Viscosity of the supercooled liquid in multi-component Zr-based metallic glasses

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Abstract. The effect of Al and Zr on the viscosity of the supercooled liquid in melt-spun Zr-Ti-Nb-Cu-Ni-Al glassy ribbons has been evaluated by parallel plate rheometry. The change of composition drastically affects the viscosity of the samples. The viscosity of the supercooled liquid and the fragility parameter ($D^*$) increase with increasing Al or decreasing Zr contents, indicating an improved glass-forming ability. At the same time, the temperature of the glass transition shifts to higher values. A clear correlation between fragility parameter and glass transition has been found. This correlation provides a guide for the estimation of $D^*$ for this particular system when the glass transition is known.

1. Introduction
Among new potential candidates for engineering applications, multi-component Zr-based metallic glasses have been extensively investigated in recent years thanks to the positive combination of interesting mechanical properties [1-3] with high thermal stability against crystallization and wide supercooled liquid region [4,5]. Changes in composition [6], addition of oxygen [7] and incorporation of transition [8] and noble metals [9] cause variations in the thermal stability and lead to the formation of a metastable quasicrystalline phase (QC) in the first stage of crystallization. The precipitation of second-phase QC particles embedded in the glassy matrix further improves the mechanical properties of the single-phase glassy alloys [10,11]. This gives Zr-based metallic glasses additional application opportunities as precursor for nanocomposite materials. The effectiveness of improvement strongly depends on the volume fraction as well as on the grain size of the phase formed [10-12]. Therefore, the engineering application of this type of composite requires the ability to produce a controlled microstructure. In order to control the microstructure, the knowledge of the thermal stability, the crystallization behavior, as well as the temperature dependence of the viscosity characterizing the material, are a necessary prerequisite. Since thermal stability, microstructure evolution during heating and viscosity are strictly correlated with the chemical composition [13], a detailed knowledge of the influence of composition on these features is very important. Accordingly, the aim of this paper is to investigate the influence of Al and Zr on the viscosity of the supercooled liquid (SCL) for Zr-Ti-Nb-Cu-Ni-Al melt-spun glassy ribbons.

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2. Experimental
Pre-alloyed ingots with nominal composition \((\text{Zr}_{0.616}\text{Ti}_{0.087}\text{Nb}_{0.027}\text{Cu}_{0.15}\text{Ni}_{0.12})_{100-x}\text{Al}_x\) \((x = 7.5, 5, 2.5\) and \(0)\) and \(\text{Zr}_y(\text{Ti}_{0.186}\text{Nb}_{0.055}\text{Cu}_{0.324}\text{Ni}_{0.258}\text{Al}_{0.174})_{100-y}\) \((y = 52, 54.5, 57\) and \(62)\) were prepared from pure elements (purity > 99.9 wt.%) by arc melting in a titanium-gettered argon atmosphere. The ingots were remelted several times in order to achieve homogeneity in composition. Ribbons with a cross section of about 0.05x3 mm\(^2\) were prepared in a single-roller Bühler melt spinner at a wheel velocity of 15 m/s under an argon atmosphere. The amount of oxygen, evaluated by carrier gas hot extraction using a Leco TC-436DR analyzer, was found to be between 0.035 and 0.062 wt.%. The structure of the samples was studied by X-ray diffraction (XRD) using a Philips PW 1050 diffractometer (Co-K\(_\alpha\) radiation). The viscosity of the supercooled liquid as a function of the temperature was measured isochronally (heating rate 20 K/min) by parallel plate rheometry using a Perkin-Elmer TMA7 thermal mechanical analyzer under a purified argon atmosphere. Before each measurement, the samples were first heated above the glass transition to the temperature \(T_x - 20\) K in order to achieve the same relaxed isoconfigurational state and to completely fill the area between the plates.

3. Results and discussion
The characterization of the Zr-Ti-Nb-Cu-Ni-Al glassy alloys prepared by melt spinning has been previously reported [13,14]. However, some key features have to be quoted here. The as-spun ribbons are amorphous and their crystallization behavior is characterized by a distinct glass transition followed by several exothermic events, indicating successive transformations into different phases. The devitrification of the ribbons with high Zr or low Al contents is characterized by the formation of a metastable quasicrystalline phase during the first stage of the crystallization process. With increasing Al or decreasing Zr content the temperature range of stability of the quasicrystals decreases and their formation is progressively hindered. The temperature of the glass transition and the crystallization temperatures related to the crystallization events shift to higher values with increasing Al or decreasing Zr content.

As a typical example, figure 1 shows how the viscosity of the supercooled liquid can be evaluated by parallel plate rheometry measurements. Figure 1(a) displays a characteristic isochronal TMA curve, which represents the variation of the height of the sample as a function of temperature or time. The viscosity \(\eta\) can be derived from the change of the height of the sample versus time through Stefan’s equation [15], where \(F\) is the applied load, \(a\) is the radius of the plates and \(h\) is the height of the sample. This allows viscosity measurements in the range from \(10^5\) to \(10^9\) Pa s [15,16].

