Materialia 9 (2020) 100505

Contents lists available at ScienceDirect

Materialia

journal homepage: www.elsevier.com/locate/mtla

Full Length Article

Anomalous behavior of glass-forming ability and mechanical response in a series of equiatomic binary to denary metallic glasses

Jung Soo Lee^a, Hyun Seok Oh^{a,b}, Wan Kim^a, Chae Woo Ryu^a, Jin Yeon Kim^a, Hye Jung Chang^{c,d}, J.L. Gu^e, K.F. Yao^e, B.S. Murty^f, Eun Soo Park^{a,*}

^a Department of Materials Science and Engineering, Seoul National University, Seoul 08826, Republic of Korea

^b Department of Materials science and Engineering, Massachusetts Institute of Technology, MA 02139, USA

^c Advanced Analysis Center, Korea Institute of Science and Technology, 5 Hwarang-ro 14-gil, Seongbuk-gu, Seoul 02792, Republic of Korea

^d Division of Nano and Information Technology, KIST school, University of Science and Technology, Seoul 02792, Republic of Korea

^e School of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China

^f Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras, Chennai 600036, India

ARTICLE INFO

Keywords: Metallic glass Configuration entropy Glass-forming ability Local structural irregularity Mechanical response

ABSTRACT

Herein, we systematically investigated the impact of configuration entropy (CE) on the glass-forming ability (GFA) and mechanical response in a series of equiatomic binary Cu₅₀Zr₅₀ to denary (CuNiBeCoFe)₅₀(ZrTiHfTaNb)₅₀ metallic glasses (MGs) with similar atomic size difference and enthalpy of mixing. Interestingly, the senary (CuNiBe)₅₀ (ZrTiHf)₅₀ MG with a medium CE of 1.79R exhibits the maximum GFA among the MGs, which means that higher CE by itself is not a sufficient condition for higher GFA, although it should be a major design parameter according to the confusion principle. The mechanical response analysis was comprehensively performed using nanoindentation test including statistical analysis of pop-in event to elucidate deformation dynamics of shear-avalanches, and the analysis result was compared with the intensive structure data obtained by high energy X-ray scattering analysis. The nanohardness and the Young's modulus (E) in MG with higher CE are shown to outwardly increase which is dominantly due to increased 3-atom connections of cluster polyhedra as well as lower fragility. However, the severe local structural irregularity and the compositional complexity in MG with higher CE promotes the manifestation of relatively chaotic behavior as well as the loss of MG's property inheritance, which results in the unexpected local softening of MG and ultimately modulating the response towards ductile deformation. Thus, the denary MG with the highest CE of 2.30R exhibits an abnormally low incremental rate in the cut-off values of strain burst size as well as measured E. Consequently, it can be concluded that the CE could be one of the crucial factors in designing an MG to alter its characteristics towards achieving desirable properties such as high GFA and enhanced plasticity.

1. Introduction

It has been over a half century since metallic glasses (MG) were discovered. Although we understand much better today, significant gaps in our knowledge for active commercialization of MGs remain. In particular, the composition-related variations in essential properties such as glass-forming ability (GFA), mechanical stability and processability remain critical issues. Therefore, various researches have been conducted to overcome the challenges to expand the use of MGs [1–9].

Recently, high-entropy bulk metallic glasses (HE-BMGs) have been developed encompassing the characteristics of bulk metallic glasses (BMGs) and high-entropy alloys (HEAs). Unable to draw accurate multicomponent phase diagrams, one of the simplest ways of designing

Corresponding author.

E-mail address: espark@snu.ac.kr (E.S. Park).

https://doi.org/10.1016/j.mtla.2019.100505 Received 17 August 2019; Accepted 13 October 2019 Available online 18 October 2019 2589-1529/© 2019 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

HE-BMGs, substituting the constituent elements with elements that have similar chemical properties in a prototypical BMG have been employed. However, such an alloy design through substitution is reported to deteriorate the GFA, for example, from maximum diameter for glass formation (D_{max}) of 25 mm for $Pd_{40}Ni_{40}P_{20}$ [10] to 10 mm for $Pd_{20}Pt_{20}Ni_{20}Cu_{20}P_{20}$ [11] by substitution of Pd with Pt and Ni with Cu. On the other hand, enhancement in other properties of HE-BMGs have been reported compared to those of conventional BMG counterparts, such as improved yield strength exceeding 2 GPa for equiatomic Ti₂₀Zr₂₀Cu₂₀Ni₂₀Be₂₀ HE-BMG compared to non-equiatomic Ti-Zr-Cu-Ni-Be BMGs [12], better thermal stability with slower crystallization kinetics for Zr-Ti-Hf-Cu-Ni-Be and Er-Gd-Y-Al-Co HE-BMGs [13,14], superior soft magnetic property for $\rm Fe_{25}Co_{25}Ni_{25}(B,\,Si)_{25}$ with excellent yield strength greater than 3 GPa and large plastic strain of about 3% [15], and enhanced corrosion resistance and low Young's modulus value close to that of the cortical bone for $Ca_{20}Mg_{20}Zn_{20}Sr_{20}Yb_{20}$ HE-BMG [16]. It was typically explained that the enhancements in HE-BMGs are





mainly attributed to the core effects of HEAs, namely, the high-entropy effects. However, very little attention has been focused on the effect of configuration entropy on the MG's properties.

In this study, we systematically investigated the impact of configuration entropy on the GFA and the mechanical response in a series of equiatomic binary Cu₅₀Zr₅₀ to denary (CuNiBeCoFe)₅₀(ZrTiHfTaNb)₅₀ MGs, while minimizing the effect of δ (parameter representing the atomic size difference) and ΔH_{mix} (enthalpy of mixing). First, the comparison of GFA parameters, defined by easily measurable characteristic temperatures of MGs obtained using calorimetric analysis, was carried out to observe the influence of configuration entropy on the GFA. Second, the mechanical response analysis was comprehensively performed using nanoindentation test including statistical analysis of pop-in event to elucidate the deformation dynamics of shear-avalanches. We then carefully compared the results with the intensive structure data obtained by high energy X-ray scattering analysis, which was employed for the qualitative analysis of the atomic-level structure of the MGs. Consequently, we learned that the severe local compositional complexity caused by increased configuration entropy results in an unexpected GFA variation as well as anomalous mechanical responses due to the pronounced local structural instability. Our results allow us to propose a novel strategy for designing an MG to alter its characteristics towards desirable properties such as high GFA and enhanced plasticity.

2. Experimental

Master alloy ingots of $Cu_{50}Zr_{50}$, $(CuNi)_{50}(ZrTi)_{50}$, $(CuNiBe)_{50}(ZrTiHf)_{50}$, $(CuNiBeCo)_{50}(ZrTiHfTa)_{50}$, and $(CuNiBeCoFe)_{50}(ZrTiHfTaNb)_{50}$ (in at.%), denoted as CZ2, CZ4, CZ6, CZ8, and CZ10, respectively, hereafter, were prepared by arc-melting high purity (>99.9%) Cu, Ni, Be, Co, Fe, Zr, Ti, Hf, Ta, and Nb under Ti-gettered argon atmosphere. The ingots were re-melted at least five times to ensure compositional homogeneity. Thereafter, melt-spinning technique was employed to produce ribbon specimens, where the ingots were re-melted using an induction heater in quartz tubes and were quickly ejected with an over-pressure of 50 kPa through a 1 mm-diameter nozzle onto a copper wheel rotating with a surface velocity of approximately 40 m/s. The melt-spun ribbons have thickness of $25\pm5 \,\mu\text{m}$ and width of $2\pm0.2 \,\text{mm}$.

