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Ultrafast heating of metallic glasses reveals disordering of the amorphous structure

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ABSTRACT

Studies of the transition from the supercooled liquid into the high temperature liquid of a glass forming metal is commonly hindered by incipient crystallization processes. In this contribution we show that a metallic glass exhibits a significant sudden increase in the specific heat while crossing the transition from the supercooled liquid into the high temperature liquid without crystallizing. At this increase, high temporal resolution X-ray studies show that the liquid structure changes and the crystallization behavior also deviates from the common $Zr_2(Cu,Al)$-phase formation. We associate the increase in specific heat capacity with the disordering of the amorphous structure like a scenario of a first order liquid—liquid phase transition.

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1. Introduction

When a glass forming liquid is quenched below its liquidus temperature, the system departs from equilibrium and its time-scales for relaxation processes increase until they are in an experimentally accessible time regime. If the system is quenched fast enough, the atoms are incapable to order into a crystalline structure and thus the configurational liquid freezes into a solid glass. During reheating of an amorphous solid, the devitrification is complex and classical nucleation theory is expected to fail due to the absence of equilibrium [1]. The complexity arises especially due to the strongly temperature dependent dynamics in the supercooled liquid in terms of the viscosity which, in fragile glass formers, changes several orders of magnitude in a relatively small temperature interval [2]. This drastic change is accompanied with a number of decoupling phenomena which occur during cooling such as the breakdown of the Stokes-Einstein-Relation, a fragility transition and the separation of the primary and the secondary relaxation process [3—7]. A possible explanation for these phenomena is a first-order liquid—liquid phase transition (LLPT) which overlaps with the aforementioned processes as shown in MD-simulations [8].

From an experimental point of view, the rapidly decreasing time scales above the glass transition temperature diminish the number of experiments which allow reliable measurements. Incipient crystallization often restricts quantitative measurements of the supercooled liquid close to the glass transition temperature or to high temperatures close to the melting temperature. In fact, previous experimental studies could verify the existence of a LLPT in the Zr-based glass former Vit. 1 close to the melting point of the crystalline structure [9,10]. However in these two studies, either the metallic glass former was never in the solid glass state but only in the liquid or the metallic glass crystallized upon heating.

Recently, studies of crystallization behavior could be extended far above the glass transition temperature for good glass formers by using a so called Chip Differential Scanning Calorimetry or Ultrafast Scanning Calorimetry [11]. This technique reaches heating rates of up to 10^5 K/s and enables thermodynamic measurements as in a conventional calorimeter but the sample weights are limited to the order of μg. Another technique was invented by Johnson et al. using a rapid capacitor discharge [12,13]. This method is based on ohmic heating and can be combined with, for instance, an in-situ deformation procedure enabling the study of viscosity or enthalpy at heating rates of 10^5—10^6 K/s.

In this work, we heated up metallic glasses very rapidly using a capacitor discharge while we measured the specific heat capacity and performed in-situ X-ray measurements. In order to prove the existence of a LLPT, we increased the temporal resolution of the

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detector using a fast chopper system [14]. At the transition from the supercooled to the high temperature liquid, we observe a pronounced increase, suggesting a subsequent maximum, in the specific heat capacity and a change in the liquid structure. We associate this observation with a first order LLPT causing a disordering of the amorphous structure.

2. Experimental methods

The metallic glass was obtained by rapid quenching out of the melt via melt-spinning. The obtained ribbons exhibit sizes of $(35-45) \times (1.5-3.0) \times (0.03-0.07)$ mm^3 and masses of $18-27$ mg. They were clamped into polished copper holders which were connected to the discharge circuit. The composition was tested via energy dispersive X-ray spectroscopy (EDX) with a Supra 35 Zeiss scanning electron microscope with an EDX addition. For every measurement, we used a fresh sample from the same ribbon of the actual composition of $Zr_{64.0}Cu_{28.2}Al_{7.8}$.

A rapid capacitor discharge with a capacity of 1 mF was used to heat up the samples homogeneously above the glass transition temperature (equivalent to the setup described in reference 12). The time constant of our discharge circuit is $\tau = R \cdot C = 0.36$ ms, with the resistance of the discharge circuit R and the capacity C. This time constant leads to heating rates in the order of 10^5-10^6 K/s. These rates can be varied by modifying the amount of energy stored in the capacitor. The conditions for homogeneous heating can also be found in reference 12.

The temperature was monitored using the fast pyrometer Kleiber KGA 740 with a response time of 6 μs in the temperature range of $433-1273$ K. High temperature investigations were performed using the fast pyrometer Impac IGA 740 which has the same specifications as the Kleiber KGA 740, particularly the same response of 6 μs, but it detects the temperature in a higher temperature interval of $573-2573$ K. Both pyrometers are single color pyrometers. This means that the emissivity is considered to be constant over the entire temperature regime. In our measurements across such large temperature interval the emissivity of metallic glasses does change. In order to take this effect into account, we quantified the absolute error in the temperature detection at high temperatures (see Supplementary Information). The absolute temperature error at the melting temperature of $Zr_{64.0}Cu_{28.2}Al_{7.8}$ at $T_m = 1179 \pm 1$ K was detected to be 28 ± 4 K in a first run and 41 ± 5 K in a second run. Whilst the absolute temperature value is compromised when the emissivity changes, relative temperature changes are still monitored reliably. Additionally, due to the air atmosphere in most of the measurements, the samples tend to oxidize and consequently change the emissivity. Therefore, we do not consider the temperature measurement after 10^{-2} s and above 1300 K to be reliable.

