Original Article

Nanoindentation of zirconium based bulk metallic glass and its nanomechanical properties

Karuppasamy Pandian Marimuthu, Kwangmin Lee, Jungmoo Han, Felix Rickhey, Hyungil Lee*

Department of Mechanical Engineering, Sogang University, Seoul, 04107, Republic of Korea

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Nanoindentation experiments with a Berkovich tip are performed on zirconium based bulk metallic glass (Zr-BMG, Zr_{64}Cu_{34}Al_{12}Ni_{10}) to study its deformation and mechanical properties (elastic modulus and hardness) at nanoscale. Further to reveal indentation-size effect (ISE), the influence of loading rate and peak and cyclic loads on evaluated nanomechanical properties are investigated in detail. The loading rate has significant effect on serration flow (pop-in), which gets predominant at higher loads. According to the Oliver-Pharr method, hardness becomes peak load-independent, whereas elastic modulus increases with the load. The same phenomenon is observed with sinus and progressive multicycle indentation methods. However, observation of significant pile-up (the ratio of elastic and total energy $W_e/W_t \approx 0.33 < 0.5$) questions the application of the Oliver-Pharr method to Zr-BMG; therefore, evaluated nanomechanical properties are corrected with the projected contact area measured by atomic force microscopic (AFM) and finite element analysis to reduce ISE.

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1. Introduction

Bulk metallic glasses (BMGs) are amorphous alloys and have excellent physical and mechanical properties such as high hardness, strength and good wear and corrosion resistance [1,2]. In recent years, investigations have been devoted for developing advanced BMGs to obtain the emerging functional materials. Unlike crystalline materials, combination of a wide range of metals with diverse chemical compositions produces unusual microstructures. As a result, BMGs exhibit novel structural properties with unconventional deformation behavior. Due to the amorphous structure, BMGs have a completely different plastic deformation mechanism when compared with crystalline alloys [2]. However, at room temperature, catastrophic growth of unhindered shear bands due to highly localized plastic deformation shows the inherent brittleness of BMGs when deforming in a bulk form. Although, much research works has been done to improve the structural properties of BMGs [3–8], the maximum dimensions of BMG are still small for large scale industrial and engineering applications [9]. Therefore, it is important to know the mechanical properties and thermal stability of BMGs for manufacturing reliable and quality products.

Nanoindentation techniques have become a significant tool for determining mechanical properties such as elastic modulus, hardness, fracture toughness and plastic and creep...
parameters of materials at a small/nano scale. So far, deformation mechanisms of BMGs have been investigated by using indentation techniques to determine their mechanical properties [8,10–14]. Guo et al. [10] measured the indentation fracture toughness of various BMGs by using nanoindentation techniques with Berkovich tip as conventional crack-tip opening displacement (CTOD) testing methods are complex due to specific specimen geometry and size requirements. Vincent et al. [13] employed both micro-and nano-indentation techniques and revealed the microstructure-dependent deformation and mechanical properties of zirconium-based BMGs (Zr–Cu–Al–Ni alloy system). The variation in mechanical properties of Zr-based BMGs due to hydrogen addition were studied with nanoindentation techniques, too [4]. As the deformation mechanism of BMG is unconventional, certain BMG shows different deformation behaviors from another BMG [15,16]. Therefore, it is inappropriate to derive or apply similar nanoindentation techniques such as Oliver-Pharr (OP) method [17] for different BMGs without prior understanding of their deformation mechanism. It was also revealed that BMG shows a significant indentation-size effect (ISE) i.e. change in mechanical properties with increasing indentation depth (18,19). Although, previous studies report the general effect of test conditions, i.e. loading rate [20,21], peak loads on mechanical properties, detailed understandings on the deformation behaviors of each BMG would promote an accurate prediction of its nanomechanical properties.

As Zr-based BMGs are the emerging engineering materials [22], investigating the deformation behaviors of Zr_{65}Cu_{15}Al_{10}Ni_{10} (at. %) (Zr-BMG) by nanoindentation become a topic of interest in this study. Compared with other multi-constituent BMGs (i.e. Mg- and Hf-based BMGs), Zr-based BMGs has high glass-forming ability and super plasticity at room temperature. Some interesting phenomena such as metastable phase formation, rapid solidification, deformation-induced nano-crystallization and associated mechanical property enhancement were also observed in these Zr-based BMGs [22]. In addition, sports goods, structural frames and electronic castings [23,24] were also practically manufactured by using Zr-based BMGs [25]. In healthcare-related products such as thin film metallic glass (TFMG)-coated needles, bio-implants [26,27], Cu-bearing Zr-BMGs show good antimicrobial (antibacterial) behaviors. Based on compression tests at room temperature, Qiu et al. [22] reported a high ductility (~25%) in Zr_{65}Cu_{15}Al_{10}Ni_{10} due to the formation of multiple shear bands by nanocrystallization.

