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# The Scavenging Effect of Different Rare-Earth Elements in the Low-Purity Zr<sub>50</sub>Cu<sub>40</sub>Al<sub>10</sub> Alloy

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- Krzysztof Pajor<sup>a,\*</sup>, Bogdan Rutkowski<sup>a</sup>, Łukasz Gondek<sup>b</sup>, Piotr Błyskun<sup>c</sup>, Manfred Reehuis<sup>d</sup>, Krzysztof Wieczerzak<sup>e</sup>, Tomasz Kozieł<sup>a</sup>
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<sup>a</sup> AGH University of Science and Technology, Faculty of Metals Engineering and Industrial Computer Science,
 Al. Mickiewicza 30, 30-059 Krakow, Poland

<sup>b</sup> AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Al. Mickiewicza
 30, 30-059 Krakow, Poland

<sup>c</sup> Warsaw University of Technology, Faculty of Material Science and Engineering, Wołoska 141, 02-507 Warsaw,
 Poland

13 <sup>d</sup> Helmholtz-Zentrum Berlin, Hahn-Meitner-Platz 1, 14109, Berlin, Germany

<sup>e</sup> EMPA, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Mechanics of Materials
 and Nanostructures, Feuerwerkerstrasse 39, Thun CH-3602, Switzerland

16 \*Corresponding author: kpajor@agh.edu.pl

# 17 Keywords

18 Bulk metallic glasses, rare-earth elements, glass forming ability, oxygen content, neutron diffraction;

# 19 Abstract

20 Glass forming alloys are very sensitive to oxygen contaminations. Here, the oxygen scavenging effect 21 of five rare-earth elements (RREs) was studied when added to the Zr<sub>50</sub>Cu<sub>40</sub>Al<sub>10</sub> alloy, synthesized from 22 commercially available zirconium. The effects of precise REEs additions (Y, Sc, Lu, Gd, Nd) with 23 respect to the measured oxygen content, based on the stoichiometric relationship in the  $M_2O_3$  oxide are 24 reported. Additionally, the influence of double and triple RRE-to-oxygen ratios on the critical diameter 25  $(D_c)$  and other glass forming ability (GFA) indicators were investigated. To evaluate the GFA and phase 26 transformations during heating, differential thermal analysis was performed along with neutron 27 diffraction. The combination of these two techniques allowed to identify crystallization products and 28 distinguish the differences in phase transformations of low and high oxygen-content alloys. 29 Microstructural analysis was carried out by means of electron microscopy (SEM, STEM), supported by 30 X-ray diffraction. The best oxygen scavengers were found to be rare-earths that form cubic sesquioxides, 31 i.e. Y, Sc and Lu, allowing to increase  $D_c$  in the high oxygen  $Zr_{50}Cu_{40}Al_{10}$  alloy from 2.5 mm up to 8 32 mm (double stoichiometric concentration of Y-to-oxygen). Our results indicate that low purity alloys 33 can be easily vitrified, highlighting their potential for wide commercialization.



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# 36 I. INTRODUCTION

37 Bulk metallic glasses (BMGs) are solid materials characterized by a non-equilibrium and non-ergodic 38 nature, and possessing extraordinary properties compared to their crystalline counterparts [1]. Sufficient 39 cooling rates are always necessary to bypass the crystallization process and to vitrify the molten alloy. BMGs lack long-range order of structure and crystal defects as opposed to crystalline materials, which 40 41 gives them high hardness and strength, large elastic limit, and even pronounced plasticity under specific 42 conditions [2,3]. For the past decades, great efforts have been made to explain and to explore the 43 mechanical, physical and chemical phenomena of BMGs. Furthermore, improving their glass forming 44 ability (GFA) has also been an important aspect in their development. The first metallic glasses required 45 high cooling rates (about  $10^4 \div 10^6$  K/s) to attain amorphous ribbons with thicknesses of only a dozen micrometers [4]. Understanding the thermodynamic and kinetic factors allowed to synthesize metallic 46 47 glasses in bulk form, having at least 1 mm in diameter [5,6]. The critical cooling rates of today's BMGs 48 are far below 100 K/s, providing options for wider commercialization. Among many glass-forming 49 systems, Zr-based BMGs are of particular interest due to their relatively low critical cooling rates and 50 cost-efficient production [7,8].

51 The Achilles' heel of BMGs is the strict processing conditions that require high purity of both the protective atmosphere and constituent elements. These conditions demand low oxygen levels, as oxygen 52 53 is the detrimental factor in many systems, as it lowers GFA [9,10]. Oxygen forms oxides with highly 54 reactive elements, which are perfect sites for heterogeneous nucleation during solidification, decreasing 55 the incubation time for crystallization by orders of magnitude [11]. It not only makes it impossible to 56 obtain fully amorphous BMGs, but also ruins their mechanical properties [3,12–14]. As Zr has a very 57 strong affinity to oxygen, it is not possible to completely eliminate this impurity from the raw material 58 or avoid some contaminations during BMG manufacturing. Furthermore, high purity and Hf-free 59 zirconium, with oxygen content below 100 wt. ppm, is regarded as a strategic material for the nuclear 60 power plant industry, due to its very low neutron capture cross-section [15]. This causes Zr of such 61 purity to be commercially unavailable, with manufacturers offering Zr of slightly lower purity and containing Hf. These materials, depending on the manufacturing method, can have an oxygen content 62 ranging from about 150 wt. ppm (Zr crystal bar) up to several thousand wt. ppm (Zr sponge). 63

An alternative way to increase the GFA of BMGs is designing new alloys with micro-additions of elements that form less harmful types of oxides. This effect can be achieved by doping Zr-based alloys with elements possessing higher oxygen affinity, e.g. rare-earth elements (REEs). These metals have lower Gibbs free energies of oxide formation at solid-liquid transformation temperatures, therefore they can "scavenge" oxygen and form rare-earth oxides (REOs) [16,17]. The most stable type of REOs is

 $M_2O_3$  (sesquioxide), where 2 atoms of REE bind 3 atoms of oxygen. Kündig et al. [18] studied this

70 correlation and obtained the maximum amorphous thickness in the Zr<sub>52.5</sub>Cu<sub>17.9</sub>Ni<sub>14.6</sub>Al<sub>10</sub>Ti<sub>5</sub> alloy for 71 stoichiometric and double stoichiometric Sc additions. There are many reports suggesting improved 72 GFA of Zr-based BMGs doped with REEs, however, typically the obtained results were not directly correlated with oxygen content [18,19,28–34,20–27]. Fig. 1 shows the crystallographic structures of 73 74 lanthanide sesquioxides. Depending on the temperature and ionic radius, REOs form various crystallographic structures, however, from the solidification point of view, the difference between 75 76 liquidus and glass transition temperatures at ambient pressure is crucial. In this region, REOs occur in 3 77 polymorphic types: *cubic* (including Y and Sc oxides) where all metal cations are surrounded by 6 78 oxygen anions, monoclinic, whose cations are mixed with six or seven-fold coordination, and hexagonal, 79 with seven-fold coordination [17]. The structure of the REOs can affect nucleation during solidification 80 [35]. Based on the reviewed literature and crystallographic structures of REOs, five REEs were selected 81 for detailed investigations. Yttrium and scandium (cubic oxide formers) were selected, as they are well-82 known dopants, causing different glass formation effects. Lutetium and neodymium oxides are 83 characterized by cubic and hexagonal structures, respectively, whereas gadolinium oxide exhibits a polymorphic transformation of a monoclinic to cubic structure at a temperature of  $1425 \pm 20$  K [17]. 84 85 The use of purely monoclinic REOs is problematic as they are formed by elements with low boiling 86 points (Sm and Eu) or by radioactive elements (Pm), therefore they were not studied here.

87 In our previous works [19,36], efforts were made to characterize and enhance the GFA in the 88  $Zr_{50}Cu_{40}Al_{10}$  alloy through Y additions. It was found that the critical diameter  $D_c$  (diameter with a 89 maximum amorphous thickness) strongly depends on the oxygen content, and the proper Y doping of a 90 low purity (high oxygen) alloy allows to obtain a similar  $D_c$  value (improved from 3 mm to 7 mm) as in 91 the high purity (low oxygen) alloy (8 mm). These results are promising in terms of steering BMGs 92 towards real engineering applications, while still using commercially available Zr.

Following this approach, Y and other REEs, i.e. Sc, Lu, Gd and Nd, were studied within this work.
Moreover, the calculating method for REE addition quantity selection was revised, complementing the
results for yttrium.



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Fig. 1 The scheme of polymorphic transformation in lanthanide sesquioxides: A – hexagonal, B –
 monoclinic, C – cubic, H – high-temperature hexagonal, X – high-temperature cubic. Yellow area
 represents liquidus and glass transition temperature range typical for Cu-Zr-Al BMGs. Adapted with
 permission from reference [17].

