Local atomic arrangements and their topology in Ni-Zr and Cu-Zr glassy and crystalline alloys

I. Kaban^{1,2,*}, P. Jónvári³, V. Kokotin⁴, O. Shuleshova¹, B. Beuneu⁵, K. Saks⁶, N. Mattern¹, J. Eckert^{1,2}, A.L. Greer⁷

¹IFW Dresden, Institute for Complex Materials, P.O. Box 270116, 01171 Dresden, Germany

²TU Dresden, Institute of Materials Science, 01062 Dresden, Germany

³Wigner Research Centre for Physics, Institute for Solid State Physics and Optics, P.O. Box 49, 1525 Budapest, Hungary

⁴Access e.V., Intzestraße 5, 52072 Aachen, Germany

⁵Laboratoire Léon Brillouin, CEA-Saclay, 91191 Gif sur Yvette Cedex, France

⁶Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 04001 Kosice, Slovak Republic

⁷Department of Materials Science & Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK

Abstract

Different experimental techniques (X-ray diffraction, neutron diffraction with isotopic substitution, extended X-ray absorption spectroscopy) and theoretical methods (reverse Monte-Carlo simulation, molecular dynamics modelling, Voronoi analysis) have been applied to elucidate the atomic structure of Ni-Zr and Cu-Zr alloys in glassy and crystalline states and to explain differences in the glass-forming abilities of the $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ compositions. Both glasses show similar strong topological ordering, but it is established that the degree of chemical ordering is much more pronounced in $\text{Ni}_{64}\text{Zr}_{36}$ glass than in $\text{Cu}_{65}\text{Zr}_{35}$ glass. The short-range atomic order and topology in the glassy and crystalline structures are remarkably different, and these differences are presumed to hinder crystal nucleation and growth, hence promoting glass formation upon fast cooling of the $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ liquid alloys. The larger differences observed for the $\text{Cu}_{65}\text{Zr}_{35}$ alloy in glassy and crystalline states are suggested to play a decisive role in increasing its bulk-glass-forming ability.

Keywords: Ni-Zr, Cu-Zr; metallic glass; crystal; structure; glass forming ability

1. Introduction

Nickel and copper are neighbours in the periodic table and have many similarities; for example, they both have the face-centred cubic (cubic close-packed) crystal structure, very similar densities, atomic sizes, and electronegativities [1]. Upon alloying with zirconium, nickel forms eight and copper forms six stable intermetallic compounds with complicated crystal structures, giving complex Ni-Zr [2] and Cu-Zr

* Corresponding author. E-mail address: i.kaban@ifw-dresden.de (I. Kaban)

[3] binary phase diagrams. In both binary systems, the ability to form glassy ribbons by melt-spinning or thin glassy discs by splat-quenching over a wide concentration range (30-80 at.% Zr in Ni-Zr and 30-75 at.% Zr in Cu-Zr) was established in 1970-80 [4-6]. Recently, bulk metallic glass (BMG) formation has been found in the Cu-Zr binary system at or around the compositions $\text{Cu}_{65}\text{Zr}_{35}$ [7,8,9], $\text{Cu}_{60}\text{Zr}_{40}$ [7,10], $\text{Cu}_{56}\text{Zr}_{44}$ [9], $\text{Cu}_{50}\text{Zr}_{50}$ [9,11], $\text{Cu}_{45}\text{Zr}_{55}$ [10,12]. In contrast, bulk glass formation has not yet been observed in the binary Ni-Zr system.

Since the discovery of the first bulk metallic glass [13] it has been widely accepted that BMG formation can take place only in systems with three or more components. Over the years, other empirical and semi-empirical criteria such as the size difference of the constituent atoms, a negative heat of mixing between the main constituents, the competition of crystalline phases, a large value of the reduced glass transition temperature $T_{\text{rg}}=T_{\text{g}}/T_{\text{l}}$, where T_{g} is the glass transition temperature and T_{l} is the liquidus temperature, chemical short-range ordering (SRO) and topological spatial ordering, etc. have been suggested to explain and predict the glass-forming ability (GFA) in metallic systems [14-20]. Lopez et al. [21] showed that the GFA in Ni-Zr and Cu-Zr systems can be related to the size mismatch and chemical interactions between the constituent atoms. However, the ability to form bulk glasses in the Cu-Zr system does not follow from that study. Based on thermodynamic assessments, Abe et al. [22] established that the driving force for crystallization is higher for the Ni-Zr system (over a wide composition range) than for the Cu-Zr system. Consequently, the critical cooling rates R_{C} are lower for the Cu-Zr system, implying better GFA. For both systems the minimal R_{C} was found around 35 at.% Zr [22]. These estimations were made under the assumption that the viscosity of Ni-Zr and Cu-Zr liquids, which is one of the crucial parameters determining nucleation rate and growth velocities of crystalline phases [23], is virtually the same in both systems. Recent quasielastic neutron scattering measurements of the $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{64.5}\text{Zr}_{35.5}$ liquid alloys near their melting temperatures yielded indeed quite close values of the Ni and Cu self-diffusion coefficient [24,25]. In view of these findings it is important to identify the structural peculiarities of the $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ alloys in their amorphous and crystalline states and to search for an explanation of their differing GFAs. The current renewed interest in structural investigation of metallic glasses is also stimulated by the aim to understand the stability of the glasses and their properties, in particular mechanical properties, and, more importantly, to tailor them.

Molecular-dynamics (MD) simulation studies suggest that the ability to form BMGs by particular Cu-Zr compositions is related to a specific atomic ordering in the liquid, the supercooled liquid and the amorphous state [26-30]. For example, Lee et al. [26] found that the MD model for $\text{Cu}_{65}\text{Zr}_{35}$ glass consists of various polyhedral clusters, among which about 15% are ideal icosahedra. Using MD simulations, Cheng et al. [27] demonstrated that the increase in dynamic viscosity and its deviation from Arrhenius-type behaviour upon cooling of Cu-Zr liquids is related to the increasing icosahedral order. Jakse and Pasturel [28] observed that the composition dependence of the icosahedral local symmetry as well as of the dynamic viscosity in MD-simulated Cu-Zr liquids exhibits a maximum around the $\text{Cu}_{64}\text{Zr}_{36}$ composition. Qualitatively similar results have been obtained in the molecular dynamics study of Cu-Zr alloys carried out by Mendelev et al. [29]. Recently Almyras et al. [30] performed a cluster analysis of the

structural models for Cu-Zr glasses and found that they are composed of interconnected clusters with icosahedral and dodecahedral symmetry. Mattern et al. [31] studied Cu-Zr glasses by reverse Monte-Carlo (RMC) simulation and analysed the model configurations. It was found that there is a large variety of polyhedra, with ideal icosahedra comprising only a small fraction.

In the present work we investigate relations between the structure and glass-forming ability of the $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ alloys (at.%). To determine the atomic structure of the $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ metallic glasses, we apply state-of-the-art experimental techniques such as high-energy synchrotron X-ray diffraction (XRD), neutron diffraction with isotopic substitution (NDIS), and extended X-ray absorption fine structure (EXAFS) spectroscopy. Structural models fitting the whole set of experimental data for each glass are generated by RMC simulation. The structure of crystalline phases for the $\text{Ni}_{64}\text{Zr}_{36}$ alloy ($\text{Ni}_{10}\text{Zr}_7$, $\text{Ni}_{21}\text{Zr}_8$ and Ni_7Zr_2) and the $\text{Cu}_{65}\text{Zr}_{35}$ alloy ($\text{Cu}_{10}\text{Zr}_7$, Cu_8Zr_3 and $\text{Cu}_{51}\text{Zr}_{14}$) is investigated by molecular-dynamics calculations. Faber-Ziman partial pair distribution functions, coordination numbers, and mean interatomic distances are extracted from the RMC and MD models. Chemical and topological atomic ordering in glasses is discussed in the framework of the Bhatia-Thornton formalism. The topology of model atomic configurations is studied with the Voronoi tessellation method.

