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Tailored gradient nanocrystallization in bulk metallic glass via ultrasonic vibrations

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ABSTRACT

To advance materials with superior performance, the construction of gradient structures has emerged as a promising strategy. In this study, a gradient nanocrystalline-amorphous structure was induced in Zr₄₆Cu₄₆Al₈ bulk metallic glass (BMG) through ultrasonic vibration (UV) treatment. Applying a 20 kHz ultrasonic cyclic loading in the elastic regime, controllable gradient structures with varying crystallized volume fractions can be achieved in less than 2 s by adjusting the input UV energy. In contrast to traditional methods of inducing structural gradients in BMGs, this novel approach offers distinct advantages: it is exceptionally rapid, requires minimal stress, and allows for easy tuning of the extent of structural gradients through precise adjustment of processing parameters. Nanoindentation tests reveal higher hardness near the struck surface, attributed to a greater degree of nanocrystal formation, which gradually diminishes with depth. As a result of the gradient dispersion of nanocrystals, an increased plasticity was found after UV treatment, characterized by the formation of multiple shear bands. Microstructural investigations suggest that UV-induced nanocrystallization originates from local atomic rearrangements in phase-separated Cu-rich regions with high diffusional mobility. Our study underscores the tunability of structural gradients and corresponding performance improvements in BMGs through ultrasonic energy modulation, offering valuable insights for designing advanced metallic materials with tailored mechanical properties.

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1. Introduction

Bulk metallic glasses (BMGs) show attractive properties such as high elastic strain limit, giant yield stress, and excellent corrosion resistance far exceeding those of conventional crystalline alloys [1–3]. While these exceptional properties in BMGs originate from their amorphous nature, the structural long-range disorder in BMGs also yields low fracture toughness, poor compressive plasticity and near-zero tensile ductility at ambient temperatures due to the strain softening and localized plastic flow in shear bands [4,5]. And this is the main obstacle in the way of utilization of BMGs as structural materials [6,7].

One practical strategy to mitigate the brittle failure of BMGs involves fine-tuning of their structure through thermomechanical

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processing (TMP) [8]. When subjected to mechanical [9,10] or thermal [11–13] treatments, the BMG can undergo a rejuvenation process, transitioning to higher energy (less-relaxed) states. This augmented free volume content in the rejuvenated BMG promotes shear band operation, thereby enhancing overall plasticity. Conversely, TMP can potentially reverse the structural evolution towards relaxation, resulting in more stable energy states [14]. Sometimes, modulations in structure and properties can be also observed as a result of competition between relaxation and rejuvenation, as reported during cryogenic thermal cycling [15,16] and ultrasonic hammering [17] of BMGs.

Another structural evolution during the TMP of BMGs is nanocrystal precipitation, forming a composite nanocrystal/amorphous structure [18,19]. The TMP-induced nanocrystallization can be achieved through controlled devitrification during thermal annealing [20] or mechanical deformation [21]. While thermally-induced nanocrystals are typically brittle intermetallic compounds, mechanically-induced nanocrystals [22,23] lead to significant work hardening, substantially enhancing plasticity through interactions with shear bands [24].



Research Article





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Achieving deformation-induced nanocrystallization in BMGs often requires the utilization of large strains and high pressures. During conventional plastic deformation techniques such as uniaxial compression [25] and high-pressure torsion [26] of BMGs, shear stress can reduce energy barriers for diffusion, increase atomic mobility within shear bands, and trigger local atomic rearrangements in these regions of highly localized plastic strain, leading to the formation of nanocrystallites [27,28]. However, plastic deformation approaches have their drawbacks. First, plastic strains are destructive and bring permanent deformation in treated BMGs. Second, the volume fraction of the nanocrystallites cannot be well-tuned by the processing variables. Further, the precipitated nanocrystallites are either volumetric and dispersed throughout the sample, or just confined to a thin surface layer with thicknesses ranging from a few hundred nanometers in the case of slurry erosion [29], to a few tens of micrometers in the case of surface mechanical attrition treatment (SMAT) [30]. Thus, achieving spatially gradient nanocrystallization induced by mechanical deformation remains challenging.

Another important issue to address is whether BMGs can undergo nanocrystallization when exposed to small mechanical strains well within the elastic limit or not? There are a few reports suggesting volumetric nanocrystal formation through elasto-static loading [31] and ultrasonic excitation [32] at loads below yield stress for long exposure times. However, the extended exposure to elastic stimulation in these studies resulted in a low nanocrystal number density, making them indistinct in X-ray diffraction (XRD) patterns. Moreover, the precise mechanism driving nanocrystal precipitation in BMGs during elastic deformation remains poorly understood.

In this study, we investigate the rapid development of a gradient nanocrystalline-amorphous structure in $Cu_{46}Zr_{46}Al_8$ (at.%) BMG induced by UV treatment under low elastic stresses. Notably, the crystallized volume fraction peaks at the struck surface, exhibiting a monotonic increase with the applied ultrasonic vibration energy. This demonstrates the remarkable tunability of nanocrystallization through the modulation of ultrasonic energy. Additionally, microstructural analyses reveal the nucleation of nanocrystallites from Cu-rich nano-sized regions within the as-cast glassy sample, providing compelling evidence for the role of chemical heterogeneities in elastic deformation-triggered nanocrystallization.

2. Experimental procedure

2.1. Sample preparation

The composition used in this study was $Cu_{46}Zr_{46}Al_8$ (at.%), prepared from pure metals with a purity exceeding 99.99 %. The master alloy underwent five repeated melting cycles in a vacuum arc remelting furnace under a protective atmosphere of argon gas (purity of 99.999 %), with titanium gettering, to ensure homogeneity. BMG rods of Ø3 mm × 70 mm were produced via suction casting in a water-cooled copper mold and then cut into 1.25 mm thick disks. Samples were polished using an automatic polishing system (LMP-3S, China) to reduce disk thickness to 1.0 mm, ensuring parallelism of top and bottom surfaces. Similarly, BMG rods of Ø2 mm × 70 mm were prepared and cut into cylindrical compression test samples with a length of 3 mm, ensuring parallel and orthogonal ends to minimize geometric constraints [33].

