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## Metals & corrosion



# Effect of cooling rate during solidification on structure and mechanical properties of Cu<sub>45</sub>Zr<sub>48</sub>Al<sub>7</sub> glass-forming alloy

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## ABSTRACT

The CuZr-based bulk metallic glass matrix composites have attracted great attention in recent years owing to their unique mechanical properties compared to bulk glassy samples. The vital effect of B2 CuZr phase on mechanical properties was previously confirmed in CuZr-based alloys with equiatomic concentrations of copper and zirconium. In this paper, the structures and mechanical properties of the Cu<sub>45</sub>Zr<sub>48</sub>Al<sub>7</sub> alloy, which has hypereutectoid composition with respect to stoichiometric B2 CuZr phase, were studied. This alloy exhibits high glass-forming ability, but low tendency to form the B2 CuZr phase during solidification. However, we demonstrated that depending on the cooling rate during solidification, governed by sample diameter, either bulk metallic glass or bulk metallic glass matrix composite can be produced. In order to allow partial crystallization of the B2 phase during solidification with the volume fraction allowing to observe the strain hardening effect, the minimum cooling rate should be lower than 40 K/s. The composite consisting of a glassy outer layer and a crystalline core composed of the B2 phase exhibits fracture strength of the same level as the bulk glassy sample (above 1800 MPa) obvious work-hardening with a plastic deformation of about 6%.

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## Introduction

The first bulk metallic glass (BMG), with each dimension of at least 1 mm, was developed in 1974 [1] and since then the critical size has been subsequently increasing until the development of Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> alloy by Inoue group with a critical cooling rate of 0.067 K/s and a critical diameter of 72 mm [2]. Pdbased alloys are considered to have the greatest glassforming ability (GFA). However, due to the extremely high cost of palladium, their commercial applications are excluded. Among the various glass-forming systems developed over the past decades, the Zr- and Cu-based systems are very attractive due to their high GFA, high fracture strength and relatively low costs of elements compared to other glass-forming systems [3, 4]. Due to the atomic-size mismatch between Cu and Zr (atomic radii of 1.27 Å and 1.58 Å, respectively [5]) and the large negative heat of mixing (-23 kJ/mol) [6], these two elements will always be present in their reciprocal alloys, Zr being present in Cu-based glassforming alloys, and vice versa.

Bulk metallic glasses exhibit outstanding properties like high elasticity, superior strength, good corrosion and wear resistance, compared to their crystalline counterparts. However, their major drawback is room temperature brittleness, related to the stress localization into shear bands, which limits their potential engineering applications [7–9]. In order to overcome this shortcoming, the concept of bulk metallic glass matrix composites (BMGMCs) with ductile crystalline phases embedded in the glassy matrix have emerged. Many attempts have been made to form BMGMCs. Initially, a presence of crystalline phase was generated by partial devitrification of the monolithic glass during annealing. However, partially nanocrystalline structure generally does not improve toughness, when compared to monolithic glass. The composites can be also formed either by ex-situ introduction of particles/ fibers prior to casting [9–11] or in-situ precipitation of the crystalline phase during solidification [9, 12, The main advantages of in-situ formed BMGMCs are simple processing route and good bonding at the interface between the amorphous matrix and reinforcing precipitates.

The idea underlying the development of BMGMCs is related with possible manipulation of shear bands nucleation and propagation during deformation by utilizing the presence of ductile crystalline precipitates. Their presence favors greater plastic strains by enabling dislocation motion within a ductile crystalline phase and by ensuring that the shear bands never reach an unstable condition in the amorphous matrix. These requirements are fulfilled if the shear modulus of the crystalline phase is lower than that of the glassy matrix [14].

The vast majority of BMGMCs exhibit several percent of plastic strain, but undesired strain-softening during deformation is observed rather than workhardening. This phenomenon, which is highly undesirable in engineering applications, is associated with lack of any strengthening mechanisms within the glassy matrix or in-situ formed precipitates.

In the last years, the Cu-Zr-based BMGMCs with in-situ formed B2 CuZr phase, have emerged great research interest because of possible martensitic transformation of a cubic B2 CuZr into monoclinic B19' CuZr phase, which can increase both strength and plastic strain during deformation. The vital effect of the B2 CuZr phase in the Cu<sub>475</sub>Zr<sub>475</sub>Al<sub>5</sub> alloy cast in form of 2-mm-diameter rods was first reported by Das et al. in 2005 [16]. Unlike other types of BMGMCs, the CuZr-based composites comprise the shape-memory B2 CuZr crystalline phase, which undergoes martensitic transformation during deformation into the B19' phase [10–16]. In other words, these composites are characterized by the transformation-induced plasticity (TRIP) effect, similar to certain conventional crystalline alloys.