2. Experimental details

A $\text{Cu}_{65}\text{Zr}_{35}$ master alloy was prepared by arc-melting pure Cu (99.99%) and Zr (99.9%) under a Ti-gettered Ar atmosphere. Three $\text{Ni}_{64}\text{Zr}_{36}$ master alloys were prepared by arc-melting using pure Zr (99.8%), $^{\text{nat}}\text{Ni}$ (99.97%), ^{58}Ni (enrichment 99.8%) and ^{60}Ni (enrichment 99.8%). Glassy ribbons were produced by single-roller melt spinning on a Cu wheel under Ar atmosphere.

The chemical composition of the glassy ribbons was determined by energy-dispersive X-ray (EDX) spectrometry and by inductively coupled plasma optical emission spectrometry (ICP-OES). The EDX analysis was performed using a LEO GEMINI 1530 scanning electron microscope (SEM) equipped with Bruker AXS spectrometer. The measurements were carried out at 30 keV on the sample area of 3 – 4 mm². The ICP-OES was performed using an Iris Advantage High Resolution Thermo Jarrell spectrometer with at least three specimens for each composition. The results of the EDX and ICP-OES analyses are summarized in Table 1. The concentrations determined by the two methods are in good agreement. The compositions of the Cu-Zr and Ni-Zr glasses prepared with natural Cu and Ni are practically equal to the nominal values. The concentrations of Ni and Zr in the ^{58}Ni - and ^{60}Ni -containing glasses deviate by about 0.4 – 0.8 at.% from the given values.

The X-ray diffraction measurements were performed at the BW5 beamline [32] at HASYLAB (DESY, Hamburg) with a photon energy of 100 keV in transmission geometry. The raw experimental data were corrected for detector dead-time, background, polarization, absorption, and variation in detector solid angle [33]. The neutron diffraction measurements were carried out with the 7C2 diffractometer at the Léon Brillouin Laboratory (CEA-Saclay, France). The wavelength of the incident radiation was 0.73 Å. Structure factors were obtained by correcting the measured intensities for detector efficiency, background scattering, absorption, multiple and incoherent scattering. The EXAFS measurements were

carried out at the beamlines A1 (Ni-Zr glass) and X1 (Cu-Zr glass) at HASYLAB. The EXAFS spectra were collected in transmission and fluorescence modes. The EXAFS-modulations were extracted from the recorded spectra using the programme VIPER [34].

3. XRD, ND, and EXAFS

The total structure factor measured in a single diffraction experiment is a weighted sum of the partial structural factors $S_{ij}(Q)$:

$$S(Q) = \sum_{i \leq j} w_{ij} S_{ij}(Q). \quad (1)$$

In the Faber-Ziman formalism [35,36], the weighting coefficients $w_{ij}^{X,N}$ are determined by the composition and the radiation in the following way:

$$w_{ij}^X(Q) = (2 - \delta_{ij}) c_i c_j \frac{f_i(Q) f_j(Q)}{\langle f(Q) \rangle^2}, \quad w_{ij}^N = (2 - \delta_{ij}) c_i c_j \frac{b_i b_j}{\langle b \rangle^2}. \quad (2)$$

The upper indices X and N stand for XRD and ND, respectively; δ_{ij} is the Kronecker delta; c_i is the mole fraction of the i -th constituent; $f_i(Q)$ is the atomic form-factor, and b_i is the coherent neutron scattering length; $\langle f(Q) \rangle = \sum_i c_i f_i(Q)$, $\langle b \rangle = \sum_i c_i b_i$. For an n -component alloy, $n(n+1)/2$ partial structure factors $S_{ij}(Q)$ can theoretically be separated from the same number of independent diffraction measurements via a matrix inversion of the system of equations of type (1).

Information on chemical order can effectively be separated from that on topological order within the Bhatia-Thornton formalism [36-38]. The concentration-concentration structure factor $S_{CC}(Q)$, which describes the concentration fluctuations, is related to the Faber-Ziman partial structure factors by:

$$S_{CC}(Q) = c_1 c_2 [1 + c_1 c_2 \{S_{11}(Q) + S_{22}(Q) - 2S_{12}(Q)\}]. \quad (3a)$$

The number-number structure factor $S_{NN}(Q)$, which describes the fluctuations of atomic positions without distinguishing between the species, is related to the Faber-Ziman partial structure factors by:

$$S_{NN}(Q) = c_1^2 S_{11}(Q) + c_2^2 S_{22}(Q) + 2c_1 c_2 S_{12}(Q). \quad (3b)$$

EXAFS spectroscopy is the most useful alternative or additional source of information for determination of local atomic order [39,40]. The EXAFS signal $\chi(k)$ measured as a function of the wave number k of the photoelectron ($k = \sqrt{2m_e(E - E_0)}/\hbar$; m_e is the electron mass, and $\hbar$ is the reduced Planck constant) is related to the partial pair correlation functions through the expression:

$$\chi_i(k) = \sum_j \chi_i^j = \sum_j 4\pi\rho_0 c_j \int_0^R r^2 \gamma_{ij}(r, k) g_{ij}(r) dr. \quad (4)$$

Here, the subscript i refers to the absorber atom; $\gamma_{ij}(r, k)$ is the photoelectron backscattering matrix, which gives the k -space contribution of a j -type backscatterer at a distance r from the absorber atom. The upper limit of integration, R , is usually below 4 Å, in line with the fact that EXAFS is a short-range technique giving mainly information on the first coordination shell. The elements of the backscattering matrix $\gamma_{ij}(r, k)$ can be calculated for each i - j pair by dedicated programmes (e.g. FEFF [41]). EXAFS is element-sensitive and provides information on the environment of absorbing atoms; $\gamma_{ij}(r, k)$ depends on both the phase and amplitude of the backscattered waves. Therefore, in favourable cases it is possible to distinguish between different types of backscatterers even if their distance from the absorber is very similar.

It has been shown in various studies, e.g. [42-46], that simultaneous modelling of diffraction and EXAFS experimental data using reverse Monte-Carlo simulation [47] allows significantly more information to be extracted on the atomic ordering in non-crystalline substances than is possible from separate investigations. Detailed descriptions of the RMC technique can be found in Refs. [47-50].

4. Simulation methods

4a) Reverse Monte-Carlo simulation of glassy structures

Due to the availability of several Ni isotopes with remarkably different coherent scattering lengths [51] and differences in the weighting coefficients $w_{ij}^{X,N}$ for the $\text{Ni}_{64}\text{Zr}_{36}$ composition (Table 2), the total structure factors measured by XRD and ND are quite distinguishable (Fig. 1a), enabling separation of partial structure factors from the system of Eqs. (1). The partial $S(Q)$'s for the $\text{Ni}_{64}\text{Zr}_{36}$ metallic glass obtained from the total $S(Q)$'s measured with XRD and ND on ^{58}Ni - and ^{60}Ni -containing samples are plotted in Fig. 2. For comparison, the partial structure factors for the $\text{Ni}_{63.7}\text{Zr}_{36.3}$ metallic glass determined by Lefebvre et al. [52] using neutron diffraction on the samples prepared from natural Ni, ^{60}Ni isotope and the rare ^{62}Ni isotope are also shown in Fig. 2. There is a good agreement between the respective partial structure factors at lower Q -values, while the uncertainty of our partial $S(Q)$'s, especially for the Zr-Zr correlations, is notably larger at high Q .

