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Dynamic fragility and reduced glass transition temperature as a pair of parameters for estimating glass forming ability

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ABSTRACT

The paper considers the development of the glass forming ability (GFA) parameter proposed by Senkov $F_1 = (T_g - T_o) / (0.5(T_l + T_g) - T_o)$ (where T_g is glass transition temperature, T_l is liquidus temperature and T_o is the temperature at which the configurational entropy becomes zero). As a result of more accurate development we introduced the parameter $F_2 = 16F_1 - \log 0.5(T_l - T_g) - 14$ that has similar correlation with the critical cooling rate R_c as F_1. The advantage of F_2 in relation to F_1 is that this parameter is more sensitive. Starting from the idea that fragility and glass forming ability should be related, we develop a relation from which the GFA parameter $F_K = (T_g - T_o) / (T_l - T_o)$, that was presented only as idea by Takeuchi et al., follows. The nature of F_K is different from the reduced glass transition temperature T_{rg} and there is no correlation between these two parameters. The influence that T_{rg} has on GFA has been taken into account by defining a new parameter $F_{KA} = 16F_K / 17 + T_{rg} / 17$. The parameter F_{KA} has the best correlation with R_c for a large group of metallic and nonmetallic glasses ($R^2 = 0.951$). The parameters F_1 and F_K exactly indicate that in the case when different glass forming alloys have the same R_c, the relationship between fragility and reduced glass transition temperature $1/T_{rg} = const/m + 1$ is fulfilled. When T_{rg} is a constant, the parameters F_1, F_K and F_{KA} are single functions of fragility and behave as $1/m$.

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1. Introduction

Glass forming ability (GFA) is the easiness to vitrify a liquid on cooling. The main indicator of GFA is the critical cooling rate R_c, above which no crystallization during solidification can occur. R_c represents the minimum cooling rate necessary to obtain fully amorphous solid from melts. Lower R_c correlates to higher GFA, but the basic problem is that R_c is generally difficult to measure [1–4]. For this reason, many studies have introduced glass stability parameters (GS), which are based upon the characteristic temperatures, and then tried to correlate these parameters with the critical cooling rate. The characteristic temperatures can be determined by standard DTA and DSC measurements, and as a result, GS parameters are easy to obtain. A satisfactory degree of correlation between the determined GS parameter and R_c would allow one to use the given GS parameter to assess GFA. The most popular are those GS parameters that involve three characteristic temperatures: T_g — glass transition temperature, T_x — onset temperature or T_c — maximum of the crystallization peak temperature, and T_m — melting temperature or T_l — liquidus temperature. The Hruby parameter [5] $K_H = (T_x - T_g)/(T_m - T_x)$ and the parameter proposed by Lu and Liu [6,7] $K_{LL} = T_x/(T_g + T_l)$ are among the best known and have been widely used. Recently, a number of new GS parameters that involve three characteristic temperatures have been proposed [8–15] for estimating GFA. GS parameters that include only two characteristic temperatures are also used with variable success. The most popular among them are supercooled region $\Delta T_{xg} = T_x - T_g$ and reduced glass transition temperature $T_{rg} = T_g/T_l$.

It is well known that glass forming ability is related to liquidus viscosity η_L. Sarjeant and Roy [16] proposed an equation in which critical cooling rate is related to liquidus viscosity η_L, melting temperature T_m and molar volume V. Ota and Wakasugi [17] obtained R_c–η_L diagrams for some borate systems. In this work and the work of Wakasugi et al. [18] it was found that the ratio T_x/T_l increases with the increase in viscosity. On the other hand, the authors [17] obtained linear relationship between R_c and T_x/T_l for the considered systems and proposed T_x/T_l as the GFA parameter.

High viscosity generally is related to good glass forming alloys and their liquids are characterized as "strong". On the other hand, there are marginal glass formers with more fragile liquids and low viscosity. "Strong" liquids exhibit Arrhenius behavior of viscosity with temperature, while the plots of "fragile" liquids show deviations.

According to Angell [19–23], the fragility index m is the slope of the viscosity curve near glass transition temperature:

$$m = \left.\frac{d(\log\eta)}{d\left(T_g/T\right)}\right|_{T=T_g}. \tag{1}$$

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The large m value indicates that the liquid behaves fragile.

There are only a few studies that analyze the correlation between fragility and GFA.

It has been suggested in [24,25] that GFA is a function of fragility and reduced glass transition temperature T_{rg}. Senkov [26] recently studied this problem using temperature dependence of relaxation time τ for glass forming liquids as a starting point

$$\tau = \tau_o \exp\left(\frac{DT_o}{T - T_o}\right). \quad (2)$$

The constant D and the pre-exponential factor τ_o, as well as the finite temperature T_o at which the configurational entropy becomes zero, are three parameters that can be determined by fitting. It was found that there exists a correlation between the critical cooling rate and fragility of glass forming liquids in combination with reduced glass transition temperature. The author proposed a new glass forming ability parameter $F_1 = \frac{T_g - T_o}{0.5(T_l + T_g) - T_o}$.