2.2. UV treatment

UV treatment involved an ultrasonic vibration setup consisting of a transducer, booster, and horn connected to a control unit for parameter adjustment. The schematic illustration of UV treatment is demonstrated in Fig. 1(a). At the outset, the mold was securely fixed to the workbench, and samples were inserted into the mold hole, which was slightly larger in diameter and shallower in depth than the sample height to allow free movement. During the process, the horn made contact with the sample's top surface under a preset pressure, and 20 kHz vibrations were applied. Various UV energies ranging from 50 to 400 J were employed (see Table S1 in the Supplementary Material), resulting in processing times of ~0.6 to 1.95 s and powers of ~83 to 205 W. The vibration amplitude and static stress were maintained at low values, specifically 40 μ m for vibration amplitude and 400 kPa for static stress, to ensure the elastic nature of cyclic strains imposed by horn.

2.3. Thermal measurement

The infrared imaging camera (Fotric 280d, China) with dataacquisition frequency of 30 Hz was used to capture thermal images from the BMG sample during UV treatment. AnalyzIR software analyzed temperature changes during treatment. Additionally, due to the continuous pressure applied between the horn and the sample, a K-type thermocouple with a sampling frequency of 1000 Hz was put on the struck surface to monitor temperature fluctuations throughout the process on the struck surface.

2.4. Structural characterizations

The XRD characterization was performed using a Rigaku Miniflex 600 XRD instrument with Cu-K_{α} radiation. The scanned area included UV-processed struck surfaces without polishing, as well as different depths of UV-200 and UV-400 samples. These depths were achieved by polishing away 0.1 or 0.05 mm of treated samples each time, enabling us to collect XRD data at various depths.

A power-compensated differential scanning calorimetry (DSC, Perkin-Elmer DSC 8000 instrument, US), operating under a continuous flow of high-purity argon, was adopted to examin thermal properties. The heating rate was 20 K/min, and the cooling rate was 60 K/min for all experiments. The DSC measurements were done on UV-treated disks and small disks of the same size $(Ø3 \times 1 \text{ mm})$ for the as-cast sample cut from the cast rod. In each DSC run, the specimen was first heated until it fully crystallized and then cooled to room temperature. A second heating scan was performed in the same protocol, and the signal from the fully crystallized sample was used as baseline correction by subtracting it from the signal from the first scan [17,34]. Additionally, the as-cast sample was annealed in the DSC furnace by heating the as-cast sample to 783 K at a rate of 20 K/min, followed by cooling at a rate of 60 K/min. DSC analysis was conducted using a minimum of three samples for each processing condition, and standard deviations were calculated to measure thermal properties.

Scanning electron microscopy (SEM, Quanta FEG 450, FEI, US) was used in this study. SEM was utilized to examine highmagnification characterizations using secondary electron imaging on the lateral surface of the UV-400 sample and analyze the fracture surface morphology of the as-cast, annealed, and UV-400 samples after compression test. Furthermore, a double spherical aberration-corrected transmission electron microscope (TEM; FEI Titan Cubed Themis G2 300, FEI, Netherlands) was used to analyze microstructures of as cast, annealed, and UV-treated samples at the nano scale. The TEM samples were prepared using a focused ion beam (FIB) on the FEI Scios dual beam system, with a sampling area of 5 μ m imes 1.5 μ m and a depth of 2 μ m cut across the intended regions of study. During the FIB sample preparation, a protective Pt layer was deposited on the samples. The energy dispersive X-ray spectroscopy (EDS) analysis was conducted in scanning mode (STEM) employing a high-angle annular dark-field (HAADF) detector.

2.5. Mechanical testing

Nanoindentation (TI 980, Bruker, Germany) was used to measure changes in hardness and elastic modulus from the surface to the interior of the UV-treated sample. The testing was performed on the cross-section of the disk sample, with measurements taken at intervals of 100 μ m. Furthermore, measurements were taken at each depth ten times to ensure data accuracy. Nanoindentation testing was conducted at each point using a Berkovich triangular pyramid indenter with a tip radius of 20 nm. A maximum load of 10 mN was applied at a loading rate of 0.5 mN/s.

Uniaxial compression tests were conducted on the as-cast, annealed, and UV-treated samples using a UMT-5105 (SanSi, China) universal testing machine at a strain rate of $1 \times 10^{-5} \text{ s}^{-1}$. The compression test samples were 2 mm in diameter and 3 mm in height. To ensure result reproducibility, compression tests were performed on three samples for each treatment condition.

3. Results

Fig. 1(b) shows stress profiles during UV treatment at varying ultrasonic energies. It is evident that at a constant ultrasonic energy, the compressive stress steadily increases with the duration of UV exposure. Furthermore, with increased ultrasonic energy, the maximum compressive stress applied to the BMG surface also escalates, reaching ~78 MPa in the sample treated with 400 J ultrasonic energy for 1.95 s (UV-400). It is important to note that these stress levels are significantly lower than the yield strength (~1.8 GPa) of the studied BMG composition. Prior studies have similarly reported small stress levels during UV treatments [35–37]. Additionally, Fig. 1(c) shows an overall view of the sample treated by the highest ultrasonic energy applied (400 J). As can be seen, there is no sign of plastic deformation in the treated sample and no shear bands are detectable on the surrounding surface

Table 1

Thermal properties in as-cast and UV-400 samples, with a maximum error of ± 1 K for the determination of T_g and T_x .

