Changes in short-range order of Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ and Zr$_{55}$Cu$_{20}$Al$_{10}$Ni$_{10}$Ti$_{5}$ BMGs upon annealing

Mihai Stoica$^{a,*}$, Nele Van Steenberge$^{b,1}$, Jozef Bednarčík$^{c}$, Norbert Mattern$^{a}$, Hermann Franz$^{c}$, Jürgen Eckert$^{a,2}$

$^a$ IFW Dresden, Institute for Complex Materials, Helmholtzstr. 20, D-01069 Dresden, Germany
$^b$ Departament de Física, Universitat Autònoma de Barcelona, 08913 Bellaterra, Spain
$^c$ HASYLAB at Deutsches Elektronen-Synchrotron (DESY), Notkestr. 85, D-22607 Hamburg, Germany

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**A B S T R A C T**

The need for a fundamental understanding of the flow in metallic glasses has motivated a variety of experimental investigations involving temperature and strain-rate sensitivity tests and assessing the dependence of flow on microstructure and heat treatment. In order to elucidate the deformation mechanism and to increase the ductility of BMGs, the local variations in structure and/or composition play an important role. Such kind of structural modification can be induced by annealing at temperatures slightly below the glass transition temperature $T_g$. The present work deals with two well-known Zr-based BMGs: Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ and Zr$_{55}$Cu$_{20}$Al$_{10}$Ni$_{10}$Ti$_{5}$. Both BMGs show increased ductility after annealing, but the microstructural modifications are different.

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1. Introduction

The absence of long-range order in bulk metallic glasses (BMGs) offers them unique physical, chemical and mechanical properties compared to conventional metallic materials, making them a promising class of engineering materials. In particular, their exceptionally high yield strength gives them potential for structural applications [1]. The need for a fundamental understanding of the flow in metallic glasses has motivated a variety of experimental investigations involving temperature and strain-rate sensitivity tests and assessing the dependence of flow on microstructure and heat treatment. In order to elucidate the deformation mechanism and to increase the ductility of BMGs, local variations in structure and/or composition are important [2,3]. Such kind of structural modification can be induced by annealing at temperatures usually above the glass transition temperature $T_g$ [4]. It was believed that annealing contributes to the hardening of BMGs and at the same time destroys the ductility, because upon annealing a decrease in free volume is noticed [5]. However, the microstructural modification of BMGs, which seems to drastically influence the mechanical behavior, is not easy to understand. There can be a phase separation into compositionally different amorphous phases, which is much more subtle than in case of crystalline alloys which have easily observable features such as grain boundaries and second-phase particles [6,7]. Also, the short-range order (SRO) and especially the changes in the SRO induced by annealing, for example, are quite difficult to be characterized with conventional techniques, particularly for multicomponent alloys which have $n(n+1)/2$ independent pair correlations ($n$ is the number of components). SRO usually refers to distances up to 0.5 nm. The medium-range order (MRO) of 0.5–2 nm [6,7] is also difficult to be adequately characterized, but in the last years some progress has been made with the help of new techniques like fluctuation microscopy or in situ X-ray diffraction using synchrotron radiation [8,9].

Very recently, Van Steenberge et al. [10] showed that annealing treatment may promote the ductilization of Zr$_{55}$Cu$_{10}$Al$_{10}$Ni$_{5}$ BMG if the annealing is done for a very short time at a temperature 75 K lower than the glass transition temperature. After annealing within the supercooled liquid region (above $T_g$ but below the crystallization temperature $T_x$) the plasticity decreases, being not better than for as-cast samples [10]. The enhancement of ductility is supposed to be caused by the occurrence of phase separation preceding the crystallization process or by the appearance of nanocrystallization. In any case, one has to deal with small changes in MRO and SRO of the BMG, changes which can be revealed by analyzing the position of the broad diffraction maxima upon integration of X-ray diffraction patterns taken in transmission configuration. In the present work two Zr-based glasses were investigated: Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ and Zr$_{55}$Cu$_{20}$Al$_{10}$Ni$_{10}$Ti$_{5}$. The samples were prepared and annealed in advance at IFW Dresden and investigated using synchrotron X-ray
radiation in transmission configuration at Hasylab Hamburg. The present work aims to discuss the different mechanical behavior of these two glasses, using the synchrotron diffraction data.