One of the biggest challenges in designing BMG-MCs with the in-situ formed B2 CuZr phase is to control the volume fraction of this phase in the ascast state. Upon cooling, the binary  $Cu_{50}Zr_{50}$  alloy solidifies congruently to the CuZr phase with a cubic B2 CsCl-type structure at 935 °C (1208 K) and this phase is thermodynamically stable down to 715 °C (988 K) [17, 18]. If the system is given enough time, the B2 CuZr phase decomposes eutectoidally to the orthorhombic Cu<sub>10</sub>Zr<sub>7</sub> and tetragonal CuZr<sub>2</sub> brittle phases, which are equilibrium phases at room temperature. Therefore, in order to understand the formation of BMGMCs, the competition between glass formation, precipitation of the B2 CuZr and room temperature equilibrium phases should be considered. Cooling rate equal to or higher than the critical cooling rate (CCR) for glass formation leads to vitrification at  $T_{g}$  temperature. On the other hand, low cooling rates result in the formation of the B2 CuZr phase during solidification, but further eutectoid decomposition of this phase into the

low-temperature equilibrium phases is possible. Therefore, in order to obtain both phases, B2 CuZr and amorphous, moderate cooling rates are necessary. This competition can be reflected in differential scanning calorimetry (DSC) analysis, where initially amorphous CuZr-based alloy is subjected to heating. Once the exothermic event(s) related to crystallization of an amorphous phase is finished, an eutectoid transformation of the crystallization products into the B2 CuZr phase, accompanied by endothermic peak should occur prior to the melting event. Song et al. [14] showed that locations of onset crystallization  $(T_r)$ , endset B2 phase formation  $(T_f)$  and liquidus  $(T_{\rm I})$  temperatures affect the formation of each phase. The glass-forming ability is proportional to the  $T_x/T_L$ ratio, whereas the B2 CuZr phase formation is proportional to  $T_{\rm f}/T_{\rm I}$  and inversely proportional to  $T_{\rm r}/T_{\rm f}$ . Therefore, the tendency to formation of BMGMCs with the B2 CuZr phase can be formulated using a dimensionless *K* parameter [14]:

$$K = \frac{T_{\rm f}}{T_{\rm L}} \tag{1}$$

Depending on the *K* value, the CuZr-based alloys can be classified into three types [14]:

- Type I: K < 0.7;</li>
- Type II: 0.77 < *K* < 0.9;
- Type III: K > 0.94.

If the endothermic peak associated with the formation of the B2 CuZr phase is shifted to low temperatures (Type I alloys), the glass-forming ability becomes very limited. The application of high cooling rates (small diameter samples) enables casting of amorphous-crystalline composites, but it can cause an undesired transformation of the B2 CuZr into martensite, due to thermal stresses during rapid quenching [19]. On the other hand, high values of K parameter (Type III) mean that the time/temperature window for the formation of B2 phase during solidification is very limited, but BMGMC with larger dimensions can be obtained. For Type II alloys, the formation of BMGMCs is possible, because of sufficient time necessary to form the B2 CuZr phase during solidification [14].

The glass-forming ability of a binary Cu–Zr system is very limited, but it can be significantly increased by the addition of transition metals such as Ti, Ni or Al. The addition of up to 8% of aluminum to the  $Cu_{50}Zr_{50}$  alloy increases the supercooled liquid region by as much as 30 K [20]. Because the B2 CuZr phase is an equiatomic phase, the majority of reports on the BMGMCs containing B2 CuZr phase is on the  $(Cu_{0.5}Zr_{0.5})_{100-x}M_x$  relation, where *M* stands for any alloying elements. In this paper, the microstructures and mechanical properties of the  $Cu_{45}Zr_{48}Al_7$  alloy, which has hypereutectoid composition with respect to stoichiometric B2 CuZr phase, were studied.

Cooling rate during solidification in a given casting method is a crucial factor. Based on the physical properties and a difference between melting and glass transition temperatures of most BMGs, Lin and Johnson [21] obtained a simple equation for expressing the cooling rate (CR):

$$\operatorname{CR}\left(\frac{K}{s}\right) = \frac{10}{R^2} \tag{2}$$

where R is the dimension (diameter, thickness) expressed in cm.

On the other hand, Löffler et al. [22] proposed

$$\operatorname{CR}\left(\frac{K}{s}\right) = \frac{20}{d^2} \tag{3}$$

where *d* is the casting thickness expressed in cm.

Comparing both equations, it is clear that for the same Dc value, the CCR based on Eq. (3) is twice than that of the obtained from Eq. (2). However, the cooling rate during solidification may vary on the casting parameters—initial temperature of the copper mold, mold geometry, melting current etc. Based on the relation between water-cooling system temperature (WCST) and rod diameter, the minimum cooling rate during solidification can be obtained according to the following formula [23]:

$$CR = \frac{10^{-0.0059 \cdot WCST + 4.9746}}{\{d(mm)\}^{0.0195 \cdot WCST - 3.6351}}$$
(4)

This formula was derived based on the microstructural observations of the as-cast Fe-25 wt% Ni in the rod axis, so it corresponds to the minimum cooling rate during solidification.

## Materials and methods

The Cu<sub>45</sub>Zr<sub>48</sub>Al<sub>7</sub> alloy was synthesized in an arc melter (Edmund Bühler GmbH) on a water-cooled copper hearth under a purified Ti-gettered argon atmosphere using raw metals with at least 99.9% purity. Before melting, the chamber was evacuated to  $< 5 \times 10^{-2}$  mbar, backfilled with high purity (6N) Ar. The flushing and backfilling cycle was repeated three times to minimize the oxygen concentration in the chamber. Next, a series of rod samples with length of 55 mm with diameters from 3 to 8 mm were produced using a water-cooled suction unit. Standard water-cooling system temperature (290 ± 1 K) was used to ensure efficient heat removal. Same device and casting procedure was used for estimation of cooling rate during solidification in our previous work [23].