The nanomechanical properties such as elastic modulus and indentation hardness of Zr_{65}Cu_{15}Al_{10}Ni_{10} BMG are evaluated by using nanoindentation techniques based on three nanoindentation modes namely (i) standard single indentation with constant loading rate, (ii) progressive multi-cyclic indentation and (iii) sinus mode indentation. Further to reveal ISE on the nanomechanical properties, the effects of loading rate and peak and cyclic loads on the nanomechanical properties are investigated. Numerical simulations with linear Drucker-Prager (DP) model are also performed to compare the experimental load-depth curves with numerical curves. Accordingly, appropriateness of OP method for Zr-BMG that exhibits a significant pile-up around the indentation mark is assessed to obtain consistent nanomechanical properties.

2. Material and methodology

2.1. Material

Zr–Cu–Al–Ni alloy with the composition of Zr_{65}Cu_{15}Al_{10}Ni_{10} (at. % - atomic weight percentage) (Avention, South Korea) was fabricated with hot-press method by applying high heat and pressure on the mixed-powder particles. The specimen dimension is 15 × 15 × 2 mm³, and the surfaces were mechanically grinded and polished with MetPrep3/PH-4™ polisher (Allied High-tech Products Inc., USA) to reduce the surface roughness Ra to be less than 5% of maximum indentation depth h max. In the step by step grinding/polishing processes (Chinwoo Tech Co., Ltd., South Korea), 220 and 600 diamond grit sandpapers, 800 and 2400 grit SiC sandpapers, 3 μm diamond suspension and 0.05 μm final preparation solutions were used. Ra was measured with atomic force microscopy (AFM) (NX10, Park systems, South Korea) in the polished samples and an average Ra of 14 nm is obtained. We observe the polished surfaces using optical microscope and AFM. In addition, the flatness of the sample is confirmed based on the line image from AFM measurements. To determine the phase structure of the sample, X-ray diffraction (XRD) measurements of as-cast alloys were obtained by using a Rigaku X-ray diffractometer with Cu Kα radiation. Measurements were taken with a scanning speed of 2°/min and a diffraction angle θ with a range of 10°–90°. The chemical composition of microstructure was analyzed by using energy-dispersive X-ray spectroscopy (EDS) inside the field emission scanning electron microscope (FE-SEM) apparatus (JSM-7100F, JEOL Ltd., Japan).

2.2. Nanoindentation experiments and methods

The nanoindentation experiments were performed at room temperature using Ultra Nanoindentation Tester (UNHT³, Anton Paar, Switzerland) with a diamond Berkovich tip. UNHT³ is appropriate for performing nanoindentation test at low loads and depths with less thermal drift as it uses a top referencing for measuring the displacement data of the indenter. Based on dynamic mechanical analysis (DMA) using a reference material i.e. Fused silica (FS) (National Physics Laboratory, UK), the tip area function is determined by adjusting a spline interpolation of A c and h c, and an extremely low frame compliance of the indentation system is estimated as c f = 0.58 μN/m. A linear load P was applied with a constant loading rate dp/dt (during both loading and unloading cycles); to reduce the error from creep in nanoindentation [28], the maximum load P max was held for a hold period of 10 seconds before unloading. The zero-contact point, where load and depth are zero, was identified with a stiffness threshold of 150 mN/mm and an initial contact load of 0.02 mN in each test. Around 15 indentations were performed for each test configuration to check the reproducibility of experimental load-depth (P–h) curves; mean load-depth curves were derived from more than five data sets with a high level of reproducibility.

To observe the effect of dp/dt and P max on the indentation response of Zr_{65}Cu_{15}Al_{10}Ni_{10}, standard indentation tests are performed with (i) different dp/dt, constant P max and (ii) various P max, constant dp/dt. Grid indentation technique was
applied with 20 µm gap between each indent. Nanoindentation est parameters are listed in Table 1. Data acquisition frequency was varied between 5–10 Hz according to the loading rate. Residual imprints (indents) after load removal were observed with an optical microscope with a lens of 100X optical magnification, FE-SEM and AFM. In addition, to understand the effect of indentation depth on evaluated mechanical properties, sinu mode and progressive multicyclic (PMC) mode indentations were also performed.