Samples	$T_{\rm g}~({\rm K})$	$T_{\rm x}$ (K)	$\Delta T_{\rm x}$ (K)	$\Delta H_{\rm cry}$ (J/g)	$\Delta H_{\rm rel}~({\rm J/g})$
As-cast	706	783	75	58.25	7.47
UV-400	704	786	82	57.63	4.46

(see inset in Fig. 1(c)), further confirming the elastic nature of UV treatment in this study. While BMGs commonly exhibit ultrasonic-vibration-induced plasticity (UVIP) at low stresses due to cyclically induced atomic-scale dilations and activation of liquid-like regions in BMGs [38,39], instances of its absence have been reported in the ultrasonic processing of Zr-based [17], La-based [40] and CuZr-based [32] BMGs. This discrepancy can be attributed to the applied UV energies, where insufficient energy may fail to initiate UVIP, while higher energies are effective in activating it. For instance, Zhang et al. [41] observed UVIP in La₆₄Al₁₄Cu₂₂ BMG composition when the UV energy exceeds ~500 J. Moreover, Chen et al. [42] have argued that the energy threshold necessary for UVIP activation increases monotonously with aging time in annealed La₆₀Ni₁₅Al₂₅ BMGs.

3.1. Calorimetric and temperature measurements

The DSC traces in Fig. 1(d) display the thermal behavior of ascast and UV-400 samples. Both samples exhibit characteristic features of an amorphous structure, as evidenced by distinct glass transition traces and sharp crystallization peaks. The corresponding calorimetric parameters, including glass transition (T_g) and crystallization (T_x) onset temperatures, as well as crystallization enthalpy (ΔH_{cry}), are extracted and compiled in Table 1. Notably, the DSC data indicate an expanded supercooled liquid region ($\Delta T_x = T_x - T_g$) following UV treatments, indicating enhanced thermal stability



Fig. 1. (a) Schematic illustration of UV treatment process setup. (b) Stress-time curves measured by force gauge during UV treatment of four samples. (c) SEM morphology of the UV-400 sample, with an inset showing an enlarged view of the sample edge. (d) DSC traces comparing the thermal behavior of the as-cast and UV-400 samples. (e) Specific heat capacity curves of the as-cast and UV-400 samples. (f) Average and surface temperature profiles and captured thermal infrared images during UV treatment of UV-400 sample.



Fig. 2. (a) XRD patterns of as-cast, annealed and UV-treated samples. (b) XRD patterns of UV-400 sample treated under different conditions.

through UV application [40]. Furthermore, both the as-cast and UV-400 samples demonstrate primary (single-peak) crystallization with nearly identical $\Delta H_{\rm cry}$ values. This suggests that ultrasonic vibration has a limited impact on the non-isothermal crystallization process.

The DSC thermograms also provide insight into the structural relaxation preceding the glass transition, allowing for a quantitative assessment of the degree of structural rejuvenation/relaxation induced by TMP [8,43]. It is evident from the specific heat traces in Fig. 1(e) that the UV-400 sample displays smaller exothermic peak in contrast to the as-cast sample by initiating exothermic signal from higher temperatures. The relaxation enthalpy ($\Delta H_{\rm rel}$), as measured from the specific heat exotherms prior to the glass transition [44], is detailed in Table 1. It is evident that $\Delta H_{\rm rel}$ in the UV-400 sample (4.46 J/g) is approximately 40 % smaller than in the as-cast sample (7.47 J/g). These findings strongly suggest that UV treatment primarily induces structural relaxation in the treated sample, rather than rejuvenation.

The structural relaxation in the UV-treated sample may have occurred as a result of the temperature rise induced by UV treatment. In this regard, Fig. 1(f) displays the real-time temperature profiles and thermographic images at three different process times taken by an infrared (IR) imaging camera for UV-400 condition. It can be seen that the temperature of struck surface reaches to a maximum of 582 K ($\sim 0.82T_g$), while the average temperature is as low as ~ 400 K ($\sim 0.57T_g$). In order to further determine the low-temperature properties, a thermocouple was used to measure the temperature on the struck surface (see Fig. S1 in the Supplementary Materials), showing that the maximum temperature rise is 571 K which is close to the maximum temperature rise is considerably lower than T_g , but it is high enough to annihilate unstable free volumes and relax the BMG to more stable energy states.

Table 2

Diffraction data extracted from XRD patterns in Fig. 2. The maximum error for determining peak position, FWHM, and *D* are \pm 0.014°, \pm 0.05°, and \pm 1 nm, respectively.

Samples	Peak position (°)	FWHM (°)	D (nm)	V _{cry} (%)
As-cast	39.02	5.05	-	0
UV-50	39.04	0.55	15.5	17.91
UV-100	39.06	0.61	14.0	23.8
UV-200	38.94	0.56	15.2	34.42
UV-300	38.98	0.55	15.7	41.96
UV-400	38.90	0.54	15.8	49.87
Annealed	39.20	0.23	36.7	73.35
UV-400-LN (60 h)	38.90	0.54	16.0	9.80
UV-400-LN (10 s)	38.98	0.56	15.3	28.04

3.2. XRD characterizations

Fig. 2(a) displays the XRD patterns of the as-cast and UVtreated samples, with the XRD pattern of the sample annealed at $T_{\rm X}$ included for comparison. The peak positions and full-width at half maximum (FWHM) data for the main peaks are extracted and summarized in Table 2. The XRD pattern of the as-cast sample exhibits a broad diffraction peak characteristic of an amorphous structure, lacking sharp crystalline peaks. In contrast, both UVtreated and annealed samples display XRD patterns consisting of a broad peak and sharp peaks corresponding to Bragg diffraction of crystalline phases, indicating the coexistence of amorphous and crystalline phases. The main crystalline peaks in the UV-treated and annealed samples are identified as $Cu_{10}Zr_7$ and $Cu_{1.74}Zr_{2.26}$, known stable phases [45,46]. The greater number of crystalline peaks with higher intensities for the annealed sample indicates a higher extent of crystallization compared to the UV-treated samples. Furthermore, the main peak position remains nearly constant across all samples, unaffected by UV energy and annealing treatment. Notably, the FWHM values for the UV-treated samples consistently exhibit smaller values compared to the annealed sample. Nonetheless, the FWHM does not show a notable change with an increase in UV energy. Correspondingly, the average grain size (*D*) of crystallites is estimated using the Scherrer equation [47]:

$$D = 0.9\lambda / (2\beta\cos\theta) \tag{1}$$

where λ is the X-ray wavelength, β is denoting the FWHM, and θ is the diffraction angle. As shown in Table 2, the *D* values in all UV-treated samples are approximately 15 nm, showing independence from the applied UV energy and remaining smaller than the annealed sample (~37 nm).