The situation is less favourable in case of the $\text{Cu}_{65}\text{Zr}_{35}$ alloy where the weights of Cu-Cu and Cu-Zr partial structure factors in the total $S(Q)$ are rather similar for XRD and ND for the sample with natural Cu (Fig. 1b). This cannot be improved significantly by the use of ^{63}Cu or ^{65}Cu isotopes, as can be seen from Table 2. Therefore, we applied RMC simulation for the separation of the partial structure factors and corresponding pair distribution functions of the $\text{Cu}_{65}\text{Zr}_{35}$ metallic glass. Furthermore, due to the availability of reliable partial structure factors for the $\text{Ni}_{63.7}\text{Zr}_{36.3}$ glass [52], we can estimate the input experimental information required for a plausible RMC modelling, which is especially important for investigation of the $\text{Cu}_{65}\text{Zr}_{35}$ metallic glass.

In the present study, the simulation runs were carried out with boxes containing 24976 atoms. The number density ρ of the $\text{Cu}_{65}\text{Zr}_{35}$ system is $0.0637 \text{ \AA}^{-3}$ [31] and that of the $\text{Ni}_{64}\text{Zr}_{36}$ system is $0.0655 \text{ \AA}^{-3}$ [53]. The minimum interatomic distance in the models is $2.20 \text{ \AA}$ for Ni-Ni and Cu-Cu pairs, $2.35 \text{ \AA}$ for Ni-Zr and Cu-Zr pairs, and $2.60 \text{ \AA}$ for Zr-Zr pairs. EXAFS backscattering coefficients were calculated using the FEFF8.4 programme [41].

The partial structure factors and pair distribution functions for the $\text{Ni}_{64}\text{Zr}_{36}$ metallic glass obtained with the simultaneous RMC simulation of the six experimental data-sets (XRD, ND on the $^{\text{nat}}\text{Ni}$, ^{58}Ni , and ^{60}Ni -containing samples, EXAFS at Ni and Zr absorption-edges) show excellent agreement with the NDIS results of Lefebvre et al. [52] in Fig. 2; the corresponding fits are plotted in Fig. 3. It is noteworthy that the three partial correlation functions of the $\text{Ni}_{64}\text{Zr}_{36}$ metallic glass can be separated by the RMC simulation (not shown) of the neutron diffraction data from ^{58}Ni - and ^{60}Ni -containing glasses and EXAFS at the Zr K-edge, because the information contained in these three datasets is sufficiently contrasting. Hence, the partial pair distributions in an alloy can be obtained if a proper combination of the input information is modelled with the RMC technique. Similarly to the $\text{Ni}_{64}\text{Zr}_{36}$ glass, we were able to separate the partial pair distribution functions for the $\text{Cu}_{65}\text{Zr}_{35}$ glass (Fig. 4) if the XRD and ND structure factors were fitted simultaneously with the Zr K-edge curve (the quality of fit is comparable to that for the $\text{Ni}_{64}\text{Zr}_{36}$ glass in Fig. 3).

4b) Molecular dynamics simulation of crystalline structures

Molecular dynamics has been used to investigate the partial pair distribution functions and topology of the crystalline phases competing with glass formation: $\text{Ni}_{10}\text{Zr}_7$, $\text{Ni}_{21}\text{Zr}_8$, Ni_7Zr_2 for the $\text{Ni}_{64}\text{Zr}_{36}$ alloy and $\text{Cu}_{10}\text{Zr}_7$, Cu_8Zr_3 and $\text{Cu}_{51}\text{Zr}_{14}$ for the $\text{Cu}_{65}\text{Zr}_{35}$ alloy [2,3]. The MD simulations were performed using the LAMMPS code [54] and the NPT ensemble at anisotropic zero pressure. The initial atomic configurations were generated using crystallographic parameters from the FIZ Karlsruhe Inorganic Crystal Structure Database [55]. The simulation boxes contained 6264 to 9504 atoms depending on the number of atoms in the unit cell. Periodic boundary conditions were applied in all three dimensions and the MD time-step was set to 2 fs. The embedded atom method (EAM) potentials of Sheng [56] and the Finnis-Sinclair EAM potentials of Mendelev [57] were used for the Cu-Zr and Ni-Zr alloys, respectively. Time-averaged (10000 MD time-steps) pair distribution functions were calculated for all six crystalline structures relaxed within 5 ns at 300 K. The averaged velocity of the atoms was $3.16 \text{ \AA ps}^{-1}$ for Cu, $3.28 \text{ \AA ps}^{-1}$ for Ni and $2.64 \text{ \AA ps}^{-1}$ for Zr.

5. Results and Discussion

5a) Partial pair correlations and atomic ordering

The partial pair distribution functions $g_{ij}(r)$ obtained by RMC simulation of the six data-sets for the $\text{Ni}_{64}\text{Zr}_{36}$ glass (XRD, EXAFS at Ni and Zr absorption edge, and ND on $^{\text{nat}}\text{Ni}$, ^{58}Ni - and ^{60}Ni -containing samples) and of the four data-sets (XRD, EXAFS at Cu and Zr K-edge, and ND) for the $\text{Cu}_{65}\text{Zr}_{35}$ glass are

compared in Fig. 5. The average interatomic distances r_{ij} were determined from the position of the first peak on the $g_{ij}(r)$ functions. The coordination numbers N_{ij} were obtained by integration of the partial radial distribution functions $4\pi r^2 \rho g_{ij}(r)$ from the left-hand edge of the first peak r_0 to the first minimum r_m on its right-hand side. The integration limits and values of r_{ij} and N_{ij} are listed in Tables 3 and 4. The uncertainty of interatomic distances is around 0.02 Å; the uncertainty of coordination numbers is around 10%.

The structure of both metallic glasses is characterized by dense atomic packing with an average coordination number of about 12. The mean coordination numbers (CN) for each component are: $N_{\text{Ni}} = 10.9 \pm 1.1$, $N_{\text{Zr}} = 14.3 \pm 1.5$ in the $\text{Ni}_{64}\text{Zr}_{36}$ glass; $N_{\text{Cu}} = 11.3 \pm 1.2$, $N_{\text{Zr}} = 13.4 \pm 1.4$ in the $\text{Cu}_{65}\text{Zr}_{35}$ glass. Though these values suggest a similarity in the atomic packing of the two glasses, there are differences in the respective interatomic distances (Table 3) and partial coordination numbers (Table 4, Fig. 6). In particular, the remarkably shorter Zr-Zr distance in the $\text{Cu}_{65}\text{Zr}_{35}$ glass (3.07 ± 0.02 Å) as compared to the $\text{Ni}_{64}\text{Zr}_{36}$ glass (3.27 ± 0.02 Å) and the larger r_{CuZr} (2.73 ± 0.02 Å) compared to r_{NiZr} (2.68 ± 0.02 Å) indicate a more compact local atomic packing in the Cu-Zr glass. As is characterized rather simply by comparing the corresponding ratios of coordination numbers and concentrations, bonding preferences are different in the two alloys. In the $\text{Ni}_{64}\text{Zr}_{36}$ glass, the ratio of N_{NiZr} and N_{NiNi} is $5.0/5.9 \approx 0.85$, while the ratio of Zr and Ni concentrations $c_{\text{Zr}}/c_{\text{Ni}}$ is $36/64 \approx 0.56$, indicating strong heteroatomic bonding. No such clear tendency can be observed around Cu in the $\text{Cu}_{65}\text{Zr}_{35}$ glass: $N_{\text{CuZr}}/N_{\text{CuCu}} \approx 0.61$, which is significantly closer to $c_{\text{Zr}}/c_{\text{Ni}} = 35/65 \approx 0.54$. The distribution around Zr is more random in the $\text{Ni}_{64}\text{Zr}_{36}$ glass (compare, $N_{\text{ZrZr}}/N_{\text{ZrNi}} \approx 0.63$; $N_{\text{ZrZr}}/N_{\text{ZrCu}} \approx 0.68$).

