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Gaining sight after being blind: A tribute to Jing Zhu

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ABSTRACT

This contribution to the Festschrift for Professor Jing Zhu concentrates on *in-situ* electron microscopy, a topic which is key in her scientific work. In particular this paper delineates the possibilities of utilizing *in-situ* transmission electron microscopy to unravel size effects in the structure-property relationship. We have focused on *in-situ* compression, tension and cyclic fatigue experiments on non-crystalline metallic materials, also called metallic glasses (MG). *In-situ* quantitative compression tests revealed intrinsic and strong size effects of taper-free metallic glass nanopillars inside a transmission electron microscope (TEM) on different MG compositions. The deformation is defect-nucleation-controlled in larger pillars but becomes propagation-controlled in smaller pillars. A unique increase in strength and strain hardening was observed for smaller sized specimens in tension which is different compared to compression experiments with the same MG compositions. Under cyclic loading a very interesting new phenomenon was observed of increasing deformability depending on the number of cycles and size. The increase in deformability increases with increasing diameter whereas the number of cycles to reach half of the peak stress is decreasing with increasing diameter. The proposed experimental technique of loading and unloading cycles opens a new route to increase the ductility of metallic glasses.

1. Introduction

Since electron microscopy lies in the focal point of the scientific work of Jing Zhu, one of the international leaders at Tsinghua University, for this special issue it is decided to concentrate on *in-situ* transmission electron microscopy observations of the structure-property relationship of amorphous materials. As it goes without saying, microscopy in the field of materials science is devoted to linking microstructural observations to properties. However, the actual linkage between the microstructure studied by microscopy on one hand and the physical property of a material on the other hand is almost elusive. The reason is that various physical properties are determined by the collective behavior of moving defects rather than by the behavior of a single stationary defect. For instance, there exists a vast but also bewildering amount of electron microscopy analyses concerned with post-mortem observation of *ex-situ* deformed materials, which try to link observed patterns of defects to the mechanical property. However, in spite of the enormous efforts which have been put in both theoretical and experimental work since the theoretical concept of a crystal dislocation was introduced in 1934, a clear physical picture that can

predict even one simple stress-strain curve based on these microscopy observations is still lacking. In fact there does not exist an easy and unique back transformation from microscopy observations to properties.

There are at least three reasons which hamper a straightforward correlation between microscopic structural information and materials properties, both from fundamental and practical viewpoints. First, in materials we are facing non-equilibrium effects. Defects determining the physical performance are usually not in thermodynamic equilibrium and their behavior is very much non-linear. Non-linearity and non-equilibrium are both tough problems in materials physics and in fact unsolved from a physics viewpoint. Second, metrological considerations of quantitative electron microscopy of materials pose very critical questions to the statistical significance of the electron microscopy observations. In particular, in situations where there is only a small volume fraction of defects present or where there is a very inhomogeneous distribution, statistical sampling may be a serious problem. Third, even when statistical sampling is adequate, still the physical property might be determined, not by its mean value, say grain size and grain size distribution, but by the extremes, e.g. in a

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nanostructured metallic material with many nano-grains but still having one singular big grain, macroscopic yielding is determined by the local plasticity in that largest grain and not by the many nano-sized grains present! For the development of flow stress as a function of strain the situation might be completely different depending on the work-hardening rate. Therefore statistical averaging of grain-size distributions is not the right thing to do when explaining the onset of plasticity in metallic systems. As a consequence, my advise is: do not only magnify to the highest point-point resolution in TEM – which is quite popular these days – but also *de-magnify* so as to clarify and not falsify the essentials in the structure-property relationship.

Nevertheless, the situation is not hopeless because *in-situ* rather than post-mortem observations are currently feasible. A very nice example supporting my point of view was published by Jing Zhu and her collaborators, including my excellent former post-doc Chang Qiang Chen who was educated at Tsinghua. It was shown that the electric-field-induced mechanical resonance of an individual nanotube or nanowire can be explored as a versatile technique for *in-situ* measurement of Young's modulus of the nanotube/nanowire in electron microscopes [1–3]. In particular the size dependence of the Young's modulus in <0001> oriented ZnO nanowires was experimentally revealed and a core-shell composite nanowire model was proposed as explanation. These are typical experiments by which microscopy not only confirms the fairly widely used driving argument '*seeing is believing*' but rather goes a step further of '*gaining sight after being blind*', i.e. providing physical explanations and in-sights by turning microscopy from a 'peep-show' and show-box into a measuring tool for unraveling the structure-property relationship. Therefore the latter expression was chosen as an appropriate working title of this contribution for Jing Zhu which the author adopted more or less from his former supervisor, colleague and good fellow friend in microscopy Gareth Thomas (1932–2014) UC-Berkeley and NCEM, USA [4,5].

Besides this example by Jing Zhu et al. to obtain the correct Young's modulus in the elastic regime via electromechanical resonances through *in-situ* microscopy, obviously, also the dynamics of moving defects due to plasticity could be more relevant to understand the mechanical response of materials than the static structure [6]. Direct observation of dislocation-grain boundary interactions during indentation has become possible through *in-situ* pico-indentation in a transmission electron microscope, results obtained with this technique are presented in [7–10] pertaining to the study of deformation mechanisms in metals and alloys with grain sizes of the order of a few hundred nanometers.

The observation of the mechanical response introduced by conventional nanoindentation has been restricted to post-mortem studies of the deformed material, mostly by atomic force microscopy, indenter-based scanning probe microscopy, or scanning and transmission electron microscopy. This post-mortem approach entails some significant limitations to the analysis of the deformation mechanisms. Most importantly, it does not allow for direct observation of the microstructure during indentation and thus lacks the possibility to monitor the precise nature of the deformation events and the evolution of defect structures as the indentation proceeds. Moreover, the deformed microstructure observed after indentation is generally different from that of the material under load, due to recovery during and after unloading. In the case of post-mortem analysis by transmission electron microscopy, the preparation of the indented surface in the form of a thin foil often leads to mechanical damage to the specimen or relaxation of the stored deformation due to the proximity of free surfaces, thereby further obscuring the indentation-induced deformation.

The present contribution avoids all these intrinsic problems of statistical sampling of the 'representative volume of defects', 'inhomogeneities' and 'statistics of the extremes' by concentrating on *in-situ* TEM studies of self-averaging systems, i.e. on amorphous materials which are also called 'metallic glasses' (MG).

2. Amorphous materials and metallic glasses

As oxymoronic as it sounds, metallic glasses exist and, as materials, pose remarkable properties, since in their tightly-packed glassy structure, the displacement of atoms at room temperature is obstructed by the potential energy barrier. A metallic glass also absorbs less energy upon stress-induced deformation compared with crystals, and with no lattice dislocations present, their mechanical properties combine to produce an exceptionally strong material.

