Thermal behavior and melt fragility number of Cu\textsubscript{100-x}Zr\textsubscript{x} glassy alloys in terms of crystallization and viscous flow

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Abstract. Six Cu\textsubscript{100-x}Zr\textsubscript{x} amorphous alloys (x in the range 35.7 – 60 at. percent) were prepared via chill block melt spinning (CBMS) method under low pressure Helium atmosphere. Their crystallization and viscous flow behavior was studied with the aid of Perkin Elmer DSC 2C and Perkin Elmer TMS 2 devices, respectively. The viscous flow temperature dependencies at a heating rate of 20 K min\textsuperscript{-1} were interpreted on the basis of the free volume model. The DSC and TMS data were used to determine the fragility number \( m \) of Angell in three different ways as a function of alloy composition. It has been shown that the fragility number goes over a maximum and has a minimum at x very near to the alloy composition Cu 64Zr36 in good agreement with the results of Donghua Xu et al. and Wang D et al. The experimental techniques and model interpretation used provide a tool for understanding the glass forming ability (GFA) and relaxation phenomena in metallic glasses.

1. Introduction

The binary alloy system Cu-Zr has been known for its relative ease of glass formation. Donghua Xu et al. [1] and D. Wang et al. [2] have found that bulk metallic glass indeed forms in Cu\textsubscript{100-x}Zr\textsubscript{x} alloy series (x in the range 34-40 at.%) and that the glass forming ability has a pronounced dependence on the alloy composition. The above cited authors [1,2] have also shown that a very narrow composition window of 2.5 at.% around the composition Cu\textsubscript{64}Zr\textsubscript{36} exists in which the formation of bulk binary metallic glass can be reached (high GFA).

The purpose of this study was to perform a systematic study of crystallization and viscous flow behavior of a series of Cu\textsubscript{100-x}Zr\textsubscript{x} in a wide composition range of 37.5 \( \leq x \leq 60 \) at.\%, respectively, in order to disclose the composition dependence of the main crystallization- and viscous flow features of this binary glass forming metallic system. They were used to study the glass forming ability (GFA) in terms of melt fragility number according to the ideas of Angell and Moynihan [3, 4]. Their ideas were further developed to correspond also to the free volume model (FVM) adapted to describe the viscosity temperature dependence under constant heating rate conditions [5].

2. Experimental and experimental results

The Cu\textsubscript{100-x}Zr\textsubscript{x} master alloys were obtained by melting pure Cu and Zr constituents using a BN crucible. The amorphous samples in a ribbon-like form were produced according to the CBMS method under low pressure He atmosphere. The thickness and the width of the amorphous ribbons obtained
varied between 0.018 ± 0.029 and 1.16 ± 1.55 mm, respectively. Their full amorphousness was proved by using XRD. The crystallization and viscous flow behaviour of the samples at a heating rate of 20 K min⁻¹ were studied with the aid of Perkin Elmer DSC 2C and TMS 2 devices, respectively, as described in [6]. Fig. 1 and Fig. 2 represent the DSC traces of crystallization and the viscous flow temperature dependencies of the amorphous alloy samples studied as a function of Zr concentration, respectively.

**Figure 1**: DSC crystallization traces of Cu₁₀₀₋ₓZrₓ amorphous alloys as a function of composition x at a heating rate of 20 K min⁻¹.

**Figure 2**: Viscosity temperature dependence of Cu₁₀₀₋ₓZrₓ amorphous alloys as a function of composition at a heating rate of 20 K min⁻¹.