More importantly, as the UV energy increases, the intensity of the main crystalline peak in UV-treated samples gets lower. By employing a pseudo-Voigt function [48] to fit the XRD patterns and deconvolute the crystalline and amorphous diffraction peaks, the crystalline volume fraction (V_{cry}) can be determined. V_{cry} is calculated as $V_{cry} = A_{cry} / (A_{am} + A_{cry}) \times 100$ [49], where A_{am} and A_{cry} respectively represent the integrated areas of the amorphous and crystalline peaks, and presented in Table 2. It is observed that with the increase in the UV energy, the $V_{\rm cry}$ gradually increases, reaching a maximum of 49.87 % in UV-400, which is approximately two third of the V_{cry} value achieved in the annealed BMG (73.35 %). The observed trend indicates that the increase in UV energy enhances the nucleation of crystallites, leading to an increase in $V_{\rm cry}$, while exerting minimal influence on their growth, as reflected in a constant D value. This significant finding suggests the tunability of nanocrystal density by varying the UV energy.

Based on the temperature measurements illustrated in Figs. 1(f) and S1, the maximum temperature rise on the struck surface of UV-400 is considerably lower than T_g . Following the general principle that the precipitation of thermally-induced nanocrystals requires reaching temperatures above T_x to overcome the energy barrier for crystal nucleation [50], it appears that nanocrystal precipi-

tation in UV-treated samples is not predominantly driven by thermal factors.

To further explore thermal effects on UV-induced nanocrystallization, we conducted UV treatment at liquid nitrogen (LN) temperature, where the impact of thermal effects is minimal. Two samples were immersed in LN for different durations, 60 h and 10 s, respectively, followed by exposure to UV energy of 400 J. It should be noted that while it is widely recognized that cryogenic cycling treatment can significantly alter the structure and performance of MGs [13,15], holding MG sample for an extended period of time at 77 K (LN temperature) may not have a significant effect on the structure of MGs [12]. A comparison of the XRD patterns in Fig. 2(b) reveals that while low-intensity peaks are eliminated from the XRD patterns in UV treatment under LN condition, the higherintensity peaks persist, albeit with reduced intensities and smaller V_{cry} values compared to the UV-400 sample (see Table 1). Interestingly, even after 60 h of pre-soaking at LN, the V_{cry} is ~10 % and crystallization cannot be completely suppressed. This observation distinctly suggests that although temperature facilitates nanocrystallization, the process is primarily activated by ultrasonic vibration rather than being solely thermally driven. Furthermore, the main contribution of cryogenic treatment in this study to the significant reduction of $V_{\rm cry}$ is making the diffusion more sluggish due to processing at quite low temperatures. It is expected that higher $V_{\rm crv}$ values can be attained under LN condition with larger applied UV energies.

3.3. HRTEM characterizations

Fig. 3(a and b) compares the HRTEM images, selected area electron diffraction (SAED) and the fast Fourier transformer (FFT) patterns corresponding to the HRTEM images for the as-cast and UV-400 samples. The schematic illustration of the FIB sampling region for UV-400 (adjacent to the struck surface) is also shown in Fig. 3(b). The HRTEM image for the as-cast sample reveals a maze structure that contains certain local regions with uneven contrast,



Fig. 3. HRTEM images and corresponding SAED patterns, along with FFT analysis of as-cast (a) and UV-400 samples (b). Detailed view of the HRTEM image in (b) is shown in (c). Auto-correlation function analysis of different regions in (c) is presented in (d). FFT and IFFT patterns corresponding to region 2 in (c) are displayed in (e), while FFT patterns corresponding to regions 1 and 3 in (c) are shown in (f).

suggesting microstructural heterogeneities in the as-cast sample. The diffuse halo rings devoid of any spots in SAED pattern and FFT image are an indication of a fully amorphous structure for the ascast sample. In contrast, the HRTEM image of UV-400 sample contains maze structure and also lattice fringes that contrast typical of crystalline structure. In addition, the corresponding SAED and FFT patterns display diffuse halo rings with several irregular bright spots, suggesting the coexistence of amorphous and nanocrystal structures.

Fig. 3(c-e) further delves into the microstructural characterization of the HRTEM image for the UV-400 sample. The yellow lines in Fig. 3(c) demarcate different grains while white lines denote the orientation for each grain. It is evident that 5 grains can be recognized in the HRTEM image with different orientations of atomic planes, some of which neighbor each other. The grains are labeled as G1-G5. To further investigate local atomic order, autocorrelation function analysis using Gatan DigitalMicrograph is employed on selected regions in each grain as well as in the amorphous matrix. As the images in Fig. 3(d) show, regions 1-5 have obvious highly-ordered lattice fringes with different orientations and longrange ordering occurs in these regions with length scales of several nm. In contrast, region 6 does not contain any lattice structure, corroborating the fully amorphous nature of the matrix with no long-range periodicity. Further, the atomic planes of regions 1, 3, 4, and 5 have regular periodic order, implying that the corresponding grains are individually grown with no consumption of other grains. However, the autocorrelation function analysis of region 2 contains an irregular pattern of lattice fringes (Fig. 3(e)). This observation suggests that G2 has grown by consuming another grain. This is supported by the FFT analysis of this area (Fig. 3(e)), which contains two sets of bright spots existing close to each other, denoting an orientation mismatch between two grains. Further, the inverse FFT (IFFT) analysis clearly confirms that several dislocations exist inside this region.

