



Local atomic structure of Zr–Cu and Zr–Cu–Al amorphous alloys investigated by EXAFS method

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ARTICLE INFO

Article history:

Received 30 July 2010

Received in revised form

29 September 2010

Accepted 24 October 2010

Available online 4 November 2010

Keywords:

Amorphous materials

Metallic glasses

Atomic scale structure

EXAFS

ABSTRACT

We report on extended X-ray absorption fine structure (EXAFS) study of rapidly quenched Zr–Cu and Zr–Cu–Al glassy alloys. The local atomic order around Zr and Cu atoms was investigated. From the EXAFS data fitting the values of coordination number, interatomic distances and mean square atomic displacement were obtained for wide range of compositions. It was found that icosahedral symmetry rather than that of corresponding crystalline analogs dominates in the local atomic structure of Zr–Cu and Zr–Cu–Al amorphous alloys. Judging from bonding preferences we conclude that addition of Al as an alloying element results in considerable deviation from random mixing behavior observed in binary Zr–Cu alloys.

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1. Introduction

Binary alloys from Zr–Cu system are known to form glassy phase on quenching in a wide range of compositions [1,2]. While glass forming ability (GFA) in binary Zr–Cu is relatively high the addition of Al results in considerable decrease of the critical cooling rate allowing formation of bulk metallic glasses (BMGs) and remarkable increase in strength [2,3]. This effect is attributed to both structural modifications as well as bonding character changes resulting from Al addition [4,5]. Recently, Georgarakis et al. [6] showed that addition of Al strongly modifies the atomic structure of Zr–Cu glasses which deviates from the ideal solution behavior. The structure of Zr–Cu and Zr–Cu–Al glasses was previously studied by means of X-ray diffraction [7–11], extended X-ray absorption fine structure (EXAFS) [12,13] as well as molecular dynamics simulations [4,5,14–16]. The atomic order in these materials is usually described in terms of interconnected icosahedral clusters organized in more extended structures obeying sequence of magic numbers [5,11,17]. In this work the local atomic structure of Zr–Cu–Al amorphous alloys is investigated in detail by means of EXAFS method

[18,19]. The effect of alloy composition on short range order is presented and discussed.

2. Experimental

Master alloys of investigated alloys were obtained by arc-melting of pure elements using multiple remelting to assure homogeneity. Samples in form of ~40 μm thick ribbons were produced from master alloys by rapid quenching of liquid using single-roller melt spinning setup operating in argon atmosphere. The alloy compositions (at.%) used in present study were: Zr₆₇Cu₃₃, Zr₄₀Cu₆₀, Zr₃₆Cu₆₄, Zr₇₀Cu₂₀Al₁₀, Zr₆₀Cu₃₀Al₁₀, Zr₅₀Cu₄₀Al₁₀. The EXAFS experiment was carried out on X1 beamline of HASYLAB (Hamburg, Germany). The measurements were performed in transmission mode at liquid nitrogen temperatures to minimize the thermal disorder. Both Cu and Zr K-edges were investigated using double crystal Si(111) monochromator. The energy calibration was performed using standard Zr on Cu foils. The EXAFS oscillations were extracted from the raw absorption data with ATHENA program [20]. Non-linear fitting was carried out using Viper software [21]. The fits have been made in the 2.5–11 Å⁻¹ range. The FEFF8 code [22] was used for calculation of the photoelectron scattering amplitudes and phases. Tetragonal Zr₂Cu intermetallic compound sample was used to obtain the passive electron amplitude reduction factors S₀². The resulting values of S₀² equal to 0.40 for Cu and 0.44 for Zr were set in all others fits.