The as-cast rod samples were cut according to the procedure given in Fig. 1. In order to minimize possible differences in cooling rate, the initial and final parts of the rod length were discarded from the tests. Samples for microscopic observations (referred to as LM) were taken at 10 mm and 45 mm from the bottom end. Additionally, two samples were cut for mechanical testing (S1, S2), and samples for X-ray diffraction (XRD) and differential scanning calorimetry (DSC) analyses were placed between them.

The structures of as-cast and deformed samples were characterized using an X-ray diffractometry (Panalytical Empyrean) with CuK<sub> $\alpha$ </sub> radiation (1.5406 Å). Differential scanning calorimetry (Netzsch DSC F1 Pegasus) at a constant heating rate of 20 K/min was used to measure characteristic temperatures of phase transformations (glass transition  $T_{g'}$  onset crystallization  $T_{x'}$  peak  $T_{p'}$  solidus  $T_{s'}$  and liquidus  $T_{L}$ ). The  $T_{g}$  temperatures were estimated as inflection points on the DSC curves. Moreover, start and final temperatures of the phase transformation ( $T_{s}$  and  $T_{f'}$  respectively) related with formation of the B2 CuZr during heating were determined. Based on DSC measurements, the reduced glass-transition temperature



Figure 1 Scheme of cutting and taking samples for testing.

 $(T_{rg} = T_g/T_L$  [24]) and the tendency to form bulk metallic glass composite with a B2 CuZr phase during solidification ( $K = T_f/T_L$  [14]) were calculated.

Standard grinding and polishing procedures (final polishing with colloidal silica suspension) were applied to reveal crystal structures. Volume fractions of crystalline areas were estimated on light microscopy images using ImageJ software. Microstructural examinations were carried out using light microscopy (LM, Nikon ECLIPSE LV150N) and scanning electron microscopy (SEM, FEI Versa 3D) techniques. SEM observations were carried out using back-scattered electron (BSE), energy-dispersive spectroscopy (EDS, Ultim Max, Oxford Instruments) and electron backscatter diffraction (EBSD, Symmetry S-2, Oxford Instruments) detectors. The EBSD analyses were performed in cross-sections, i.e., in planes perpendicular to the cylindrical axis.

High-resolution scanning transmission electron microscopy (HRSTEM) studies were carried out using a FEI, Titan<sup>3</sup> G2 60–300 microscope operated at 300 kV. The images were captured in bright field (BF) and fast Fourier transforms (FFT) were applied to solve the diffractions. The studies were performed on TEM lamellae, prepared via focused ion beam milling using the ZEISS NEON CrossBeam 40EsB. Room temperature compression tests were performed at an initial strain rate of  $1 \times 10^{-4}$  s<sup>-1</sup> using an Instron 5982 testing machine. The height-to-diameter aspect ratio of the bulk compression specimens was kept to 2.0 and both ends of the specimens were carefully ground to make them parallel. Mean values of yield strength ( $\sigma_{0,2}$ ), fracture strength ( $\sigma_{max}$ ) and plastic strain ( $\varepsilon_{p}$ ) were calculated from three tested specimens for each rod diameter, so extra rod samples dedicated for mechanical testing were produced. The  $\sigma_{0,2}$  was calculated as the amount of stress that resulting in a plastic strain of 0.2%. Fracture surface observations after compression tests were carried out using SEM equipped with a secondary electron (SE) detector.

## Results

Minimum cooling rates during solidification estimated from Eq. (4) are presented in Table 1 (values obtained from Eqs. 2 and 3 are given for comparison). As the relation between CR and rod diameter for a constant water-cooling system temperature was proven as

Table 1         Minimum cooling	
rates during solidification	
estimated from Eqs. (2–4)	

Cooling rate (K/s)	Rod diameter						
	3 mm	4 mm	5 mm	6 mm	7 mm	8 mm	
<b>From Eq.</b> (4)	199	112	71	49	36	28	
From Eq. (2)	111	63	40	28	20	16	
From Eq. (3)	222	125	80	56	41	31	



Figure 2 XRD patterns of as-cast  $Cu_{45}Zr_{48}Al_7$  alloy with a diameter between 3 and 8 mm.

exponential decay [23], the highest decrease of cooling rate is noticed for the lowest diameter.

Figure 2 shows XRD patterns of the Cu<sub>45</sub>Zr<sub>48</sub>Al<sub>7</sub> alloy cast in 3- to 8-mm-diameter rod samples. Typical amorphous halos without any detectable sharp Bragg peaks were recorded for the 3-, 4- and 5-mm-diameter samples. The crystalline B2 CuZr phase (CsCl-type bcc-based structure), with the main intensity peak at  $2\theta = 39^{\circ}$  corresponding to the (110) plane was detected for higher diameter samples. Minor peak can be observed for the 6 mm sample, indicating low volume fraction of B2 phase. For the 8-mm-diameter sample, apart from the B2 phase, the crystalline AlCu<sub>2</sub>Zr phase (Cu<sub>2</sub>MnAl-type fcc structure) was also identified.

