Chapter 4

Thermo-mechanical Properties of Glass Forming Alloys


It is more systematic to divide this Chapter into two sections. After a general overview, firstly we shall introduce thermodynamic analyses and some results (section 4.2) and secondly, we shall introduce concepts of shear band formation and direct observations, by electron microscopy, in section 4.3.

4.1 Introduction

Crystallisation in metallic glass alloys can occur in two ways, either from the melt (during cooling) or from glass during heating. The former case is important in the control and design of glass forming alloys, but the latter is important when considering thermal stability and related properties of metallic glasses.

As described in Chapter 3, criteria (albeit often empirical rules) for metallic glass formation, which outline necessary parameters and thermometric properties and relationships as being important for such formation have found increasing recent interest. It is noticeable that temperature plays a very important role in understanding glass forming ability. An example of this is the ratio between the glass transition temperature ($T_g$) and the melting temperature ($T_m$) of a system: $T_g/T_m$, which is deemed to be required to be higher than 0.6 for good glass forming systems. The difference between the first crystallisation start temperature ($T_x$) and the glass transition temperature; $\Delta T_x = T_x - T_g$ is also considered to be important, with a larger difference generally correlating to better glass forming ability.
Prior to crystallization during heating, metallic glasses experience “structural relaxation”, related to short-range ordering phenomena and volume contraction around the glass transition temperature, i.e. the temperature at which, during heating, the material becomes soft, or upon cooling, becomes brittle. This phenomenon occurs in amorphous materials when the atoms in the non-equilibrium state of amorphyicity gain appreciable mobility, which may occur upon heating. When considering the next physical change upon heating for glassy metals, i.e. crystallisation and the activation energy, $E$, for this, the Kissinger equation is often quoted as here in equation 4.1. Where $T_p$ is the peak crystallization temperature, $k$ is Boltzmann’s constant and $\phi$ is the heating rate. A dependence of $T_x$ of heating rate is therefore expected.

$$\ln\left(\frac{T_p^2}{\phi}\right) = \frac{E}{kT_p} + \ln K$$  \hspace{1cm} (4.1)

Many physical properties may be affected by structural relaxation and subsequent crystallisation and it is of course useful to understand how and when these changes are brought about. Thermodynamic analyses can aid in this quest. To gain information as regards glass transition temperature, crystallisation temperature(s) (and associated formation enthalpies), melting temperature, volumetric changes due to crystallisation and responses to loading at elevated temperatures, no current single test permits the collection of all this information. However, several standard thermo-analytical tests do exist that allow such information to be attained in part. They will be addressed in this chapter and their relevance to the investigation of metallic glasses will be assessed as regards the various processing routes.

The glass forming alloy series introduced in Chapter 3, based predominantly upon Cu-Ti-Zr has been developed and studied in some detail since the mid-1990s with respect to its thermal properties and glass forming ability [1]. Additional elements and partial substitutions have been reported to improve the glass forming ability of such compositions. A recent paper revisited the glass forming alloy Cu_{47}Ti_{33}Zr_{11}Ni_{8}Si_{1} with respect to its glass forming ability, and the overestimation thereof [2]. Glassy metal production is not (yet) a well understood technology, and the definition of what is amorphous may differ depending on the chosen analytical method. As Venkataraman et al. [2] point out; even when using some of the most highly technological analytical techniques (such as (HR)TEM), the result can be very dependent on the sample preparation technique, or factors such as recrystallization induced through exposure to high energy electron beams (TEMs generally operate at 200-400 kV). It is no surprise, therefore, that published data can appear not only differing, but sometimes contradictory.

Park et al [3] studied the effect of Sn addition to Cu-Ti-Zr-Ni-Si, however the analysis concentrates mainly on the effect on glass forming ability (defined by casting thickness), with no (HR)TEM analysis given, nor any attempt made to assess the
crystallisation beyond the enthalpies for crystallisation. In the coming results, we attempt to elaborate, not only on the thermal properties and response to mechanical deformation of this and other alloys, but also in section 4.3, we direct attention towards the characteristics of full fracture of this and other glass forming alloys.

An adjunct to the fascinating thermo-mechanical properties of metallic glasses is the material response to deformation. This is an important factor when considering possible applications or functions and also a subject area which is still shrouded with some confusion. In the case of amorphous materials, it is well understood that shear bands form in bulk metallic glasses (BMGs) as a plastic response to deformation at low temperatures [4,5]. Significant progress has been made in recent years in the understanding of the associated deformation and fracture in amorphous metals together with possible control of shear band propagation by virtue of (nano-)crystalline additions in order to suppress the tendency for instantaneous catastrophic failure [6,7,8,9,10]. However, it is also apparent that there is still much inconsistency, and whilst many sound hypotheses and proofs abound, clarity is often lacking when comparing published results. Zhang et al. [11] review the (High Resolution) Transmission Electron Microscopy ((HR)TEM) analysis of shear band thickness and find the range to be 10 – 20 nm for several BMG compositions. TEM should be a suitable tool for this kind of analysis of shear band formation in metallic glasses, since their thicknesses are very low and it may be expected that shear bands may lead to (nano-scale) structural changes in amorphous materials. However, this methodology often requires post-experimental sample preparation which can invalidate TEM observations [12,13].

Analysis of inhomogeneous deformation of metallic glasses in compression and their response thereto has been extensively studied [14, 15], since it is believed that this is the easiest manner in which to avoid catastrophic instability [16]. This consequently means that tensile fracture in BMGs has received less attention, mainly due to the high instability associated with plane stress and plane strain investigations. Some interesting tensile investigations have been reported [17], and in-situ TEM has been shown to be an excellent tool for observing the formation of nanocrystals and their effects [8].

It has been widely believed that shear in metallic glasses can develop high local temperatures [18, 19], leading to a range of fracture surface features in metallic glasses [20], which can be simple flat and almost featureless shear planes; characteristic vein patterns formed by the meniscus instability [21] initiated from the surface edges or homogeneously inside a deformed layer; or wide and very elongated veins extending along the shear surface from the edge of the shear step of bulk samples [20]. Again, there remains uncertainty over why there are differences in fracture surfaces with respect to both fracture due to compression and tension [7] although Zhang et al attempt to compare differences in compressive and tensile fracture surfaces in [22]. Analysis of these features, however, suggests that the heat developed during deformation in metallic glasses means that much more material is involved
in the formation of a so-called ‘liquid-like layer’ (LLL) [11] than the accepted width of a shear band (10 – 20 nm) [11, 12].