2.2.1. Quasi-static indentation methods
In quasi-static indentation, the hardness and elastic modulus of Zr65Cu15Al10Ni10 in each test can be calculated by using the Oliver-Pharr (OP) method [6,13,17]. The indentation hardness H is here determined by

\[ H = \frac{P_{\text{max}}}{A_c} \]  

(1)

where \( A_c \) is the projected contact area at \( P_{\text{max}} \). For a perfect Berkovich tip, \( A_c \) can be determined from the contact depth \( h_c \) and a tip geometry factor \( C_c = 24.5 \), which was previously obtained from the best fit of indentation data [17]. Hence, \( A_c \) is expressed as

\[ A_c = 24.5h_c^2 \]  

(2)

and the corresponding \( h_c \) is calculated from the indentation load-depth (P-h) curves as

\[ h_c = h_{\text{max}} - h_b = h_{\text{max}} - \frac{P_{\text{max}}}{S} \]  

(3)

where \( h_{\text{max}} \) is maximum indentation depth. The sink-in depth \( h_s \) is related to the geometric constant \( \epsilon = 0.76 \) for Berkovich indenter tip), the initial unloading stiffness (slope) \( S \) and \( P_{\text{max}} \). The initial slope \( S \) can be determined from the elastic unloading curve as

\[ S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A_c} \]  

(4)

Here, reduced modulus \( E_r \) is expressed by the elastic moduli of the specimen \( E \) and of the indenter \( E_I \) and the corresponding Poisson’s ratios \( v \) and \( v_I \)

\[ \frac{1}{E_r} = \frac{1 - v^2}{E} + \frac{1 - v_I^2}{E_I} \]  

(5)

Accordingly, the elastic modulus of the specimen \( E \) can be determined by

\[ E = \frac{S \sqrt{\pi} E_I \left(1 - v^2\right)}{2 \sqrt{\pi} E - S \sqrt{\pi} \left(1 - v_I^2\right)} \]  

(6)

2.2.2. Sinus mode indentation methods
In sinus mode indentations, a small oscillated force that follows sine wave is added to the quasi-static force. With respect to time \( t \), the force and displacement signals can be denoted as follows [29].

\[ P(t) = P_b \sin(\omega t) \]  

(7)

\[ h(t) = h_b \sin(\omega t + \phi) \]  

(8)

where \( P_b \) and \( h_b \) are the force and displacement amplitudes, respectively and \( \omega \) is the angular frequency. \( \phi \) is the phase angle between excitation and response. The stiffness \( S \) can be determined as follows

\[ S = \frac{P_b}{h_b \cos \phi} \]  

(9)

Based on Eq. (9), \( S \) can be determined with increasing \( h \). Therefore, the mechanical properties can be calculated at various \( h \) based on Eqs. (1) & (6), and then the variation of hardness and elastic modulus with increasing \( h \) can be plotted. Nanoindentation test parameters are listed in Table 1. The sinus mode indentation is performed under constant strain rate condition as defined below [30]

\[ \dot{\epsilon} = \frac{\dot{h}}{h} = \frac{1}{2} \left( \frac{\dot{P}}{P} - \frac{\dot{H}}{H} \right) \approx \frac{\dot{P}}{P} = \text{constant} \, \text{s}^{-1} \]  

(10)

By maintaining constant \( \dot{P}/P \) with pyramid shaped indenter, constant value for indentation strain rate can be achieved if a steady-state value of hardness is reached and \( \dot{h} = 0 \) [30].

2.3. Finite element modelling
Since the Berkovich nanoindentation can be modelled by replacing the Berkovich tip with an equivalent conical indenter [31], an axisymmetric two-dimensional (2D) finite element (FE) model is created, and detailed explanation on mesh refinement study can be found in Refs. [28,32,33]. The ideally sharp conical indenter with an angle (between indenter
and sample surface) \( \theta = 19.7^\circ \) is modelled by using rigid surfaces in Abaqus/Standard [34] (Fig. 1). The FE model contains about 15,600 nodes and 15,300 elements 4-node continuum axisymmetric elements (CAX4). Axisymmetric boundary conditions (BCs) are applied to the nodes on the z-axis. On the other hand, the bottom nodes are fixed in the z-direction, while they are free to move in radial direction (r-direction). The rigid indenter is allowed to move only in the depth direction (z-direction). Surface-to-surface contact is defined between the indenter and the specimen, and Coulomb-type friction is assumed with coefficient of friction \( \mu = 0.2 \) [11]. Nanoindentation simulations are performed with load control in the dynamic analysis. Cyclic indentation responses of BMG are also simulated with a maximum of 10 cycles as described in the experimental section.