## 101 II. EXPERIMENTAL

## 102 A. Material

103 The Zr-Cu-Al alloy with a nominal composition of  $Zr_{50}Cu_{40}Al_{10}$ , as well as the Zr-Cu-Al-REE alloys 104 were synthesized by means of arc melting (Edmund Bühler GmbH) from a mixture of low purity (high 105 oxygen level) zirconium (99.8 wt. %) and high purity other components (at least 99.99 wt. %). Prior to 106 melting, the surfaces of individual metal pieces were ground off and cleaned in acetone. The chamber 107 was evacuated and flushed with high purity argon (6N). The ingots were thrice remelted under a Ti-108 gettered argon atmosphere to obtain composition homogeneity, and then suction cast into copper molds

- 109 ( $\emptyset$  3 10 mm). The water cooling system temperature was set to  $17 \pm 1$  °C [4].
- 110 B. Oxygen analysis and REEs addition

111 Oxygen content analysis of the reference and doped alloys was performed via the inert gas fusion method (LECO RO 416 DR). At least 5 samples from each alloy were cut off from the synthesized  $\emptyset$  3 mm 112 113 ingots and tested according to the ASTM E1409 standard. The ppm weight of oxygen was converted to atomic percentage, from which the REE concentration necessary to bind all oxygen was calculated, 114 115 based on the stoichiometric amount of the sesquioxide. As all REE form REE<sub>2</sub>O<sub>3</sub> oxides, it will be 116 further referred to it as the 2/3 variant. Additionally, double (4/3), as well as triple (6/3) amounts of REE with respect to its stoichiometric ratio were calculated. Due to the high affinity of REEs to oxygen, it 117 118 was necessary to consider additional oxygen coming from the REE dopants.

119 C. Structure analysis

120 Structural analysis of as-cast alloy cross-sections was performed using X-ray diffraction (XRD, Panalytical Empyrean) with Cu K<sub> $\alpha$ 1</sub> and Cu K<sub> $\alpha$ 2</sub> monochromatic radiation ( $\lambda$ =1.5406 Å and 1.5444 Å, 121 122 respectively) at a voltage of 40 kV and current of 40 mA. The analyzed data were collected in the 20 123 range from 20 to 100°, with a step size of 0.03342°. The D<sub>c</sub> for glass formation was determined by XRD 124 analysis and supported by cross-section observations using light microscopy (Leica DMLM/LP). 125 Samples were considered to be amorphous when no crystalline peaks were registered on the XRD diffractograms. Moreover, the microstructure of each sample was observed and thresholds of 5 % and 1 126 127 % were established for the crystalline area in the central part of the rods and in the whole area, 128 respectively. Scanning electron microscopy (SEM) observations were carried out using a Phenom XL 129 microscope equipped with an energy-dispersive X-ray spectrometer (EDX). Oxide distribution analysis was performed by means of ImageJ 1.52a commercial software (National Institutes of Health, USA). 130 131 The oxides' mean size was represented by the circular-equivalent diameter (1) and shape factor (2). 132 Calculations were performed based on 10 images of each sample (size of rods corresponding to the  $D_c$ value) captured at a magnification of 5000x (field of view 53.61 x 53.61 µm). Observations, as well as 133 134 EDX analyses, were performed using a voltage of 20 kV.

135 (1)  $d_{eq} = ((4*Area)/\pi)^{0.5}$ 

136 (2) 
$$\xi = (4\pi^* \text{Area})/(\text{Perimeter}^2)$$

High-resolution scanning transmission electron microscopy (HR-STEM) studies were carried out using 137 a FEI, Titan Cubed G2 60-300 microscope, equipped with an EDX detector (ChemiSTEM). The field 138 emission gun was operated at 300 kV. The experiments were performed to analyze the structure and 139 140 chemistry of the rare-earth oxides. The images were captured in bright field (BF) and fast Fourier 141 transforms (FFT) were applied to solve the diffraction. The studies were performed on TEM lamellae, prepared via focused ion beam (FIB) milling, using the ZEISS NEON CrossBeam 40EsB. Prior to 142 143 extraction utilizing the FIB crossbeam system, a protective gold layer was applied onto the lamellae. 144 The initial lamella width of ~15  $\mu$ m was later thinned to a thickness of ~80 nm using Ga<sup>+</sup> ions.

145 D. Phase transformations during heating, GFA of alloys

146 Differential thermal analysis (DTA) was carried out using a DTA Setaram Labsys on thin slices of the

147 middle part of the as-cast alloys (highest glassy diameter samples were tested) placed in 100  $\mu$ l alumina

- pans at a constant heating rate of 20 K/min and protective argon (5 N purity) gas flow of 20 ml/min. All
- 149 characteristic temperatures were determined by the DTA software:  $T_g$  glass transition (estimated as

150 the inflection point on the DTA curve),  $T_x$  – onset of crystallization,  $T_p$  – peak of crystallization,  $T_s$  and  $T_{\rm f}$  - start and finish of the eutectoid transformation,  $T_{\rm m}$  - solidus temperature,  $T_{\rm l}$  - liquidus temperature. 151 152 Based on these values, GFA indicators were evaluated:  $\Delta T_{xg} = T_x - T_g$ ,  $\Delta T_{rg} = (T_x - T_g)/(T_1 - T_g)$ ,  $\chi =$  $((T_x - T_g)/(T_1 - T_x))^*(T_x/(T_1 - T_x))^{1.47}$ . Among many indicators, the above-mentioned have the highest 153 154 correlation with the critical diameter in Zr-based alloys [37]. Neutron diffraction (ND) measurements 155 were carried out at the BER II reactor (Helmholtz-Zentrum Berlin). The E2 instrument was used with an incident neutron wavelength of  $\lambda = 2.3814$  Å. The ND patterns were recorded in the diffraction angle 156 range 26° - 102°, with a step size of 0.05°.  $\varnothing$  5 mm × 55 mm rods were placed inside quartz tubes, 157 which were then inserted into a high-temperature furnace (ILL-type). The tubes were evacuated and 158 159 flushed with high purity Ar (6N). The protective Ar atmosphere was maintained during the entire 160 experiment to prevent sample oxidation. As the quartz tubes introduced an amorphous background, empty tubes were measured under the same conditions, allowing to extract scattering signals originating 161 162 entirely from the investigated samples. The diffraction patterns were collected at a temperature step of 20 K and heating ramp of 10 K/min. After temperature stabilization (10 min), the diffraction pattern was 163 164 acquired during 15 min.

## 165 III. Results

166 A. Oxygen analysis and chemical compositions of doped alloys

Fig. 2 shows oxygen analysis results carried out for the reference (undoped) and doped alloys. In our 167 168 previous works, the oxygen content in the  $Zr_{50}Cu_{40}Al_{10}$  alloy was 918 wt. ppm [19,36]. Here, a slightly 169 higher value (988 wt. ppm) was obtained due to Zr coming from another batch (Cu and Al are the same). 170 The nominal contents in atomic % of each REE with the stoichiometric value to bind all oxygen (2/3), as well as double (4/3) and triple stoichiometric (6/3) REE-to-oxygen ratios were calculated as 0.302 at. 171 172 %, 0.604 at. % and 0.906 at. %, respectively (Tab. I). Due to high REE-oxygen affinity, it is clear that 173 the commercially available REEs also contain some dissolved oxygen, and even careful cleaning of the components' surface cannot eliminate oxygen coming from the dopants. To compensate this effect, the 174 175 actual additions of REEs should be higher than nominal. Thus, an additional oxygen analysis was 176 performed for the 4/3 variant that enabled to estimate the oxygen coming from each REE. The smallest oxygen content difference between the doped and undoped alloy was measured for Sc and Gd, while 177 178 considerable contamination was noticed for Y, Lu and Nd additions, giving a total value of 1091, 1109 179 and 1225 wt. ppm of oxygen level, respectively. Each REE addition was recalculated with respect to the 180 measured oxygen content for all REE-to-oxygen ratios. Successive values are not linear, as the 181 compensation level increases with their content. For Nd, the dopant (atomic) concentrations were 13.9 %, 31.5 % and 55.3 % (0.042, 0.190 and 0.501 percent points) higher compared to the nominal values 182 183 of the 2/3, 4/3 and 6/3 variants. The smallest differences can be observed for Gd, which was only 0.44 at. % (0.004 p.p.) higher in the triple stoichiometric variant. All REE dopants are presented in Table I. 184



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Fig. 2 Oxygen analysis of reference and doped alloys with double stoichiometric REE-to-oxygen ratio.
 Oxide structure: C – cubic, B – monoclinic, A – hexagonal.



