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Thermal expansion of amorphous $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ in the vicinity of the glass transition

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Abstract. The thermal expansion of non-crystalline $Zr_{65}Al_{7.5}Cu_{17.5}$ Ni_{10} has been studied in the range of the glass transition and in the undercooled liquid using a dilatometric device. The measuring technique used permits reliable experimental results up to 40 K above the glass transition temperature. The linear thermal expansion coefficient obtained is almost constant in the glassy state with a value of 8.0×10^{-6} K^{-1}. It discontinuously increases at the glass transition temperature yielding a value of 20.0×10^{-6} K^{-1} in the undercooled liquid. The results are compared with specific heat measurements of the amorphous material in this temperature range and are interpreted in the framework of a cluster model.

PACS. 65.70.+y Thermal expansion and density changes; thermomechanical effects. – 61.43.Dq Amorphous semiconductors, metals, and alloys

1 Introduction

There is an important need to characterize and to understand the glass transition with an exact knowledge of the thermodynamic data in the vicinity of the glass transition and in the region of the undercooled melt [1]. One important thermodynamic quantity is the thermal expansion coefficient. In recent years multicomponent metals have been discovered which can be processed around the glass transition temperature T_g [2]. For one of these, $Zr_{41}Ti_{13}Ni_{10}Cu_{13}Be_{23}$, thermal expansion data were derived by He *et al.* [3] in the glassy state and at the glass transition temperature, respectively, by measuring the volume change of a bulk cuboid. Further results were obtained by Ohsaka *et al.* [4] using an imaging device to detect the temperature dependent volume change of a spherically shaped sample in an electrostatic levitator. The aim of this letter is to present new results on a similar, here ZrAlCuNi-based, amorphous metallic alloy for which the linear thermal expansion is measured by a different measurement method and to compare the results obtained with heat flow data from differential scanning calorimetry (DSC).

2 Experimental details

Amorphous $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$-alloys have been prepared from ultra pure elements by arc-melting in a Zr-gettered Argon atmosphere and subsequent rapid cooling by copper mold casting in a vacuum atmosphere. Bulk amorphous samples were produced with dimensions of 1 mm × 30 mm × 10 mm. About 200 mg of amorphous material was filled into a quartz pot of 0.28 inches diameter together with angular shaped Al_2O_3-powder (Perkin-Elmer 0419-0197, mesh-size mainly 30-40 μm diameter). The pot with the powder and the sample was mechanically shaken to densify the powder. A schematic view of the system is shown in Figure 1. After inserting a plunger into the pot within an Ar-glove box, the vertical position of the plunger with changing temperature is detected in a differential mechanical analyser (Perkin-Elmer DMA7). To prevent sample oxidation the entire equipment operates in a second glove box under Argon atmosphere. By considering the thermal expansion of the measurement instruments and the Al_2O_3-powder the additional plunger displacement that is only caused by the sample can be determined. This is achieved by reference measurements

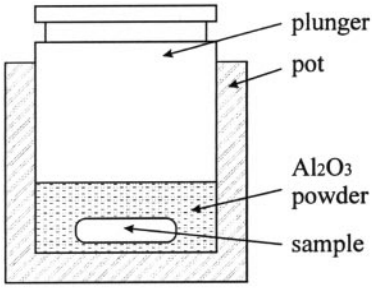

Fig. 1. Schematic picture of the quartz dilamometer used within the DMA-7.

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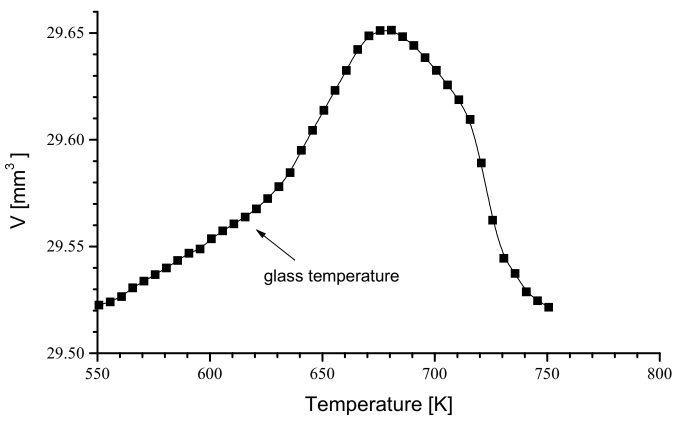

Fig. 2. Sample volume V of a relaxed amorphous $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$-sample.

