Yielding and intrinsic plasticity of Ti–Zr–Ni–Cu–Be bulk metallic glass

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Abstract

Bulk metallic glass with composition Ti_{40}Zr_{25}Ni_{8}Cu_{9}Be_{18} exhibits considerably high compressive yield stress, significant plasticity (with a concomitant vein-like fracture morphology) and relatively low density. Yielding and intrinsic plasticity of this alloy are discussed in terms of its thermal and elastic properties. An influence of normal stresses acting on the shear plane is evidenced by: (i) the fracture angle (<45°) and (ii) finite-element simulations of nanoindentation curves, which require the use of a specific yield criterion, sensitive to local normal stresses acting on the shear plane, to properly match the experimental data. The ratio between hardness and compressive yield strength (constraint factor) is analyzed in terms of several models and is best adjusted using a modified expanding cavity model incorporating a pressure-sensitivity index defined by the Drucker–Prager yield criterion. Furthermore, comparative results from compression tests and nanoindentation reveal that deformation also causes strain softening, a phenomenon which is accompanied with the occurrence of serrated plastic flow and results in a so-called indentation size effect (ISE). A new approach to model the ISE of this metallic glass using the free volume concept is presented.
1. Introduction

The interest for bulk metallic glasses (MGs) has been steadily increasing during recent years, triggered in part by their unique mechanical properties, in many cases superior to their crystalline counterparts. Namely, MGs can be twice as strong as steels, exhibit more elasticity and fracture toughness than ceramics and be less brittle than conventional oxide glasses (Telford, 2004; Yavari et al., 2007). Amongst the different families of MGs, the Ti-based ones have recently attracted attention due to their relatively low-cost, good glass forming ability, large compressive strength and reasonable Young's modulus (Ma et al., 2004; Kim et al., 2004; Guo et al., 2005; Park et al., 2005; Zhang et al., 2007; Kim et al., 2008). In addition, these alloys exhibit a rather low density, making them suitable candidates for lightweight applications (e.g. automotive or aerospace industries; Duan et al., 2008). It should be noted that, in spite of these interesting properties, some aspects of the mechanical behaviour of these MGs have not been systematically addressed yet.

One of the main technological drawbacks of MGs is that they typically show limited plasticity at room temperature. This actually hinders further advancement in the applicability of these materials. Nevertheless, compared to other MGs, some Ti-based amorphous alloys exhibit moderate plastic deformation, not far from the commercially available Zr-based, Ni-based, Cu-based or Pd-based MGs (Kim et al., 2004; Park et al., 2005; Zhang et al., 2007; Lewandowski et al., 2005, 2006; Wang, 2006).

In an attempt to understand the reason for the dissimilar intrinsic plasticity of different existing families of MGs, it has been recently suggested that the mechanical toughness of these materials can be correlated with the ratio between the elastic shear modulus and the bulk modulus, \( \mu / B \) (Lewandowski et al., 2005, 2006; Wang, 2006). Namely, alloys with low \( \mu / B \) ratios (like Zr-based, Pt-based or Pd-based glasses) are relatively tough, whereas those with larger \( \mu / B \) values (like Mg-based, Nd-based or Ce-based alloys) tend to fracture in a brittle manner, similar to oxide glasses. Another interesting correlation has been established between the glass transition temperature, \( T_g \), and the yield strength: MGs with higher \( T_g \) values tend to be mechanically harder (Yang et al., 2006). This correlation results from the similarities between the glass transition in MGs and the physical processes governing plastic deformation of MGs.

Plastic flow in MGs is accompanied by dilatation, i.e., net creation of free volume (Spaepen, 1977; de Hey et al., 1998; van Aken et al., 2000). This results in a decrease of viscosity and a concomitant strain softening. In nanoindentation experiments, this softening can manifest by the occurrence of an indentation size effect (ISE), i.e. a progressive decrease of hardness as the indentation proceeds (van Steenberge et al., 2007; Manika and Maniks, 2006; Jana et al., 2004; Zhang et al., 2005). It should be noted that the ISE is typically rather pronounced in crystalline materials and has been ascribed to a variety of factors, such as surface effects (Gerberich et al., 2002), friction between the indenter and the sample (Li et al., 1993) or, more recently, strain gradient hardening (Nix and Gao, 1998; Huang et al., 2004; Al-Rub and Voyiadjis, 2004; Huang et al., 2006; Lele and Anand, 2008). The latter considers that, as a result of the shear field created by the indenter, the crystal lattice becomes distorted and, in order to form the residual indentation imprint, the so-called geometrically necessary dislocations have to be created. For large indentations, the strain variation between two extremes is more gradual and the statistically stored dislocations can easily accommodate the shear stress without need of the geometrically necessary dislocations, thus reducing strain gradient effects. Since no dislocations are formed during deformation of MGs, alternative approaches (like strain softening associated with a net production of free volume) need to be considered to understand the ISE in these materials.

Although dislocation networks cannot be created in MGs to accommodate plastic strains, plastic flow in these materials at room temperature and moderate strain rates is typically inhomogeneous and proceeds via formation and propagation of shear bands (Anand and Su, 2005; Jiang et al., 2008; Schuh et al., 2007). These bands locally nucleate in regions where the deformation-induced creation of free volume cannot be fully compensated by thermal diffusive relaxation (Spaepen, 1977). As a result, the excess free volume coalesces and the viscosity significantly reduces. Consequently, shear bands manifest as sudden load drops in macroscopic compression curves or pop-in events in nanoindentation experiments (Concustell et al., 2005).
Another peculiarity of MGs is that yielding cannot be simply described by the usual von Mises or Tresca criteria, as for crystalline metals, since normal stress components acting on the shear plane and/or hydrostatic pressure also play a role at the onset of plasticity (Schuh and Nieh, 2004; Lund and Schuh, 2004; Ogata et al., 2006). The dependence of yielding on normal stresses seems to be related to atomic friction and the dilatation events that occur during plastic flow in MGs (Lund and Schuh, 2004; Schuh and Lund, 2003). To account for the normal-stress or pressure dependence of the shear stress, both the Mohr–Coulomb (Schuh and Lund, 2003; Lund and Schuh, 2004; Vaidyanathan et al., 2001) and the Drucker–Prager (Patnaik et al., 2004; Zhang et al., 2006; Ai and Dai, 2007) yield criteria have been used in the literature.