The amorphous structure of the as-spun ribbons was primarily confirmed by X-ray diffractometer (XRD; Bruker D2 Phaser) using monochromatic Cu K α radiation. Thermal analysis was carried out during continuous heating with various heating rate of 10, 20, 40, 80 and 160 K/min to determine the glass transition temperature (T_g) and the crystallization onset temperature (T_x) of as-spun ribbons using differential scanning calorimetry (DSC, Perkin Elmer DSC8500) and the liquidus temperature (T_l) on ingot samples using TGA/DSC 1 STARe system (Mettler Toledo). The microstructure of MGs was examined using high resolution transmission electron microscopy (HRTEM, Thermo Fisher Scientific Titan 80–300). The samples for HRTEM observation were carefully prepared by mechanical polishing and Ar ion milling (Gatan PIPS II model 695) at 3.0 keV under LN₂ cooling. The selected area diffraction patterns (SAD patterns) were analyzed thoroughly using PASAD-tools in the Gatan Digital Micrograph software [17].

For the in-depth analysis on the local atomic structure, high energy X-ray scattering (XRS) was carried out at room temperature at the 6-ID-D beam line of the Advanced Photon Source, Argonne National Laboratory, using monochromatic X-ray beam with the wavelength of 0.123686 Å (corresponding energy of ~100 keV) in transmission mode. A two-dimensional stationary detector comprised of 2048 × 2048 pixels with each pixel size of $200 \,\mu\text{m} \times 200 \,\mu\text{m}$ was employed. Calibration of the beam center, detector tilt angles and the distance between the sample and the detector was carried out using CeO₂ powder. Correction of the dark current and re-binning of the data were performed using FIT2D software [18]. PDFgetX2 software [19] was utilized to generate the pair distribution function, denoted as g(r), from the high energy XRS data by

correcting background contribution and Compton scattering, and subsequently through Fourier transformation. The XRS results were compared with those obtained at the 5A beamline of the Pohang Accelerator Laboratory (PAL) with the wavelength of 0.6927 Å (corresponding energy of \sim 17.8 keV).

Quasi-static nanoindentation was performed using Hysitron TI 750 Triboindenter with a 2 μ m radius conical type indenter at least 100 times for each alloy composition. Maximum indentation force of 8 mN was reached in 40 s, held for 2 s, and was withdrawn in 5 s at constant loading rates. The obtained load versus depth curves were fitted to second degree polynomial equation and were subtracted by the fitted curve to easily distinguish the pop-ins. A MATLAB based code was used to appropriately determine the noise level from the holding time signals that contain the instrumentally generated noise in order to identify the small pop-ins. Further processing was performed to calculate the strain burst sizes of the pop-ins and analyze the distribution characteristics using cumulative probability distribution function.

3. Results

3.1. Alloy design of CZ2 to CZ10

It is well known that the formation zones of bulk metallic glasses (BMGs) and solid-solution phases in multi-component alloys (so-called high-entropy alloy, HEAs) under the factors of the atomic size difference (δ) and the enthalpy of mixing (ΔH_{mix}) are completely opposite. For example, to form BMGs, the alloys should have higher δ and largely negative ΔH_{mix} , which satisfy Inoue's empirical rules for glass formation. However, to form the solid solution, the alloys should have high configuration entropy (S_{conf}), lower δ and not too positive or negative ΔH_{mix} . Thus, to investigate the effect of S_{conf} under the minimization of the effect of δ and ΔH_{mix} in glass-forming alloys, first, we carefully designed a series of equiatomic binary $\mathrm{Cu}_{50}\mathrm{Zr}_{50}$ (CZ2) to denary (CuNiBeCoFe)₅₀(ZrTiHfTaNb)₅₀ (CZ10) alloy. In detail, CZ2 with $D_{\text{max}} = 2 \text{ mm}$ was chosen for the alloy composition with lowest S_{conf} , and then subsequent element additions chemically and topologically similar to Cu, viz., Ni, Be, Co, and Fe, and Zr, viz., Ti, Hf, Ta, and Nb (as shown in Table 1 [20,21] and Fig. S1 in the Supplementary material) were made to this composition whilst maintaining equiatomic ratio to achieve high S_{conf} condition up to denary CZ10. It should be noted that such a substitution strongly affects S_{conf} but only weakly influences $\Delta H_{\rm mix}$ because the $\Delta H_{\rm mix}$ among the constituent and substituting elements is almost zero in each group, allowing us to explore the effect of S_{conf} on GFA.

Fig. 1 shows δ , ΔH_{mix} , and S_{conf} in a series of equiatomic binary CZ2 to denary CZ10. To obtain the values of δ , ΔH_{mix} , and S_{conf} of the alloys, the following equations were used.

$$\delta = \sqrt{\sum x_i \left(1 - \frac{r_i}{\sum x_i r_i}\right)^2} \tag{1}$$

$$\Delta H_{\rm mix} = \sum_{i \neq j} 4\Delta H_{ij}^{\rm mix} x_i x_j \tag{2}$$

$$S_{conf} = -R \sum x_i \ln x_i \tag{3}$$

where x_i is the mole fraction, r_i is the atomic radius of the *i*th element, $\Delta H_{ij}^{\text{mix}}$ is the mixing enthalpy of liquid in *i*th and *j*th binary system and *R* is the universal gas constant. The calculated results are listed in Table 2. As shown in Fig. 1, δ (multiplied by 100 for convenience) and ΔH_{mix} of the alloys are close to each other with the values -11.5 ± 1.3 and -27 ± 5 kJ/mol, respectively, whereas S_{conf} monotonically increases from 5.76 (0.69*R*) J/K mol for CZ2 to 19.14 (2.30*R*) J/K mol for CZ10. Indeed, it can be noted that the series of alloys from CZ2 to CZ10 in this study can allow us to investigate the influence of S_{conf} on the GFA and the mechanical responses under controlled δ and ΔH_{mix} .

Table 1

Mixing enthalpy of binary systems (kJ/mol) and atomic radii (Å) of considered elements in this study. The atomic radii are shown on the diagonal positions.

Element	Cu	Ni	Be	Co	Fe	Zr	Ti	Hf	Та	Nb
Cu	1.28	4	0	6	13	-23	-9	-17	2	3
Ni		1.25	-4	0	-2	-49	-35	-42	-29	-30
Be			1.13	-4	-4	-43	-30	-37	-24	-25
Со				1.25	-1	-41	-28	-35	-24	-25
Fe					1.24	-25	-17	-21	-15	-16
Zr						1.60	0	0	3	4
Ti							1.46	0	1	2
Hf								1.58	3	4
Ta									1.43	0
Nb										1.43



Fig. 1. Graphs showing δ , ΔH_{mix} , and S_{conf} for CZ2 to CZ10. δ and ΔH_{mix} values fall within the range of 11.5 ± 1.3 and 27 ± 5 kJ/mol, respectively.

3.2. Vitrification of CZ2 to CZ10

Since the alloys were designed by substituting the elements from Cu₅₀Zr₅₀ composition with topologically and chemically similar elements following the empirical rules for glass formation, the alloys from CZ2 to CZ10 were expected to exhibit considerable GFA. Fig. 2 shows the XRD traces of the as-spun ribbons of the alloys from CZ2 to CZ10. All XRD traces showed broad diffraction peaks in the 2 theta range of 33-47°, representing a typical amorphous structure. The peak positions are located within 2° deviation even under drastic compositional change from binary CZ2 to denary CZ10. Furthermore, TEM analysis was employed to verify the amorphous nature of the as-spun samples since XRD technique has limitations in examining the presence of crystalline precipitates of small volume fraction, especially those in nanoscale regime. Fig. 3 presents (a) a HRTEM image, (b) SAD pattern (inset: intensity profile) and (c) corresponding fast Fourier transformed (FFT) patterns obtained from as-spun CZ10 ribbon. Despite the alloy being composed of 10 elements in equiatomic ratio, the random atomic arrangement of

Table 2 δ , ΔH_{mix} , and S_{conf} calculated by Eq. (1)–(3) for CZ2 to CZ10.