The mechanical behavior of Zr\(_{65}\)Cu\(_{15}\)Al\(_{10}\)Ni\(_{10}\) is assumed to be isotropic. To consider its pressure dependent behavior of BMGs, a linear Drucker-Prager (DP) pressure-dependent model is applied to the FE model [12]; the dilatancy angle for the linear DP model is assumed to be zero. The mechanical properties (\( E \), zero pressure yield strength \( \sigma_y \), and friction angle \( \beta \)) of Zr\(_{65}\)Cu\(_{15}\)Al\(_{10}\)Ni\(_{10}\) are obtained based on a trial and error method by matching FE load-depth curves with experimental curves.

A small weight ratio of oxygen is also observed in the EDS analysis. Elemental analysis based on XRD usually provides only qualitative results; for quantitative analysis, ICP-MS (inductively coupled plasma-mass spectroscopy) method is recommended. Although there is small deviation in measured values due to chemical fluctuation, we emphasize that the nanomechanical properties of Zr-BMG are comparable to the chemical composition measured i.e. Zr\(_{65.9}\)Cu\(_{15.8}\)Al\(_{8.5}\)Ni\(_{9.8}\) (at. %) in this work. Based on the XRD measurements, the amorphous structure of Zr-BMG is confirmed as reported in the previous studies on the alloys with similar chemical composition [6,22,35]. Huang et al. [36] analyzed the possible scenario of heterogenous microstructure and density fluctuations in various BMGs and reported a weaker microstructural inhomogeneity in similar Zr\(_{64.13}\)Cu\(_{15.75}\)Al\(_{10.12}\)Ni\(_{10}\). Here, we assume that the effect of (even weaker) microstructural inhomogeneity on the measured nano-mechanical properties is insignificant.

### 3. Results and discussion

#### 3.1. Microstructural analysis of Zr\(_{65}\)Cu\(_{15}\)Al\(_{10}\)Ni\(_{10}\)

To confirm the designed chemical composition of Zr\(_{65}\)Cu\(_{15}\)Al\(_{10}\)Ni\(_{10}\) (at. %) that provided by the vender, EDS spectrum of as received Zr-BMG specimen is analyzed. The comparison of SEM and EDS layered images of residual indents shows that the chemical elements are evenly distributed over the sample as shown in Fig. 2. The SEM-EDS results at different indented locations give an average global composition of Zr\(_{65}\) (71–75 wt.%), Cu\(_{15}\) (13–16 wt.%), Al\(_{10}\) (2.6–3.2 wt.%) and Ni\(_{10}\) (6.6–8.9 wt.%) with small chemical fluctuation in the sample.

The nanoindentation load-depth \((P-h)\) curves of Zr\(_{65}\)Cu\(_{15}\)Al\(_{10}\)Ni\(_{10}\) are extensively investigated in this section. Degree of plastic flow i.e. serration flow of BMGs mainly depends on employed loading rates \(dP/dt\) [37]. By varying \(dP/dt\) as 5, 10, 20, 40, 60, 100 mN/s, Fig. 3a shows obtained \(P-h\) curves for \(P_{\text{max}} = 50\) mN. Formation of shear bands occurs around the indentation imprint (Fig. 3) as freely moved atoms accumulate at a certain region due to large free volume in amorphous BMG [13]. When the applied strain rate is smaller than the net-generation rate of free volumes in amorphous alloys, individual shear bands form along the sliding plane [2,38]. Consequently, serration flows, which can be compared with pop-in events in nanoindentation, are often observed with \(dP/dt\) smaller than 20 mN/s, whereas, higher loading rates suppress the serration flows (i.e. amplitude of the pop-in event gets smaller [20]) as shown in Fig. 3b as reported in
previous studies [2,20,37]. The deformation mechanism in amorphous alloys can be explained by bridging between serration and plasticity [2]. Although, the serration flow is observed with different loading rates, P-h curves are likely to coincide especially in the loading part. It coincides because serration distances are small (around 5–10 nm). Hence, the loading part of the P-h curve is approximated using Kick’s law \( P = C h^2 \) for sharp indenter [39]; we obtain the coefficient \( C = 153 \text{ GPa} \) by regressing the mean experimental P-h curve. Similarly, the numerical P-h curve is obtained by assigning the elastic behavior with \( E = 130 \text{ GPa}, \nu = 0.367 \) [12], and plastic behavior with linear Drucker-Prager model parameters \( \sigma_s = 2.7 \text{ GPa}, \beta = 14^\circ \) [12]. The values of elastic (E) and plastic (\( \sigma_s, \beta \)) parameters are determined by obtaining a good match between unloading and loading curves of numerical and experimental data based on trial and error method. The error is reduced in a least square sense. Fig. 3a includes both Kick’s law approximation and the numerical P-h curve for \( \text{Zr}_{65}\text{Cu}_{15}\text{Al}_{10}\text{Ni}_{10} \). In addition, SEM images of residual indent for each loading rate are compared in Fig. 3c. It is noted that the shear band formation is predominant with lowest loading rates. Therefore, further experiments with various peak and

