Structural behavior of Cu$_x$Zr$_{100-x}$ metallic glass ($x = 35–70$)

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Received 12 January 2007; received in revised form 25 June 2007
Available online 27 September 2007

Abstract

The structural behavior of rapidly quenched amorphous Cu$_x$Zr$_{100-x}$ alloys was investigated in a wide composition range between 35 and 70 at.% Cu content. High-energy X-ray diffraction patterns, atomic pair correlation functions, mass density and the thermal stability behavior of the alloys all exhibit monotonic changes with composition. Partial pair correlation functions were determined assuming that they remain unchanged in the different amorphous Cu$_x$Zr$_{100-x}$ alloys and only the weight fractions become altered with changes in composition. The experimental results can be well described by a solid solution-like replacement of Cu and Zr atoms in the whole composition range. No indications are observed neither for the existence of a special atomic arrangement at a particular chemical composition nor for the presence of phase separation in the glassy state of the binary Cu–Zr system.

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PACS: 61.43.Dq; 61.46.+w; 64.70.Nd

Keywords: Amorphous metals, metallic glasses

1. Introduction

In the last 15 years new bulk metallic glass (BMG) forming alloys were developed in Zr-, Lu-, Ti-, Ni-, Pd-, Mg-, Al-, Fe-, Cu-based systems [1,2]. These multi-component alloys can be obtained in a glassy state in mm or cm-dimension by copper mold casting due to low critical cooling rates of $10^2$–$10^6$ K/s. The preparation of BMG’s enables now to explore the exceptional mechanical properties of metallic glasses [3]. The glass forming ability (GFA) is related to several thermodynamic and kinetic properties like a high reduced glass transition temperature $T_{rg}$ (ratio of the glass transition temperature $T_g$ to the liquidus temperature $T_l$), strong negative enthalpy of mixing of the constituents, and low enthalpy differences between undercooled liquid and competing crystalline phases [1,4]. From the point of view of the atomic structure, size effects and special clusters arrangements are discussed to stabilize the under-cooled liquid [5–8].

Recently, BMGs could also be prepared for some particular compositions in the binary Cu–Zr system. Glassy samples of 2 mm thickness were reported for the alloys Cu$_{66}$Zr$_{34}$ [9], Cu$_{65.5}$Zr$_{34.5}$ [10], Cu$_{50}$Zr$_{50}$[11], and Cu$_{46}$Zr$_{55}$ [12]. Furthermore extraordinary plasticity was observed for binary and ternary Cu-based BMG’s [13–17]. These findings renewed the interest in structural investigations of the Cu–Zr system. It is well known from earlier work that Cu–Zr glass can be prepared in a wide composition range [18–21]. Partial atomic pair correlation functions of amorphous Cu–Zr alloys were determined by anomalous X-ray scattering [22,23] but the accuracy suffers from the weak energy dependence of the atomic form amplitudes. Phase separation into two amorphous phases was reported to exist between $x = 50$ and 65 at.% Cu [24–26]. Other results [27,28] are in contradiction to the assumption of phase separation in amorphous Cu–Zr alloys. Recently, the presence of icosahedral clusters in bulk glass forming

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Cu$_{66}$Zr$_{34}$ was concluded from the analysis of extended X-ray absorption fine structure (EXAFS) measurements [29]. The aim of this work was to reinvestigate the structural behavior of amorphous Cu–Zr alloys. The analysis of the concentration dependence of the short-range order should give evidence whether or not special clusters exist at compositions with high GFA.