3. Results and discussion

Fig. 1 presents the experimental k^3 -weighted $\chi(k)$ functions for Cu and Zr K-edge measured for all investigated alloys. In order to establish the symmetry of local atomic order in investigated sys-

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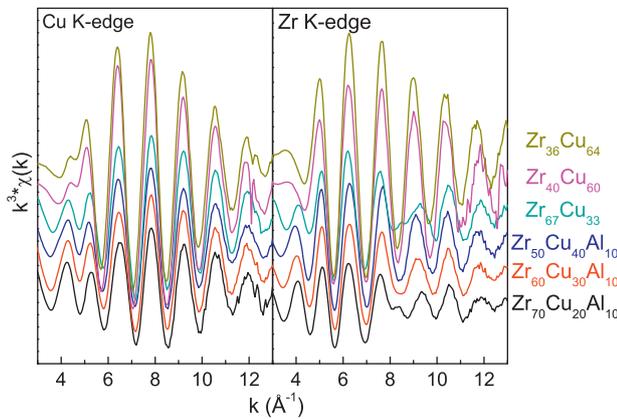


Fig. 1. Experimental k_3 -weighted $\chi(k)$ functions for investigated amorphous alloys measured for Cu (left) and Zr (right) K-edge.

tems we started with comparison of an experimental Cu K-edge EXAFS spectrum for binary $Zr_{67}Cu_{33}$ glass with EXAFS oscillations simulated for two structural models. The first model was a unit cell of tetragonal Zr_2Cu compound (crystalline polymorph of $Zr_{67}Cu_{33}$ alloy) while the second one was Cu-centered icosahedral cluster with stoichiometry Zr_8Cu_5 . Fig. 2 shows comparison between the experimentally measured EXAFS oscillations and the two simulated curves. While in case of tetragonal Zr_2Cu compound the experimental and the calculated oscillations are in antiphase the theoretical curve corresponding to the icosahedral cluster matches the experiment almost perfectly. As similar observation was made in case of the other systems investigated in this work we conclude that the local atomic symmetry of Zr–Cu and Zr–Cu–Al amorphous alloys has mainly icosahedral character and does not resemble the symmetry of their crystalline analogs. This conclusion is in agreement

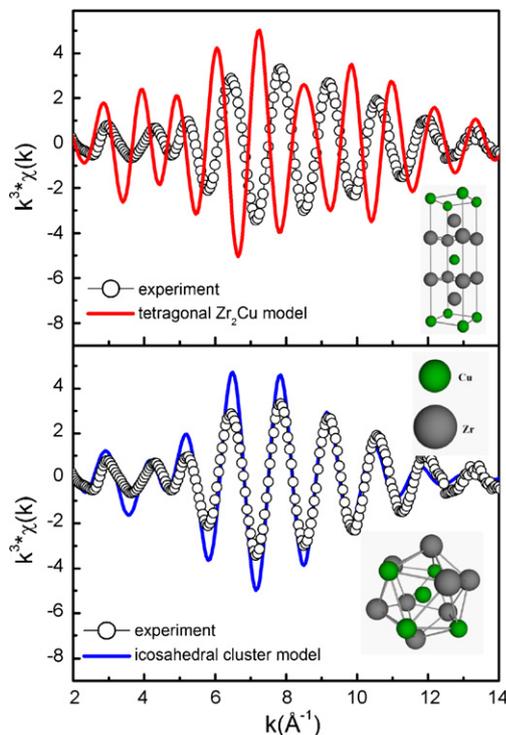


Fig. 2. Comparison between the experimental Cu K-edge k_3 -weighted $\chi(k)$ function measured for $Zr_{67}Cu_{33}$ amorphous alloy and the results of calculation for two models of local structure: unit cell of tetragonal Zr_2Cu compound (top) and Cu-centered icosahedral Zr_8Cu_5 cluster (bottom).

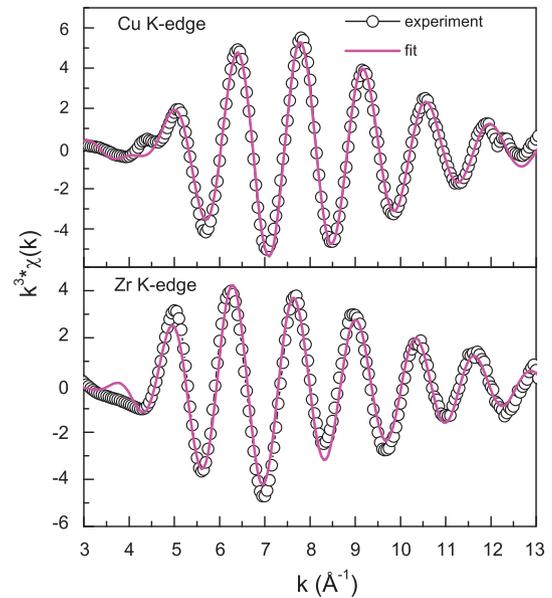


Fig. 3. Cu (top) and Zr (bottom) K-edge EXAFS fitting for $Zr_{36}Cu_{64}$ metallic glass.