Alloy notation	δ	$\Delta H_{\rm mix}$ (kJ/mol)	S_{conf} (J/K mol)
CZ2	11.26	-23.00	5.76 (0.69R)
CZ4	10.34	-28.00	11.53 (1.39R)
CZ6	12.77	-31.67	14.89 (1.79R)
CZ8	11.68	-28.44	17.29 (2.08R)
CZ10	11.00	-24.40	19.14 (2.30R)



Fig. 2. XRD patterns obtained from as-spun CZ2 to CZ10 ribbon specimens.

constituent elements in HRTEM image (Fig. 3(a)) and the diffuse halo SAD and FFT patterns (Fig. 3(b) and (c), respectively) strongly demonstrate the formation of fully amorphous structure. In particular, the intensity profile of the electron diffraction processed by PASAD software (inset of Fig. 3(b)) exhibits no sharp peaks related to the presence of distinguishable crystallites even in nanometer scale. It should be noted that the series of alloys from CZ2 to CZ10 in this study can be fabricated as a fully amorphous phase for ribbon specimens, which means that the critical cooling rate for glass formation is under 10^5 K/s.

3.3. GFA evaluation of CZ2 to CZ10

Fig. 4 shows the DSC thermograms of CZ2 to CZ10 MGs indicated with T_g , T_x , and T_l . The measured T_g and T_x show a gradual increase along the series, which reflect on the greater metastable liquid stability and resistance to crystallization, respectively. And an increase in S_{conf} of the alloys from CZ2 to CZ10 leads to a noticeable change in normalized heat exchanges that occur during crystallization, resulting in a significant decrease in peak intensities. However, T_l initially decreases with an increase in S_{conf} from 1258 K for CZ2 to 1107 K for CZ6, and then increases up to 1498 K for CZ10. Consequently, some representative GFA parameters were calculated using the measured characteristic temperatures; reduced glass transition temperature $T_{rg} (= T_g/T_l)$ [22], γ parameter (= $[T_x]/[T_g + T_l]$) [23], and ε parameter (= $[\Delta T_m^i + \Delta T_x + T_x]/T_m^{mix}$, where $\Delta T_m = T_m^{mix} - T_l$, $\Delta T_x = T_x - T_g$ and $T_m^{mix} = \sum_i^n n_i \cdot T_m^i$, with n_i and T_m^i being mole fraction and melting temperature, respectively, of the *i*th component of an n-component alloy) [24]. The characteristic temperatures and the calculated GFA parameters for CZ2 to CZ10 MGs are listed in Table 3. Although the GFA parameters are not the absolute



Fig. 3. (a) HR-TEM image of as-spun CZ10 ribbon. (b) Corresponding selected area diffraction (SAD) pattern. (c) Fast Fourier transformation pattern confirming the non-crystalline nature of the ribbon.



Fig. 4. DSC traces obtained from as-spun CZ2 to CZ10 ribbons. Black, red, and orange arrow heads indicate the T_{g} , T_{x} , and T_{l} , respectively.

measures of GFA, they represent the GFA of the alloys well with reasonable theoretical justification [22–24]. Fig. 5 shows the variation of calculated GFA parameters in the series of CZ2 to CZ10 MGs. As shown in Fig. 5, the parameter values show a steady increase from CZ2 to CZ6, and then decrease to CZ10 (dotted lines). As a matter of fact, the maximum diameters for glass formation of CZ2 and CZ6 were reported to be 2 mm [25] and 15 mm [26], respectively. Furthermore, it was confirmed in this study that CZ10 was not able to vitrify when casted into 1 mm rod specimen using water-cooled copper mold suction casting technique



Fig. 5. A graph showing calculated GFA parameters ($T_{\rm rg}$, γ , and ϵ) for CZ2 to CZ10 MGs.

(not shown). Thus, it can be understood that the trend of GFA and GFA parameter was identified in the series of CZ2 to CZ10. Interestingly, the senary CZ6 with medium S_{conf} exhibits the maximum GFA in the series of alloys, which means that higher S_{conf} by itself is not a sufficient condition for higher GFA. In general, higher S_{conf} is expected to hinder the glass formation due to slower atomic diffusion and increased resistance to crystallization as also stated by the confusion principle [27]. However, as shown in this work, higher S_{conf} does not always lead to the formation of an amorphous phase. This indicates that apart from S_{conf} .

Table 3The characteristic temperatures

The characteristic temperatures $(T_{g}, T_{x}, T_{l} \text{ and } T_{m}^{mix})$, calculated GFA parameters $(T_{rg}, \gamma, \text{ and } \epsilon)$ for CZ2 to CZ10 MGs.

Alloy notation	T_g (K)	T_x (K)	T_l (K)	T_m^{mix} (K)	T_{rg}	γ	ε
CZ2	676	725	1258	1743	0.537	0.375	0.722
CZ4	690	733	1293	1786	0.534	0.370	0.711
CZ6	690	764	1107	1869	0.623	0.425	0.856
CZ8	753	796	1357	2034	0.555	0.377	0.745
CZ10	776	897	1498	2083	0.518	0.394	0.770

there are other factors such as δ and ΔH_{mix} controlling the phase selection in the alloys. Furthermore, in this study, under the minimization of the effect of δ and ΔH_{mix} , it was be evaluated that the characteristic temperature for glass formation, especially T_l , drastically changes depending on the alloy composition. Although T_m^{mix} continuously increases from 1743 K for CZ2 to 2083 K for CZ10, T_l decreases from 1258 K for CZ2 to 1107 K for CZ6 and then increases to 1498 K for CZ10. Therefore, CZ6 exhibits the largest relative decrease of melting temperature ($\Delta T^* = \Delta T_m / T_m^{\text{mix}} = 0.41$) and the highest GFA parameters (T_{rg} , γ and ε parameter), implying the longest onset time for the nose of C curve and consequently has the lowest critical cooling rate in the series of CZ2 to CZ10 [23,24]. As a result, it can be understood that S_{conf} is a crucial design parameter for the glass formation. However, the precise contributions of each design parameter for GFA is still uncertain, which merits further investigation.

3.4. Structural response of CZ2 to CZ10 MGs

The structural stability of MGs with amorphous structure can be quantified by calculating the fragility index (*m*). In general, stronger the liquid (lower *m*), higher is the amorphous stability, which is related to the denser random packed structure and higher GFA [14]. The more fragile MG (higher *m*) will allow local stress concentration to dissipate quickly via formation of multiple shear bands, slowing down and branching the shear band propagation thereby resulting in enhanced ductility. In particular, *m* can be formulated with *v* (Poisson's ratio) and *K/G* (the ratio of bulk and shear moduli) in various glass-forming alloys: $v = -0.179+0.312 \log m$ and $v = 0.22+0.27 \log K/G$ [28].

The dynamic fragility (m_{dyn}) can be formulated as [29]

$$m_{dyn} = \left[d \log x/d \left(T_g/T \right) \right]_{T=T_a},\tag{4}$$

where *x* can be dynamic variables such as viscosity (η) and relaxation time (τ). It is important to note that the m_{dyn} describes the rate of change in the mass transport or relaxation properties such as η , τ and fluidity at T_g [14].