Metallic glasses are currently the focus of extensive studies in view of their potential applications [11,12]. Tremendous efforts have been dedicated to characterize, understand, and possibly control the atomic and micro-scale mechanisms underlying the unique properties of MGs, e.g. the very high yield strength but near zero plasticity at room temperature. One of the explanations of the deformation behavior in MGs under applied stresses is related to the movements of the shear transformation zones (STZs). According to this hypothesis, the basic carriers of plasticity in MGs are STZs, each of which is a local atomic region containing tens to hundreds of atoms and embedded within an elastic medium [13–15]. However, the dynamics and correlation of the local flow units, and their spatiotemporal evolution into macroscopic shear bands (SBs) are still under drastic and sometimes emotional debates. Whether STZs exist or how they manifest in deformation still remains unsettled. In our view the dynamical, i.e. rather stochastic and collective interactions among defects, essentially characterized by density fluctuations that produce local stress fluctuations in a MG, are responsible for intrinsic versus extrinsic size effects.

So far, size effects on mechanical properties have been widely investigated in different kinds of materials, including polycrystalline and single-crystalline metals, polymers and concretes. Size effects in plasticity of crystalline metals have been investigated to a large extent, at least for pure metallic systems and size-dependent strengths have been reported in nanoindentation, micro-torsion, micro-bending, and micro-compression experiments, and were attributed to different phenomena, e.g. hardening by geometrically necessary dislocations, dislocation interactions with surfaces, and dislocation starvation. For a recent review reference is made to [16].

Size effects in the mechanical behavior of metallic glasses have received less attention but it is gaining importance because of applications of thin (protecting) layers in electronic devices and products [11,17]. At low homologous temperatures relative to the glass-transition temperature plastic deformation in MGs occurs inhomogeneously with the strain being localized within a small number of discrete shear bands [18]. Strain softening is believed to be the reason for this localization. Although the strain in the shear bands can be quite high, the overall ductility of bulk MGs is low, and MGs typically fracture by massive shear-off along the shear bands. Strain softening is not unique and not limited to metallic glasses. In general, if strain softening accompanies the generation of the initial shear bands, one would expect a substantial machine spring-back when MGs are tested, similar to that observed in whisker tests. But there is a substantial difference between crystalline and amorphous materials: work hardening in crystalline metals eventually takes over after a possible initial period of strain softening, whereas in MGs work hardening typically does not develop. Consequently, it raises the following question: is there a transition from unstable shear band propagation to homogeneous yet ductile deformation with decreasing specimen size of MGs [19–25]?

So far a major drawback of experimental research on size effects in amorphous and crystalline pillars is that almost all *ex-situ* deformation followed by post-mortem microscopy does not allow a direct observation of the microstructure during mechanical loading and thus lacks the possibility to monitor deformation events and the evolution of microstructures as the deformation proceeds [10]. A favorable exception is the early work by Ma and collaborators [26]. In addition, the microstructure observed after deformation is generally different from that of the material under loading, due to recovery during and after unloading

[27].

Furthermore, the appearance of a tapering angle due to the focused ion beam (FIB) milling procedure may have a large influence on the deformation behavior and stress/strength measurements of nanopillars under compression test. It is notable that tapering is inevitable for FIB milled pillars with diameters down to less than 300 nm. The tapering might be critical for MG pillars as shear band initiation mostly occur close to the corner of the top surface where the pillar has the least cross-sectional area due to tapering effects. This stress concentration is further intensified by possible frictional forces between the top surface of the pillar and a flat punch indenter. This affects not only SB nucleation but also makes stress analysis rather difficult [28]. This is especially so for the *ex-situ* experiments when the events in the stress–strain curve cannot be correlated to particular individual SBs through *in-situ* microscopy observations.

In the past we investigated the size dependence of the deformation behaviors of various amorphous metallic glasses: $\text{Cu}_{47}\text{Ti}_{33}\text{Zr}_{11}\text{Ni}_6\text{Sn}_2\text{Si}_1$, $\text{Zr}_{50}\text{Ti}_{16.5}\text{Cu}_{15}\text{Ni}_{18.5}$, $\text{Zr}_{61.8}\text{Cu}_{18}\text{Ni}_{10.2}\text{Al}_{10}$, and $\text{Al}_{86}\text{Ni}_9\text{Y}_5$. Tapered and taper-free MG nanopillars with diameters down to sub-100 nm are made and tested quantitatively *in-situ* inside a transmission electron microscope [16,24]. The major consideration of compositional variation was the change of bulk modulus and Poisson's ratio that may affect the deformation mode and ductility of MGs at the nanoscale. Lewandowski et al. [29] suggested that the ratio between the shear modulus and bulk modulus is a relevant parameter to categorize intrinsic brittle behavior of bulk metallic glasses, i.e. the higher the ratio or the smaller Poisson's ratio the more brittle the material may behave. This was taken as a starting point in our choice concerning materials addressing the questions whether also at smaller dimensions the ductile-to-brittle transition will depend on that ratio and whether a size effect does exist. In this contribution some striking new results on the tension–compression performance as a function of the MG composition are presented which have not been observed before.

It should be realized that the term size-effect is used to distinguish all the cases when materials change the properties by reducing the dimensions of the specimen. Nowadays, material technologies emphasize miniaturization. Nano-system fabrication and developments are very interesting and challenging fields of scientific research bridging microelectronic, physics, chemistry, mechanics. Recent progresses have allowed highly integrated and high-performance micro- and nano-electromechanical devices and the further development of such systems depends critically on the choice of appropriate materials.

In this regard, properties of metallic glasses at nanoscale are providing a significant and unique potential (see [12]). Understanding mechanical properties of MGs at nanoscale is therefore a high impact issue of material research. The investigations on different compositions in tension and in compression should be addressed in particular. With respect to the size it is interesting also to reveal the influence of initial MG structure and temperature treatments on the transition thresholds. In summary, potential applications of this research on metallic glasses as we will show, are feasible and it offers a bright prospective for future work in materials science.

3. *In-situ* compression, tension and cyclic tests in TEM

In-situ picondentation inside a TEM requires a special specimen stage designed to move an indenter towards an electron-transparent specimen on the optic axis of the microscope. The first indentation holder was developed in the late 1990s by Wall and Dahmen [30,31] for a high-voltage microscope at the National Center for Electron Microscopy (NCEM) in Berkeley, California. In the following years, several other stages were constructed at NCEM with improvements made to the control of the indenter movement but without a transducer dedicated to measuring load and displacement [32–34].

