Mechanical behaviour of metallic glasses related to thermal properties

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Abstract. The relationship between mechanical properties, the glass transition temperature and the heat content needed to reach it is discussed for various glass-formers to prove aspects of the mechanism of shear band propagation. Temperature profiles around shear bands are determined by means of finite element modelling. The results are used to interpret serrations and the effect of specimen size.

1. Introduction
Deformation of metallic glasses is homogeneous close to the glass transition temperature, $T_g$, and inhomogeneous at low temperature occurring in localized shear bands [1]. In this case failure apparently starts with shear offset at a favourite site causing local temperature rise above $T_g$, maturation of the shear band which ends up in a crack [2, 3]. The energy released during yielding and failure (the resilience) was compared with the thermal energy needed to bring the glass at temperatures above $T_g$ evidencing three lengthscales: one related to the volume of unitary area where localization occurs, another to the volume providing mechanical energy, and a third one where temperatures in excess of $T_g$ are experienced. These conclusions were drawn using data for Vitreloy 1 (Vit 1, Zr41.25Ti13.75Ni10Cu12.5Be22.5) obtained with the fusible coating method [4] and the findings were validated by means of finite element (FE) modelling of the shear band and its surroundings [5]. The correlation of the resilience with thermal energy for practically all known metallic glasses was shown.

The ongoing discussion is extended here by considering deformation in alloys which do not display a manifest $T_g$, the energetics of serrations which often precede failure during compression testing as well as specimen size, and a comparison with properties of other families of glass-formers.

2. Temperature profile around a shear band
The FE calculation assumes the heat source smeared in the shear band is a thin slab of width 10 nm adjacent to a thicker domain, the heat reservoir, where heat conduction occurs [5]. A spatial temperature profile at $1.5 \cdot 10^{-8}$ s after shearing is shown in Fig. 1a where the maximum is still above the melting point of the alloy (937 K) and the thickness of the slab above $T_g$ is 560 nm. Five profiles are projected in the plane in Fig 1b. The temperature decreases rapidly in time and space from left to right but a region of some hundred nanometers thickness remains above $T_g$ still after $4 \cdot 10^{-8}$ s. The cooling rate from the melting point to $T_g$ is of the order of $10^{10}$ K/s well suited to keep the zone glassy after shearing. These times are of the same order as that estimated for shearing therefore the band is not adiabatic, as already pointed out [6].
3. Further evidence of high temperatures in fractured metallic glasses

There is wide evidence that the liquid state is reached at fracture surfaces where filaments, drops, vein and river patterns appear [1, 3, 7, 8]. Fig. 2 reports images of surfaces of an Al$_{87}$Ni$_7$Ce$_6$ ribbon cold rolled to fracture between stainless steel plates. The rolled surface has aligned steps due to shear bands; the fracture surface is vein-like (Fig. 2a). In Fig 2b at the bottom of the step on the left, unbroken ligaments are seen resulting from tearing. Differential scanning calorimetry of such fragments did not differ from that of the original ribbon indicating that no extensive crystallization occurred during deformation. The T$_g$ for this alloy ($\approx$ 510 K) is lower than that of Vit1, so the times for heat dissipation must be longer but short enough to preserve amorphicity.

4. Energetics of shear bands

Shear displacement occurs at some flaw of the material. Then, the temperature rises and the shear band propagates with loss of traction. Elastic energy is contributed to the band from a distance of tens
to hundreds of micrometres [4, 5]. The resilience of metallic glasses \( U_r = \sigma_y^2/2E \), with \( \sigma_y \) the yield stress and \( E \) the Young modulus, estimates the energy released at fracture. \( U_r \) versus the energy needed to reach \( T_g \) \( (3R\Delta T_g/V) \) with \( R \) the gas constant, \( \Delta T_g \) the difference between \( T_g \) and the testing temperature, and \( V \) the molar volume) shows a clear correlation as reported in Fig. 3a for bulk metallic glasses. The line is drawn according to the energy ratio (44) for Vit 1. Clearly, shear band propagation is related to \( T_g \) for many alloys in the same way. The above ratio shows that elastic energy is localized in a thinner zone estimated of the order of micrometers [5], a lengthscale compatible with the size of

the molten zone in fusible coating experiments [2] and of veins and other features on the fracture surfaces of metallic glasses. For a comparison with other glasses, a plot of the quantity \( H_v^2/(2E) \) (with \( H_v \) the hardness, used as a measure of strength; the relationship between hardness and yield stress is assumed as \( \sigma_y = 3H_v \)) is reported versus thermal energy in Fig. 3b. The correlation is kept for metallic and some inorganic, e.g. selenide, glasses indicating a common mechanism for failure contrary to other glasses (e.g. borates and phosphates) for which a different mechanism of failure can be suggested.

![Figure 3](image1.png)

**Figure 3.** The resilience (a) and the quantity \( H_v^2/(2E) \) (b) versus the volumetric heat needed to bring the material from room temperature to \( T_g \). The lines are described in the text. Full symbols: bulk metallic glasses; open symbols: triangles, selenides; circles, borates; rhombi, silicates.

![Figure 4](image2.png)

**Figure 4.** The strain undergone by bulk metallic glasses as a function of the ratio of the measurement (room) temperature, \( T_{amb} \) to \( T_g \).
5. Effect of temperature on strain
It has been suggested that a critical strain level is necessary to activate shear transformation zones determining the yield stress [1] and a universal criterion has been proposed [9]. With the set of data collected for bulk metallic glasses this is checked in Fig. 4 which confirms the earlier finding. Although weakly, temperature favours reaching the activation barrier for shearing.

6. Serrations and specimen size
The shear band energetics summarized above was derived for catastrophic failure. Plastic behaviour via a series of serrations implies stress drops of the order of 1% and elastic deformation with energy release of the order of $10^{-4} R$ per serration. Steps of various sizes are produced on the surface of samples [6, 10]. The size of the molten fusible coating scales with the shear offset of each band becoming undetectable below about 1 µm [3]. This can imply that the amount of energy released is progressively decreased. Lower temperatures are attained and the fast dissipation described above prevents fracture. Actually, $T_g$, or perhaps the softening temperature of the glass since the highly viscous liquid just above $T_g$ can still offer some traction, may just be reached. The glassy state is recovered, although with local dilatation, as well as renewed resistance to strain.

Finally, for samples of limited size, e.g. well below that needed for releasing enough elastic energy at yielding to reach high temperatures (hundreds of micrometres), the local heating will be less, but also there will be no possibility of dissipating it. This may be a reason for the transition to the homogeneous deformation mode reported recently [11].

7. Conclusions
This work contributes to the current discussion on the deformation of metallic glasses starting from the results of a FE calculation of the temperature profile around a shear band, and from evidences of melting on fracture surfaces. Then, the correlation between resilience and thermal energy is shown to be general for bulk metallic and some inorganic glasses suggesting a similar mechanism of formation of critical shear bands. The implications for the energetics of serrations are discussed and a suggestion is put forward for the homogeneous deformation in small sized specimens.

8. Acknowledgments
Work performed for “Progetto D23, Bando Regionale Ricerca Scientifica Applicata 2004”. Fondazione S. Paolo is acknowledged for support to CdE NIS.

9. References
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