Direct proofs of those temperature rises have been published, with the analytical methods including high speed camera observations in compressive and impact testing [23, 24]. Recently Lewandowski and Greer [25] found a very elegant fusible-coating method to confirm experimentally the local temperature increase in the vicinity of a shear band formed in amorphous material, using a thin tin coating on their surface which melts up to some distance from a developed shear band. In the model calculation they consider a shear band to be a planar source of heat with density $Q$ (J/m$^2$) at time $t = 0$. The temperature increase at a distance $x$ to the both sides of shear band located at $x = 0$ is given by:

$$\Delta T = \left( \frac{Q}{2\rho C\sqrt{\pi \kappa}} \right) \frac{1}{\sqrt{t}} \exp\left( \frac{-x^2}{4\kappa t} \right)$$

(4.2)

where $\rho$ is the material density, $C$ the specific heat of the material and $\kappa$ the material thermal diffusivity. Their measurements approved this relatively simple model as well as an estimation of amount of released heat $Q$ calculated from the uniaxial yield stress $\sigma_y$ and shear displacement $\delta$ [19, 36]:

$$Q = \beta \sigma_y \delta,$$

(4.3)

where $\beta$ is a constant of value < 0.35 in the case of 45º shear. Further experimental study [19] confirmed this model, showing that a linear dependence between shear displacement and width of melted coating area exists for three different metallic glasses with $\beta = 0.30$.

Given that heat is developed during shear in metallic glass, it may be safe to assume that crystallisation may occur within that heat affected area. Published data shows that it does occur [7] but also does not occur [17]; however to the best of our knowledge, no explanation has been offered for these differing findings until this work [26].

In the upcoming work we attempt to address the problems outlined above by adopting the model engaged for the tin-coating investigations [25], but apply it to the glass transition temperature of a given material. We also attempt to estimate the thickness of the LLL by complimentary TEM and scanning electron microscopy (SEM) observations. Due to the nature of in-situ TEM testing, the samples must be very thin and therefore the results should not be tacitly assumed valid for normal “bulk” samples although the compositions chosen are from BMG compositions. We address discrepancies in experimental and model findings and discuss the formation of a range of fracture surfaces developed under macroscopically identical conditions for several BMGs, namely $\text{Cu}_{47}\text{Ti}_{33}\text{Zr}_{11}\text{Ni}_6\text{Sn}_2\text{Si}_1$ [3], $\text{Zr}_{50}\text{Cu}_{30}\text{Ni}_{10}\text{Al}_{10}$ [27] and $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_{5}$ (VIT105) [28].
4.2 Thermo(mechanical) Analyses

4.2.1 Thermal Mechanical Analysis (TMA)

Any analysis of the thermal properties of a material involves the application of heat to the samples and measuring the response of the material thereto. In TMA, a static load is applied to the material while the heat is applied. The elongation of the sample can be translated to engineering strain and plotted as a function of temperature the gradient is therefore the coefficient of thermal expansion, $\alpha$ (K$^{-1}$). Due to structural changes upon heating, several interesting numbers can be retrieved. Figure 4.1 show the results of engineering strain as a function of temperature for different stresses for Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_6$Sn$_2$Si$_1$ alloy measured at heating rate 10 K/min. It is clear to see from the Figure 4.1 and Table 4.1 that the applied stress has a marked effect on the ‘material properties’. Given that the material is amorphous, it can be considered isotropic, but all measurements were taken in the casting direction. The equipment set-up (Setaram TGA 92) can be seen in Figure 4.2.

![Figure 4.1: Static dilatometric curves measured on Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_6$Sn$_2$Si$_1$ alloy amorphous ribbon using the heating rate of 10 K/min and different loads. Two distinct gradients ($\alpha_1$ and $\alpha_2$, Table 4.1) are seen for all curves. The steepest gradient, $\alpha_2$, represents the highest thermal extension, induced through reduced viscosity resulting in visco-plastic behaviour around the glass transition temperature, $T_g$.](image)

It is also possible to estimate the viscosity of the ribbons during deformation by plotting the strain as a function of time to reveal the strain rate. When this is divided through the shear stress (we assumed here $\tau = 0.6*\sigma$), the average viscosity in the $\alpha_1$ region was found to be $5 \times 10^{12}$ Pa.s, while the average viscosity in the $\alpha_2$ region was found to be $5 \times 10^{10}$. This is a significant drop in viscosity for the material when it is heated above $T_g$. 

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Table 4.1: Thermal properties of Cu\textsubscript{47}Ti\textsubscript{13}Zr\textsubscript{11}Ni\textsubscript{6}Sn\textsubscript{2}Si\textsubscript{1} alloy melt-spun ribbon gained from TMA analysis shown in Figure 4.1

<table>
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<th></th>
<th>5.5 MPa</th>
<th>24 MPa</th>
<th>43 MPa</th>
<th>78 MPa</th>
<th>115 MPa</th>
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<td>4.03</td>
<td>4.08</td>
<td>4.53</td>
<td>4.22</td>
<td>4.49</td>
</tr>
<tr>
<td>T\textsubscript{g} [°C]</td>
<td>453</td>
<td>463</td>
<td>461</td>
<td>457</td>
<td>456</td>
</tr>
<tr>
<td>$\alpha_2 \times 10^{-3}/K$</td>
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<td>18.5</td>
<td>19</td>
<td>18.5</td>
<td>19</td>
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<tr>
<td>T\textsubscript{x1} [°C]</td>
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<td>485</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T\textsubscript{x2} [°C]</td>
<td>517</td>
<td>517</td>
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</tbody>
</table>

4.2.2 Dynamic Thermo-Mechanical Analysis (DTMA)

4.2.2.1 DTMA Concepts and Calibration

DTMA is a thermal analysis technique, which performs tensile sinusoidal variations of the load on a sample. Essentially the sample is ‘hung’ with one end fixed and the other end attached to an oscillating bar (Figure 4.2). The frequency and amplitude of oscillation can be controlled accurately to measure the response of the material. If this is performed with increasing temperature then the structural changes associated with the temperature rise can be recorded.

Before one can perform such an analysis it is necessary to calibrate the system to determine the system stiffness. This is done by annealing a fully amorphous section of metallic glass ribbon for a long time (2 hours) at a temperature below $T_g$. The annealed sample may then be placed in the DTMA equipment and, at ambient temperature, a static load is applied. This load is then supplemented by an oscillating load (of less magnitude than the static load). After a certain number of oscillations this load is then increased for an equivalent
duration, before another incremental rise until such a time that the oscillating load is greater than the static load. This data can then be plotted on an extension vs. time plot and the average extension can be recorded from the FFT smoothed data (Figure 4.3A). By plotting applied load ($P$) as a function of (average) extension ($\delta$) the stiffness ($S_{\text{system}}$) of the system can be equated from the gradient of the line ($S = P/\delta$).