In the work described in this paper, a holder developed by Hysitron (Hysitron, Inc., Minneapolis, MN) in collaboration with NCEM for a

JEOL microscope was used. The latter holder is commonly referred to as depth-sensing indentation. A piezoelectric tube allows high-precision movement of the tip of the indenter in three dimensions, the indentation direction being perpendicular to the electron beam. The indenter itself can be a Berkovich-type diamond tip, which is boron-doped in order to be electrically conductive in the TEM or a flat punch. The goniometer of the TEM provides a single tilt axis, so that suitable diffraction conditions can be set up prior to indentation. The indenter tip itself is mounted to a miniature transducer coupled to the piezo tube. Here, the piezo tube functions only as a fine positioner and is held static during indentation to avoid the previously described complications. By capitalizing upon its electrostatic actuation and capacitive displacement sensing capabilities, the transducer is able to deliver calibrated loads in excess of 1300 μN and measured displacements up to 5000 nm. By adopting a parallel loading configuration and a very stiff load frame, the displacement signal generated by the transducer is a direct measure of the penetration depth. This displacement signal is inputted into a digital feedback system operating at a feedback loop rate of several tens of kHz. The primary purpose of the feedback system is to control the electrostatic actuation voltage to the transducer with the aid of a proportional–integral–derivative (PID) algorithm to meet the displacement demand, which also provides the benefit of damping the transducer in the high vacuum environment of the TEM, resulting in a settling time reduction by a factor of ~ 5000 . The indentation can be programmed to follow a predefined displacement profile as a function of time.

As the size of the “target” decreases, the inability to actually see what occurs during testing can be troublesome. The geometry of the specimens used for *in-situ* picondentation has to comply with two basic requirements: (i) an electron-transparent area of the specimen must be accessible to the indenter in a direction perpendicular to the electron beam, and (ii) this area of the specimen must be rigid enough to support indentation without bending or breaking. With the so-called picondent TEM holder equipped on our JEOL 2010F TEM it is possible to acquire quantitative mechanical data while simultaneously monitoring the microstructural evolution of the sample with the TEM.

In-situ TEM compression experiments on the amorphous pillars were performed using the picondent with a diamond flat punch either of 1 or 2 μm in diameter. The indenter should have unique features, which are particularly critical to the present study. The miniature capacitive load–displacement transducer permits high resolution load and displacement measurements (resolution of ~ 0.3 μN in load, ~ 1 nm in displacement). In addition, a rapid instrument response and data acquisition rate (as said before, the controller is operating in a continuous loop and samples data at 20 kHz) allows discrete flow events to be well-resolved. The experiments are run in two typical control modes: displacement control, which shows a great sensitivity, and load control, which has an advantage when evaluating sudden displacement jumps. The displacement and/or load rate are programmed in such a way that a nominal strain rate of $\sim 10^{-2} \text{ s}^{-1}$ is applied. Together with the high data acquisition rate, this all makes it possible to evaluate the development of a single shear band SB event in an amorphous material [21,24,35–37].

In addition to compression experiments we explored deformation in tension. Tensile experiments allow circumventing some artifacts (tapering, shear band formation due to friction). *In-situ* TEM tension experiments are performed by using the abovementioned Hysitron picondent TEM holder with an in house-made Al alloy tip sample holder and W indenter tip. We have also designed a Fe-alloy base tip sample holder but that was a bit too heavy leading sometimes to instabilities during the experiment. The Al-alloy based holder was designed and developed in order to achieve good calibration and to avoid undesirable mechanical noise during tensile experiments. Tungsten tip was designed and made first by electrochemical polishing and later on milled by Focused ion beam (FIB) to a desired shape. TEM pictures of testing in compression and tension testing are displayed in Fig. 1 (see also tensile designs made by Kiener and Minor [38] as well as Shan and

Fig. 1. (a) TEM picture of compression testing; (b) FIB milled W tensile tip and nanopillar for tensile testing (scale bar 1 μm).

co-workers [39].

On the making of these pillars for *in-situ* TEM examination, it has to be emphasized that there are at least two different artifacts known as redeposition and tapering effects that occur during FIB milling procedure by Ga ions and have an influence first on the quality and the geometry of the MG pillars and make the analysis of the experiments rather difficult. The influence of the redeposition effect on the FIB microfabrication process by conventional top FIB milling method is significant. There are several parameters such as beam current, ion beam spot size, milling speed could also key factors that determines this process. Not fully controllable portions of material can be redeposited on the walls of the sample and will form an undesirable pattern on the surface of the sample. A FIB milling artifact, already mentioned, which significantly influences the analyses of compression tests is tapering effect.

An important characteristic that has to be chosen properly is the FIB milling current [40]. The smaller the size of the desired pillar, the smaller FIB current must be used to decrease the FIB damage of the surface and the rounding of the shape of the edge. We have designed a reproducible procedure not only to make small pillars but also to find a way to calculate the cross-section of the pillars accurately. The latter is relevant for an accurate determination of the applied stress fields [41]. Fig. 2 shows the dependence of the pillar diameter on the FIB current for the metallic glass (MG) pillars of different compositions. The error bars indicate the milling error. With decreasing pillar diameter the FIB current should be decreased so as to mill better shaped pillars. On the other hand the milling time also plays an important role in the preparation. By lowering the FIB current the milling time increases. Therefore, for the best performance, it is necessary to keep the suitable time range and to use the proper FIB currents for the different pillar diameters. It should be noted that the physically controlling parameter should be the beam diameter or the aperture size rather than the FIB current and Fig. 2 is chosen because of the accuracy.

Indeed the difference in composition may also affect the details of the preparation process. In general harder (MG) materials will take longer but to reach smaller diameters a harder material is preferable, e.g. for Zr-based materials the smallest diameter was equal to 70 nm but for the Al-base MG only 120 nm was attained. This phenomenon is related to the limitations of the milling process itself. When the sizes of milled features approach tens of nanometers, the damage by Ga ions becomes more relevant. The softer the material the less accurate becomes the milling. The shape of the desired mill becomes rather out of control and not very much reproducible.

4. Cyclic deformation of metallic glasses

The main drawback of metallic glasses that hamper applications is

Fig. 2. Dependence of the pillar diameter vs. FIB current for MG pillars of different composition: (a) $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ and (b) $\text{Zr}_{61.8}\text{Cu}_{18}\text{Ni}_{10.2}\text{Al}_{10}$. The error bars indicate the error measured in TEM.

their brittleness at room temperature caused by strain localization in narrow areas called shear bands (SBs). Various attempts to enhance the deformability of MGs were focused on the development of alloy systems and compositions so as to enhance a uniform distribution of SBs [42]. A unique strains as high as 70% in compression was reported as well as an enhancement of the plasticity limit in tension, either in thin metallic glass foils even at room temperature [43,44]. Several toughening

Fig. 3. TEM video frames showing the deformation of a $\phi 552$ nm MG pillar after each of the first 5 cycles (a)–(f).

mechanisms were considered in the explanation of the experimental observations, including a high Poisson's ratio or μ/B ratio, spinodal phase separation [45], nanometer-scale heterogeneities [46], nanocrystallization within shear bands [47], extreme amounts of the free volume content [48] and sluggish atomic movement kinetics [49]. In fact toughening means here the increase in deformability. In mechanics toughness is usually measured through notched specimens, but here we use to relate toughness to the mechanical work absorbed up to failure. In the following we use deformability when referring toughness.

