



Communication Synthesis of Bulk Zr₄₈Cu₃₆Al₈Ag₈ Metallic Glass by Hot Pressing of Amorphous Powders

Tianbing He¹, Nevaf Ciftci², Volker Uhlenwinkel^{2,3} and Sergio Scudino^{1,*}

- ¹ Leibniz IFW Dresden, Institute for Complex Materials, Helmholtzstraße 20, 01069 Dresden, Germany; t.he@ifw-dresden.de
- ² Leibniz Institute for Materials Engineering IWT, 28359 Bremen, Germany; ciftci@iwt.uni-bremen.de (N.C.); uhl@iwt.uni-bremen.de (V.U.)
- ³ Faculty of Production Engineering, University of Bremen, 28359 Bremen, Germany
- * Correspondence: s.scudino@ifw-dresden.de

Abstract: The critical cooling rate necessary for glass formation via melt solidification poses inherent constraints on sample size using conventional casting techniques. This drawback can be overcome by pressure-assisted sintering of metallic glass powders at temperatures above the glass transition, where the material shows viscous-flow behavior. Partial crystallization during sintering usually exacerbates the inherent brittleness of metallic glasses and thus needs to be avoided. In order to achieve high density of the bulk specimens while avoiding (or minimizing) crystallization must be identified. Here, by carefully selecting the time–temperature window for powder consolidation, we synthesized highly dense $Zr_{48}Cu_{36}Ag_8Al_8$ bulk metallic glass (BMG) with mechanical properties comparable with its cast counterpart. The larger ZrCu-based BMG specimens fabricated in this work could then be post-processed by flash-annealing, offering the possibility to fabricate monolithic metallic glasses and glass–matrix composites with enhanced room-temperature plastic deformation.

Keywords: bulk metallic glasses; powder metallurgy; hot pressing; gas atomization; mechanical properties

1. Introduction

Bulk metallic glasses (BMGs) are materials with liquid-like structure [1] exhibiting high strength and hardness, large strain elastic limit (~2%), and good wear and corrosion resistance [2], which represent an attractive combination of properties for applications in the field of structural materials. The necessity for rapid heat extraction and the corresponding high cooling rates essential for glass formation by melt solidification set an inherent limit to the achievable dimensions of bulk metallic glass specimens [3]. This aspect is explained in Figure 1a, which shows a schematic continuous cooling transformation (CCT) diagram for a glass-forming system. Since the cooling rate decreases with increasing sample dimension [4], there will exist a critical sample size and a corresponding critical cooling rate (i.e., the lowest cooling rate for vitrification), R_c , for glass formation that avoids the intersection of the cooling curve with the crystalline nose to form glass [5]. Solidification of larger specimens will lead to partial or full crystallization. Such crystallization usually occurs with the formation of brittle intermetallic phases, which further reduces the limited plastic deformation of metallic glasses at room temperature [6]. Although there has been significant progress toward the synthesis of larger BMG specimens via the development of alloys with high glass-forming ability [7], most of the glass-forming systems are still limited to the millimeter scale [8]. The restriction in sample size obviously limits the potential applications of BMGs.



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Figure 1. (a) Schematic continuous cooling transformation (CCT) diagram for a glass-forming system showing the critical cooling rate, R_c , for glass formation; (b) schematic continuous heating transformation (CHT) diagram for conventional heating rates showing the principles of consolidation of amorphous powders. T_L = liquidus temperature; SCL = supercooled liquid; τ = incubation time.