![Figure 4.3: (A) Graph showing a section of DTMA curve used for system stiffness calibration. The sinusoidal part of the curve represents the displacement of the annealed amorphous ribbon due to an oscillatory load. This data is smoothed by Fast Fourier Transform (FFT) and the average value for each ‘step’ is recorded and plotted vs. time in (B) which reveals the effect of load on the system displacement. The gradient of this curve is given as the system stiffness, $S_{\text{system}}$.](image-url)
4.2.2.2 DTMA of Metallic Glass Ribbons

A typical DTMA analysis for increasing temperature is shown in Figure 4.4A. A focus of the area around \( T_g \) is shown in Figure 4.4B so that the displacement due to the oscillating load can be seen clearly. Once this data is collected, it may be treated so as to remove the system stiffness contribution and this was achieved here by formulating a simple MATLAB programme. The result is that a relative change in strain/unit load may be plotted, as shown in Figure 4.4C. To aid clarity only a few examples are shown, and fundamentally this provides a comparison between Cu\(_{47}\)Ti\(_{33}\)Zr\(_{11}\)Ni\(_{8}\)Si\(_{1}\) alloy and Cu\(_{47}\)Ti\(_{33}\)Zr\(_{11}\)Ni\(_{6}\)Sn\(_{2}\)Si\(_{1}\) alloys. It can be seen that for all samples there is a significant reduction in strain (or conversely an increase in stiffness, i.e. Young’s Modulus) prior to the glass transition. This is seen to be dependant upon the applied stress (larger stress = larger change in strain). Thereafter, the strain increases rapidly signifying a significant reduction in Young’s modulus (and viscosity) before the material crystallises and the strain reduces again before a second crystallisation event is witnessed. The correlation between the crystallisations for Cu\(_{47}\)Ti\(_{33}\)Zr\(_{11}\)Ni\(_{6}\)Sn\(_{2}\)Si\(_{1}\) alloy is excellent – no deviation is seen despite the differing stresses applied. The alloying effect of Sn is also clear to see. \( T_x-T_g \), which we remember is a significant factor in metallic glass forming ability, is seen to increase with the addition of Sn.
Figure 4.4: (A) DTMA curves for Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_6$Sn$_2$Si$_1$ alloy with the dotted-box area in (A) shown in (B). (C) provides relative strain/unit load vs. temperature curves for Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_6$Sn$_2$Si$_1$ and Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_6$Sn$_2$Si$_1$ alloys for differing applied stresses as relayed in the Figures themselves.

4.2.3 Differential Scanning Calorimetry (DSC) and Transmission Electron Microscopy

One further method to realise the values of \( T_g \), \( T_x \), and \( T_m \), as well as the enthalpies associated with those thermometric properties is a method known as Differential Scanning Calorimetry (DSC). In this case, no load is applied to the sample and the measurement methodology is rather simple. In essence, this method consists of two little pans, one containing a sample whose thermodynamic data is unknown and the second is a reference pan. This is left empty. The two samples are then heated at a constant heating rate. Generally, in practice this rate varies between 10 and 40 K/min, although heating rates can be much lower
than 10 K/min. In this range (10-40 K/min), the lower rates lead to more accurate readings in crystallisation activity due to lower heat lag and the dependency given in equation (4.1), however DSC sensitivity can become poor at lower heating rates. The essential part of this analysis is that the reference sample and the analysed sample are kept at the same heating rate (and therefore same temperature) throughout the analysis, and the extra (or surplus) energy required to heat the extra mass of the analysed sample is measured, with endothermic (energy absorbing) or exothermic (energy release) reactions being recorded. An endothermic reaction correlates to melting, whilst exothermic reactions signify crystallisation occurrences. With DSC analysis, this energy release may be evaluated. Each crystallisation has a unique enthalpy associated with it and therefore affords a method of identifying chemical possibilities for that particular crystallisation.

In this section, we combine the knowledge gained through the various thermo-analyses outlined thus far and combine this with TEM. The results thereof are concerned with Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_8$ BMG alloy, which as noted repeatedly already is part of a series first developed by Johnson et al [1]. Many other works have been published in connection with this system and its recrystallization; however slight differences in production route or the state of the raw material can lead to widely differing results and indeed differing degrees of amorphisation. The crystallisation temperature $T_x$ (exothermic reaction) is not strictly intrinsic properties of a system, but instead is found to lie within a range as can be derived from equation 4.1. From a detailed reading of published data, for most BMG alloys this range has been found to be in the order of 50 K. This is highlighted in the DSC trace shown in Figure 4.5. Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_8$ ribbon was heated to discover information regarding the material’s thermo-dependant properties. Not only does this DSC traces for the ribbon yield information surrounding $T_g$ (found to be ~648 K) and $T_x$ found to be ~725 K), but also shows the enthalpy of formation for area of the first crystallisation, $\Delta H$ to be -11.28 J/g. The glass transition and crystallisation temperatures are considerably lower for this alloy than those presented in the DTMA sections, which signify a greater thermal stability for the BMGs with small additions of Sn and Si.

![Figure 4.5: DSC trace for Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_8$ metallic glass ribbon](image-url)
Figure 4.6: [A] TEM micrograph showing a Ti rich crystal in an amorphous matrix; the HRTEM image of which is shown in [B].

Figure 4.7: TEM micrographs of the two matrices found to develop in a Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_8$ melt spun ribbon. Energy filtering reveals: in [SERIES A], a chemically homogeneous matrix; and in [SERIES B], a matrix exhibiting spinodal decomposition. Both cases show the presence of a Ti-rich grain.
Figure 4.8: TEM observation of in-situ heating of Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_{8}$ ribbon. Small crystals form uniformly initially away from the sample edge (i.e. in the thicker area) as < 10 nm size grains and up to 525 °C these crystals do not appear to vary much in size, or density. At 525 °C grains form in the thinner section of the sample and grow to be considerably larger (~100 nm) than the grains in the ‘bulk’ (~10-20 nm). The large grains in the thin sample area were found, by energy filtering, to be Ti-rich.

EDS analysis was conducted and yielded results such that the matrix was seen to be very close to that of nominal, with a matrix composition of (in atomic %) Cu$_{48}$Ti$_{33}$Zr$_{11}$Ni$_{8}$, whilst crystals found in the matrix were seen to be titanium rich, with a composition (in atomic %) of Cu$_{22}$Ti$_{66}$Zr$_{11}$Ni$_{4}$. Diffraction patterns from the matrix showed it to be amorphous. This was confirmed by high resolution TEM (HRTEM) imaging, which shows there were indeed crystals, embedded in an amorphous matrix (Figure 4.6).

The matrix has been found to take two forms. These are represented in Figure 4.7. The first is a homogeneous matrix (series A, Figure 4.7), the second shows some decomposition (series B, Figure 4.7) (possibly spinodal, due to the vein-like appearance of the microstructure) or segregation. By virtue of Energy-Filtering analysis in the TEM, it was
possible to show the vein-like structure to be Ti rich (white) and most likely Cu regions. Both pictorial series comprise an overview, a zero-loss (ZL) image and a Ti map to highlight the points outlined here. Again, the presence of Ti rich crystals is clearly evident in both cases.

