Towards the Better: Intrinsic Property Amelioration in Bulk Metallic Glasses

Baran Sarac1, Long Zhang1,2, Konrad Kosiba1, Simon Pauly1, Mihai Stoica1,3 & Jürgen Eckert4,5

Tailoring the intrinsic length-scale effects in bulk metallic glasses (BMGs) via post-heat treatment necessitates a systematic analyzing strategy. Although various achievements were made in the past years to structurally enhance the properties of different BMG alloys, the influence of short-term sub-glass transition annealing on the relaxation kinetics is still not fully covered. Here, we aim for unraveling the connection between the physical, (thermo)mechanical and structural changes as a function of selected pre-annealing temperatures and time scales with an in-house developed Cu46Zr44Al8Hf2 based BMG alloy. The controlled formation of nanocrystals below 50 nm with homogenous distribution inside the matrix phase via thermal treatment increase the material’s resistance to strain softening by almost an order of magnitude. The present work determines the design aspects of metallic glasses with enhanced mechanical properties via nanostructural modifications, while postulating a counter-argument to the intrinsic property degradation accounted for long-term annealing.

The today’s tendency for creating high performance materials is towards generating advanced alloys with controllable properties1–3. Bulk metallic glasses (BMGs) are within this category due to their high thermodynamical metastability when quenched at sufficiently high cooling rates from the liquid state, where the precipitation of the second phase(s) can be tuned by the selected processing method4,5. Among metallic glasses, multicomponent CuZr-based alloys possess excellent glass-forming ability (cooling rates as low as 1–10 K/s) in combination with high strength (up to 2.5 GPa)6, a large elastic limit of 2%, and decent fracture toughness (as high as 100 MPa m−1/2)7. As opposed to conventional metallic alloys such as steels, due to the lack of grain boundaries, these materials exhibit strain softening behaviour at room temperatures with an accumulation of deformation into very narrow shear bands8. Lately, BMGs with additions of rare-earth elements showing high glass forming ability (GFA) and plasticity9,10 have been developed. These new-generation materials can meet the prospects of different sectors such as energy, safety, transportation, medicine etc. owing to their enhanced elastic and plastic behavior at room and elevated temperatures.

Recent investigations on the effect of long-term isothermal treatment of BMGs below the glass transition temperature conducted by different groups11–13 clearly identified the modifications of mechanical and thermal properties due to structural relaxation. This irreversible process is accounted for the annihilation of free volume via densification caused by annealing8. The decrease in free volume creates an additional endotherm on the differential scanning calorimetry (DSC) curve in the glass transition region without changing the glass transition temperature $T_g$ or the exothermic enthalpy for crystallization $\Delta H$ of the BMG alloy. On the contrary, Van Steenberge et al.14 and Stoica et al.15 postulated the idea of low-temperature annealing through continuous heating of BMGs. This heating protocol increases the tendency for structural reordering of Cu and Zr atoms, and as a result, create considerable plasticity under compression. The concept behind the improved plasticity is linked to the short-term heat treatment at sub-$T_g$ temperatures, where the structural modifications occur in the chemical and topological short-range order12. This mechanical property enhancement is achieved by continuous heating until the target temperature is reached, and rapid cooling of the sample immediately after the desired processing temperature is stabilized. By this method, the excess free volume within the BMG can be retained within the material. Subtle

1IFW Dresden, Institute for Complex Materials, Helmholtzstr. 20, D-01069 Dresden, Germany. 2Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 110016 Shenyang, China. 3Politehnica University of Timisoara, P-ta Victoriei 2, RO-300006 Timisoara, Romania. 4Erich Schmid Institute of Materials Science, Austrian Academy of Sciences (ÖAW), Jahnstrasse 12, A-8700 Leoben, Austria. 5Department Materials Physics, Montanuniversität Leoben, Jahnstrasse 12, A-8700 Leoben, Austria. Correspondence and requests for materials should be addressed to B.S. (email: b.sarac@ifw-dresden.de)
structural changes such as phase separation on the nano-scale or nucleation of nanocrystals distributed homogeneously throughout the specimen account for the mechanical property enhancement of BMGs. Furthermore, metallic glasses can undergo β relaxation as low as 0.6 $T_g$, which was shown to increase the macroscopic plasticity of BMGs through atomic diffusion.  

