Thermochimica Acta 510 (2010) 137–143

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Sensitivity of the Hruby, Lu–Liu, Fan, Yuan, and Long glass stability parameters to the change of the ratios of characteristic temperatures T_x/T_g and T_m/T_g

Ana F. Kozmidis-Petrović*

University of Novi Sad, Faculty of Technical Sciences, Trg D. Obradovića 6, 21000 Novi Sad, Serbia

ARTICLE INFO

Article history:
Received 18 March 2010
Received in revised form 4 July 2010
Accepted 6 July 2010
Available online 14 July 2010

PACS:
64.70.kj
64.70.pe
64.70.ph
64.70.Q–

Keywords:
Glass stability
Sensitivity
Supercooled region
Reduced glass transition temperature
Glass-forming ability

ABSTRACT

The glass stability (GS) parameters, recently introduced by Fan (Φ), Yuan (β) and Long (ω), which are based upon the three characteristic temperatures: T_g—glass transition temperature, T_x—onset of the crystallization peak (or T_c—maximum of the crystallization peak), and T_m—melting temperature, are expressed in this paper via the ratios $r = T_x/T_g$ and $m = T_m/T_g$. In an earlier paper, we applied the same procedure on the Hruby (K_H), Weinberg (K_W) and Lu–Liu (K_{LL}) parameters. Thus, the GS parameters are more directly related to the supercooled region and reduced glass transition temperature. The objective was to find out how these GS parameters are sensitive to the changes of r and m, and whether this is reflected on the correlation of the given parameter with the glass-forming ability (GFA). The theoretically derived relation $d\beta/dr > dK_H/dr > dK_{LL}/dr$ always holds, and $d\beta/dr > dK_H/dr > d\omega/dr > dK_{LL}/dr$ is also probable, while the order of sensitivity to m is $d\beta/dm > d\omega/dm > dK_{LL}/dm$. Testing on one series of oxide glasses and two series of bulk metallic glasses confirmed in full these relations. The parameter β is the most sensitive to the changes of both r and m, while K_{LL} is generally least sensitive. Partial sensitivity of a GS parameter to r and m is not related to the coefficient of correlation between the GS parameter and GFA, whereas the ratio $dGS/dr : dGS/dm$ can explain the magnitude of the correlation coefficient.

1. Introduction

Glass stability (GS) on heating is assessed on the basis of various parameters. Those relying on three characteristic temperatures: T_g—glass transition temperature, T_x—onset of the crystallization peak (or T_c—maximum of the crystallization peak), and T_m—melting temperature, have been used most widely [1]. Since these temperatures can be easily determined by standard DTA and DSC measurements, these GS parameters can also be easily obtained. On the other hand, the glass forming ability (GFA) is estimated upon the critical cooling rate R_c, maximal section thickness, or diameter D_{max}. The R_c is a quantity hard to measure and also the D_{max} cannot be measured in a sufficiently precise way [2–4]. Hence, of essential importance are the correlations between the GS parameters expressed via characteristic temperatures and GFA [2–9]. A satisfactory degree of correlation between the determined GS parameter and R_c (that is D_{max}) would allow one to use the given GS parameter to assess the GFA. Besides the well-known parameters such as the supercooled region $\Delta T_{xg} = T_x - T_g$, reduced glass transition temperature $T_{rg} = T_g/T_m$ [10], Hruby parameter $K_H = (T_x - T_g)/(T_m - T_x)$[11], Lu and Liu parameter $K_{LL} = T_x(T_g + T_m)$ [6,12], a number of new GS parameters for assessing the GFA have been recently proposed. Thus, Fan et al. [13] proposed the parameter $\phi = T_{rg}(\Delta T_{xg}/T_g)^a$, where $a = 0.143$; Yuan et al. [2] proposed the parameter $\beta = T_x T_g/(T_m - T_x)^2$, and Long et al. [14] introduced the parameter $\omega = T_g/T_c - 2T_g/(T_g + T_m)$. In our previous work [15], by introducing the substitutions $r = T_c/T_g$ (or $r = T_x/T_g$) and $m = T_m/T_g$ we showed that K_H and K_{LL} can be expressed via these temperature ratios. At that, the use of T_c instead of T_x, as was demonstrated in [5,9], does not affect significantly the obtained results. In this way, by using the substitutions r and m, the GS parameters are expressed indirectly via the reduced glass transition temperature and supecooled region. Because the parameter m represents the reciprocal value of T_{rg}, and the parameter r can be correlated to ΔT_{xg}, as was shown in the work of Lu and Liu [6] or in a recent work by Zhang et al. [16]. Namely, in order to enable the comparison for different glasses, the value of the supercooled region is divided by T_g [6], which gives $(T_x - T_g)/T_g = r - 1$. In [16], the authors introduced the factor of crystallization resistance $T_g/(2T_x - T_g)$, which can be expressed as $1/(2r - 1)$. The introduction of r and m allows us to present GS parameters in the form of 3D graphs, of which those for K_H and K_{LL} were shown in our previous work [15]. The reported graphs made it possible to observe the difference in the sensitivity of these two parameters to the changes in r and m. As we

* Tel.: +381 216350770; fax: +381 216350770.
E-mail address: analeto@yahoo.com.

