Thermo-mechanical Study of the Cu-Zr Ribbon with 2% V Addition for Amorphous-nano Crystalline Composites

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Abstract
The structure, thermal stability and dynamic viscosity of the CuZrV amorphous alloy around T₉ were studied. This kind of amorphous alloys are potential amorphous-crystalline composites with the lowered glass forming ability and increased ability for the nano-crystallization. The structure and thermal properties of amorphous alloys were determined. To determine the dynamic viscosity the mechanical properties and GFA were studied in an amorphous state of the material in the form of ribbons using multiplied tensile tests experiments. The results of the experimental viscosity were interpreted on the base of the free volume model (FVM). The obtained values of the parameters were used to estimate glass forming ability (GFA) in terms of the Angell parameter mₐ and characteristic temperatures measured by DSC as well as to determine dynamic viscosity and flow defect concentration.

Keywords: CuZrV amorphous alloys, viscous flow, glass transition, glass forming ability, Free Volume Model

Introduction

Amorphous metallic alloys (glassy metals) represent new class materials in materials science. Recently most studies concern amorphous alloys revealing high glass forming ability (GFA), which can easily form metallic glasses by suction casting sizing from several mm to several cm [1, 2]. The other leading subject concerns formation and properties of the composite, amorphous-crystalline structures which should reveal enhanced mechanical properties, especially avoiding catastrophic fail in the tensile tests due to local plasticity introduced by the deformable crystalline particles [3, 4]. In that range of investigations the Cu-Zr alloys with different additions stabilizing the deformable β phase are of a special interest [5]. One of the less known addition to the amorphous Cu-Zr alloys are small V additives. During the heat treatment of metallic glasses, they undergo fine changes of a short range atomic ordering leading to the decrease of the internal free energy of the system. Extremely sensitive to the structural relaxation are the coefficients of atomic transport, especially the viscosity η. This is why one of the most important characteristics of amorphous phase of the metallic glasses is the temperature dependence of their coefficient of viscous flow [6] which drastically decreases at the glass transition temperature T₉ and further decreases until the primary crystallization temperature Tₓ is reached. The mechanical properties of the glassy alloys have inspired great interest. Commonly, metallic glasses reveal high strength but their applicability depends on the ductility, which at low temperatures is commonly the weakest point of most compositions [7]. Large, homogenous deformation at the temperature range between 0.8T₉ and primary crystallization Tₓ, that is in the range of Newtonian flow remains the most promising way of the amorphous alloys
processing. This is why the study of viscosity in its connection to the application properties is of great importance from both scientific and practical point of view [6].

Many methods could be applied to measure viscosity from the equilibrium melt down to undercooled liquid near \( T_g \), such as parallel-plate rheometry, beam bending and capillary flow method [8–12]. In this work, we study the thermal stability and viscosity around \( T_g \) using tensile tests equipment what determined the required form of the investigated samples to be the thin ribbons of the \( \text{Cu}_{40}\text{Zr}_{58}\text{V}_2 \) nominal composition. At the presented stage of the investigations the study concerns seldom the glassy state of the alloy. For the interpretation of the results the Russew Free Volume Model was applied [6].

A short theoretical background of the applied model is as follows.

The basic assumption of the free volume model (FVM) used for interpretation of the viscosity experimental data is that viscous flow takes place through thermally activated events at specific sites in the structure, called flow defects (\( c_f \)). The most generalized temperature dependence of the viscosity (\( \eta \)) of an amorphous alloy can be represented as [13]:

\[
\eta = \eta_0 T \exp \left( \frac{Q_\eta}{RT} \right) \frac{1}{c_f}
\]  

(1)

Here \( Q_\eta \) is the activation energy for the viscous flow, \( \eta_0 \) is a pre-exponential factor and \( c_f \) is the concentration of the flow defects. The equilibrium concentration of flow defects \( c_{f,eq}(T) \) is given by Zhu et all. [14]:

\[
c_{f,eq}(T) = \exp \left( -\frac{B}{T - T_0} \right)
\]  