In particular, the mechanical and physical properties of BMG alloys are considerably influenced by the casting conditions and post-thermal treatment.  

The annealing induced structural modifications on the course of heat treatment was investigated for various annealing temperatures as well as for different time scales. After annealing, the samples were subsequently cooled down to the room temperature at constant rates of 100 K/s to minimize the possibility of formation of undesirable phases (such as Cu10Zr7 and CuZr2).  

Figure 1 shows the continuous DSC curves of the samples that were previously isothermally annealed for 5 min at $T_a$ as well as 25 K, 50 K, 75 K, and 100 K below the glass transition temperature. For comparison, the continuous heating curve of the reference (as-cast) state is presented. To understand the influence of above-$T_g$ annealing and long-term sub-$T_g$ annealing, a sample that was isothermally annealed for 5 min at 50 K above its glass transition, and a sample produced by annealing for half an hour at 50 K below $T_g$ are presented, respectively.  

The findings show that distinct relaxation mechanisms evolve at different temperatures. $T_c$, the crystallization temperature, increases by several degrees (up to 2 K) after pre-annealing (Fig. 1a). On the other hand, $T_g$, $\Delta H$ and the specific heat $\Delta C_p$ are marginally affected by the thermal history when the alloy is pre-annealed below its $T_g$ for 5 min (Fig. 1b and Table 1). Significant $T_c$ and $T_x$ drops by 30 K and 25 K together with drops in $\Delta C_p$ and $\Delta H$ were observed for the sample treated at 773 K. Structural relaxation for half an hour below $T_g$ decreases $T_c$ and $T_x$ by 5 K and 15 K, respectively, while not reducing $\Delta H$. Interestingly and opposite to previous literature findings, the enthalpy recovery in the calorimetric glass transition region $\Delta H_r$ was found to be smaller for the samples subjected to short-term annealing at sub-$T_g$ temperatures (except for the HT 623 K sample) compared to the as-cast state sample and the sample annealed at $T_g$ (723 K) (see Table 1 and Fig. 1b inset). This finding is possibly due to the inherent structural modifications (viz. phase decomposition, nanocrystallization etc.) during heat treatment.  

Relatively higher temperature (or longer term) annealing creates an additional endotherm corresponding to an increased $\Delta H_r$, which finally decreases significantly for annealing above $T_g$. Thus, thermal analysis clearly shows that the thermal treatment of the HT 648 K, HT 673 K, and HT 698 K samples for very short durations has no major impact on changing $T_g$, $T_c$, and $\Delta H$ in contrast to annealing above $T_g$. However, a remarkable drop in the $\Delta H$ values is observed for these three samples.  

Isothermal thermomechanical analysis (TMA) at sub-$T_g$ (Fig. 2a) were conducted to investigate the relaxation kinetics of the selected BMG alloy as a function of the viscosity change. TMA can provide a highly sensitive mechanical analysis (displacement and temperature precision of 2 nm and ±1 K, respectively) so that even small fluctuations (caused by nanocrystallization, nanodefect formation, or nanosegregation) within the sample can be carefully traced. This measurement allows us to understand the connection between the
| Sample     | $T_g$ (±2 K) | $\Delta c_p$ (±0.01 Jg$^{-1}$K$^{-1}$) | $T_x$ (±2 K) | $\Delta H$ (±0.7 Wg$^{-1}$) | $\Delta H_r$ (±1.0 Wg$^{-1}$) |
|------------|--------------|-------------------------------------|--------------|--------------------------|---------------------------|
| As-cast    | 723          | 0.26                                | 785          | −54.8                    | 9.0                       |
| HT 623 K   | 719          | 0.25                                | 784          | −54.4                    | 8.0                       |
| HT 648 K   | 720          | 0.23                                | 785          | −54.6                    | 7.2                       |
| HT 673 K   | 720          | 0.20                                | 784          | −54.3                    | 5.7                       |
| HT 698 K   | 717          | 0.28                                | 785          | −54.7                    | 6.6                       |
| HT 723 K   | 717          | 0.22                                | 782          | −54.9                    | 7.8                       |
| HT 773 K   | 689          | 0.17                                | 759          | −48.4                    | 2.9                       |
| HT 673 K*  | 713          | 0.27                                | 775          | −53.8                    | 7.8                       |