The $S_{\text{CC}}(Q)$ and $S_{\text{NN}}(Q)$ Bhatia-Thornton structure factors for the $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ glasses calculated from the Faber-Ziman structure factors using Eqs. (3a,b) are compared in Fig. 7. Almost the same number density correlations up to high Q -values are observed in the $S_{\text{NN}}(Q)$ curves for both the $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ glasses. On the other hand, notable differences are observed for the concentration-concentration structure factors. While several strong peaks are present in $S_{\text{CC}}(Q)$ for the $\text{Ni}_{64}\text{Zr}_{36}$ glass, the oscillations are rather weak over the whole Q -range for the $\text{Cu}_{65}\text{Zr}_{35}$ glass. It can thus be concluded that the $\text{Ni}_{64}\text{Zr}_{36}$ glass is characterized by pronounced topological and chemical ordering, while the $\text{Cu}_{65}\text{Zr}_{35}$ glass is topologically ordered and chemically rather disordered.

A glass is formed if the nucleation and/or growth of the stable or metastable crystalline phases is suppressed by sufficiently fast cooling of the liquid. It is therefore important to compare the atomic ordering in the $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ glasses and the crystalline phases which might compete with glass formation on cooling of the corresponding liquids. Bearing in mind the Ni-Zr and Cu-Zr phase diagrams [2,3] as well as the composition of crystalline phases found in glassy matrix by cooling at the margin of glass formation (see for example refs. [8,9,58]), the following crystalline phases were taken to be the competitors to glass formation: $\text{Ni}_{10}\text{Zr}_7$, $\text{Ni}_{21}\text{Zr}_8$, Ni_7Zr_2 in the $\text{Ni}_{64}\text{Zr}_{36}$ alloy and $\text{Cu}_{10}\text{Zr}_7$, Cu_8Zr_3 , $\text{Cu}_{51}\text{Zr}_{14}$ in the $\text{Cu}_{65}\text{Zr}_{35}$ alloy. The MD-simulated partial pair distribution functions for these crystalline structures are plotted along with the RMC-simulated partial pair distribution functions for the $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$

glasses in Fig. 8a and Fig. 8b, respectively. The average interatomic distances r_{ij} and partial coordination numbers N_{ij} , determined from the $g_{ij}(r)$ functions in the same way as those for the glasses, are listed in Table 3 and Table 4.

It is worth noting that very large differences are seen between the Cu-Cu, Cu-Zr and Zr-Zr pair distribution functions of the $\text{Cu}_{65}\text{Zr}_{35}$ glass and all of the $\text{Cu}_{10}\text{Zr}_7$, Cu_8Zr_3 , and $\text{Cu}_{51}\text{Zr}_{14}$ crystalline phases (Fig. 8b). The differences seem to be not so obvious in the case of Ni-Zr alloys by visual observation of the partial distribution functions, in particular for the Ni-Zr pairs (Fig. 8a). To get a quantitative picture, it is useful to compare the mean interatomic distances and partial coordination numbers for the two systems (Tables 3 and 4). A relative difference in the first coordination number for the ij atomic pairs in the glassy and crystalline state is given in Table 4 by the parameter ε calculated as

$$\varepsilon = \frac{|N_{ij}^{\text{glass}} - N_{ij}^{\text{cryst}}|}{N_{ij}^{\text{glass}}} \cdot 100\% \quad (5)$$

There is a remarkable difference in the Ni-Ni mean bond length for the $\text{Ni}_{64}\text{Zr}_{36}$ glass compared to $\text{Ni}_{10}\text{Zr}_7$ crystal, and in the Zr-Zr distance for the $\text{Ni}_{64}\text{Zr}_{36}$ glass compared to $\text{Ni}_{21}\text{Zr}_8$ and Ni_7Zr_2 crystals. The Ni-Zr mean interatomic distance is quite similar in all Ni-Zr alloys. A significant difference in coordination numbers for the glassy and crystalline Ni-Zr structures is observed at least for two of the three atomic pairs for each composition (see Fig. 8a, Tables 3a and 4a for details).

Comparison of the bond lengths and coordination numbers in the $\text{Cu}_{65}\text{Zr}_{35}$ glass and Cu-Zr crystalline phases also reveals a notable difference for at least two of the three atomic pairs. The Zr environment in the $\text{Cu}_{65}\text{Zr}_{35}$ glass is found to be particularly different from those in the $\text{Cu}_{10}\text{Zr}_7$, Cu_8Zr_3 and $\text{Cu}_{51}\text{Zr}_{14}$ crystalline phases (see Fig. 8b, Tables 3a and 4b for details).

5b) Local and spatial topology of atomic arrangements

In view of the differences in the short-range atomic ordering observed in the Ni-Zr and Cu-Zr glassy and crystalline structures it is interesting to compare the topology of local atomic arrangements. For this, we have used Voronoi tessellation analysis [59, 60]. The Voronoi cell or polyhedron of an atom contains all points in space which are closer to the centre of the atom than to any other atom (also called the Dirichlet region [61] and, in the case of a regular atomic structure, the Wigner-Seitz cell [62]). The Voronoi tessellation thus produces convex polyhedral cells, which have planar faces and completely fill space. The different coordination polyhedra surrounding a central atom can be characterized by the Voronoi index $\langle n_3, n_4, n_5, n_6, \dots \rangle$ where n_i denotes the number of i -edged faces of the polyhedron and $\sum_i n_i$ is the coordination number.

The Voronoi analysis applied to the atomic configurations in the $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ metallic glasses generated by RMC revealed a large variety of polyhedra (> 700 different structures) in both systems. The populations of the more common structures (with populations more than 0.5% of the total

number of polyhedra) are listed in Table 5 and presented in Fig. 9. As the supercooling and glass-forming ability observed in metallic alloys have often been discussed in relation to icosahedral short-range order, it is interesting to take a more detailed look at the icosahedral and icosahedral-like structures in our models. In this work, the ideal icosahedron is defined as polyhedron having (0, 0, 12, 0) index and, therefore, consisting of 12 pentagons, which can be regular or distorted. To take into account thermal vibrations of atoms, distorted icosahedra are defined as the polyhedra, which can be received by small transformation of the ideal ones [63].

Icosahedral structures (ideal and distorted icosahedra) are formed predominantly around Ni and Cu atoms. The populations of distorted icosahedra are relatively large and approximately equal in the two alloys: 20.46% in $\text{Ni}_{64}\text{Zr}_{36}$ and 21.32% in $\text{Cu}_{65}\text{Zr}_{35}$. The population of ideal icosahedra is rather small in both alloys (Table 5, Fig. 9), but in $\text{Cu}_{65}\text{Zr}_{35}$ (5.66%) it is more than twice that in $\text{Ni}_{64}\text{Zr}_{36}$ (2.54%).

The distribution of polyhedra found in the $\text{Ni}_{10}\text{Zr}_7$, $\text{Ni}_{21}\text{Zr}_8$, Ni_7Zr_2 crystalline structures is plotted in Fig. 10a while that for the $\text{Cu}_{10}\text{Zr}_7$, Cu_8Zr_3 , $\text{Cu}_{51}\text{Zr}_{14}$ crystal structures is shown in Fig. 10b. These figures also show the distributions of the more common polyhedra (with populations more than 1% of the total) in the RMC atomic configurations for the $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ glasses. Significant differences in the type and distribution of polyhedra appearing in the glassy and crystalline structures are observed in both systems. It is noteworthy that the population of the ideal icosahedra (0,0,12,0) is rather large in the crystalline phases, in particular 33.3% in the Ni_7Zr_2 , 17.2% in the $\text{Ni}_{21}\text{Zr}_8$, 27.3% in the Cu_8Zr_3 , and 18.5% in the $\text{Cu}_{51}\text{Zr}_{14}$. Besides, there is a large population of the icosahedra-like polyhedra – 18.2% of the (0,0,12,4) and 9.1% of the (0,0,12,5) polyhedra – in the Cu_8Zr_3 crystalline phase. The other polyhedra observed in the Ni-Zr and Cu-Zr crystalline structures are quite different from ideal icosahedra.