**Fig. 2** – Zr–Cu–Al–Ni alloy: comparison of SEM image with EDS layered image along with EDS spectrum.

**Fig. 3** – Nanoindentation load-depth (P-h) curves of zirconium based bulk metallic glass (Zr-BMG) for different (a) loading rate \( \frac{dP}{dt} = 5, 10, 20, 40, 60, 100 \text{ mN/s} \). Loading curve is approximated based on both Kick’s law and FE method (b) observation of serration flow with slower \( \frac{dP}{dt} = 5 \text{ mN/s} \). (c) SEM images of residual indent at each loading rate.
cyclic loads are conducted with a loading rate of 40 mN/s to reduce the effect from the serration flows.

We observed the effect of peak loads on the P-h curves varying $P_{\text{max}}$ = 5, 10, 20, 30, 50, 80, 100 mN. The mean loading curves for each load almost coincide with those approximated with Kick’s law; hence, it confirms a high-level of reproducibility of experimental curves as shown in Fig. 4a. Similarly, numerical simulations are performed with the material properties of Zr$_{65}$Cu$_{15}$Al$_{10}$Ni$_{10}$ and the numerical P-h curves almost reproduce the experimental results as shown in Fig. 4b. A comparison of residual indent for $P_{\text{max}}$ = 20, 50, 80, 100 mN (in Fig. 4c) confirms a gradual increase in indent size with the load. Surface damages due to the accumulation of shear bands, which control the compressive plasticity in BMGs [40], are observed at higher loads $P_{\text{max}}$ = 80, 100 mN. Similar damages are also observed during the cyclic indentation as discussed in the following section.

A representative P-h curve of sinus mode indentation and the corresponding SEM image of residual imprint are presented in Fig. 5a and b. The test is performed with a constant strain rate of 0.05 s$^{-1}$ up to $P_{\text{max}}$ = 100 mN. By continuously measuring the material stiffness $S$, the variation of hardness and elastic modulus are calculated with increasing indentation depth. Numerical simulation of sinus mode indentation is not performed in this work. Fig. 5c compares P-h curves between experiments (black line) and simulations (red line) of progressive multi-cyclic indentation. A comparison of experimental P-h curves of enlarged views at lower and higher loads confirms that the size of serration steps increases with gradually increasing loads (or penetration depth); similar phenomenon was observed in prior nanoindentation studies on Zr-BMG [35,37,41]. The surface damages are observed in some tests for higher loads $P ≥ 80$ mN (cycles ≥ 8) as shown Fig. 5d.