(2)

where \( B \) and \( T_0 \) are two model parameters, which can be related to the empirical constants \( B_{\text{VFT}} \), and \( T_{0,\text{VFT}} \) in the classical empirical Vogel-Fulcher-Tammann equation. Combining equation (1) and (2), the so-called ‘hybrid’ temperature dependence of quasi-equilibrium viscosity \( \eta_{eq} \) is obtained [14]:

\[
\eta_{eq}(T) = \eta_0 T \exp \left( \frac{Q_\eta}{RT} \right) \exp \left( -\frac{B}{T - T_0} \right)
\]  

(3)

Equation (3) describes the change of viscosity of glass forming undercooled (metallic) melts in the structural state, where the flow defect concentration follows immediately the changes of temperature. Taub and Spaepen, [15] were the first, who have found, that the defect concentration changes cause linear increase of glassy metals viscosity along with increasing the time of isothermal annealing far from their metastable equilibrium. In that case, it follows from eq. (4), that the concentration \( c_f \) of flow defects decreases inversely proportional to the time of annealing, e.g.:

\[
\frac{dc_f}{dt} = -k_c c_f^2
\]  

(4)

Duine et al. [16] have shown that alloy \( \text{Pd}_{40}\text{Ni}_{40}\text{P}_{20} \) possess a very high thermal stability around its glass transition temperature thus a term taking into account the production of flow defects should be included in (5):

\[
\frac{dc_f}{dt} = -k_c (c_f^2 - c_{f,eq}^2)
\]  

(5)

Russew et al. [6,17] have transform equation (5) to \( dc_f/dt = (dc_f/dT)_q \) in order to describe the change of \( c_f \) in the glassy alloy with temperature under non-isothermal conditions and at a constant heating rate, \( q \) in the temperature range around the glass transition temperature \( T_g \). The solution becomes to equation (6):
where \( c_{f,0} \) is the initial defect concentration and \( R \) is the universal gas constant. Combining equation (1) with equation (6) one obtains the temperature dependence of viscosity \( \eta \) in the high temperature range near \( T_g \). The Free Volume Model interpretation of the viscosity experimental data allows specifying the model parameters \( \eta_0, Q_\eta, \nu_r, Q_r, c_{f,0}, B \) and \( T_0 \) in equations (1) and (6) by using multi-parameter regression analysis. This is an equation of Bernoulli [18] of the 2\(^{nd}\) order.

Angell [19] has pointed out also 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 (7):

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

where \( m_A \) is the melt fragility number of Angell and can be used as a measure of the glass forming ability (GFA). Equation (7) bases on the assumption that the melt viscosity of glass forming substances follows Vogel-Fulcher-Tammann (VFT) temperature dependence. In the case of FVM interpretation, the viscosity temperature dependence should be presented by the “hybrid” eq.(3). In this case:

\[
m_A = 0.434 \left[ \frac{B T_g}{T_g - T_o} + \frac{Q_\eta}{RT_g} - 1 \right]
\]

The Free Volume Model interpretation of the experimental data allows to specify the parameters in eq. (6) \( Q_\eta, B \) and \( T_0 \), and \( T_g \) is easily interpreted as the temperature at the cross point of \( \eta_{\text{nonequilibrium}} \) and \( \eta_{\text{quasiequilibrium}} \).

**Experiments**

The alloys were prepared by the arc melting from the high purity at least 99,99 components. The ribbons were made by the typical melt spinning method with the solidification on the brass disc of the 300 mm diameter in the controlled atmosphere of Ar. The rotation speed was 33 m/s. The ribbons were 5 mm wide and 20-30 \( \mu \)m thick. For comparison also massive samples were prepared by the melt suction method 1-3 mm in diameter.