**Table 1.** DSC features and FVM fitting parameters of the viscosity data.

| Parameters | Dimension | Zr, at.% |
|------------|-----------|----------|
|            | 35.7      | 38.2     | 44   | 50    | 54   | 60   |
| \( \nu \) \( \text{s}^{-1} \) | 2.8x10⁹⁵ | 1.1x10⁷⁷ | 4x10⁶⁶ | 8x10⁶⁶ | 2x10¹⁴ | 1.6x10¹⁴ |
| \( Q_r \) \( \text{kJ mol}^{-1} \) | 116 | 128 | 95 | 102 | 96 | 92 |
| \( \epsilon_{f,0} \) \( \text{kJ mol}^{-1} \) | 2.5x10⁰⁷ | 2.9x10⁰⁷ | 8x10⁰⁸ | 7.8x10⁰⁷ | 7x10⁰⁵ | 7.7x10⁰⁵ |
| \( T_o \) \( \text{K} \) | 529 | 510 | 481 | 460 | 409 | 410 |
| \( Q_{\eta} \) \( \text{kJ mol}^{-1} \) | 238 | 248 | 334 | 275 | 195 | 193 |
| \( B \) \( \text{K} \) | 4290 | 4640 | 5620 | 5480 | 4810 | 4790 |
| \( T_{\eta} \) \( \text{K} \) | 734 | 716 | 692 | 676 | 642 | 632 |
| \( T_{\eta} \) (DSC) \( \text{K} \) | 775 | 761.6 | 742.1 | 725.4 | 696.5 | 685.3 |
| \( \eta \) \( \text{Pa s K}^{-1} \) | 1.1x10¹⁸ | 4.4x10¹⁰ | 4x10³⁰ | 4.2x10²⁵ | 3x10¹⁷ | 3.8x10¹⁷ |
| \( \eta(T_o) \) \( \text{Pa s} \) | 8.37x10¹⁰ | 1.48x10¹¹ | 1.39x10¹⁰ | 4.26x10¹⁰ | 1.06x10¹¹ | 7.67x10¹⁰ |
| \( \eta(T_{\eta}) \) \( \text{Pa s} \) | 2.51x10⁹ | 9.20x10⁸ | 5.65x10⁸ | 3.4x10⁸ | 4.95x10⁸ | 8.65x10⁸ |

The non-equilibrium \( \ln(\eta) \) vs. \( T^{-1} \) curve for each alloy composition in Fig.2 consists of two almost linear parts of different slopes before and after the glass transition and a much steeper curve presenting the quasi-equilibrium viscosity temperature dependence described by the “hybrid” equation (3) – see the next paper section. The viscosity experimental data were fitted according to the combined using eqns.(1) and (4). The DSC crystallization features and the viscosity fitting parameters obtained are
given in Table (1). The glass transition temperature $T_g$ is the cross point of the non-equilibrium and quasi-equilibrium viscosity curves for every alloy composition, respectively.

3. Theoretical approach and discussion of experimental results

According to Russew et al. [5] the viscosity temperature dependence in the framework of the Free Volume Model (FVM) is given by:

$$\eta = \eta_0 T \exp \left( \frac{Q_\eta}{RT} c_f \right),$$

(1)

where $Q_\eta$ is the activation energy of viscous flow, $\eta_0$ is a pre-exponential factor, and $c_f$ is the concentration of the so-called flow defects. The equilibrium concentration of these defects is given by:

$$c_{f,eq}(T) = \exp \left( - \frac{B}{T - T_o} \right),$$

(2)

where $B$ and $T_o$ are two model parameters. Combining eqns. (1) and (2) one obtains the so-called “hybrid” temperature dependence of the quasi-equilibrium viscosity:

$$\eta_{eq}(T) = \eta_0 T \exp \left( \frac{Q_\eta}{RT} \right) \exp \left( \frac{B}{T - T_o} \right).$$

(3)

During continuous heating, $c_f$ changes following a bi-molecular kinetics along with the time of heating. The equation describing the changes of $c_f$ along with the increasing temperature at a heating rate $q$ in a broad temperature range around the glass transition temperature $T_g$ is:

$$c_f^{-1} = \left[ c_{f,0}^{-1} + \frac{q}{Q} \int \frac{dP}{dT} \right] \int \frac{dP}{dT} \exp \left( - \frac{Q}{RT} \right) \exp \left( \frac{B}{T - T_o} \right).$$