with previous EXAFS [11,23–26], and *ab initio* molecular dynamics studies [4,14,15,17] providing evidences of icosahedral structural motifs in Zr–Cu and Zr–Cu–Al glasses. The icosahedral cluster was used as initial structural model for EXAFS fitting. Fig. 3 shows the results of k -space fitting of Cu and Zr absorption edge EXAFS oscillations for $Zr_{36}Cu_{64}$ metallic glass. The fitting carried out for all of investigated compositions allowed determination of coordination numbers, interatomic distances and means square atomic displacement values for Cu and Zr as central atom independently.

The bonding preferences of different atomic species can be determined from their partial coordination numbers. Table 1 summarizes the values obtained from EXAFS fitting for partial coordination numbers of Zr and Cu atoms. The most straightforward way of illustrating the bonding preferences is looking at the deviation from randomness in atomic arrangement. For this purpose we introduce a quantity N_{RAND} defined as a partial coordination number obtained theoretically assuming dense packing of atoms around central (absorbing) atom [27] and fully random distribution of different atomic species in its first coordination shell. N_{RAND} can be interpreted as an upper limit for partial coordination number due to additional disorder and resulting free volume present in real systems. Here we propose a parameter $\Delta N = (N_{EXAFS} - N_{RAND})/N_{RAND}$ (where N_{EXAFS} stands for partial coordination number from EXAFS fitting) as a quantitative measure of deviation from randomness in atomic arrangement. The positive value of ΔN indicates excess and the negative ΔN indicates a deficit of a given kind of atoms creating bonds with the absorbing atom. Fig. 4 shows values of ΔN plotted as a function of Zr to Cu content ratio for binary Zr–Cu and ternary Zr–Cu–Al with 10% Al addition. In case of binary Zr–Cu alloys the values of ΔN are close to zero for all atomic pairs indicating nearly fully random mixing. On the other hand for the Al bearing

Table 1
Partial coordination numbers in Zr–Cu and Zr–Cu–Al amorphous alloys (± 0.5).

Alloy	N_{Cu-Cu} [Å]	N_{Zr-Zr}	N_{Zr-Cu}	N_{Cu-Zr}	N_{Cu-Al}	N_{Zr-Al}
$Zr_{67}Cu_{33}$	2.6	10.2	4.0	8.6	–	–
$Zr_{40}Cu_{60}$	6.2	6.4	8.8	5.7	–	–
$Zr_{36}Cu_{64}$	6.7	4.1	11.8	5.3	–	–
$Zr_{70}Cu_{20}Al_{10}$	3.3	11.1	0.4	5.1	2.4	1.9
$Zr_{60}Cu_{30}Al_{10}$	3.4	10.0	1.9	5.6	2.5	2.5
$Zr_{50}Cu_{40}Al_{10}$	3.7	8.8	2.8	5.8	2.2	3.2