2. Experimental

Pre-alloyed ingots were prepared by arc-melting elemental Cu and Zr with a purity of 99.9% or better in a Ti-gettered argon atmosphere. For reaching homogeneity, the samples were remelted several times. From these pre-alloys, 3 mm wide and 25 μm thick amorphous ribbons were prepared by means of rapid quenching from the melt using a single-roller melt-spinner under argon atmosphere. Chemical compositions were analyzed by the titration technique. The amorphous structure was checked by X-ray diffraction (XRD) using a Bruker D8 diffractometer with Cu Kα radiation. Parallel beam geometry was applied for a precise determination of the position of the first maximum of the XRD patterns. To analyze the short- and medium-range order, high-energy X-ray diffraction experiments were conducted at the synchrotron beam-line BW5 (HASYLAB Hamburg, wavelength of $\lambda = 0.01250$ nm) at room temperature. Differential scanning calorimetry (DSC) experiments were performed employing a Netzsch DSC 404 calorimeter using a heating rate of 20 K/min. The mass density was determined at room temperature by the Archimedes principle by weighing samples in air and in dodecane (C$_{12}$H$_{26}$).

3. Experimental results

The amorphous state of the as-quenched ribbons was confirmed for all compositions by the presence of only diffuse maxima in the XRD pattern, as well as by the crystallization behavior. The values of the analysis of the chemical composition of the ribbons are given in Table 1. There is an overall agreement with the nominal values.

The thermal behavior of the amorphous Cu–Zr alloys is shown in Fig. 1 by their DSC traces recorded upon constant-rate heating. The glass transition and the crystallization are observable by the respective endothermic and exothermic heat flow events. The endothermic peak at $T = 1005$ K for $x = 40–55$ at.% Cu corresponds to the transformation into the high temperature phase CuZr in accordance with the phase diagram [30]. The composition dependence of the glass transition temperature $T_g$ and the crystallization temperature $T_x$ is shown in Fig. 2. Both temperatures monotonically increase with increasing Cu-content in accordance with [19,20]. The shape of the first DSC event remains unchanged for the different composition. The large supercooled liquid region as defined by $T_x - T_g$ as well as the relatively high values of the reduced glass transition temperature $T_{rg} (T_{rg} = T_g / T_l$ where $T_l$ is the liquidus temperature) point to high glass forming ability of binary Cu–Zr alloys (Table 1).

Fig. 3 shows the structure factor $S(q)$ of the amorphous Cu$_{100-x}$Zr$_x$ alloys in the as-prepared state ($q = 4\pi \sin \theta / \lambda$ is the absolute value of the scattering vector). The $S(q)$ curves were obtained from the measured diffraction curves by applying the usual corrections for background, absorption, multiple scattering, Compton scattering and normalization procedure to extract the elastic scattering intensity in abso-