The structure of crystalline phase can be characterized from the HRTEM images. The FFT patterns of regions 1 and 3 are shown in Fig. 3(f) as a representative of crystalline regions, which consist of sharp diffraction spots of atomic planes along the $[-1 \ 0 \ -5]$ and [-5 - 6 - 4], respectively, confirming the existence of Cu₁₀Zr₇ phase with an orthorhombic system and space group of C2ca [51]. This crystalline phase is also detectable in other TEM images taken from the surface adjacent to struck surface (see Fig. S2) and in the microstructure of the annealed sample (see Fig. S3). It is worth noting that the Cu₁₀Zr₇ phase is thermodynamically and kinetically the most preferential crystalline structure precipitated during conventional devitrification of Cu_{47.5}Zr_{47.5}Al₅ MG, followed by CuZr₂ and metastable CuZr B2 phases [46,52,53]. While polymorphic precipitation of CuZr B2 nanocrystals is often observed during the deformation of Cu-Zr-Al BMGs [23,54,55], our extensive analysis of several HRTEM images of the UV-treated sample (not shown here) persuades us to conclude that CuZr B2 phase does not have any possibility to evolve by the UV treatment applied. It is important to note that the precipitation of Cu₁₀Zr₇, while being an equilibrium crystalline phase that requires long-range diffusion, is also reported during ultrasonic excitation of Cu_{46.75}Zr_{46.75}Al_{6.5} [32] and ion irradiation of Zr_{50.7}Al1_{2.3}Cu₂₈Ni₉ [56] BMGs. Further, Shibazaki et al. [19] have observed the formation of Cu-rich nanocrystals during high-pressure annealing of Zr₅₀Cu₄₀Al₁₀ BMG.

The atomic-level structural modifications induced by UV treatment can be also investigated by calculating the reduced density function (RDF) using the FFT patterns in Fig. 3(a and b). The RDFs are computed by using the well-known PASAD package [57] and displayed in Fig. S4. As can be seen, short-range ordering (SRO) and medium-range ordering (MRO) make up the typical atomic ordering in the as-cast and UV-400 samples. The first two sub-peaks of RDFs correspond to Cu–Cu and Zr–Al atomic pairs, with the calcu-

lated positions of, respectively, $r_{Cu-Cu} = 2.54$ Å and $r_{Zr-Al} = 3.06$ Å in the as-cast sample. These interatomic distances are generally in agreement with the data for Zr-Cu-Al MGs reported by the previous studies [53,58-60]. Interestingly, the sub-peaks for Cu-Cu and Zr-Al atomic pairs in the UV-400 sample shift, respectively, by ~0.03 and ~0.08 Å toward smaller r values, indicating that UV treatment reduces the average atomic distance between the first nearest neighboring atoms. Similarly, the positions of the MRO peaks in the UV-400 sample have shifted to shorter r, possibly due to the formation of densely packed interpenetrating clusters [61]. Therefore, these results suggest that the main mechanism of structural relaxation induced by UV, identified from calorimetric studies, is volumetric shrinkage caused by a decrease in the average atomic bond lengths. An increase in ordering upon deformation at the SRO and MRO length scales has been previously observed in cold-rolling of Cu₅₀Zr_{47.5}Ti_{2.5} MG ribbons [23] and high-pressure annealing of Zr₅₀Cu₄₀Al₁₀ BMG [19].

3.4. Structural gradient

To investigate the structural gradient in UV-treated samples, we conducted XRD analysis at various depths beneath the struck surface. Fig. 4(a and b) compares the XRD plots from the struck surface to different distances beneath the surface in UV-200 and UV-400 samples. It is evident that the intensity of crystalline peaks in both samples gradually decreases with increasing distance from the struck surface, eventually leading to fully amorphous structures within the detection limits of XRD at 300 and 450 μ m away from the struck surface in UV-200 and UV-400, respectively. This observation highlights the tailored nanocrystal formation via UV treatment, where the extent of structural gradient, measured as the distance from the treated surface, can be well controlled by the UV energy input. Furthermore, the calculated values of D and $V_{\rm crv}$ extracted from the XRD data (see Table S2) indicate that the structural gradient arises from a reduction in V_{cry} (enhanced nucleation) while the D (growth) remains almost consistent across different depths. This trend mirrors the effect of UV energy on the crystallization behavior of the struck surface (see Fig. 2(a)).

In order to explore the possibility of nanocrystallization at distances farther away from the struck surface, we characterized the microstructure of UV-400 at 600 μ m beneath the struck surface (see Fig. S5). Interestingly, lattice fringes of nanocrystallites with multiple directions were observed from the HRTEM image. The corresponding FFT diffraction pattern of this atomic configuration also shows a diffuse halo together with visible bright specks, denoting the coexistence of amorphous and crystalline structure in the current depth of sample. Regarding the 1 mm thickness of the treated sample, it can be therefore concluded that the application of 400 J of UV energy for a very short time of ~1.95 s results in a gradient nanocrystallization throughout ~60 % of sample thickness.

While gradient crystallization has been noted in SMAT of Tibased BMGs [30], the structural gradient attained through UV treatment in this study exhibits distinct characteristics. Primarily, UV treatment induces a structural gradient based on the crystallized volume fraction, in contrast to the size-related gradient observed during SMAT. Additionally, the extent of the crystallization gradient in our work (600 μ m in the case of UV-400) is significantly larger compared to the ~80 μ m achieved by the SMAT. Importantly, such a substantial extent of structural gradient has not been reported thus far in the deformation-induced crystallization of BMGs.