Table 1. DSC data for samples with different thermal histories at a heating rate of 20 K/min, followed by short-term annealing after reaching their target temperature. Note that the highest standard deviation values among the samples were taken into account. *Held for 30 min at constant temperature.

thermomechanical and structural properties via the change in the viscosity value, and the influence of this change on the room-temperature mechanical behaviour.

The samples were heated to $T_g$ of the CuZr-based BMG ($T_g = 723$ K measured by DSC) under vacuum, as well as to temperatures lower than the glass transition temperature ($T_g = 50$ K, $T_g = 75$ K), respectively. The temperature was held constant until the viscosity rises and reaches to the thermal equilibrium again. The viscosity at a certain temperature as a function of time was calculated by applying the Stefan's equation:

\[
\Delta H_r (\pm 1.0 \text{ Wg}^{-1})
\]
where $F$ is the load applied by the plunger, $r$ is the radius of the sample, and $h$ is the height of the sample. The aspect ratio of the sample $h/r$ was selected as 0.25 following\(^2\), and thereby the influence of the viscosity component of the liquid normal to the plates can be neglected.

The viscosity starts to drop around 635 K with increasing temperature. The change in viscosity differs with respect to the final temperature, where the isothermal TMA experiment at the glass transition temperature (723 K) shows an almost order of magnitude lower viscosity. Following this, it rises again and returns back to its original value which might be interlinked with the structural modifications (such as nanocrystallinity) within the structure.

The dark yellow dashed line shows the first point where the temperature reaches to 723 K. The scattered data is indicated by dark yellow pentagons in Fig. 2a, where the minimum viscosity is reached at $T_{\text{iso, HT}}=707$ K. This clearly means that structural changes already starts to occur before the desired constant temperature is reached. As the isothermal temperature is lowered, the dashed line shifts to the left (i.e., shorter times), and the time until the material reaches the target temperature becomes comparable with the temperature at which structural changes start to occur. The blue dashed line in Fig. 2b and left inset indicate the point above which the samples reach their isothermal temperature ($T_{\text{iso}}$). Green squares show the amount of available or overconsumed time (indicated by plus and minus signs, respectively) for the sample with respect to the blue dashed line. When the isothermal temperature is selected as 648 K or lower, no visible change in viscosity was observed for 30 min of waiting time. This temperature can be regarded as the threshold temperature below which no remarkable structural alterations are observed. However, this event might be due to the fact that the change in viscosity is overlapping with the device noise. For this reason, the minor decrease in the sample height for the mentioned sample was used to estimate the time of 3000 sec for the viscosity. The schematic time-temperature-transformation curve (right inset to Fig. 2b) shows the process path of the samples after casting (linear red line). The samples are subsequently annealed at sub-$T_g$ for a short duration and do not intersect the crystallization curve (blue path) as opposed to the ones intersecting the curve with a possibility of crystallization (green path). The drop in viscosity followed by a subsequent rise in isothermal TMA measurements at sub-$T_g$ temperatures show marked deviations of the viscosity data compared to the ones shown in the Angell plot\(^2\). Our results suggest that the stabilization of a nanocrystalline phase below $T_g$ (see Fig. 3) causes this viscosity change.

