This appears to be very small, and would seem to call the proposed mechanism into question.

Currently, there is no mathematical framework presented in the literature for modelling transformation toughening in metallic glass composites. However, there exists a body of literature surrounding the transformation toughening behaviour in zirconia-based ceramics [6]. Developed in its original form by McMeeking and Evans [7], the method considers the surface tractions required to compress the transformed particle into its original space in the matrix in an Eshelby-type model.

The original model considers only the mode I case. Furthermore, the shape change component of the transformation strain is neglected – only the volume component is considered. This is due to self-accommodation of martensite variants, which usually results in negligible shape change. Later work on the subject recognized that shape change is important in nucleation of martensites even if it then contributes little to the stresses in the

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matrix. In zirconia, it should be noted, the volume change component is rather more significant.

In order to adapt the model to shear banding in metallic glasses, a number of assumptions and adaptations must be made. First, we model shear bands as mode II cracks, a model found in prior literature [8]. This requires us to adapt the mathematics for the mode II case. We then take into account the shape change component of the transformation.

The objective of this adaptation is to develop a mathematical framework that will allow us to model the transformation toughening behaviour in these metallic glasses, and to determine whether the proposed mechanism can be supported despite the low volume change involved in the transformation.

We begin by calculating the extent of the transformation zone, which is determined from the stress needed to cause a particle to transform and the stresses around the shear band tip. For this purpose, considering the full shape strain is valid since one full martensite variant must nucleate before other corresponding variants can form.

Mathematics as explained by Evans and Heuer [9] are used. Details of the method used can be adapted from the original paper, so we will not reproduce the full working here. The paper uses mode I expressions for the stresses around the crack tip, resulting in a value for the transformation radius r_c of

$$r_c \left(\frac{e^T E_p}{K_I} \right)^2 = \frac{4.1}{\pi} \left(\frac{\cos \frac{\theta}{2} \left[\pm 1 + 1.25 \xi \left| \sin \frac{\theta}{2} \cos \frac{\theta}{2} \right| \right] (1 + \beta)}{\beta [1 + 3\xi^2] - 3.6(1 + \beta)F} \right) \tag{1}$$

where e^T is the volume component of the transformation strain, e^S is the shear component of transformation strain, E_p is the Young modulus of the particle, E_m is the Young modulus of the matrix, ξ is the value of e^S/e^T, β is given by E_p/E_m, and K_I is the applied stress intensity factor at the crack tip (before transformation). We define a plane polar co-ordinate system r, θ about the crack tip, with the plane defined as perpendicular to the shear band front – see Figure 1 below.

We instead use mode II expressions for the stresses around the crack tip [10]:

$$\sigma_{1_1} = K_{II} r^{\frac{1}{2}} \sin \frac{\theta}{2} \left[-2 - \cos \frac{\theta}{2} \cos \frac{3\theta}{2} \right] + o\left(r^{-\frac{1}{2}} \right) \tag{2}$$

$$\sigma_{1_2} = K_{II} r^{\frac{1}{2}} \cos \frac{\theta}{2} \left[1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right] + o\left(r^{-\frac{1}{2}} \right) \tag{3}$$

$$\sigma_{2_2} = K_{II} r^{\frac{1}{2}} \cos \frac{\theta}{2} \sin \frac{\theta}{2} \cos \frac{3\theta}{2} + o\left(r^{-\frac{1}{2}} \right) \tag{4}$$
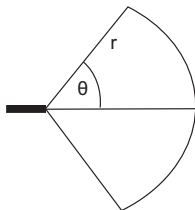
where K_{II} is the applied stress intensity factor at the shear band tip (before transformation). Using this adaptation, we can determine a mode II transformation zone radius of

$$\sqrt{r_c} = - \frac{K_{II} \left[\cos \frac{\theta}{2} \left(1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right) e^S - \frac{4.8}{3} \sin \frac{\theta}{2} e^T \right]}{\Delta G_0 + \beta E_p \left[\frac{\frac{1}{3} e^{T2}}{1.2 + 1.2\beta} + \frac{6 e^S e^S}{7.2(1+\beta)} \right]} \tag{5}$$

where ΔG_o is the free energy change per unit volume from parent to martensite phase.

This gives us the transformation zone before the shear band begins to advance. Once it advances, we must consider several regions, as shown in Figure 2. We model in the way described in Ref. [11], using Eq. (5) for the region ahead of the shear band tip until the distance from the shear band plane reaches a maximum, w, which we call the zone height. From here, we consider straight zone sides at distance w from the shear band plane, and also take into account the shear band edges, for a shear band advance distance Δa.