In this work, the mechanical properties of the newly developed Ti-based metallic glass are comprehensively investigated by compression tests and nanoindentation (i.e., in geometrically constrained specimens) and compared with those of other MG families. In particular, the intrinsic plasticity and yield stress are discussed in terms of the thermal and elastic properties of the alloy, in an attempt to confirm the validity of the aforementioned universal correlations governing the mechanical behaviour of MGs. An influence of local normal stresses acting on the shear plane is evidenced by the fracture angle ($\approx 39.5^\circ$). This effect is incorporated in the finite-element simulations of the nanoindentation curves, which include the Mohr–Coulomb yield criterion. In addition, the ratio between hardness and yield stress (i.e., the constraint factor) is also discussed in terms of the pressure-sensitivity of the glass. Furthermore, nanoindentation experiments using the continuous stiffness method (CSM) reveal the occurrence of mechanical softening, which manifests in a so-called indentation size effect, i.e., an overall decrease of hardness with the indentation penetration depth. This effect is modeled in a semi-quantitative manner using the free volume concept.

2. Experimental methods

A master alloy with composition Ti$_{40}$Zr$_{25}$Ni$_{8}$Cu$_{9}$Be$_{18}$ (at.%) was prepared by arc-melting a mixture of high purity (99.9 wt.%) elements in an Ar atmosphere. Rods of 3 mm diameter were obtained from the arc-melt by copper mould casting. The sample was structurally characterized by X-ray diffraction (XRD) using Cu $K_{\alpha}$ radiation. The thermal stability of the system was investigated by differential scanning calorimetry (DSC). The elastic properties were evaluated using ultrasonic measurements (pulse-echo overlap technique) along with density assessment (Archimedes’ method).

To evaluate the mechanical properties, cylindrical specimens with a 2:1 aspect ratio were cut, polished and tested under compression, at room temperature, using a loading rate of $1.8 \times 10^{-4}$ s$^{-1}$. Quasi-static nanoindentation experiments were also carried out at room temperature, in the load control mode, using a Berkovich’s pyramidal-shaped indenter tip and maximum loads of 10 and 100 mN. Prior to nanoindentation, the samples were carefully polished to mirror-like appearance using diamond paste. The indentation function consisted of a loading segment of 250 s, followed by a load holding segment of 20 s and an unloading segment of 50 s. The thermal drift was always kept below $\pm 0.05$ nm s$^{-1}$. From the load–displacement curves, the hardness values were evaluated at the end of the load holding segments using the method of Oliver and Pharr (Oliver and Pharr, 1992; Fischer-Cripps, 2002). Proper corrections for the contact area (calibrated using a fused quartz specimen), instrument compliance and initial penetration depth were applied to obtain reliable values of hardness and reduced elastic modulus.

The nanoindentation curves were modeled using a finite-element analysis software (Strand7, developed by G + D Computing Pty Ltd.). The measured values of Poisson’s ratio, yield stress and Young’s modulus were used for the calculations and a frictionless contact between the indenter and the specimen was assumed. In the simulations, the Berkovich indenter was treated as a conical indenter with a cone half-angle (70.3°) that provides the same area to depth relationship as the actual indenter in question. This allows the use of axial-symmetric elastic equations. Although contact solutions for pyramidal indenters have been reported in the literature, the conversion to an equivalent axial-symmetric solution is widely used and accepted (Fischer-Cripps, 2002). It should be noted, for example, that comparison with experimental results in the form of load–displacement curves on materials with known properties is very good. Namely, in the case of fused silica, the finite-element
results using axial-symmetric equations compare with the experimental results by less than 1% difference in the total penetration and the shapes of the curves are almost indistinguishable (Fischer-Cripps, 2004). Furthermore, due to the axis-symmetric nature of the geometry, only a half-sectional plane of the geometry needs to be included in the mesh design. A detailed view of the initial mesh (i.e., of the undeformed state) is shown in the animations provided as supplementary files (Electronic Annex 1). Note that a larger density of nodes was designed in the vicinity of the contact so that rapid spatial variations in stress and displacements could be accurately calculated. A very high Young’s modulus (1100 GPa), a Poisson’s ratio of 0.07 and an isotropic, pressure-independent, behaviour are assumed for the diamond indenter. Both the elastic and elasto-plastic responses (employing the conventional Tresca and the pressure-dependent Mohr–Coulomb yield criteria – with variable internal friction coefficient) were numerically calculated and the results compared with the experimental load–displacement data. Output from the simulations also included stress and displacement contour mappings of the deformed region beneath the indenter. In addition, the dynamic continuous stiffness method (CSM), up to a maximum load of 450 mN, was employed to investigate the dependence of the dynamic hardness as a function of the penetration depth during nanoindentation. In brief, this method consists in applying a small oscillation to the force signal at a relatively high frequency (45 Hz), so that the stiffness can be continuously evaluated during loading (Mukhopadhyay and Paufler, 2006). Finally, the indented regions and fracture surfaces were examined by means of optical and scanning electron microscopes (SEM).

3. Results

3.1. Structural, thermal and elastic properties

The XRD pattern recorded for the Ti-based MG is shown in Fig. 1a. The pattern consists of broad halos with absence of well-defined peaks, indicating that the rods are amorphous without detectable crystalline phases. Further evidence for the amorphous character of the sample is obtained from the DSC scans, as the one shown in Fig. 1b. The curve reveals the existence of a broad exothermic peak at low temperatures, which corresponds to the enthalpy release during structural relaxation. For the heating rate of 40 K/min, the glass transition temperature is \( T_g = 610 \) K. The crystallization enthalpies, evaluated from the areas of the first and second crystallization peaks, are \( \Delta H_1 = -38 \) J/g and \( \Delta H_2 = -21 \) J/g, respectively, in good agreement with other amorphous alloys with similar composition reported in the literature (Ma et al., 2004; Kim et al., 2004).

![Fig. 1. (a) X-ray diffraction pattern of the as-cast Ti_{40}Zr_{25}Ni_{16}Cu_{9}Be_{18} alloy, showing the absence of sharp, crystalline peaks and (b) differential scanning calorimetry curve of the Ti-based alloy, measured at a heating rate of 40 K/min. The glass transition temperature, \( T_g \), is indicated in the figure.](image-url)
The values of density and elastic constants of this alloy are presented in Table 1. It is noteworthy that the Ti-based amorphous alloys are lighter than most families of MGs. For instance, the density of the investigated Ti$_{40}$Zr$_{25}$Ni$_{8}$Cu$_{9}$Be$_{18}$ MG is 15–20% lower than for Zr-based (Wang et al., 1999) and rare-earth (Zhang et al., 2004) MGs, 30% lower than for Cu$_{47.5}$Zr$_{47.5}$Al$_{5}$, about 55% lower than for some Pd-based MGs (Wang et al., 1999; Johnson and Samwer, 2005) and more than 60% lower than for Pt-based MGs (Johnson and Samwer, 2005). Also remarkable is that the Young’s modulus displayed by this alloy is higher than for most rare-earth MGs – which exhibit $E$ around 30 GPa (Zhang et al., 2004) – Cu-based ($E \approx 85$ GPa) or Au-based ($E = 70$ GPa) MGs (Johnson and Samwer, 2005) and similar to Zr-based, Pd-based or Pt-based MGs (Zhang et al., 2004; Wang et al., 1999). Note that the ratio between the shear modulus and the bulk modulus, $\mu/B$, is higher than for Pd-based and Pt-based MGs ($\mu/B \approx 0.18$) but lower than for some (more brittle) rare earth-based MGs ($\mu/B \approx 0.43$ for Mg-based and Ce-based MGs) or oxide glasses ($\mu/B > 0.7$) (Lewandowski et al., 2006).