3.5. Mechanical property characterizations

We systematically investigated the effects of gradient nanocrystallization on mechanical properties through nanoindentation and



Fig. 4. (a) XRD patterns from the UV-struck surface to the inner layer of UV-200. (b) XRD patterns from the UV-struck surface to the inner layer of UV-400. (c) Typical nanoindentation load-displacement curves of the UV-400 struck surface and opposite surface. The inset illustrates the test area for nanoindentation. (d) Changes in hardness and elastic modulus across the cross-section of UV-400.

uniaxial compression tests. In Fig. 4(c), the nanoindentation loaddisplacement curves for the indentation area adjacent to the struck surface and adjacent to the opposite surface in the UV-400 sample are presented. Notably, the area adjacent to the struck surface exhibits a significantly lower indentation depth compared to the region adjacent to the opposite surface, indicating higher hardness induced by nanocrystallization. Figs. 4(d) and S6 provide the hardness and elastic modulus data determined from the load-displacement curves across the sample thickness. Both hardness and elastic modulus reach their maximum values of 9.46 ± 0.11 GPa and 128.7 ± 1.46 GPa, respectively, at the area adjacent to struck surface. These properties gradually decrease with increasing displacement into the surface until reaching a relatively steady state at distance of \sim 0.25 mm away from the struck surface. This observed trend aligns well with the gradient reduction in $V_{\rm cry}$ seen in the XRD plots in Fig. 4(a). Nonetheless, the gradient depth for hardness and elastic modulus is more confined compared to the $V_{\rm cry}$, which demonstrates a reduction in the crystallinity intensity up to a depth of \sim 0.4 mm.

The compressive stress-strain curves of the as-cast and annealed samples, as well as the sample treated with a UV energy of 400 J on both sides, are presented in Fig. 5. These curves are utilized to determine various mechanical properties including yield stress (σ_y), fracture strength (σ_f), plastic strain (ε_p), and fracture strain (ε_f), summarized in Table 3. Plasticity in the as-cast sample is 0.221 % and reduces to 0.07 % in the annealed sample, but the values of ε_f for these two samples are almost similar. Significantly, when the sample is subjected to UV treatment, the values of ε_p and ε_f remarkablyrise to, respectively, 2.16 % and 3.67 %, accompanied by serrated flow. Additionally, the values of σ_y and σ_f in the annealed and UV-treated samples slightly decrease compared

Table 3 Plastic strain (ε_p), fracture strain (ε_f), yield stress (σ_y), and fracture strength (σ_f) values for the as-cast. UV-400, and annealed ClassZracAle BMG samples.

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Samples	$\varepsilon_{\rm p}$ (%)	$\varepsilon_{\rm f}$ (%)	$\sigma_{\rm y}~({ m MPa})$	$\sigma_{\rm f}~({\rm MPa})$
As-cast Annealed UV-400	$\begin{array}{c} 0.221\pm0.12\\ 0.071\pm0.016\\ 2.16\pm0.10 \end{array}$	$\begin{array}{c} 1.775 \pm 0.09 \\ 1.737 \pm 0.12 \\ 3.67 \pm 0.14 \end{array}$	$\begin{array}{c} 1824\pm12\\ 1760\pm16\\ 1776\pm14 \end{array}$	$\begin{array}{c} 1937\pm25\\ 1784\pm20\\ 1826\pm20 \end{array}$

to the values in the as-cast sample. Thus, UV treatment gave increases in plasticity without a drastic loss in flow stress.

The schematic illustration in Fig. 5(a) depicts the outcome of thermal annealing, which yields $Cu_{10}Zr_7$ nanograins of approximately equal size over the entire specimen, resulting in a homogenous microstructure. Given that the $Cu_{10}Zr_7$ intermetallic compound has a smaller Poisson's ratio ($\nu = 0.326$ [62]) compared to the $Cu_{46}Zr_{46}Al_8$ BMG ($\nu = 0.366$ [63]), the presence of a high degree of uniformly dispersed nanocrystals (with a V_{cry} of ~73 %) leads to the deterioration of the plasticity and fracture strength in the annealed sample. This behavior is commonly observed in Zrbased BMG composites where V_{cry} exceeds 60 % [5].

In contrast, UV treatment results in a heterogenous composite structure with gradient distribution of higher number-density of Cu₁₀Zr₇ nanocrystals toward the outer surface. Regarding the 3-mm height of specimen used in compression test, applying a UV energy of 400 J on both sides yields a nanocrystallization depth of ~0.6 mm from each side (i.e., a total depth of ~1.2 mm). As a result, roughly 40 % of the sample height contains a gradient nanocrystallization. This extensive structural gradient can effectively alter the deformation behavior and enhance plasticity.

By examining fracture surfaces following the compression test, it is possible to investigate the mechanism of increased



Fig. 5. (a) Compressive stress-strain curves for as-cast, annealed, and UV-400 samples (treated on both sides). (b, c) SEM images of the lateral fractured surface in the as-cast and UV-400 samples. (d, e) Morphology of the fractured surface in the as-cast and UV-400 samples.

plasticization induced by UV treatment. Fig. 5(b and c) shows the SEM micrographs of lateral fracture surfaces in the as-cast and the UV-400 samples, respectively. The as-cast sample shows one single shear band, implying that shear was fully accommodated by a single band. However, the UV-treated sample clearly displays primary shear bands apparently parallel to the fracture surface and secondary shear bands branching off from the primary ones. These secondary shear bands interact strongly with the primary shear bands and other secondary ones, consequently having an impingement effect that delays the fracture. Moreover, the SEM images from the fracture surface of as-cast and UV-treated samples (Fig. 5(d and e)) reveal marked differences in fracture morphologies. The fracture morphology of the as-cast sample exhibits dimple patterns separated by smooth areas, typical of monolithic BMGs [4]. However, the UV-treated sample displays a vein-like pattern, characteristic of significant plasticity in BMGs [64].