Table 1

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cu (at.%)</th>
<th>Zr (at.%)</th>
<th>$\sigma$ (g cm$^{-3}$)</th>
<th>$\rho_0$ (nm$^{-3}$)</th>
<th>$T_g$ (K)</th>
<th>$T_x$ (K)</th>
<th>$T_g/T_l$</th>
<th>$w_{CuCo}$</th>
<th>$w_{CuZr}$</th>
<th>$w_{ZrZr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{66}$Zr$</em>{34}$</td>
<td>34.77</td>
<td>65.23</td>
<td>7.01</td>
<td>51.2</td>
<td>616</td>
<td>657</td>
<td>0.51</td>
<td>0.079</td>
<td>0.202</td>
<td>0.517</td>
</tr>
<tr>
<td>Cu$<em>{60}$Zr$</em>{40}$</td>
<td>39.88</td>
<td>60.12</td>
<td>7.17</td>
<td>53.9</td>
<td>634</td>
<td>679</td>
<td>0.53</td>
<td>0.106</td>
<td>0.220</td>
<td>0.454</td>
</tr>
<tr>
<td>Cu$<em>{55}$Zr$</em>{45}$</td>
<td>44.94</td>
<td>55.05</td>
<td>7.26</td>
<td>55.5</td>
<td>648</td>
<td>692</td>
<td>0.56</td>
<td>0.139</td>
<td>0.233</td>
<td>0.394</td>
</tr>
<tr>
<td>Cu$<em>{50}$Zr$</em>{50}$</td>
<td>49.86</td>
<td>50.14</td>
<td>7.33</td>
<td>57.1</td>
<td>666</td>
<td>710</td>
<td>0.58</td>
<td>0.177</td>
<td>0.243</td>
<td>0.336</td>
</tr>
<tr>
<td>Cu$<em>{45}$Zr$</em>{55}$</td>
<td>54.14</td>
<td>44.86</td>
<td>7.47</td>
<td>59.2</td>
<td>682</td>
<td>724</td>
<td>0.60</td>
<td>0.221</td>
<td>0.249</td>
<td>0.281</td>
</tr>
<tr>
<td>Cu$<em>{40}$Zr$</em>{60}$</td>
<td>58.92</td>
<td>40.08</td>
<td>7.53</td>
<td>60.8</td>
<td>711</td>
<td>750</td>
<td>0.63</td>
<td>0.271</td>
<td>0.250</td>
<td>0.230</td>
</tr>
<tr>
<td>Cu$<em>{35}$Zr$</em>{65}$</td>
<td>63.92</td>
<td>35.08</td>
<td>7.75</td>
<td>63.7</td>
<td>737</td>
<td>776</td>
<td>0.66</td>
<td>0.329</td>
<td>0.244</td>
<td>0.182</td>
</tr>
<tr>
<td>Cu$<em>{30}$Zr$</em>{70}$</td>
<td>69.93</td>
<td>30.07</td>
<td>7.86</td>
<td>65.9</td>
<td>–</td>
<td>770</td>
<td>–</td>
<td>0.395</td>
<td>0.233</td>
<td>0.138</td>
</tr>
</tbody>
</table>
The shape of the $S(q)$ curves corresponds to that of many metallic glasses and also to Cu–Zr alloys reported in earlier papers [21–23]. When looking in more detail, systematic changes in $S(q)$ with composition are visible. The peak positions become shifted and the shape of the second and third maxima are altered as a function of the Cu concentration $x$. The composition dependence of the position of the first maximum of the structure factor $q_1$ is shown in Fig. 4. The value of $q_1$ shifts linearly to higher $q$-values with increasing Cu content in a good agreement with earlier reported values [20]. In contrast to crystalline material the position of $q_1$ is not directly related to an inter-atomic distance and the linear shift does not necessarily indicate altered nearest neighbor distances as can be seen by the atomic pair correlation functions.

Fig. 5 shows the change of the structure factor $\Delta S/\Delta x$ versus for the different compositions. The general behavior...
of the change in the structure factor is similar over the whole composition range. There is no indication for any anomaly of $\Delta S/\Delta x$ versus composition. The behavior points to a continuous structure development over the whole composition range rather than the presence of a special atomic configuration at certain compositions. The main part of the observable changes in the total structure factor comes from the variation of the weights $w_{ij}$ (Table 1) of the individual partial structure factors $S_{ij}$ with composition [31]:

$$S(q) - 1 = \sum_i \sum_j w_{ij} \cdot (S_{ij} - 1)$$

with $w_{ij} = c_i \cdot c_j \cdot f_i \cdot f_j \left(\sum_i c_i \cdot f_i\right)^2$, (1)

where $c_i$ is the concentration, and $f_i$ is the atomic form amplitude of the $i$-atom.

From the structure factor $S(q)$ the atomic pair correlation functions $g(r) = \rho(r)/\rho_0$ were calculated by the Fourier transform of $S(q)$ between $0 \leq q \leq 180$ nm$^{-1}$ according to [31]

$$4\pi \cdot r \cdot \rho_0 \cdot (g(r) - 1) = \frac{2}{\pi} \int (S(q) - 1) \cdot q \cdot \sin(q \cdot r) \cdot dq,$$