We now have a model for the transformation zone. In order to determine the toughening effect of this transformation zone, we adapt the work of McMeeking and Evans [7] applied in the mean field case. For full details of the method, consult their original paper; our approach follows their work closely. We use the above zone shape instead of the simpler expression given in their paper. We also work in the mode II case; this means replacing the mode I expressions for the weight function $\mathbf{h}$ [8] with

$$\mathbf{h}_{II} = \begin{pmatrix} h_x \\ h_y \end{pmatrix} = \frac{1}{2\sqrt{2\pi}\sqrt{r}(1 - v)}$$
$$\left\{ \begin{array}{c} \sin \frac{\theta}{2} \left[2 - 2v + \cos \frac{\theta}{2} \cos \frac{3\theta}{2} \right] \\ \cos \frac{\theta}{2} \left[1 - 2v + \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right] \end{array} \right\} \tag{6}$$

where v is Poisson's ratio for the glass. We consider the case of the transformation zone around an extending crack, and hence an important parameter is the crack aspect ratio $\Delta a/w$.

The original paper suggests that the change in stress intensity factor caused by the transformation can be found via an integral given by

$$\Delta K_I = \left[\frac{E}{1 + v} \right] \int_{S_p} \mathbf{n} e^T \mathbf{h} + \frac{v e^T \mathbf{n} \mathbf{h}}{1 - 2v} dS \tag{7}$$

where $\mathbf{n}$ represents the zone normal and dS is the surface element around the edge of the transformation zone. Note that many of the explicit results during the
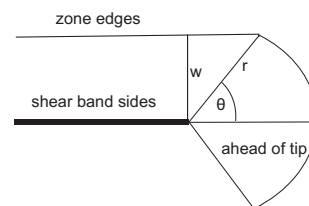

Figure 1. Co-ordinate system.

Figure 2. Calculation regions.

working produce extremely lengthy expressions and we will not reproduce them all here.

We calculate dS via

$$dS = \sqrt{dr^2 + r^2 d\theta^2} \tag{8}$$

and $\mathbf{n}$ via

$$\mathbf{n} = \begin{pmatrix} n_x \\ n_y \end{pmatrix} = \begin{pmatrix} -r' \sin\theta - r\cos\theta \\ r'\cos\theta - r\sin\theta \end{pmatrix} \tag{9}$$

To calculate the transformation strain, we have used experimental data for the CuZr system obtained from a paper by Schryvers et al. [5]. We obtain

$$e^T = \begin{pmatrix} 0.00137 & 0.124 \\ 0.124 & 0.00137 \end{pmatrix} \tag{10}$$

We integrate Eq. (7) over the three main regions, as shown in Figure 2. The integral ahead of the crack tip is just given by calculating the above using Eq. (5) for radius (and hence obtaining $\mathbf{h}$, dS and $\mathbf{n}$ from Eqs. (6), (8, and 9)), and then evaluating Eq. (7) from $-\frac{\pi}{3}$ to $\frac{\pi}{3}$ (which is where the distance from the crack plane is at a maximum).

For the zone sides, we give the radius as

$$r_{c_2} = \frac{w}{\sin\theta} \tag{11}$$

We can then calculate $\mathbf{h}$ from Eq. (6), dS through equation Eq. (8) and use $n = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$. We calculate the contribution to stress intensity factor via Eq. (7), evaluated from $\frac{\pi}{3}$ to $\arctan[\Delta a/w + \pi/2]$. We calculate for a range of values of $\Delta a/w$ (see Table 2 and Fig. 3).

We also calculate for a range of values of $\Delta a/w$ the contribution from the crack sides. Here, we can set $dr = da$, $n = \begin{pmatrix} 0 \\ -1 \end{pmatrix}$ and $dS = da$. We evaluate for the case $\theta = 2\pi$ from $a = 0$ to $a = \frac{\Delta a}{w}w$. We tabulate also in Table 2 and Figure 3.

We calculate the sum of these three terms to get the total contribution of the transformation zone to toughening. We use values for the material shown in the original work on this subject, a $Cu_{47.5}Zr_{47.5}Al_5$ alloy. The material characteristics are shown in Table 1 [12,13].

Figure 3 shows a number of clear trends in the contribution of transformation to toughening as the shear band advances. Important to note is that a negative value implies a reduction in stress intensity and hence toughening, a positive contribution favours propagation of the shear band.

We can draw a number of observations from Figure 3. First, the contribution from the volume strain alone is insignificant compared to that from the shape strain. Secondly, the shape strain contribution peaks rapidly with shear band advance and then rapidly

decreases. These observations lead to a number of conclusions.

First, if there is no significant shape change component to toughening (such as is often assumed in the literature, due to variant self-accommodation), we have negligible toughening even at the steady-state value. If we input a sample initial applied stress intensity factor of 5 MPa m$^{1/2}$ and a crystalline volume fraction of 0.1, we get -0.2 MPa m$^{1/2}$ for the component caused by the shape strain and $+1.12$ MPa m$^{1/2}$ if we consider both components. As such, this model suggests volume change alone cannot be the mechanism behind toughening in the $Cu_{47.5}Zr_{47.5}Al_5$ alloy.