The DSC studies (Fig. 3) confirmed presence of the amorphous phase in all studied variants, including 8-mm-diameter sample. The studied samples exhibit a distinct glass transition temperature, followed by a



Figure 3 DSC curves of the  $Cu_{45}Zr_{48}Al_7$  alloy samples recorded at a heating rate of 20 K/min.

supercooled liquid region and two exothermic peaks related to crystallization of the amorphous phase, with onset crystallization temperature  $T_x = 760 \pm 1$  K and peak crystallization temperatures of about 763 and 870 K. The enthalpy of crystallization of the first exothermic event is much higher compared to the second one (Table 2). With further heating three endothermic events were recorded, with the last one related to melting process ending at a temperature of about 1160 K. The two preceding events, which are much weaker compared to last one, are most likely related to the formation of the B2 CuZr phase during heating, because the composition of this alloy is hypereutectoid with respect to the stoichiometric B2 CuZr phase.

For the 8-mm-diameter sample, it was possible to cut the specimens for DSC measurements from the outer part of the rod as well as the central one. There is a clear difference in DSC scans; typical thermal events



Characteristic		Rod diameter							
formations measured		3 mm	4 mm	5 mm	6 mm	7 mm	8 mm		
$Cu_{45}Zr_{48}Al_7$ alloy with rs of 3 to 8 mm along							outer	central	
rameters describing	$T_{\rm g}$ (K)	699	704	707	706	704	707	_	
s-forming ability $(T_{rg})$	$T_{x}(\mathbf{K})$	760	760	760	759	759	761	_	
lency to formation	$T_{p1}$ (K)	761	761	762	761	760	763	_	
2 CuZr during	$T_{p2}(K)$	872	868	873	872	871	866	-	
ation (K)	$T_{\rm B2(1)}({\rm K})$	988	989	989	989	987	987	-	
	$T_{\rm B2(2)}({\rm K})$	1072	1070	1071	1072	1072	1070	_	
	$T_{\rm f}({\rm K})$	1085	1081	1084	1084	1080	1081	-	
	$T_{\rm s}\left({\rm K}\right)$	1129	1136	1131	1134	1136	1134	1132	
	$T_{\rm L}({ m K})$	1160	1165	1161	1164	1163	1165	1166	
	$\Delta H_1$ (J/g)	-47.4	-45.2	-42.5	-41.6	-44.6	-31.0	-	
	$\Delta H_2$ (J/g)	-10.4	-10.3	-11.5	-10.7	-11.1	-8.1	-	
	$\Delta H_{\mathrm{B2(1)}} (\mathrm{J/g})$	12.4	9.7	8.6	8.5	9.5	7.1	-	
	$\Delta H_{\mathrm{B2(2)}} (\mathrm{J/g})$	19.6	21.2	16.2	16.1	17.6	12.2	-	
	$\Delta H_{\rm top}  ({\rm J/g})$	98.5	98.8	76.5	80.2	98.3	92.0	81.4	
	$T_{rg}$	0.60	0.60	0.61	0.61	0.61	0.61	-	
	K	0.94	0.93	0.93	0.93	0.93	0.93	_	

Table 2 tempera of trans for the C diamete with par the glass and tend of the B solidific

for the initially amorphous alloys were observed for the specimen cut from the outer part (close to surface) of the rod, while for the central part only melting event could be noticed.

The ability to form CuZr-based BMGMC in the Cu45Zr48Al7 alloy was estimated at 0.93-0.94, so it can be classified to low susceptible alloys, with possible B2 formation for larger sample dimensions.

Figure 4 shows LM images of Cu<sub>45</sub>Zr<sub>48</sub>Al<sub>7</sub> alloy cast in form of as 4-, 5- and 6-mm-diameter rods. Sparse spherical precipitations distributed randomly within a featureless matrix were observed. The morphology of the dendritic precipitation in its central part was revealed by scanning electron microscopy (Fig. 4c, d). Approaching the interface between crystal and matrix, the dendrites become finer and finally cannot be resolved using SEM, so high-resolution transmission electron microscopy was employed to examine both phases. The interface between glassy matrix and crystalline precipitate for the 5 mm sample is shown in Fig. 5a and corresponding HRSTEM image (Fig. 5b). The FFT pattern from disordered region (matrix) confirmed its amorphous structure (Fig. 5c), while FFT taken from dendrite (Fig. 5d) confirmed existence of the B2 CuZr phase.

The micrographs of the end faces of 7- and 8-mmdiameter samples are depicted in Fig. 6. The mean volume fraction of crystalline areas for 7-mm-diameter sample was 14%, but they tend to form coarser areas at the upper part of the rod (Fig. 6b). Increase of the sample diameter up to 8 mm brought about crystallization of whole central part of the cast (Fig. 6c, d) with the amorphous (featureless) phase remaining only at the outer part of the rod (Fig. 6e). In this case nice grain boundaries and dendritic morphology of crystals could be observed within resolution of LM (Fig. 6f) and SEM (Fig. 6g). Mean volume fraction of crystalline areas was measured as 43%.