Figure 2c shows the thermal expansion measurement of the CuZr BMG. $T_g$ and $T_s$ were found to be around 710 and 773 K, which is in good agreement with the data taken from the DSC curve conducted with the same heating rate (Fig. 2c bottom inset). The employed dilatometer has an ultra-high temperature precision of 0.1 K, and a displacement resolution $\Delta l$ of 8 nm. Hence, the structural modifications as a function of volumetric shrinkage can be identified during heating. The point where the curve deviates from linearity was selected as the temperature onset for the structural changes within the sample. The volumetric shrinkage, which is determined from the vertical difference between the two red dashed lines in Fig. 2c top inset, was calculated to be $3 \times 10^{-3}$ (0.03%). This value is an order of magnitude smaller than the volumetric structural relaxation induced by the crystallization (0.5%), which is calculated from the vertical difference between the same heating and cooling $dl/dt$ data. XRD patterns obtained for the as-cast state, as well as for the samples with different thermal histories were compared to explore the influence of thermal treatment on the crystallization behaviour of BMGs. However, even after higher temperature or longer heat treatment, the samples showed broad patterns and no detectable diffraction peaks (Fig. 2d). This finding ascertains that the change in heat recovery can only be correlated with nano-scale structural modifications which cannot be identified by conventional XRD investigations.

Transmission electron microscopy (TEM) unraveled the change in the deformation pattern with respect to the annealing temperature. The as-cast reference sample’s corresponding high-resolution TEM (HR-TEM) image (Fig. 3a), and the inverse fourier transform (IFT) of the correlated images (Fig. 3b) revealed an amorphous maze-like pattern. On the other hand, the sample exposed to a heat treatment at 673 K for 5 min (HT 673 K) displayed nanocrystals which are below 50 nm in size that are dispersed homogenously (average of 20% by volume) within the amorphous matrix (Fig. 3c,d). The lattice constant from the place of local rearrangements was measured to be 0.326 nm corroborating the lattice spacing of the B2 CuZr phase found from X-ray diffraction\(^2\). In fact, B2-CuZr was previously found to primarily precipitate during sub-$T_g$ annealing for long terms (on the order of hours)\(^2\). No compositional difference between the local ordered region and matrix could be detected by energy dispersive x-ray analysis (EDX) in scanning transmission electron microscopy (STEM) mode. These findings confirmed that the phase precipitation is polymorphic\(^2\). Although the high temperature CuZr phase is normally stabilized above 700 K during fast quenching from the liquid state or during above-$T_g$ heat treatment\(^2\), our findings suggest that the precipitation of the B2 CuZr nanocrystals are triggered by the high nucleation rates obtained at sub-$T_g$ temperatures where the rate of atomic diffusion and growth of nanocrystals are limited\(^2\).

Figure 3e depicts the bright-field image of a nanocrystallite with dimensions of around 50 nm formed by the same heat treatment. A remarkable contrast difference between different regions in the nanocrystals can be identified, which can be attributed to the superposition of lattice fringes from different B2 CuZr nanocrystals (as shown in Fig. 3f). The resultant patterns found on the nanocrystal precipitates within the glassy BMG matrix are named as moiré fringes\(^3\). The overall length of these fringes are measured to be around 5 nm, which indirectly suggests the grain size of these nanocrystals. The yellow and blue arrows show two different interference patterns with fringe spacings of 2.6 nm and 0.8 nm, respectively.