3.2. Mechanical characterization

3.2.1. Compressive stress–strain curve and fracture behaviour

A typical true stress–true strain curve obtained during uniaxial compression of the as-cast Ti$_{40}$Zr$_{25}$Ni$_{8}$Cu$_{9}$Be$_{18}$ alloy, carried out at room temperature at a rate of $1.8 \times 10^{-4}$ s$^{-1}$, is shown in Fig. 2. The obtained Young’s modulus is $E_{\text{Compr}} = 98$ GPa, the yield stress is $\sigma_y = 1.72$ GPa and the total strain is $e_t = 0.056$. Concerning the elastic strain, the obtained value (2.2%) is not far from the universal value reported for most MGs ($e_e = 0.026$; Johnson and Samwer, 2005). After yielding, clear serrations in the compression curve are observed, as can be seen in the inset of Fig. 2. The occurrence of inhomogeneous plastic flow indicates the formation of shear bands (Schuh et al., 2007). Some of these shear bands can be observed at the outer surface of the deformed specimen (see Fig. 3a). In these shear bands there is a sudden decrease of viscosity (Spaepen, 1977), which brings about load drops and a

<table>
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<tr>
<th>$\rho$ (g/cm$^3$)</th>
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Table 1

Summary of the elastic properties ($\nu$, $\mu$, $B$ and $E_{\text{Acoustic}}$ denote the Poisson’s coefficient, shear modulus, bulk modulus and Young’s modulus, respectively) of the as-cast Ti$_{40}$Zr$_{25}$Ni$_{8}$Cu$_{9}$Be$_{18}$ alloy evaluated from acoustic measurements. The density of this alloy, $\rho$, determined using the Archimedes’ technique, is also presented.

Fig. 2. Stress–strain curve obtained during compression of the as-cast Ti$_{40}$Zr$_{25}$Ni$_{8}$Cu$_{9}$Be$_{18}$ alloy, carried out at room temperature at a rate of $1.8 \times 10^{-4}$ s$^{-1}$. The inset shows the occurrence of serrated flow along with a progressive mechanical softening after yielding.
concomitant mechanical softening. In fact, an overall mechanical softening of the Ti-based MG takes place as deformation proceeds, as can be also seen in the inset of Fig. 2.

Fracture occurs after a plastic strain, $\varepsilon_p$, of around 0.034. The fracture angle, $\theta_C = 39.5 \pm 0.5^\circ$ (see Fig. 3a), is lower than the value obtained in most polycrystalline metallic specimens ($\theta_C = 45^\circ$) but...
is within the range of fracture angles typically reported for MGs deformed under compression (Zhang et al., 2003a,b). Some insight into the mechanisms responsible for mechanical failure can be obtained by imaging the fracture surface of the deformed specimen using SEM. The observations reveal that vein-like patterns form at the fracture surface (see Fig. 3b), suggesting that local heating accompanies shear during mechanical failure. In the investigated alloy, the width of the dimples (or the wavelength of the vein features) ranges between 5 and 10 μm. This type of morphology is frequently encountered in MGs deformed under compression, particularly when they exhibit significant plasticity (Kusy et al., 2006). Conversely, a so-called river-like pattern is usually observed at the fracture surface of brittle MGs and is associated with a much faster fracture. Actually, it has been recently claimed that the river-like fracture surface of brittle MGs is also constituted of multiple dimples, similar to those observed in vein-like morphologies, but with much smaller sizes (Xi et al., 2005), suggesting that plasticity is very short-ranged in those systems. Indeed, the size of the dimples seems to be indicative of the extent of the plastic zones in the MG, i.e., the size of regions below which it is likely to have plastic flow without premature fracture (Ashby and Greer, 2006). Hence, as expected, the dimples in the Ti$_{40}$Zr$_{25}$Ni$_{8}$Cu$_{9}$Be$_{18}$ alloy are indeed much larger than in brittle Ce-based or Mg-based MGs (Xi et al., 2005).

3.2.2. Nanoindentation

Typical load ($P$) – displacement ($h$) curves obtained by nanoindentation performed under quasi-static conditions, using maximum loads of 10 and 100 mN, are shown in Fig. 4a and b, respectively. Similar to compression tests, serrated plastic flow also occurs during depth-sensing nanoindentation experiments and manifests as pop-in events in the indentation loading curves. These serrations are less clearly seen for larger maximum applied load (e.g. 100 mN), mainly because of lack of resolution of the experimental setup (note that the pop-in events represent discontinuous displacements of the order of tens of nm or less).

The pop-in events can be also visualized if the indentation strain rate is plotted as a function of the indentation time (see Fig. 4c). The indentation strain rate is calculated as

$$\dot{e}_i = \frac{1}{h} \frac{dh}{dt},$$

where $h$ is the penetration depth into the specimen (Schuh et al., 2004; van Steenberge et al., 2007). As it typically occurs in nanoindentation experiments, $\dot{e}_i$ at the beginning of the loading segments is relatively high (in our case $\dot{e}_i > 0.2$ s$^{-1}$) and it progressively decreases as the indentation proceeds ($\dot{e}_i \approx 2 \times 10^{-3}$ s$^{-1}$ at the end of the loading segments). The indentation strain rate is, in fact, multiaxial but it can be related to the effective uniaxial strain rate by $\dot{e}_u = 0.09 \dot{e}_i$ (Schuh et al., 2004).

In turn, the estimated uniaxial strain rate during nanoindentation is proportional to the effective shear strain rate governing deformation, $\dot{\gamma}$, roughly by a factor $\sqrt{3}$, i.e. $\dot{\gamma} = 0.16 \dot{\gamma}_i$ (Schuh et al., 2004). It should be noted that for the conditions of our experiments $\dot{\gamma}$ during indentation loading segments tends to approach a value of about $3.2 \times 10^{-4}$ s$^{-1}$. For this effective shear strain rate, the deformation map developed by Schuh et al. (2004) predicts that plastic deformation during nanoindentation at room temperature should be inhomogeneous, as it is indeed observed experimentally. Also noteworthy is that from these quasistatic indentation experiments with maximum loads of 10 and 100 mN the calculated hardness is $H = 6.9$ and 6.3 GPa, respectively, whereas the Young's modulus is $E_{\text{Nanoindent}}\approx 110$ GPa, not much different than the value obtained from the compression tests.