Based on this understanding, we carefully carried out m_{dyn} calculation by analyzing the temperature dependence of τ from CZ2 to CZ10 MGs to more precisely compare the structural change when S_{conf} increases. Fig. 6 shows the variation of T_g as a function of ln Φ for CZ2 to CZ10 MGs (here, Φ =heating rate). By using Vogel–Fulcher–Tammanntype function, the T_g variation depending on Φ can be formulated



Fig. 6. Variation of T_g as a function of ln Φ for CZ2 to CZ10 MGs.

as [30–32]

$$\ln \Phi = \ln A + D \cdot \frac{T_g^0}{T_g^0 - T_g}.$$
(5)

Here, *D* and T_g^0 are obtained from the plot of ln Φ and T_g , respectively [14]. Consequently, the dynamic fragility (m_{dyn}^r) can be formulated as the following equation

$$m_{dyn}^{r} = \left[D \cdot T_{g}^{0} \cdot T_{g} \right] / \left[\ln 10 \left(T_{g} - T_{g}^{0} \right)^{2} \right].$$

$$\tag{6}$$

In Fig. 6, ln A, D and T_g^0 values are listed in their respective alloy color scheme which were obtained by the best fit between ln Φ and T_g using Eq. (5). Here, the m_{dyn}^r values (calculated for T_g measured at $\Phi = 20$ K/min) of CZ2 to CZ10 MGs continuously decrease from 64.5 to 20.9 with an increase in the S_{conf} , which means that CZ10 is a stronger glass than CZ2. As mentioned earlier, it is well known that *m* of a glass-forming liquid is closely linked to a fundamental property of the corresponding glass phase; GFA, Poisson's ratio and elastic moduli (*K/G*) [14]. However, interestingly, the linear trend between *m* and GFA does not hold in the series of CZ2 to CZ10 MGs. Thus, it is necessary to consider why these differences occur in the series of CZ2 to CZ10 MGs by systematically checking other relevant property changes and through detailed structural analysis.

3.5. Nano-indentation test of CZ2 to CZ10 MGs

During nanoindentation test, plastic shearing can be stabilized due to the confinement from the surrounding material even in extremely brittle MGs without any compressive plasticity. This behavior is very useful for the analysis of the characteristics of the intermittent shear avalanches (=pop-in events) during deformation in most MGs [33]. Fig. 7 shows the load versus displacement curves of as-spun CZ2 to CZ10 ribbons measured by nanoindentation test. The results show a systematic decrease in the maximum depths along the series from the binary CZ2 MG to the denary CZ10 MG. The overall trend of the nanohardness and the reduced Young's modulus (E_r) of the series from CZ2 to CZ10 is shown to increase from 7.1 ± 0.2 to 10.8 ± 0.3 GPa and from 89.4 ± 1.0 to 109.9 ± 2.5 GPa, respectively. For MGs, the Vicker's hardness (H_{ν}) and the Young's modulus (E) are reported to be directly correlated



Fig. 7. Load and displacement curves for CZ2 to CZ10 MGs. A table below lists the nanohardness and the E_r , respectively.



Fig. 8. A graph showing nanohardness and E_r for CZ2 to CZ10 MGs. The arrows indicate the direction and magnitude of change in property value with respect to the preceding MG enclosed within the boxes.

 $(H_v = E/20)$ [34]. However, a close examination of the values reveals an anomaly variation, which can clearly be observed by comparing the values of CZ4 and CZ6 MGs as well as CZ8 and CZ10 MGs. Fig. 8 shows the nanohardness and E_r of as-spun CZ2 to CZ10 ribbons measured by nanoindentation tests. To help visualize the differences in the tendency of the nanohardness and E_r , dotted lines and arrows were drawn in Fig. 8. The arrows indicate the direction and magnitude of change in property value with respect to the MGs enclosed within the boxes. The nanohardness shows a monotonic increment pattern, whereas E_r exhibits alternating pattern with relative increment ($\Delta E_r^{CZ4-CZ2} = 15.2$ GPa and $\Delta E_r^{CZ8-CZ6} = 14$ GPa) and decrement($\Delta E_r^{CZ6-CZ4} = -5.4$ GPa and $\Delta E_r^{CZ10-CZ8} = -3.3$ GPa) occurring consecutively. Thus, it can be recognized that like GFA, the linear trend between *m* and elastic moduli does not apply to the investigated alloys. A detailed analysis of anomalous moduli variation will be discussed in Section 4.2.

4. Discussion

4.1. Influence of configuration entropy on the atomic-level structure

Using molecular dynamics simulations, it was demonstrated that the different atomic correlations of atomic packing motifs/clusters in amorphous structure can be characterized by the second peak of the pair distribution function (PDF) curve in MGs as well as in liquids [35]. In general, a PDF plot shows the distribution profile around a central atom. However, by normalizing the x-axis by r_1 (first peak position or average bond length), we can get the relative distribution profile that can give us the information regarding the atomic-level structure. According to Ding et al. [35], specific r/r_1 ratios, $\sqrt{4}$, $\sqrt{3}$, $\sqrt{8/3}$, and $\sqrt{2}$, represent the most probable relative distance between two second-nearestneighboring atoms in g(r) and those values correspond to 1, 2, 3, and 4 atom-connection of polyhedra, respectively. Through atomic-level structure simulation techniques, g(r) can clearly be decomposed for each of the atomic-connection types. However, such simulation is difficult to be applied in this study due to the multicomponent nature of the alloys. Thus, we try to obtain g(r) from the total structure factor, S(Q) (Fig. S2 in the Supplementary material) measured through high energy X-ray scattering (XRS) study.

g(r) can be obtained by the Fourier transformation [36]

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho_0} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dQ$$
(7)

where ρ_0 is the average atomic number density. Fig. 9(a) shows the g(r) normalized by r_1 of respective CZ2 to CZ10 MGs obtained from high



Fig. 9. (a) A plot of g(r) normalized by the first peak position (r_1) for CZ2 to CZ10 MGs. The r/r_1 values $\sqrt{4}$, $\sqrt{3}$, and $\sqrt{8/3}$ represent the 1, 2, and 3 atom-connection of clusters, respectively. (b) Schematic diagram of binary and denary MGs indicating the probabilities of dissimilar constituent element atom occupying neighboring atomic position giving rise to severe local compositional complexity.

energy XRS at the 6-ID-D beam line of the Advanced Photon Source, Argonne National Laboratory. Fig. S3 in the Supplementary material shows g(r) normalized by r_1 of respective alloys obtained at the 5A beamline of PAL, which exhibits similarity to those in Fig. 9(a). The detailed data processing method for the pair distribution function, g(r) are described elsewhere [36–38].