Figure 7 and Table 3 depict mechanical properties of the Cu45Zr48Al7 alloy tested in compression at a strain rate of  $1 \times 10^{-4}$  s<sup>-1</sup>. This alloy exhibits fracture strength above 1700 MPa, but the fracture behavior strongly depends on the structure. Compressive stress-strain curves without a distinct plastic strain were recorded for the sample diameter up to 6 mm, which is typical behavior for most monolithic BMGs. On the other hand, composites (7 and 8 mm dia. samples) exhibit relatively large plastic strain and work-hardening, as the flow stress increases with the increasing strain after yielding. The higher volume fraction of the B2 phase, the lower yield strength and the higher plastic strain. The composite containing of about 43% of B2 phase shows yield strength 1352 ± 66 MPa, fracture strength  $1848 \pm 198$  MPa and plastic strain above 6%.

Figure 8 shows comparison of XRD patterns of as-cast and deformed 6 and 8 dia. samples. Similar

Figure 4 a–c The overall view of the cross-section of the  $Cu_{45}Zr_{48}Al_7$  alloy observed by light microscopy: a 4 mm dia., b 5 mm dia., c 6 mm dia., d, e SEM images of the 5 mm dia. sample.



Figure 5 STEM images of the 5-mm-diameter sample: a amorphous-crystalline interface; b–d HRSTEM images of the interface (b), amorphous (c) and crystalline (d) areas. Insets show FFT images of amorphous and crystalline phases.





Figure 6 a-d The overall view of the cross-section of the 7 mm (a, b) and 8 mm (c, d) samples observed by light microscopy. Micrographs a and c were recorded at the bottom part, b and d at the upper part of the rods. e-g Microstructures of the 8 mm dia. sample observed close to surface (e) and in the rod axis (f, g).



patterns with a broad amorphous halo and a weak peak coming from B2 phase was noticed for 6-mmdiameter samples. On the other hand, a broad maximum originating from the glassy phase superposed by reflections of the B19' martensite were recorded for 8 mm sample. More reflections from the B2 phase could be observed on the deformed samples which is a result of non-homogeneous distribution of this phase along the rod length.

SEM observation of the fractured surfaces allowed to observe vein-like melted patterns (Fig. 9) for all samples, with characteristic droplets and layers of solidified liquid (depicted by white arrows). This phenomenon is related to the storage of elastic deformation energy, which is released during the formation of the shear bands in the form of heat. As a result, it leads to a local temperature increase to very high values, estimated even at several thousand degrees [25, 26]. More developed fracture surface was observed for partially crystalline 8-mm-diameter sample (Fig. 9c, d). In this case, numerous shear bands were observed on the lateral surface (Fig. 10). The propagation of shear bands is blocked by the B2 particle, which hinders shear bands movement at the interface between the glassy matrix and the precipitate. Inside the particle, there are parallel stripes marked with arrows



**Figure 7** Compressive engineering stress–strain curves for the as-cast  $Cu_{45}Zr_{48}Al_7$  alloy tested at a strain rate of  $1 \times 10^{-4}$  s<sup>-1</sup>. The curves are shifted relative to each other for clarity of presentation.

(Fig. 10b), which indicates the occurrence of a martensitic transformation from B2 to B19' CuZr phase during deformation.

Microstructure observations performed on the metallographic specimen prepared from fractured 7-mm-diameter sample confirmed the deformationinduced martensitic transformation. Characteristic martensitic laths were observed inside the separated spherical precipitates (Fig. 11a) and large crystalline regions (Fig. 11b). EBSD analysis confirmed presence of the B19' CuZr phase. Figures 12a, b show SEM micrographs recorded in the forward scatter detector (FSD) image and Inverse Pole Figure (IPF) map, respectively. It is known, that between parent B2 and B19' phases the  $[100]_{B2}$  ||  $[100]_{B19'}$ ,  $(011)_{B2}$  ||  $(001)_{B19'}$  and  $(01-1)_{B2} \mid \mid (010)_{B19'}$  orientation relationships should be fulfilled [30, 31]. In the areas between B19' CuZr phase, the B2 phase could not be indexed during EBSD analysis, so direct comparison of pole figures of parent and child grains was not possible. In order to confirm this, the idealized pole figures of the cubic B2 CuZr phase (Fig. 12c) was rotated to fulfil this relationship and good agreement with experimental pole figures of multivariant B19' CuZr phase can be noticed (Fig. 12d).

#### Discussion

The glass-forming ability of a binary Cu-Zr system is limited, but aluminum is known to significantly improve it. Since the B2 CuZr phase has an equiatomic composition, most of the developed CuZr-based BMG-MCs have the same content of these elements. However, Al can be also dissolved in this phase. Pauly et al. [11] proposed polymorphous crystallization mechanism of the B2 CuZr phase formation during solidification of the  $Cu_{47}$  <sub>5</sub> $Zr_{47}$  <sub>5</sub> $Al_5$  melt, with a maximum solubility of approximately 4 at% Al in B2 CuZr dendrites. The Cu<sub>45</sub>Zr<sub>48</sub>Al<sub>7</sub> alloy has hypereutectoid composition with respect to the stoichiometric B2 CuZr phase. DSC measurements showed that this alloy exhibits low tendency to form B2 CuZr phase during solidification, as the K parameter is  $0.93 \div 0.94$ , which places it in type III alloys [14]. However, we proved that by tailoring of the cooling rate during solidification, governed by changing the sample diameter, it is possible to obtain the BMGMC with a different volume fraction of the B2 CuZr phase. With increasing rod diameter, the axial cooling rate exponentially decreases, and a good agreement with relation of 20/{d(cm)}<sup>2</sup> was noticed for the standard (290 ± 1 K) water-cooling system temperature.