2. Experimental procedures

The investigated BMGs were prepared in several steps. First, two master alloys with nominal compositions Zr55Cu30Al10Ni5 and Zr55Cu20Al10Ni10Ti5, respectively, were prepared from pure elements by arc-melting. The master alloys were further crushed and small pieces of 3–4 g were used to produce amorphous rods with 3 mm diameter and a length of 50 mm. The casting was performed under Ar atmosphere, using induction melting and injection copper mold casting. In order to check the thermal stability of the cast samples, small slices of the BMGs were heated up to a temperature of 873 K under Ar flow in a Perkin-Elmer differential scanning calorimeter (DSC). The heating rate was set at 20 K/min. From the DSC traces, the glass transition temperature $T_g$ and the crystallization temperature $T_c$ for both glasses were measured. The rods were further annealed at $T_{ann} = 623$ K, which is for both alloys lower than $T_g$. Several samples of both compositions with identical geometries (3 mm diameter and 30 mm length) were one by one introduced and kept for 5 min in a pre-heated furnace. Afterwards, the samples were cooled fast to room temperature by dropping them in water. The as-cast and the annealed rods were cut into small cylinders of 6 mm length and the end surfaces were carefully polished plan-parallel. The amorphous structure of as-cast and annealed samples was proved by X-ray diffraction in transmission configuration using synchrotron radiation at the BW5 beamline at HASYLAB Hamburg. The energy of the radiation was set to 103.8 keV, which corresponds to a wavelength $\lambda = 0.0191441$ nm. The X-ray spot size was 1 mm $\times$ 1 mm, large enough to average a significant portion of the specimen. The measurements were repeated in three different positions of the rod (beam passed through the rod perpendicularly to its axis) and after integration the wave vector $Q$ and the interplanar distance $d$ were measured. The $Q$ value as measured for as-cast sample, while the position of the Bragg peak is $2\theta d = \frac{4\pi}{\lambda}$ the case of crystalline materials, the Bragg condition for the first diffraction peak is $2d\sin \theta = \lambda$ (d the interplanar distance), so the wave vector $Q$ can be written as $Q = 2\pi/d$. This approach cannot be completely transferred to amorphous materials, i.e. the position of the wave vector is not directly correlated with an interatomic distance, but it is helpful to understand what structural modification may take place in the MRO and SRO.

As one can observe from Fig. 3 (Zr55Cu30Al10Ni5 BMG), the position of the first halo after annealing remains at the same value as measured for as-cast sample, while the position of the second halo shifts by 0.12 nm$^{-1}$ towards higher Q values. The Zr55Cu30Al10Ni10Ti5 BMG behaves completely different (Fig. 4): upon annealing, the entire spectrum shifts towards lower Q values, shown by annealed samples is larger than those measured for as-cast samples. Interesting is that the Zr55Cu30Al10Ni5 BMG shows increased values of Young modulus (72.3 GPa instead of 69.5 GPa) and fracture stress after annealing, while for Zr55Cu20Al10Ni10Ti5 BMG these values decrease (for example, Young modulus decrease from 77.4 GPa to 73.1 GPa).

From the stress–strain curves it is rather difficult to estimate with a good accuracy the values of Young's modulus. All data should be considered within the errors of $\pm$4 GPa. The errors were calculated taking in account the stiffness of the machine used for compression tests and the incertitude on measuring the cross-section of the measured samples. In this light, the modifications in the stress–strain curves for each alloy composition are more qualitative than quantitative. Generally, more accurate values of elastic constants can be obtained if an ultrasonic measurement is employed. Unfortunately, due to the small dimensions of the investigated samples, this method brings also errors, comparable with the differences between the values for as-cast and annealed samples. Anyway, Fig. 2 gives at least a qualitative image of how the mechanical behavior changes upon annealing.

The synchrotron X-ray diffraction patterns for the Zr55Cu30Al10Ni5 and Zr55Cu20Al10Ni10Ti5 as-cast and annealed samples are presented in Figs. 3 and 4, respectively. All investigated samples are fully amorphous, with no traces of Bragg peaks in the X-ray patterns. The plots are presented as a function of the wave vector $Q$, which is defined as $Q = (4\pi \sin \theta)/\lambda$ ($\lambda$: wavelength). In the case of crystalline materials, the Bragg condition for the first diffraction peak is $2d\sin \theta = \lambda$ (d the interplanar distance), so the wave vector $Q$ can be written as $Q = 2\pi/d$. This approach cannot be completely transferred to amorphous materials, i.e. the position of the wave vector is not directly correlated with an interatomic distance, but it is helpful to understand what structural modification may take place in the MRO and SRO.