Therefore, it can be concluded that the gradient dispersion of Cu₁₀Zr₇ nanocrystals induced by the UV treatment alters the plasticization mechanism from single shear banding to multiple shear banding, along with branching and arresting of shear bands. This unique behavior may result from the complex flow stress fields, presumably originating from the spatial variations of the number density of nanocrystals. This, in turn, suppresses the catastrophic shear banding and promotes the formation of multiple shear bands. Experimental support for this hypothesis is found in the anomalous rotation of primary shear bands toward the horizontal direction. As depicted in Fig. S7, primary shear bands nucleate from the struck surface, where stress concentrations may occur due to the gradient increase in crystalline content toward the struck surface. Interestingly, these shear bands exhibit different inclination angles with respect to the loading axis. The initial band, formed at the early stage of deformation, has a minimum angle of 40.03°, while the shear plane at the fracture surface shows a maximum angle of 44.64°. The inclination angles are smaller than the maximum shear plane of 45° with respect to the loading axis, consistent with observations during compression test of BMGs [4,65]. This mechanism, characterized by enhanced plasticity due to the rotation of shear bands, bears some resemblance to the shear delocalization through shear band deflection observed in stress-induced [66] and thermally-induced [67,68] gradient rejuvenation of Zr-based BMGs.

4. Discussion

Earlier investigations into the effects of ultrasonic excitation in MGs primarily employed ultrasonic field annealing treatments. These studies revealed structural instabilities such as remarkable reduction of T_g and T_x [69] and enhanced crystallization process [70]. Later, a series of experiments by Ichitsubo et al. [71-76] explored the effects of high-frequency acoustic waves during the determination of elastic moduli for Pd-based and Zr-based BMGs at elevated temperatures. The results revealed that crystallization could occur at temperatures near $T_{\rm g}$, accelerated by structural instabilities induced by atomic motions linked to β (secondary) relaxation, that are stochastically resonant with the ultrasonic (sub-)MHz field [76]. The repetitive atomic jumps toward more energetically favorable sites related to β relaxation gradually alter the energy landscape, ultimately leading to crystallization. This hypothesis gained support from the frequency-dependent manifestation of β relaxation [73,74,77], where the relaxation shifted from temperatures significantly below T_g at low frequencies (a few Hz) to temperatures above Tg when MHz frequencies were applied. Recently, ultrasonic-induced crystallization has been also observed during ultrasonic vibration loading of Zr_{46.75}Cu_{46.75}Al_{6.5} [32] and La₆₄Al₁₄Cu₂₂ [41] BMGs at room temperature. However, the underlying mechanism behind this phenomenon remains poorly understood.

While the concept of β relaxation plays a key role in explaining ultrasonic-induced instabilities during ultrasonic field annealing treatment, our observations suggest an alternative scenario for UV treatment, supported by several compelling reasons. Firstly, the accelerated crystallization observed in BMGs during ultrasonic field annealing is induced by radiofrequency (MHz) Lorentz forces, which involve infinitesimal mechanical strains on the order of 0.0001 % [74]. In contrast, UV treatment utilizes microscale strains with a strain amplitude of ~0.5 %-1 % [17], perturbing BMGs through 20,000 cycles of mechanical vibrations per second. Secondly, crystallization in ultrasonic field annealing occurs at temperatures above T_g , whereas our study shows nanocrystallization at temperatures that UV treatment induces nanocrystallization even at liquid nitrogen temperatures.

Additionally, in the Zr-Cu-Al BMG composition used in our study, the β relaxation peak obtained from dynamical mechanical analysis measurements is not a prominent feature. Instead, it is observed to manifest as an excess wing, nearly merging into α (primary) relaxation [78]. The activation energy for β relaxation (E_{β}) in MGs can be estimated using the empirical relation $E_{\beta} = 26$ $RT_{\rm g}$, where R is the gas constant [78]. For the as-cast Cu₄₆Zr₄₆Al₈ BMG with a $T_{\rm g}$ of 706 K, the calculated E_{β} is ~1.6 eV, significantly larger than E_{β} for Pd-based MGs (~ 1 eV) [74]. This substantial difference in activation energies indicates a higher energy barrier for



Fig. 6. (a, b) HRTEM images captured from UV-400 samples at a depth of \sim 500 μ m beneath the struck surface. (c) HAADF image of the as-cast sample. (d) EDS mapping illustrating the constituent elements in the STEM mode for the as-cast sample. (e) Schematic representation depicting the nucleation pathway in CuZrAl BMG with chemical heterogeneities under UV treatment.

the activation of β relaxation at low frequencies in the Cu₄₆Zr₄₆Al₈ alloy compared to the Pd-based MGs, which exhibits a broad hump for β relaxation. Moreover, considering the frequency dependence of β relaxation and the fact that temperature during UV treatment at the frequency of 20 kHz still remains far below T_g , it appears insufficient to activate β relaxation in this context.

To delve into the underlying mechanism of nanocrystal formation during UV treatment, we conducted detailed TEM characterizations on the UV-400, particularly focusing on region ~500 μ m farther away from the struck surface. This region exhibits lower nanocrystal number density and is assumed to be at the early stages of nanocrystal precipitation. Notably, in the HRTEM images depicted in Fig. 6(a and b), we observe the nucleation of lattice fringes (depicted by white dashed interfaces) within dark contrast regions (areas demarcated by yellow dashed interfaces), while brighter contrasts do not show detectable lattice fringes.