A straightforward way to circumvent the size limitation is the synthesis of BMGs using methods not involving solidification; these include thermoplastic joining [8] and ultrasonic welding [9] or, alternatively, powder metallurgy (PM) via the consolidation of amorphous powders [10]. Due to the great flexibility of the PM approach, a multitude of BMGs including Zr- [10], Cu- [11], Ni- [12], Al- [13], and Ti-based [14] ones with size exceeding 10 mm have been developed. The results indicate that highly dense BMG specimens with mechanical properties comparable with the corresponding material prepared by casting can be synthesized by using powder metallurgy. Consolidation of amorphous powders is frequently carried out by simultaneously applying high pressures and high temperatures, examples are warm extrusion [10], hot pressing [15], and spark plasma sintering (SPS) [11]. Regardless of the composition and the method used, the crucial aspect is to achieve full densification without inducing crystallization and thus further embrittlement of the glassy specimens. Consolidation of amorphous powders below the glass transition temperature (T_g) is extremely difficult because the glassy particles are typically hard in this temperature regime. However, densification into bulk specimens can be efficiently achieved at temperatures within the supercooled liquid (SCL) region $\Delta T_x = T_x - T_g$ (T_x = crystallization temperature), where the material exhibits a pronounced decrease of viscosity [16]. The viscous-flow behavior characteristic of metallic glasses at these temperatures not only assists particle bonding and densification [17] but also promotes the process of crystallization even at temperatures below T_x [18]. The accurate selection of the consolidation parameters, in particular temperature and holding time, is thus crucial in order to achieve high density without inducing crystallization [19]. The use of the proper time-temperature window for consolidation is described in the schematic continuous heating transformation (CHT) diagram for conventional heating rates in Figure 1b. The glassy powder is heated at temperatures within the SCL region, where it is kept constant for a period not exceeding the incubation time τ (i.e., the time needed to start the crystallization process at a given temperature).

In this study, we further explore the process of consolidation of amorphous powders by analyzing the effectiveness of hot pressing for the synthesis of $Zr_{48}Cu_{36}Al_8Ag_8$ BMGs. We first studied the crystallization behavior and the temperature dependence of the viscosity of the powder in order to select the proper consolidation parameters. Highly dense $Zr_{48}Cu_{36}Al_8Ag_8$ BMGs were then produced by hot pressing and, finally, the mechanical properties of the bulk specimens were evaluated via room-temperature compression tests. The $Zr_{48}Cu_{36}Al_8Ag_8$ composition was selected because it shows a relatively large SCL region [20], which may facilitate the optimization of the consolidation parameters. More importantly, ZrCu-based BMGs are promising precursors for the formation of ductile ZrCu shape memory crystals in the glassy matrix via post-processing by flash-annealing at high heating rates (e.g., ~100 K/s) [21]. These kinds of composites are reported to show a transformation-induced plasticity under deformation; thus, the toughness of the alloy is significantly increased in comparison with the monolithic BMG [22].

2. Materials and Methods

Metallic glass powder with the nominal composition $Zr_{48}Cu_{36}Al_8Ag_8$ (at.%) was synthesized by argon gas atomization. The mass median particle diameter (D₅₀), measured using a laser diffraction system (Malvern, Mastersizer 2000), is 100 µm (for powder morphology and size distribution see Figure 2). Although smaller particle size may assist the densification process [23], particle sizes of about 100 µm have been successfully used for the fabrication of $Zr_{57}Cu_{20}Al_{10}Ni_8Ti_5$ glassy specimens by SPS [24]. Additionally, given the narrow particle size distribution of the present powder (Figure 2b), the use of a smaller particle fraction, such as below 20 µm, would have resulted in an excessive amount of unused powder. The chemical composition of the powder (Table 1), analyzed by inductively coupled plasma–optical emission spectroscopy (ICP-OES, Thermo Fisher IRIS Intrepid II XUV), indicates that the actual composition matches the nominal composition.



Figure 2. (a) Particle morphology and (b) particle size distribution of the gas-atomized $Zr_{48}Cu_{36}Al_8Ag_8$ glassy powder.