The dependence of hardness on the maximum indentation load can be studied in detail using the continuous stiffness method (CSM). From a total of ten CSM curves measured up to 450 mN, the dynamic hardness, $H$, has been evaluated as a function of the applied load. The average $H$ (plotted in Fig. 5a as a function of the penetration depth) is found to progressively decrease as the indentation proceeds, i.e., from about 7.8 (at 1 mN) to 6.3 GPa (at 450 mN). The decrease of hardness with the penetration depth is, in fact, well-known in crystalline metals (Manika and Maniks, 2006) but not so often reported for MGs (van Steenberge et al., 2007; Manika and Maniks, 2006; Jana et al., 2004; Zhang et al., 2005). In MGs, this effect has been ascribed to the overall strain softening that occurs during plastic deformation (van Steenberge et al., 2007). A detailed discussion of this effect within the framework of the free volume model is presented in Section 4.4. Finally, it should be noted that although no clear pop-in events are observed in the CSM nanoindentation experiments, shear bands surrounding each of
the indents obtained by this method are easily observed by SEM (see Fig. 3c). Again, this is in agreement with the deformation map proposed by Schuh et al. (2004) since although these indentations are carried out using a dynamic approach, the average steady state value of the shear strain rate (for su-
Sufficiently long indentation times is found to be around $4.4 \times 10^{-3}$ s$^{-1}$ (Section 4.4), still within the inhomogeneous region of the plastic flow map. The absence of serrations in the CSM curve shown in Fig. 5a is mainly due to the lack of experimental resolution to resolve them and the fact that the presented curve is actually the average of the ten CSM curves and pop-in events are localized at different penetration depths in each of them.

Fig. 5. (a) Dependence of the dynamic hardness, $H$, on the total penetration depth, $h$, during nanoindentation measurements carried out on the as-cast Ti$_{46}$Zr$_{22}$Ni$_{8}$Cu$_{9}$Be$_{13}$ alloy using the continuous stiffness method (CSM) up to a maximum load of 450 mN; (b) dependence of $H$ on $h^{-1/2}$ and linear fit of the data (discontinuous line) from where the value of $H_0$ (strain gradient independent, i.e. conventional, hardness) can be evaluated; (c) log ($H$) – log ($h$) plot, showing a linear fit of the experimental data, from which the indentation size effect exponent, $m$, can be evaluated.
4. Discussion

4.1. Correlation between thermal/elastic properties and the overall mechanical behaviour

As stated in the introduction, based on extensive data collected for different families of MGs, some works have been reported in the literature wherein universal correlations between \( \sigma_y \) and \( T_g \) (Yang et al., 2006) and between the plastic strain and the \( \mu/B \) ratio of MGs are established (Lewandowski et al., 2005, 2006; Wang 2006). In this sense, it is noteworthy that the value of yield stress obtained for the as-cast Ti40Zr25Ni8Cu9Be18 is lower than for Co-based, Fe-based or Ni-based MGs (all of which exhibit higher \( T_g \) than Ti40Zr25Ni8Cu9Be18) whereas it is higher than for rare earth or Mg-based MGs (which exhibit a lower \( T_g \) than the alloy investigated here). In fact, by comparing the thermal energy for glass transition and the mechanical energy for shearing, a relationship between \( \sigma_y \) and \( T_g \) was recently derived (Yang et al., 2006):

\[
\sigma_y = 50 \frac{\Delta T_g}{V},
\]

where \( \Delta T_g \) is the temperature difference between \( T_g \) and room temperature and \( V \) is the molar volume of the MG. Using Eq. (2) and after calculating the molar volume for the Ti40Zr25Ni8Cu9Be18 alloy it is found that \( \sigma_{y,calc} = 1.68 \text{ GPa} \), a value which is not far from the measured one (\( \sigma_{y,expt} = 1.72 \text{ GPa} \)).

In turn, the relatively good plasticity of the investigated alloy can be understood in terms of its rather low \( \mu/B \) ratio. Namely, it is usually observed that MGs with \( \mu/B < 0.41 \) show some plasticity and tend to fracture in a ductile manner (i.e. exhibiting vein-like patterns, like the one shown in Fig. 3b (Lewandowski et al., 2005, 2006; Wang 2006). This stems from the competition between the resistance against plastic deformation, proportional to \( \mu \), and the resistance to dilatation that occurs in the region of a crack tip, which is proportional to \( B \). Since Ti40Zr25Ni8Cu9Be18 presents a low \( \mu/B \) ratio (i.e. \( \mu/B = 0.314 \)), a relatively plastic behaviour is expected and is indeed observed experimentally (Fig. 2).

4.2. Pressure-sensitive yielding

From the compression tests of the Ti-based MG rods, a fracture angle around 39.5 ± 0.5° was estimated (instead of 45°, as it would be generally the case for polycrystalline metallic specimens) – see Fig. 3a. This is an indication that yielding is influenced by the internal pressure and/or local normal stresses acting on the shear plane (Vaidyanathan et al., 2001; Anand and Su, 2005; Schuh et al., 2007). This effect is captured by the Mohr–Coulomb yield criterion, which can be expressed as follows:

\[
\tau_y = c - \beta_{M-C} \sigma_n,
\]

where \( \tau_y \) is the shear stress on the slip plane at yielding, \( c \) is the shear strength in pure shear (also termed cohesion), \( \beta_{M-C} \) denotes the internal friction coefficient of the glass and \( \sigma_n \) is the normal stress acting on the shear plane. Using a geometrical reasoning it is easy to demonstrate that the fracture angle can be related to \( \beta_{M-C} \) as follows:

\[
\beta_{M-C} = \frac{\cos 2\theta_c}{\sin 2\theta_c}.
\]

From this equation, the friction coefficient, \( \beta_{M-C} \), for the investigated Ti40Zr25Ni8Cu9Be18 alloy is estimated to range between 0.212 and 0.176, which is in agreement with values evaluated from other studies of yielding in MGs (Lund and Schuh, 2003; Lewandowski and Lowhaphandu, 2002).

Further evidence for the influence of pressure and/or normal stresses at yielding is obtained from numerical simulations of the load–displacement nanoindentation curves. As shown in Fig. 6, the indentation loading curve calculated using the elastic Hertz theory deviates significantly from the experimental one. Also a disagreement is encountered between the experimental curve and the simulated one using the elastic-perfectly plastic formalism with a pressure-independent (Tresca) yield criterion. In this case, for a given load, the corresponding calculated penetration depth is larger than the experimental one. Conversely, the overall load–displacement indentation response is well repro-
duced if the Mohr–Coulomb yield criterion with a pressure index \( \beta_{MC} = 0.194 \) (which corresponds to \( h_C = 39.5 \)) is introduced in the simulations (see Fig. 6). Hence, the simulations reveal that the indentation load at a given indentation depth increases when a pressure-sensitivity index is introduced, a result which confirms the analysis, performed by Narasimhan, based on expanding cavity model, of the stress and displacement fields in a hollow sphere subjected to internal pressure (Narasimhan, 2004).