As the glass transition temperature \((T_g)\) is reached and the glassy solid transforms into the SCL, the curve in figure 1(b) displays a strong viscosity drop. At \(T_x\), when the crystallization sets in, the viscosity abruptly

![Figure 1](image)

**Figure 1.** Derivation of the viscosity from parallel plate rheometry measurements through Stefan’s equation.
increases with increasing temperature, indicating the loss of liquid-like behavior. The minimum value of the viscosity, i.e. $T_x$ in figure 1(b), (not shown here) increases with increasing Al or decreasing Zr content, indicating a strong composition dependence of the viscosity. The values of $T_g$ and $T_x$ evaluated from the viscosity measurements are in good agreement with the data determined from constant-rate heating DSC scans [13,14] given the different heating rate used for the experiments (20 K/min for $\eta$ and 40 K/min for DSC).

The viscous flow of the SCL in the temperature range between $T_g$ and $T_x$ can be well described with the Vogel-Fulcher-Tammann (VFT) equation [15], as shown in figure 2(a), where $\eta_0$ is a constant, $D^*$ is the fragility parameter and $T_0$ is the VFT temperature [15]. The concept of fragility, proposed by Angell [17], is a classification scheme describing the effect of temperature on the viscosity. In the VFT equation (figure 2) the VFT temperature $T_0$ is the temperature where the barriers with respect to flow go to infinity and $D^*$ is a measure of the fragility of the (supercooled) liquid. It is found that $D^*$ is on the order of 2 for the most fragile liquids and yields 100 for the strongest glass formers, such as SiO$_2$ [18].

In the present work, the Zr-Ti-Nb-Cu-Ni-Al glassy ribbons are characterized by values of $D^*$ ranging between 5 and 11 (figure 2(b)), indicating that this type of metallic glass is rather fragile. The fragility parameter as well as the glass transition temperature increase linearly with increasing Al or decreasing Zr content, which suggests a correlation between $D^*$ and $T_g$. From this correlation the empirical equation $D^* = 0.087 (T_g - 537)$, linking the fragility parameter to the glass transition, has been derived. This equation provides a guide for the estimation of $D^*$ for this particular system when the glass transition is known.

Figure 3 shows the fragility parameter $D^*$ as a function of the glass transition temperature $T_g$ for different metallic glasses. Al-based glasses and the present Zr-Ti-Nb-Cu-Ni-Al ribbons both belong to the fragile-type of metallic glasses, which display a fragility parameter below 12. The low values of $D^*$ characterizing these metallic glasses is a signal of their poor glass-forming ability. On the other hand, Zr-Ti-Cu-Ni-Be and Zr-Cu-Ni-Al metallic glasses, which can be cast into fully glassy samples of several millimeters, are characterized by values of $D^*$ exceeding 20 and, therefore, can be considered as strong glasses.

As already mentioned, the variation of Al or Zr content drastically affects the thermal stability as well as the microstructure evolution upon heating [13,14]. Increasing Al or decreasing Zr shifts $T_g$ and $T_x$ to...
Gher temperatures and increases both the viscosity and the fragility parameter of the supercooled liquid. Most likely, the increase of Al or the decrease of Zr content both lead to the increase of the packing density of the amorphous solid. In turn, this may increase the viscosity and enhance the thermal stability, therefore, leading to an increase of $T_g$ and $T_x$ as well as of $D^*$. This is corroborated by the XRD investigations for the as-spun ribbons, revealing that the values of the scattering vector ($q_p = 4\pi \sin \theta_{\text{max}} / \lambda$) related to the position of the first diffuse amorphous diffraction maximum shifts to higher values with increasing Al or decreasing Zr content [figures 4(a) and 4(b)], which indicates that varying the amount of Al or Zr induces shorter interatomic distances, therefore, increasing the packing density.

4. Summary
Zr-Ti-Nb-Cu-Ni-Al glassy ribbons with different Al and Zr content have been produced by melt spinning and the effect of composition on the viscosity of the supercooled liquid has been investigated by parallel plate rheometry. The fragility parameter ($D^*$) has been derived from viscosity measurements through the Vogel-Fulcher-Tammann equation, which describes well the viscous flow

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Fragility parameter $D^*$ as a function of the glass transition temperature for different metallic glasses.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Effect of (a) Al and (b) Zr content on the scattering vector $q_p = 4\pi \sin \theta_{\text{max}} / \lambda$, related to the position of the first diffuse amorphous diffraction maximum.}
\end{figure}
in the supercooled liquid regime. The results indicate that the variation of Al and Zr significantly affects the viscous flow of the melt-spun glassy ribbons. The ribbons are characterized by values of $D^*$ ranging between 5 and 11, indicating that this type of metallic glass is fragile. The fragility parameter as well as the glass transition temperature increase linearly with increasing Al or decreasing Zr contents, which suggests a correlation between $D^*$ and $T_g$. From this correlation the empirical equation $D^* = 0.087 (T_g – 537)$, linking the fragility parameter to the glass transition, has been derived. This equation provides a guide for the estimation of $D^*$ for this particular system when the glass transition is known.

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