Table 1. Chemica	l composition	of the Zr ₄₈	Cu ₃₆ Al ₈ Ag ₈	glass	powder	(at.%)
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Zr	Cu	Al	Ag	0
47.83 ± 0.35	36.11 ± 0.11	7.97 ± 0.03	8.00 ± 0.04	0.09 ± 0.01

The Zr₄₈Cu₃₆Al₈Ag₈ powder was consolidated under argon atmosphere into cylindrical specimens (dimensions: 10 mm diameter and about 10 mm height) by uniaxial hot pressing at different temperatures (743, 753, and 758 K) using an electro-hydraulic universal axial pressing machine (WEBER PWV 30 EDS, Figure 3a,b). We used a pressure of 900 MPa, which represents the upper limit of pressure usable in our hydraulic pressing machine in the temperature range used in this work, and 10 min holding time, which is a good compromise between good densification and minimum crystallization for a series of metallic glass powders, including Ni_{52.5}Nb₁₀Zr₁₅Ti₁₅Pt_{7.5} [25], Zr₇₀Cu₂₄Al₄Nb₂ [26], and Zr₅₅Cu₃₀Ni₅Al₁₀ [27]. A copper coil was used to heat the powders at a heating rate of about 40 K/min. During heating, the temperature was continuously monitored by a thermocouple, which was inserted in the dedicated cavity of the mold (Figure 3b). To reduce the friction effects arising during hot pressing and demolding, a thin layer of boron nitride was sprayed on the surface of the mold cavity and punches. A mold with a cylindrical cavity (inner diameter of 10 mm, which in turn determines the shape and diameter of the specimens) and cylindrical punches with corresponding size (10 mm) made of Inconel 718 alloy were used. After compaction, the samples were demolded by raising the lower punch (demolding) and then cooled in air. A schematic of the hot-pressing process is shown in Figure 3c. Phase characterization was performed by X-ray diffraction (XRD) using a Panalytical X'pert Pro diffractometer with a Co K α radiation source ($\lambda = 0.1789$ nm) operating

at 40 kV and 40 mA. The thermal stability of the samples was investigated isochronally (heating rate 40 K/min) and isothermally by differential scanning calorimetry (DSC) using a PerkinElmer DSC 7 calorimeter under a continuous flow of purified argon. Isothermal DSC measurements were carried out by heating at 40 K/min to different temperatures (673, 743, 753, and 763 K) followed by isothermally annealing for a maximum of 30 min. At 743 K, the crystallization is complete after 30 min; therefore, we set this time as the longest annealing time. The change of viscosity of the supercooled liquid as a function of the temperature was measured isochronally (heating rate 40 K/min) by parallel plate rheometry using a PerkinElmer TMA7 thermal mechanical analyzer (Waltham, MA, USA) operating under a high-purity argon atmosphere.



Figure 3. (**a**) The hot-pressing setup and (**b**) close view of the controlled atmosphere chamber. (**c**) Schematic of the hot-pressing process.

The microstructure of the samples was investigated by optical microscopy (OM, Nikon Epiphot 300) and scanning electron microscopy (SEM, Zeiss Gemini 1530, Oberkochen, Germany). Density measurements were conducted according to the Archimedeans principle using a precise balance (Sartorius MSA225S, Göttingen, Germany) with an accuracy of 0.01 mg. The relative density (or porosity) was calculated by comparing the experimental and theoretical density. Oxygen content of the specimens was analyzed by the carrier gas hot extraction method using a Leco ON-836 analyzer. Oxygen contamination increases from 0.09 ± 0.01 at.% in the atomized powder to 0.21 ± 0.01 at.% in the sample synthesized at 753 K. Such an increase, however, does not preclude the densification process. X-ray computed tomography (CT) was carried out using a GE Phoenix Nanotom device (140 kV voltage, 100 μ A current, and 1250 ms detector timing). The radiographic images with a spatial resolution of 3.33 μ m were then reconstructed using the VG Studio Max 2.2 software. The mechanical properties of the material hot pressed at 753 K were evaluated by room-temperature quasistatic compression tests (strain rate 1×10^{-4} s⁻¹). The tests were performed on cylindrical specimens (3 mm diameter and 6 mm length produced by wire

erosion from the 10 mm diameter cylinders hot pressed at 753 K) using an Instron 5869 testing facility. Polished tungsten carbide (WC) disks were used as platens, and a Fiedler laser extensometer monitored the strain directly at the samples. Both ends of the specimens were carefully ground to make them parallel to each other before the tests. Five samples were tested to ensure the reproducibility of the results.