Table I Nominal and actual REEs additions in Zr<sub>50</sub>Cu<sub>40</sub>Al<sub>10</sub> alloys

RFE-to-	Nominal	Actual REEs additions (at. %)							
oxygen ratio	REEs additions (at. %)	Sc	Y	Lu	Gd	Nd			
2/3	0.302	0.304	0.319	0.322	0.303	0.344			
4/3	0.604	0.613	0.675	0.689	0.606	0.794			
6/3	0.906	0.926	1.074	1.109	0.910	1.407			

#### 189 B. Structure analysis

190 Figure 3 shows the XRD patterns of the doped alloys. Colored and grey diffractograms represent 191 amorphous and partially crystalline samples, respectively. It should be noted that the critical diameter of the undoped alloy was below 3 mm [19], so in each case a positive effect of REE addition on the 192 193 GFA was observed, however, the impact differed depending on the used dopant. The best results, in 194 terms of the diameter of the suction-cast rods with an amorphous structure, were obtained for Y 195 additions, achieving a  $D_c$  as high as 8 mm in stoichiometric and double stoichiometric variants (Fig. 3b), 196 which is the same as in the low oxygen undoped alloy [19]. Promising values were additionally obtained 197 from alloys containing Lu, being another representative of a cubic REO. In this case, there are some visible peaks on the XRD pattern at  $2\theta = 29.7^{\circ}$  corresponding to Lu<sub>2</sub>O<sub>3</sub> (space group Ia $\overline{3}$ ), however, the 198 199 oxide's volume fraction was far below 1 %. The critical diameters for 2/3, 4/3 and 6/3 variants were evaluated as 3, 5 and 6 mm, respectively (Fig. 3c). Moderate improvement of GFA was observed for Sc 200 201 additions, reaching 4 mm, 4 mm and 5 mm for the stoichiometric (2/3), double (4/3), and triple 202 stoichiometric (6/3) variants, respectively (Fig. 3a). Minor improvement of GFA was observed for Gd 203 and Nd additions (Fig. 3d-e). The lack of crystalline peaks was only registered for 3 mm triple 204 stoichiometric (6/3) variants, while for stoichiometric (2/3) and double stoichiometric (4/3) variants, the 205  $\tau_3$  phase was identified. In most alloys, the  $\tau_3$  phase was detected, however, due to the lack of data, the peaks were indexed by comparing the corresponding peak positions with those available in Ref. [12]. 206 207 The B2 CuZr phase was identified in Y- and Sc-doped alloys, as well as for higher additions of Lu and Nd. Interestingly, in the case of the Y4/3 sample, a strong B2 CuZr peak at 69.9° (211) indicated a single 208 209 large grain or texturing.



210 •  $r_3$  ( $Zr_{51}Cu_{28}Al_{21}$ ) • B2 CuZr \*  $Lu_2O_3$  (Ia3) 211 Fig. 3 XRD patterns of amorphous (colored) and partially crystalline (grey) samples doped with: a) Sc, 212 b) Y, c) Lu, d) Gd, and e) Nd (for interpretation of the references to color in this figure legend, the 213 reader is referred to the web version of this article).

#### 214 C. Microstructure observations

215 Figure 4 shows selected cross-sectional SEM backscattered electron (BSE) images of the triple 216 stoichiometric doped casts with  $D_c$  and  $D_c+1$  mm (complete documentation of images is included in the 217 appendix A1 to A4). The results of EDX measurements are presented in Table II, but these should be 218 treated as qualitative analysis, rather than quantitative, because of small size of precipitates. Due to the 219 different atomic numbers of REE forming oxides, those containing Sc and Y (shown in [36]) give dark 220 contrast in the BSE mode in the matrix, while oxides containing Lu, Gd and Nd are bright. EDX results of the REOs (spots 1, 4, 7, 9) confirmed increased oxygen levels. The Lu oxide also contains aluminum 221 222 (spot 4), whereas other rare-earth oxides are too small for precise quantitative analysis (spots 7 and 9). 223 The trace amount of the  $\tau_3$  phase (Zr<sub>51</sub>Cu<sub>28</sub>Al<sub>21</sub>) was observed in each case (spots 3, 6, 8 and 11), even 224 if no diffraction peaks were detected. Similar to oxide formation,  $\tau_3$  also appears in the melt before 225 solidification. The  $\tau_3$  phases are dendritic in shape and their distribution along the cross-section is 226 spiraled due to turbulent flows during casting [12]. Moreover, the presence of the B2 CuZr phase was 227 noticed in all samples (except Gd) with a diameter above the  $D_c$  and its chemical composition is close 228 to the nominal composition of the alloy (spots 2, 5, 10). This phase was mainly observed in the central 229 part of the samples, i.e. with the lowest cooling rate.



230

Fig. 4 SEM-BSE images of alloys doped with Sc, Lu, Gd and Nd in triple stoichiometric (6/3) REE-to oxygen ratio: a) the critical diameter, b) 1 mm above the critical diameter. EDX spots marked as red
 points.

Table II EDX analysis of alloys doped with Sc, Lu, Gd and Nd in triple (6/3) stoichiometric REE-tooxygen ratio.

Chemical composition (at. %.)						
Spot	Zr	Cu	Al	REE	0	
1	6.0	2.5	1.0	(Sc) 30.4	60.1	
2	49.5	39.3	11.2	-	-	
3	50.6	30.8	18.6	-	-	
4	5.4	5.3	-	(Lu) 41.9	47.4	
5	59.5	39.2	11.3	-	-	
6	49.5	30.3	20.2	-	-	
7	18.0	9.5	5.5	(Gd) 29.0	38.0	
8	50.1	29.5	20.4	-	-	
9	18.5	9.3	5.6	(Nd) 21.6	45.0	
10	53.1	34.1	12.8	-	-	
11	52.8	26.3	20.9	-	-	

236

237 The size distribution (here expressed by the circular-equivalent diameter) of the oxides is presented in Fig. 5. Cubic sesquioxides (Sc, Y and Lu) are significantly larger compared to the other oxides. While 238 239 the size distributions of Sc and Lu oxides are wide, the distribution of  $Y_2O_3$  is much narrower with a 240 strong visible mean size. However, a more irregular distribution of  $Y_2O_3$  on the cross-section was 241 observed, therefore images were acquired from areas enriched in these oxides. The number of counts 242 was higher compared to other REOs, giving a Gaussian oxide size distribution and the mean size of 2.64  $\mu$ m. The mean values of the shape factor  $\xi$ , given in eq. (2) for Y<sub>2</sub>O<sub>3</sub>, indicate a more developed shape 243 244 than squares (the cubes have a coefficient of  $\xi = 0.785$  and spheres  $\xi = 1.0$  [38]). Gd and Nd oxides are 245 closer to a square shape, however, due to their size (mean equivalent diameter  $< 1 \mu m$ ) this factor can

- be slightly overestimated. The coefficients determining appropriate Gauss fitting for each case are above
- 247 0.90, indicating a very good correlation of the model with the experimental data.





Fig. 5 Circular-equivalent diameter distribution of REOs in all REE-to-oxygen ratios alloys with the

critical diameter and 1 mm higher: a) Sc, b) Y, c) Lu, d) Gd, e) Nd, where  $\overline{d}$  - mean diameter,  $\xi$  - mean shape factor, NC - number of counts, R<sup>2</sup> - coefficient of determination.

252 HR-STEM images of oxides with corresponding FFT patterns are shown in Fig. 6 ( $Y_2O_3$  in Ref. [36]).

FFT reflection indexing revealed a cubic structure (space group  $Ia\bar{3}$ ) for Sc, Lu and Gd oxides. In the Lu sesquioxide, the area for FFT was taken from the boundary between the glassy matrix and the oxide,

therefore together with the oxide diffraction an "amorphous halo" is clearly visible. The  $Nd_2O_3$  oxide

256 was identified to be from the trigonal crystal system ( $\overline{P3}m1$ ), however, it can also be classified as a

257 primitive hexagonal unit cell containing five atoms [39]. Moreover, in this sample, an additional pattern

258 was detected (red reflects), coming from the phase that surrounds the oxide (visible in Fig. 7 in HAADF

contrast). This pattern is most probably related to the presence of the  $\tau_3$  phase, however, due to the lack of database reference, it cannot be solved. The crystal structures and lattice parameters of the studied sesquioxides are summarized in (Appendix) Table AI.

262 Fig. 7 shows high-angle annular dark-field (HAADF) images and EDX elemental distribution maps.

263 The Gd and Nd oxides are surrounded by other phases enriched in Al and depleted in Cu, which

264 corresponds to the composition of the  $\tau_3$  phase. This area is also characterized by a slightly higher

265 oxygen level compared to the glassy matrix.



Fig. 6 HRSTEM-BF images, with corresponding FFT patterns of the oxides in alloys doped with Sc,
 Lu, Gd and Nd in triple stoichiometric ratio. Zone axis: Sc [211], Lu [001], Gd [112], Nd [110]. Red
 points in FFT for N<sub>2</sub>O<sub>3</sub> are reflections corresponding to the τ<sub>3</sub> phase.