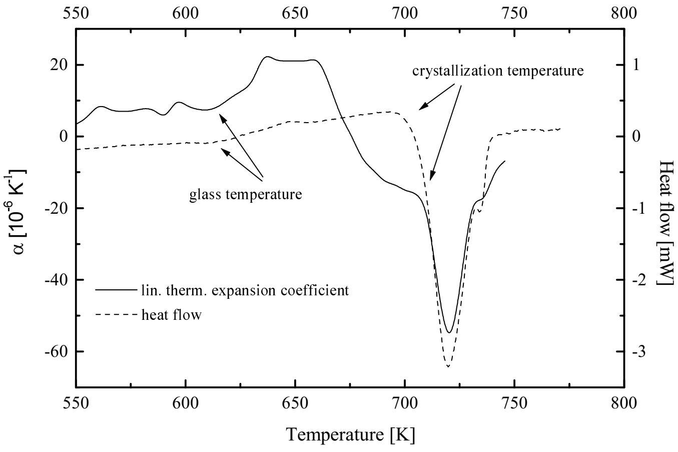

Fig. 3. Linear thermal expansion coefficient α of $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ in comparison with the heat flow signal from a specific heat measurement relative to the crystalline phase.

without a sample using the same mass of Al_2O_3-powder and thus obtaining the plunger displacement $h_c(T)$ caused by the powder. Furthermore, it is necessary to know the mass m and the density ρ of the amorphous sample at the beginning temperature T_0 of the experiment which one can easily measure using the Archimedes method. The plunger displacement $h_s(T)$ due to the sample volume is then calculated from the measured total height $h_p(T)$ by:

$$h_s(T) = \left(\underbrace{(h_p(T) - h_p(T_0))}_{\Delta h_p} - \underbrace{(h_c(T) - h_c(T_0))}_{\Delta h_c} \right) + \frac{m}{\rho(T_0) A} \tag{1}$$

where A is the area of the basal plane inside the dilatometer.

This resulting height $h_s(T)$ then directly corresponds to the sample volume $V(T)$ and its changes with temperature:

$$V(T) = A h_s(T). \tag{2}$$

Differential scanning calorimetry (Perkin-Elmer DSC7) was carried out in an Ar-environment.

3 Results

Figure 2 shows the results of volume measurements $V(T)$ on a relaxed amorphous $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$-sample as a function of increasing temperature at a scanning rate of 5 K/min. The volume first increases constantly up to a temperature of about 615 K. Above this temperature it increases more rapidly up to 665 K. From there the volume increases nearly constantly and exhibits a maximum around 675 K before dropping dramatically around 725 K. For samples kept at temperatures below this maximum the entire process is reversible as we have observed by using the same sample in two subsequent heating cycles. The general behavior is more apparent, if one calculates the linear thermal expansion coefficient α as a temperature derivative of the volume change, as shown in Figure 3. The linear thermal expansion coefficient α of the sample volume V, assuming an isotropic material, is determined by:

$$\alpha = \frac{1}{3V} \frac{\partial V}{\partial T} \cdot \tag{3}$$

For temperatures lower than the glass transition temperature which, known from DSC-studies [5], is located at 612 K (heating rate 5 K/min), the linear thermal expansion coefficient α for $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ is found to be constant with a value of $\alpha = 8.0 \times 10^{-6}$ K^{-1}. At the glass transition temperature the thermal expansion coefficient increases abruptly to a value of $\alpha = 20.0 \times 10^{-6}$ K^{-1} and stays constant up to about 665 K. This change is not surprising since, at T_g , the glassy solid becomes an undercooled liquid which can access additional configurational states of lower density, resulting in a drastic increase in the linear thermal expansion coefficient. It is interesting to note that there exists a small overshoot effect in the glass transition region as also observed in the measurements of the heat flow [6]. At higher temperatures, above 670 K, an initial rapid decrease of the linear expansion is observed before the sample crystallizes above 700 K. This initial decrease of α can be explained by two easily obtained light microscopy pictures of the sample surface taken before and after the measurement, as shown in Figure 4. Above the glass transition temperature the viscosity is known to decrease strongly within a small temperature interval [7–9]. Correspondingly, the $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$-sample softens and starts to penetrate into spaces between the Al_2O_3-powder particles which takes place above 665 K. This can be deduced from the black areas at the surface which now represent the indents caused by the powder particles. This mechanism leads to a continuous loss