0040-6031/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2010.07.007

have shown, the relative changes of the K_{LL} parameter (dK_{LL}/K_{LL}) are smaller compared to those of the Hruby and Weinberg [17] parameters, whose sensitivity was also analyzed. The objective of the present work was to establish how much the change in r and m, each in its turn, influences the changes in GS parameters. In other words, the aim was to find out which of the GS parameters is more sensitive to the change of the supercooled region and which to the T_{rg} value. To put it in another way, we wanted to identify the GS parameters that are more sensitive to the changes in r, and those which are more sensitive to the change in m, including their ratio, as well as to establish whether this is reflected on the correlation between the given parameter and GFA. Since the quantities r and m are directly related to ΔT_{xg} and T_{rg}, the sensitivity of GS parameters to the changes in r and m reflect the sensitivity to the change in the supecooled region and T_{rg}. Nascimento et al. [9] showed that for the oxide glasses considered, in contrast to T_{rg}, the supercooled region correlated well with GFA. For these glasses, a very good correlation was found between the Hruby parameter and GFA. Also, very good correlations between K_{LL} and GFA have been found for the oxide glasses from [9] and for those from [18]. With bulk metallic glasses (BMGs), the GFA is often estimated based on the values of ΔT_{xg} and T_{rg} [16,19,20], although for bulk glasses there exist different findings for the correlation between these two parameters and GFA [21]. Studies [21,22] have shown that T_{rg} has a better correlation with GFA than with ΔT_{xg}. One of the results of the work by Lu and Liu [6] is that the supecooled region alone cannot effectively reflect the relative GFA for metallic glasses, as well as that GFA of metallic glasses is somewhat more dependent on T_{rg}. The studies presented in [6] showed that K_{LL} is more strongly correlated with GFA than with T_{rg}. Bearing in mind their good correlations with the GFA, the K_H and K_{LL} parameters were used in the present work to determine their sensitivity to the partial changes of r and m. Since the newly defined parameters Φ, β and ω also showed good correlation with GFA for BMGs [13,2,14], we also included them in our analysis.

Let us point out that the newly defined parameters that appeared in [16,23–25] will be the subject of our future analysis.

2. Theoretical derivation

As was shown in our previous paper [15], when K_H and K_{LL} are expressed via r and m one obtains

$$K_H = \frac{r-1}{m-r} \tag{1}$$

$$K_{LL} = \frac{r}{m+1} \tag{2}$$

The relations from [13,2,14], defining the parameters Φ, β and ω can also be transformed and expressed via r and m, which gives

$$\phi = \frac{(r-1)^a}{m} \tag{3}$$

$$\beta = \frac{r}{(m-r)^2} \tag{4}$$

$$\omega = \frac{1}{r} - \frac{2}{m+1} \tag{5}$$

In order to determine the change of the investigated GS parameters in relation to r and m, we take derivatives of Eqs. (1)–(5) with respect to both r and m. Thus we obtain

$$\frac{dK_H}{dr} = \frac{m-1}{(m-r)^2} \tag{6}$$

$$\frac{dK_H}{dm} = -\frac{r-1}{(m-r)^2} \tag{7}$$

$$\frac{dK_{LL}}{dr} = \frac{1}{m+1} \tag{8}$$

$$\frac{dK_{LL}}{dm} = -\frac{r}{(m+1)^2} \tag{9}$$

$$\frac{d\phi}{dr} = \frac{a}{m}(r-1)^{a-1} \tag{10}$$

$$\frac{d\phi}{dm} = -\frac{(r-1)^a}{m^2} \tag{11}$$

$$\frac{d\beta}{dr} = \frac{m+r}{(m-r)^3} \tag{12}$$

$$\frac{d\beta}{dm} = -\frac{2r}{(m-r)^3} \tag{13}$$

$$\frac{d\omega}{dr} = -\frac{1}{r^2} \tag{14}$$

$$\frac{d\omega}{dm} = \frac{2}{(m+1)^2} \tag{15}$$

We are going to compare only the absolute values of the changes, so that the minuses on the right-hand sides of Eqs. (7), (9), (11), (13) and (14) will be omitted, since they suggest only the direction of the change.