3. Results

3.1. Selection of the Hot-Pressing Parameters

As previously mentioned, the production of highly dense BMG specimens while avoiding crystallization via PM processing, requires the identification of the optimal processing parameters. This includes the knowledge of T_x and T_g at the heating rate used during hot pressing, the incubation time, τ , for crystallization at a given temperature and the temperature dependence of viscosity.

Although the crystallization behavior of metallic glass powders can be significantly affected by the pressure applied during consolidation [28], the range of temperature where consolidation will take place can be successfully identified at atmospheric pressure by DSC. The isochronal (40 K/min) DSC scan for the $Zr_{48}Cu_{36}Al_8Ag_8$ glassy powder is presented in Figure 4a, showing the characteristic features of metallic glasses: an endothermic event due to the glass transition followed by an exothermic peak with onset T_x due to crystallization. The temperature onset of the glass transition, estimated as the intersection of the extrapolated horizontal line below the transition with the steepest tangent of following heat flow signal [29], is $T_g = 709$ K, whereas T_x , corresponding to the upper temperature limit for hot pressing, is 800 K. This gives an SCL region ΔT_x of 91 K, where consolidation can take place.



Figure 4. (a) Isochronal differential scanning calorimetry (DSC) scan (40 K/min) and viscosity vs. temperature (40 K/min) for the $Zr_{48}Cu_{36}Al_8Ag_8$ glassy powder; inset: change of the sample height as a function of temperature; (b) isothermal DSC scans of the powder carried out at 673, 743, 753, and 763 K; (c) isochronal DSC scans (40 K/min) for the $Zr_{48}Cu_{36}Al_8Ag_8$ glassy powder and bulk specimens hot pressed (HP) at different temperatures; (d) XRD patterns of as-atomized powder and hot-pressed samples.

The viscosity, η , as a function of temperature was derived from the change of the sample height (inset in Figure 4a) using Stefan's equation, which has been successfully used for describing the viscosity of the SCL of a series of Zr-based metallic glass ribbons [16], rods [30], and powders [31]:

$$\eta = \frac{2Fh^3}{3\pi r^4 (dh/dt)} \tag{1}$$

where *F* is the applied load (2.6 N), *r* is the radius of the plates (1.5 mm), and *h* is the height of the sample (100 μ m). The viscosity initially decreases rather slowly between 500 and 700 K (Figure 4a), most likely due to structural relaxation [30]. As the glass transition temperature is reached, the curve displays a stronger viscosity drop than the previous relaxation step, compatible with the viscous-flow behavior characteristic of metallic glasses above the glass transition temperature [16]. At about 765 K, crystallization sets in and the viscosity gradually increases with increasing temperature, indicating the loss of liquid-like behavior [16].

During an isochronal DSC at a given heating rate, crystallization is observed at a characteristic value of T_{x} , whereas during an isothermal DSC at a given temperature crystallization sets in after the so-called incubation time, τ [32]. Since hot pressing of the glassy powders is carried out isothermally at temperatures within the SCL region, the time-temperature processing window should ensure both decreased viscosity of the powder and an incubation time compatible with the holding time necessary for effective powder compaction. The incubation time, τ , at different temperatures (for 40 K/min heating rate) was thus determined by isothermal DSC measurements. The isothermal DSC scans (Figure 4b) show an exothermic peak due to crystallization and an incubation time that increases with decreasing the annealing temperature. At 763 K, crystallization starts after 5 min (extrapolated peak onset time [33]). Hot pressing requires a holding time of about 10 min; such a short incubation time would be, therefore, insufficient for sample consolidation avoiding crystallization. The incubation time then increases from about 8.5 min at 753 K to 18.5 min at 743 K, values more compatible with the experimental requirements for hot pressing. The incubation time exceeds 30 min when the isotherm is performed at a temperature lower than $T_{\rm g}$ (673 K); however, at this temperature, the glass does not show the liquid-like behavior necessary for powder consolidation (Figure 4a). We therefore selected 743 and 753 K as hot-pressing temperatures for the glassy specimens.