The influence of sample size on compressive deformation response has been studied for several amorphous alloy systems [21,23,24,50–52]. For a recent review reference is made to [16]. It was found that the yield strength is independent of sample size ranging from tens of nanometers to one micrometer but the plasticity increases as sample sizes decreases. It was observed that there exists a critical energy density above which catastrophic fracture would occur. This critical energy density depends on the composition of MG but it is independent of sample size.

MG Al-based alloy with a composition of $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ was selected for this study in comparison with conventional crystalline Al alloys. Al-based MGs exhibit much higher yield strength without loss of ductility and corrosion resistance [53]. Despite studies on μm and sub- μm scale, size effects on nanometer scale of these MGs have not been investigated in detail before. We found strong size effects with the achievement of excellent mechanical properties [54]. It is also well known that the ductility of MGs at the large scale depends strongly on the sample geometry [40] and, as a consequence, on the aspect ratio [55] ρ (height to diameter ratio), e.g. at mm-scale buckling occurs when $\rho > 5$, shear banding $2.5 < \rho < 5$, and barreling when $\rho < 2.5$.

Despite the absence of a crystallographic lattice structure these amorphous materials exhibit failure under fatigue at room temperature, with an endurance limit as low as 4% of the yield strength [56]. A question to be addressed is: what happens during cyclic deformation when down-sizing the specimen to a couple of hundred nanometers? Recently, several studies have reported on the cyclic compression of crystalline nanopillars but not so many on metallic glassy pillars inside TEM [57–59].

Milne et al. have demonstrated that compressive and cyclic loads can be applied to individual nanostructures, enabling the observation of nanoscale deformation and fatigue of Al crystalline pillars of 350 nm diameter [60]. In crystalline Al nanopillars 15% of the stress reduction was explained by the formation and re-arrangement of grains. However this effect is not expected for Al-base MG pillars, since there are no grain boundaries or dislocations present.

Here we report some new finding on $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ that was prepared by melt spinning. Ribbons of 0.3 mm in thickness were mechanically polished down to a wedge shape of around 3 μm thickness suitable for

further focused ion beam (FIB) milling. Taper-free nanopillars were cut by using an in-house developed FIB milling technique [40]. A different set of rectangular taper-free nanopillars with diameters ranging from 110 nm to 900 nm was successfully fabricated for different experiments including compression tests, aspect ratio investigations and cyclic experiments by means of a dual beam FIB/SEM microscope (Lyra, Tescan, CZ). First, a series of rectangular micro-sized beams were milled on the microwedge. Then, out of these beams, nanopillars were fabricated step by step with decreasing FIB current at different milling stages. First, a series of micro-sized beams were milled on the microwedge at 10° tilt angle of the stage with respect to the ion beam at high FIB current (~ 10 nA). Then, nanopillars were fabricated from these beams step-by-step with decreasing FIB current at different milling stages down to 1 pA.

Cyclic deformation experiments were performed in such a way that unloading was followed after each loading cycle when reaching the corresponding yield stress and subsequently one stress drop (due to shear band propagation) was registered. To ensure reproducibility of the cyclic experiments, several samples, order of 3–5, were investigated.

Typical behavior of thick $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ pillars (diameter typically larger than $\phi 300$ nm) show catastrophic failure in single cycle compression due to localized deformation in shear banding, which is the characteristic behavior of metallic glasses at macroscopic dimension. Cyclic experiments for three pillars of different diameters were executed, $\phi 552$ nm, $\phi 357$ nm, and $\phi 186$ nm. Fig. 3 displays the observations of the pillar with a diameter of $\phi 552$ nm. In Fig. 3 it looks like that the pillar is slightly bended and alignment is an issue. Therefore several experiments have to be carried out to get statistics. Alignment has been studied explicitly in [28].

By applying cyclic deformation, the ductility of the large samples ($\sim \phi 500$ nm) was significantly increased, i.e. up to $\sim 100\%$ true strain in total in 10 cycles of compression and yet without break-down (Fig. 4(a)). Moreover, both the yield- and peak stresses continuously decrease from the first cycle of compression to the successive cycles. That is to say, noticeable strain softening was observed in cyclic deformation of MG pillars. True stresses and strains were derived as based on minimum cross section as suggested by Kiener et al. [61], see also [41]. Close-up examinations indicate that strain softening occurred in each individual cycle of compression, i.e. an observable decrease of flow stress was recorded in each of the true stress–strain curves. The same phenomena, i.e. strain induced ductility and softening, were observed on thinner Al-MG pillars as shown in Fig. 4(b) and (c). The primary difference among the three pillars of different sizes is the compression cycles needed to convert them from brittle fracture to ductile failure. Thicker pillars need a larger number of deformation cycles to become ductile. As the diameter of pillars decreases to a

Fig. 4. True stress–strain curves of cyclic loading-unloading tests: (a) 10 cycles compression of $\phi 552$ nm pillar, (b) 5 cycles compression of a $\phi 357$ nm pillar and (c) 2 cycles compression of a $\phi 186$ nm pillar.

threshold value (about 300 nm for $\text{Al}_{86}\text{Ni}_{10}\text{Y}_5$ MG), thin pillars may deform in a fully ductile manner even in a single compression cycle.

Fig. 5(a) shows the dependence of the yield stress on the number of deformation cycles whereas Fig. 5(b) indicates the occurrence of softening and deformability effects in MG. For larger pillars the number of the cycles that is necessary to reach plastic flow was higher than for the

Fig. 5. (a) Yield stress versus number of the cycle. Solid line is the theoretical curve (b) number of cycles versus diameter of the pillar. The increase in deformability (here also referring to toughness) increases with increasing diameter (open squares, right side) whereas the number of cycles to reach half of the peak stress is decreasing with increasing diameter (solid squares, right side).

smaller pillars. For each pillar size there is a certain number of cycles at which a more ductile behavior is attained. In order to avoid catastrophic failure a 10% load drops of the ultimate load have been selected as a reference point for the experiments. The reduction in yield stress to 50% has been chosen as a quantitative characteristic to describe softening effects for each pillar size. The maximum value observed of the load drops for the small pillar diameters is 10%.

Since it is rather difficult to observe structural features in MG during compression, the discussion on the deformation mechanism of MGs is still under severe debate. We stick to the most commonly accepted theoretical description explaining the processes from a mechanistic viewpoint. The distribution of free volume in MGs is affected by the chemical composition and related to the glass transition temperature. When compressing MG a certain fraction of the material γ_k is activated as free volume in the k th cycle resulting in a local shear transformation zones whereas the rest of the material of concentration $1-\gamma_k$ is only elastically strained. The collective behavior of these shear transformation zones, which combines the integration of the local shears, determines the macroscopic response in elastic, viscoelastic and plastic regimes.

For a large-sized sample, there is limited influence of free surface, and volume effects will predominant the influence on the deformation behavior. But when we downsize the specimen we argue that free

surfaces become more important. Upon decreasing the size of the sample down to 100 nm, the total number of STZs decreases, assuming the same interaction of free atoms during compression as for bulk specimens. On the other hand, with decreasing sample size down to hundreds of nanometers, the distribution of the free volume density may also become rather inhomogeneous.

