Structure of Zr_{52}Ti_{5}Cu_{18}Ni_{15}Al_{10} Bulk Metallic Glass at Elevated Temperatures

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The structural behavior of the Zr\textsubscript{52}Ti\textsubscript{5}Cu\textsubscript{18}Ni\textsubscript{15}Al\textsubscript{10} bulk glass has been investigated in situ by means of high-temperature X-ray synchrotron diffraction. The crystallization starts with the formation of an extremely fine nanostructure followed by the transformation into tetragonal NiZr\textsubscript{2}-type crystals plus an unknown phase. Both phases are metastable and transform at about 1123 K into the stable equilibrium, A Debye temperature \( \theta = 412 \) K was estimated for the glassy, and \( \theta = 162 \) K for the liquid state of the Zr\textsubscript{52}Ti\textsubscript{5}Cu\textsubscript{18}Ni\textsubscript{15}Al\textsubscript{10} alloy. The short-range order of the glass, of the supercooled liquid state, and of the equilibrium melt at \( T = 1193 \) K is found to be quite similar. The results point to the formation of complex chemically ordered clusters already in the melt.

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1. Introduction

Bulk metallic glasses are characterized by a high glass-forming ability and the existence of a wide supercooled liquid region.\textsuperscript{1,2} Inoue employed empirical rules for easy glass formation which relate to differences in atomic size and enthalpy of mixing of the constituents in such multicomponent metallic alloys.\textsuperscript{3} Despite the well-established effect of the frustration of the nucleation of competing crystalline phases by five or more kinds of atoms with different sizes, \textsuperscript{4,5} experimentally determined atomic pair correlation functions of bulk glasses exhibit no enhanced disorder or other specific features compared to conventional metallic glasses.\textsuperscript{6,7} Sato et al.\textsuperscript{8} observed structural changes in the supercooled liquid state of Zr\textsubscript{52}Al\textsubscript{15}Ni\textsubscript{15} using X-ray diffraction at temperature of \( T = 720 \) K.

The aim of this work is to analyze the temperature dependence of the structure of a bulk metallic glass up to its melt. The glass transition and the phase formation during crystallization were followed \textit{in situ} by high-temperature X-ray synchrotron diffraction. Based on the diffraction data a quantitative comparison is given between the structure of the amorphous solid state, the supercooled liquid, and the equilibrium melt above the liquidus temperature of the alloy.

2. Experimental Procedure

Samples of the Zr\textsubscript{52}Ti\textsubscript{5}Cu\textsubscript{18}Ni\textsubscript{15}Al\textsubscript{10} bulk glass were prepared in form of rods with 3 mm diameter and 50 mm length by copper mold casting of arc-melted prealloys. Discs of 1 mm height were cut from the rods for differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The DSC experiments were performed using discs of 1 mm in height employing a Netzsch DSC 404 calorimeter. Heating runs under high purity argon atmosphere up to the characteristic temperature above the first exothermic crystallization event were carried out to induce primary crystallization. After reaching the respective temperature, the samples were immediately cooled down to room temperature at \(-100 \) K/min. \textit{In situ} XRD measurements at elevated temperatures were conducted at the high energy beam-line BW5 at the storage ring DORIS (HASYLAB, Hamburg). The experimental set-up consisting of a platinum heater furnace in helium atmosphere and image plate detector combined with the short wave length (\( \lambda = 0.01040 \) nm) enables to record intensities in transmission up to scattering vectors \( q \) of 200 nm\(^{-1}\) with a measuring time of 20 s per diagram.\textsuperscript{9} The sample was held for 130 s at the corresponding temperature (20 s for exposure and additional 110 s for data read out time), and then heated up to the next temperature within 10 s. Immediately thereafter the measurement was started again. The mass density \( \sigma = (6.60 \pm 0.01) \) g cm\(^{-3}\) was determined by the Archimedes principle by weighing samples in air and in dodecan (C\textsubscript{12}H\textsubscript{26}).

3. Results and Discussion

Figure 1 shows the thermal behavior of the alloy as obtained by differential scanning calorimetry. At this rate of 10 K/min, the calorimetric glass transition temperature \( T_g \) is 675 K and the crystallization temperature \( T_x \) is 737 K (both characteristic temperatures are here defined as the onset temperatures of the respective endothermic or exothermic DSC heat flow events). This yields a supercooled region \( \Delta T_x = T_x - T_g \) of 62 K. The split first DSC peak points to a two step crystallization process. At higher temperatures only weak thermal events are visible. The liquidus temperature of the alloy is 1144 K, as determined from DSC experiments (not shown here in detail).