3.2. Microstructure and Mechanical Properties of Hot-Pressed Specimens

The microstructures of the BMGs hot pressed at 743 and 753 K are shown in Figure 5a,b, respectively. The specimen hot pressed at 743 K exhibits considerable porosity (about 3%), while porosity is significantly reduced in the sample consolidated at 753 K (1%). The isochronal DSC scans of the bulk BMGs hot pressed at 743 and 753 K (Figure 4c) show the same characteristics of the parent $Zr_{48}Cu_{36}Al_8Ag_8$ powder: a distinct glass transition followed by the exothermic event at higher temperature due to crystallization. The temperature of glass transition (T_g) is slightly affected by the consolidation process, while T_x is shifted to lower temperatures. This behavior can be ascribed to the change of composition of the glass as a result of partial crystallization during hot pressing. Partial crystallization indeed occurs during consolidation, as demonstrated by the reduced crystallization enthalpy (ΔH , corresponding to the area of the exothermic events in Figure 4c) of the BMG specimen hot pressed at 753 K (about 34 J/g) compared with the parent metallic glass powder ($\Delta H = 43 \text{ J/g}$). The size of the crystals, however, must be very small and below the detection limit of the X-ray diffractometer, as the XRD patterns in Figure 4d exclusively show the broad diffraction maxima characteristic of glassy materials. Improved densification can be achieved by hot pressing at 758 K (Figure 5c) but at the expense of the amount of glassy phase, which is drastically reduced; this is confirmed by the absence of the crystallization event in the corresponding DSC scan (Figure 4c) and by the presence of visible crystalline peaks in the XRD pattern (Figure 4d). Therefore, although the decrease of viscosity attained at 758 K assists the sintering process, it also accelerates atomic mobility

and the process of crystallization. Figure 5d shows the CT 3D view of the monolithic BMG consolidated at 753 K: no pores can be detected under the current spatial resolution (3.33 μ m), while an unidentified impurity (detected by the different X-ray absorptivity compared with the surrounding Zr₄₈Cu₃₆Al₈Ag₈ glass) with a volume fraction of less than 0.1 vol.% is observed.



Figure 5. Microstructure of the $Zr_{48}Cu_{36}Ag_8Al_8$ BMGs hot pressed at (a) 743 K, (b) 753 K, and (c) 758 K; (d) μ -CT (computed tomography) reconstruction of the $Zr_{48}Cu_{36}Al_8Ag_8$ powder hot pressed at 753 K showing minor impurities but no porosity.

The sample synthesized at 753 K represents the optimized material with the best compromise between high densification and minimum crystallization, while the sample synthesized at 758 K is highly dense but almost fully devitrified, and the sample hot pressed at 743 K is still amorphous but with significant residual porosity. We therefore analyze the mechanical behavior of the sample HP at 753 K because we want to compare its properties with the corresponding material synthesized by casting [20], which is highly dense and fully amorphous. Figure 6a shows the representative compressive stress-strain curves of the Zr₄₈Cu₃₆Al₈Ag₈ bulk specimen hot pressed at 753 K along with the corresponding material synthesized by casting [20]. The hot-pressed BMG exhibits a fracture strength of 1864 \pm 37 MPa and fracture strain of 1.8% \pm 0.1% with no visible plastic deformation (characteristics evaluated from five compression tests, Figure 6b). The mechanical properties of the Zr₄₈Cu₃₆Al₈Ag₈ BMG synthesized by powder metallurgy in this work are quite comparable with those of the corresponding BMG fabricated by casting (curve labeled "cast" in Figure 6a [20]): beside the tiny plastic deformation of the cast material, which is not present in the HP specimen, the curves display almost identical slope in the elastic regime (i.e., similar Young's modulus; 99 \pm 1 GPa and 101 GPa for the HP and cast samples, respectively) and comparable fracture strength.