The structure and composition was controlled with the SEM/EDS FEI QUANTA 3D FEGSEM scanning, electron microscope (SEM) equipped with the EDAX EDXS XRD detector. Further, the structure both ribbons and massive samples was investigated by XRD. The diffraction patterns were collected using diffraction of high-energy synchrotron radiation (87.1 keV) in transmission geometry at the HZG materials science beamline P07B at DESY in Hamburg, Germany. To ensure a good statistics and to get rid of texture effect, the sample was continuously rotated 180\(^{\circ}\) around the \( \alpha \)-axis. Such an approach allowed to obtain data from the whole measured volume. Afterwards, the obtained 2D patterns were integrated employing the Fit2D software and showed in a graph of relative intensity vs. 2Theta angle.
photons was limited to $0.5 \times 0.5 \text{ mm}^2$. The detector was placed at a distance of 1100 mm from the sample. The Plexiglas support was used to fit the ribbon samples.

To determine thermal stability of the amorphous ribbons the DSC 404 F1 Pegasus (Netzsch company) and DuPont 910 were used in the temperature range 473-1400 K, with the heating rate 20 K/min and with the controlled Ar gas atmosphere. The ceramic $\text{Al}_2\text{O}_3$ cups were used and to avoid possible oxidation the low vacuum was made before controlled atmosphere was introduced to the measuring cell. Several measurements was performed on the different parts of the ribbons to avoid differences resulting from the slightly different cooling rates. The temperature dependence of $\eta$ were investigated by Perkin Elmer thermo-mechanical device TMS-2 shown in Fig. 1 with a home-made silica glass assembly for high temperature measurements.

In Fig. 1 the supporting silica glass tube (rigid frame) (1), silica glass probe with a hook at the end where the load is applayed (and connecting moving grip to LVDT) (2), furnace (3), unmovable wedge shaped grip of Invar alloy (4), stationary silica glass hook (5), specimen of fixed initial length of 4 mm (6), unmovable wedge shaped grip of Inver alloy (7) and the thermocouple (8) are shown. The special tool, where the ribbon is set to wedge shaped grips with fixed length is shown more clear at Fig. 2.

The measurements were carried out under loads ranging between 50 g and 130 g. The temperature accuracy ($\pm 1\text{K}$) of the TMS-2 was calibrated by using the strips of pure Sn, Pb, Zn and Al of known melting points.
Results

Structure and crystallization process of the ribbons
The experimental composition of the ribbon in wt.%, verified with the EDS is shown in Tab.1.

Table 1 Chemical composition of the investigated alloy in weight %.

<table>
<thead>
<tr>
<th>elements</th>
<th>Experimental composition, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ribbon</td>
<td>Cu</td>
</tr>
<tr>
<td>1</td>
<td>41.9</td>
</tr>
</tbody>
</table>

As was established the V content 1.9 at.% is very near to the assumed 2 at.%, while the Cu/Zr proportion 50.4/47.7 (in at.%) was shifted in the Cu direction, suggesting in case of crystallization the two phase CuZr + Cu_{10}Zr_{7} composition at high temperatures while below 988 K CuZr phase should decompose into Cu_{10}Zr_{7} and CuZr_{2} phases (Fig.3).

Fig 3. Equilibrium Phase diagram of the Cu-Zr binary system [20].

Fig 4. Microstructure on the polished edge section of the investigated ribbon. SEM, BSE mode, magnification 5000x.
The general view of the ribbon in the SEM/BSE technique from the edge side is shown in Fig. 4. At the SEM magnification no crystalline phase was detected. As a powerful tool for the crystalline nano-phase determination the XRD with use of the synchrotron radiation was used (Fig. 5). Two XRD curves are compared in the figure, the upper concerning the investigated ribbon and the bottom the massive, mostly crystalline sample prepared also by the suction method. As is visible from the upper curve the sample reveals amorphous microstructure however very small amount of crystalline phase, marked by arrows in the Fig. 5, were also present. Due to the bottom curve, the nanoparticles may be identified as the CuZr phase. There is no method to estimate the amount of the crystalline phase, however, it’s amount is below 1 vol.%. 