(4)

where $P(T) = \frac{v_r \exp \left( - \frac{Q}{RT} - \frac{B}{T - T_o} \right)}{q}$, $Q(T) = \frac{v_r \exp \left( - \frac{Q}{RT} \right)}{q}$, $v_r$ is the attempt frequency, $Q$ is the activation energy of relaxation, $c_{f,0}$ is the initial concentration of flow defects, and $R$ is the universal gas constant. Combining eqns. (1) and (4) one obtains the viscosity temperature dependence around $T_g$. The model parameters can be determined by using multi-parameter regression analysis of the viscosity experimental data. The glass transition is the main feature of amorphous materials obtained via rapid solidification from the melt. It is believed that the value of the viscosity at the glass transition temperature equals $10^{12}$ Pa. s, although this is only a very rough estimate – see Table 1. Angell [3, 4] has pointed out that not the absolute value of the melt viscosity but the rate of viscosity change at $T_g$ is the most important factor determining the glass forming ability of different substances including classical silicate glasses and amorphous metallic alloys. This is mathematically presented as:

$$m_A = \left[ \frac{d(\log \eta)}{dT} \right]_{T=\T_g},$$

(5)

where $m$ is the so-called melt fragility number of Angell [3,4]. Eq. (5) is based on the assumption that melt viscosity of glass forming substances follows Vogel-Fulcher-Tammann (VFT) temperature dependence and at $T=T_g$ the viscosity value is $10^{12}$ Pa. s. In the case of FVM interpretation [3] the viscosity temperature dependence should be presented by the “hybrid” eq.(3) instead of VFT-type equation. In this case:

$$m_A = 0.434 \left[ \frac{BT_g}{(T_g - T_o)} + \frac{Q_\eta}{RT_g} - 1 \right].$$

(6)
and the Angell's melt fragility number \( m_A \) can be easily calculated with the aid of FVM model parameters – see Fig. 3.

Another simple way to calculate the melt fragility number \( m_M \) is given by Moynihan [5,6]:

\[
\frac{\Delta T_g}{T_g} \approx \frac{2}{m_M},
\]

where \( \Delta T_g = T_{on} - T_g \). It is based on the assumption that \( \ln(\eta_{T_o}/\eta_{T_m}) = \mu = 2 \) which is again a very rough estimate, and that the VFT equation describes the quasi-equilibrium viscosity. This can be easily corrected having the possibility to calculate the real \( \mu = \ln(\eta_{T_o}/\eta_{T_m}) \) value (ranging in this case from 3.5 to 5.3 instead of 2), and taking into account that the “hybrid” eq. (3) should replace the VFT equation:

\[
m_M = 0.434 \left[ \frac{BT_{on}}{(T_g - T_o)(T_{on} - T_o)} + \frac{Q_g}{R} \left( \frac{2}{T_g} - \frac{1}{T_{on}} \right) - \mu - 1 \right],
\]

where \( T_{on} \) is the onset temperature of crystallization of the alloys studied. Unfortunately, in this case it is not possible to use only the DSC crystallization traces in order to calculate the melt fragility number. Fig.3 represents the composition dependence of the melt fragility numbers of Cu\(_{100-x}\)Zr\(_x\) alloys studied.

**Figure 3**: Dependence of melt fragility numbers on the Cu\(_{100-x}\)Zr\(_x\) alloy composition: \( \Delta \) – melt fragility number calculated according to eq. (6); O – melt fragility number calculated according to eq. (8); □ – melt fragility number calculated according to eq. (7) - classical Moynihan.

### 4. Conclusions

- The binary Cu\(_{100-x}\)Zr\(_x\) metallic amorphous alloy system (37.5 \( \leq x \leq 60 \) at.%) shows strong dependence of crystallization and viscous flow features on the Zr content.
- The FVM can be successfully used for a quantitative interpretation of viscous flow behavior of the alloys studied. The FVM parameters describing the experimental data provide the possibility to calculate the “hybrid” temperature dependence of the quasi-equilibrium viscosity and to use it instead of VFT-type equation to calculate the melt fragility number according to Angell and Moynihan.
- The melt fragility number calculated in three different ways goes over a maximum and has a local minimum at the Cu\(_{60}\)Zr\(_{36}\) alloy composition in good agreement with experimental evidence [1,2].

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