From the DSC values attained, it is possible to attempt knowledge-driven in-situ heating with TEM (Figure 4.8). Heating began just above the given first crystallisation temperature of 450 °C. Imperfect thermal contact (described in section 4.3) between the specimen holder and specimen however, limited crystallisation until the recorded temperature was 490 °C. Beyond this temperature, a clear densification of crystals is seen in the sample, however it appears retarded at some distance from the sample edge, until heating above 535 °C is achieved, at which point rapid crystallisation occurs of, once again, Ti-rich composition, revealed by Energy Filtering analysis.

By the size of the crystals grown, which will not grow larger than the thickness of the ribbon, it follows that the thickness dependent crystallisation of Cu₄₇Ti₃₄Zr₁₁Ni₈ is limited to a thickness of 100 nm and requires and activation temperature of 45 °C higher than the first crystallisation, which, using equation 4.1 signifies that an activation energy 5 kJ.mol⁻¹ higher is required to overcome the thickness-dependant crystallisation compared to the uniform crystallisation that takes place in the bulk of the sample.

4.2.3.1 First Crystallisation after T_g in Cu-based metallic glass ribbon

In order to avoid decomposition, and improve glass forming ability, the Cu₄₇Ti₃₄Zr₁₁Ni₈ alloy with Si and Sn additions can be selected. Rather than in-situ heating, for the alloy Cu₄₇Ti₃₃Zr₁₁Ni₆Sn₂Si₁, TEM studies have been conducted on DSC heated metallic glass ribbons. The crystallisation of the alloy, beyond the glass transition temperature, found by DTA and DTMA analysis is not seen to be driven by nucleation. The material heated to just above the glass transition temperature (733 K) is seen to remain fully amorphous (Figure 4.9), although thermo-mechanical testing revealed some structural relaxation leading to a lowering in the Young’s Modulus. In previous in-situ studies the (re)crystallisation of a variant of this alloy, without the Sn addition, has shown the alloy to begin with the nucleation of clear Ti-rich crystallites [29] and confirmed by [30]. In the current investigation, the alloy instead reveals only a sharpening of the first and second order amorphous diffraction rings (Figure 4.10). Coupled with TEM analysis, this signals a blanket refinement of the microstructure. This does not appear to be driven by a particular element or element pair, although the nano-crystals that form may be clearly seen in Figure 4.10, giving contrast to the microstructure that was not originally there. High resolution TEM (Figure 4.11) confirms this that some short-medium range ordering appears to develop.
Figure 4.9 (left) Diffraction pattern, (centre) line profile thereof and (right) TEM micrograph for metallic glass ribbon heated to 460 °C

Figure 4.10 (left) Diffraction pattern, (centre) line profile thereof and (right) TEM micrograph for metallic glass ribbon heated to 510 °C

Figure 4.11: HRTEM and accompanying FFT evidence of short/medium range ordering in Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_6$Sn$_2$Si$_1$ metallic glass ribbon at 510 °C
4.3 Shear band formation in Metallic Glass Ribbons

4.3.1 Experimental Procedures

Alloys were prepared as described in Chapter 3. In order to directly observe the evolution of shear bands during tensile deformation, in situ tensile experiments were performed at both room and elevated temperatures in a TEM. Such experiments require a specimen stage that is capable of straining TEM specimens while maintaining a controllable temperature of the order of (recorded) 723 K (close to $T_g$ as described in section 4.1). At present, only one type of stage with combined heating and straining capability is commercially available (Gatan Inc., Pleasanton, CA). The design of this stage relies on direct physical contact between a heating element and the specimen to control the specimen temperature. The temperature of the specimen is tacitly assumed to be equal to the furnace temperature as measured by a thermocouple. This is approximately valid at high temperatures (~ 1000 °C) when the specimen is mostly heated by radiation. However, at the intermediate temperatures used in this study, radiation is negligible, and the specimen temperature can only reach the furnace temperature if the thermal contact between the two is very good. The requirement that the specimen be movable for tensile testing results in poor thermal contact; moreover, the degree of contact fluctuates during the course of a tensile experiment. This was confirmed by Wouter Soer’s calibration measurements in low vacuum on TEM tensile specimens with a thermocouple spot-welded close to the electron-transparent area [31]. Applying a thermally conductive paste between the heating element and the specimen greatly improved the performance of the holder. However, such viscous agents are not suitable for high vacuum systems such as TEMs. This has already been observed in section 4.2.3 where the temperature of the chamber does not precisely correlate with the temperature expected from the thermal-(mechanical) analyses. Therefore, the TEM chamber was held at temperature for at least 30 minutes before the deformation experiments were begun.

Two sample dimensions were chosen for the in-situ straining measurements, as shown in Figure 4.12. In the in-situ set-up of the JEOL 2010, one end is ‘clamped’ while the other is extended at a desired extension rate. In these experiments, that strain rate was varied, but most results are shown for 0.1 $\mu$m/s (corresponding to $10^{-5}$ s$^{-1}$) extension rates as this allows a reasonable propagation time without losing imaging capabilities. Larger strain rates will also be discussed.
4.3.2 Results

4.3.2.1 In-situ TEM straining of Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_6$Sn$_2$Si$_1$ BMG ribbon

As an initial cautionary note, the in-situ TEM straining observation of metallic glass ribbons has been found to be a far from easy experiment, since, in non-notched samples, the prediction of where a shear band may initiate must be fortunate. However, in-situ testing has been found to provide a means by which the propagation of a shear band and its associated fracture tip may be followed and analysed. Figure 4.13 portrays a typical result for Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_6$Sn$_2$Si$_1$ alloy. In Figure 4.13A the ‘state’ of the crack tip at 368 µm extension (= 4.08 % strain) is shown. The fracture opening is preceded by material-thinning induced through the progression of the shear band. The shear band itself was initiated at around 3% strain, as may be expected for amorphous materials. After imaging at 368 µm extension, the sample was then re-strained for a further 3 µm to 371 µm extension (4.12 % strain) accompanied with video recording. The time taken for this displacement to occur was 30 seconds (extension rate = 0.1 µm.s$^{-1}$). No jerky motion was seen in this case, but instead the ‘opening’ of the crack tip was seen to be ‘constant’, however in some cases, applied load resulted in no discernable change at the crack tip for up to 5 µm normal extension. This is complimentary to macroscale observations in shear band propagation. Imaging the ‘new’ crack tip allows measurement of the crack-tip displacement and crack-tip characteristics (Figure 4.13B). Little change in the ‘microstructural appearance’ of the crack-opening was seen. Characteristics of the area in and around the projected shear band include narrow (10 -
20 nm) featureless bands, at the edge of the fracture surface. The next region is shown to be a ‘speckled’ band 20-50 nm in width. The features in the speckled region are 2-5 nm in size, but could not be resolved as crystals in HRTEM investigations. It may, therefore, be reasonable to consider the smooth, (bright) bands to be characteristic of the shear band, while in the speckled region, the nano-scale features can be attributed to very local meniscus instability.