![Fig. 5. XRD on the investigated ribbon (upper curve) revealing amorphous character of the sample and from the “suction cast” massive 3 mm in diameter sample (lower curve) revealing predominant crystallization of the CuZr and Cu10Zr7 phases. Synchrotron radiation.](image)

![Fig. 6a. Glass transition and crystallization process in the investigated ribbon containing 2 at.% of V. DSC DuPont 910.](image)
The heat flow DSC curves are presented in Fig. 6a and b. The effects observed are typical for the metallic glasses. After small relaxation effect the increase of the heat capacity related to the glass transition takes place at 729 K (Fig. 6a insert). The large, primary crystallization effect at 766 K proceeded by the additional exothermic transition which may be related to the growth of the existing nano-crystals of CuZr phase at 747 K (Fig. 6a). The endothermic effect at 1014 K relates to the Cu_{10}Zr_{7} + CuZr_{2} → CuZr transition (Fig. 6b). Melting starts at T_m 1156 K (Fig. 6b). Liquidus temperature T_l was assumed to be at the peak temperature at 1167.9 K.

The characteristic temperatures are given in Tab. 2. Some parameters recognised as related to the glass forming ability are also given in Tab. 2. As is known, there is no universal one. The following parameters were calculated: ΔT_{rg} related rather to the stability of the amorphous phase of the glass, T_{rg} connected to the resistivity for the crystallization of the kinetic character and an universal GFA parameter for many glass-forming systems γ = T_x / (T_g + T_l).

Table 2 Characteristic parameters detected from the DSC heat flow signals. Heating rate 20 K/min.

<table>
<thead>
<tr>
<th>Amorphous ribbon</th>
<th>Parameter</th>
<th>Temperature [K]</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>V2</td>
<td>T_g [K]</td>
<td>729.0</td>
<td>devitrification</td>
</tr>
<tr>
<td></td>
<td>T_{x1} [K]</td>
<td>746.6</td>
<td>first crystallization effect</td>
</tr>
<tr>
<td></td>
<td>T_{x2} [K]</td>
<td>766.2</td>
<td>dominant crystallization effect</td>
</tr>
<tr>
<td></td>
<td>ΔH [J/g]</td>
<td>43.5</td>
<td>glass crystallization enthalpy</td>
</tr>
<tr>
<td></td>
<td>T_p [K]</td>
<td>1014.0</td>
<td>Cu_{10}Zr_{7} + CuZr_{2} → CuZr peak transition</td>
</tr>
<tr>
<td></td>
<td>T_m [K]</td>
<td>1155.5</td>
<td>melting temperature</td>
</tr>
<tr>
<td></td>
<td>T_l [K]</td>
<td>1167.9</td>
<td>liquidus temperature</td>
</tr>
<tr>
<td>GFA</td>
<td>ΔT_{rg} = T_x - T_g</td>
<td>17.6</td>
<td>glassy phase stability</td>
</tr>
<tr>
<td></td>
<td>T_{rg} = T_g / T_l</td>
<td>0.624</td>
<td>stability against crystallization</td>
</tr>
<tr>
<td></td>
<td>γ = T_x / (T_g + T_l)</td>
<td>0.394</td>
<td>calculated glass forming ability</td>
</tr>
</tbody>
</table>
Dynamic viscosity investigations – Experimental procedure

Typical experimental elongation \( (l(T) - l_0) \) temperature (time) curves for the amorphous alloys are shown in Fig. 7.