3.3. Evaluation of nanomechanical properties

3.3.1. Elastic modulus

At each $P_{\text{max}}$, the variation of unloading stiffness $S$ with increasing contact depth $h_c$ at $P_{\text{max}}$ are plotted as shown in Fig. 6a, where $h_c$ is calculated based on OP method [Eq. (3)]. As like in Eq. (4), a linear relationship between $E_r$, $S$ and $h_c$ at $P_{\text{max}}$ can be obtained by replacing $A_r$ with 24.5 $h_c$. Consequently, $E_r$ can be obtained from the slope of best-fit line. Linear regression yields non-zero intercept, which is very close to origin. For better comparison, a linear regression line with zero intercept is also plotted. At smaller depths, effect of finite indenter-tip radius causes smaller deviations between the regression lines. However, a best-fit value of intercept $= -0.013$ mN/nm can be large enough to influence on the estimated elastic modulus at smaller depths [42]. It is suggested to introduce a correction offset ($≈14$ nm) with contact depth to consider the effect of indenter-tip radius. Using a linear regression with zero intercept, we calculate the load independent elastic modulus $E_0$ from the slope of best-fit line as 144 GPa by assuming negligible tip radius effect on $E_0$. In addition, $E$ is measured at each $P_{\text{max}}$ based on the Eq. (6) as listed in Table 2. It should be emphasized that, for $P_{\text{max}} = 50$ mN, the effect of loading rate on measured $E$ values is negligible as the average value of $E = 154 ± 5$ GPa from the tests with a range of $\dot{d}P/\dot{dt}$ similar to those obtained with $\dot{d}P/\dot{dt} = 40$ mN/s and $P_{\text{max}} = 50$ mN. The same can be applied to the cases with another $P_{\text{max}}$, too. Regardless of the magnitude of $P_{\text{max}}$, the numerical approximation gives rather smaller $E = 130$ GPa, which is based on the trial and error method of matching load-depth curves. This is further discussed in Section 3.4.

On the other hand, a strong indentation depth (or peak load) dependency of $E$ is observed as listed in Table 2; in which, $E$ increases with $h$. A converged constant value of elastic modulus is not obtained up to the maximum depth around 800 nm. Results from the sinus mode and progressive multi-cyclic mode indentations also support the results obtained with the single indentation mode as shown in Fig. 6b. It is interesting to note that the all three modes of indentation provide similar trends of indentation size effect (ISE) on elastic modulus; this can be attributed to the significant pile-up around the indent (Figs. 3 and 4). ISE in amorphous alloys may originate from the strain-induced softening due to the continuous creation and coalescence of excessive free volume upon indentation [43]. While, the other reason may be that the material properties calculated by the Oliver-Pharr method are significantly affected by the pile-up as the ratio of elastic and total energy $W_{\text{e}}/W_t ≈ 0.33$ (Table 2), which can be readily obtained from the indentation load-depth curve, for Zr-BMG is less than 0.5. $W_{\text{e}}/W_t$ is closely related to the plasticity index i.e. material with $W_{\text{e}}/W_t = 1$ tends to show elastic behavior, whereas the material with $W_{\text{e}}/W_t ≈ 0$ shows fully plastic regime [12]. Rodriguez et al. [12] stated that the OP method leads to very large errors in $A_r$ estimations for very ductile materials ($W_{\text{e}}/W_t < 0.5$) and/or materials with low pressure sensitivity, while the OP method can be conventionally used to estimate $A_c$ if $W_{\text{e}}/W_t > 0.5$. Since $W_{\text{e}}/W_t$ for Zr-BMG is measured as 0.33, inaccurate determination of $A_c$ by the OP method can introduce, significant error in calculated properties. This error can be rectified by including the pile-up effect, through AFM or microscopy measurements of the projected area of the residual imprint [12].

3.3.2. Hardness

A polynomial relation can be obtained between the $P_{\text{max}}$ and $h_c$ in nanoindentation as follows [43].

$$P_{\text{max}} = a_0 + a_1 h_c + a_2 h_c^2$$  \hspace{1cm} (11)

where $a_0$, $a_1$, $a_2$ are constants, and parameter $a_2$ can be used to measure a load-independent hardness $H_a$ [42,44,45]. Fig. 7a shows the experimental results of $h_c$ at various $P_{\text{max}}$, and the polynomial regression is presented as a solid line with $(a_0$, $a_1$, $a_2) = (−0.454, 0.0105, 1.89 × 10^{-4})$. For Berkovich indenter, the load-independent hardness $H_a = a_2/24.5$ is measured as 7.71 GPa for Zr$_{65}$Cu$_{15}$Al$_{10}$Ni$_{10}$. Unlike the elastic modulus, the hardness does not show any significant ISE (Fig. 7b, in which

$^1$ For the linear regression with non-zero intercept, $E_0$ is calculated as 148 GPa. The difference between the values of $E_0$ with zero and non-zero intercept is less than 3% for considered bulk metallic glass; therefore, it is concluded that the effect of tip radius on $E_0$ is negligible in this study.
Fig. 4 – Nanoindentation load-depth \( (P-h) \) curves for different maximum indentation loads \( P_{\text{max}} = 5, 10, 20, 30, 50, 80, 100 \) mN from (a) experiments and (b) FE analyses. Mean experimental curves are obtained from more than five experimental data at each \( P_{\text{max}} \) and coincides of loading part confirms the reproducibility of experimental results.