Figure 6. (a) Representative room-temperature stress–strain curves under compression for the $Zr_{48}Cu_{36}Al_8Ag_8$ bulk specimen hot pressed at 753 K and the corresponding material synthesized by casting [20]. For clarity, the curve of HP 753 K was offset along the horizontal axis. (b) The five compressive stress–strain curves of the $Zr_{48}Cu_{36}Al_8Ag_8$ BMG hot-pressed at 753 K used to derive average strength and corresponding error.

4. Discussion

The small size of the BMG specimens synthesized by conventional casting is the most critical limitation to the exploitation of the remarkable properties of BMGs in structural applications. The restriction in sample size can be overcome by processing metallic glass powders via pressure-assisted sintering at low temperatures [27], where atomic mobility is sluggish and crystallization sets in after a much longer time compared with during the solidification of glass-forming melts, consequently giving more time for material processing. Long incubation times for crystallization is only one of the requirements for the fabrication of BMGs by PM. For example, at temperatures below T_{g} , crystallization can be drastically delayed (see red isothermal curve labeled "673 K" in Figure 4b). However, in order to achieve optimal densification, metallic glass powders have to be processed at temperatures above T_{g} , where the viscosity is low. Low viscosity implies high atomic mobility (and, thus, short incubation times), meaning that an optimal combination between viscosity and incubation time has to be found to achieve high density of the bulk specimens, while avoiding (or minimizing) crystallization. This approach is highlighted in Figure 7a, which shows the shrinking curves vs. holding time for the isothermal stage of hot pressing at 743 and 753 K (i.e., within the SCL region) along with the crystallized fractions derived from the areas of the corresponding isothermal DSC peaks in Figure 4b.

In order to effectively compare the results for hot pressing at 743 and 753 K, in the experiment summarized in Figure 7a, the curves are shifted to start the isothermal stage at 0 min. The densification of the powders is more effective at 753 K, as demonstrated by the larger shrinking at this temperature than for hot pressing at 743 K. This can be ascribed to the lower viscosity at 753 K (4.3×10^6 Pa s) compared with the value at 743 K $(4.8 \times 10^6 \text{ Pa s}; \text{ see Figure 4a})$. Low values of viscosity assist particle deformation, as described in Figure 7b, which schematically shows the variation of the contact area and densification caused by the viscous-flow behavior for a spherical metallic glass particle part of an ensemble of particles with cubic packed structure [34]. The shrinkage curves in Figure 7a indicate that densification is at first faster, most likely because of the extremely high effective pressure exerted on the initially small area of contact between the particles. Shrinkage then progressively slows down at later stages, when the low viscosity is unable to counterbalance the reduced effective pressure due to the increase of the contact area, as shown in Figure 7b. Figure 8 displays a visual confirmation of the change of the particle shape in the SCL region when pressure is applied. The image shows the fracture surface of a sample unintentionally fractured upon release of the pressure during hot pressing at 743 K. The characteristics shown in the figure for the 743 K sample are valid for the 753 K as well, with the only difference being the different relative density of the specimens. This demonstrates that the present Zr₄₈Cu₃₆Al₈Ag₈ particles indeed behave as a highly viscous



material at these temperatures, and their shape changes from spherical to polygonal, filling the space between particles (compare Figures 2a and 8).

Figure 7. (a) Shrinking curves as a function of the holding time for the isothermal stage of hot pressing (represented by the shadowed area) of the $Zr_{48}Cu_{36}Al_8Ag_8$ powder at 743 and 753 K along with the crystallized fractions derived from the areas of the corresponding isothermal DSC peaks in Figure 4b. Note that the curves are shifted so that the isothermal stage starts at 0 min for both experiments. The vertical dashed line represents the time when the pressure was released. (b) Schematic representing the variation of contact area for a particle in an ensemble of particles with cubic packed structure and corresponding to the shrinking curves in (a). The sphere is progressively deformed, increasing the sintering process, corresponding to the blue curves in (a). Crystals embedded in the glassy matrix are represented as dark blue pentagons.