It should be noticed that our simulation results are also in agreement with other works in the literature that have shown the influence of pressure on the indentation behaviour of Zr-based MGs, either by introducing the Mohr–Coulomb (Vaidyanathan et al., 2001) or the Drucker–Prager (Patnaik et al., 2004) yield criterion in the finite-element simulations. In fact, the Mohr–Coulomb and Drucker–Prager pressure-dependent criteria have the same similarities and differences as the Tresca and von Mises pressure-independent criteria (Keryvin, 2007). Therefore, both yield criteria can be used to properly capture the pressure-sensitivity features of MGs.

Further outcome from the numerical simulations can be obtained by plotting the displacement and stress (in this case \( \sigma_{\text{zz}} \) component) contour mappings. The contour mappings corresponding to maximum load (100 mN) are shown in Fig. 7, while the evolution of these mappings during an overall load–unload process are presented as animations in the Electronic Annex 1 of the online version of this article (both when using the Tresca and the Mohr–Coulomb yield criterion). Remarkably, both types of plots suggest that, although the maximum depth of the indenter into the specimen is larger when the Tresca criterion is employed (see also Fig. 6), the extent of the plastic zone underneath the indenter is actually larger for the simulations using the Mohr–Coulomb criterion. This result, which has been obtained by a few authors (Patnaik et al., 2004; Narasimhan, 2004), is the consequence of the combined action of hydrostatic pressure and normal stresses acting on the shear plane upon yielding. Also worth mentioning is that, as the plastic zone boundary is approached, \( \sigma_{\text{zz}} \) becomes slightly tensile (rather than compressive) and then progressively decreases again with further increase in distance. Remarkably, the peak value of this tensile strength is reduced in the Mohr–Coulomb simulations (i.e., when a pressure-sensitivity index is incorporated), as predicted by Narasimhan (2004).

4.3. Ratio between hardness and yield stress: Constraint factor

In general, the hardness evaluated from indentation tests can be used as an indicative measure of the material’s yield strength. In fact, it has been empirically observed that in isotropic materials, when the mean pressure beneath the indenter attains a constant value upon further loading (plastic regime),
the hardness is directly proportional to the yield stress obtained from compression tests, i.e., $H = C\sigma_y$, where $C$ is the so-called constraint factor (Fischer-Cripps, 2002). For rigid, sharp and frictionless indenters, ductile crystalline metals display $C$ values between 2.7 and 3. Conversely, in conventional brittle oxide glasses the constraint factor is $C_{/C25} = 1.6$. From the data in Fig. 5a it is possible to estimate the asymptotic value of $H$ that would be attained if sufficiently large loads were applied. Indeed, by analogy to the strain gradient hardening model developed to describe the ISE in crystalline metallic alloys (Nix and Gao, 1998), Lam and Chong showed that the depth dependence of $H$ in MGs could be reasonably well adjusted using the following equation (Lam and Chong, 2001):

$$H = H_0 \left(1 + \frac{h^*}{\sqrt{h}}\right),\quad (5)$$

where $H_0$ is the conventional (i.e. strain gradient independent), hardness, and $h^*$ is a material constant. A fit of our experimental data using this equation (see Fig. 5b) yields $H_0 = 5.7$ GPa. The resulting constraint factor calculated from $H_0$ is $C = 3.3$. This value is close to typical values obtained in crystalline metals ($C = 3$) and is similar to the values reported for Ni-based, Pd-based (Zhang et al., 2006) and some Zr-based MGs (Keryvin, 2007).

Several models exist in the literature, which provide a more or less complex relationship between $H$ and $\sigma_y$. One possibility is to consider the slip-line field theory (Lockett, 1963), which is in principle valid for rigid and perfectly plastic materials. From numerical simulations on various conical indenters with variable apex angle, this theory shows that

$$H = \frac{\sigma_y}{\sqrt{3}} (1.41 + 2.72\theta),\quad (6)$$

where $\theta$ is the equivalent half-apex angle of the cone-shaped indenter. Using a value $\theta = 70.3^\circ$, a constraint factor $C = 2.74$ is obtained, thus considerably smaller than the experimental one. Since MGs are

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**Fig. 7.** (a) Displacement contour underneath the indenter (with respect to the initial position of the region of material that gets first in contact with the indenter), plotted in the $r$–$z$ plane, corresponding to $P_{\text{Max}} = 100$ mN obtained via finite element simulations using the elasto-plastic Mohr–Coulomb yield criterion; (b) displacement contour beneath the indenter obtained using the conventional Tresca yield criterion; (c) circumferential stress ($\sigma_{\text{rhh}}$) contour in the $r$–$z$ plane developed beneath the indenter for $P_{\text{Max}} = 100$ mN, obtained using the Mohr–Coulomb yield criterion; and (d) circumferential stress contour analogous to (c) but using the Tresca yield criterion (with $\beta_M/C0 = 0.194$); Note that the overall mesh distribution (nodes and plates) and also the rigid indenter are displayed in the images.
prone to deform in an elastic-perfectly plastic manner, it is also possible to use the formalism developed by Dao et al. (2001) based on finite-element analysis of non strain hardening materials:

\[ H = \frac{2N}{B} \sigma_y \left[ N' + \ln \left( \frac{E_r}{\sigma_y} \right) \right], \]  

where \( N, N' \) and \( B \) are constants that depend on the type of indenter (for a Berkovich tip \( N = 6.618 \), \( N' = -0.875 \) and \( B = 15 \) (Dao et al., 2001; Zhang et al., 2006) and \( E_r \) is the reduced elastic modulus, which includes contributions from both the indenter and the sample (Fischer-Cripps, 2002). Using \( E_r = 112 \text{ GPa} \) (as determined from the quasistatic indentations) the calculated \( C \) is 2.91, hence closer to the experimental value than what is predicted by the slip-line theory.

An alternative approach is to use the expanding cavity model, developed for elastic–plastic materials, which assumes a quasi-static expansion of an internally pressurized spherical core. Once the indentation geometry is included in the formalism, it can be shown that (Johnson, 1970; Keryvin, 2007)

\[ H = \frac{4}{3} \sigma_y + \frac{2}{3} \sigma_y \ln \left( \frac{1}{3} \frac{E_r}{\sigma_y} \cot \theta \right). \]  

Approximating the Berkovich indenter as a conical indenter with equivalent half-apex angle \( \theta = 70.3^\circ \), this equation yields \( C = 2.7 \), which is again considerably lower than experimental constraint factor. To account for this discrepancy, one can try to include the pressure-sensitivity of MGs in the expanding cavity model. Indeed, in Section 4.2 it has been shown that hydrostatic pressure or normal stresses have a strong influence in the shear stress on the slip plane at yield. This is likely to cause an effect in the value of \( \sigma_y \). A modified expanding cavity model that incorporates the Drucker–Prager yield criterion has been developed by Narasimhan (Narasimhan, 2004), who showed that the indentation hardness was enhanced when larger pressure-sensitivity indexes were included in the analysis.