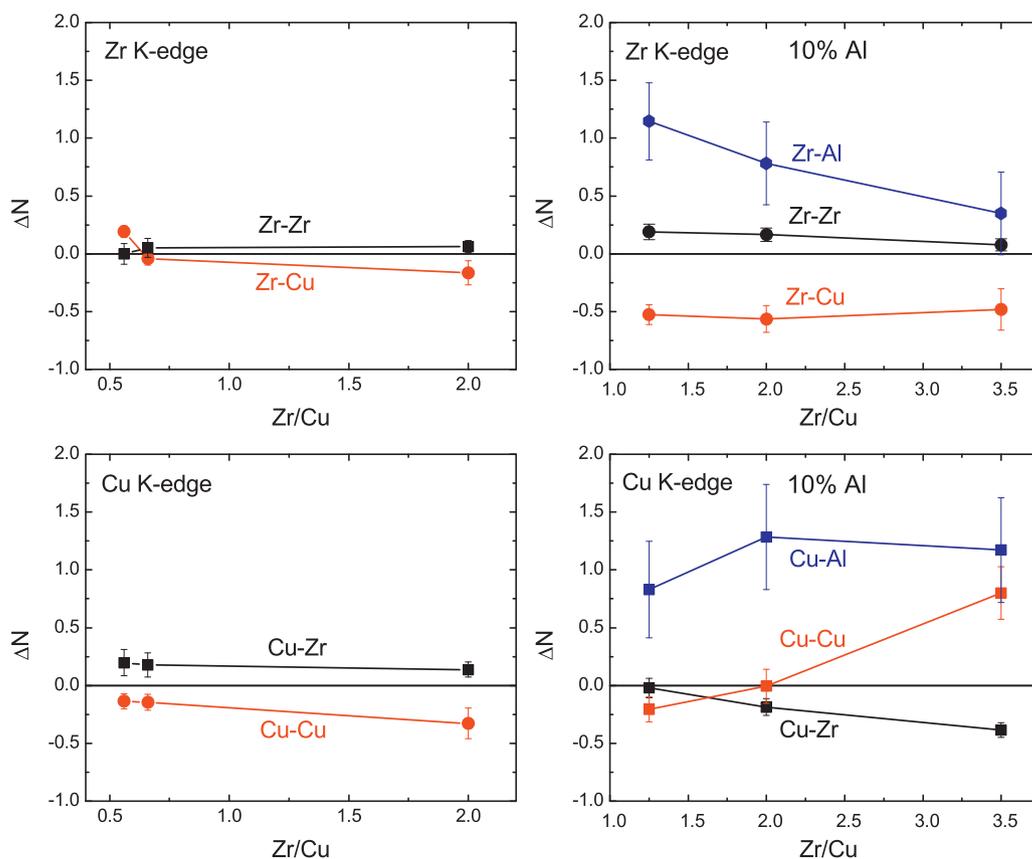


Fig. 4. ΔN plotted as a function of Zr to Cu content ratio for binary Zr–Cu (left) and ternary Zr–Cu–Al with 10% Al addition (right).

glasses a considerable deviation from randomness is observed [6]. For those alloys excess Zr–Al and Cu–Al bonds are formed at the expense of Zr–Cu pairs. The effect of excess Zr–Al bonds can be explained by strongly negative enthalpy of mixing ΔH_{mix} between Zr and Al equal to -44 kJ/mol compared to -23 kJ/mol in Zr–Cu and -1 kJ/mol in Cu–Al systems however the presence of additional Cu–Al pairs can not be justified by this simple argumentation. According to *ab initio* studies [5] addition of Al atoms results in complex rearrangement in the icosahedral clusters structure and their interconnections introducing covalent-like bondings contributing to enhanced glass forming ability and strengthening of the alloy. Besides changes in bonding preferences those structural rearrangements should affect also the interatomic distances.

The interatomic distances resulting from EXAFS fitting are listed in Table 2. Comparing these values to the sum of Goldschmidt radii ($R_{Zr} = 160$ pm, $R_{Cu} = 128$ pm, $R_{Al} = 143$ pm) one can see that Zr–Zr, Cu–Cu and Zr–Al bond distances are slightly shortened by 1–3%, Zr–Cu bonds are shortened by about 8% while Cu–Al distances are considerably elongated by approximately 20%. Also a small ($\sim 3\%$) decrease in distance between Zr and Cu atoms on addition of Al can be observed. The observed elongation of Cu–Al bonds is in contrary to previously published theoretical results for $Zr_{47}Cu_{46}Al_7$ glass

where about 6% decrease of Cu–Al distances was reported [4]. This discrepancy might be due to the different stoichiometry of alloys studied and might reflect high compositional sensitivity of the local atomic structure.

During EXAFS fitting process the distribution of interatomic distances was assumed to have gaussian character. The mean square atomic displacement σ^2 (Debye–Waller factor) was evaluated parallel with coordination numbers and interatomic distances. We have found that values of σ^2 for each of the atomic pairs do not vary significantly with alloy composition in Zr–Cu and Zr–Cu–Al alloys. The average values of σ^2 for binary and ternary alloys are shown in Table 3. While the uncertainty of σ^2 is relatively large (± 0.005 \AA^2) one can notice that addition of Al results in increase of σ^2 for Cu–Cu pairs and that the distribution of distances of newly formed, energetically favorable Zr–Al bonds is more narrow than in case of other bond types.