For smaller diameters (up to 6 mm) it is lower than 1%, with individual spherical precipitates. In case of 7 mm dia. sample, corresponding the axial cooling rate of 36 K/s, a composite consisting of about 14% of a crystalline B2 CuZr phase was successfully produced. Increase in the sample diameter to 8 mm (axial

Table 3	Mechanical
propertie	es of the Cu <sub>45</sub> Zr <sub>48</sub> Al
allov test	ted in compression

Rod diam- eter (mm)	$\sigma_{0.2}$ (MPa)	$\sigma_{\rm max}$ (MPa)	ε <sub>p</sub> (%)	Volume fraction of crystalline areas (%)	Minimum (axial) cooling rate during solidification
3	_	$1830 \pm 44$	_	<1	199
4	_	$1776 \pm 98$	_	<1	112
5	-	$1834 \pm 34$	_	<1	71
6	$1559 \pm 140$	$1720 \pm 91$	$1.7 \pm 0.7$	<1	49
7	$1297 \pm 377$	$1798 \pm 71$	$4.9 \pm 3.4$	14	36
8	$1352\pm66$	$1848 \pm 198$	$6.1\pm3.2$	43	28



**Figure 8** XRD patterns of as-cast and deformed  $Cu_{45}Zr_{48}Al_7$  alloy with a rod diameter of 6 and 8 mm.

Figure 9 SEM images of the fractured surface for the 5 mm (**a**, **b**) and 8 mm (**c**, **d**)

diameter samples.

cooling rate of 28 K/s) enabled to obtain BMGMC composed of amorphous outer layer and crystalline core with total volume fraction of crystalline areas of about 43%. XRD studies proved that in this alloy, the cubic AlCu<sub>2</sub>Zr phase is formed, which is most probably located between the dendrite arms. With increasing volume fraction of the precipitates they may impinge each other leading to form coarse crystalline areas, as observed in Fig. 6c, d. Han et al. reported a percolation threshold for dual-phase Cu-Zr-Al-Co BMG composites between 10 and  $31 \pm 2 \text{ vol}\%$  [27], and we observed this phenomenon for the composite containing 14% of crystallites (Fig. 6b). In addition, we noticed a difference between bottom and top ends which is probably related by difference of the cooling rates. The residual heat coming from the excess melt above the rod leads to lower cooling rate and coarse crystalline areas.

In contrast to the CuZr-based BMGMCs with equiatomic concentrations of Cu and Zr, we observed two endothermic events preceding the melting process on DSC curves. This is related to shifting the composition out of the eutectoid composition, so a two-stage



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Figure 10 SEM images of the lateral surfaces 8-mm-diameter sample.



Figure 11 SEM images of metallographic specimen prepared on the cracked sections of the 7-mm-diameter sample.

transformation during heating is necessary to reach a B2 CuZr phase stability region. With the applied heating rate of 20 K/min, the first endothermic event starts at about 873 K (peak temperature ~ 988 K), while endset temperature of second event ( $T_f$ ) is approx. 100 K higher. Both endothermic peaks disappeared in the 8 mm dia. sample cut from the central part of the rod consisting of the B2 CuZr phase. In this case no solidstate transformations were recorded and only melting event was noticed. It confirms that the B2 CuZr phase was stable from room temperature up to the solidus temperature.

No significant changes in mechanical properties of the suction-cast  $Cu_{45}Zr_{48}Al_7$  alloy were noticed for sample diameters between 3 and 6 mm, as the volume fraction of precipitates was below 1%. The fracture strength is in the range of 1800 MPa, but no distinct plastic strain can be expected. With increasing volume fraction of the B2 CuZr phase successfully stabilized to room temperature, the beneficial effect of B2 CuZr phase on the mechanical properties of BMG-MCs can be noticed. For 7 mm dia. sample containing 14% of B2 crystallites, the mean fracture strength was approx. 1800 MPa, but distinct plastic strain was observed (5%). These values were even higher for the composite containing 43% of crystalline area  $(\sigma_{\rm max} = 1848 \pm 195 \text{ MPa} \text{ and } \varepsilon_{\rm p} = 6.1 \pm 3.2\% \text{ for } 8 \text{ mm} \text{ dia.}$ sample). However, the yield strength, which depends mostly on the volume fraction of the glassy phase, decreased from  $1559 \pm 140$  MPa to  $1350 \pm 66$  MPa with increasing sample dimeter from 6 to 8 mm. It should be noted here that any casting defects significantly affect mechanical properties leading to high estimation error. The best 8 mm dia. sample exhibited fracture strength above 2 GPa and a plastic strain above 8%. Our results are similar to those obtained in Cu-Zr-Al alloy with equiatomic concentrations of Cu and Zr [13, 28–31], so the key point is to stabilize the B2 CuZr phase down to room temperature.