The yield function in the Drucker–Prager criterion can be expressed in its linear form as (Patnaik et al., 2004; Zhang et al., 2006; Keryvin, 2007; Zhang et al., 2005):

\[ \Phi(\sigma_{ij}) = \sigma_{eq} + \sigma_m \tan \alpha_{D-p} - \left( 1 - \frac{1}{3} \tan \alpha_{D-p} \right) \sigma_y = 0, \]  

where \( \sigma_m \) and \( \sigma_{eq} \) are the hydrostatic stress and the von Mises equivalent stress, respectively, \( \sigma_y \) is the yield stress in uniaxial compression and \( \alpha_{D-p} \) is the pressure sensitivity index. It should be noted that the cohesion and friction coefficients from the Mohr–Coulomb criterion can be related to the Drucker–Prager pressure sensitivity index as follows (ABACUS/Standard, Theory Manual. Hibbit Karlsson and Sorenson Inc., RI, 1996):

\[ \tan \alpha_{D-p} = \frac{\sqrt{3} \sin \left[ \tan^{-1} (\beta_{M-C}) \right]}{\sqrt{1 + \frac{1}{3} \sin^2 \left[ \tan^{-1} (\beta_{M-C}) \right]}} \]  

\[ \frac{(1 - \frac{1}{3} \tan \alpha_{D-p}) \sigma_y}{C} = \frac{\sqrt{3} \cos \left[ \tan^{-1} (\beta_{M-C}) \right]}{\sqrt{1 + \frac{1}{3} \sin^2 \left[ \tan^{-1} (\beta_{M-C}) \right]}}. \]

Hence, according to Eq. (10), \( \beta_{M-C} = 0.194 \) corresponds to, approximately, \( \alpha_{D-p} = 18.4^\circ \).

Assuming that the indentation hardness \( H \) is equal to the stress component \( \sigma_{zz} \) it can be shown that (Zhang et al., 2006; Narasimhan, 2004)

\[ H = \sigma_y \left( 1 - \frac{1}{3} \tan \alpha_{D-p} \right) \left[ \left( 1 + \frac{2}{3} \tan \alpha_{D-p} \right) \frac{\zeta}{q} - 1 \right] \]  

where \( \zeta \) is the ratio between the plastic zone radius and the contact radius and \( q \) is defined as

\[ q = \frac{\tan \alpha_{D-p}}{1 + (2/3) \tan \alpha_{D-p}}. \]

The value of \( \zeta \) can be determined, using Johnson’s expanding cavity model, as follows (Johnson, 1970):
Using the values of $E$, $\nu$ and $\sigma_{D-p}$ of the currently investigated Ti–Zr–Ni–Cu–Be alloy, this modified expanding cavity model predicts $C = 3.1$, which is now in better agreement with the experimental value.

Finally, it is interesting to note that, from the Mohr–Coulomb yield criterion (Eq. (3)), using simple geometrical reasoning (Vaidyanathan et al., 2001) and bearing in mind that $H = C\sigma_y$, the shear yield stress can be expressed as

$$
\tau_y = \frac{H}{C} \sin \theta_c \cos \theta_c - \beta_{M-C} \frac{H}{C} \sin^2 \theta_c.
$$

(15)

With the experimental constraint factor, $C = 3.3$, and using the values estimated for $\beta_{M-C}$ and $\theta_c$, Eq. (15) yields $H \approx 8\tau_y$ in our case. Note that this value of $H$ is higher than what would be predicted by the pressure-independent Von Mises ($H = \sqrt{3}C\tau_y$) or Tresca ($H = 2C\tau_y$) yield criteria. This result could be anticipated from the finite-element simulations since a smaller penetration depth (i.e., higher hardness) is obtained when calculations are performed including the Mohr–Coulomb instead of a pressure-insensitive yield criterion (see Fig. 6).

4.4. Mechanical softening and indentation size effect: Free volume considerations

The nanoindentation experiments, both in quasistatic (Fig. 4) and dynamic (Fig. 5) regimes, show that $H$ decreases as the indentation load is increased. In spite of the lack of dislocations in MGs, the ISE has been occasionally reported in these materials (van Steenberge et al., 2007; Manika and Maniks, 2006; Jana et al., 2004; Zhang et al., 2005). It is known that flow events in MGs are accompanied by dilatation, i.e., creation of free volume (Spaepen, 1977). This mechanism results in strain softening during plastic deformation (as it is also evidenced in the compression tests Fig. 2) and, hence, it is likely to play a crucial role in the ISE. The ISE can be quantified using a power law of the type

$$
H = \beta \exp (m \gamma),
$$

(14)

Using the values of $E$, $m$, and $\beta$ estimated for the Ti–Zr–Ni–Cu–Be alloy, this modified expanding cavity model predicts $C = 3.1$, which is now in better agreement with the experimental value.

Here $\Omega$ is the atomic volume (approximately $1.5 \times 10^{-29}$ m$^3$ in our case), $\nu_0$ is the local strain of a flow event, $\nu_0$ is the volume of a locally sheared region, $k_B$ is the Boltzmann constant, $\tau$ is the shear stress, $k_f = k_f_0 \exp \left(\frac{\Delta F}{k_B T}\right)$ is a temperature-dependent rate constant of plastic flow (in which $k_f_0$ is proportional to the Debye frequency and $\Delta F$ is the Helmholtz free energy required to operate a shear flow) and $\Delta F$ is the volume fraction of flow units. The hyperbolic function results from subtracting the backward flux due to thermal fluctuations from the net forward flux of atoms in the direction of the stress. This equation was originally derived for high temperature viscous flow where shear transformation zones are rather spherical and uncorrelated (homogeneous flow). However, the main change when plastic flow becomes inhomogeneous is that the value of $\Delta F$ changes, from being close to 1 in homogeneous flow to a lower value in low-temperature inhomogeneous flow (Spaepen, 1977).
In Section 4.3 it has been shown that for the Ti-based MG hardness is proportional to the shear stress by $H = 8 \sigma$. Then Eq. (17) can be rewritten to

$$H = \frac{16k_BT}{\epsilon_0 \nu_0} \sinh^{-1} \left( \frac{i\omega}{2\epsilon_0 \nu_0 \Delta \epsilon k_f} \exp \left( \frac{\Delta F_0}{k_BT} \right) \right).$$

(18)

The inverse hyperbolic sine function can be simplified using that $\sinh^{-1}(y) = \ln(y + \sqrt{y^2 + 1}) \approx \ln(2y)$ for $y \gg 1$. Filling in $k \approx 10^{-2} \text{s}^{-1}$ (as obtained experimentally), and representative orders of magnitude for $\frac{\Delta F_0}{\epsilon_0 \nu_0} \approx 0.1$, $\Delta f \approx 0.8$, $\epsilon_f \approx 10^{-8}$, $\exp(\frac{\Delta F_0}{k_BT}) \approx 10^{25}$ and $k_f \approx 10^{24} \text{s}^{-1}$ (Schuh et al., 2004; de Hey et al., 1998; van Aken et al., 2000; Daniel et al., 2002), this simplification is found to be valid and it leads to the following expression for $H$

$$H = \frac{16k_BT}{\epsilon_0 \nu_0} \left( \frac{\Delta F_0}{k_BT} + \ln \left( \frac{i\omega}{\epsilon_0 \nu_0 \Delta \epsilon k_f} \right) - \ln(c_f) \right).$$

(19)

Eq. (19) predicts that for a given strain rate the hardness will decrease with increasing free volume and flow defect concentration. In other words, accumulation of free volume brings about a mechanical softening of the metallic glass.