Fig. 7 HAADF-EDX elemental distribution maps of the alloys doped with Sc, Lu, Gd and Nd in triple
 (6/3) stoichiometric REE-to-oxygen ratio.

#### D. Thermal analysis

275 The DTA measurements performed on the highest glassy diameter samples are plotted in Fig. 8. All 276 curves exhibit similar behavior with two exothermic peaks, followed by two endothermic events above 277 1000 K. The first exothermic peak, related to the onset of crystallization, is preceded by a distinct glass 278 transition temperature T<sub>g</sub>. The last endothermic event corresponds to melting, while the preceding peak 279 is related to the eutectoid transformation of the crystallization products into the B2 CuZr phase, which is thermodynamically stable at high temperatures [40]. All characteristic temperatures, together with the 280 281 GFA indicators, are summarized in Table III. To assess the suitability of a given REE on the GFA, the 282 obtained data for the low and high oxygen (LO and HO, respectively) undoped alloy [19] are also shown. 283 Compared to the HO Zr<sub>50</sub>Cu<sub>40</sub>Al<sub>10</sub> alloy (B in Ref. [19]) the glass transition temperature did not change

- significantly. A slight decrease of 1-2 K was noticed for most cases, with a more pronounced decrease
   observed only for Y2/3, Lu6/3, Nd4/3 and Nd6/3.
- 286 The crystallization onset temperature T<sub>x</sub> clearly increased compared to the undoped HO variant, giving
- 287 an increase in the supercooled liquid region  $\Delta T_{xg}$ . The largest  $\Delta T_{xg}$  was noticed for Y additions, reaching
- 288 60, 66 and 70 K for stoichiometric, double- and triple stoichiometric variants, respectively. A moderate
- 289 increase in  $\Delta T_{xg}$  was noticed for Sc, Lu and Nd additions, while the weakest effect was observed for Gd.
- 290 The full width at half maximum (FWHM) of the first crystallization peaks are 5.48 K and 7.12 K for
- 291 LO and HO alloys, respectively. The FWHM is inversely proportional to the nucleation rate, which
- means a larger FWHM is related to a higher crystallization barrier, causing slower crystallization [41].
- Firstly, the FWHM increases with the doping of rare-earths, excluding Y2/3 and Nd4/3 alloys, where the overlapping of the additional effect prevented the correct measurement of these values (insets in
- Fig. 8). Interestingly, the second exothermic peak temperature strongly depends on the dopant type and
- 296 concentration. In the case of Y and Nd additions, it strongly decreases with increased dopant 297 concentrations, while an opposite effect was observed for Gd and no significant changes were noticed 298 for Sc and Lu.
- A clear difference in melting behavior of the studied samples was noticed. In the undoped LO alloy,
- 300 only one uniform melting peak was registered, while for the HO sample the melting peak was split into
- 301 two peaks, suggesting the shifting of the alloy to an off-eutectic composition [19]. It was observed that
- 302 HO alloy doping with REE generally allows to avoid the splitting effect, however, it is visible again for
- 303 higher concentrations of Y and Sc (6/3). A distinct splitting was also observed for all Nd additions.
- 304 All doped samples exhibit higher GFA compared to the undoped HO sample ( $\Delta T_{xg} = 40 \text{ K}$ ;  $\Delta T_{rg} = 0.090$
- and  $\chi = 0.252$ ). In the case of Sc additions, all  $\Delta T_{rg}$ ,  $\Delta T_{xg}$  and  $\chi$  parameters decreased despite increasing
- 306 D<sub>c</sub>. Doping with Nd caused a strong increase in GFA, as  $\Delta T_{rg}$  and  $\chi$  increased up to 0.145 and 0.497,
- 307 respectively, however, D<sub>c</sub> reached only 3 mm.
- 308



 $\begin{array}{ll} \mbox{310} & \mbox{Fig. 8 DTA curves of the studied alloys with additions of Y, Sc, Lu, Gd and Nd. Insets show \\ \mbox{311} & \mbox{crystallization peaks for Y2/3 and Nd4/3; Characteristic temperatures: $T_g - glass transition, $T_x - onset$ \\ \mbox{of crystallization, $T_{p1}$, $T_{p2}$ - first and second peak of crystallization, $T_s$ and $T_1$ - start and finish of the \\ \mbox{eutectoid transformation, $T_m$ - solidus, $T_1$ - liquidus; FWHM - full width at half maximum of the \\ \mbox{s12} & \mbox{crystallization peak.} \end{array}$ 

315Table III Characteristic temperatures and GFA indicators of reference (LO – low oxygen content, HO316– high oxygen content) and doped  $Zr_{50}Cu_{40}Al_{10}$  alloys. D – diameters of the rods from which the317samples were taken (red ones – alloys with critical diameter below 3 mm). Data of references alloy318(LO and HO) reprinted with permission from [19].

D			Characteristic temperatures (K)							GFA indicators		
Alloy	(mm)	$T_{g}$	$T_{x}$	$T_{p1}$	$T_{p2}$	$T_s$	$T_{\mathrm{f}}$	$T_{m}$	$T_1$	$\Delta T_{xg}$	$\Delta T_{\text{rg}}$	χ
LO [19]	8	711	779	781	936	1054	1076	1131	1157	68 K	0.152	0.521
HO [19]	3	720	760	764	966	1049	1123	1150	1163	40 K	0.090	0.252
Y2/3	6	714	774	781	969	1059	1085	1119	1154	60 K	0.136	0.455
Y4/3	8	719	785	787	937	1054	1077	1123	1156	66 K	0.151	0.535
Y6/3	8	719	789	792	915	1058	1078	1113	1152	70 K	0.162	0.604
Sc2/3	4	719	766	772	964	1053	1073	1132	1160	47 K	0.107	0.317
Sc4/3	4	719	772	775	966	1053	1073	1130	1159	53 K	0.120	0.378
Sc6/3	5	718	770	771	966	1050	1072	1134	1159	52 K	0.118	0.365
Lu2/3	3	718	766	769	961	1051	1074	1127	1156	48 K	0.110	0.332
Lu4/3	5	719	770	776	973	1050	1073	1127	1155	51 K	0.117	0.367
Lu6/3	6	715	778	788	959	1042	1069	1122	1153	63 K	0.144	0.491
Gd2/3	3	719	765	768	941	1052	1072	1120	1154	46 K	0.106	0.320
Gd4/3	3	719	764	768	948	1052	1073	1121	1150	45 K	0.104	0.318
Gd6/3	3	719	763	768	965	1057	1080	1119	1145	44 K	0.103	0.318
Nd2/3	3	719	763	766	961	1054	1073	1102	1154	44 K	0.101	0.301
Nd4/3	3	713	763	766	939	1049	1073	1105	1145	50 K	0.116	0.362
Nd6/3	3	703	765	767	914	1049	1074	1104	1132	62 K	0.145	0.497
	T (D <sup>2</sup>	0 (00)	٨T			$T \rightarrow (D^2)$	0.005					$\mathbf{T}$ $\mathbf{T}$ $\mathbf{N}^{1}$

 $\begin{array}{l} 319 \qquad \Delta T_{xg} = T_x - T_g \; (R^2 = 0.698), \; \Delta T_{rg} = (T_x - T_g)/(T_1 - T_g) \; (R^2 = 0.665), \; \chi = ((T_x - T_g)/(T_1 - T_x))^* (T_x/(T_1 - T_x))^{1.47} \\ 320 \qquad (R^2 = 0.663) \end{array}$ 