Figure 12 EBSD analysis of the deformed 7-mm-diameter sample: a SEM micrograph in the FSD image; b SEM FSD image and IPF map with highlighted area of pole figures analysis; c idealized pole figures of the cubic B2 CuZr phase rotated to fit

the theoretical crystallographic orientation relationship;  $\mathbf{d}$  experimental pole figures of the monoclinic B19' CuZr phase (generated from highlighted area of **b**).

The work-hardening behavior was observed for the BMGMCs. XRD studies of the deformed samples supported by SEM observations and EBDS analysis on the metallographic specimens prepared from the fractured samples confirmed existence of the B19' CuZr monoclinic phase along with primary B2 CuZr and amorphous phases. The martensite laths of B19' phase were observed both within individual spherical precipitates and the large crystalline areas (see. Figure 11).

#### Conclusions

The Cu<sub>45</sub>Zr<sub>48</sub>Al<sub>7</sub> hypereutectoid alloy with respect to the stoichiometric CuZr eutectoid composition is characterized by high glass-forming ability ( $T_{rg}$  = 0.6) and low tendency to formation of the B2 CuZr phase during solidification (*K* = 0.93). Depending on the cooling rate during solidification, either bulk metallic glass or bulk metallic glass matrix composite with a remarkable fraction of the B2 CuZr phase can be produced. If the axial cooling rate is 40 K/s or higher, the glassy matrix with spare B2 precipitates were observed, so no strain hardening effect could be observed in compression. Decrease of a cooling rate, governed by increase of a sample diameter, allowed formation of the B2 phase during solidification. The composites consisting of a glassy outer layer and a crystalline core exhibit obvious work-hardening behavior. The fracture strength of a composite containing 43% of a crystalline phase, composed mainly of B2 CuZr with a minor AlCu<sub>2</sub>Zr phase is of the same level as the bulk glassy sample (above 1800 MPa), but it has a plastic deformation of about 6%. The B2  $\rightarrow$  B19' deformationinduced martensitic transformation was confirmed to contribute to work-hardening, which is extremely important feature in designing load-bearing materials.

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## Author contributions

TK contributed to conceptualization, methodology, formal analysis, visualization, data curation, supervision, and writing—original draft. GC contributed to XRD analysis, SEM and EBSD observations, visualization, and writing—review & editing. BR contributed to TEM observations, visualization, and writing—review & editing. AW-M contributed to DSC analysis, visualization, and writing—review & editing. KP contributed to alloy synthesis and casting, light microscopy observations, visualization, and writing—review & editing. PB contributed to conceptualization, and writing—review & editing.

#### Data availability

The raw/processed data required to reproduce these findings are available on https://doi.org/10.58032/AGH/UFTAVQ.

## Declarations

**Conflict of 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.

Ethical approval Not Applicable.

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## References

- Chen HS (1974) Thermodynamic considerations on formation and stability of metallic glasses. Acta Met Mater 22:1505–1511
- [2] Inoue A, Nishiyama N, Kimura H (1997) Preparation and thermal stability of bulk amorphous Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> alloy cylinder of 72 mm in diameter. Mater Trans JIM 38:179– 183. https://doi.org/10.2320/matertrans1989.38.179
- [3] Dai CL, Guo H, Shen Y et al (2006) A new centimeterdiameter Cu-based bulk metallic glass. Scr Mater 54:1403– 1408. https://doi.org/10.1016/j.scriptamat.2005.11.077
- [4] Zhou BW, Zhang XG, Zhang W et al (2010) Synthesis and mechanical properties of new Cu-based Cu–Zr–Al glassy alloys with critical diameters up to centimeter order. Mater Trans 51:826–829. https://doi.org/10.2320/matertrans. MBW200928
- [5] Xu D, Duan G, Johnson WL (2004) Unusual glass-forming ability of bulk amorphous alloys based on ordinary metal copper. Phys Rev Lett 92:245504–245511. https://doi.org/ 10.1103/PhysRevLett.92.245504