While a satisfactory explanation of the above structural data requires more detailed theoretical study involving *ab initio* and molecular dynamics simulations we have demonstrated that Al addition in Zr–Cu binary system results in considerable structural rearrangement. The rearrangement involves both the bonding preferences as well as interatomic distances and their distribu-

Table 2
Interatomic distances in Zr–Cu and Zr–Cu–Al amorphous alloys (± 0.02 \AA).

Alloy	R_{Cu-Cu} [\AA]	R_{Zr-Zr} [\AA]	R_{Zr-Cu} [\AA]	R_{Cu-Zr} [\AA]	R_{Cu-Al} [\AA]	R_{Zr-Al} [\AA]
Zr ₆₇ Cu ₃₃	2.51	3.12	2.70	2.72	–	–
Zr ₄₀ Cu ₆₀	2.51	3.14	2.71	2.77	–	–
Zr ₃₆ Cu ₆₄	2.51	3.14	2.72	2.77	–	–
Zr ₇₀ Cu ₂₀ Al ₁₀	2.60	3.05	2.60	2.68	3.25	2.88
Zr ₆₀ Cu ₃₀ Al ₁₀	2.54	3.11	2.64	2.68	3.25	2.94
Zr ₅₀ Cu ₄₀ Al ₁₀	2.54	3.15	2.66	2.68	3.31	2.99

Table 3
Mean square atomic displacement in Zr–Cu and Zr–Cu–Al amorphous alloys (± 0.005 [Å²]).

Alloy	$\sigma_{\text{Cu–Cu}}^2$ [Å ²]	$\sigma_{\text{Zr–Zr}}^2$ [Å ²]	$\sigma_{\text{Zr–Cu}}^2$ [Å ²]	$\sigma_{\text{Cu–Zr}}^2$ [Å ²]	$\sigma_{\text{Cu–Al}}^2$ [Å ²]	$\sigma_{\text{Zr–Al}}^2$ [Å ²]
Zr ₆₇ Cu ₃₃	0.006	0.018	0.014	0.015	–	–
Zr ₄₀ Cu ₆₀	0.009	0.018	0.015	0.014	–	–
Zr ₃₆ Cu ₆₄	0.009	0.015	0.014	0.014	–	–
Zr ₇₀ Cu ₂₀ Al ₁₀	0.025	0.020	0.010	0.009	0.012	0.006
Zr ₆₀ Cu ₃₀ Al ₁₀	0.018	0.022	0.009	0.010	0.015	0.005
Zr ₅₀ Cu ₄₀ Al ₁₀	0.017	0.022	0.009	0.011	0.015	0.005

tion. These atomic-level structural modifications underlay changes in macroscopic properties resulting from Al addition in Zr–Cu alloys such as enhanced GFA and increased strength. We note that the present results support the recent findings concerning deviation from ideal solution behavior on Al addition in Zr–Cu system deduced from pair distribution functions calculated from X-ray diffraction spectra.

4. Conclusions

The local atomic order in Zr–Cu and Zr–Cu–Al amorphous alloys was investigated by means of EXAFS technique for Zr and Cu K-edge. The comparison between the experimental and calculated EXAFS signal indicates that icosahedral symmetry rather than that of corresponding crystalline analogs dominates investigated glassy systems. We have found that the addition of Al results in considerable structural rearrangement involving bonding preferences, interatomic distances and structural disorder. Basing on a quantitative analysis of Zr and Cu bonding preferences we demonstrate that addition of Al as an alloying element results in considerable deviation from random mixing behavior while almost ideally random mixing takes place in binary Zr–Cu alloys. Most of the bond lengths we found to be shortened by several percent while Cu–Al distances are elongated by about 20% with respect to the sum of their Goldschmidt radii.

The random mixing behavior in all investigated Zr–Cu alloys having different GFA [6] might indicate that bonding preferences alone are not enough to predict their GFA. In forthcoming article we will discuss the correlation between the details of local atomic structure of Zr–Cu and Zr–Cu–Al amorphous alloys and their GFA and thermal properties.

Acknowledgments

We kindly acknowledge Dr. Adam Webb from X1 beamline at HASYLAB for his professional assistance during EXAFS measurements.

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