Fig. 5 – Load-depth curve from (a) sinu mode nanoindentation (b) corresponding residual indent. (c) \( P-h \) curve from cyclic mode indentation. Experimental \( P-h \) curve (black line) is compared with those from FE analysis (red line). (d) Observed surface damages at higher loads \( P \geq 80 \) mN (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).
Fig. 6 – (a) Variation of initial unloading stiffness $S$ with increasing contact depth $h_c$ at $P_{\text{max}}$. $h_c$ is calculated based on OP method. At smaller depths, effect of finite indenter-tip radius can cause deviations from the data points. However, the deviation is very small. (b) Variation of elastic modulus with indentation depth.

Table 2 – Effect of peak load on experimental results ($dP/dt = 40$ mN/s).

<table>
<thead>
<tr>
<th>$P_{\text{max}}$ (mN)</th>
<th>$h_{\text{max}}$ (nm)</th>
<th>$W_r/W_t$</th>
<th>$h_c$ (nm)</th>
<th>$S$ (mN/nm)</th>
<th>$E$ (GPa)</th>
<th>$H$ (GPa)</th>
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<tr>
<td>5</td>
<td>173 ± 3</td>
<td>0.36</td>
<td>142</td>
<td>0.126</td>
<td>137 ± 11</td>
<td>8.18 ± 0.2</td>
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<td>10</td>
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<td>0.35</td>
<td>212</td>
<td>0.188</td>
<td>143 ± 7.4</td>
<td>7.84 ± 0.2</td>
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<td>302</td>
<td>0.280</td>
<td>153 ± 4.3</td>
<td>7.97 ± 0.2</td>
</tr>
<tr>
<td>30</td>
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<td>0.33</td>
<td>372</td>
<td>0.345</td>
<td>156 ± 3.4</td>
<td>8.08 ± 0.1</td>
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<tr>
<td>50°</td>
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<td>0.32</td>
<td>491</td>
<td>0.449</td>
<td>155 ± 3.1</td>
<td>7.88 ± 0.2</td>
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<tr>
<td>80</td>
<td>733 ± 8</td>
<td>0.33</td>
<td>625</td>
<td>0.570</td>
<td>155 ± 6.6</td>
<td>7.88 ± 0.2</td>
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<tr>
<td>100</td>
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<td>0.32</td>
<td>701</td>
<td>0.663</td>
<td>163 ± 3.5</td>
<td>7.88 ± 0.2</td>
</tr>
</tbody>
</table>

Bold values highlight the size of the indentation to readily interpret ISE.

* Effect of loading rate on measured values is negligible: $E = 154 ± 5$ GPa and $H = 8.22 ± 0.2$ GPa.

Fig. 7 – (a) Plot of $P_{\text{max}}$ vs. $h_c$. Solid lines regress the data. (b) Variation of hardness with indentation depth. Hardness becomes depth-independent at larger indentation depth.

Experimental results from all three indentation modes are compared. The hardness of $\text{Zr}_{65}\text{Cu}_{15}\text{Al}_{10}\text{Ni}_{10}$ is obtained as $H = 7.88$ GPa, which is close to $H_c$ measured based on Fig. 7a. By contrast, FE results give a much larger hardness $H_{\text{FE}} = 8.23$ GPa; this can be attributed to the substitution of the conical indentation for Berkovich indentation, especially when significant pile-up occurs. Kim et al. [32] showed that $A_c$ from Berkovich indentation is larger than the conical indentation at equal indentation depths. In addition, the current FE model unable to simulate the surface damage due to the formation of the shear band around the indentation.