Figure 2 shows the interference functions \( I(q) \) of the as-prepared alloy and those after heating in the DSC apparatus. For these measurements, the samples were constant-rate heated at 10 K/min to different temperatures and rapidly cooled at \(-100 \) K/min to room temperature. Subsequently, X-
the supercooled region (721 K) exhibits only small changes in the second diffuse maximum. The state heated up to a temperature typical for amorphous metallic alloys with a shoulder or beginning crystallization of the as-cast amorphous material. The diffraction pattern of the sample heated up to a temperature above the main split DSC peak (823 K) shows crystalline reflections. A careful analysis reveals that tetragonal Ni$_2$Zr and an unknown phase form upon heating to this temperature. From the interference functions $I(q)$ the atomic pair correlation functions $g(r) = \rho(r)/\rho_0$ were calculated by the Fourier transform of $I(q)$ between 0 \leq q \leq 150 \text{ nm}^{-1}$ according to:

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

where $\rho(r)$ is the atomic pair density distribution function and $\rho_0$ is the mean atomic density. The measured interference function $I(s)$ and the estimated $g(r)$ curves represent in the 5-component alloy the weighted sum of the 15 partial functions $I_{ij}(s)$ and $g_{ij}$:\

$$I(s) = \sum_i \sum_j w_{ij} \cdot I_{ij}$$

and

$$g(r) = \sum_i \sum_j w_{ij} \cdot g_{ij}$$

with

$$w_{ij} = c_i \cdot c_j \cdot f_i \cdot f_j / \left( \sum_i c_i \cdot f_i \right)^2.$$

An interpretation of the data for the multi-component alloy is therefore difficult and ambiguous. Figure 3 shows the calculated $g(r)$ curves. For the as-cast state, two components of the first maximum of $g(r)$ are visible. Referring to the atomic diameters of the elements and the weighting factors $w_{ij}$ the submaxima can be attributed mainly to the zirconium-metal neighborhood at $r_{Zr-M} = 0.265 \text{ nm}$, and to the zirconium-zirconium at $r_{Zr-Zr} = 0.310 \text{ nm}$, respectively. The samples annealed within the supercooled liquid (721 K) are very similar to the as-cast state. After heating to temperatures above
the first DSC peak (823 K) the \( g(r) \) curve clearly exhibits changes in the short-range order which are related to crystallization. The first maximum of \( g(r) \) is broadened and in the second and third maximum additional distances are visible. The broadening of the first maximum is probably due to the superposition of different first neighbor distances in the two phases. The broadening of the first maximum is probably due the superposition of different first neighbor distances in the two phases. The first maximum of crystallization. The first maximum of crystallization starts in agreement with the DSC curve. Tetragonal NiZr\(_2\) and an unknown phase are formed by an eutectic-type crystallization from the supercooled liquid and/or the metastable first crystallization phase. These metastable clusters and the remaining glassy phase transform during the second stage of crystallization into metastable NiZr\(_2\) and other still unknown phases. For the Zr\(_{52}\)Ti\(_5\)Cu\(_{18}\)Ni\(_{15}\)Al\(_{10}\) alloy under investigation the transformation at higher temperatures as indicated by distinct separate exothermic DSC peaks typical for crystallization. That really an extremely fine grain size is formed in this state which relates to a still “amorphous-like” diffuse diffraction pattern has been shown by high resolution transmission electron microscopy (TEM).\(^{14,16}\) Analyzing the small-angle scattering data of annealed Zr\(_{54.5}\)Ti\(_{5}\)Al\(_{10}\)Cu\(_{20}\)Ni\(_{8}\) points to diffusion controlled primary crystallization leading to nanocrystals/clusters with a mean diameter of 2.6 nm.\(^{16}\) The atomic pair correlation functions of these annealed states are similar to that of cubic NiZr\(_2\) which is a metastable phase. These metastable clusters and the remaining glassy phase transform during the second stage of crystallization into tetragonal NiZr\(_2\) and other still unknown phases. For the Zr\(_{52}\)Ti\(_5\)Cu\(_{18}\)Ni\(_{15}\)Al\(_{10}\) alloy under investigation the transformation starts at 751 K during heating with 10 K/min or during isothermal heating after 14 min at \( T = 710 \) K as can be seen in Fig. 1 and Fig. 5.