where $\rho(r)$ is the atomic pair density distribution function and $\rho_0$ is the mean atomic density ($\rho_0 = N_1 \sigma/m$; $\sigma$, mass density; $m$, average atomic mass; $N_1$, Loschmidt constant). Fig. 6 shows the calculated $g(r)$ curves. The atomic pair correlation functions of the Cu$_4$Zr$_{100-x}$ glasses exhibit systematic changes with composition. For all $g(r)$ curves, two components of the first maximum are visible. The positions and the integrals of the two components of the first maximum in $g(r)$ were estimated by a fit of two Gaussian curves to the radial distribution function $4\pi r^2 p(r)$ between 0.24 and 0.35 nm as shown in the inset of Fig. 6. The positions of the two maxima in the first neighborhood are nearly constant (Table 2) and can be mainly attributed to the zirconium–copper ($r_{Zr-Cu}$) and to the zirconium–zirconium ($r_{Zr-Zr}$) distances. The Cu–Cu contributions are not resolved in the total $g(r)$ curve. Therefore, the integration over the total radial atomic pair density function gives only a weighted, averaged nearest neighbor number $N^1$ in the interval between $r_1$ and $r_2$

$$N^1 = \int_{r_1}^{r_2} 4\pi r^2 \cdot \rho(r).$$

The obtained values (areas) for the two submaxima of the first neighborhood $N^1_{Zr-Cu}$ and $N^1_{Zr-Zr}$ are given in Table 2. These numbers exhibit a monotonic behavior with composition $x$ pointing to a continuous substitution of Zr by Cu atoms. The total nearest neighbor number $N^1$ (Table 2) increases with the Cu content in accordance with the behavior of the mean atomic density $\rho_0$ (Table 1). The mass density of crystalline Cu–Zr compounds CuZr$_2$, CuZr, Cu$_{10}$Zr$_{7}$, and Cu$_2$Zr$_3$ [31] is about 1% higher than that of the corresponding amorphous alloys.

### Table 2

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$q_1$ (nm$^{-1}$)</th>
<th>$r_{Cu-Zr}$ (nm)</th>
<th>$r_{Zr-Zr}$ (nm)</th>
<th>$N_{Zr-Cu}$</th>
<th>$N_{Zr-Zr}$</th>
<th>$N^1$</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{12}$Zr$</em>{88}$</td>
<td>25.79</td>
<td>0.2744</td>
<td>0.3114</td>
<td>1.9</td>
<td>10.5</td>
<td>12.4</td>
<td>0.003</td>
</tr>
<tr>
<td>Cu$<em>{10}$Zr$</em>{90}$</td>
<td>26.20</td>
<td>0.2754</td>
<td>0.3110</td>
<td>7.0</td>
<td>5.2</td>
<td>13.1</td>
<td>0.003</td>
</tr>
<tr>
<td>Cu$<em>{9}$Zr$</em>{91}$</td>
<td>26.52</td>
<td>0.2739</td>
<td>0.3111</td>
<td>3.7</td>
<td>7.9</td>
<td>13.1</td>
<td>0.003</td>
</tr>
<tr>
<td>Cu$<em>{8}$Zr$</em>{92}$</td>
<td>26.98</td>
<td>0.2754</td>
<td>0.3111</td>
<td>4.2</td>
<td>7.9</td>
<td>13.1</td>
<td>0.003</td>
</tr>
<tr>
<td>Cu$<em>{7}$Zr$</em>{93}$</td>
<td>27.34</td>
<td>0.2733</td>
<td>0.3123</td>
<td>5.2</td>
<td>7.9</td>
<td>13.1</td>
<td>0.003</td>
</tr>
<tr>
<td>Cu$<em>{6}$Zr$</em>{94}$</td>
<td>27.86</td>
<td>0.2733</td>
<td>0.3135</td>
<td>5.2</td>
<td>7.9</td>
<td>13.1</td>
<td>0.003</td>
</tr>
<tr>
<td>Cu$<em>{5}$Zr$</em>{95}$</td>
<td>28.22</td>
<td>0.2733</td>
<td>0.3123</td>
<td>8.0</td>
<td>5.2</td>
<td>13.2</td>
<td>0.003</td>
</tr>
<tr>
<td>Cu$<em>{4}$Zr$</em>{96}$</td>
<td>28.63</td>
<td>0.2731</td>
<td>0.3114</td>
<td>10.1</td>
<td>5.2</td>
<td>13.2</td>
<td>0.003</td>
</tr>
</tbody>
</table>