The question becomes rather more interesting if we allow the shape change to contribute, neglecting for the moment self-accommodation of variants. We then observe a significant contribution to the stress intensity factor at the shear band tip, but in such a manner as to make propagation easier. However, we also note that propagation is favoured significantly more during the early stage of shear band advance than when it grows longer. As such, we propose an alternate mechanism whereby propagation of new shear bands is favoured over extension of existing longer ones. This leads to propagation of multiple shear bands, distributing shear through the material and hence promoting ductility.

We have so far considered the transformation zone as a region with a discrete boundary, with all particles transforming inside the zone and none without. As understanding of transformation toughening has advanced, it has become clear that considering the transformation zone as a whole and neglecting the reverse transformation [6] gives a subtly wrong estimate of the toughening. A case with a full-width transformation zone behind the shear band is known as "supercritical", and is what we have considered here. The "subcritical" case, where some of the outer transformation zone is not fully transformed in the shear band wake, however, should in this case simply reduce the contribution to stress intensity factor as the crack advances further – i.e. increase the height of the peak and contribute to the proposed toughening mechanism.

It should be noted that the model as proposed is a mean-field model, which considers the particle-containing region around the shear band to be a homogeneous region and averages the effects of individual particles transforming. This should still give a reasonably accurate output in the general case. A further assumption to identify is that we have neglected the effects of the ends of the transformation zone, where the zone sides and the shear band edges are joined. However, this should be negligible with longer shear bands and, running the ahead-of-tip calculations from π to $-\pi$, we obtain a value of zero – showing the contribution prior to shear band advance to be zero, and in fact suggesting a
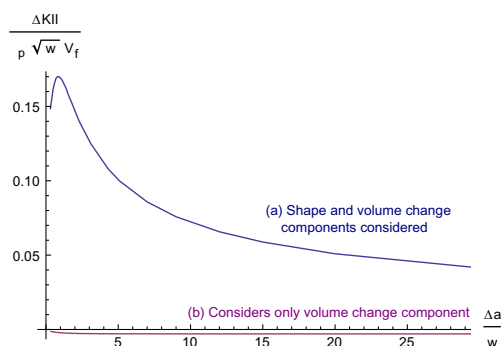
Table 1. Material properties for $Cu_{47.5}Zr_{47.5}Al_5$.

Poisson's ratio	E_p (GPa)	E_m (GPa)	ΔG (J mol^{-1})	e^T	e^S
0.373 [12]	82 [12]	82 [12]	2.702*T–1408.52 [13]	0.00137 [5]	0.124 [5]

Values are evaluated for $T = 298$ K and with a sample initial stress intensity factor of 5 MPa m$^{1/2}$.

Table 2. Stress intensity factor change with crack advance.

$\Delta w/a$	$\Delta K_{II}/(E_p \times V_f \times w^{1/2})$	$\Delta w/a$	$\Delta K_{II}/(E_p \times V_f \times w^{1/2})$
0.3	1.48E−01	1.8	1.52E−01
0.5	1.62E−01	2.3	1.40E−01
0.6	1.66E−01	3.1	1.25E−01
0.7	1.69E−01	4.3	1.08E−01
0.8	1.70E−01	5.1	9.98E−02
0.9	1.70E−01	7	8.58E−02
1	1.69E−01	9	7.58E−02
1.1	1.68E−01	12	6.57E−02
1.2	1.66E−01	15	5.88E−02
1.3	1.64E−01	20	5.09E−02
1.4	1.62E−01	30	4.14E−02
1.5	1.59E−01	50	3.19E−02

Figure 3. Contribution to toughening.

positive contribution from the region at the zone end as the shear band advances.

Also worth considering is the impact of size effects on the toughening behaviour. Size effects in bulk metallic glasses can have a significant impact on plasticity, as observed in the recent review by Greer and De Hosson [14]. In this instance, it is perhaps most interesting to consider particle size – we have assumed an ideal thermoelastic martensite and hence no interfacial energy term [15], but it now seems likely that the interfacial effects may play a significant part in the toughening behaviour, and this bears further investigation. We also note, however, that our approach may break down when the particle size approaches the transformation zone size.

To conclude, we establish a mathematical model for transformation toughening behaviour in the Cu$_{47.5}$Zr$_{47.5}$Al$_5$ bulk metallic glass composite, based on the mathematics developed for use in zirconia-based ceramics and a model of shear bands as mode II cracks. We demonstrate that, considering volume change alone, this mechanism cannot explain the unusual ductility of the composite, contributing only −0.2 MPa m$^{1/2}$ if we set an initial applied stress intensity of 5 MPa m$^{1/2}$. We propose a mechanism whereby, if shape change components are considered, ductility is enhanced via propagation of shorter shear bands being favoured over more mature, longer ones (by 1.12 MPa m$^{1/2}$ with an initial applied stress intensity of 5 MPa m$^{1/2}$). This leads to the propagation of multiple short shear bands and hence distribution of shear, leading to ductility.

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