An extension of 3 µm in the tensile loading direction ($\Delta l_n$) is found to translate to a crack propagation displacement ($\Delta l_p$) of 338 nm, heralding an approximate relationship of $\Delta l_n \approx 10 \Delta l_p$ during plastic deformation. This relationship was confirmed over further observations, although instances whereby application of load led to no propagation in the direction of the shear band was also seen as stated above.

Upon further straining, the shear band propagates away from the electrochemically polished hole to the thicker ‘bulk’ sample and this in turn leads to a change in stress state, which results in the formation of shear band branching since the character of the stress conditions at the surface (plane stress) are different to the conditions inside (plane strain) the sample, which means that not all shear bands which form lead to fracture, as seen in Figure 4.14.

Figure 4.13: (A) TEM micrograph of a shear band and its crack opening after 4.08% strain in Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_6$Sn$_2$Si$_1$ alloy. The inset shows that the Shear Band Propagation (SBP) direction relative to the Tensile Axis (TA) was found to be (~)90°. The white circle corresponds with the black circle in (B), a TEM micrograph of the crack opening progress at 4.12 % strain.
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The formation of secondary shear bands occurs when there is a temporary halt in the progression of the shear band due to competing planes of maximum shear stress. In the in-situ observations here, the crack propagation along the primary shear band (in the plane of maximum shear stress) and the occurrence of the secondary shear band in the opposing plane were simultaneous.

Figure 4.14: (A) and (B) TEM micrographs revealing shear band branching in Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_6$Sn$_2$Si$_1$ ribbon at 4.4 % strain. The white ellipse in (A) highlights the secondary shear band, while the white ellipse in (B) highlights an area of speckled appearance.
In one, special, case, crystallisation due to shear band formation was found. In this case, the propagation rate was much greater, since, during the image collection, 25 full frames are recorded per second. Figure 4.15B reveals the rapid crack propagation that occurred in 1 full frame with respect to Figure 4.15A. Upon sighting this rapid propagation, the progressive loading was stopped immediately and the full extent of the crack movement was imaged. The length over which the crack existed was > 600 nm.
At the head of this ‘crack’, a meniscus was found, which signifies liquid-like behaviour, and all resolvable material ahead of this tip was shown to be amorphous (HRTEM – Figure 4.16A). The edges of the sample close to the meniscus revealed crystallinity which must be developed due to the rapid segregation of the shear surfaces and a heat associated with that. Figure 4.16B shows the crack tip developed in the Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_6$Sn$_2$Si$_1$ ribbon shown in Figure 4.13B. The difference is clear and the area around this crack tip remains amorphous. The results of this rapid propagation will be discussed later.

4.3.2.2 In-situ TEM straining of Zr$_{50}$Cu$_{30}$Ni$_{10}$Al$_{10}$ BMG ribbon plus ‘post-mortem’ SEM

The shear band initiation and crack propagation of this alloy was found to be similar to that outlined above, however in some cases “full fracture” is induced rapidly; here we define full fracture as the fracture, induced by deformation due to shear banding of the sample through its full thickness between any two free ends. Given the nature of the test, this does not mean that the sample is necessarily in ‘half’ since electrochemical polishing often results in more than one hole. In all cases where this kind of fracture occurred, the initial shear band was not seen before full fracture occurred, however the resultant sample surface was found to be the same in all cases and the result was one of edge thinning and short corrugated veins were observed at one end of the fractured plane, as seen in Figure 4.17A. HRTEM raises questions over possible crystallisation or atomic ordering during shear band propagation as shown in
Figure 4.17B, which is a micrograph from the vein tip shown in Figure 4.17A. Surprisingly, these veins were only seen at one end of the fractured section.

Figure 4.17: (A) TEM micrograph revealing a ~20 nm triple point vein tip and B a high resolution TEM image of the vein tip revealing possible nanometre scale ordering, but this in unconfirmed in the FFT inset for Zr$_{50}$Cu$_{30}$Ni$_{10}$Al$_{10}$ ribbon

Post-mortem SEM (Figure 4.18 A and B) reveals that the end at which the veins appeared was the end of final contact. The two fracture surfaces overlap one another in these figures because of sample retraction when the load was removed from the tensile stage. It is not believed that this added extra deformation to the sample.
Figure 4.18: SEM micrographs revealing the corresponding fracture surfaces of (A) “top” and (B) (mirrored) “bottom” sections of a section of Zr50Cu30Ni10Al10 ribbon which underwent ‘full fracture’ driven by shear band propagation (C) fracture surface revealing no liquid-like behaviour and (D) fracture surface at propagation end revealing material shear, but no liquid-like behaviour, except at the final points of contact which are highlighted by the white arrows.

The fact that the ribbon is less than 2 µm in thickness may play a role in the development of a liquid like layer since no veins appear on the fracture surface itself (Figure 4.18) and this will be discussed later. Several other interesting features can be seen in this analysis. The shear band propagates in tearing mode from left to right in the images of Figure 4.18 in a direction approximately perpendicular to the tensile stress component, while the shear band planes are inclined to the ribbon surface plane. The shear band initially appears to
propagate as a straight-line. As the sample thickness increases a few secondary shear bands appear, all in roughly parallel planes. The shear crack propagates in a jump-like motion (as observed by TEM). A jump site may be detected via a characteristic set of secondary shear bands at the place when failure stops momentarily to select a new plane for further propagation. As seen for Cu₄₇Ti₃₃Zr₁₁Ni₆Sn₁₂Si₁ alloy (Figure 4.14), the branches are developed at these jump sites and the point at which the shear offset is developed occurs very rapidly indeed.

4.3.2.3 In-situ TEM straining of Zr₅₂.₅Cu₁₇.₉Ni₁₄.₆Al₁₀Ti₅ (VIT105) BMG ribbon and the effect of in-situ heating, plus ‘post-mortem’ SEM

Glass forming alloy VIT105 (Zr₅₂.₅Cu₁₇.₉Ni₁₄.₆Al₁₀Ti₅) has been the subject of many recent investigations, and here we examine it in in-situ tensile testing as described above, however here we make three changes to the procedure. Firstly, the samples are also prepared with a ‘dog-bone’ geometry (Figure 4.12); secondly, the extension rate is higher (1 µm/s = strain rate ~10⁻⁴ s⁻¹) and thirdly, elevated temperature (with respect to room temperature) experiments were conducted. The aim of the raised temperature investigation was to bring the alloy temperature as close to \( T_g \) as possible, without inducing crystallisation; however, one of the drawbacks of in-situ TEM heating is control of the sample temperature. In these results, the sample chamber was elevated to above 773 K (\( T_x \) for this alloy has been found to be 714 K) but no crystallisation was seen. Therefore the actual sample temperature must still have been below \( T_x \). Although the exact sample temperature is unknown, it can be safely assumed that the alloy underwent (limited) structural relaxation.