During the discharge, the voltage and the current were also measured. The latter one was detected via the Rogowski coil CWT30 with a bandwidth from 0.6 Hz to 16 MHz.

In-situ X-ray measurements during the fast heating procedure were performed at the synchrotron beamline P07 at PETRA III/DESY in Hamburg. The energy of the beam was 70 keV which corresponds to a wavelength of 0.17712 Å. We used a Perkin Elmer XRD 1621 flat panel detector with 2048×2048 pixels. The maximum read out frequency of this detector was 15 Hz which corresponds to a temporal resolution of 67 ms. Every measurement at the synchrotron beamline was performed in air.

The temperature increase of the sample due to the discharge and relaxation processes in the supercooled liquid region, particularly at high heating rates, occur on a millisecond timescale (see below). The temporal resolution of the aforementioned detector is insufficient to resolve structural changes on such fast timescales.

Therefore, we installed a chopper system between the sample and the detector to increase the read out frequency. For detailed information about the chopper system, we refer to the Supplementary material and reference 14. The chopper system causes a split of the detector image into 13 separate sections which are equal in size and each of them correspond to a different time window of about 5 ms. Therefore, this setup causes an increase of the temporal resolution up to 195 Hz.

3. Results

In our measurements, we charged the capacitor with different voltages in order to control the heating rate and to study the crystallization in different regions of the supercooled liquid.

Sample A of the metallic glass $Zr_{64.0}Cu_{28.2}Al_{7.8}$ was heated up with a rate of $\phi = 0.9 \cdot 10^6$ K/s until 770 K due to the capacitor discharge. After the discharge is over the temperature remains almost unchanged and eventually starts decaying. The temperature curves of the samples B and C exhibit both a pronounced increase after 50 ms and 4 ms, respectively, afterwards the temperatures are beyond the detection limit of 1273 K. These rises can be clearly separated from the original one caused by the capacitor discharge which takes about 1 ms (inset of Fig. 1). Sample D was heated with the highest rate $\phi = 1.6 \cdot 10^6$ K/s. Unfortunately, the temperature profile exhibits an unusual distortion after $5 \cdot 10^{-4}$ s which is not considered reliable. However, the sample did not fuse and X-ray diffraction patterns were recorded.

The diffraction intensity in the X-ray measurements of sample A shows broad diffraction peaks in the entire time regime of 1.2 s as an indication of its amorphous nature (Fig. 2a). 55 ms after the original discharge, the temperature of the sample B increases again accommodated by the transformation of the broad diffraction peaks into sharp peaks which characterize the crystalline phase $Zr_2(Cu,Al)$ (Fig. 2b). The $Zr_2(Cu,Al)$ is the bct C11b phase. This intermittent crystalline $Zr_2(Cu,Al)$ phase disappears at 0.7 s and is replaced by diffuse peaks in the q-range of the first and second initial amorphous maximums. However, several crystalline peaks are visible as well which can be identified to correspond to the ZrO_2-phase [15]. The diffuse maxima which occurred at 0.7 s transform 0.25 s later into sharp peaks which also correspond to the ZrO_2-phase. The assignment of the crystalline phases results from a comparison with literature data (see Supplementary Information). The same behavior of sample B can be observed for the faster heated sample C, but the intermittent phase already occurs 5 ms after the discharge started and lasts only for 0.1 s. The
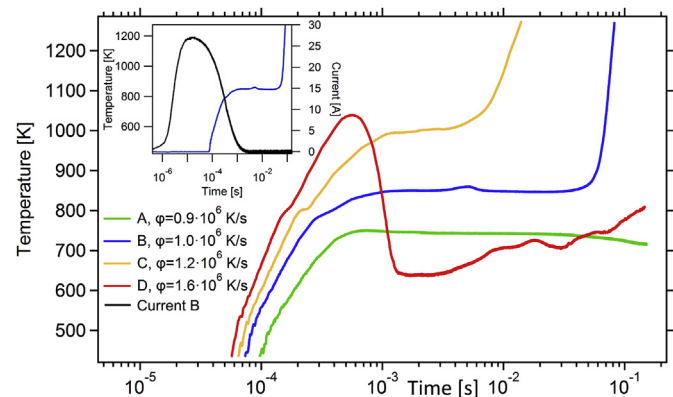

Fig. 1. Temperature versus the logarithm of time during ultrafast heating for four heating rates. Inset: Temperature of sample B compared to the current flowing through the sample.