To characterize the spatial arrangement of the ideal (0, 0, 12, 0) icosahedra in the model atomic configurations, we have calculated the ratio between the number of all atoms incorporated in the ideal icosahedra and the number of such icosahedra, i.e. determined the average number of atoms belonging to each icosahedron only, therefore not shared with other ones. This number is 9.5 for the $\text{Ni}_{64}\text{Zr}_{36}$ glass and 7.9 for the $\text{Cu}_{65}\text{Zr}_{35}$ glass. Since only 13 atoms of an icosahedron can be connected to other icosahedra, these values mean that each ideal icosahedron is connected to other icosahedra by sharing on average 3.5 atoms in $\text{Ni}_{64}\text{Zr}_{36}$ and 5.1 atoms in $\text{Cu}_{65}\text{Zr}_{35}$, leading to the conclusion that the icosahedra in the Cu-Zr glass are more strongly interconnected. The distribution of ideal icosahedra and their networking in the atomic configurations for the $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ metallic glasses obtained by RMC simulation are shown in Fig. 11. In the crystalline state, the interconnection of ideal icosahedra is rather similar for the both systems. The average number of shared atoms is 7.7 in $\text{Ni}_{21}\text{Zr}_8$, 9.9 in Ni_7Zr_2 , 8.7 in $\text{Cu}_{51}\text{Zr}_{14}$ and 9.7 in Cu_8Zr_3 .

5c) Atomic structure and glass-forming ability of $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ alloys

Empirical criteria apparently are of little help in understanding the differences in the glass-forming ability of the $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ alloys. The size mismatch, which introduces crystal instability, increases bond strength and hinders atomic transport [18], is similar in the Ni-Zr and Cu-Zr systems. Also, the

reduced glass-transition temperature, related to the homogeneous nucleation rate of crystals [14], is almost the same in both alloys: $T_g \approx 0.60$ for $\text{Ni}_{64}\text{Zr}_{36}$ [2,64] and $T_g \approx 0.59$ for $\text{Cu}_{65}\text{Zr}_{35}$ [3,65].

It is usually accepted that a negative heat of mixing ΔH , reflecting attractive interactions of unlike atoms, promotes glass formation by increasing the local packing efficiency and reducing the atomic diffusivity. However, a negative heat of mixing also favours compound formation, which limits diffusivity but competes against glass formation. Calculations with Miedema's approach [15] reveal that the negative heat of mixing in the amorphous phase is significantly larger for $\text{Ni}_{64}\text{Zr}_{36}$ (-56 kJ/mol) than for $\text{Cu}_{65}\text{Zr}_{35}$ (-21 kJ/mol). This comparison suggests that making the heat of mixing more and more negative does not necessarily keep improving the GFA.

$\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ glasses show strong topological ordering, while the degree of chemical ordering is much more pronounced in Ni-Zr glass than in Cu-Zr glass (Fig. 7). Recent structural investigations of the Ni-Zr [66] and Cu-Zr [66,67] melts demonstrate that these structural features are characteristic for the liquid state as well as for the supercooled liquid state. Indeed, $S_{NN}(Q)$ and $S_{CC}(Q)$ Bhatia-Thornton partial structure factors for the liquid $\text{Ni}_{64}\text{Zr}_{36}$ [66] were established to show remarkable oscillations both at ~ 40 K below as well as at ~ 300 K above the melting temperature. The $S_{NN}(Q)$ partial structure factors for the liquid $\text{Cu}_{33.3}\text{Zr}_{66.7}$, $\text{Cu}_{50}\text{Zr}_{50}$ and $\text{Cu}_{58.8}\text{Zr}_{41.2}$ alloys at ~ 50 K above and up to 100 K below the respective melting temperature [66,67] exhibit distinct oscillations similar to those for the $\text{Cu}_{65}\text{Zr}_{35}$ glass. We are not aware of any $S_{CC}(Q)$ experimental partial structure factors for the liquid Cu-Zr alloys, but taking into account the present results for the $\text{Cu}_{65}\text{Zr}_{35}$ glass it is natural to suppose that the Cu-Zr melts are chemically rather disordered.

The most striking finding of our study is a fundamental difference in the chemical atomic ordering (Fig. 8, Tables 3 and 4) and topology of local atomic arrangements (Fig. 10) between the $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ glasses and the crystalline phases which, in accordance with the equilibrium phase diagrams [2,3], could compete with glass formation. This difference is assumed to have a twofold effect on the solidification of $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ liquids, hindering first crystal nucleation and then growth, as fundamental structural rearrangement of atoms is required. Obviously, due to particularly large differences observed between the $\text{Ni}_{21}\text{Zr}_8$ and Ni_7Zr_2 crystal structures and $\text{Ni}_{64}\text{Zr}_{36}$ glass (and also between the Cu_8Zr_3 and $\text{Cu}_{51}\text{Zr}_{14}$ crystal structures and $\text{Cu}_{65}\text{Zr}_{35}$ glass), these crystalline phases can be relatively easily suppressed by glass formation. On the other hand, it is more difficult to prevent the formation of $\text{Ni}_{10}\text{Zr}_7$ and $\text{Cu}_{10}\text{Zr}_7$ crystallites along with glass.

The different GFAs of the $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ alloys can be explained by the different degrees of dissimilarity between the glassy and crystalline structures for these compositions (Fig. 8), and consequently different crystallization driving forces as calculated in Ref. [22]. The differences in the partial pair distribution functions observed for the $\text{Ni}_{64}\text{Zr}_{36}$ alloy (Fig. 8a) seem to be sufficient to permit glass formation (stifle crystallization) at the high cooling rates achievable by melt spinning, while the remarkably larger differences in the $g_{ij}(r)$'s for the $\text{Cu}_{65}\text{Zr}_{35}$ alloy most likely play a decisive role in its bulk-glass-forming ability.

Conclusions

We have performed a comparative structural study of Ni-Zr and Cu-Zr alloys in the glassy and crystalline states. XRD, ND and EXAFS data from the $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ metallic glasses were all fitted consistently using reverse Monte Carlo simulation. The partial structure factors, pair distribution functions, coordination numbers and most probable interatomic distances were extracted from the atomic configurations obtained by the RMC simulation. The $\text{Ni}_{64}\text{Zr}_{36}$ metallic glass is established to be characterised by pronounced topological and chemical short-range atomic ordering with preferred Ni-Zr bonding. The $\text{Cu}_{65}\text{Zr}_{35}$ glass shows topological order with more compact packing, but it is chemically rather disordered (consistent with a smaller negative heat of mixing).

The model atomic configurations for both $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ glasses show a large variety of polyhedra, about 25% of which have icosahedra-like structures. The number of ideal icosahedra is relatively small in both systems, but in the $\text{Cu}_{65}\text{Zr}_{35}$ model it is twice that in the $\text{Ni}_{64}\text{Zr}_{36}$ model. Also, the ideal icosahedra are significantly more interconnected in the $\text{Cu}_{65}\text{Zr}_{35}$ model than in the $\text{Ni}_{64}\text{Zr}_{36}$ model.