Fatigue failure of crystalline materials is usually related to subcritical crack growth described by Paris law [62]. Such an approach assumes that all structures contain flaws, and that cracks may initiate and propagate early in service life. Here we assume that after each unloading cycle, the stresses that were concentrated near the STZs areas are released. The structure will be changed after the first cycle and there is a lower probability that the next compression cycle will start near the former flow defect area, since that was already strengthened.

The local strengthening effect is followed by the release of the residual stresses upon unloading, i.e. resulting in softening. Here we propose that a visco-elastic model is appropriate to describe the softening. According to the Maxwell–Weichert model we assume a number of units N_k , each consisting of a spring and damping term placed in series. It follows that the relaxation modulus in response to instantaneous loading during the k th cycle can be formulated as:

$$E_Y(t) = \sum_{i=1}^{N_k} E_{Y,i} \exp\left(-\frac{E_{Y,i} t}{\eta_i}\right) = \sum_{i=1}^{N_k} E_{Y,i} \exp\left(-\frac{t}{\tau_i}\right), \quad (1)$$

where η_i is the damping coefficient determining the relaxation time τ_i :

$$\tau_i = \frac{\eta_i}{E_{Y,i}}. \quad (2)$$

The general expression for the stress as it depends on the relaxation modulus and the total stress is described by an elastic part of fraction $1 - \gamma_k$ and a visco-elastic part of fraction γ_k related to the STZ:

$$\sigma_k = (1 - \gamma_k) \sigma_k^e + \gamma_k \sigma_k^v, \quad (3)$$

where $\dot{\epsilon}$ is the strain rate and t' is an integration variable. The visco-elastic part simplifies to:

$$\sigma_k^v = \dot{\epsilon} \int_0^{t_0} E_{Y,k}(t - t') dt', \quad t_0 < t, \quad (4)$$

yielding :

$$\begin{aligned} \sigma_k^v &= \dot{\epsilon} \int_0^{t_0} \sum_{i=1}^{N_k} E_{Y,k,i} \exp\left(-\frac{t - t'}{\tau_i}\right) dt' \\ &= \dot{\epsilon} \sum_{i=1}^{N_k} E_{Y,k,i} \tau_i \exp\left(-\frac{t}{\tau_i}\right) \left(\exp\left(\frac{t_0}{\tau_i}\right) - 1 \right), \quad t_0 < t \end{aligned} \quad (5)$$

Or

$$\sigma_k^v = \dot{\epsilon} \sum_{i=1}^{N_k} \eta_i \exp\left(-\frac{E_{Y,k,i} t}{\eta_i}\right) \left(\exp\left(\frac{E_{Y,k,i} t_0}{\eta_i}\right) - 1 \right), \quad t_0 < t. \quad (6)$$

Assuming that the units of our system are equal to each other $i_1 = i_2 = \dots = i_N$ we arrive at the simplified equation of stress:

$$\sigma_k = (1 - \gamma_k) E_{Y,k} \epsilon + \gamma_k \dot{\epsilon} \eta \exp\left(-\frac{E_{Y,k} t_k}{\eta}\right) \exp\left(\frac{E_{Y,k} t_0}{\eta} - 1\right). \quad (7)$$

Taking into account that after the first cycle $t = t_0$, and the concentration of activated events at the k th cycle is γ_k , i.e. equal to N_k/N_0 , and assuming that the process of compression is continuous with respect of the time, then:

$$t = \frac{\Lambda}{s} \quad (8)$$

where Λ is the total displacement for each cycle k and s is the speed of compression. The basic description of number of defects during the cyclic deformation at larger scale can be described by

$$\gamma_k = k^\psi \left(\frac{d_k}{d_0} - 1 \right)^\psi \quad (9)$$

where the parameter ψ is found equal to 1.3 from a fit to experiment. Eq. (9) is valid only for the limited number of cycles (k). The component k^ψ includes the chemical composition dependence, where ϕ is constant determined from boundary conditions.

According to experimental fit the apparent Young's modulus E_Y also changes with the number of cycles

$$E_{Y,k} = E_Y (k^\phi)^{-1}, \quad (10)$$

with $E_Y = 57$ GPa [41]. The equation for the yield stress as a function of the number of cycles becomes:

$$\begin{aligned} \sigma_k &= \left(\frac{1 - k^\phi}{k^\phi} \right) \left(\frac{d_k}{d_0} - 1 \right)^\psi E_Y \epsilon + \dot{\epsilon} \eta k^\phi \left(\frac{d_k}{d_0} - 1 \right)^\psi \exp\left(-\frac{E_Y \Lambda}{\eta s k^\phi}\right) \exp\left(\frac{E_Y t_0}{\eta k^\phi} - 1\right). \end{aligned} \quad (11)$$

The theoretical curve of σ^k has been plotted (Fig. 5(a)) as a function of k^ϕ (with η and ψ as the basic parameters) and it is seen that the theoretical curve (black line) plotted according to this model describes the experimental decaying behavior very well. It should be noted that detailed estimates of the parameters in the modified Kelvin–Maxwell–Weichert model (with a spring representing the elastic areas of concentration $1 - \gamma_k$ and a dashpot (representing the γ_k concentration of viscoelastic STZs in parallel) can be obtained by fitting to the experimental results of the relaxation modulus. However, the point here was to get a physical explanation for the decaying behavior in Fig. 5(a) which is due to the visco-elastic part.

The central question addressed in this study is then: What actually means the *yield stress* in a metallic glass upon repeated loading and unloading? Is this related to the stress level at which shear bands are formed and get reactivated? Is it linked to the stress, at which several non-correlated local shear events happen? In principle two mechanisms can be operational: homogeneous flow (at high temperatures and low strain rates) when the whole volume of the sample statistically contributes to plastic deformation, and non-homogeneous flow (low temperatures and high strain rates) when deformation gets localized into shear bands. If non-correlated deformations of STZ are assumed, a decreasing yield stress upon repeating loading and unloading is expected. Residual stresses are frozen in the microstructure from a previous loading that will contribute to the external stress and help to activate STZs. The existence of a residual stress supports the idea, that *homogeneous* deformation is actually a more or less visco-elastic deformation of STZ. It is reversible at its first moment, but due to a relaxation of internal stresses around STZ due to structural relaxation and/or visco-elastic deformation of neighborhood STZs this deformation becomes irreversible due to the 'loss of memory' in its surrounding. The increase in ductility might be explained in terms of absorbed mechanical energy. The energy per unit of volume which involved in deformation is equal to $\int \sigma d\epsilon$. Each compression cycle leads to softening $\sigma_{n+1} < \sigma_n$. Assuming that energy per unit of volume is about constant before failure the ductility with each cycle should increase $\epsilon_{n+1} > \epsilon_n$.