The current findings raise the question whether the nanocrystallization confirmed by the TEM study leads to changes in the mechanical properties on the macroscopic scale. For this purpose, by using the test setup shown in Fig. 4a, 3-point bending tests were performed. BMG samples at the selected thicknesses of 0.5 $\pm$ 0.05 mm are

\[ \eta = \frac{-2Fr^3}{3\pi r^4 (dh/dt)} \]
estimated to exhibit 5–6% bending plasticity. The high extent of plasticity observed allows to determine the changes (i.e., amount of stress drop, plasticity, final strain at fracture) in the plastic regime with high accuracy and in a systematic manner. The findings revealed that the samples subjected to 5 min of heat treatment at 623, 648, 673 K followed by fast water quenching show a resistance to softening in the plastic regime in contrast to the as-cast reference sample (Fig. 4b). Thus, after reaching their ultimate flexural strength \( \sigma_{UFS} \) the strength drop for the heat treated \((\Delta \sigma = \sigma_{UFS} - \sigma_f)\) samples became remarkably smaller (see Table 2). For the same samples, a higher elastic modulus \( E \) and \( \sigma_{UFS} \) was observed at only a slight expense of strain at rupture \( \varepsilon_f \). On the contrary, thermally treated samples 25 K below or at \( T_g \) showed a degraded \( \sigma_{UFS} \) with almost no plasticity. Particular attention should be given to the duration of the heat treatment. The HT 673 K sample with 5 min thermal treatment has higher \( \sigma_{UFS} \) and larger \( \varepsilon_f \) compared to the sample annealed for 30 min that shows catastrophic deformation below its elastic limit. High yield strength with limited plasticity was observed for the samples annealed above-\( T_g \) (HT 773 K), which can be attributed to the possible increase in the volumetric density of the crystals.

The extensive bending plasticity observed for the as-cast state sample and the samples heat treated at 648 K and 673 K was reflected on the fracture surface of the specimens. The tensile side exhibits dimples which are created by the coalescence of microvoids during ductile fracture (Fig. 4c top figure). Vein patterns with partially molten ridges are the characteristics of the compressive side. The smooth region (pointed by a blue arrow) is regarded as being due to stable shear-type deformation before failure. The fracture morphologies can be evidently seen in Fig. 4d. Sharp transition exists between uneven and smooth regions deformed under tension and compression, respectively. The extensive plastic strain for the mentioned samples is attributed to the amount of shear band formation. To show this correlation, another sample was deformed up to 80% of its average fracture strain, and the load was subsequently released (Fig. 4e). Sample analysis via high-resolution SEM reveal that the tensile side of the deformed specimen exhibits longer shear bands. Secondary and tertiary branching can be observed for the tensile side compared to shorter and less noticeable shear bands on the compressive side. The results are suggesting the precipitation of more nanocrystals on the tensile regions of the bent samples analogous to the stress-driven nanocrystallization process at room temperatures. To conclude, the bend-tests of the 648 K and 673 K heat-treated samples show the highest resistance against softening which can be linked with the homogenous nanocrystal formation during thermal treatment in addition to the stress-induced nanocrystals generated during bending.
In this contribution, we developed a viable strategy to improve the overall toughness of BMGs by precipitating B2 CuZr nanocrystallites homogenously within the amorphous matrix through short durations of heat treatment at sub-$T_g$ temperatures. The controlled structural modifications are reflected on the continuous DSC curves. The enthalpy recovery data in the calorimetric glass transition region $\Delta H_r$ are found to be decreasing for short terms of annealing at relatively lower annealing temperatures as opposed to the structures exposed to high temperature or long-term sub-$T_g$ annealing. The isothermal TMA analysis displays a slight change in viscosity (approximately an order of magnitude). During the dilatometric measurement with continuous heating, the volumetric shrinkage measured between the initiation temperature of the structural modifications $T_{str, modif}$ and $T_g$ is found to be an order of magnitude smaller than the volumetric shrinkage ensuing between $T_g$ and $T_x$. These findings corroborate the slight structural modifications are taking place within the sample which happens before the growth of the nanocrystals, where in the latter case the glass is structurally relaxed by free volume annihilation.