321 To relate the DTA curve peaks with phase transformations occurring during heating, neutron diffraction 322 studies of LO and HO undoped alloys were carried out up to the liquid phase stability region. ND patterns, together with DTA traces (Fig. 9), allowed to distinguish five regions. The amorphous structure 323 324 was confirmed in region (1) for both samples, however, additional diffraction peaks corresponding to 325 the  $\tau_3$  (Zr<sub>51</sub>Cu<sub>28</sub>Al<sub>21</sub>) and B2 CuZr phases were detected for the HO variant. The  $\tau_3$  phase exists in the 326 entire temperature range (along 5 regions), and its peaks shifted due to thermal expansion by 327 -0.00076 °/K, -0.00064 °/K, -0.00057 °/K and -0.00050 °/K for the first, second, third and fourth peak 328 represented by dashed red lines, respectively. In region (2), amorphous phase crystallization occurred 329 and the first sharp peaks on the ND patterns appear at 725 K, corresponding to the first exothermic peaks 330 on DTA. It should be noted that DTA analysis was carried out at a constant heating rate of 20 K/min, so 331 the phase transformations are shifted to higher temperatures compared to the ND patterns. In the LO 332 sample, the CuZr<sub>2</sub> phase (tetragonal, I4/mmm) appeared along with the AlCu<sub>2</sub>Zr (cubic,  $Fm\overline{3}m$ ) and 333 transition phase [35,36]. The crystallization onset temperature for the HO sample is about 20 K lower 334 compared to the LO alloy, and the  $Zr_6Al_7Cu_{16}$  phase (triclinic, P1) was identified instead of the AlCu<sub>2</sub>Zr. 335 The remaining glassy phase region (2) transformed into the B2 CuZr phase at the upper temperature range. In region (3), the metastable B2 CuZr phase, formed in the low temperature range, further 336 337 transforms upon heating into stable CuZr<sub>2</sub> and AlCu<sub>2</sub>Zr phases. Furthermore, at approx. 950 K, the 338 AlCuZr phase (orthorhombic, Imma) appears in the LO alloy. In the next stage, at about 1075 K, further transformation of crystalline CuZr<sub>2</sub> and AlCu<sub>2</sub>Zr phases into the B2 CuZr phase, which is 339 340 thermodynamically stable at high temperatures, was noticed. The intensity of this phase in region (4) is dominant, however, AlCuZr and the remaining CuZr<sub>2</sub> phase were also observed. Further heating leads 341

to melting of the sample. The crystalline diffraction peaks disappear at about 1150 K in the LO alloys, while the HO alloy is characterized by a wide range of melting between 1150 K and 1175 K. ND allowed to show the amorphous halo coming from the molten alloy and to compare it with the "halo" coming from the glassy phase. Once again, the presence of the  $\tau_3$  phase was observed in the glassy matrix and it is stable up to the liquid phase stability region. The individual traces taken from each region are presented in the appendix files (Fig. A5).

348



- 350 Fig. 9 Neutron diffraction patterns collected along the temperature with differential thermal analysis
- divided into 5 regions: a) LO alloy (194 wt. ppm), b) HO alloy (918 wt. ppm). Dashed red lines represent the  $\tau_3$  phase. TP – transition phase. (For interpretation of the references to color in this figure

legend, the reader is referred to the web version of this article). DTA curves adapted with permission
 from reference [19].

#### 355 IV. Discussion

#### 356 A. Determining the critical diameter

357 Alloys from the ZrCu-based family are considered as high glass formers [7]. In addition to research 358 focused on the mechanical and chemical properties of BMGs, those related to increasing the volume of material vitrification are also of great importance. This requires the use of universal methods of 359 360 comparison, which can be divided into direct and indirect methods. The GFA is most quantified directly using the minimum cooling rate required to avoid crystallization upon solidification (resulting in glass 361 formation). As it is difficult to experimentally measure the critical cooling rate, more often the critical 362 363 casting size (in our case, critical diameter D<sub>c</sub>) is used as a direct GFA indicator. Generally, there are two methods allowing to measure the D<sub>c</sub>, namely discrete and continuous. The first one is the most common, 364 365 due to its simplicity, where rods are cast with a gradually increasing diameter and the D<sub>c</sub> is determined by means of microstructure observations and/or XRD analysis. This method is limited by the size of 366 gradual changes, usually 1 mm. The XRD pattern can be used to determine the level of crystallinity, 367 however, in this work, such estimations were not possible due to the lack of data of the crystalline  $\tau_3$ 368 369 phase. Nevertheless, it was possible to distinguish diameters close to the real D<sub>c</sub> (higher peak intensities 370 for higher diameter samples, e.g., Y2/3) and slightly below the D<sub>c</sub> value (lower peak intensities for higher diameter samples, e.g. Sc2/3). The resolution of D<sub>c</sub> estimation could be increased, however, this 371 372 would involve an increase in the number of produced casts. An alternative way to determine D<sub>c</sub> is the 373 continuous method, which consists of casting into cone-shape molds and investigating the microstructure along the longitudinal section. This way, a wide range of diameters can be measured on 374 375 a single cast. However, the biggest disadvantage of this method is heat distribution disturbance caused 376 by potential turbulent liquid flow during casting. Laws et al. [42] showed that the real critical casting 377 diameter obtained from parallel-edged molds should be lower than those from conical molds, however, 378 our previous works show a reverse correlation [19,36,43]. This effect can be stronger in the case of 379 inclusion occurrence (e.g. oxides) in liquid alloys that facilitate heterogenous crystallization. Therefore, 380 in this study the discrete method based on microstructural and phase analysis was used, bearing in mind the shortcomings of this method. 381

382 It should be noted that, depending on the selected approach, samples containing trace amounts of 383 crystallites embedded in the amorphous matrix could be classified as BMG or partially crystalline. The 384 criterium of an amorphous structure is often defined as the lack of diffraction peaks on XRD/ND patterns. During microstructural observations, the threshold of 5 % crystallinity is used, which is similar 385 386 to the detection limit in the XRD method. In this work, the XRD method was combined with 387 microstructural investigations to determine the D<sub>c</sub>. Within the BMG community, some believe that 388 glasses are materials that do not contain any crystalline phases, and if such a crystalline phase should 389 appear, it should be referred to as a bulk metallic glass composite (BMGC) [44]. There is a common 390 definition of a composite, which is the combination of at least two different materials that exhibits improved properties as a whole than the sum of those components [45]. We believe that this is not the 391 392 case in critical diameter measurements, as the crystalline phase is not introduced intentionally to 393 improve BMG properties, therefore we do not classify it as a composite. Moreover, a 3-5 vol. % 394 crystalline phase threshold is frequently used in various classifications.

The positive effect of REEs on the D<sub>c</sub> is undeniable, however, their influence on the BMGs differ. There are several works considering rare-earths additions on the glass forming ability of Zr-based bulk metallic glasses, including Y [20–25,36], Sc [18,26,27], Lu [28,29], Nd [29–31] and Gd [29,31,32]. The majority of these reports show a combination of scavenging and alloying effects of REEs, as these elements were added in a discrete manner and in relatively large amounts (x = 1, 2 etc.). In previous studies, we have shown that the  $Zr_{50}Cu_{40}Al_{10}$  alloy based on Zr with 99.8 wt. % purity has about 0.1 wt. % of oxygen,

- 401 thus the critical diameter is below 3 mm, while for high purity (99.95 wt. %) Zr (0.02 wt. % of oxygen)
- 402 it is 8 mm [19]. More comprehensive studies were performed by Kündig et al. [18], where the effect of
  403 REEs additions in amounts related to the oxygen content were studied. Alloys were cast with different
  404 additions of various elements (including Sc) and showed the optimal concentration in stoichiometric
  405 and double-stoichiometric of Sc with respect to the measured oxygen level.
- 406 Here, attempts were made to measure the pure scavenging effect of yttrium, scandium, lutetium,
- 407 neodymium and gadolinium additions on GFA in the  $Zr_{50}Cu_{40}Al_{10}$  alloy synthesized from commercially
- 408 available zirconium. Results of the critical diameter determination for each doping variation are 409 summarized in Fig. 10. Two dashed lines represent critical diameter values (8 and 2.5 mm) obtained for
- 409 summarized in Fig. 10. Two dashed lines represent critical diameter values (8 and 2.5 mm) obtained for 410 LO (194 wt. ppm) and HO (918 wt. ppm)  $Zr_{50}Cu_{40}Al_{10}$  alloys, respectively [19]. In fact, the D<sub>c</sub> of the
- HO alloy was not determined directly (the smallest rod diameter D = 3 mm was partially crystalline),
- 412 but based on the extrapolation of the  $\gamma$  indicator [36].
- 413 According to Inoue and Takeuchi [46], the  $D_c$  of the  $Zr_{50}Cu_{40}Al_{10}$  alloy is 10 mm, which means that the
- 414 authors were able to obtain an oxygen content less than 194 wt. ppm. Our results show that Y additions
- 415 (double and triple stoichiometric variation) allowed to obtain a  $D_c$  value on the same level as in the LO
- 416 alloy, i.e. 8 mm. This result is even better than in our previous report on Y addition in the  $Zr_{50}Cu_{40}Al_{10}$
- 417 alloy, where a  $D_c$  of 7 mm was obtained (empty circles on Fig. 10) [36]. This improvement was achieved
- 418 by considering the additional oxygen from the rare-earth elements. We have also studied half-419 stochiometric and stoichiometric ratios with respect to oxygen content, achieving  $D_c$  as high as 4 and 5
- 420 mm, respectively. These results, after recalculating the Y-to-oxygen ratio, are depicted in Fig. 10 as
- $\begin{array}{ll} 421 & \text{empty circles. It is visible that Y additions up to its double stoichiometric concentration (4/3) increased \\ 422 & \text{the } D_c, \text{ with no further improvements noticed with increasing Y. Furthermore, this element exhibited} \end{array}$
- $423 \qquad \text{the strongest influence on the } D_c \text{ among all studied dopants.}$
- 424 Sc and Lu additions are characterized by a moderate increase in critical diameter. For these elements,
  425 the highest amorphous diameters of 5 and 6 mm were noticed for triple stoichiometric Sc and Lu
- 426 concentrations, respectively. In these cases, it is difficult to estimate the real  $D_c$ , as in most
- 427 diffractograms, amorphous halos are preceded by low-intensity peaks (Fig. 3). For Lu additions, a single
- 428  $Lu_2O_3$  (*Ia3*) peak was observed in all diffractograms. We suppose that the signal could be registered 429 from large oxides. As SEM observations of the Lu-doped samples did not reveal any other crystalline
- 430 phases and the volume fraction of Lu oxides did not exceed 5 %, we decided to consider the XRD pattern
- 431 with visible peaks at  $2\theta = 29.7^{\circ}$  (Fig. 3c) as amorphous.
- 432 The weakest effects on glass formation were gained from Nd and Gd additions. In both cases, the 433 stoichiometric and double stochiometric ratios showed no effect, and even 3 mm samples were partially
- 434 crystalline. Only the triple stoichiometric variants allowed to obtain fully glassy 3 mm diameter samples.
- 435 Unlike cubic  $Sc_2O_3$ ,  $Y_2O_3$  and  $Lu_2O_3$  oxides, these two rare-earth elements are known to form other
- $436 \qquad \text{structures, i.e. monoclinic for } Gd_2O_3 \text{ and hexagonal } Nd_2O_3. \text{ However, } Gd_2O_3 \text{ also turned out to be cubic,}$
- 437 as it was not possible to undercool its monoclinic form to ambient temperature and most probably it438 succumbed the polymorphic transformation around the glass transition temperature.
- 439 These results show that the least detrimental kind of sesquioxides for vitrification processes are the cubic
- 440 ones. It should be noted that measuring the oxygen level in the reference alloy might be insufficient, as
- 441 REEs alone easily bind oxygen due to their high chemical affinity. Therefore, oxygen present in all
- 442 elements needs to be taken into account.