The partial pair distribution functions of crystalline phases for the $\text{Ni}_{64}\text{Zr}_{36}$ alloy ($\text{Ni}_{10}\text{Zr}_7$, $\text{Ni}_{21}\text{Zr}_8$ and Ni_7Zr_2) and the $\text{Cu}_{65}\text{Zr}_{35}$ alloy ($\text{Cu}_{10}\text{Zr}_7$, Cu_8Zr_3 and $\text{Cu}_{51}\text{Zr}_{14}$) were calculated by molecular-dynamics simulation. In both systems, differences have been found in the local atomic order on the level of pair distribution functions, coordination numbers and mean interatomic distances as well as in the topology of atomic arrangements between the glassy and the crystalline structures. The differences are significantly larger in the case of $\text{Cu}_{65}\text{Zr}_{35}$, which is assumed to be the most decisive factor increasing its bulk glass-forming ability.

Rather large populations of the ideal (0,0,12,0) icosahedra found in the MD-simulated atomic configurations for the $\text{Ni}_{21}\text{Zr}_8$ and Ni_7Zr_2 as well as for the Cu_8Zr_3 and $\text{Cu}_{51}\text{Zr}_{14}$ crystalline structures suggest that icosahedral order does not necessarily favour glass formation in the Ni-Zr and Cu-Zr alloys.

Acknowledgments

We thank H. Teichmann, B. Opitz, A. Voß, S. Donath, J. H. Han for technical assistance. The staffs at HASYLAB (DESY) and LLB (CEA-Saclay) are kindly acknowledged for technical support during experiments. P. Jónvári is indebted to T. Fukunaga for helpful discussions and to the OTKA (Hungarian Basic Research Found) for financial support (Grant No. 083529). K. Saksl acknowledges financial support of the Slovak Grant Agency for Science (Grant No. 2/0128/13).

References

- [1] <http://www.webelements.com>
- [2] Abe T, Onodera H, Shimono M, Ode M. Mater Trans 2005;46:2838.
- [3] Arias D, Abriata JP, Bull Alloy Phase Diagrams 1990;11:452.
- [4] Ray R, Giessen BC, Grant NJ. Scripta Metall 1968;2:357.
- [5] Altounian Z, Strom-Olsen JO. Phys Rev B 1983;27:4149.
- [6] Buschow KHJ. J Phys F: Met Phys 1984;14:593.
- [7] Xu D, Lohwongwatana B, Duan G, Johnson WL, Garland C. Acta Mater 2004;52:2621.
- [8] Wang D, Li Y, Sun BB, Sui ML, Lu K, Ma E. Appl Phys Lett 2004;84:4029.
- [9] Li Y, Guo Q, Kalb JA, Thompson CV. Science 2008;322:1816.
- [10] Inoue A, Zhang W. Mater Trans Jpn Inst Metals 2004;45:584.
- [11] Tang MB, Zhao DQ, Pan MX, Wang WH. Chinese Phys Lett 2004;21:901.
- [12] Duan G, Xu D, Zhang Q, Zhang G, Cagin T, Johnson WL, Goddard WA. Phys Rev B 2005;71:224208.
- [13] Drehman AJ, Greer AL, Turnbull D. Appl Phys Lett 1982;41:716.
- [14] Turnbull D. Contemp Phys 1969;10:473.
- [15] Miedema AR, Boom R, De Boer MR. J Less-Common Met 1975;41:283.
- [16] Cahn RW, J Phys Colloq C9 1982;12:55.
- [17] Inoue A, Zhang T, Masumoto T. J Non-Cryst Solids 1993;156-158:473.
- [18] Egami T. J. Non-Cryst Solids 2003;317:33.
- [19] Miracle DB. Nature Mater 2004;3:697.
- [20] Sheng HW, Luo WK, Alamgir FM, Bai JM, Ma E. Nature 2006;439:419.
- [21] Lopez JM, Alonso JA, Gallego LJ. Phys Rev B 1987;36:3716.
- [22] Abe T, Shimono M, Ode M, Onodera H. J Alloys Comp 2007;434-435:152.
- [23] Kelton KF, Greer AL. Nucleation in Condensed Matter: Applications in Materials and Biology. Amsterdam: Elsevier Pergamon Materials Series; 2010.
- [24] Holland-Moritz D, Stüber S., Hartmann H, Unruh T, Meyer A. J Phys: Conf Series 2009;144:012119.
- [25] F. Yang, private communication
- [26] Lee S-C, Lee C-M, Lee J-C, Kim H-J, Shibutani Y, Fleury E, Falk ML. Appl Phys Lett 2008;92:151906.
- [27] Cheng YQ, Sheng HW, Ma E. Phys Rev B 2008;78:014207.
- [28] Jakse N, Pasturel A. Phys Rev B 2008;78:214204.
- [29] Mendeleev MI, Kramer MJ, Ott RT, Sordélet DJ, Besser MF, Kreyssig A, Goldman AI, Wessels V, Sahu KK, Kelton KF, Heyers RW, Caneparì S, Rogers JR. Phil Mag 2010;90:3795.
- [30] Almyras GA, Papageorgiou DG, Lekka ChE, Mattern N, Eckert J, Evangelakis GA. Intermetallics 2011;19:657.

- [31] Mattern N, J3v3ri P, Kaban I, Gruner S, Elsner A, Kokotin V, Franz H, Beuneu B, Eckert J. *J Alloys Comp* 2009;485:163.
- [32] Bouchard R, Hupfeld D, Lippmann T, Neuefeind J, Neumann H B, Poulsen H F, R3tt U, Schmidt T, Schneider J R, S3ssenbach J, von Zimmermann M. *J Synchrotron Rad* 1998; 5:90.
- [33] Poulsen HF, Neumann H-B, Schneider JR, Neuefeind J, Zeidler MD, *J Non-Cryst Solids* 1995;188:63.
- [34] Klementev KV. *J Phys D: Appl Phys* 2001;34:209.
- [35] Faber TE, Ziman JM, *Phil Mag* 1965;11:153.
- [36] Waseda Y. *The Structure of Non-Crystalline Materials*. New-York: McGraw-Hill International Book Co; 1980.
- [37] Bhatia AB, Thornton DE. *Phys Rev B* 1970;2:3004.
- [38] Salmon PS, Martin RA, Mason PE, Cuello GJ. *Nature* 2005;435:75.
- [39] Newville M. *Fundamentals of XAFS*. Chicago: Consortium for Advanced Radiation Sources, University of Chicago; 2004.
- [40] Rehr JJ, Albers RC. *Rev Mod Phys* 2000;72:2000621.
- [41] Ankudinov AL, Ravel B, Rehr JJ, Conradson SD. *Phys Rev B* 1998;58:7565.
- [42] Kaban I, J3v3ri P, Hoyer W, Welter E. *J Non-Cryst Solids* 2007;353:2474.
- [43] Kaban I, J3v3ri P, Stoica M, Eckert J, Hoyer W, Beuneu B. *Phys Rev B* 2009;79:212201.
- [44] Luo WK, Ma E. *J Non-Cryst Solids* 2008;354:945.
- [45] Sugiyama K, Muto T, Kawamata T, Yokoyama Y, Waseda Y. *Phil Mag* 2011;91:2962.
- [46] Cheng YQ, Ma E. *Prog Mater Sci* 2011;56:379.
- [47] McGreevy RL, Pusztai L. *Molec Simul* 1988;1:359.
- [48] McGreevy RL. *J Phys: Condens Matter* 2001;13:R877.
- [49] Evrard G, Pusztai L. *J Phys: Condens Matter* 2005;17:S1.
- [50] Gereben O, J3v3ri P, Temleitner L, Pusztai L. *J Optoelectron Adv Mater* 2007;9:3021.
- [51] <http://www.ncnr.nist.gov/resources/n-lengths/>
- [52] Lefebvre S, Quivy A, Bigot J, Calvayrac Y, Bellisent R. *J Phys F: Met Phys* 1985;15:L99.
- [53] Itoh K, Watanabe T, Otomo T, Sugiyama M, Mori K, Fukunaga T. *J Alloys Comp* 2009;483:213.
- [54] <http://lammps.sandia.gov>
- [55] FIZ Karlsruhe Inorganic Crystal Structure Database; <http://icsd.fiz-karlsruhe.de>; ICSD Collection Codes: 240191 (Ni₁₀Zr₇); 402864 (Ni₂₁Zr₈); 2778 (Ni₇Zr₂); 164881 (Cu₁₀Zr₇); 396 (Cu₈Zr₃); 629471 (Cu₅₁Zr₁₄).
- [56] <https://sites.google.com/a/gmu.edu/eam-potential-database/Home/AlCu>
- [57] <http://www.ctcms.nist.gov/potentials/Zr-Ni.html>
- [58] Wang WH, Lewandowski JJ, Greer AL, *J Mater Res* 2005;20:2307.
- [59] Voronoi G. *J Reine Angew Math* 1908;134:198.
- [60] Bernal JD. *Nature* 1960;185:68.
- [61] Dirichlet GL. *J Reine Angew Math* 1850;40:209.