Figure 8. Surface morphology of a $Zr_{48}Cu_{36}Al_8Ag_8$ bulk specimen consolidated at 743 K fractured upon release of the pressure during hot pressing showing the shape changes from spherical to polygonal.

Different temperatures correspond to characteristic values of viscosity and incubation time, τ (see the red curves of crystallized fraction in Figure 7a). Hot pressing at 743 K can be carried out without exceeding the incubation time; however, densification is not optimal, and the specimens consolidated at this temperature display significant residual porosity (Figure 5a). Porosity can be reduced by hot pressing at 753 K (Figure 5b), by taking advantage of the reduced viscosity. This, however, promotes crystallization (schematically described in Figure 7c), which sets in after a shorter incubation time at 753 K. The extent of crystallization at 753 K is, however, limited, and hot pressing at this temperature represents an optimal compromise between good densification and reduced crystallization of the glass.

The attractive properties of metallic glasses can find a wide spectrum of possible applications (Table 2). Except for applications that are not limited by the sample size, such as components for nano- and micromachines or microelectromechanical systems (MEMS) [35], the applications listed in Table 2 require a size of the specimens far exceeding the millimeter-scale size usually achievable by solidification [36]. The necessity of scaling up

the size of the BMG specimens is thus of primary importance. Powder metallurgy is a very flexible method to achieve this aim. Table 3 summarizes the microstructural characteristics and mechanical properties of different BMGs synthesized by powder metallurgy. One can observe that the size of the BMGs can be easily scaled up to tens of millimeters by pressure-assisted sintering of glassy powders and, in contrast to solidification of glassforming melts, this aspect is rather independent of the glass composition. Particularly significant is the production of Al-based BMGs, which are marginal glass formers [37], having a critical diameter of only 1 mm by solidification [13]; powder consolidation by SPS is able to produce bulk $Al_{86}Ni_6Y_{4.5}Co_2La_{1.5}$ specimens with size up to 10 mm [13]. Table 3 shows that, if a full amorphous powder is selected, the size of the particles has no significant influence on the propensity to crystallization during sintering. Similarly, the glass transition and crystallization temperatures and the width of the SCL region have very little impact on sample size, relative density, and mechanical properties: all PM BMGs are highly dense (relative density of about 99% or higher) with full amorphous structure or minimum crystallization (below the detection limit of XRD), and high strength comparable with the cast counterparts.

Table 2. Properties and potential applications of bulk metallic glasses (BMGs) [36].

Property	Application				
High strength	Machinery structural materials				
High hardness	Cutting materials				
High fracture toughness	Die materials				
High impact fracture energy	Tool materials				
High fatigue strength	Bonding materials				
High elastic energy	Sporting goods materials				
High corrosion resistance	Corrosion resistance materials				
High wear resistance	Writing appliance materials				
Good soft magnetism	Soft magnetic materials				
High frequency permeability	High magnetostrictive materials				
Self-sharping property	Penetrator				
High wear resistance and manufacturability	Medical devices materials				

Table 3. Microstructural features and mechanical properties of BMGs synthesized by powder metallurgy. σ_f is the fracture strength, σ_r is the relative strength with respect to the cast counterpart ($\sigma_r = \sigma_f / \sigma_{cast} \times 100\%$, where σ_{cast} is the fracture strength of the cast BMG with same composition), and ρ_r is the relative density. T_g = glass transition temperature, T_x = crystallization temperature, and ΔT_x = supercooled liquid region.

