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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

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ABSTRACT

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.

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, this 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 $Zr_{55}Cu_{30}Al_{10}Ni_5$ 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

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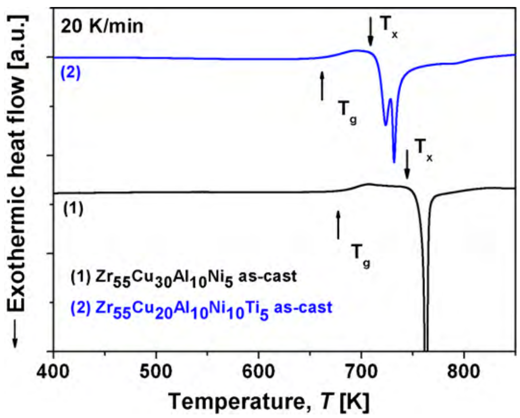

Fig. 1. DSC curves (heating rate 20 K/min) for as-cast $Zr_{55}Cu_{30}Al_{10}Ni_5$ and $Zr_{55}Cu_{20}Al_{10}Ni_{10}Ti_5$ BMGs.

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 $Zr_{55}Cu_{30}Al_{10}Ni_5$ and $Zr_{55}Cu_{20}Al_{10}Ni_{10}Ti_5$, 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_x 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 λ = 0.0119441 nm. The X-ray spot size was 1 mm × 1 mm, large enough to average a significant portion of the specimens. The measurements were repeated in three different positions of the rod (beam passed through the rod perpendicularly to its axis) and after integration the diffraction image recorded by the MAR 2D detector no differences were observed. After synchrotron investigation, the small cylinders were subjected to compression tests, using an INSTRON machine equipped with a laser extensometer. The tests were performed in track-control mode at a constant speed of 10^{-3} mm/s, at room temperature.

3. Results

Fig. 1 shows the DSC curves for both as-cast BMGs. The glass transition temperature T_g and the crystallization temperature T_x were measured as the onset temperatures of the glass transition and the crystallization events, respectively, during heating with a constant rate of 20 K/min. The extension of the supercooled liquid region, defined as the difference between the glass transition temperature and the crystallization temperature, $\Delta T_x = T_x - T_g$ was also calculated. The thermal stability data are summarized in Table 1.

Fig. 2 presents the stress–strain curves measured upon compression for as-cast and annealed $Zr_{55}Cu_{30}Al_{10}Ni_5$ and $Zr_{55}Cu_{20}Al_{10}Ni_{10}Ti_5$ BMG samples. It is worth to mention that the compression experiments were done for four samples of each kind, but here only one curve per sample is presented. This is because all samples of one kind behaved almost similarly, with the differences within the measurement errors. Apparently, both BMGs become more "deformable" upon annealing, in the sense that the strain

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

	T_g [K]	T_x [K]	ΔT_x [K]	T_{ann} = 623 K
$Zr_{55}Cu_{30}Al_{10}Ni_5$	685	761	76	T_g − 62 K
$Zr_{55}Cu_{20}Al_{10}Ni_{10}Ti_5$	669	714	45	T_g − 46 K

shown by annealed samples is larger than those measured for as-cast samples. Interesting is that the $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG shows increased values of Young modulus (72.3 GPa instead of 69.5 GPa) and fracture stress after annealing, while for $Zr_{55}Cu_{20}Al_{10}Ni_{10}Ti_5$ 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 ±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 $Zr_{55}Cu_{30}Al_{10}Ni_5$ and $Zr_{55}Cu_{20}Al_{10}Ni_{10}Ti_5$ 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 $Q = (4\pi \sin\theta)/\lambda$ (λ: 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.

As one can observe from Fig. 3 ($Zr_{55}Cu_{30}Al_{10}Ni_5$ 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 $Zr_{55}Cu_{20}Al_{10}Ni_{10}Ti_5$ BMG behaves completely different (Fig. 4): upon annealing, the entire spectrum shifts towards lower Q values,

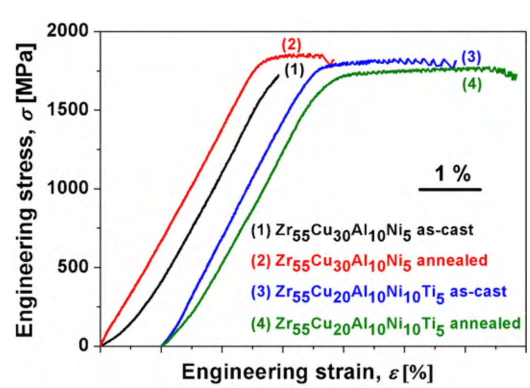

Fig. 2. Stress–strain curves measured in compression for as-cast and annealed $Zr_{55}Cu_{30}Al_{10}Ni_5$ and $Zr_{55}Cu_{20}Al_{10}Ni_{10}Ti_5$ BMGs (cylinders with 3 mm diameter and 6 mm length). The curves are grouped and shifted for better visibility.

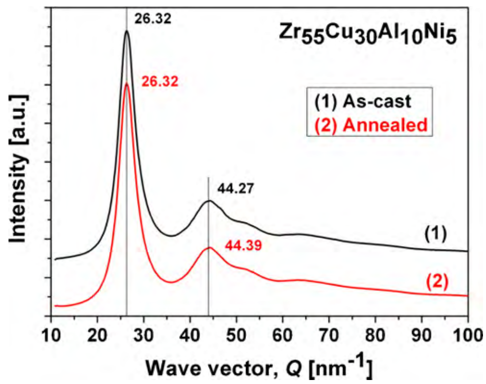

Fig. 3. Synchrotron X-ray diffraction patterns for as-cast and annealed $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG.

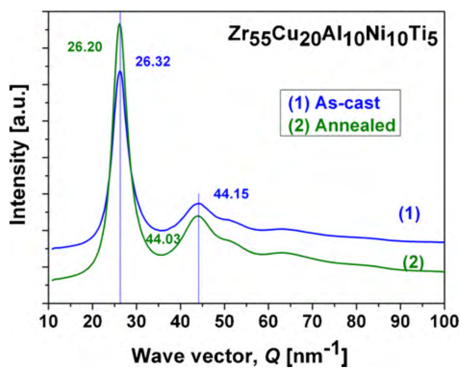

Fig. 4. Synchrotron X-ray diffraction patterns for as-cast and annealed $Zr_{55}Cu_{20}Al_{10}Ni_{10}Ti_5$ BMG.

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 plot 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 $Zr_{55}Cu_{30}Al_{10}Ni_5$ 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 $Zr_{55}Cu_{20}Al_{10}Ni_{10}Ti_5$ 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 $Zr_{55}Cu_{30}Al_{10}Ni_5$ and $Zr_{55}Cu_{20}Al_{10}Ni_{10}Ti_5$ 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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