As shown in Fig. 9(a), the normalized PDF curves corresponding to CZ2 and CZ4 MGs are very similar with each other and the highest position of the second peaks seem close to $\sqrt{3}$ (related to the 2 atom-connection by sharing the edge of polyhedra). However, with an increase in $S_{conf},$ the position systematically shifts towards $\sqrt{8/3}$ (related to the 3 atom-connection by sharing a face of polyhedra) and clearly separates to two sub-peaks from CZ6 to CZ10 MGs. Although the exact atomic-level structure and the fractions for each of the atomic-connections cannot be evaluated from Fig. 9(a), the nearidentical curves might suggest a similar overall atomic-level structure of the corresponding MGs and the shift of the second peak might suggest an increased fraction of 3 atom-connection for the MGs with higher S_{conf} . In other words, two neighboring coordination polyhedra in MGs with higher S_{conf} prefer to connect to each other through face rather than edge connection. Thus, the examined MGs can be classified into three groups by main atomic-connection of polyhedra, 2-1 atom connections for CZ2 and CZ4, 3-2 atom connections for CZ6 and CZ8, and 3-1 atom connections for CZ10. In particular, it should be noted that the increased fraction of 3-atom connections in CZ10 MG causes a large deviation of polyhedra connectivity, which is related to the severe local structural irregularity in the degree of disorder. On another note, the short-range order in amorphous structure has also been identified via the common coordination polyhedra (so-called atomic packing motifs/clusters) constituted by a center atom with surrounding neighboring atoms [35,39–41].

Since the distance corresponding to the second peak in the PDF curve of MGs is just beyond a layer above the packing of atoms in the nearest neighbor shell constituting the cluster, the second-nearest neighbor correlations might be a useful departure point for the characterization of medium-range order in amorphous structure, which is closely related to the local structural stability of an amorphous phase. Fig. 9(b) schematically shows the high S_{conf} condition developed through the addition of principal elements in the present study that would give rise to a severe local compositional complexity because of the higher probability of different element atom occupying a neighboring position (probability (P) of 1/2 for a binary system, and P of 9/10 for a denary system as shown in Fig. S4 in the Supplementary material) even though the atoms exhibit similar δ and ΔH_{mix} . This in turn could severely distort the atomic clusters owing to different chemical nature and bond lengths, possibly restricting the connection of more atomic clusters with severe deviation of polyhedra connections, which can be identified with a distinct separation of second sub-peak in Fig. 9(a). Thus, it can be understood that the more severe local compositional complexity as well as structural irregularity in MGs with higher S_{conf} enhances the local structural instability via distortion of the atomic clusters.

4.2. Anomalous moduli variation of HE-MG

Mechanical response is one of the efficient ways to understand the structural changes in glass-forming alloys qualitatively [14]. In order to better understand the anomalous results in Section 3.5, the Young's moduli of the MGs were calculated using the equation proposed by Wang [42],

$$\frac{1}{M} = \sum \left(f_i \cdot \frac{1}{M_i} \right) \tag{8}$$

where *M* is the elastic constant of the MG, f_i is the fraction of element *i*, and M_i is the elastic constant of the element *i* [43]. The calculated moduli (*E* and *G*) and measured *E* are listed in Table 4. To further scrutinize the difference between the experimental and the calculated elastic moduli, E_r was converted to *E* using the relation given below [44],

$$\frac{1}{E_r} = \frac{(1-v^2)}{E} + \frac{(1-v_i^2)}{E_i}$$
(9)

where E_i is the *E* of the indenter, v_i is the *v* of the indenter. Since a diamond indenter was used, the values of E_i and v_i were taken as 1141 GPa and 0.07, respectively. The conversion was done by considering the Poisson's ratio of the MGs as 0.34, an average value of 83 compositions from the supplementary of Ref. [45], except for CZ2 MG whose Poisson's ratio was already reported as 0.36 [42]. The converted *E* values from measured E_r are also listed in Table 4 as measured *E*.

Fig. 10(a) shows the variation of calculated moduli (*E* and *G*) for CZ2 to CZ10. First, it can be noticed that the variation of calculated moduli is similar with that of the measured moduli in Fig. 8. Furthermore, the tendency of outward increment is similar to that of the nanohardness, i.e., the calculated Young's moduli and shear moduli monotonically increase. Since the overall property of the MGs is primarily influenced by the constituent elements, the enhancement of nanohardness and Young's modulus in the examined MGs with higher S_{conf} seems reasonable due to the substitution of pre-constituent elements with elements possessing better inherent mechanical properties. However, as shown in Fig. 10(b),



Fig. 10. Plots showing (a) calculated *G* and *E*, and (b) calculated and measured *E* for CZ2 to CZ10 MGs. The arrows indicate the direction and magnitude of change in property value with respect to the preceding MG enclosed within the boxes. In (b), the grey dotted and the solid lines represent the linear fits of the calculated and measured *E*, respectively.

the difference between the calculated and the measured *E* values for CZ2 MG is 5.0 ± 1.0 GPa, which keeps increasing up to 22.8 ± 2.7 GPa for CZ10 MG. In other words, as S_{conf} of the system increases in the series of CZ2 to CZ10 MGs, the alloy with higher S_{conf} seems to exhibit lower Young's modulus values compared to the predicted values which have been derived solely from the elemental modulus values. Eq. (8) is based on the previous observation that the elastic properties of MGs are correlated to the weighted average of the elastic constants of the constituent elements [34,46,47]. The deviation of the calculated and the measured E in high-entropy MGs (HE-MGs) implies the loss of the inheritance in HE-MGs, which could be an inevitable effect of MGs with high S_{conf} . Two approaches are conceivable for explaining the deviation of moduli of HE-MGs. First, the total number of the bonds between the same elements may decrease with increasing S_{conf} . As schematically described in Fig. S4, a bonding forms between two atoms, and the fraction of the like-like atom bonding (such as A-A, B-B) is inversely proportional to the number of principal elements (and hence, S_{conf}). For example,

Table 4 Calculated moduli (*E* and *G*), measured $E_r \kappa$, and S_e for CZ2 to CZ10 MGs.

Alloy notation	Calculated <i>E</i> (GPa)	Calculated G (GPa)	Measured E (GPa)	к	S _c
CZ2	89.3	39.1	84.3 ± 1.0	1.46	0.0202
CZ4	111.1	46.0	101.8 ± 1.4	1.48	0.0254
CZ6	114.4	46.8	96.1 ± 7.0	1.45	0.0419
CZ8	128.0	51.4	111.2 ± 9.4	1.36	0.0390
CZ10	130.3	51.5	107.5 ± 2.7	1.55	0.0625



Fig. 11. (a), (c), and (e) the correlation between subtracted depth ($\Delta h_s = h_{exp} - h_{fit}$) and depth (*h*) for single indentation test of CZ2, CZ6 and CZ10 MGs, respectively. (b), (d), and (f) the correlation between pop-in size (Δh) and depth (*h*) for the series of nanoindentation test of CZ2, CZ6 and CZ10 MGs, respectively.

the portion of the like-like atom bonding in Fig. S4 is only 10% in the equiatomic denary MG, while it is 50% in the equiatomic binary MG. It is well known that the solvent-solvent bonded cluster, here like-like atom bonded cluster, provides the weakest junction in MGs, where the elastic deformation mainly occurs [46,48], which is the physical origin of the inheritance of mechanical properties mentioned above (Eq. (8)). This means that the portion of like-like atom bonded cluster for the inheritance decreases with increasing S_{conf} , which may lead to the deviation in Fig. 10(b). Therefore, although the overall property may follow the trend of the constituent elements, HE-MGs may exhibit anomalous properties due to the loss of inheritance. Second, Cheng and Ma [49] have shown that the elastic modulus of MGs depends sensitively on the internal amorphous structure, which is strongly influenced by the degree of local structural ordering. In the reference, higher S_{conf} condition (achieved via faster cooling rate) locally decreases the fraction and connectivity of icosahedra, ultimately lowering the shear modulus. Hence, it can be understood that the anomalous moduli variation occurs with increasing S_{conf} , especially in HE-MGs due to the aforementioned enhanced distortion of the atomic clusters.