- [62] Wigner E, Seitz F. Phys Rev 1933;43:804.
- [63] Hermann H, Kokotin V, Eckert J. EPL 2012;98:16003.
- [64] Russew K, Sommer F, Duhai P, Bakonyi I. J Mater Sci 1992;27:3565.
- [65] Mattern N, Schöps A, Kühn U, Acker J, Khvostikova O, Eckert J. J Non-Cryst Solids 2008;354:1054.
- [66] Kordel T. PhD Thesis, Ruhr-Iniversität Bochum 2011.
- [67] Holland-Moritz D, Yang F, Kordel T, Klein S, Kargl F, Gegner J, Hansen T, Bednarčik J, Kaban I, Shuleshova O, Mattern N, Meyer A. EPL 2012;100:56002.

Table 1. Nominal and measured compositions (in at.%) of the metallic glasses studied in this work. EDX – energy dispersive X-Ray analysis, ICP-OES – inductively coupled plasma with optical emission spectrometry.

Nominal composition	EDX		ICP-OES	
	composition	exp. error	Composition	exp. error
$\text{Cu}_{65}\text{Zr}_{35}$	$\text{Cu}_{65.05}\text{Zr}_{34.95}$	± 0.29	$\text{Cu}_{65.17}\text{Zr}_{34.83}$	± 0.12
$^{\text{nat}}\text{Ni}_{64}\text{Zr}_{36}$	$\text{Ni}_{64.17}\text{Zr}_{35.83}$	± 0.12	$\text{Ni}_{64.01}\text{Zr}_{35.99}$	± 0.11
$^{58}\text{Ni}_{64}\text{Zr}_{36}$	$\text{Ni}_{64.88}\text{Zr}_{35.12}$	± 0.31	$\text{Ni}_{64.82}\text{Zr}_{35.18}$	± 0.16
$^{60}\text{Ni}_{64}\text{Zr}_{36}$	$\text{Ni}_{63.29}\text{Zr}_{36.71}$	± 0.24	$\text{Ni}_{63.47}\text{Zr}_{36.53}$	± 0.28

Table 2. XRD and ND weight coefficients for $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ alloys (see Eqs. 1,2).

Irradiation / isotope	$\text{Ni}_{64}\text{Zr}_{36}$			$\text{Cu}_{65}\text{Zr}_{35}$		
	W_{NiNi}	W_{NiZr}	W_{ZrZr}	W_{CuCu}	W_{CuZr}	W_{ZrZr}
XRD ($Q = 0 \text{ \AA}^{-1}$)	0.307	0.494	0.199	0.329	0.489	0.182
ND / $^{\text{nat}}\text{Cu}$ / $^{\text{nat}}\text{Ni}$	0.517	0.404	0.079	0.445	0.444	0.111
ND / ^{63}Cu / ^{58}Ni	0.611	0.342	0.048	0.391	0.469	0.141
ND / ^{65}Cu / ^{60}Ni	0.168	0.484	0.348	0.538	0.391	0.071
ND / ^{62}Ni	3.47	-3.21	0.74	—	—	—

Table 3. Mean interatomic distances r_{ij} (Å) in the $\text{Ni}_{64}\text{Zr}_{36}$ (a) and $\text{Cu}_{65}\text{Zr}_{35}$ (b) glasses and related crystalline phases. The uncertainty of the interatomic distances is around 0.02 Å.

a) Ni-Zr system	r_{NiNi}	r_{NiZr}	r_{ZrZr}
$\text{Ni}_{64}\text{Zr}_{36}$ glass	2.54	2.68	3.27
$\text{Ni}_{10}\text{Zr}_7$ crystal	2.65	2.72	3.33
$\text{Ni}_{21}\text{Zr}_8$ crystal	2.55	2.69	3.15
Ni_7Zr_2 crystal	2.57	2.69	3.35

b) Cu-Zr system	r_{CuCu}	r_{CuZr}	r_{ZrZr}
$\text{Cu}_{65}\text{Zr}_{35}$ glass	2.60	2.73	3.07
$\text{Cu}_{10}\text{Zr}_7$ crystal	2.58	2.77	3.23
Cu_8Zr_3 crystal	2.51	2.90	3.12 3.51
$\text{Cu}_{51}\text{Zr}_{14}$ crystal	2.51	2.84	3.31 3.78

Table 4. Coordination numbers in the $\text{Ni}_{64}\text{Zr}_{36}$ (a) and $\text{Cu}_{65}\text{Zr}_{35}$ (b) glasses and related crystalline phases: N_{ij} – partial coordination number, N_i – average coordination number for i -th component, N – average coordination number for alloy. The integration limits ($r_0 - r_m$) and the number densities ρ used in the

calculations are given. The value $\varepsilon = \frac{|N_{ij}^{\text{glass}} - N_{ij}^{\text{cryst}}|}{N_{ij}^{\text{glass}}} \cdot 100\%$ gives a relative difference in the first coordination number for an ij -atomic pair in the glassy and crystalline state. The uncertainty of coordination numbers is around 10%.

a) Ni-Zr system	$(r_0 - r_m)$ $N_{\text{NiNi}} / \varepsilon$	$(r_0 - r_m)$ $N_{\text{NiZr}} / \varepsilon$	$(r_0 - r_m)$ N_{ZrNi}	$(r_0 - r_m)$ $N_{\text{ZrZr}} / \varepsilon$	N_{Ni}	N_{Zr}	N
$\text{Ni}_{64}\text{Zr}_{36}$ glass $\rho = 0.0655 \text{ \AA}^{-3}$	(2.20 – 3.26) $\text{\AA}$ 5.9	(2.35 – 3.42) $\text{\AA}$ 5.0	(2.35 – 3.42) $\text{\AA}$ 8.8	(2.60 – 3.92) $\text{\AA}$ 5.5	10.9	14.3	12.1
$\text{Ni}_{10}\text{Zr}_7$ crystal $\rho = 0.0652 \text{ \AA}^{-3}$	(2.25 – 3.19) $\text{\AA}$ 4.2 / 29%	(2.25 – 3.45) $\text{\AA}$ 6.6 / 32%	(2.25 – 3.45) $\text{\AA}$ 9.4 / 7%	(2.85 – 3.69) $\text{\AA}$ 5.7 / 4%	10.8	15.1	12.6
$\text{Ni}_{21}\text{Zr}_8$ crystal $\rho = 0.0734 \text{ \AA}^{-3}$	(2.05 – 3.21) $\text{\AA}$ 7.5 / 27%	(2.10 – 3.39) $\text{\AA}$ 4.7 / 6%	(2.10 – 3.39) $\text{\AA}$ 12.2 / 39%	(2.53 – 3.67) $\text{\AA}$ 2.1 / 62%	12.2	14.3	12.8
Ni_7Zr_2 crystal $\rho = 0.0772 \text{ \AA}^{-3}$	(2.02 – 3.05) $\text{\AA}$ 8.1 / 37%	(2.22 – 3.47) $\text{\AA}$ 4.0 / 20%	(2.22 – 3.47) $\text{\AA}$ 13.9 / 58%	(2.71 – 3.89) $\text{\AA}$ 2.0 / 64%	12.1	15.9	12.9