444Fig. 10 The critical diameters of doped alloys vs. REE-to-oxygen ratio. Dashed lines show  $D_c$  of LO445and HO  $Zr_{50}Cu_{40}Al_{10}$  alloys [19]. Empty circles represent yttrium additions in half-, stoichiometric-446and double stoichiometric ratios recalculated to the real Y-to-oxygen ratio taking Y native oxygen447content into account.

#### 448 B. Structure and microstructure investigations

In-depth microstructure investigations were performed via SEM and TEM observations, supported by 449 450 EDX analysis, and neutron diffraction studies. SEM observations (Fig. 4) in combination with XRD 451 studies (Fig. 3) were applied to estimate the  $D_c$  of alloys. We proved that the  $\tau_3$  phase in the HO alloy is stable in liquid state, which was confirmed via ND (Fig. 9). The dendritic shape indicate its formation 452 453 prior to solidification [19]. Diffraction was carried out up to 1273 K (1000 °C), where peaks from this 454 phase still existed. It means that the  $\tau_3$  phase probably has a much higher melting point compared to the 455 matrix. There are some works that have studied the  $\tau_3$  phase [12,47–49], however, future research 456 towards constructing its unit cell and recognizing its basic physical properties should be performed. Based on our results and other reports, it is clear that the  $\tau_3$  phase can affect the crystallization process 457 458 via the heterogenous nucleation mechanism.

459 Interestingly, in the case of doped alloy samples with diameters 1 mm larger than  $D_c$ , the  $\tau_3$  phase is still the main crystalline phase. Only for higher REE-to-oxygen variants does the B2 CuZr phase become 460 461 dominant. Zhou et al. showed that the size and lattice parameter of the  $\tau_3$  phase increase with increasing 462 oxygen levels [47]. According to that study, this phase consumes oxygen from the solution, allowing 463 the rest of the liquid to vitrify. It should be noted that, in contrast to the B2 phase, which crystallizes through a massive transformation (without changing the chemical composition with respect to the 464 465 mother phase – spots 2, 5 and 10 in Fig. 4 and Table II), the  $\tau_3$  phase (Zr<sub>51</sub>Cu<sub>28</sub>Al<sub>21</sub>) is enriched with Al at the expense of Cu, compared to the nominal composition of the studied  $Zr_{50}Cu_{40}Al_{10}$  alloy. It means 466 that the  $\tau_3$  phase changes the alloy's chemical composition in the liquid phase, causing deterioration of 467 468 the GFA. This effect is more pronounced in the case of higher oxygen levels, as the volume fraction of 469 the formed  $\tau_3$  phase is higher, and consequently more aluminum will be consumed from the matrix. The 470 solubility of oxygen in the  $\tau_3$  phase is not exactly known. According to Zhou et al. [47], it should be

- 471 between 830 and 1900 wt. ppm and exceeding the solubility limit decreases the GFA even more strongly.
- 472 These observations are visible in our results, as additions of REEs with a weak scavenging effect lead 473 to the appearance of the  $\tau_3$  phase (Fig. 3 and A 1 to A 4). Furthermore, we noted higher liquidus 474 temperatures on DTA curves of alloys doped with lower amounts of rare-earths, which means that the 475 chemical composition was shifted from deep eutectic composition.
- Differences in the effect of REE on the  $D_c$  can be explained by two effects. First is the ability of REEs 476 to scavenge oxygen from the alloy. The addition of rare-earths to the Zr-Cu-Al alloy, due to higher 477 478 affinity to oxygen than other constituent elements, leads to oxygen being captured from the melt and the 479 formation of  $M_2O_3$ -type oxides. Scandia, yttria, lutetia, gadolinia and neodymia are stable up to 2758 K, 2712 K, 2763 K, 2693 K and 2593 K[17], respectively, which is in the range of the arc melting process. 480 481 Even if the oxides were melted during the remelting process, they could spontaneously form during solidification. This effect can be recognized by comparing crystallization products in  $D_c+1$  mm samples. 482 In the case of Sc and Y additions, only marginal amounts of the  $\tau_3$  phase were confirmed (Fig. 3 a,b, 483 484 A1), which means that most oxygen was bound in the oxide, and not dissolved in the matrix. The effect of oxygen scavenging of Gd and Nd is very weak, causing pronounced formation of the  $\tau_3$  phase. We 485 486 suppose that some amount of Gd and Nd is dissolved in the matrix, however, more detailed chemical
- 487 analysis is necessary to prove it.
- 488 The second effect is related to heterogeneous nucleation, which is induced by the presence of 489 sesquioxides dispersed in the melt. This means that REOs can also affect the crystallization process (but 490 to a lesser degree), where we observed some B2 CuZr phase growth on the mentioned oxides (especially 491 visible in Fig. A1e-f). Therefore, in doped alloys with a similar level of crystallinity, the B2 phase occurs 492 in a more dispersive form. This observation is in agreement with other studies, where the glassy matrix 493 can be reinforced by in situ or ex situ mechanisms [50]. Each oxide has a different structure (at least 494 lattice parameter) affecting the contact angle, resulting in different D<sub>c</sub> values. Our results show that Y 495 additions provide improved GFA results in low purity alloys. However, in the case of BMGCs, where 496 the B2 CuZr phase is desirable, Sc doping is more suitable for enhancing phase formation. Lu additions 497 give ambiguous results. Despite the presence of the  $\tau_3$  phase in D<sub>c</sub>+1 mm samples, these alloys obtain a 498 relatively high critical diameter. The oxides' chemical composition show a large amount of aluminum 499 (Table II and Fig. 7), which indicates the presence of the complex phase, however, diffraction clearly
- 500 points to the Lu<sub>2</sub>O<sub>3</sub> ( $Ia\bar{3}$ ) sesquioxide. The composition and structure of Lu oxides should be further 501 studied, since this REE facilitates glass formation in high oxygen Zr-based alloys.
- A shift in the matrix's chemical composition, caused by  $\tau_3$  phase formation, can be observed in the melting range of the ND diffractograms (Fig. 9). In the case of the LO alloy, this event is very narrow (possibly congruent melting point), while for the HO alloy it is much wider. Compared to DTA, individual events in ND are at slightly lower temperatures, as DTA is characterized by a continuous temperature rise (20 K/min) during analysis, while in ND samples were heated with a rate of 10 K/min and often kept isothermally for 25 min. This provides incubation time for phase transformations, especially in the case of the onset crystallization temperature  $T_x$  [44].
- 509 At a low temperature range, the  $\tau_3$  and B2 CuZr phases in HO alloy can be distinguish due to too large 510 diameter of the as-cast alloy (twice the  $D_c$ ). The differences between the HO and LO alloys are mainly visible at the crystallization event, where in the first stage of crystallization the glassy phase decomposes 511 512 into two equilibrium phases: tetragonal CuZr<sub>2</sub> (in both alloys) and cubic AlCu<sub>2</sub>Zr (in LO alloy) or 513 triclinic Zr<sub>6</sub>Al<sub>7</sub>Cu<sub>16</sub> (in HO alloy). The AlCu<sub>2</sub>Zr and Zr<sub>6</sub>Al<sub>7</sub>Cu<sub>16</sub> phases have similar chemical 514 compositions and densities (6.787 g/cm<sup>3</sup> and 6.753 g/cm<sup>3</sup> [51,52], respectively), however different 515 angles and spacings between crystallographic planes, as well as in atom positions in the elemental cell. To the best of our knowledge, the presence of the Zr<sub>6</sub>Al<sub>7</sub>Cu<sub>16</sub> phase in Zr-Cu-Al BMGs is shown here 516 517 for the first time, and we believe it is related to high oxygen content. Its privileged crystallization over 518 AlCu<sub>2</sub>Zr may be induced by  $\tau_3$  phase occurrence or residual oxygen in the matrix. This hypothesis 519 should, however, be studied further. Additionally, two peaks (at  $2\theta = 54^{\circ}$  and  $72^{\circ}$ ) were noted to be
- 520 stable in both LO and HO variants, coming from the metastable transition phase (TP) that only exists
- 521 during the crystallization event. Similar observations were obtained by Soubeyroux et al. [53], where *in*