4.3. Abnormal deformation dynamics of HE-MGs

Similar to the slip avalanche in crystalline materials [50], shear banding behavior leads to an intermittent shear avalanche phenomenon in MGs which is related to the elastic properties [51] and the inhomogeneities [47] in MGs. Shear bands initiate and propagate by elastic coupling of shear transformation zones (STZs) that correspond to the spatio-temporally occurring shear avalanches [52], ultimately generating the pop-ins. It has been reported in other previous studies [52–56] that the characterization of plastic deformation can be achieved by statistical analysis of the strain burst sizes (S). Under nanoindentation test, strain bursts (= pop-in events) can occur by constrained shear localization within the self-organized criticality (SOC) or the formation of shear bands beyond SOC [57]. The former events (=smaller pop-ins) follow the power-law distribution, whereas the latter events (=larger pop-ins) generate the truncation, when we plot the cumulative probability distribution of strain burst sizes (P(>S)) [56]. Thus, it can be noticed that P(>S) in MGs has been described by a truncated power-law function, and explained by means of the formation and percolation of deformation units during deformation [52-56]. Inspired by these investigations, statistical analysis of shear avalanches has been carried out with pop-ins collected from the processed nanoindentation data to observe the changes in the characteristic behavior of CZ2 to CZ10 MGs. For the data processing, we first eliminated the effect of addition generated from the increment of indentation depth (*h*) in the pop-in events by subtraction of the baseline, which can be obtained by fitting the loaddisplacement curves using a second degree polynomial function. As a result, the pop-in size (Δh) reflects the depth drop of shear band formation and propagation. Fig. 11(a), (c) and (e) shows the correlation between the subtracted depth ($\Delta h_s = h_{exp} - h_{fit}$) and h for single indentation of CZ2, CZ6 and CZ10 MGs, respectively. The results indicate a simultaneous occurrence of reduction in the number and the increment in the magnitude of Δh for a single indentation performed as the MGs possess higher S_{conf} . In corollary, the increasing Δh occurring over a wide range of depths along the series can easily be seen by comparing the Δh versus h plots for multiple indentations in Fig. 11(b), (d), and (f). This change in the mechanical response is due to the transition from unjamming to jamming state of concordant regions in this series of MGs.

After the calculation of strain burst sizes ($S = \Delta h/h$), P(>S) was used to fit the distribution to the following empirical relation [53],

$$P(>S) = AS^{-(\kappa-1)} \exp\left(-\left(S/S_c\right)^2\right)$$
(10)

where S_c is the cut-off strain burst size, κ is a scaling exponent, and A is a normalization constant. Fig. 12 shows P(>S) for CZ2 to CZ10 MGs along with the correspondingly colored power-law fitted solid lines and S_c indicated by the arrow heads, which exhibit power-law scaling behavior



Fig. 12. Cumulative probability distributions of strain burst sizes of the CZ2 to CZ10 MGs. Solid scattering points represent experimental results measured from the nanoindentation and solid lines are the fitting curves by Eq. (10). The arrow heads mark the corresponding S_{c} .

within SOC, and truncation beyond SOC. The aspects of SOC transition have been statistically characterized by truncated power-law equations and/or maximum-likelihood exponent methods [58,59]. Table 4 lists κ and S_c values of CZ2 to CZ10 MGs. It was reported that a system that exhibits SOC behavior more dominantly will possess larger S_c . On the contrary, a system that shows relatively chaotic shear avalanche behavior possesses smaller S_c . As it can be observed, S_c steadily increases in the series of CZ2 to CZ10 MGs from 0.0202 for CZ2 MG, to 0.0419 for CZ6 MG, and finally to 0.0625 for CZ10 MG, indicating relative chaotic to SOC behavior transition with increasing S_{conf} . It should be noted that the cluster connections by face-sharing, 3 atom-connection of cluster polyhedra show the stiffest elastic response during deformation [35]. Thus, the S_c variation from CZ2 to CZ10 can be reasonably understood by the atomic-level structure variation.

Fig. 13(a)-(e) shows the histograms obtained from the nanoindentation tests in the series of the MGs (a) CZ2, (b) CZ4, (c) CZ6, (d) CZ8, and (d) CZ10. The dotted lines signify the respective S_c whereas the solid curves represent the strain burst size distribution profiles obtained from the power-law fittings. It can clearly be understood that the large strain burst sizes occur for HE-MGs which coincide well with the higher S_c values. Furthermore, the analogous slip avalanche behavior of (CZ2, CZ4) and (CZ6, CZ8) and the subsequent small difference of corresponding S_c values ($\Delta S_{-CZ4-CZ2}^{CZ4-CZ2} = 0.0052$ and $\Delta S_{-CZ6}^{CZ8-CZ6} = -0.0029$) could be caused by the similarity of the overall atomic-level structure as shown in normalized g(r) of Fig. 9(a). Fig. 13(f) shows κ and S_c values obtained from the fitting of cumulative probability distribution using Eq. (10). The κ values are within the range of 1.46±0.1, which are close to the mean field value of 1.5 [60], an evidence of randomly packed amorphous state. Previous studies reported higher S_c values for harder MGs [14,52]. This is reasonable since harder MGs are able to withstand harsher stress condition and maintain the SOC behavior, resulting in higher S_c values. Indeed, even in this work, harder MGs showed higher S_c values as reported. However, considering the similar overall atomic-level structure of CZ2 and CZ4 MGs and CZ6 and CZ8 MGs and the relatively large difference in nanohardness between them (Δ nanoharndess^{CZ4-CZ2} = 1.7 GPa and Δ nanoharndess^{CZ8-CZ6} = 1.7 GPa), the change in S_c is abnormally small, indicating a low rate of increment of S_c . In detail, the severe local structural irregularity and the compositional complexity in MG with higher S_{conf} seems to influence the S_c , by promoting the manifestation of relatively chaotic behavior due to the aforementioned enhanced distortion of the atomic clusters, which results in the unexpected local softening by weakened jammed state of STZs, and ultimately modulating the



Fig. 13. (a)–(e) histograms collected from the series of nanoindentation test with the MGs (a) CZ2, (b) CZ4, (c) CZ6, (d) CZ8, and (d) CZ10. The bin size for *S* in histogram is 10^{-3} . (f) κ and S_c values obtained from the fitting of cumulative probability distribution using Eq. (10). The κ values are within the range of 1.46±0.1, which are close to the mean field value of 1.5.

response towards ductile mechanical deformation. Thus, an effective alloy design utilizing the influence of S_{conf} to tune the properties could be applied to develop MGs possessing adequate GFA and considerable ductility, which merits further investigation for identifying more precise contribution of each term.