Further examination using HAADF-STEM imaging (Fig. 6(c)) and corresponding EDS maps (Fig. 6(d)) of the as-cast sample show that the dark contrasts observed in the HRTEM images correspond to Cu-rich regions, indicative of nanoscale phase separation. Chemical composition analysis from the EDS maps reveals that the white (Cu-rich) and dark (Cu-depleted) regions in the HAADF-STEM image exhibited compositions of $Cu_{57}Zr_{39}Al_4$ and $Cu_{40}Zr_{55}Al_5$, respectively, consistent with the local stoichiometry of phase-separated regions in $Cu_{46}Zr_{56}Al_8$ BMG reported elsewhere [79]. This finding confirms that phase-separation-produced compositional fluctuations serve as preferential sites for crystal nucleation, a phenomenon commonly observed during the devitrification of silicate glasses [80] and other metallic glass systems such as Zr-based [81,82] and Al-based [83] MGs.

These direct observations provide insights into potential scenario for nucleation pathway during UV treatment of BMGs containing chemical heterogeneities. As schematically illustrated in Fig. 6(e), Cu atoms are unevenly distributed in the parent CuZrAl BMG, with high concentrations in certain regions. In the amorphous Cu-Zr system, similar to the Ni-Zr system, Cu atoms exhibit significantly higher diffusivity compared to Zr atoms at typical temperatures of measurements [50,84]. This diffusional asymmetry leads to the nucleation rate being controlled by the fast component (Cu atoms) due to their smaller atomic size and higher diffusivity, while the subsequent growth rate is inhibited by the slow component (the Zr atoms), thereby promoting crystallization on finer scales [50]. In the context of UV treatment, we speculate that such an asymmetry (with $D_{Cu} >> D_{Zr}$) extends into the solid state because ultrasonic excitation can significantly enhance the atomic mobility in MGs [85]. Consequently, this facilitates the nucleation of nanocrystals from Cu-rich clusters, accompanied by structural densification at the atomic level.

Another important aspect to consider is the high propensity of the glass for the $Cu_{10}Zr_7$ phase formation during UV treatment, which seems to emanate from the following factors: (i) chemistry–local Cu-enrichments ($Cu_{57}Zr_{39}Al_4$) in the as-cast state results in Cu:Zr ratio (1.46) very close to the ratio in $Cu_{10}Zr_7$ (1.43); (ii) atomic-level structural affinity–as the atomic structure at the SRO length scales in the as-cast $Cu_{46}Zr_{46}Al_8$ MG (see Fig. S4) resembles the coordination of the SRO of $Cu_{10}Zr_7$ crystalline phase (see Fig. 6 in Ref. [53]), straining of MG by UV treatment could trigger atomic rearrangements which cause precipitation of $Cu_{10}Zr_7$ nanocrystals rather than CuZr B2 phase; (iii) topological ordering—the $Cu_{10}Zr_7$ phase has a remarkable number of pentagon in Voronoi polyhedral similar to the $Cu_{47.5}Zr_{47.5}Al_5$ MG [53].

An additional issue worth discussing is the underlying reason for the observed gradient evolution in the structure and hardness of UV-treated samples. This phenomenon may stem from the hammering effect during ultrasonic vibration loading [17,86,87], where the contact between the horn and sample is intermittently lost. In addition to the cyclic compressive loading of sample, these intermittent high-velocity impacts also serve as a new source of excitation. Consequently, UV treatment shares similarities with ultrasonic impact treatments such as SMAT [30,88,89] and ultrasonic impact peening [90], wherein a gradient variation in strain and strain rate exists from the struck surface to the deeper matrix. However, due to the longer contact duration (depth) between the horn and sample in UV treatment, the structural and property gradient fields are deeper compared to the ultrasonic impact treatments. Further, the attenuation of ultrasonic wave transmission throughout the sample thickness [91] may also contribute to the structural gradient observed in our study.

It is important to note that achieving a structural gradient during UV treatment depends on the UV processing variables and the inherent physical properties of the treated BMG. For example, UV treatment of certain BMGs such as $Zr_{55}Al_{10}Ni_5Cu_{30}$ under low UV energies (~200 J) induces rejuvenation with no structural and property gradients and only brings about uniform variations in hardness values across the cross-section of the UV-treated sample [17]. Conversely, applying high UV energies of 700 J brings a full crystallization of $La_{64}Al_{14}Cu_{22}$ MBG, accompanied by UVIP [41]. Thus, structural gradient induced by the UV treatment may occur within a specific processability window where an effective strain gradient is satisfied. Further research is warranted to precisely delineate this window for tuning structural gradients in different BMG compositions using UV treatment—an approach valued for its rapid and straightforward nature.

5. Conclusions

In conclusion, our study investigated the nanocrystallization behavior of Zr₄₆Cu₄₆Al₈ BMG during ultrasonic elastic loading at various UV energies. Calorimetric measurements confirmed that structural relaxation is occurring during UV treatment. Temperature measurement revealed that the temperature rise on the struck surface is below T_{g} , suggesting UV, rather than thermal factors, drives nanocrystal formation in UV-treated samples, which was further supported by UV treatment under LN conditions. Structural characterization revealed a gradient nanocrystalline structure induced by UV treatment, with the crystallized volume fraction peaking at the struck surface and demonstrating tunability through ultrasonic energy modulation. Nanoindentation tests showed higher hardness near the struck surface, gradually decreasing with depth. The gradient dispersion of Cu₁₀Zr₇ nanocrystals altered deformation behavior, enhancing plasticity through the formation of multiple shear bands and thus delaying fracture. It was suggested that diffusional asymmetry between Cu-rich and Cu-depleted regions, driven by nano-sized phase separation, could be the primary mechanism describing crystal nucleation in UV-treated samples

Data availability

Data will be made available on request.

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.

CRediT authorship contribution statement

Yu Zhang: Writing – original draft, Visualization, Data curation. **Sajad Sohrabi:** Writing – review & editing, Writing – original draft,

Visualization, Methodology, Data curation. Xin Li: Validation, Formal analysis. Shuai Ren: Writing - review & editing, Validation, Formal analysis. Jiang Ma: Writing - review & editing, Supervision, Resources, Funding acquisition, Data curation.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jmst.2024.05.027.

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