![Fig. 7 Experimental elongation \( (l(T) - l_0) \) versus temperature curves in various loads for Cu_{40}Zr_{58}V_2 glassy alloy at heating rate at 20 K/min.](image)

The overall strain of a glassy alloy ribbon reached at temperature \( T \) under applied tensile stress at continuous heating conditions is given by:

\[
\varepsilon(T) = \left[ l(T) - l_0 \right] / l_0 = \varepsilon_{el}^{\sigma}(T) + \varepsilon_{am}^{\sigma}(T) + \varepsilon_{rel}^{\sigma}(T) + \varepsilon_{an}^{\sigma}(T) + \varepsilon_{vf}^{\sigma}(T)
\]

(9)

where \( l_0 \) and \( l(T) \) are the initial length and the current length of the specimen at temperature \( T \), respectively, \( \varepsilon_{el}^{\sigma}(T) \) is the elastic strain of the ribbon divided by Young’s modulus of the material \( E(T) \). It is worth adding that \( \varepsilon_{am}^{\sigma}(T) \) represents the possible anelastic contribution to the overall strain, \( \varepsilon_{rel}^{\sigma}(T) \) takes into account the contribution of any relaxation effects to the overall strain, \( \varepsilon_{an}^{\sigma}(T) \) represents the contribution of the thermal expansion to the overall strain, while \( \varepsilon_{vf}^{\sigma}(T) \) takes into account the viscous flow contribution to the overall strain. It is shown that the subtraction of the strains obtained at different loads gives:

\[
\Delta \varepsilon_{1,2}(T) = \varepsilon_{\sigma_1}(T) - \varepsilon_{\sigma_2}(T) \equiv \varepsilon_{\sigma_1}^{vf}(T) - \varepsilon_{\sigma_2}^{vf}(T)
\]

(10)

where \( \Delta \varepsilon_{1,2}(T) \) is caused by the effective stress \( \Delta \sigma_{1,2} = \sigma_1 - \sigma_2 \). Applying the Newtonian relation for viscous flow \( \eta = \tau / \dot{\varepsilon} \) and taking into account that the shear stress \( \tau = \sigma / 3 \) one obtains

\[
\Delta \dot{\varepsilon}_{1,2}(T) = \frac{\Delta \tau_{1,2}}{\eta(T)}
\]

(11)

where \( \Delta \dot{\varepsilon}_{1,2}(T) = \dot{\varepsilon}_1(T) - \dot{\varepsilon}_2(T) \) is difference of the strain rates \( \dot{\varepsilon}_1 \) and \( \dot{\varepsilon}_2 \), caused by the different applied shear stresses \( \tau_1 \) and \( \tau_2 \), while \( \Delta \tau_{1,2} = \tau_1 - \tau_2 \).

The typical temperature dependences of the strain rates \( \Delta \dot{\varepsilon}(T) \) caused by the shear stresses difference \( \Delta \tau_{1-2} = \frac{1}{3} (\sigma_1 - \sigma_2) \) are shown in Fig. 8. These curves are obtained by numerical differentiation of the temperature dependences of the strain differences.
Fig. 8 Temperature dependence of the strain rates obtained at different load differences (100 g -50 g (1); 130 g – 50 g (2), 130-100 g (3)) for Cu_{40}Zr_{58}V_{2} glassy alloy at 20 K/min.

The strain rates increase smoothly up to approximately 730 K for the CuZrV alloy. On reaching these temperatures, a rapid increase in the strain rates is observed because of reaching $T_g$ of the alloy studied. A passage over a maximum is observed after reaching the onset temperature of crystallization.

Fig. 9 illustrates the shear viscosity values calculated in accordance with eq. (11) (points) from strain rates (Fig. 8). The solid line represents the best-fit curve of all data, obtained at the different load differences.

A common feature of the viscosity curves, obtained by measuring under a constant heating rate, is the presence of two almost linear parts and curved transitional portion between them. The steeper part of the temperature dependence is approaching the quasi-equilibrium structural state of under-cooled liquid of the alloys described by the “hybrid” equation (3). The other one in the lower temperature region is the non-equilibrium viscosity of the vitrified alloy. In the temperature range of crystallization beginning, the viscosity values are influenced by the increasing volume fraction of crystallized regions.
In Fig. 10 experimental data (points) are presented together with the viscosity values calculated using the Free Volume Model equations (solid line) for the studied alloys.

A combination of equations (1) and (4) is used to obtain the non-equilibrium viscosity curve and eq. (3) – for obtaining the quasi-equilibrium viscosity curve (steeper curve –broken line). The intersection of the non-equilibrium and quasi-equilibrium curves for studied alloy determines the glass transition temperature $T_g$.