The diffraction curves of the amorphous state of the sample within the temperature range 293 K \( \leq T \leq 733 \) K exhibit only small changes with increasing temperature. Figure 6 shows the temperature dependence of the height of the in-
terference function $I(q)$ for the position of the first maximum $q_1$. A linear decrease of $I(q_1)$ with increasing temperature is observed for the glass up to $T_g$. At the glass transition thermal activation leads to additional motions of the atoms which is reflected by the observed increase of the slope of $dI(q)/dT$ for temperatures above $T_g$ (Fig. 6). As long as no crystallization sets in, the temperature dependence of the structure factor of the preannealed sample is reversible, i.e. the same data are recorded for thermal cycling by cooling and subsequent reheating. For temperatures $T > 733$ K, the beginning crystallization is detected sensitively by an increase of $I(q_1)$ as shown in Fig. 6 (indicated by the $\star$ for the pattern measured at $T = 743$ K). An extrapolation of the temperature dependence of $I(q_1)$ from the supercooled liquid state to higher temperatures is in agreement with the experimentally obtained values for the molten Zr$_{52}$Ti$_5$Cu$_{18}$Ni$_{15}$Al$_{10}$ alloy at temperatures above the liquidus temperature.

The temperature dependence of X-ray intensities is usually well described within the framework of the Debye theory. The interference function at the temperature $T_2$ can be calculated from any temperature $T_1$ by:

$$I_{T_2}(q) = 1 + (I_{T_1}(q) - 1) \cdot \exp(-2(W_{T_2}(q) - W_{T_1}(q))) \quad (4)$$

where $\exp(-2W_T)$ is the Debye-Waller factor

$$W_T = \frac{3\hbar^2q^2}{2m_0k_BT} \cdot \left(\frac{T}{\Theta}\right)^2 \cdot \int_0^{\Theta/T} \left(\frac{1}{2} + \frac{1}{e^z - 1}\right) z dz \quad (5)$$

with $\hbar$ being Planck’s constant, $k_B$ being Boltzmann’s constant, $m_0$ the atomic mass, and $\Theta$ being the Debye temperature. This type of expression is commonly used within the framework of the Ziman theory for describing the temperature dependence of the electrical conductivity of liquid metals.\(^{18,19}\) The application of this theory to metallic glasses was suggested by Sinha\(^{20}\) and further developed by Nagel.\(^{21}\) Applying eq. (4) to the temperature dependence of the height of the first maximum of $I(q)$, the Debye temperatures were determined to be $412 \pm 12$ K for the glass, and $162 \pm 50$ K for the liquid, respectively. The applicability of the Debye approach to the glassy and the liquid state was checked in the following way: The interference function $I_{T_2}^*(q)$ was calculated from the experimental curve $I_{T_1}(q)$ measured at $T_1$ and compared to the corresponding experimental data $I_{T_2}(q)$ as shown in Fig. 7. There is a good agreement between the calculated and experimental curves in general, which confirms that thermal oscillation effects only and no structural change were detected within the temperature range up to 733 K, but this is of course restricted to a limited time scale. The comparison shown in Fig. 7 again shows that Debye theory applies much better to the glassy state than to the liquid one.

Figure 8 compares the atomic pair correlation functions $g(r)$ of the glassy and the liquid state of the Zr$_{52}$Ti$_5$Cu$_{18}$Ni$_{15}$Al$_{10}$ alloy. The curve for the melt ($T = 1193$ K) is quite similar to that of the glass. All the structural features of the first and second coordination shells are identical. There is only a broadening and a decrease of the

![Fig. 6](image1.png)  
Fig. 6 Height of the first maximum in $I(q)$ versus temperature.

![Fig. 7](image2.png)  
Fig. 7 Interference function $I(q)$ of glassy and liquid Zr$_{52}$Ti$_5$Cu$_{18}$Ni$_{15}$Al$_{10}$ at different temperatures (open circles: experimental values at $T = T_2$; lines: calculated from values at $T = T_1$).

![Fig. 8](image3.png)  
Fig. 8 Atomic pair correlation function $g(r)$ of (a) glassy and liquid Zr$_{52}$Ti$_5$Cu$_{18}$Ni$_{15}$Al$_{10}$ [this work], and (b) Fe$_{80}$B$_{20}$.\(^{21}\)
height of the oscillations due to the enhanced thermal excitation in the melt. The similarity of the short-range order points to the existence of chemically well defined clusters already in the melt. These structural results are in accordance with measurements of the viscosity of the melt which is found to be three orders of magnitude higher for bulk glass-forming alloys compared to that of simple metals.\(^{22}\)

4. Conclusions

The short-range order of the Zr\(_{52}\)Ti\(_5\)Cu\(_{18}\)Ni\(_{15}\)Al\(_{10}\) bulk glass was found to be rather similar to its melt. The glass transition is expressed by a reduction of the Debye temperature which might be linked to the softening of phonons upon melting. The crystallization of the glassy alloy starts with by formation of an extremely fine nanostructure followed by transformation into further metastable phases. The equilibrium phases are formed at relative high temperatures. The existence of complex chemically ordered clusters in the melt as well as low driving forces for the equilibrium phases are concluded from the temperature dependent structural investigations.

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REFERENCES