3.4. Correction of evaluated properties

According to the Oliver-Pharr method, hardness $H$ shows insignificant ISE and the value $H = 7.88$ GPa was obtained for $\text{Zr}_{65}\text{Cu}_{15}\text{Al}_{10}\text{Ni}_{10}$, whereas elastic modulus $E$ shows significant ISE. Here $E$ increases monotonically from 130 to 165 GPa with $P_{\text{max}}$ in the range of 5–100 mN (Table 2) due to the significant pile-up around the indentation. The observation of significant pile-up (the ratio of elastic and total energy $W_r/W_t \approx 0.33 < 0.5$) thus questions the application of the Oliver-Pharr method to Zr-BMG. Huang et al. [18] also concluded that ISE in nanoin-
dentation of BMG is attributed to the pile-up and suggested to account the effect of pile-up to the OP method. Therefore, the nanomechanical properties evaluated by the OP method are corrected with the AFM measured projected contact area of residual imprint $A_{\text{res}}$, based on the assumption that $A_{\text{res}}$ is equal to $A_c$ at $P_{\text{max}}$ [14,46]. From 3D-mapping of the residual imprint for $P_{\text{max}} = 50$ mN, we observe significant pile-up near the contact edges as shown in Fig. 8a. Therefore, the Sobel edge enhancement method with normalized parameters [12] is used to measure $A_{\text{res}}$ from the AFM topology image (Fig. 8b). Profiles of residual imprints for different $P_{\text{max}} = 20$, 50, 100 mN are compared in Fig. 8c, in which the material pile-up is highlighted. By substituting $A_{\text{res}}$ instead of $A_c$ in Eq. (1) and Eq. (6), the nanomechanical properties are re-calculated for various $P_{\text{max}}$ as listed in Table 3. Although, the elastic modulus yet shows small ISE, we conclude that the nanomechanical properties of considered Zr$_{65}$Cu$_{15}$Al$_{10}$Ni$_{10}$ are around $E = 125 \pm 3$ GPa, $H = 6.60$ GPa, and the DP model parameters $\sigma_0 = 2.7$ GPa, and $\beta = 14^\circ$. These experimental values are comparable with the previously reported data [16,27]. However, the values of elastic modulus reported in this work is larger than that from conventional compression tests [22]; this is an example of the ‘smaller is the stronger’ pattern and so called ‘size effects’ [29,47]. To validate these properties, the experimental load-depth curve for $P_{\text{max}} = 50$ mN is compared with those from FE analysis for evaluated nanomechanical properties as shown in Fig. 8d. A good match between numerical and experimental load-depth curves is obtained. It is again concluded that OP method tends to overestimate $E$ and $H$ of the material e.g. BMGs that shows significant pile-up. The results presented in this work based on AFM measurements provide further insight to understand the mechanical behaviors of similar BMGs. Accordingly, the effect of experimental uncertainties in material property evaluation also can be reduced for these materials.

### Table 3 – Corrected experimental results by AFM measurements.

<table>
<thead>
<tr>
<th>$P_{\text{max}}$ (mN)</th>
<th>Projected contact area ($\mu$m$^2$)</th>
<th>$S$ (mN/nm)</th>
<th>$E$ (GPa)</th>
<th>$H$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OP</td>
<td>AFM</td>
<td>OP</td>
<td>AFM</td>
</tr>
<tr>
<td>20</td>
<td>2.51 ± 0.05</td>
<td>3.04</td>
<td>0.280</td>
<td>153 ± 4.3</td>
</tr>
<tr>
<td>50</td>
<td>6.35 ± 0.13</td>
<td>7.65</td>
<td>0.449</td>
<td>155 ± 3.1</td>
</tr>
<tr>
<td>100</td>
<td>12.70 ± 0.24</td>
<td>15.60</td>
<td>0.663</td>
<td>163 ± 3.5</td>
</tr>
</tbody>
</table>

### 4. Summary and conclusion

Nanomechanical properties, including elastic modulus and hardness of zirconium based bulk metallic glass (Zr$_{65}$Cu$_{15}$Al$_{10}$Ni$_{10}$) were obtained by nanoindentation experiments and numerical simulations. Experimental results from three different nanoindentation modes, namely (i) standard single indentation with a linear loading rate, (ii) progressive multi-cyclic indentation and (iii) sinus mode indentation, were compared to analyze the indentation size effect (ISE) on measured properties. Numerical simulations with the
linear Drucker-Prager (DP) model were also performed, and a good match between experimental and numerical load-depth curves were obtained. The effects of loading rates and peak loads on the nanomechanical properties were also investigated in detail. The occurrence of serration flows was observed depending on the employed loading rate. SEM images of residual imprints for various modes of indentation and peak loads were compared. Finally, based on experimental and numerical studies, the nanomechanical properties of Zr65Cu15Al10Ni10 were evaluated as $E = 125 \pm 3$ GPa, $H = 6.60$ GPa, and DP model parameters $\sigma_0 = 2.7$ GPa, and $\beta = 14^\circ$.

As damage around the indentation imprint was observed for higher loads >80 mN, future work will be focused on identifying the causes of these damages, especially in the multi-cyclic indentation. It is expected to improve the understanding of (contact) fatigue and fracture properties of Zr65Cu15Al10Ni10. In addition, wear properties will be investigated based on nano-scratch tests.

**Conflicts of interest**

The authors declare no conflicts of interest.

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**References**