**Table 2.** Mechanical properties extracted from the 3-point bending test. The term $T/T_g$ defines the normalized annealing temperature with respect to $T_g$ of the as-cast BMG. $\sigma_f$ is the fracture strength of the bent specimens. $\Delta \sigma$ is the ratio of strength drop between $\sigma_{UFS}$ and $\sigma_f$. Note that the highest standard deviation values among the samples were taken into account.

| Sample | $T/T_g$ | $E$ (±1 GPa) | $\sigma_{UFS}$ (±50 MPa) | $\sigma_f$ (±50 MPa) | $\Delta \sigma$ (±1.2%) | $\varepsilon_f$ (±0.1) |
|--------|---------|-------------|--------------------------|---------------------|--------------------------|----------------------|
| As-cast| –       | 97          | 2709                     | 2305                | 14.9                     | 6.1                  |
| HT 623 K | 0.86    | 98          | 2745                     | 2639                | 3.9                      | 4.9                  |
| HT 648 K | 0.90    | 104         | 2816                     | 2593                | 7.9                      | 5.6                  |
| HT 673 K | 0.93    | 103         | 2778                     | 2679                | 3.6                      | 5.6                  |
| HT 698 K | 0.97    | 103         | 2535                     | 2535                | –                        | 2.7                  |
| HT 723 K | 1.00    | 105         | 2447                     | 2447                | –                        | 2.4                  |
| HT 773 K | 1.07    | 106         | 2942                     | 2933                | –                        | 4.4                  |
| HT 673* K | 0.93   | 106         | 1729                     | 1729                | –                        | 1.8                  |

**Discussion**

In this contribution, we developed a viable strategy to improve the overall toughness of BMGs by precipitating B2 CuZr nanocrystallites homogeneously within the amorphous matrix through short durations of heat treatment at sub-$T_g$ temperatures. The controlled structural modifications are reflected on the continuous DSC curves. The enthalpy recovery data in the calorimetric glass transition region $\Delta H_r$ are found to be decreasing for short terms of annealing at relatively lower annealing temperatures as opposed to the structures exposed to high temperature or long-term sub-$T_g$ annealing. The isothermal TMA analysis displays a slight change in viscosity (approximately an order of magnitude). During the dilatometric measurement with continuous heating, the volumetric shrinkage measured between the initiation temperature of the structural modifications $T_{str, modif}$ and $T_g$ is found to be an order of magnitude smaller than the volumetric shrinkage ensuing between $T_g$ and $T_x$. These findings corroborate the slight structural modifications are taking place within the sample which happens before the growth of the nanocrystals, where in the latter case the glass is structurally relaxed by free volume annihilation.

Figure 4. (a) The deformation setup for the bending test. The plunger was pushed at a strain rate of 0.001 mm/sec towards the fixed base holder. *In-situ* visualization of the experiment was carried by the VEDDAC video extensometer. (b) Stress-strain curves of the as-cast state and heat treated samples. Error bars are inserted for stress and strain values at equivalent data intervals for each sample. (c) Tensile (top) and compressive (bottom) sections of the bent specimen showing different fracture morphologies (yz axis). (d) Overall fractography of the broken sample. (e) Shear bands observed on the tensile and compressive sides of the shear surface (xy axis).
devitrification of the matrix phase is detected by the (S)TEM measurements for the analyzed HT 673 K sample. The HT 673 K sample \( (T_f/T_g = 0.93) \) with homogeneously dispersed nanocrystals (of sizes below 50 nanometers, and a volume fraction of \(~20\%\) exhibit the highest resistance to softening with a maximum stress drop of only 3.6\% (as opposed to the drop of 14.9\% for the reference as-cast sample) with final strain values comparable to the as-cast state sample. The contrast difference between different regions in the nanocrystals is observed in the HT 673 K sample, where the detected lattice fringes are due to the overlapping of different B2 CuZr nanocrystals which form during the heat treatment process.

In summary, the thermal stability of the BMG changes with the chosen annealing temperature and time. Intrinsic property amelioration can be achieved by the controlled and homogenous nanocrystallization proposed within this study. We envision that the presented method can enable us to design tough metallic glasses with tailorable properties.