5. Conclusions

Our study highlights the influence of S_{conf} on mechanical responses as well as GFA in a series of equiatomic binary CZ2 to denary CZ10 MGs under minimization of the effect of δ and ΔH_{mix} . The higher S_{conf} in this study causes improved overall amorphous phase stability (increased fraction of 3-atom connections in cluster polyhedral and lower *m*), but, simultaneously, increased the severe local structural instability (increased deviation of polyhedra connectivity and decreased likelike atom bonding probability), which results in anomalous GFA and mechanical responses (elastic moduli and deformation dynamics). First, the senary CZ6 with medium S_{conf} of 1.79R exhibits maximum GFA in CZ2 to CZ10, which means that higher S_{conf} by itself is not a sufficient condition for higher GFA, although it might be a major design parameter according to the confusion principle. CZ6 exhibits the largest relative decrease of melting temperature ($\Delta T^* = 0.41$) and highest GFA parameters ($T_{rg} = 0.623$, $\gamma = 0.425$ and $\varepsilon = 0.856$), which is related to the longest onset time for the nose of C curve and consequently has the lowest critical cooling rate within the series of investigated MGs. Second, the overall trend of nanohardness and *E* from CZ2 to CZ10 MGs is shown to outwardly increase which is dominantly due to the increased 3-atom connections of cluster polyhedra as well as lower *m*. However, if we carefully analyze, the linear trend between *m* and elastic moduli does not apply in CZ2 to CZ10 MGs, i.e., the increment and decrement

alternate for the values of E_r and lowering of measured E with widening deviation from calculated E occur. In particular, considering the similar overall atomic-level structure of CZ2 and CZ4 MGs and CZ6 and CZ8 MGs and the relatively large difference in nanohardness between them (about 1.7 GPa), the change in S_c is abnormally small, indicating a low rate of increment of S_c . These results help us conclude that the severe local compositional complexity (calculated by like-like atom bonding probability) and the structural irregularity (observed by increased deviation of polyhedra connectivity) in MGs with higher S_{conf} promotes the manifestation of relatively chaotic behavior as well as the loss of MG's property inheritance, which results in the unexpected local softening of amorphous phase, and ultimately modulating the response towards ductile deformation. Hence, it can be concluded that S_{conf} could be one of the crucial factors that should be considered while designing an MG in order to tune the vital properties for engineering applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that support the findings of this study are available from Prof. Park (email: espark@snu.ac.kr) upon reasonable request.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (Ministry of Science, ICT and Future Planning) (No. NRF-2018M3A7B8060601). One of the authors (E.S. Park) also benefited from the Center for Iron and Steel Research (RIAM) and Institute of Engineering Research at Seoul National University. Part of this research used resources of the Advanced Photon Source, operated for the DOE Office of Science by Argonne National Laboratory under contract No. DE-AC02-06CH11357 and Pohang Light Source (X-ray scattering measurements at the 5A beamline) in Pohang Accelerator Laboratory, Korea.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mtla.2019.100505.

References

- [1] D.C. Hofmann, J.-Y. Suh, A. Wiest, G. Duan, M.-L. Lind, M.D. Demetriou, W.L. Johnson, Designing metallic glass matrix composites with high toughness and tensile ductility, Nature 451 (7182) (2008) 1085.
- [2] H. Guo, P. Yan, Y. Wang, J. Tan, Z. Zhang, M. Sui, E. Ma, Tensile ductility and necking of metallic glass, Nat. Mater. 6 (10) (2007) 735.
- [3] J. Das, M.B. Tang, K.B. Kim, R. Theissmann, F. Baier, W.H. Wang, J. Eckert, "Work-hardenable" ductile bulk metallic glass, Phys. Rev. Lett. 94 (20) (2005) 205501.
- [4] Y. Wu, Y. Xiao, G. Chen, C.T. Liu, Z. Lu, Bulk metallic glass composites with transformation-mediated work-hardening and ductility, Adv. Mater. 22 (25) (2010) 2770–2773.
- [5] J. Shen, Q. Chen, J. Sun, H. Fan, G. Wang, Exceptionally high glass-forming ability of an FeCoCrMoCBY alloy, Appl. Phys. Lett. 86 (15) (2005) 151907.
- [6] P. Jia, H. Guo, Y. Li, J. Xu, E. Ma, A new Cu–Hf–Al ternary bulk metallic glass with high glass forming ability and ductility, Scr. Mater. 54 (12) (2006) 2165–2168.
- [7] J. Qiao, H. Jia, P.K. Liaw, Metallic glass matrix composites, Mater. Sci. Eng.: R: Rep. 100 (2016) 1–69.
- [8] J.J. Kruzic, Bulk metallic glasses as structural materials: a review, Adv. Eng. Mater. 18 (8) (2016) 1308–1331.
- [9] M.M. Khan, A. Nemati, Z.U. Rahman, U.H. Shah, H. Asgar, W. Haider, Recent advancements in bulk metallic glasses and their applications: a review, Crit. Rev. Solid State Mater. Sci. 43 (3) (2018) 233–268.
- [10] Y. He, R. Schwarz, J. Archuleta, Bulk glass formation in the Pd–Ni–P system, Appl. Phys. Lett. 69 (13) (1996) 1861–1863.