In the example shown here, full fracture did not occur. The shear band detected in (HR)TEM (Figure 4.19A) shows a typical crack opening behaviour as seen already with other amorphous alloys and remained amorphous (HRTEM 4.19A), while post-straining SEM analysis showed the presence of many secondary shear bands. The fracture surface (Figure 4.19B), however, did not reveal any liquid-like behaviour. Material involved in the shear process does not have an appearance which would suggest it has experienced significant heating, but it has clearly been sheared across the fracture surface and remains intact with the surface. The individual features on the fracture surface range in sizes from a few hundred nanometers up to 1 micrometer. It is interesting to note that a shear displacement, \( \delta \), which develops in the secondary shear bands (for example Figure 4.19B) does not ‘travel’ past the centre of the ribbon, and secondly, that in these images where this occurs, the effect is not mirrored on the ribbon underside. This may suggest that a certain amount of the (secondary) shear band deformation may be absorbed plastically.
Figure 4.19: (A) HRTEM image showing the crack opening; (B) is an SEM micrograph of a similar area in the same sample revealing no evidence of surface feature heating/melting despite full surface separation for Zr\textsubscript{52.5}Cu\textsubscript{17.9}Ni\textsubscript{14.6}Al\textsubscript{10}Ti\textsubscript{5} ribbon.

Figure 4.20: (A) TEM micrograph revealing a triple point vein formed in Zr\textsubscript{52.5}Cu\textsubscript{17.9}Ni\textsubscript{14.6}Al\textsubscript{10}Ti\textsubscript{5} alloy. The inserted SAED ring is taken in the area highlighted by the black circle and shows the vein to be fully amorphous. This was confirmed at the vein tip by (B) HRTEM and FFT (inserted) thereof.

The formation of veins in the full fracture sample was again seen because of meniscus instability and their length is spread over a wider scale, and much longer veins than those seen in the previous case. This suggests that more material is involved in the formation of a liquid-like layer during deformation. Figure 4.20A shows one of these triple point veins.
Their lengths range from 200-600 nm and could be found across the whole length of the fracture surface. Figure 4.20B confirms these vein nipples to be amorphous for a sample heated to 703 K in a TEM chamber.

If the unheated sample is viewed in ‘post mortem’ SEM, the result show typical fracture surfaces associated with failure in metallic glasses. Figure 4.21A shows such a surface. The veins witnessed in TEM are again visible during SEM analysis and their average height and density may therefore be calculated as will be discussed in section 4.3.3.1. While the shear angle was seen to be consistently around 53º, the primary shear plane on which it propagated was seen to alternate (Figure 4.21B).

When the sample chamber is heated to 430 ºC, the veins which develop are found to be characteristically different. Figure 4.22A shows a series of short veins developed during tensile fracture at elevated temperature, while some veins are clearly faceted at the root and are much longer (up to 2 µm) (Figure 4.22B). HRTEM again, however, revealed no crystallisation.

**Figure 4.21**: SEM micrographs revealing (A) the formations of triple point veins and secondary shear bands and (B) alternating shear planes in VIT105 glassy ribbon as indicated by the white arrows
Figure 4.22: (A) A series of veins exhibiting their inter-vein spacing (B) a very elongated vein produced during failure of VIT105 ribbon elongated in a TEM chamber at 430 °C

The fracture surface again revealed many triple-point veins up to 2 µm in length, as seen in the TEM and there was also evidence of shorter veins and material melting, since the surface artefacts form liquid-like balls (spheroid drops) as shown in Figure 4.23A, compared to the surface debris artefacts in Figure 4.19B which do not exhibit liquid-like features. The fracture angle, in a given plane, was found to be 53° (Figure 4.23B) which is in excellent agreement with previous research on the fracture angle of metallic glasses in tension.

Figure 4.23: SEM micrographs revealing: (A) short triple-point vein tips (> 1 µm) and apparent melting with the presence of spheroid drops ~ 300-500 nm in diameter adhered to the fracture surface and (B) the fracture angle for Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_{5} alloy pulled in tension to failure at 10^{-4} s^{-1} side-on vein tips can be seen on the fracture surface

4.3.3 Discussion

4.3.3.1 Experimental analysis of the liquid-like layer thickness

The term “liquid-like layer” (LLL) is currently quite frequently used in the literature in connection with catastrophic shear fracture of metallic glasses. However, more than 30 years ago, Takayama and Maddin [32], suggested a “grease” model giving a good simulation of the
actual fracture morphology of metallic glass ribbon. Recently, Zhang and Greer concluded in their review [11], that the shear localization in metallic glasses is the cause of the temperature rise and not its consequence. Therefore, the shear band formation is only the first stage of catastrophic failure and it takes a time of the order of a nanosecond [25]. In the following stages of the catastrophic shear failure, a subsequent temperature increase due to the thermal diffusion from the shear band to the surrounding volume and a redistribution of local stresses due to the shear deformation take part. The vein pattern morphology on the fracture surface is formed during the very last stages of the fracture when there are appropriate conditions for meniscus instability to occur. These conditions include appropriate thickness, viscosity and surface tension of the LLL, as well as the presence of a normal stress component [21].

We used the combination of TEM and SEM observations of features on the fracture surfaces exhibiting vein patterns to estimate the lowest limit of the amount of material, which is active during the last moments of failure. Quantitative analysis of a group of TEM observations of veins similar to Fig. 4.20A allows us to estimate the average height of a vein as: 0.31 µm and to approximate its profile as an isosceles triangle with a same base in accordance with scanning tunnelling microscope observations [33]. A linear density of veins on the fracture surface may be directly estimated using one of the statistical methods of quantitative stereology [34] applied to SEM micrographs, similar to Figure 4.25, where the fracture surface of VIT105 ribbon exhibits a characteristic vein pattern area.

By simply counting the number of intersections of veins with randomly applied grid lines inside the vein pattern area, calculating the average number of these intersections per unit length and multiplying by a constant \(\pi/2\) gives us the average linear density of veins on a fracture surface of VIT105 alloy = 1.25 µm/µm². Multiplying this average linear vein density by the average vein profile estimated from TEM observations we get the volume of 0.061 µm³ per each µm² of fracture surface. Assuming that the major part of the liquid-like layer is, during failure, moving into the veins and that the vein pattern is mirrored at the opposite side of the fractured surface [32], we estimated the lower limit of liquid like layer thickness to be 120 nm.