Al₈₆Ni₉Y₅ taper-free metallic glass has shown extremely high values (around 300 nm) for the transition threshold of the ductility. In metallic glasses with these dimensions, such a high plasticity has never been observed before. It is relevant to note that we did not observe any change in the amorphous state due to the preparation conditions (FIB) and after deformation. It can be concluded that the deformation in MG, which becomes apparent through softening and deformability effects, is revealed and characterized through the cyclic micro- and nanopillar tests. The proposed experimental technique of loading and unloading cycles is capable of determining the mechanical properties in metallic glasses, and opens a new route to the characterization of the deformation behavior of metallic glasses down to the 100 nm sizes.

Fig. 6. (a) TEM micrograph of a shear band and its crack opening after 4.08% strain in $\text{Cu}_{47}\text{Ti}_{33}\text{Zr}_{11}\text{Ni}_6\text{Sn}_2\text{Si}_1$ alloy. The inset shows that the Shear Band Propagation (SBP) direction relative to the Tensile Axis (TA) was found to be ($\sim$)90°. The white circle corresponds with the black circle in (b), a TEM micrograph of the crack opening progress at 4.12% strain.

5. *In-situ* tension versus *in-situ* compression

In-situ TEM tensile experiments on amorphous materials are very rare. As a cautionary note, the *in-situ* TEM straining observations of metallic glass ribbons we did in the past [47] have 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 analyzed. As an example Fig. 6 portrays a typical result for a metallic glass. In Fig. 6(b) the ‘state’ of the crack tip at 368 μm extension (= 4.08% strain) is shown. The shear band itself was initiated at around 3% strain, as may be expected for amorphous materials. In our observations we also found small crystals (<5 nm in diameter) in the close vicinity (say 10 nm) of a shear band. In the example shown in Fig. 6, where crystallization processes are seen, they are driven by temperature increase from the shear band motion. The most important influencing factor in this case is not the maximum temperature, but the time during which the heated volume stays at an elevated temperature. The time scale varies with the square of shear displacement. However, for large shear displacements the time at which the material is elevated above the crystallization temperature is still less than 1 μs , which may be adequate for crystal growth but is insufficient for crystal nucleation, since the activation energy for nucleation is larger than the activation energy for crystal growth in amorphous alloys. This explains why crystals only appear in a very narrow band at the shear band edge and also why those crystals are of nanometer size. See also [47].

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 are formed will lead to fracture, as seen in Fig. 7.

Obviously size-effects are far more difficult to study through these *in-situ* straining experiments because of wedge-shaped specimen geometry. As a consequence we turn to pillars and in particular we discuss tensile experiments of $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ and $\text{Zr}_{61.8}\text{Cu}_{18}\text{Ni}_{10.2}\text{Al}_{10}$ MG pillars with diameters ranging from 100 to 500 nm. Upon testing specimens of larger diameter, the load increases proportionally up to yielding followed by brittle failure. The fracture surface shows a major shear phenomenon under 45°, i.e. similar to the behavior of mm-sized MG specimens. The localization of the fracture could occur stochastically on the specimen surface over entire length, depending on the local concentration of smaller pre-shear which contribute to major shear band.

The localization of shear bands differs between thin and thicker pillars. The latter show more localized areas with shear bands, which propagate to one major shear band. The ultimate stress in smaller specimens is higher in comparison with larger diameter specimens. An increase of true strain up to 8% was observed for this diameter range of 200 nm MG pillar specimens. The smallest specimen diameter in the range down to 100 nm shows more plasticity, necking and an increased strain hardening effect (Fig. 8). Fracture behavior is similar to plastic crystalline materials, i.e. without a 45° fracture plane as occurs in larger specimens. The plastic strain reached is around 8%. The most important observation of tensile experiments is that no clear size effect is seen on the yield stress but a clear increase in the ultimate strength is observed with decreasing the diameter of MG pillars (Fig. 8).

Even though some bulk metallic glasses can exhibit compressive strains of over 25%, they still fracture abruptly under uniaxial tensile stresses. This fact indicates that metallic glasses exhibit a tension–compression asymmetry as far as plasticity is concerned. The latter is usually interpreted by continuum mechanics, which neglects the atomic structure of materials. However, metallic glasses show an asymmetry

Fig. 7. (a) and (b) TEM micrographs revealing shear band branching in $\text{Cu}_{47}\text{Ti}_{33}\text{Zr}_{11}\text{Ni}_6\text{Sn}_2\text{Si}_1$ 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.

Fig. 8. Video frames recording the deformation of a $\phi 100$ nm $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ MG pillar in tension at displacement rate controlled mode. Grabbed video frames show the deformation structures before, during and after tension (a)–(d). True stress–strain curve (e).

that can be linked to the amorphous structure and pre-treatments.

Fig. 9 shows that $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ MG specimen does not exhibit the usual tensile behavior, i.e. release of intermittent shear bands and hardening effects (Fig. 9). Some local failure for this specimen was observed at different places (not shown) where shear bands are released and some of the shear bands released at the surface (Fig. 9). This is consistent with our compression experiments (Fig. 10). With increasing volume under compression the interaction between STZs has a larger chance to

Fig. 9. True stress–strain curve of $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ MG specimen of $\phi 200$ nm in tension at displacement rate controlled mode.

Fig. 10. (a) TEM picture of $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ MG specimen of $\phi 250$ nm in compression at displacement rate controlled mode; (b) true stress–strain curve.

occur which leads to the build-up and propagation of larger shear bands.

The comparison of stress level in compression and tensile experiments for two different compositions $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ and $\text{Zr}_{61.8}\text{Cu}_{18}\text{Ni}_{10.2}\text{Al}_{10}$ MGs is displayed in Fig. 11. At both compositions there is no size effect of the yield stress observed, i.e. the same in tension and in compression, similar to the observations in compression for other metallic glasses [25]. However both compositions show strain hardening upon reducing the specimen size (Fig. 11 – black curves) under tension. There are several differences between the materials: Al-based specimens harden more than Zr-based, almost up to the same ultimate strength as for the bulk. Both the tensile and compressive stresses increase the number of interactions among STZs. The specimens possess the same apparent Young's modulus under tension and compression. However, the experiments show that ultimate strength under tension is higher than under compression.

In our explanation of the asymmetry between tensile and compression experiments the stress state of the starting material plays a predominant role. Generally speaking, in making comparisons between the mechanical performance of materials it is of utmost importance to know precisely the residual stress state at the start of an experimental test, under compression as well as under tension. In this regards, the effect of ion irradiation caused by FIB in the preparation stage of specimens has to be considered.