If one assumes that each flow event, on average produces a certain amount of free volume, i.e., $dx = a_x d\epsilon$, where $a_x$ is the proportionality factor which a priori can be temperature dependent (van Aken et al., 2000), then a free volume production term, $P$, can be readily obtained

$$\left( \frac{dc_f}{dt} \right)_{def} = P = a_x \epsilon_c \ln^2 c_f.$$  

(20)

During the indentation process, the change in free volume in the specimen may be approximated by (Heggen et al., 2005)

$$\frac{dc_f}{dt} = -k_r c_f (c_f - c_{f,eq}) + a_x \epsilon_c \ln^2 c_f \approx a_x \epsilon_c \ln^2 c_f,$$

(21)

where $k_r$ is a temperature-dependent rate constant for structural relaxation and $c_{f,eq}$ is the equilibrium flow defect concentration. Neglecting the first term implies that the production term $P = a_x \epsilon_c \ln^2 c_f$ is the dominant factor in the kinetics of structural relaxation at temperatures far below $T_E$. This is plausible since the value of $k_r$ decreases very rapidly with decreasing temperature. Furthermore, it is believed that the duration of the local temperature rise associated with shear band formation is very short compared with the overall time scale of the nanoindentation experiment (Lewandowski and Greer, 2006).

Fig. 4c shows that, for a given $h$, the strain rate is higher for 100 mN than for 10 mN. According to Eq. (21), this means that, at a certain indentation depth, the production of free volume is more pronounced for larger maximum applied loads. As a result, a lower $H$ will be obtained for indentations performed up to higher $P_{\text{Max}}$ (van Steenberge et al., 2007).

Combining Eqs. (1) and (21), the change in free volume as a function of indentation depth can be expressed as

$$\ln(c_f) = \left[ \frac{1}{\ln(c_{f,ini})} - a_i \ln \left( \frac{h}{h_{ini}} \right) \right]^{-1},$$

(22)

where $c_{f,ini}$ is the concentration of defects present in the material before deformation and $h_{ini}$ the initial indentation depth.

Since $H$ is continuously measured in CSM experiments, these types of curves are very suitable to investigate the ISE. In fact, the obtained data can be used to estimate the amount of free volume locally generated in the metallic glass during the indentation test. It turns out that the shear strain rate in CSM experiments is roughly constant ($\dot{\gamma} = 4.5 \times 10^{-3} \text{s}^{-1}$) in the depth range between 0.2 and 2 $\mu$m (see Fig. 8a). Bearing in mind that the pressure-sensitivity in this alloy results in $H \approx 8\tau_p$ (see Section 4.3), it is possible to use Eq. (17) to evaluate the change in $c_f$ that is required to cause the softening (and concomitant ISE) observed during the course of the CSM indentation experiments. The depth...
dependence of \( 2D \text{fcf} \text{ kf} (\text{e}_0 \text{v}_0) \), calculated from Eq. (17) using the estimated values of \( \dot{\gamma}, \text{e}_0 \text{v}_0 \) and \( \tau \) is shown in Fig. 8b. Since the degree of inhomogeneity in plastic flow of MGs depends on the strain rate (Schuh et al., 2004, 2007) and \( \dot{\gamma} \) is rather constant once the steady state is achieved (i.e., for \( 0.1 \text{ \mu m} < h < 2 \text{ \mu m} \)), it is likely that \( \Delta f \) does not vary significantly within this penetration depth range. Analogously, \( (\text{e}_0 \text{v}_0) \) and \( k_f \) should remain essentially constant during the steady state of CSM experi-

Fig. 8. (a) Dependence of (a) the shear strain rate, \( \dot{\gamma} \), and (b) \( 2D \text{fcf} \text{ kf} (\text{e}_0 \text{v}_0) \) (see definition in the text) on the penetration depth during the continuous stiffness mode (CSM) indentation experiments. Shown in (c) is the dependence of the measured values hardness, \( H \), on the penetration depth, \( h \). The line in (c) is a fit of the experimental data using Eqs. (19) and (22) (see text).
ments. Then Fig. 8b indicates that $c_{f(h=2 \, \mu m)} \approx 9 \cdot c_{f(h=0.1 \, \mu m)}$. Taking characteristic values of reduced free volume frozen during the as-cast procedure, $\langle \gamma \rangle / \gamma^* \approx 0.05$ (Gao et al., 2007; Flores and Dauskardt, 2001), such an increase in $c_f$ is equivalent to an increase of reduced free volume of around 10%. Interestingly, this value is of the same order of magnitude as the free volume increase ($\approx 4.4\%$) reported for a Zr–Cu–Ni–Al–Nb amorphous alloy subjected to cold rolling to a thickness reduction of 32% (Kanungo et al., 2004).

Furthermore, substituting $\ln(c_f)$ in Eq. (19) by its expression in Eq. (22) results in a relationship between $H$ and the indentation depth $h$ that can be used to fit the experimental variation of hardness with the penetration depth. Using the measured values of $\dot{\varepsilon}$ and $\tau$ and plausible values for $\frac{\partial f}{\partial \Omega}$, $\Delta f$, $\exp \left( \frac{\Delta f}{s \varepsilon_0 \ell} \right)$ and $k_{f0}$ from the literature (Argon, 1979; Schuh et al., 2004; van Aken et al., 2000; Daniel et al., 2002) – see Table 2 – the experimental variation of $H$ vs. $h$ can be fitted with accuracy, as it is shown in Fig. 8c. As a result of the fit, the obtained initial penetration is $h_{ini} = 8$ nm, the amount of reduced free volume at the beginning of the indentation tests is $\langle \gamma \rangle / \gamma^* = -(\ln (c_{f,ini}))^{-1} \approx 0.055$ and $a_\kappa = 0.006$. It should be noted that varying the value of $\Delta f$ within a reasonable range, e.g. between 0.5 and 1, also allows proper fitting of the experimental data and does not result in significant variations in the fitted values of $c_{f,ini}$, $\gamma^*$ and $a_\kappa$. The fitted value for $h_{ini}$ is reasonable since in the first nanometers of indentation the response of a flat specimen under an indenter is fully elastic. In turn, the obtained initial amount of reduced free volume is also in good agreement with the estimations made on other families of as-cast MGs (Gao et al., 2007; Flores and Dauskardt, 2001). Finally, it is worth mentioning that, based on Spaepen’s original model for the plastic flow of MGs (Spaepen, 1977), the creation of free volume for deformations under high stresses can be expressed as

$$
\left( \frac{dv_f}{dt} \right)_{creation} = \frac{\gamma \nu^*}{\nu_f} \frac{k_B T}{S} \frac{\Omega}{\varepsilon_0 v_0} \dot{\varepsilon}.
$$