There is another approach to estimate the thickness of liquid like layer [11], based on the fact that meniscus instability process starts at air in a liquid like layer of thickness of 2-20 times the vein spacing at their initialization place [21]. Measuring the value of average vein spacing at the places similar to the area around the initiation core shown in Figure 4.26A, we received the value of 0.27 µm, which results in an estimation of thickness of liquid like layer between 0.5 and 5 µm.

Both these estimations substantially exceed the thickness of a single shear band, which verifies our expectation that much more material is taking part in the last stage of the failure process, than the volume of a single shear band.
The fact that veins are seen to develop on some fracture surfaces and not on others, and the fact that the appearance of the fracture surfaces can be so very varied, means that the local temperature and/or active stress components must be different in the various cases. There is clear evidence of elevated temperatures, since the (last point of contact) failure becomes ductile in appearance due to necking. The question of course is how high is this local temperature? In order for ductile fracture to occur in metallic glasses, visco-plastic deformation must be induced. One manner in which visco-plastic deformation is induced [35] is when the material temperature is raised. The temperature regime in which the material behaves visco-plastically can be determined through thermo-mechanical analyses. The behaviour is associated with the glass transition temperature and this temperature was found to be 674 K for VIT105 alloy. The temperature at which the crystallisation starts, $T_x$, is shown to be 714 K, however high heating rates can substantially increase this value.

Bengus et al. [36] hypothesized as early as 1993 that extreme local heating and melting at the shear crack front developed during tensile tests of amorphous alloys ribbon may occur. Their deductions were supported by the measurement of kinetics of shear crack propagation, by estimation of the amount of elastic energy released and transformed to the local heat in an extremely short time and by the observations of spheroid drops on the fracture surface of Fe$_{83}$B$_{17}$ amorphous alloy ribbon. Fractographic evidences of the local hot state of the material on the shear failure surfaces were also observed for amorphous ribbons tested in tension at very low temperatures (4.2 K) [37] and for bulk amorphous alloys tested in compression [20].

Fracture surfaces of amorphous ribbons or bulk amorphous materials studied during recent decades show a variety of fractographic features, from simple flat and almost featureless shear planes (as in Fig. 4.18 and left upper part of fracture surface in Fig. 4.25), via characteristic vein patterns formed by the meniscus instability [21] initiated from the surface edges (bottom part of Fig. 4.25) or homogeneously inside a deformed layer (Fig. 4.26A), to the wide and very elongated veins extending along the shear surface from the edge of the shear step of bulk samples [20]. However, from all these observations it seems that much more material is involved up to the final fracture process than corresponds to the generally accepted width of the shear band ~ 20 nm [12], confirmed recently also by MD calculations [38]. Moreover, some TEM observations confirmed a presence of crystalline nuclei of different size near shear crack tip or fracture surface [7, 8, 12].

According to the contemporary concept of shear band formation in amorphous metals [11, 19, 25], immediately after instantaneous shear band development, the surrounding amorphous material is heated up from the environment temperature $T_0$ due to heat diffusion. The volume where the local temperature is higher than the glass transition temperature $T_g$ may
be deformed easily due to substantially decreased viscosity, when both tensile and shear stress components exist.

The size of this volume for alloy VIT105 may be estimated using equation 4.2. We assumed \( \sigma_y = 1850 \text{ MPa}, \rho = 6600 \text{ kg m}^{-3} \) [39], \( C = 420 \text{ Jkg}^{-1}\text{K}^{-1}, \kappa = 3 \times 10^{-6} \text{ m}^2\text{s}^{-1} \) and \( T_g = 674 \text{ K} \) [40]. Figure 4.24 conveys our calculations. Figure 4.24A shows one half of the temperature increase profile in the vicinity of a single shear band with a shear displacement, \( \delta = 5 \mu m \) (a value near to that observed in Fig. 4.25) at three different times 3, 12 and 50 ns, respectively. The horizontal line made at \( \Delta T = 376 \text{ K} \) corresponds to the limit when the temperature increase from room temperature reaches the glass transition temperature \( T_g \). From Fig. 4.24A it can be concluded that the volume which may be considered to be at the temperatures over \( T_g \) is dependent on time. At a time shortly after shear band development (3 ns), the temperature increase is relatively high, however the “heat affected volume” is small. After 50 ns, all material is cooled down under \( T_g \). If one would like to know the maximal distance to which the material is overheated over the glass transition temperature, the differentiation of equation 4.2 gives the value of maximum temperature increase together with the time at which this maximum is reached. This calculation is shown in Fig. 4.24B for four different shear displacements 1, 5, 10 and 50 \( \mu m \). It is seen that 5 \( \mu m \) shear displacement may induce, at time 17 ns, the visco-plastic layer with a thickness slightly exceeding 0.6 \( \mu m \). A 1 \( \mu m \) shear displacement offers only a 0.13 \( \mu m \) layer for a much shorter time and the larger displacements such as 10 and 50 \( \mu m \), usually observed on the fracture surfaces of bulk amorphous samples, may form much thicker “liquid-like” layers (1.3 and 6.4 \( \mu m \)) for substantially longer times (70 ns and 1.7 \( \mu s \)).

Figure 4.24: (A) Local temperature increase in shear band vicinity calculated for a shear displacement, \( \delta \) of 5 \( \mu m \) (\( Q = 1.34 \text{ kJ/m}^2 \)) and \( t = 10, 50 \) and 130 ns for VIT105 alloy. (B) Maximum temperature increase calculated for shear displacements, \( \delta = 1, 5, 10 \) and 50 \( \mu m \).
The horizontal line $\Delta T = 740$ K that corresponds to the temperature increase over the melting temperature of VIT105 glass [40] is also present in Fig. 4.24A,B to indicate that a large displacement offers enough heat for local melting, as the spheroid drop on Fig. 4.23A testifies.

Using (4.3) and (4.4) we may calculate the half width $x_{T_g}$ of the zone around the shear band, within which the glass transition temperature would be exceeded, and the time when it happens. $x_{T_g}$ scales with $\delta$:

$$x_{T_g} = \frac{\beta}{\sqrt{2\pi\epsilon}} \frac{\sigma_y\delta}{\rho C(T_g - T_0)}; \quad (4.4)$$

And the time when $T_g$ at distance $x_{T_g}$ is reached scales with $\delta^2$:

$$t_{T_g} = \frac{1}{4\pi\epsilon\kappa} \left( \frac{\beta\sigma_y\delta}{\rho C} \right)^2 \frac{1}{(T_g - T_0)^2}. \quad (4.5)$$

When we calculate a maximal thickness of liquid-like layer using the model approach explained above, we get for 3.5 $\mu$m shear displacement in this alloy a thickness of about 450 nm in 8.5 ns. This number is almost four times greater than our experimental estimation calculated from vein profile and density. However, two corrections to the experimental observations and model assumptions can account for this discrepancy. Firstly, the assumption that all liquid-like material is transformed into the veins is not realistic; a substantial fraction of the liquid-like material must remain indistinguishable by SEM on the fracture surface as a thin uniform layer. This assumption moves the estimated value of 120 nm for thickness of LLL to a higher value. Secondly, the final fracture will not wait until a maximum thickness of LLL is developed, but instead it can begin earlier, when a suitable thickness for meniscus instability formation is achieved. This fact corrects the calculated value 450 nm towards a lower value. To conclude, these two corrections bring the experimental value (which can be regarded as a lower limit) and the model value (which can be regarded as an upper limit) towards a more realistic value of the true volume of liquid-like material generated during shear band deformation.