- 522 situ neutron diffraction experiments were performed at different temperatures for Zr-based alloys. Their
- $523 \qquad \text{conclusions were based on previous research on the crystallization of } Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10} \text{ glassy alloys}$
- 524 with different oxygen content, conducted by Eckert et al. [54]. This phase is referred to as the quasi-525 crystalline phase and its existence region is extended in alloys with higher oxygen content. These
- by the phase and its existence region is extended in anoys with higher oxygen content. These observations are in line with our results:  $\Delta T_{TP} = 100$  K and  $\Delta T_{TP} = 120$  K for low and high oxygen
- 527 alloys, respectively.

528 In the second stage of crystallization, the remaining glassy phase transforms into the B2 CuZr phase. 529 This phase is formed at temperatures below 800 K, which is far below the equilibrium formation 530 temperature (1002 K in the binary Cu-Zr alloy [55]). This phenomenon was explained by Zhang et al. [56,57], who compared the distances between the nearest neighbors of Zr-Cu and Zr-Zr in the 531 532 Zr<sub>50</sub>Cu<sub>40</sub>Al<sub>10</sub> glassy alloy, as well as in the unit cell of the B2 CuZr phase (which were very similar). They postulated that insufficient long-range atom diffusion causes decomposition of the untransformed 533 534 structure into a phase possessing a similar composition to the glassy state. This effect was more 535 pronounced with higher heating rates, when B2 CuZr crystallized predominantly at the expense of the CuZr<sub>2</sub> phase [45,58]. The ND results (Fig. 9) show that the B2 phase is visible in a much wider 536 537 temperature range in the case of the HO alloy compared to the LO alloy ( $\Delta T_{CuZr} = 60$  K and  $\Delta T_{CuZr} = 20$ K, respectively). This clearly shows the impact of oxygen, or the oxygen-rich  $\tau_3$  phase, on the kinetics 538 539 of phase transformations during heating. Thus, it can be concluded that the dispersive  $\tau_3$  phase hinders 540 the phase transformation front of low temperature equilibrium phases ( $CuZr_2$  and  $Zr_6Al_7Cu_{16}$ ), enabling the formation of the B2 CuZr phase via a massive crystallization mechanism (similar as in undercooled 541 542 liquid). With further temperature increase, the metastable B2 phase transforms into equilibrium  $CuZr_2$ 543 and AlCu<sub>2</sub>Zr phases (region 3 in Fig. 9), however, the B2 phase forms once again at temperatures above 544 1000 K. This phase is stable, together with the AlCuZr phase and some remaining CuZr<sub>2</sub> (and the  $\tau$ 3 phase in HO alloy) up to the solidus temperature. In the case of the LO alloy, the AlCuZr phase appears 545 546 already at approx. 950 K, where the exothermic peak on the DTA trace can be seen. In the HO alloy this 547 transformation is again hindered and the peak on the diffractogram is also blurred.

548 These considerations lead to the conclusion that the kinetic of cooling and heating of metallic glasses 549 can be represented by the mirror reflection rule (Fig. 11). In fact, the starting point is very similar: liquid and glass (also called frozen liquid [1]). The competition between viscosity and diffusion have a major 550 influence on the type of transformation that occurs during cooling/heating. Higher rates will increase 551 552 the importance of viscosity, hindering diffusion processes, and vice versa. If a sufficient cooling rate is provided, the metastable liquid can be undercooled below the T<sub>g</sub> temperature to form glass [7]. Similarly, 553 554 fast heating from room temperature allows to retain the glassy state up to liquidus temperature [59]. 555 Slowing down heating/cooling causes massive crystallization of the B2 CuZr with the chemical composition of the matrix [60,61]. This phase is often observed in ZrCu-based alloys if the cooling rate 556 557 condition is not fulfilled [19,40,48,61–63]. Chen et al. [45] claim that flash annealing could facilitate 558 the production of BMGCs reinforced by B2 CuZr. With even slower treatments, the first products of diffusion transformations appear at the onset of crystallization. A phase transformation between Tg and 559  $T_1$  can also occur. As the rate is closer to standard metallurgical conditions, all changes occur in a manner 560 close to equilibrium, thus the B2 phase may not occur anymore. In the case of BMGs with higher oxygen 561 562 content, the  $\tau_3$  phase will be present the in liquid and glass, so according to our previous observations,

563 with the same cooling rate, more B2 CuZr phase will form.



Fig. 11 Schematic diagram showing the phase transformation kinetics during cooling (a) and heating
 (b) of the ZrCu-based BMGs. The arrows symbolize the different cooling/heating rates. EP –
 equilibrium phases.

568 C. Thermal GFA evaluation

569 Glass forming ability evaluation based on the thermal analysis is a common approach allowing to 570 compare many BMG systems. Many efforts have been made to find a versatile GFA indicator by 571 analyzing hundreds of alloys. So far, above 20 different indicators (most of them are based on Tg, Tx and  $T_1$  temperatures) have been proposed with different  $R^2$  coefficient fit to the critical diameter [37]. 572 Here, we used three indicators with the best R<sup>2</sup> in our case:  $\Delta T_{xg} = T_x - T_g$  (R<sup>2</sup> = 0.698),  $\Delta T_{rg} = (T_x - T_y)$ 573  $(T_1 - T_g)/(T_1 - T_g)$  (R<sup>2</sup> = 0.665),  $\chi = [(T_x - T_g)/(T_1 - T_x)] * [T_x/(T_1 - T_x)]^{1.47}$  (R<sup>2</sup> = 0.663). However, such 574 575 fitting is still weak from a statistical point of view. Slightly better results can be obtained if Nd and Gd 576 are excluded, then for all indicators the  $R^2$  value becomes close to 0.878. Such a difference can be easily 577 explained by imperfect critical diameter determination by the discrete method as the gradual increase in 578 diameter does not include results between natural numbers. The most expanded  $\gamma$  indicator takes values 579 between 0.252 for the undoped HO alloy (diameter < 3 mm) and 0.521 for the LO alloy (8 mm). As predicted, casts with an intermediate  $\chi$  value have critical diameters between 3 and 8 mm. For Y 580 581 additions (Y4/3 and Y6/3), this indicator is slightly higher (0.535 and 0.604, respectively), meaning that 582 they should be characterized by better glass forming ability and higher maximum amorphous thickness, 583 compared to the LO undoped variant. This observation is consistent with XRD analysis, where the 584 intensities of crystalline peaks for the 9 mm rod sample (Fig. 3b) are smaller in comparison to the undoped 9 mm LO partially crystalline sample (Fig. 3 in Ref. [19]). For the triple variant of Y-to-oxygen 585 ratio, the melting event was split into two peaks. This change in behavior is attributed to the changes in 586 587 phase transformation products that are formed during heating. In the case of Sc, the highest values of all 588 GFA indicators were obtained for the Sc4/3 sample, though the largest D<sub>c</sub> was obtained for Sc6/3. Such a deviation was observed only for this element. For Lu, a straight correlation between GFA indicators

