Normalized value of K_{gl} parameter of glass formation ability

The parameter $K_{gl} = (T_x - T_g)/(T_m - T_x)$, introduced by Hrubý [1], is not an absolute indicator of the glass-formation ability (GFA). Being scanning-rate-dependent [2], it is only a relative measure of the ease of vitrification. According to Thornburg [2], the variation of K_{gl} with the scanning rate, β, results from the strong dependence of the devitrification onset temperature, T_x on β, while the melting temperature, T_m, as well as the glass transition temperature, T_g, remain nearly constant. These assumptions have been confirmed for glassy As_2SeTe_2 alloy. However, our results obtained for eutectic Te–Ge alloy, vitrified by both splat- and water-quenching methods, have shown a strong dependence of T_g on β, even in as narrow a range of β as 1.25 to 10° C min^{-1} [3]. Experiments were performed within a scanning rate range of 1.25 to 80° C min^{-1} [3, 4]. We present, therefore, further evidence for the dependence of K_{gl} on the scanning rate, resulting not only from the $T_x(\beta)$ relationship, but also from the existence of a defined $T_g(\beta)$ function [3, 5].

The experimental results obtained for splat- and water-quenched samples are presented in Fig. 1. It is surprising that for the same material (glass of composition $Te_{85}Ge_{15}$ at.%) the glass formation ability, expressed by the K_{gl} parameter, differs depending on the glass preparation technique. The differences increase with a rise of the scanning rate. Therefore, the values of K_{gl}, calculated from the T_x and T_g data, determined at an arbitrarily chosen scanning rate β, are meaningless. The most often used scanning rates are 10 and 20° min^{-1}; as may be seen in Fig. 1, for these β-values, splat- or water-quenched glasses of the same composition exhibit differences in the glass formation ability. Hence, the K_{gl} parameter cannot serve as a comparative indicator of the ease of vitrification of various materials, as long as the DSC-results remain non-normalized.

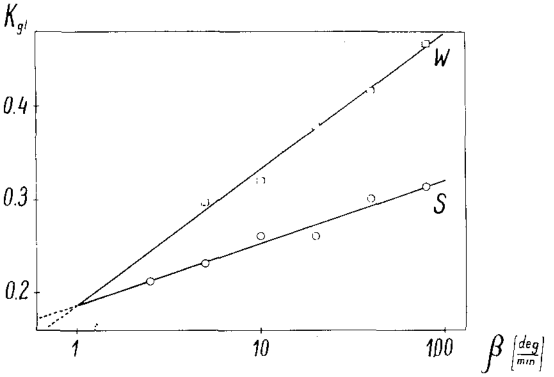

Figure 1 K_{gl} parameters calculated from DSC data for eutectic Te–Ge alloy, obtained in the glassy state by splat- and water-quenching. Equations are given in the text. Normalized K_{gl} parameter amounts to 0.18.

Previous results have shown that the mathematical expression $T = A + B \log \beta$ holds good for both the glass transition temperature, T_g [3, 5], and devitrification temperature, T_x [4], the slope B being higher for $T = T_x$ than for $T = T_g$ (i.e. $B_x > B_g$). This is true for splat- and water-quenched samples, denoted by S and W, respectively. However, for glass transition, $B_S > B_W$, whereas for the onset of devitrification, $B_S \cong B_W$. The above relationships become clear, when the cooling rate, R, of the melt during glass formation and the heating rate, β, during DSC experiments are compared. In the case of splat-cooled samples $R \gg \beta$, whereas for the water-quenched samples $R \cong \beta$. Hence, configurational changes within the glass transition region will be more sensitive to β in the case of the more non-equilibrated splatted glasses than for water-quenched ones. Differences in the initial cooling rate R influence, to a lesser degree, the start of devitrification (which takes place after glass transition if the latter becomes manifest at all), since devitrification is a monotropic process, while glass transition proceeds via a metastable super-cooled liquid.

Plots of K_{gl} versus c give straight lines, according to the least squares fit:

$$K_{gl_S} = 0.186 + 0.068 \log \beta \quad (\text{S.D.} = 0.0067),$$

$$K_{gl_W} = 0.187 + 0.146 \log \beta \quad (\text{S.D.} = 0.0068),$$

for splat- and water-quenched samples, respectively. These lines intersect at $\beta \cong 1$. Therefore, only for $\beta = 1$ may the value of K_{gl} be comparable for various materials, being independent of the vitrification method. This is in agreement with the previous conclusions concerning the necessity of normalization of the DSC results

[3]. However, it is suggested that even K_{gl} normalized to $\beta = 1$ represents only a comparable experimental parameter, without any deep physical meaning. This is the case, since the T_g values determined by DSC fail to be the real glass formation temperatures for glasses obtained at $R \gg \beta$ (e.g. splats). In this case the glass transition temperature determined by DSC represents the low-temperature edge of the transformation region, being lower than the real glass formation temperature [3], whereas the T_x value is the real temperature of the onset of devitrification (being a measure of the thermal stability of glassy state). These T_x values also have to be normalized to $\beta = 1$, for comparison of the thermal stability of various materials.

The assumption about the constancy of the melting temperature, T_m, seems to be of a general nature. In the present calculations of K_{gl} for Te–Ge alloy, the value of T_m was taken from the equilibrium diagram, and confirmed experimentally. Variations in T_m within the whole scanning rate range do not exceed the experimental error, while those for T_g and T_x amount to 27° and 42°, respectively.

In summary, it is suggested that the K_{gl} parameter, normalized to $\beta = 1$, is accepted as a comparable measure of the vitrification tendency of various materials, although no strictly defined physical meaning can be attributed to K_{gl}. The normalized value of K_{gl} for the eutectic Te–Ge alloy was found to be 0.18.

The present results were obtained on the occasion of systematic studies on transformations in glassy Te–Ge alloy; the results of the latter investigations will be published separately [4].

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On the influence of the flushing fluid during diamond drilling

Since the work of Rehbinder and co-workers became widely known in the late forties [1, 2], there has been a continued interest in the effect of a surrounding liquid environment on the mechanical properties of both metals and non-metals (see for example a recent review by Westwood [3]. In particular, it has been suggested that simple inorganic salts, soaps and other surfactants may be added to the flushing water when drilling rocks in order to produce substantial increases in the rate of penetration. Such increases have indeed been reported by many workers [1, 4–7], but there is some conflicting evidence (8, 9), and no additive is yet used in commercial practice with the specific purpose of exploiting the "Rehbinder effect". The effect was originally explained [1, 2] in terms of a reduction of the fracture surface energy of the rock by an adsorbed ion or compound, but subsequent workers [3, 6] have shown that the explanation may be more complex, and that inter alia, dislocation mobility in the material being drilled may be either increased or decreased by the additive.

In an attempt to clarify this question, we have made simple experiments on both marble (from Lasa, Ticino, Switzerland) and a pink granite (from Bohus, Sweden) with a standard 10 mm diamond-impregnated core drill, using a variety of liquids recommended in the literature. In diamond drilling, the instantaneous speed of advance is approximately proportional to the rotation speed and to the feed pressure, provided that adequate flushing is maintained. This is very important