b) Cu-Zr system	$(r_0 - r_m)$ $N_{\text{CuCu}} / \varepsilon$	$(r_0 - r_m)$ $N_{\text{CuZr}} / \varepsilon$	$(r_0 - r_m)$ $N_{\text{ZrCu}} / \varepsilon$	$(r_0 - r_m)$ $N_{\text{ZrZr}} / \varepsilon$	N_{Cu}	N_{Zr}	N
$\text{Cu}_{65}\text{Zr}_{35}$ glass $\rho = 0.0637 \text{ \AA}^{-3}$	(2.20 – 3.26) $\text{\AA}$ 7.0	(2.35 – 3.50) $\text{\AA}$ 4.3	(2.35 – 3.50) $\text{\AA}$ 8.0	(2.60 – 3.50) $\text{\AA}$ 5.4	11.3	13.4	12.0
$\text{Cu}_{10}\text{Zr}_7$ crystal $\rho = 0.0609 \text{ \AA}^{-3}$	(2.15 – 3.25) $\text{\AA}$ 4.2 / 40%	(2.35 – 3.51) $\text{\AA}$ 6.6 / 53%	(2.35 – 3.25) $\text{\AA}$ 9.4 / 17%	(2.75 – 3.55) $\text{\AA}$ 4.1 / 24%	10.8	13.5	11.9
Cu_8Zr_3 crystal $\rho = 0.0678 \text{ \AA}^{-3}$	(2.10 – 3.43) $\text{\AA}$ 7.5 / 7%	(2.35 – 3.50) $\text{\AA}$ 4.6 / 7%	(2.35 – 3.50) $\text{\AA}$ 12.3 / 54%	(2.75 – 3.29) $\text{\AA}$ 1.3 / 76% (3.29 – 3.97) $\text{\AA}$ 2.7	12.1	13.6 16.3	12.5 13.2
$\text{Cu}_{51}\text{Zr}_{14}$ crystal $\rho = 0.0705 \text{ \AA}^{-3}$	(2.10 – 3.31) $\text{\AA}$ 7.8 / 11%	(2.35 – 3.43) $\text{\AA}$ 3.9 / 9%	(2.35 – 3.43) $\text{\AA}$ 14.2 / 77%	(2.75 – 3.48) $\text{\AA}$ 0.7 / 87% (3.48 – 4.15) $\text{\AA}$ 1.7	11.7	14.9 16.6	12.4 14.75

Table 5. Fraction of major polyhedra with total fraction larger than 0.5%. The Ni, Cu and Zr columns show the fractions of the polyhedra centred on those particular species.

Polyhedron	Ni _{63.7} Zr _{36.3}			Cu ₆₅ Zr ₃₅		
	Total	Ni	Zr	Total	Cu	Zr
(0, 0, 12, 0)	2.54	2.54	0.00	5.66	5.36	0.30
(0, 0, 12, 3)	0.59	0.02	0.57	0.81	0.11	0.70
(0, 1, 10, 2)	3.28	3.17	0.11	5.07	4.19	0.88
(0, 1, 10, 4)	1.88	0.11	1.77	2.14	0.30	1.84
(0, 1, 10, 5)	1.28	0.01	1.27	1.06	0.06	1.00
(0, 2, 8, 0)	0.52	0.52	0.00	0.14	0.14	0.00
(0, 2, 8, 1)	2.99	2.99	0.00	1.37	1.37	0.00
(0, 2, 8, 2)	4.82	4.82	0.00	4.24	4.18	0.06
(0, 2, 8, 4)	2.39	1.23	1.16	3.82	2.14	1.68
(0, 2, 8, 5)	1.62	0.17	1.45	2.49	0.56	1.93
(0, 2, 8, 6)	1.19	0.02	1.17	0.91	0.08	0.83
(0, 2, 10, 3)	0.58	0.05	0.53	0.71	0.10	0.61
(0, 2, 10, 4)	0.53	0.01	0.52	0.44	0.04	0.40
(0, 3, 6, 3)	2.93	2.93	0.00	1.49	1.47	0.02
(0, 3, 6, 4)	4.19	4.06	0.13	4.14	3.80	0.34
(0, 3, 6, 6)	0.88	0.13	0.75	1.23	0.34	0.89
(0, 4, 4, 4)	1.24	1.24	0.00	0.57	0.56	0.01
(1, 2, 7, 2)	0.84	0.84	0.00	0.59	0.59	0.00

Fig. 1. Experimental total structure factors for (a) $\text{Ni}_{64}\text{Zr}_{36}$ and (b) $\text{Cu}_{65}\text{Zr}_{35}$ metallic glasses measured for different isotopes or with different radiations.

Fig. 2. Partial structure factors for $\text{Ni}_{64}\text{Zr}_{36}$ metallic glass determined by different methods: *thick blue lines* – NDIS on $^{\text{nat}}\text{Ni}$ -, ^{60}Ni -, and ^{62}Ni -containing samples (digitized from the work of Lefebvre et al. [52]); *symbols* – XRD and ND on ^{58}Ni - and ^{60}Ni -containing samples, present work; *thin red lines* – RMC modelling of the six data-sets (XRD, ND and EXAFS data). The corresponding fits are shown in Fig. 3.

Fig. 3. Experimental diffraction and EXAFS data for the $\text{Ni}_{64}\text{Zr}_{36}$ metallic glass and their RMC fits.

Fig. 4. Partial pair distribution functions for $\text{Cu}_{65}\text{Zr}_{35}$ glass obtained by the RMC simulation of the experimental XRD, ND, and Zr K-edge EXAFS data.

Fig. 5. Partial pair distribution functions for $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ metallic glasses obtained by RMC modelling.

Fig. 6. Partial and average coordination numbers for $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ metallic glasses extracted from the final atomic configurations obtained by RMC simulations. (TM = Cu, Ni).

Fig. 7. Bhatia-Thornton number-number $S_{NN}(Q)$ and concentration-concentration $S_{CC}(Q)$ structure factors for $\text{Ni}_{64}\text{Zr}_{36}$ and $\text{Cu}_{65}\text{Zr}_{35}$ metallic glasses.

Fig. 8. Partial pair distribution functions for (a) $\text{Ni}_{64}\text{Zr}_{36}$ and (b) $\text{Cu}_{65}\text{Zr}_{35}$ metallic glasses compared with the partial pair distribution functions for the stable crystalline phases of these alloys.

Fig. 9. Distribution of different types of polyhedra found in the atomic configurations of Ni₆₄Zr₃₆ and Cu₆₅Zr₃₅ metallic glasses obtained by RMC simulations.

Fig. 10. Distribution of different types of polyhedra found in the RMC-simulated atomic configurations of (a) Ni₆₄Zr₃₆ and (b) Cu₆₅Zr₃₅ glasses and MD-simulated atomic configurations for crystalline phases.

Fig. 11. Networks of ideal icosahedra in the RMC model configurations for (a) $\text{Ni}_{64}\text{Zr}_{36}$ and (b) $\text{Cu}_{65}\text{Zr}_{35}$ metallic glasses.