### 4. Discussion

The composition dependence of the parameters of the structure factor, as well as of the atomic pair correlation function points to a solid solution-like behavior of the amorphous structure. In the case of phase separation, the change of the position of the first maximum with composition (Fig. 5) should lead to an additional broadening of the first diffuse maximum. The extreme case of a splitting into two diffuse maxima as reported for Cu–Zr films in [24] is obviously not present. Fig. 7 shows the full widths at half maximum (FWHM) determined by a fit of a Lorentz function to the first maximum of $S(q)$. A continuous dependence of the width versus composition is observed with a maximum at about 55 at.% Cu. The variation of FWHM...
is caused by the changes in the weights of the partial structure factors $S_{ij}$, which have their first maximum at different positions [22, 23]. Between 50 < $x$ < 60 all the three partial structure factors contribute strongly to $S(q)$. For $x$ < 50, the main contributions come from Zr–Zr and Cu–Zr pairs, and for $x$ > 60 from Cu–Zr and Cu–Cu pairs, respectively (Table 1). In a first approximation the structure factor of an alloy within the miscibility gap should be the weighted sum of the values at the corresponding phase boundaries. Assuming a miscibility gap between 50 and 65 at.% Cu as reported in [16], the structure factor for Cu$_{55}$Zr$_{45}$ was calculated according to the lever rule by

$$S_x = \frac{2}{3} S_{50} + \frac{1}{3} S_{65},$$

and for Cu$_{60}$Zr$_{40}$ by

$$S_x = \frac{1}{3} S_{50} + \frac{2}{3} S_{65},$$

respectively. The FWHM values of these calculated sum curves are also given in Fig. 7. The widths of the calculated sum curves are significantly larger than the experimentally determined values of the corresponding alloys. The behavior of the width is therefore in contradiction to the existence of a miscibility gap between 50 and 65 at.% Cu in the glassy Cu–Zr alloys.

The observed systematic changes in the structure factor as well as in the atomic pair correlation function are in the case of solid solution behavior to a large extend related to the changes in the weights $w_{ij}$ with composition (Table 1). It is not possible to determine the exact partial coordination number $N_{ij}$ from the total atomic pair correlation function $g(r)$ due to the non-resolved superposition of the pair-wise contributions. But the three partial pair correlation functions can be extracted from the seven experimental total functions $g(r)$ by solving the linear equation system with the constraint of the least square error sum:

$$g_x(r) - \sum_i \sum_j w_{ij} \cdot g_{ij}(r) \rightarrow \min, \quad x = 35, \ldots, 70. \quad (4)$$

This procedure is based on the assumption that the partial functions do not change with composition similar to an isomorphous substitution. This is justified by the behavior of the changes of structure factor with composition at least as a first approximation.

Fig. 8 shows the calculated partial atomic pair correlation functions $g_{\text{CuCu}}$, $g_{\text{CuZr}}$, and $g_{\text{ZrZr}}$. The position of the first maximum or the nearest neighbor distances $r_{\text{Cu-Cu}} = 0.248$ nm, $r_{\text{Cu-Zr}} = 0.272$ nm, and $r_{\text{Zr-Zr}} = 0.312$ nm are in a general agreement with the data given in [22, 23]. The Cu–Cu distance $r = 0.248$ nm corresponds to the atomic diameter. The direct Cu–Cu contact present in amorphous Cu–Zr alloys deviates from the Cu environment of some of the crystalline counterparts pointing to differences in short-range order, e.g. in crystalline CuZr$_2$ the Cu atoms are not nearest neighbors at all, and in the bcc CuZr phase, the smallest Cu–Cu distance is equal to the Cu–Zr distance [32]. From the partial pair correlation function $g_{ij}$ the partial nearest neighbor numbers $N_{ij}$ can be calculated by the integration over of the first maximum analogous to Eq. (3). Fig. 9 shows the composition dependence of the partial nearest neighbor numbers. The calculated values $N_{ij}$ are proportional to the corresponding element concentration as expected for a solid solution behavior.