### Table 1
Thermal stability data measured by DSC at a constant heating rate of 20 K/min. $T_g$, $T_c$, $\Delta T$, and $T_{ann}$ stand for glass transition temperature, crystallization temperature, extension of the supercooled liquid region and annealing temperature, respectively.

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ [K]</th>
<th>$T_c$ [K]</th>
<th>$\Delta T$ [K]</th>
<th>$T_{ann}$ = 623 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr55Cu30Al10Ni5</td>
<td>685</td>
<td>761</td>
<td>76</td>
<td>T$_g$ = 62 K</td>
</tr>
<tr>
<td>Zr55Cu20Al10Ni10Ti5</td>
<td>669</td>
<td>714</td>
<td>45</td>
<td>T$_g$ = 46 K</td>
</tr>
</tbody>
</table>

![Fig. 2. Stress–strain curves measured in compression for as-cast and annealed Zr55Cu30Al10Ni5 and Zr55Cu20Al10Ni10Ti5 BMGs (cylinders with 3 mm diameter and 6 mm length). The curves are grouped and shifted for better visibility.](image-url)
Fig. 3. Synchrotron X-ray diffraction patterns for as-cast and annealed Zr55Cu30Al10Ni5 BMG.

Fig. 4. Synchrotron X-ray diffraction patterns for as-cast and annealed Zr55Cu20Al10Ni10Ti5 BMG.

by the same amount of 0.12 nm$^{-1}$. This reveals that the structural changes introduced upon annealing are different for the two studied BMGs, but both modifications induce a better deformability compared to the as-cast state. Vertical lines, as guides for eyes, were plotted in Figs. 3 and 4. They represent the $Q$-position of the first and second broad maxima for samples in as-cast state. In this way the shifting of the XRD patterns upon annealing can be observed easier.

4. Discussion

The most important aspect is to evaluate the microstructural changes which determine the modification of the mechanical behavior of both BMGs upon annealing. The as-cast and annealed Zr55Cu30Al10Ni5 BMG was investigated by means of high resolution transmission electron microscopy [10]. By this, it was proved that the as-cast fully amorphous BMG undergoes a phase separation during short-time annealing at a temperature 75 K lower than the glass transition. Once the annealing temperature approaches $T_g$, the ductility further decreases, due to the fact that one type of the glass clusters formed in the matrix gives rise to small nanocrystals which contribute to the macroscopic embrittlement of the sample. At the same time a hardening was observed, which explains the increase of Young’s modulus upon annealing.

In the case of Zr55Cu20Al10Ni10Ti5 BMG, the entire X-ray pattern shifts by the same amount towards lower $Q$ values after annealing. In contrast to crystalline materials, the position of the wave vector corresponding to the first broad maximum is not directly correlated to an interatomic distance and a linear shift does not necessarily indicate altered nearest neighbor distances. However, here the entire pattern shifts and this indicates either an increase in free volume [11,12], or a change in the SRO (topological and/or chemical). Usually, the free volume decreases upon annealing, leading to a harder and more rigid structure. In the present case, the Young’s modulus and the fracture level seem to decrease, phenomena which cannot simply be attributed only to the changes in the free volume. Most plausible is to consider that upon annealing some clusters/nanocrystals may form or, as it was already observed in the Cu–Zr alloy system [10,13], phase separation may occur. This kind of structural modification could be revealed by TEM investigations, experiments which are currently under consideration.

5. Conclusions

BMGs can undergo plastic deformation only if a particular SRO or MRO is created in such way that the LRO is still characteristic for a glass. One can suppose that the monolithic fully relaxed BMGs are brittle and the mechanical behavior is very sensitive to the thermal history of the sample. This fact may also explain why some of the as-cast BMGs show ductility and others not, even if they are of the same composition: the casting procedures (technologies, temperatures, etc.) may be different and this results in a different random arrangement of the atoms. We have shown here that one may promote the deformability by sub-$T_g$ annealing in the case of Zr55Cu30Al10Ni5 and Zr55Cu20Al10Ni10Ti5 BMGs. The structural modifications induced by annealing, as ruled-out from synchrotron diffraction data, seems to be different for the two investigated alloys.

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References