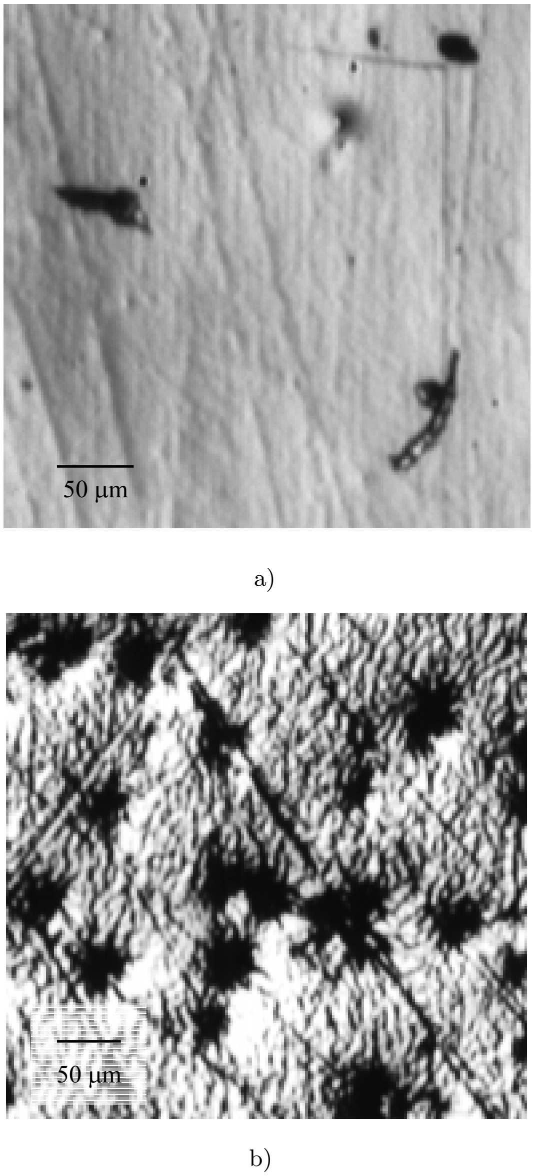

Fig. 4. Surface micrograph of an amorphous $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$-sample: a) as prepared and b) after the measurement in the dilatometer.

of volume corresponding to Figure 2 above 665 K. Thus this decrease shows the limitation of the measurement technique applied but is not related to an intrinsic effect of the amorphous material. Comparing the behavior of the DSC-measurements of the $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$-samples relative to the crystalline phase with the linear thermal expansion coefficient in Figure 3, we observe a qualitative similar behavior. This shows that both the glass transition and the crystallization of the sample can be detected from either measurement technique. Additionally, both thermodynamic quantities measured are comparable in showing the jump at T_g and the constant behavior in the region of the undercooled melt. However, no comparison is possible in the temperature range from 665 K to 709 K, as emphasized above.

4 Discussion

According to the text books (see *e.g.* J. Zarzyki, *Glasses and vitreous state*, Cambridge University Press, 1991) the observed step in the thermodynamic quantities (here: thermal expansion coefficient) around the glass transition is due to the difference in the density of the liquid structure at high temperatures and the more “open” structure in the glassy state. Due to different cooling rates a certain degree of order or the state of configuration of the liquid is frozen in. With heating this difference in configuration can even lead to an “over- or undershooting” at the glass transition. In a cluster model as given by Cohen *et al.* [10] the non-crystalline material consists of solid-like and liquid-like clusters. Below a certain temperature the fraction of solid-like clusters is dominating but decreases, however, with increasing temperature and the fraction of the liquid-like clusters increases. It consequently follows, that at a certain temperature a percolation threshold of the solid-like clusters will be reached. This temperature can be considered as the glass transition temperature at which the second derivatives of the thermodynamic functions show a step. In addition to this step a small overshoot in the thermal expansion coefficient is observed (Fig. 3). This correlates with the overshoot in the heat flow signal of the specific heat measurement [11,12] and should depend on the heating rate [13,14]. Furthermore, at even higher temperatures, the thermal expansion of the liquid dominates the thermal expansion until the material crystallizes. This interpretation is also in accordance with the interpretation deduced from anelastic relaxation measurements on the similar alloys $Zr_{65}Al_{7.5}Cu_{27.5}$ and $Zr_{65}Al_{15}Cu_{20}$ investigated recently [15,16].

5 Conclusions

In this article we presented an experimental method for the measurement of the thermal expansion coefficient of bulk amorphous materials up to 40 K into the undercooled melt. Using the amorphous alloy $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ as a model system we compared the thermal expansion results with the specific heat data of a DSC-measurement. The results were interpreted in the framework of freezing and are consistent with the investigations on anelastic relaxation measurements in such alloy classes.

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14. The study of the heating rate dependence in our measurements, however, was not possible because of two reasons: for considerable larger heating rates the heat flow between sample material and powder particles turns out to be insufficient and for significantly smaller heating rates the sample surface tends to oxidize. Therefore, to study such a heating rate dependence, a different and less sensitive alloy system may be required.
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