Methods

The BMG master alloy ingot was prepared from elements with purity higher than 99.99\% using an Edmund Bühler GmbH Arc Melter. The master alloys were subsequently heated above the liquidus temperature three times to form a homogenous mixture. The master alloys were then sliced into 10–12 g pieces, and the water-cooled copper mold casting was conducted under Ar atmosphere using an in-situ suction casting device attached to Edmund Bühler Arc Melter. The dimensions of the cast plates were \( 1.5 \text{ mm} \times 10 \text{ mm} \times 75 \text{ mm} \). The cast plates were sliced into smaller pieces (using Struers Accutom 50) and slightly ground by hand to eliminate surface oxides. The plates were scanned by 3D computer tomography (GE Phoenix Nanotom), and no porosity on the micron-level was found. The sample plates were inserted in a calibrated furnace, and brought to different temperatures below \( T_g \) under Ar atmosphere of \( 10^{-3} \text{ mbar} \). After reaching the chosen temperature, samples were isothermally treated for 5 min for temperature stabilization, and subsequently taken out of the furnace and water-quenched to room temperature. The as-cast reference and heat treated samples were ground and subsequently mirror-polished down to the desired thickness level using Buehler Metaserv 250 to eliminate any influence of possible surface crystallization and oxidation. The final dimensions of the samples had a thickness of \( 0.5 \pm 0.05 \text{ mm} \), where the width and the length of the samples were \( 4.5 \pm 0.3 \text{ mm} \) and \( 14.0 \pm 1.0 \text{ mm} \), respectively. Meanwhile, smaller pieces (about \( 20 \text{ mg} \) in weight) were prepared for calorimetric measurements. Using a PerkinElmer Pyris Diamond DSC, each piece was heated to its destination temperature at a rate of 20 K/min, kept at constant temperature for 5 min, and finally cooled down at a rate of 100 K/min. The glass transition (\( T_g \)) was measured from the inflection point of the endothermic ramp, whereas the crystallization temperature (\( T_c \)) was measured from the onset point of the exothermic signal. Viscosity measurements were conducted with a Perkin-Elmer Dynamic Mechanical Analyzer (DMA 7) with 3 mm diameter flat tip parallel plate probes. The samples (2 samples from each set) were heated up to the desired temperatures at a heating rate of 20 K/min under a constant load of 2.6 N, and were subsequently annealed isothermally for 0.5 h followed by fast cooling of 100 K/s. The relative length change \( \Delta l/l_0 \) of the \( \text{Cu}_{40}\text{Zr}_{50}\text{Al}_{10}\text{Hf}_1 \) samples was measured using a Netzsch DIL 402 C Dilatometer under a constant heating and cooling rate of 10 K/min with two identical samples. The length of the samples were \( 27.96 \pm 0.12 \text{ mm} \) with a diameter of 3 mm, where both sides were made parallel by mirror polishing. Structural characterization was conducted before and after heat treatment by X-ray diffraction using a D3290 PANalytical Xpert PRO with Cu-Kα radiation. For the mechanical property characterization, 3-point bending tests were performed with the Kammrath & Weiss Tensile/Compression Module (with 5 kN load cell) with attached bending fixtures having an effective gauge section of 10 mm. Samples with thermal histories, as well as the as-cast reference samples were deformed under strain rates of \( 10^{-3} /\text{s} \) until rupture. The imaging with the preloaded state is conducted by Keyence Digital Microscope VHX 2000. The visualization of the deformation process, and the strain correction was implemented using a video extensometer system (MicroDAC strain measurement) attached to the testing device. The fractographic analysis after rupture, as well as shear surface analysis of the bent samples right before failure were performed using an SEM Zeiss Ultra Plus and its EDX detector attached. The fractographic analysis were also conducted for different samples of \( \epsilon_f > 5.0\% \), however because of the similar deformation patterns and final strains, the images only from the as-cast sample were used to represent the other samples of interest. The specimens for the TEM observations were prepared by ion milling (Gatan 691) via liquid nitrogen cooling. The amorphous structure and nanocrystallinity of the as-cast and heat treated samples were investigated using a TEM FEI Tecnai F30. The composition was analyzed by an EDX module attached to the TEM.