Since it is clear that the shear displacement is the important influencing factor as regards LLL thickness, it is also reasonable to suggest that limiting the shear offset will limit the probability of inducing meniscus instability. Experimental observations reveal that pure shear presides up to 4 $\mu$m (Figure 4.25) and samples thinner than this value exhibit no vein morphology, despite full fracture (Figures 4.18 and 4.19). Therefore, in order to avoid catastrophic fracture by meniscus instability, for room temperature tensile deformation of metallic glass ribbons, restraining shear bands displacement to $\delta < 4$ $\mu$m may be a solution.

If the ambient temperature is brought close to $T_g$ during in-situ TEM straining, a substantial increase in the plasticity and the amount of material involved in the veins formed
was detected (see Fig. 4.22B and Fig. 4.26A). Inserting \((T_g - T_0) = 50\) K into eq. (4.4) and (4.5), we will receive an LLL thickness around 5 \(\mu m\) for 5 \(\mu m\) displacement in time 1 \(\mu s\). These values are much larger than the values calculated and observed for room temperature experiments.

Figure 4.25: SEM micrograph revealing a plan view fracture surface of VIT105 ribbon strained at room temperature to failure at \(1 \times 10^4\) s\(^{-1}\). LLL = liquid-like layer.

Figure 4.26: (A) SEM micrograph showing the initiation place for meniscus instability in heated (430 °C) VIT105 and (B) HRTEM image revealing nano-crystallization close to the fracture surface edge for Zr\(_{50}\)Cu\(_{30}\)Ni\(_{10}\)Al\(_{10}\)
Chapter 4

A variety of the fractographic features observed on the fracture surfaces of amorphous ribbons and bulk metallic glasses as well as possible crystallization events that occur near the shear band have been shown and discussed. The reasons for these variations are explained by the large number of parameters that influence the thickness of the LLL (scaling linearly with shear displacement) and lifetime of an LLL (scaling with the square of shear displacement) in the vicinity of a shear band at the moment of failure. From the above analysis, we conclude that the thickness of the liquid-like layer depends, besides the shear displacement, upon the yield stress, the glass transition temperature, ambient temperature, and local structural inhomogeneities that may initiate meniscus instability.

4.3.3.3 (Nano-)crystallization

A question remains as to why the local crystallization near a shear band is confirmed in some TEM observations [41] but not present in others [17]. In our observations we also found small crystals (< 5 nm in diameter) in the close vicinity (~10 nm) of a shear band observed in alloy Zr_{50}Cu_{30}Ni_{10}Al_{10} in one case when it underwent ‘full fracture’ (as shown in Figure 4.26B). Crystallization has also been seen in section 4.3.2.1 when the alloy Cu_{47}Ti_{33}Zr_{11}Ni_{8}Sn_{2}Si_{1} was seen to exhibit rapid crack propagation. Again the ‘crystallized zone’ comprised crystals < 5 nm in size over a width of approximately 10 nm. Conversely, the HRTEM imaging of vein tips did not confirm any crystalline phase present. In the examples outlined in this work, where crystallization processes derive, they are driven by temperature increases and not by deformation processes as reported elsewhere [7, 41]. The maximum temperature is not the most important influencing factor in this case, but the time during which the heated volume stays at an elevated temperature, which must, due to the extreme heating rates, be much higher than conventionally measured T_{x} (~775 K). As has been shown in Figure 4.24 and eq. 4.5), this time scales with the square of shear displacement, \( \delta \). However, for large shear displacements (~50 \( \mu \)m), the time at which the material is elevated above the measured \( T_{x} \) is still less than 1 \( \mu \)s, which may be adequate for crystal growth, but insufficient for crystal nucleation since the activation energy for nucleation is larger than the activation energy for crystal growth in amorphous alloys [42]. This explains why crystals only appear in a very narrow band at the shear band edge and also why those crystals are of nanometre size. In other works [7], crystal growth up to almost 50 nm has been reported. This study supports those observations since the alloys (often Al based) have poor glass forming ability and often contain nucleation sites already of nm size. The formation of larger crystals is therefore easier to facilitate.
4.4 Conclusions

Thermo-mechanical analyses have been conducted on several metallic glasses and new data and microscopy, as well as discussions about discrepancies in published works, are presented.

For these metallic glasses studied under DTA, (D)TMA, and DSC, several microscopy techniques have been combined to provide an overview of some of the important features of shear band development and shear fracture of three metallic glass forming compositions in the form of melt-spun ribbons. The analytical method involved in-situ TEM straining, combined with heating, followed by ex-situ (HR)TEM and ex-situ SEM observations.

In-situ shear band propagation has been found to be jump-like. The secondary shear bands form a branch when the primary shear band stops and one of them will become the new primary shear band with the largest shear displacement, $\delta$. These jump sites act as a place where the primary shear plane is changed. This change can be a small correction, or may result in full alternation to an opposite plane of maximum shear stress.

Both TEM and SEM observations confirm the presence of a liquid-like layer on or near the fracture surface of the ribbons. The characteristic features of this layer include protruding veins and spheroid drops which develop during the final separation.

Estimations based on quantitative fractographic observations permit an evaluation of the thickness of the liquid-like layer formed due to heat evolution after shear band development. A model based on an assumption that a shear band acts as a planar source of heat has been used to estimate a maximum thickness of the liquid-like layer and its dependence on fracture parameters. Both experimental evaluation and model calculation confirmed that the thickness of a liquid like layer present at the last moment of fracture substantially exceeds the generally accepted thickness of a shear band.

The probability of witnessing a crystal phase near the fracture surface is mainly dependent on the size of the shear displacement.

A large number of parameters may influence the thickness of a liquid like layer in the vicinity of a shear band at the moment of failure. These include the shear displacement, the glass transition temperature and local structural inhomogeneities that initiate meniscus instability, which may all lead to a variety of fracture mechanisms with characteristic fracture surface features, which explains why conflicting results appeared in the literature. From the results published here, it may be recommended to limit amorphous “features” within a material to < 4 $\mu$m in order to avoid catastrophic fracture via meniscus instability.
References

Thermo-mechanical Properties