- 590 and  $D_c$  was observed.
- 591 The Nd-doped alloys are characterized by quite high GFA thermal indicator values (similar to alloys
- 592 doped with Lu), while achieving very low critical diameters. Even for the largest Nd dose, the number 593 of oxides observed in the microstructure was low and their mean circular-equivalent diameter was lowest
- 595 of oxides observed in the incrostructure was low and their mean circular-equivalent diameter was lowest 594 among all dopants, indicating a weak scavenging effect. Neodymia has the lowest Gibbs free energy of
- formation compared to other investigated REOs (Table IV) and although it is still more negative
- 596 compared to  $ZrO_2$ ,  $Al_2O_3$  and  $Cu_2O$  phases, the scavenging effect is not so prominent. Most probably
- 597 large amounts of Nd dissolved in the matrix, as indicated by the split melting event on DTA curves (Fig.
- 598 8), thereby increasing the GFA of the glassy matrix. It means that Nd can be used as a dopant increasing
- 599 GFA in high purity alloys. Additionally, the smallest FWHM of the first crystallization event (except
- 600 for the Nd4/3 variant) was found on the DTA traces for the Nd-doped alloy, indicating that alloys 601 containing  $Nd_2O_3$  oxides facilitate crystallization.
- 602 The opposite was observed for Gd additions, where the FWHMs indicated a relatively high barrier for
- 603 crystallization, and all GFA indicators remained unchanged and have low values. According to Zhiwei
- 604 et al. [32] in the  $Cu_{46}Zr_{47-x}Al_7Gd_x$  (x = 2, 4 and 5) alloy, only 5 % of Gd contributed to GFA
- 605 improvement, while lower concentrations decreased GFA indicators compared to the undoped alloy.
- 606 Similar observations were reported by Deng et al. [29], who observed a negative effect of the Gd in the
- 607 (Cu<sub>47</sub>Zr<sub>45</sub>Al<sub>8</sub>)<sub>96</sub>Gd<sub>4</sub> alloy. Hu et al. [64] examined in greater detail the sensitivity of the supercooled
- 608 liquid region to REEs additions, including Gd. It was found that with increasing Gd dopant content
- 609 (about 1 %),  $\Delta T_x$  quickly falls compared to other elements, meaning that Gd is unsuitable in minor
- 610 additions to obtain scavenging and/or alloying effects.
- Taking into account all the above-mentioned considerations, to obtain effective oxygen scavenging in
- 612 the Zr-Cu-Al system, a rare-oxide with lower Gibbs free energy of oxide formation than  $Gd_2O_3$  and
- $Md_2O_3$  should be used. In many studies,  $ZrO_2$  or ZrO oxides have been reported to cause easier BMG crystallization via a heterogenous nucleation mechanism [18,29,31,33]. However, in the Zr-Cu-Al
- 615 systems, the Al<sub>2</sub>O<sub>3</sub> oxide is also favorable to form together with zirconium oxide (Table IV). We suppose
- that in the present system, aluminum works as a scavenger (if no REE are added), resulting in  $\tau_3$  phase
- 617 stabilization. This hypothesis, however, should be verified.
  - $\Delta_f G^\circ$  (kJ mol<sup>-1</sup>) per oxygen mole  $\Delta_{\rm f} {\rm G}^{\circ} ({\rm kJ} {\rm mol}^{-1})$ Oxide 298.15 K 1800 K 298.15 K 1800 K  $ZrO_2$  $-1042.8 \pm 1.7$ -763.7 -521.4 -368.4-520.9 $Al_2O_3$ -1562.7±1.3 -1092.2-364.1Cu<sub>2</sub>O  $-146.0\pm6.3$ --146.0- $Sc_2O_3$  $-1819.4\pm2.5$ -1384.0-606.5-461.3  $Y_2O_3$ -605.5  $-1816.6\pm2.4$ -1392.3-464.1 $Lu_2O_3$  $-1788.8\pm6.3$ -1360.3 -596.3 -453.4  $Nd_2O_3$ -1299.7 -1721.1±1.0 -573.7 -433.2  $Gd_2O_3$ -1307.1 -435.7 -1732.3±3.6 -577.4

618Table IV Gibbs free energies of oxide formation (the most stable oxide at ambient pressure) at 298.15619K (25°C) and 1800 K (1526.85°C) [16].

620

# 622 V. CONCLUSIONS

623 The effect of  $Zr_{50}Cu_{40}Al_{10}$  alloy doping with rare-earth elements on glass forming ability was studied. 624 The main outcomes are summarized as followed:

- 625 1) Rare-earths forming cubic sesquioxides, including yttrium, scandium and lutetium, are the best 626 oxygen scavengers allowing to increase the critical diameter for glass formation  $(D_c)$  in Zr-based 627 alloys. The oxygen contamination coming from rare-earth additions is unambiguous and should be 628 included into calculations to study the pure scavenging effect.
- 629 2)  $D_c$  of the  $Zr_{50}Cu_{40}Al_{10}$  alloy with high oxygen content (988 wt. ppm) can be increased from 2.5 mm 630 up to 8 mm by double stoichiometric concentration of Y-to-oxygen content (Y = 0.675 at. %), 631 achieving at least the same  $D_c$  value as in the alloy containing much lower oxygen levels (194 wt. 632 ppm).
- $\begin{array}{ll} 633 \\ 634 \end{array} \begin{array}{l} \text{O} \\ \text{O} \\ \text{O} \\ \text{O} \\ \text{O} \end{array} \end{array}$
- 636 4) The structures of rare-earth oxides were confirmed by HR-STEM investigations:  $Sc_2O_3$  (cubic 637  $Ia\overline{3}$ ),  $Lu_2O_3$  (cubic –  $Ia\overline{3}$ ),  $Nd_2O_3$  (hexagonal –  $P\overline{3}m1$ ) and  $Gd_2O_3$  (cubic –  $Ia\overline{3}$ ). In the case of Gd, 638 the monoclinic sequioxide was not obtained.
- 639 5) The most developed GFA indicator  $\chi$  took values in the range of 0.252 to 0.604 for the investigated 640 alloys. After removing the results for partially crystallized samples (HO alloy, Nd2/3, Nd4/3, Gd2/3 641 and Gd4/3), it is in good agreement with the critical diameter. This allows for the maximum 642 amorphous thickness prediction in the range between 3 and 8 mm.

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# 648 CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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797Fig. A1 SEM-BSE images of  $Zr_{50}Cu_{40}Al_{10}$  alloy doped with scandium with stoichiometric 2/3 (a)  $D_c =$ 7984 mm and (b) D = 5 mm, double stoichiometric 4/3 (c)  $D_c =$  4 mm and (d) D = 5 mm and triple799stoichiometric 6/3 (e)  $D_c =$  5 mm and (f) D = 6 mm.



801Fig. A2 SEM-BSE images of  $Zr_{50}Cu_{40}Al_{10}$  alloy doped with lutetium with stoichiometric 2/3 (a)  $D_c = 3$ 802mm and (b) D = 4 mm, double stoichiometric 4/3 (c)  $D_c = 5$  mm and (d) D = 6 mm and triple803stoichiometric 6/3 (e)  $D_c = 6$  mm and (f) D = 7 mm.



805Fig. A3 SEM-BSE images of  $Zr_{50}Cu_{40}Al_{10}$  alloy doped with neodymium with stoichiometric 2/3 (a) 3806mm, double stoichiometric 4/3 (b) 3 mm and triple stoichiometric 6/3 (c)  $D_c = 3 mm$  and (d) D = 4807mm.



809Fig. A4 SEM-BSE images of  $Zr_{50}Cu_{40}Al_{10}$  alloy doped with gadolinium with stoichiometric 2/3 (a) 3810mm, double stoichiometric 4/3 (b) 3 mm and triple stoichiometric 6/3 (c)  $D_c = 3 mm$  and (d) D = 4811mm.

813 Table AI. Crystal structures of the studied sesquioxides

Rare-earth oxide	Crystal structure	Space group	Lattice parameters
$Sc_2O_3$ [65]	cubic	Ia3	$\alpha = \beta = \gamma = 90^\circ$ , $a = b = c = 9.845$ Å
Y <sub>2</sub> O <sub>3</sub> [66]	cubic	Ia3	$\alpha=\beta=\gamma=90^\circ,a=b=c=10.604~\text{\AA}$
Lu <sub>2</sub> O <sub>3</sub> [67]	cubic	Ia3	$\alpha = \beta = \gamma = 90^\circ, a = b = c = 10.363 \text{ Å}$
Nd <sub>2</sub> O <sub>3</sub> [68]	hexagonal	P3m1	$\alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}, a = b = 3.832 \text{ Å}, c = 6.012 \text{ Å}$
Gd <sub>2</sub> O <sub>3</sub> [69]	cubic	Ia3	$\alpha=\beta=\gamma=90^\circ,a=b=c=10.811~{\rm \AA}$



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Fig. A5 Neutron diffraction patterns of  $Zr_{50}Cu_{40}Al_{10}$  alloy with a) low; b) high oxygen level. Patterns taken from each temperature regions: 1 - 573 K, 2 - 833 K (LO) and 793 K (HO), 3 - 953 K, 4 - 1113 K, 5 - 1273 K.