The logarithm of viscosity $\log \eta$ is usually plotted as a function of T_g-scaled inverse temperature that is a function of T_g/T and is called the Angell plot. Takeuchi et al. proposed in [27] the $T_g - T_o$ scaled Vogel–Fulcher–Tammann (VFT) plot instead of the Angell plot in order to derive universal features of η for the VFT-type glassy materials. The authors obtained that some of the investigated alloys show a tendency to increase the $(T_g - T_o)/(T_l - T_o)$ value with decreasing critical cooling rate R_c. Therefore, in [27] it has been suggested that the relation $(T_g - T_o)/(T_l - T_o)$ can be used as the GFA parameter. The Angell plot is incorporated in the $T_g - T_o$ scaled VFT plot and follows from it in the case of $T_o = 0$. For this reason the authors assumed that the parameter $(T_g - T_o)/(T_l - T_o)$ in the $T_g - T_o$ scaled VFT plot has the role of the parameter T_g/T_l in the Angell plot.

In this work we consider the development of the parameter F_1 and take into account the terms that were omitted in [26]. The GFA parameter F_2, which is a result of our development is more sensitive than F_1. On the other hand, starting from the idea that fragility and glass forming ability should be related, we will develop a relation from which the parameter $F_K = (T_g - T_o)/(T_l - T_o)$ follows. This was presented only as idea in [27] but, contrary to the opinion of Takeuchi et al., we will not relate this parameter to T_g/T_l. Taking into account that T_g/T_l should have the influence on GFA, we will define a new parameter F_{KA}. This parameter, besides the relation $(T_g - T_o)/(T_l - T_o)$, also includes reduced glass transition temperature as an additional term.

2. Theoretical background

2.1. The parameter F_2

Eq. (2) can be rewritten in a logarithmic form. By using the expression for D [26]

$$D = \frac{m_{\min}\left(T_g - T_o\right)}{T_o} \ln 10 \quad (3)$$

it follows that

$$\log\frac{\tau}{\tau_o} = m_{\min}\frac{T_g - T_o}{T - T_o} \quad (4)$$

where $m_{\min}$ is the minimal value of the fragility index which is expressed as $m_{\min} = \log \tau_g / \tau_o$. It was assumed that $\tau_g = 100$ s and $\tau_o \approx 10^{-14}$ s and with these values it holds that $m_{\min} \approx 16$.

From the time temperature transformation (TTT) diagram [28], the critical cooling rate R_c can be defined as

$$R_c \approx \frac{T_l - T_n}{t_n} \quad (5)$$

where t_n is the minimum time necessary to start crystallization and T_n is the corresponding "nose" temperature. Senkov assumed that t_n is proportional to the relaxation time τ_n of the supercooled liquid at $T = T_n$. As a result it holds that

$$R_c \approx \frac{T_l - T_n}{\tau_n}. \quad (6)$$

Rewriting this expression in a logarithmic form, we obtain

$$\log R_c \approx \log(T_l - T_n) - \log \tau_n. \quad (7)$$

The relaxation time τ_n can be expressed from Eq. (4) as

$$\log \tau_n = m_{\min}\frac{T_g - T_o}{T_n - T_o} + \log \tau_o. \quad (8)$$

Substituting this in Eq. (7) for critical cooling rate we obtain

$$\log R_c \approx \log(T_l - T_n) - m_{\min}\frac{T_g - T_o}{T_n - T_o} - \log \tau_o. \quad (9)$$

The "nose" temperature T_n is usually obtained as an average temperature between T_g and T_l [26] that is $T_n = 0.5\,(T_l + T_g)$, thus for R_c it holds that:

$$\log R_c \approx \log 0.5\left(T_l - T_g\right) - m_{\min}\frac{T_g - T_o}{0.5\left(T_l + T_g\right) - T_o} - \log \tau_o \quad (10)$$

Taking into account the already mentioned values $m_{\min} \approx 16$ and $\log \tau_o = -14$, we obtain the following relationship for R_c

$$\log R_c \approx \log 0.5\left(T_l - T_g\right) - 16\frac{T_g - T_o}{0.5\left(T_l + T_g\right) - T_o} + 14. \quad (11)$$

As the glass forming ability increases with decreasing R_c, it is common to define GFA parameter by an expression in which the parameter is proportional to minus $\log R_c$. Among the large number of GFA parameters, most of them are such that their values increase with decreasing R_c. From Eq. (11) we will define a new GFA parameter F_2 and will assume that $F_2 \approx -\log R_c$. Taking into account all three terms in Eq. (11), we define the parameter F_2 as

$$F_2 = -\log 0.5\left(T_l - T_g\right) + 16\frac{T_g - T_o}{0.5\left(T_l + T_g\right) - T_o} - 14. \quad (12)$$

The difference between the parameter F_2 and the criterion F_1 which has been proposed by Senkov is easy to notice. F_1 was defined in such a way that only the second term from Eq. (11) has been taken into account, that is

$$F_1 = \frac{T_g - T_o}{0.5\left(T_l + T_g\right) - T_o}. \quad (13)$$

The third term in Eq. (12) ($\log \tau_o = -14$) could be neglected in the GFA parameter, because it only causes translational displacement. In contrast, the first term can introduce a significant difference in the values of the GFA parameter and correlation with R_c, because this term includes the temperatures T_l and T_g. As a result, the parameter F_2

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