By combining Eqs. (20) and (23) it is possible to correlate $a_\kappa$ with the stiffness of the MG, $S$, as follows:

$$
a_\kappa \approx \frac{k_B T}{S} \frac{\Omega}{\varepsilon_0 v_0}. \quad (24)
$$

Using a value for $S = \frac{1}{2} \mu 1.5 \times 10^{-12}$ equal to 48 GPa (as calculated from the elastic constants reported in Table 1) and considering that $\gamma \nu^* \approx 0.8 \Omega$ (Spaepen, 1977) a value for $a_\kappa$ around 0.008 is obtained, which is in rather good agreement with fitted value for this parameter obtained from the indentation data.

It should be noted that our analysis is, in fact, representative of the average behaviour of the system. The local strain rate within shear bands is much larger than in the surrounding matrix (Schuh et al., 2007); therefore only an average shear strain rate is evaluated from the CSM curves. Furthermore, a slight reduction of $\Delta F_0$ may be expected in the previously deformed regions beneath the indenter both because of the local temperature increase within shear bands and the fact that consecutive activation of flow events requires each time a lower energy due to the presence of local strain fields and the progressive creation of free volume. In this sense, it is possible that the estimated deformation-induced average excess free volume evaluated from our analysis could be, to a certain

### Table 2

Parameters used to fit the experimentally observed variation of hardness with the penetration depth (Fig. 8c). Some of the parameters have been calculated from the experimental data while others (as indicated) have been taken from the literature. The fitted values for $h_{ini}$, $-(\ln (c_{f,ini}))^{-1}$ and $a_\kappa$ are also given in the table.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\dot{\varepsilon}(h)$</td>
<td>$1.5 \times 10^{-29}$ m$^3$</td>
<td>Calculated</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>$1.5 \times 10^{-29}$ m$^3$</td>
<td>Calculated</td>
</tr>
<tr>
<td>$\varepsilon_0 v_0$</td>
<td>2</td>
<td>van Aken et al. (2000)</td>
</tr>
<tr>
<td>$\Delta f$</td>
<td>0.8</td>
<td>Argon (1979)</td>
</tr>
<tr>
<td>$\Delta F_0$</td>
<td>1.5 eV</td>
<td>Argon (1979) and Schuh et al. (2007)</td>
</tr>
<tr>
<td>$k_{f0}$</td>
<td>$10^{24}$ s$^{-1}$</td>
<td>Daniel et al. (2002)</td>
</tr>
<tr>
<td>$\tau(h)$</td>
<td>$H(h)/8$</td>
<td>Calculated</td>
</tr>
<tr>
<td>$h_{ini}$</td>
<td>8 nm</td>
<td>Fitted</td>
</tr>
<tr>
<td>$-(\ln (c_{f,ini}))^{-1}$</td>
<td>0.055</td>
<td>Fitted</td>
</tr>
<tr>
<td>$a_\kappa$</td>
<td>0.006</td>
<td>Fitted</td>
</tr>
</tbody>
</table>
extent, overestimated and should be rather regarded as an upper limit. Despite these shortcomings, the presented interpretation of the ISE in MGs is derived here for the first time and it demonstrates that the free volume concept can give a good estimate of the ISE in MGs. More complex models may be elaborated in the future to incorporate other effects, such as an eventual strain rate sensitivity or plastic anisotropy induced by deformation.

5. Conclusions

The mechanical properties of an amorphous Ti_{40}Zr_{25}Ni_{10}Cu_{9}Be_{18} alloy have been systematically investigated by means of two complementary techniques: macroscopic compression tests and depth-sensing nanoindentation. Our study contributes to shed light on some of the fundamental issues regarding yielding and plastic deformation of metallic glasses. The main results from our work can be summarized as follows:

1. The relatively high compressive yield stress and reasonable plasticity of the investigated alloy correlate well with its glass transition temperature and the rather low ratio between the shear and bulk elastic moduli.

2. As a result of the significant plasticity, the fracture surface exhibits vein-like pattern morphology. From the relatively large size of the dimples it can be suggested that premature fracture may be circumvented in specimens with sizes smaller than 5–10 \( \mu \text{m} \). Hence, this alloy may have potential applications in sub-\( \mu \text{m} \) micro-/nano-electro-mechanical systems (MEMS/NEMS).

3. Yielding is influenced by normal stresses acting on the shear plane. This causes the fracture angle to deviate towards values smaller than 45°. Consequently, the pressure-insensitive von Mises or Tresca yield criteria are found to be inadequate to describe the onset of plasticity. Alternatively, other criteria, which take normal stresses and pressure effects into account (e.g., the Mohr–Coulomb or Drucker–Prager), are invoked to properly describe the mechanical behaviour of the glass.

4. Finite element simulations of nanoindentation curves reveal that the extent of the plastic zone underneath the indenter is larger when the Mohr–Coulomb criterion is used instead of the pressure-independent Tresca criterion.

5. The effect of internal pressure is also taken into account to obtain a constitutive picture of the deformation behaviour of the system based on compression tests and nanoindentation. Namely, the ratio between hardness and yield stress (the so-called constraint factor, \( C \)) is larger than 3 for the investigated alloy. However, with the corresponding material parameters, conventional models of contact mechanics describing nanoindentation (e.g., the slip-line field theory or the expanding cavity model) all predict \( C < 3 \). Only when an internal friction index is incorporated in the formalism \( C \) is actually enhanced to approach the experimental value.

6. Plastic flow in this alloy is inhomogeneous, as it corresponds to the range of strain rates employed in this study. Moreover, shear band activity is accompanied by a local mechanical softening, which brings about sudden load drops in the compression tests and pop-in events in the indentation loading curves.

7. An overall mechanical softening is observed during the course of the nanoindentation experiments, which causes a progressive reduction of hardness as deformation proceeds, i.e., an indentation size effect. This indentation size effect is modeled, in a semi-quantitative manner, using the free volume concept. An average increase of free volume of 10% (or less) is estimated within the indentation plastic zone in experiments performed using the continuous stiffness method.

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Appendix A. Supplementary data

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