Composition -	Powder Characteristics			Processing	Sample	Sample	σι	σ_r	0r		
	Particle Size (µm)	<i>Т</i> g (К)	<i>Т</i> _х (К)	Δ <i>T_x</i> (K)	Method	Diameter (mm)	Structure	(MPa)	(%)	(%)	Ref.
Zr ₆₅ Al ₁₀ Ni ₁₀ Cu ₁₅	<75	652	735	83	Extrusion	~10	Amorphous	1520	96.8	99.4	[10]
$Ni_{59}Zr_{20}Ti_{16}Si_2Sn_3$	<45	815	878	63	Extrusion	~12	Amorphous	2000	90.9	99.5	[12]
Cu _{47.6} Ti _{32.7} Zr _{10.5} Ni _{6.1} Sn _{2.1} Si ₁	~30	722	759	37	SPS	20	A few crystals	1810	94	98.9	[11]
$Cu_{50}Zr_{45}Al_5$	<75	714	769	55	SPS	20	Amorphous	1840	97.6	99.9	[38]
Zr ₅₇ Cu ₂₀ Al ₁₀ Ni ₈ Ti ₅	63-125	653	718	65	SPS	10	A few crystals	1677	102	100	[24]
$Cu_{46}Zr_{42}Al_7Y_5$	<53	672	773	101	SPS	15	Amorphous	1774	115	~100	[39]
Al ₈₆ Ni ₆ Y _{4.5} Co ₂ La _{1.5}	<25	545	-	-	SPS	10	Amorphous	1250	119	~100	[13]
Cu ₅₀ Zr ₄₅ Al ₅	50	711	769	58	SPS	30	Amorphous	1600	93	100	[19]
Zr ₅₅ Cu ₃₀ Ni ₅ Al ₁₀	52	684	757	73	SPS	10	Amorphous	1622	98.9	98.7	[27]
$Zr_{48}Cu_{36}Al_8Ag_8$	100	709	800	91	Hot pressing	10	A few crystals	1864	100	99	This work

The small size of the samples is not the only limitation for the use of BMGs in structural applications. Monolithic BMGs show limited plasticity at room temperature due to the fact that plastic deformation in these materials occurs via the formation and propagation of highly localized shear bands [2]. Kosiba et al. [40] reported that shear band propagation in ZrCu-based glassy specimens can be guided via the generation of designed elastic stress

fields, suggesting that the current BMG may be made ductile. BMG composites containing secondary phases in the glassy matrix is another effective way to toughen the monolithic glass via a mechanism of shear band arrest and multiplication [41]. Note that deliberately introducing tough second phases is significantly difference to the aforementioned crystallization of the glass during processing. The synthesis of ductile BMG composites requires sophisticated design of the composition, size, distribution, volume fraction, and morphology of the second phase [42]. For many glass compositions, crystallization/devitrification induced by insufficient cooling rates usually results in the formation of brittle intermetallics, which in turn is detrimental to the mechanical properties [6]. ZrCu-based BMG can be post-treated by flash-annealing at high heating rates to induce the precipitation of ductile ZrCu crystals with B2 structure [21]. The B2 crystals can undergo martensitic transformation to the B19' phase upon deformation [43], which is quite effective to impede catastrophic shear band propagation in the glassy matrix, thus enhancing the plasticity and inducing work-hardening capability with respect to the monolithic glass [44].

5. Conclusions

To conclude, by carefully selecting the time–temperature window for powder consolidation, we synthesized a near fully dense $Zr_{48}Cu_{36}Ag_8Al_8$ BMG with minimum crystallization (below the detection limit of XRD). The hot-pressed BMG exhibits a fracture strength of 1864 ± 37 MPa and a fracture strain of $1.8\% \pm 0.1\%$, which is comparable with its cast counterpart. Powder metallurgy via pressure-assisted sintering in the SCL region, where the material displays liquid-like behavior, is an effective way to overcome the size limitation inherent to glass formation via solidification. The larger ZrCu-based BMG specimens synthesized in this study can be made ductile via the generation of designed elastic stress fields in the monolithic glass by postprocessing or can be utilized as precursors for the formation of ductile and work-hardenable BMG composites via the precipitation of the B2 ZrCu phase by flash-annealing at high heating rates. Finally, this work also has important implications for the synthesis of ex-situ $Zr_{48}Cu_{36}Ag_8Al_8$ BMG composites by powder metallurgy via introducing tough and ductile second phase into the glassy matrix.

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