- [6] Takeuchi A, Inoue A (2005) Classification of bulk metallic glasses by atomic size difference, heat of mixing and period of constituent elements and its application to characterization of the main alloying element. Mater Trans 46:2817– 2829. https://doi.org/10.2320/matertrans.46.2817
- [7] Langer JS (2006) Shear-transformation-zone theory of deformation in metallic glasses. Scr Mater 54:375–379. https://doi.org/10.1016/j.scriptamat.2005.10.005
- [8] Greer AL (2009) Metallic glasses...on the threshold. Mater Today 12:14–22. https://doi.org/10.1016/S1369-7021(09) 70037-9
- [9] Lewandowski JJ, Wang WH, Greer AL (2005) Intrinsic plasticity or brittleness of metallic glasses. Philos Mag Lett 85:77–87. https://doi.org/10.1080/09500830500080474
- [10] Jiang F, Zhang ZB, He L et al (2006) The effect of primary crystallizing phases on mechanical properties of Cu<sub>46</sub>Zr<sub>47</sub>Al<sub>7</sub> bulk metallic glass composites. J Mater Res 21:2638–2645. https://doi.org/10.1557/Jmr.2006.0315
- [11] Pauly S, Liu G, Wang G et al (2009) Microstructural heterogeneities governing the deformation of Cu<sub>47.5</sub>Zr<sub>47.5</sub>Al<sub>5</sub> bulk metallic glass composites. Acta Mater 57:5445–5453. https://doi.org/10.1016/j.actamat.2009.07.042
- [12] Pauly S, Das J, Duhamel C, Eckert J (2007) Martensite formation in a ductile Cu<sub>47.5</sub>Zr<sub>47.5</sub>Al<sub>5</sub> bulk metallic glass composite. Adv Eng Mater 9:487–491. https://doi.org/10. 1002/adem.200700044
- [13] Song KK, Pauly S, Zhang Y et al (2012) Triple yielding and deformation mechanisms in metastable Cu<sub>47.5</sub>Zr<sub>47.5</sub>Al<sub>5</sub> composites. Acta Mater 60:6000–6012. https://doi.org/10. 1016/j.actamat.2012.07.015
- [14] Song KK, Pauly S, Zhang Y et al (2011) Strategy for pinpointing the formation of B2 CuZr in metastable CuZrbased shape memory alloys. Acta Mater 59:6620–6630. https://doi.org/10.1016/j.actamat.2011.07.017
- [15] Zhai H, Wang H, Liu F (2016) A strategy for designing bulk metallic glass composites with excellent work-hardening and large tensile ductility. J Alloys Compd 685:322– 330. https://doi.org/10.1016/j.jallcom.2016.05.290
- [16] Chen Y, Tang C, Jiang J-Z (2021) Bulk metallic glass composites containing B2 phase. Prog Mater Sci. https://doi. org/10.1016/j.pmatsci.2021.100799
- [17] Arias D, Abrlata JP (1990) Cu–Zr (Copper–Zirconium). Bull Alloy Phase Diagr 11:452–459
- [18] Cui X, Zu FQ, Wang ZZ et al (2013) Study of the reversible intermetallic phase: B2-type CuZr. Intermetallics 36:21– 24. https://doi.org/10.1016/j.intermet.2012.12.008
- [19] Song KK, Wu DY, Pauly S et al (2015) Thermal stability of B2 CuZr phase, microstructural evolution and martensitic transformation in Cu–Zr–Ti alloys. Intermetallics 67:177– 184. https://doi.org/10.1016/j.intermet.2015.08.015

- [20] Cheung TL, Shek CH (2007) Thermal and mechanical properties of Cu–Zr–Al bulk metallic glasses. J Alloys Compd 434–435:71–74. https://doi.org/10.1016/j.jallcom. 2006.08.109
- [21] Lin XH, Johnson WL (1995) Formation of Ti–Zr–Cu–Ni bulk metallic glasses. J Appl Phys 78:6514–6519. https:// doi.org/10.1063/1.360537
- [22] Löffler JF, Kündig AA, Dalla Torre FH (2007) Rapid solidification and bulk metallic glasses—processing and properties.
   In: Groza JR, Shackelford JF, Lavernia EJ, Powers MT (eds) Materials processing handbook. CRC Press, Boca Raton
- [23] Kozieł T, Pajor K, Gondek Ł (2020) Cooling rate evaluation during solidification in the suction casting process. J Mater Res Technol 9:13502–13508. https://doi.org/10. 1016/j.jmrt.2020.09.082
- [24] Turnbull D (1969) Under what conditions can a glass be formed? Contemp Phys 10:473–488. https://doi.org/10. 1080/00107516908204405
- [25] Sun BA, Wang WH (2015) The fracture of bulk metallic glasses. Prog Mater Sci 74:211–307. https://doi.org/10. 1016/j.pmatsci.2015.05.002
- [26] Zheng W, Huang YJ, Wang GY et al (2011) Influence of strain rate on compressive deformation behavior of a Zr–Cu–Ni–Al bulk metallic glass at room temperature. Metall Mater Trans A 42A:1491–1498. https://doi.org/10.1007/s11661-011-0632-0
- [27] Han X, Qin Y, Qin K et al (2016) Glass-forming ability and early crystallization kinetics of novel Cu–Zr–Al–Co bulk metallic glasses. Metals 6:225. https://doi.org/10.3390/ met6090225
- [28] Escher B, Kaban I, Kühn U et al (2019) Stability of the B2 CuZr phase in Cu–Zr–Al–Sc bulk metallic glass matrix composites. J Alloys Compd 790:657–665. https://doi.org/ 10.1016/j.jallcom.2019.03.139
- [29] Song KK, Pauly S, Zhang Y et al (2013) Thermal stability and mechanical properties of Cu<sub>46</sub>Zr<sub>46</sub>Ag<sub>8</sub> bulk metallic glass and its composites. Mater Sci Eng A 559:711–718. https://doi.org/10.1016/j.msea.2012.09.013
- [30] Wu D, Song K, Cao C et al (2015) Deformation-induced martensitic transformation in Cu–Zr–Zn bulk metallic glass composites. Metals 5:2134–2147. https://doi.org/10.3390/ met5042134
- [31] Pauly S, Das J, Bednarcik J et al (2009) Deformationinduced martensitic transformation in Cu–Zr–(Al, Ti) bulk metallic glass composites. Scr Mater 60:431–434. https:// doi.org/10.1016/j.scriptamat.2008.11.015

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