Obviously, the influence of irradiation is increasing with decreasing size of the specimen, since the ratio $2d_{Ga}/d$ (where constant d_{Ga} is the penetration depth of Ga ions) is increasing upon decreasing the diameter d . For the smaller diameters $2d_{Ga}/d$ is reaching values equal to 1/4 or more and the outer layer will be under compression. Therefore it is important to include the influence of the FIB ion layer for the smaller

Fig. 11. Ultimate tensile stress vs pillar diameter of $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ MG (a) and $\text{Zr}_{61.8}\text{Cu}_{18}\text{Ni}_{10.2}\text{Al}_{10}$ MG (b). Black curve indicates the hardening size effect, red graph refers to the yield stress. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

specimens. The negative compressive stress of the outer layer will generate an offset for the positive applied stress under tension. The ultimate tensile stress will therefore increase upon decreasing diameter as experimentally observed. One would expect also an offset under compressive loading, i.e. a decreasing peak stress upon decreasing diameter. This was not really observed in practice because of the experimental difficulties to perform reliable compression tests on pillars with 1 free-end and diameters smaller than 100 nm. More experimental efforts are needed to clarify this point.

Fig. 11 shows a considerable difference between the UTS values of $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ MG and $\text{Zr}_{61.8}\text{Cu}_{18}\text{Ni}_{10.2}\text{Al}_{10}$ MG upon decreasing size. The difference is about a factor of 2, i.e. much larger for $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ and $\text{Zr}_{61.8}\text{Cu}_{18}\text{Ni}_{10.2}\text{Al}_{10}$, say roughly 1500 MPa for $\text{Zr}_{61.8}\text{Cu}_{18}\text{Ni}_{10.2}\text{Al}_{10}$ and 2500 MPa for $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ at a diameter of 100 nm and the question is whether we can understand these differences in a more quantitative sense.

Our starting hypothesis is the mean projected range of defects induced by the FIB treatment that may affect the UTS. It is worth noting that thermal or charge-based effects are discarded here: in a transmission electron microscope thermal and charge conditions could surpass the FIB in intensity but no deformation was observed during static observations. Therefore the explanation is caused by the presence of defects introduced into the material during ion milling pre-treatment and the subsequent knock-on effects produced as ions traveled within the material.

Stopping Range of Ions in Matter (SRIM, version 2012.03, [63])

simulations allow us to see the effects of ions impinging upon a solid target. A typical result for SRIM of a material like Al exposed to a perpendicular 30 kV Ga ion beam shows a projected damage range of 20 nm. Depending on the material, each ion generates an approximately fixed number of defects, the shape of the ion penetration distribution is then the same as the shape of the distribution of defects created through ionic knock-on effects. The defect distribution induced can be modeled as symmetrical and triangular [64]. Sputtering has been considered within the SRIM approaches (see [65,66])

We take stress σ and strain ε interrelated by linear elasticity and we relate the stress formed in the defect-rich region to the strain via the modulus E and Poisson's ratio ν :

$$\sigma(z) = \frac{E}{1 - \nu} \cdot \varepsilon(z) \quad (12)$$

During ion exposure various types of defects will be formed. In a crystalline case it is easier to identify these defects as vacancies, self-interstitials and Ga defects. We can express the contribution of defects to strain as linear, and thus take the sum of each type of defect of concentration $C_{d_i}(z) = n_i/n$ and atomic volume Ω_i .

$$\varepsilon_d = \frac{1}{3} \sum_i \frac{\Delta\Omega_i}{\Omega} \cdot C_{d_i}(z) \quad (13)$$

where n_i/n is the number of defects over number of all lattice sites, where i , refers to the various defects like vacancies, interstitials and Ga + defects, and $\Delta\Omega_i/\Omega$ refers to the relative volume change due to specific kind of defect i . Obviously in an amorphous system the reference state is not crystalline but a state of random disorderness. Therefore the damage cascade will be less localized due to less focused knock-on collisions as it will be in the crystalline state.

To predict $C_{d_i}(z) = n_i/n$ we take the displacement energy term E_d of a metal in the Kinchin-Pease equation that relates accelerated ion energy E_a to the amount of defects formed through E_d .

$$n_d = \frac{E_a}{2E_d} \quad (14)$$

E_d is mostly measured empirically, and a large amount of literature is available on experiments to measure E_d of various materials [67], e.g. using displacement energies of 16 eV for Al the approximate amount of defects formed by a single ionic impact at 30 kV is 1000. If we estimate the ion emission parameter of the FIB apparatus used at $2.08 \cdot 10^7$ ions per second to achieve an ionic current of 10 pA, we can state that approximately $2 \cdot 10^{10}$ defects in crystalline aluminum would be generated. At low to medium dose the number of defects goes linear with the fluence.

With n_d taken from Eq. (14) and substituting its value into Eqs. (12) and (13) it seems rather trivial to predict the residual stress. However, there is at least one snake. The contribution of defects to the total strain/stress is assumed to be linear. The stress field of a single defect in an infinite linear elastic solid can be calculated based on the theory presented already 90 years ago by Love [68] and to date it can be done through atomistics. The latter predicts a stress of 0.18 MPa of a single defect in crystalline Al based alloy on the Daw-Baskes Embedded Atom Method (EAM) [69]. This would lead to an unrealistic high stress state and you may ask yourself: what is wrong here and where is the snake?

The answer lies in the actual distribution. For a uniform distribution of defects in a linear elastic medium, the material will expand/contract uniformly leading to a stress-free material (assuming no other boundary conditions and constraints, e.g. surfaces etc). For a linear elastic solid this was worked out by 'Jock' Eshelby [70] assuming a homogeneous distribution and for a non-linear elastic solid surprisingly enough only recently [71]. The effective n_d for a triangular distribution and including a free surface is only 1% of the number predicted by the Kinchin-Pease equation.

Now we are in the position to make a fair estimate of the residual stress and to check our hypothesis concerning the increase of UTS upon

decreasing size as displayed in Fig. 11. In the milling process it is reasonable to estimate that only 15% of the Ga ions will impinge the surface perpendicularly. Therefore the effective dose is 4×10^{19} ions m^{-2} and based on Kinchin–Pease equation each incoming ion will generate for the stress build-up effectively: $0.015 \times 1000 \times 4 \times 10^{19} = 6 \times 10^{20}$ defects m^{-2} for $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ MG and 3×10^{20} for $\text{Zr}_{61.8}\text{Cu}_{18}\text{Ni}_{10.2}\text{Al}_{10}$ (melting points and cohesive energies of Zr and Al differ a factor of 2). With a projected range of 20 nm at 30 kV Ga^+ and the external dimensions of the experimental pillars (diameter 100 nm, length 300 nm) the effective strain build-up is 0.013 in $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ MG and 0.007 in $\text{Zr}_{61.8}\text{Cu}_{18}\text{Ni}_{10.2}\text{Al}_{10}$ taking into account that the density of amorphous systems is about 0.9 of crystalline materials systems and a volumetric change of 12% being the average with respect to Ga ions.