To check the validity of the assumption of unchanged partial pair correlation functions, the total pair correlation functions were recalculated by the weighted sum of the partial functions $g(r) = \sum_i \sum_j w_{ij} \cdot g_{ij}$. Fig. 10 compares the calculations with the experimental curves for the two boundary compositions Cu$_{55}$Zr$_{65}$ and Cu$_{70}$Zr$_{30}$. The difference curve $\Delta g = g_{\text{mea}} - g_{\text{calc}}$ is also shown for the Cu$_{70}$Zr$_{30}$ alloy. For all curves and in the whole composition range, a
good agreement is observed. This is also expressed by low mean square root values \( \chi \)
\[
\chi^2 = \frac{\sum [g(r_k) - \sum w_{ij} g_{ij}(r_k)]^2}{\sum [g(r_k)]^2},
\]
given in Table 2. These results demonstrate that the partial \( g_{ij} \) are not or only very weakly dependent on the chemical composition between 35 and 70 at.% Cu. This is of course valid for the partial structure factors \( S_{ij} \) as well. The continuous variation with composition also means that there are no particular structural features for the Cu–Zr compositions having high glass forming ability.

The solid solution behavior of the structure of glassy Cu–Zr is also supported by the composition dependence of the mass density \( \sigma \). Fig. 11 shows the average mean atomic volume \( \bar{V} = m/N_L \sigma \) as a function of the Cu concentration \( x \). The linear relationship with concentration \( x \) is in agreement with the prediction of the Midema model [33]. The model is based on the fact that alloy formation is not only accompanied by an enthalpy change but also by a change of specific volume. The calculations by the Midema model are also given in Fig. 11 by the dashed line for the disordered system, and by the dotted–dashed line for the ordered systems. The disordered case seems to be in a better agreement with the experimental data.

Because it was no special behavior observed in the composition dependence of the structure, the high GFA of the binary Cu–Zr alloys is probably mainly determined by the thermodynamic properties of the system. Shao [34] could successfully model the glass transition by a second order phase transition. The composition dependence of the glass transition temperature \( T_g \) agrees well with experimental values of glassy Cu–Zr by modeling the liquid as a solution phase. By the CALPHAD approach also the stability of the glassy phase can be calculated in comparison with the competing crystalline phases [4,35]. The thermodynamic description of the Cu–Zr liquid by the associate model gives an additional contribution for the under-cooled liquid. The lowest driving force for crystallization is calculated for compositions around 60 at.% Cu [35] which is in a
general agreement with the glass forming composition range. However, the strong variation of the GFA within a very narrow composition ranges as reported in [10] requires further investigations.

5. Conclusions

The structural and thermal stability behavior of rapidly quenched Cu–Zr amorphous alloys was reinvestigated in a wide composition range between 35 and 70 at.% Cu. High-energy X-ray diffraction patterns, atomic pair correlation functions, and the calorimetric data exhibit monotonic changes with composition. Partial pair correlation functions could be determined assuming them to stay unchanged and the weight factors only become altered in the different amorphous Cu$_x$Zr$_{100-x}$ alloys. The experimental results are well described by a solid solution-like replacement of Cu and Zr atoms in the whole composition range. No indications are observed that would support the existence of special structure or the presence of phase separation in the glassy state of rapidly quenched Cu–Zr alloys. High glass forming ability of Cu–Zr alloys is related to composition around the deep eutectics which is expressed by high values of reduced glass transition temperature $T_{rg} > 0.55$ for Cu-content between 45 and 65 at.%.

Acknowledgments

HASYLAB is gratefully acknowledged for the support during synchrotron beam time. The authors thank J. Das, M. Frey, K.B. Kim, S. Kuszinski, A. Oswald, and B. Opitz for technical assistance and stimulating discussions.

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