References

1. Jung, H. D. et al. Novel strategy for mechanically tunable and bioactive metal implants. Biomaterials 37, 49–61 (2015).
2. Zou, Y., Ma, H. & Spolenak, R. Ultrastrong ductile and stable high-entropy alloys at small scales. Nat. Commun. 6, 1–8 (2015).
3. Zhu, R. et al. Multi-phase microstructure design of a low-alloy TRIP-assisted steel through a combined computational and experimental methodology. Acta Mater. 60, 3022–3033 (2012).
4. Qin, J. W. In-situ Dendrite/Metallic Glass Matrix Composites: A Review. J. Mater. Sci. Technol. 29, 685–701 (2013).
5. Wu, Y. et al. Designing Bulk Metallic Glass Composites with Enhanced Formability and Plasticity. J. Mater. Sci. Technol. 30, 566–575 (2014).
6. Inoue, A., Zhang, T., Kurosaka, K. & Zhang, W. High-strength Cu-based bulk glassy alloys in Cu-Zr-Ti-Be system. Acta Mater. 42, 1800–1804 (2001).
7. Ashby, M. F. & Greer, A. L. Metallic glasses as structural materials. Scripta Mater. 54, 321–326 (2006).
8. Schuh, C. A., Hufnagel, T. C. & Ramamurty, U. Overview No. 144 - Mechanical behavior of amorphous alloys. Acta Mater. 55, 4067–4109 (2007).
9. Deng, L. et al. Roles of minor rare-earth elements addition in formation and properties of Cu-Zr-Al bulk metallic glasses. J. Alloy Compd. 632, 429–434 (2015).
10. Park, E. S. & Kim, D. H. Phase separation and enhancement of plasticity in Cu-Zr-AI-Y bulk metallic glasses. Acta Mater. 54, 2597–2604 (2006).
11. Kumar, G., Rector, D., Conner, R. D. & Schroers, J. Embrittlement of Zr-based bulk metallic glasses. Acta Mater. 57, 3572–3583 (2009).
Towards the Better: Intrinsic Property Amelioration in Bulk Metallic Glasses

Abstract

Bulk metallic glasses (BMGs) exhibit intriguing mechanical properties compared to traditional metallic materials, yet their deformation mechanisms remain challenging. Here, we report significant amelioration in the intrinsic properties of BMGs through a combination of experimental and computational findings. By utilizing advanced in situ experimental techniques and performing atomistic simulations, we identify the role of short-range order and atomic composition in enhancing mechanical properties, specifically tensile plasticity. Our results reveal that by tuning the atomic structure and composition of BMGs, it is possible to significantly improve their deformation capacity.

Author Contributions

B.S. and M.S. designed the research, B.S. fabricated the samples, conducted 3-point bending, thermal analysis of the data. K.K. and S.P. has developed the BMG alloy, and involved in the writing phase of the manuscript. B.S. and M.S. designed the research, B.S. fabricated the samples, conducted 3-point bending, thermal analysis of the data. K.K. and S.P. has developed the BMG alloy, and involved in the writing phase of the manuscript. B.S. and M.S. designed the research, B.S. fabricated the samples, conducted 3-point bending, thermal analysis of the data. K.K. and S.P. has developed the BMG alloy, and involved in the writing phase of the manuscript.

Additional Information

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Sarac, B. et al. Towards the Better: Intrinsic Property Amelioration in Bulk Metallic Glasses. Sci. Rep. 6, 27271; doi: 10.1038/srep27271 (2016).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/