Based on these data and the elastic moduli and Poisson's ratio ($E = 57.10^9$ Pa, $\nu = 0.384$ for $\text{Al}_{86}\text{Ni}_9\text{Y}_5$; for $\text{Zr}_{61.8}\text{Cu}_{18}\text{Ni}_{10.2}\text{Al}_{10}$ $E = 84.10^9$ Pa, $\nu = 0.377$) we estimate an increase of the UTS in pillars with diameter of 100 nm due to a compressive stress of 2.6 GPa in $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ and 1.3 GPa in $\text{Zr}_{61.8}\text{Cu}_{18}\text{Ni}_{10.2}\text{Al}_{10}$ which turns out to be in fair agreement with experiments (Fig. 10).

This analysis provides support to our hypothesis that residual stresses play an important role in the UTS value of smaller sized pillars (range 100 nm in diameter). As expected, basically because of the difference in bond strength, the effects of residual stresses due to pre-treatment are more visible in Al-based than in Zr-based MG and therefore the ion irradiation effect has the largest impact onto the mechanical performance of smaller sized Al-based specimens under tension.

Likewise hardening under tension is expected because the interacting volume of the STZs is actually decreasing even more rapidly upon decreasing size and in fact confined due to the (relatively) increasing volume fraction of negative compressive stress. Indeed, for both MGs the larger the $d_{\text{Ga}}/2d$ ratio, the larger the hardening effect.

In summary, *in-situ* TEM tensile tests of $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ and $\text{Zr}_{61.8}\text{Cu}_{18}\text{Ni}_{10.2}\text{Al}_{10}$ MG specimens with diameters ranging between 100 and 500 nm show a predominant inhomogeneous flow characterized by shear banding. However starting at specimens with 120 nm in diameter, $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ MG exhibits a change in deformation behavior from brittle fracture to plastic behavior and inhomogeneous plasticity of necking.

The influence of chemical composition on the transition threshold in the tensile experiments was also observed, in accordance with compression tests. $\text{Zr}_{61.8}\text{Cu}_{18}\text{Ni}_{10.2}\text{Al}_{10}$ MG still shows plasticity around 60 nm, which is confirmed by the localized plastic necking. The unique increase in strength and strain hardening was observed for smaller sized specimens in tension which is different compared to compression experiments with the same MG compositions.

These observations confirm our predictions about volumetric size effect of MGs at nanoscale and can be explained by the competition between the nucleation and propagation of STZs at different stress fields and volumes. The study shows that the asymmetry in compression–tensile experiments is due to the residual stress state caused by the FIB pre-treatment. The residual stress does not seem to lead to a yield anisotropy and does not affect the size independency of the yield stress in compression. The implantation stress may lead to a local change (rejuvenation) of the glass since it may influence the hydrostatic stress fields ('free volume') rather than affecting the distribution in shear stresses (see also annihilation by thermal annealing and effects on deformation behavior in Al crystalline pillars [72]).

6. Conclusions

A metallic glass (MG) represents an exceptional class of materials which possesses rather unique properties for metals. It allows producing of large amount of stresses within the specimen, but it lacks the plasticity and undergoes shear band deformation rapidly. Therefore

investigations of size effects in metallic glasses plays important role. Size effects can be grouped into intrinsic or extrinsic. Intrinsic size effects are commonly controlled by the inner structure and materials processing. In MGs, they are represented by the collective behavior of (shear transformation zone) STZs. *In-situ* quantitative compression tests which revealed intrinsic and strong size effects of taper-free metallic glass nanopillars inside a transmission electron microscope (TEM) on different MG compositions show predominantly an inhomogeneous and intermittent plastic flow characterized by shear banding events. The deformation is defect-nucleation-controlled in larger pillars but becomes propagation-controlled in smaller pillars. Pillars with a diameter smaller than a certain diameter show a homogeneous flow behavior without shear banding during compression.

The initial structure and chemical composition of MGs also affect the deformation behavior at the nanoscale. MG pillars of different alloy systems and compositions. The $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ taper-free metallic glass showed the highest transition threshold for brittle behavior, i.e. above pillar diameter of 300 nm in compression. $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ MG shows plastic deformation becoming even more apparent through softening and deformability effects. These phenomena are revealed and characterized through the cyclic micro- and nanopillar tests. The *in-situ* TEM experimental technique of loading and unloading cycles is capable of determining the mechanical performance in metallic glasses, and opens a new route to the characterization of the deformation behavior of metallic glasses down to 100 nm sizes.

Interactions between intrinsic and extrinsic size effects in MGs are particularly interesting, although the current understanding of this topic is limited. Tapering was a serious problem in investigating the deformation behavior of micro-pillars under compression but it was more or less solved experimentally. Tensile experiments were performed in order to separate the difference between extrinsic and intrinsic size effects. The transition threshold from inhomogeneous flow which is characterized by shear banding events is shifting compare to compression experiments towards a lower diameter of the specimens. It indicates the separation of volumetric extrinsic size effect which was concluded by compression experiments and intrinsic size effects on MG composition which is related to collective behavior of STZs.

Based on the tensile experiments on $\text{Al}_{86}\text{Ni}_9\text{Y}_5$ and $\text{Zr}_{61.8}\text{Cu}_{18}\text{Ni}_{10.2}\text{Al}_{10}$ MG samples many questions about the mechanical behavior of MGs at nanoscale could be properly addressed. The change in deformation behavior from brittle fracture to necking starts at samples in tension at smaller diameters in comparison to the compression. The influence of chemical composition on the transition threshold for both regimes was also observed. It confirms our predictions about volumetric size effect of MGs at nano-scale and can be explained by the competition between the nucleation and propagation of STZs at different stress fields and volumes.

Despite of the constant yield stress in compression, tensile experiments show unique increase in strength. Strain hardening was observed for smaller sample sizes in tension. However tensile experiments at the smallest scale revealed the influence of FIB ion irradiation on specimens and suggest that it plays also a role in appearance of extrinsic size effects of MGs in tension.

From a theoretical viewpoint an interesting question to address is the influence of statistics. In crystalline materials the stress–strain response of micropillars during compression is characterized by significant stochastic effects, which are manifested through multiple strain bursts [16,73–75]. The stress–strain curves for same diameter pillars differ significantly, however, they can be enclosed within bounds, and therefore a size effect is noted. Recently it has been shown that the stochastic effects observed in the stress–strain behavior of both crystalline and glassy micropillars are successfully captured by implementing a gradient formulation in a cellular automaton and using a stochastic term to characterize the yield stress [16,45,52,76]. The numerical code was able to interpret the stochastic stress-drops observed during nano-pillar compression and the observed size-dependent

strengthening as well. In particular for glassy materials, having a proposed internal self-averaging structure when no mechanical stress is applied, this approach dealing with stochastic effects is worthy to examine in further detail.

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The author congratulates Professor Jing Zhu with her 80th birthday and trusts many fruitful and exciting years in science are still to come. This paper was given in her honor as a tribute, thanking her for her great contributions to the field of electron microscopy and to the materials science community. The author is also eager to seize this opportunity to thank for her efforts to the appointment of a honorary guest professorship at Tsinghua University.

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Supplementary materials

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