- [11] A. Takeuchi, N. Chen, T. Wada, Y. Yokoyama, H. Kato, A. Inoue, J. Yeh, Pd20Pt20Cu20Ni20P20 high-entropy alloy as a bulk metallic glass in the centimeter, Intermetallics 19 (10) (2011) 1546–1554.
- [12] Y. Tong, J. Qiao, C. Zhang, J.-M. Pelletier, Y. Yao, Mechanical properties of Ti16. 7Zr16. 7Hf16. 7Cu16. 7Ni16. 7Be16. 7 high-entropy bulk metallic glass, J. Non Crvst. Solids 452 (2016) 57–61.
- [13] M. Yang, X. Liu, H. Ruan, Y. Wu, H. Wang, Z. Lu, High thermal stability and sluggish crystallization kinetics of high-entropy bulk metallic glasses, J. Appl. Phys. 119 (24) (2016) 245112.
- [14] J.Y. Kim, H.S. Oh, J. Kim, C.W. Ryu, G.W. Lee, H.J. Chang, E.S. Park, Utilization of high entropy alloy characteristics in Er–Gd–Y–Al–Co high entropy bulk metallic glass, Acta Mater. 155 (2018) 350–361.
- [15] T. Qi, Y. Li, A. Takeuchi, G. Xie, H. Miao, W. Zhang, Soft magnetic Fe25Co25Ni25 (B, Si) 25 high entropy bulk metallic glasses, Intermetallics 66 (2015) 8–12.
- [16] H. Li, X. Xie, K. Zhao, Y. Wang, Y. Zheng, W. Wang, L. Qin, In vitro and in vivo studies on biodegradable CaMgZnSrYb high-entropy bulk metallic glass, Acta Biomater. 9 (10) (2013) 8561–8573.
- [17] C. Gammer, C. Mangler, C. Rentenberger, H. Karnthaler, Quantitative local profile analysis of nanomaterials by electron diffraction, Scr. Mater. 63 (3) (2010) 312–315.
- [18] A. Hammersley, S. Svensson, A. Thompson, Calibration and correction of spatial distortions in 2D detector systems, nuclear instruments methods in physics research section A: accelerators, spectrometers, Detect. Assoc. Equip. 346 (1–2) (1994) 312–321.
- [19] X. Qiu, J.W. Thompson, S.J. Billinge, PDFgetX2: a GUI-driven program to obtain the pair distribution function from X-ray powder diffraction data, J. Appl. Crystallogr. 37 (4) (2004) 678.
- [20] O. Senkov, D. Miracle, Effect of the atomic size distribution on glass forming ability of amorphous metallic alloys, Mater. Res. Bull. 36 (12) (2001) 2183–2198.
- [21] A. Takeuchi, A. Inoue, Classification of bulk metallic glasses by atomic size difference, heat of mixing and period of constituent elements and its application to characterization of the main alloying element, Mater. Trans. 46 (12) (2005) 2817–2829.
- [22] D. Turnbull, Under what conditions can a glass be formed? Contemp. Phys. 10 (5) (1969) 473–488.
- [23] Z. Lu, C. Liu, A new glass-forming ability criterion for bulk metallic glasses, Acta Mater. 50 (13) (2002) 3501–3512.
- [24] E.S. Park, C.W. Ryu, W.T. Kim, D.H. Kim, A novel parameter to describe the glassforming ability of alloys, J. Appl. Phys. 118 (6) (2015) 064902.
- [25] W. Wang, J. Lewandowski, A. Greer, Understanding the glass-forming ability of Cu 50 Zr 50 alloys in terms of a metastable eutectic, J. Mater. Res. 20 (9) (2005) 2307–2313.
- [26] H. Ding, Y. Shao, P. Gong, J. Li, K. Yao, A senary tizrhfcunibe high entropy bulk metallic glass with large glass-forming ability, Mater. Lett. 125 (2014) 151–153.
- [27] W.H. Wang, High-Entropy metallic glasses, JOM 66 (10) (2014) 2067–2077.
- [28] E.S. Park, J.H. Na, D.H. Kim, Correlation between fragility and glass-forming ability/plasticity in metallic glass-forming alloys, Appl. Phys. Lett. 91 (3) (2007) 031907.
- [29] L. Shadowspeaker, R. Busch, On the fragility of Nb–Ni-based and Zr-based bulk metallic glasses, Appl. Phys. Lett. 85 (13) (2004) 2508–2510.
- [30] C.A. Angell, Perspective on the glass transition, J. Phys. Chem. Solids 49 (8) (1988) 863–871.
- [31] D.V. Louzguine, S. Sobu, A. Inoue, The influence of scandium in effecting fragile to strong glass transition in aluminium-based alloys, Appl. Phys. Lett. 85 (17) (2004) 3758–3759.
- [32] R. Busch, E. Bakke, W. Johnson, Viscosity of the supercooled liquid and relaxation at the glass transition of the Zr46. 75Ti8. 25Cu7. 5Ni10Be27. 5 bulk metallic glass forming alloy, Acta Mater. 46 (13) (1998) 4725–4732.
- [33] J.I. Lee, J.W. Kim, H.S. Oh, J.S. Park, E.S. Park, Abnormal devitrification behavior and mechanical response of cold-rolled Mg-rich Mg–Cu–Gd metallic glasses, Acta Mater. 116 (2016) 238–249.
- [34] W. Wang, Elastic moduli and behaviors of metallic glasses, J. Non Cryst. Solids 351 (16–17) (2005) 1481–1485.
- [35] J. Ding, E. Ma, M. Asta, R.O. Ritchie, Second-nearest-neighbor correlations from connection of atomic packing motifs in metallic glasses and liquids, Sci. Rep. 5 (2015) 17429.
- [36] T. Egami, Atomic correlations in non-periodic matter, materials transactions, JIM 31 (3) (1990) 163–176.
- [37] B. Warren, H. Krutter, O. Morningstar, Fourier analysis of X-Ray patterns of vitreous SiO₂ and B₂O₂, J. Am. Ceram. Soc. 19 (1–12) (1936) 202–206.
- [38] W.-H. Wang, Q. Wei, S. Friedrich, Microstructure, decomposition, and crystallization in Zr 41 Ti 14 Cu 12.5 Ni 10 Be 22.5 bulk metallic glass, Phys. Rev. B 57 (14) (1998) 8211.
- [39] F.T. Frank, J. Kasper, Complex alloy structures regarded as sphere packings. I. Definitions and basic principles, Acta Crystallogr. 11 (3) (1958) 184–190.
- [40] S. Pan, J. Qin, W. Wang, T. Gu, Origin of splitting of the second peak in the pair-distribution function for metallic glasses, Phys. Rev. B 84 (9) (2011) 092201.
- [41] S.-P. Pan, S.-D. Feng, J.-W. Qiao, W.-M. Wang, J.-Y. Qin, Crystallization pathways of liquid-bcc transition for a model iron by fast quenching, Sci. Rep. 5 (2015) 16956.
 [42] W.H. Wang, Correlations between elastic moduli and properties in bulk metallic
- [42] W.H. Wang, Correlations between elastic moduli and properties in bulk metallity glasses, J. Appl. Phys. 99 (9) (2006) 093506.
- [43] WebElements. https://www.webelements.com, (accessed June.2018).
- [44] W.C. Oliver, G.M. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, J. Mater. Res. 7 (6) (1992) 1564–1583.

- [45] S.Y. Kim, H.S. Oh, E.S. Park, A hidden variable in shear transformation zone volume versus Poisson's ratio relation in metallic glasses, APL Mater. 5 (10) (2017) 106105.
- [46] D. Ma, A.D. Stoica, X.L. Wang, Z.P. Lu, B. Clausen, D.W. Brown, Elastic moduli inheritance and the weakest link in bulk metallic glasses, Phys. Rev. Lett. 108 (8) (2012) 085501.
- [47] W.H. Wang, The elastic properties, elastic models and elastic perspectives of metallic glasses, Prog. Mater. Sci. 57 (3) (2012) 487–656.
- [48] W.H. Wang, Metallic glasses: family traits, Nat. Mater. 11 (4) (2012) 275.
- [49] Y. Cheng, E. Ma, Configurational dependence of elastic modulus of metallic glass, Phys. Rev. B 80 (6) (2009) 064104.
- [50] M. Zaiser, P. Moretti, Experiment, fluctuation phenomena in crystal plasticity—a continuum model, J. Stat. Mech.: Theory 2005 (08) (2005) P08004.
- [51] J. Ye, J. Lu, C. Liu, Q. Wang, Y. Yang, Atomistic free-volume zones and inelastic deformation of metallic glasses, Nat. Mater. 9 (8) (2010) 619.
- [52] X. Bian, G. Wang, K. Chan, J. Ren, Y. Gao, Q. Zhai, Shear avalanches in metallic glasses under nanoindentation: deformation units and rate dependent strain burst cut-off, Appl. Phys. Lett. 103 (10) (2013) 101907.
- [53] X. Bian, G. Wang, H. Chen, L. Yan, J. Wang, Q. Wang, P. Hu, J. Ren, K. Chan, N. Zheng, Manipulation of free volumes in a metallic glass through Xe-ion irradiation, Acta Mater. 106 (2016) 66–77.

- [54] J.W. Kim, H.S. Oh, W. Kim, P.-P. Choi, D. Raabe, E.S. Park, Modulation of plastic flow in metallic glasses via nanoscale networks of chemical heterogeneities, Acta Mater. 140 (2017) 116–129.
- [55] W. Kim, H.S. Oh, E.S. Park, Manipulation of thermal and mechanical stability by addition of multiple equiatomic rare-earth elements in Al-Tm-Re metallic glasses, Intermetallics 91 (2017) 8–15.
- [56] T.G. Park, S.Y. Kim, H.S. Ahn, H.S. Oh, D.H. Kim, H.J. Chang, E.S. Park, Tuning correlative atomic scale fluctuation and related properties in Ni–Nb–Zr metallic glasses, Acta Mater. 173 (2019) 52–60.
- [57] Y. Cheng, E. Ma, Intrinsic shear strength of metallic glass, Acta Mater. 59 (4) (2011) 1800–1807.
- [58] Y. Zhang, J.P. Liu, S.Y. Chen, X. Xie, P.K. Liaw, K.A. Dahmen, J.W. Qiao, Y.L. Wang, Serration and noise behaviors in materials, Prog Mater. Sci. 90 (2017) 358–460.
- [59] E.K. Salje, A. Planes, E. Vives, Analysis of crackling noise using the maximum-likelihood method: power-law mixing and exponential damping, Phys. Rev. E 96 (4) (2017) 042122.
- [60] J. Antonaglia, X. Xie, G. Schwarz, M. Wraith, J. Qiao, Y. Zhang, P.K. Liaw, J.T. Uhl, K.A. Dahmen, Tuned critical avalanche scaling in bulk metallic glasses, Sci. Rep. 4 (2014) 4382.