The glass transition temperature, $T_g$ and the value of the viscosity at $T_g$, $\eta(T_g)$, the values of the model parameters in eq.(1), eq.(3) and eq.(4), $\nu$, $Q_r$, $c_{f,o}$, $T_o$, $Q_\eta$, $B$ and $\eta_o$, obtained by the regression analysis of the experimental data are given in Table 3.

**Table 3 Glass transition temperature $T_g$, calculated $m_{\text{Angel}}$ and FVM parameters of the CuZrV metallic glass.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CuZrV</th>
<th>dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$</td>
<td>9.49E+16</td>
<td>1/s</td>
</tr>
<tr>
<td>$Q_r$</td>
<td>120,296</td>
<td>kJ/mol</td>
</tr>
<tr>
<td>$c_{f,o}$</td>
<td>2.92E-7</td>
<td>-</td>
</tr>
<tr>
<td>$R$</td>
<td>8,31451</td>
<td>J/molK</td>
</tr>
<tr>
<td>$T_o$</td>
<td>510</td>
<td>K</td>
</tr>
<tr>
<td>$dT$</td>
<td>0.25</td>
<td>K</td>
</tr>
<tr>
<td>$Q_\eta$</td>
<td>255,254</td>
<td>kJ/mol</td>
</tr>
<tr>
<td>$B$</td>
<td>5221</td>
<td>K</td>
</tr>
<tr>
<td>q-value</td>
<td>0.33334</td>
<td>K/s</td>
</tr>
<tr>
<td>$\eta_o$</td>
<td>2,33E-21</td>
<td>Pa s/K</td>
</tr>
<tr>
<td>$m_{\text{Angel}}$</td>
<td>34,56</td>
<td>-</td>
</tr>
<tr>
<td>$T_g$</td>
<td>727</td>
<td>K</td>
</tr>
<tr>
<td>$\eta(T_g)$</td>
<td>9E+10</td>
<td>Pa s</td>
</tr>
</tbody>
</table>
The GFA of the studied alloy was determined on the bases FVM interpreted by the Angell melt fragility number and is given in Table 3.

Summary and Discussion

The composition of the sample revealed to be very near to the nominal one, at the equilibrium state and high temperature the alloy should be composed with the CuZr and Cu_{10}Zr_{7} phases. This was also the phase composition revealed in the rapidly solidified samples 3 mm in diameter, prepared by the melt suction method and should be expected as well in the case of the crystallization of the ribbons from the glassy state. The XRD measurements with use of the synchrotron intensive beam revealed very small amount of the crystalline nano-particles of the CuZr structure. Such small content of the crystalline phase should not have any influence on the amorphous phase properties, e.g. a dynamic viscosity, however proves that even a small V addition may promote crystallization of the CuZr phase from the melt. Lack of the CuZr_{2} phase should suggest also stabilizing influence of the V on the CuZr (β) phase at low temperature range. DSC results revealed two-step crystallization proceeded by the glass transition at 729 K (Tab. 2) what remains in a very good agreement with the \( T_{g} \) determined at 727 K by the rheometric experiments (Tab. 3). The parameters related to GFA presented in Tab. 2 suggest quite large potential for the glassy phase formation [21] in spite of the fact, that the massive samples could not be produced amorphous.

Conclusions

1. The ribbons made from the Cu_{40}Zr_{58}V_{2} alloy by the melt-spoon method revealed amorphous structure.
2. The V addition promotes crystallization of the CuZr (β) ductile phase from the melt and stabilizes it at a low temperature range.
3. The glass transition temperatures \( T_{g} \) for the investigated alloy determined by the DSC and FVM by the thermomechanical analysis are very close at 729 and 727 K respectfully proving the high precision and reliability of the model.
4. The parameters related to GFA determined by FVM model suggest quite large potential for the metallic glassy phase formation.

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