The first step is to find out whether the given GS parameter is more sensitive to the changes of r or m, that is to determine the ratio $dGS/dr{:}dGS/dm$ for each particular GS parameter. After simple rearrangement of Eqs. (6)–(15) we obtain

$$\frac{dK_H}{dr} : \frac{dK_H}{dm} = \frac{m-1}{r-1} \tag{16}$$

$$\frac{dK_{LL}}{dr} : \frac{dK_{LL}}{dm} = \frac{m+1}{r} \tag{17}$$

$$\frac{d\phi}{dr} : \frac{d\phi}{dm} = \frac{am}{(r-1)} \tag{18}$$

$$\frac{d\beta}{dr} : \frac{d\beta}{dm} = \frac{r+m}{2r} \tag{19}$$

$$\frac{d\omega}{dr} : \frac{d\omega}{dm} = \frac{(m+1)^2}{2r^2} \tag{20}$$

Since $m>1$, $r>1$ and $m>r$, the right-hand side of Eqs. (16), (17) and (19) is always greater than 1. This means that K_H, K_{LL} and β parameters are more sensitive to the changes in relation to r than in relation to m, and it always holds that

$$\frac{dK_H}{dr} > \frac{dK_H}{dm} \tag{21}$$

$$\frac{dK_{LL}}{dr} > \frac{dK_{LL}}{dm} \tag{22}$$

$$\frac{d\beta}{dr} > \frac{d\beta}{dm} \tag{23}$$

In contrast to K_H, K_{LL} and β, expressions (18) and (20) do not allow us to determine in a straightforward way whether Φ and ω are more sensitive to the change in r or in m. From Eq. (18) it follows that if $m>(r-1)/a$, then $d\phi/dr>d\phi/dm$, whereas, on the basis of Eq. (20), it is necessary that $m > r\sqrt{2}-1$ in order to have $(d\omega/dr)>(d\omega/dm)$. To assess these relations it is necessary to take the concrete values for r and m that appear in BMGs or oxide glasses. Hence we will examine on the concrete examples the sensitivity of the parameters Φ, and ω to the changes of r and m.

2.1. Comparison of the sensitivity of GS parameters to r

Further, we want to determine which of the examined GS parameters are more or less sensitive in relation to the changes of r and m. In other words, we want to find out whether it is possible to establish an order of their sensitivity to each of these two quantities.

A comparison of Eqs. (6) and (12) clearly shows that $d\beta/dr > dK_H/dr$, because $(m-r)^3 < (m-r)^2$, and because $m+r > m-1$.

If the changes dK_H/dr and dK_{LL}/dr are compared, then, on the basis of expressions (6) and (8), the following condition should be fulfilled $(m-1)/(m-r)^2 > 1/(m+1)$ in order the ratio $dK_H/dr > dK_{LL}/dr$ would hold. The condition expressed by this inequality can be transformed to

$$\frac{m-1}{m-r}\frac{m+1}{m-r} > 1 \tag{24}$$

The condition (24) is always fulfilled because $(m-1)/(m-r) > 1$, and because $(m+1)/(m-r) > 1$.

Hence, it always holds that $dK_H/dr > dK_{LL}/dr$, and it is possible to form the following order of sensitivity of GS parameters with respect to r

$$d\beta/dr > dK_H/dr > dK_{LL}/dr \tag{25}$$

As far as the change of Φ with r is concerned, its position in this order is not quite clearly determined. It is not possible apriori, without taking into account the values of r and m, derive a conclusion on whether $d\phi/dr$ is greater than the changes of the other GS parameters with r or not. The change of the parameter ω with r is somewhat different. By comparing expressions (12) and (14) it can be concluded that it always holds that $d\beta/dr > d\omega/dr$, because $m+r > 1$, and $(m-r)^3 < r^2$. From expressions (6) and (14) it is obvious that $dK_H/dr > d\omega/dr$ since $(m-1)/(m-r)^2 > 1$ and $1/r^2 < 1$. Also, from the comparison of expressions (8) and (14) it comes out that $d\omega/dr > dK_{LL}/dr$, because the values of r and m that are usually encountered with glasses are such that the necessary condition $r < \sqrt{m+1}$ is satisfied. A possible order of the changes of GS parameters with r is as follows:

$$d\beta/dr > dK_H/dr > d\omega/dr > dK_{LL}/dr \tag{26}$$

2.2. Comparison of the sensitivity of GS parameters to m

By comparing absolute values of expressions (13) and (7) it follows that it always holds that $d\beta/dm > dK_H/dm$, since $2r > r-1$ and $(m-r)^3 < (m-r)^2$, because $m-r < 1$.

Also, it can be seen that absolute value of expression (13) is always greater than the right-hand side of expression (15), so that $d\beta/dm > d\omega/dm$ always holds. By comparing expression (15) with the absolute value of Eq. (9) it is evident that $d\omega/dm > dK_{LL}/dm$, because $2 > r$. Thus, it is possible to establish the following order with respect to the magnitude of the change of GS parameters with m.

$$d\beta/dm > d\omega/dm > dK_{LL}/dm \tag{27}$$

In this order, however, the position of dK_H/dm is not clear. It is only clear that it is smaller than $d\beta/dm$, and its position with respect to the other parameters has to be estimated by taking into account the values of m and r.

By comparing absolute values of expressions (13) and (11) it is evident that $d\beta/dm > d\phi/dm$ because $2r > (r-1)^a$, and $(m-r)^3 < m^2$.

The position of $d\phi/dm$ with respect to the other terms in the relation (27) can be estimated only with the aid of the concrete values for m and r.

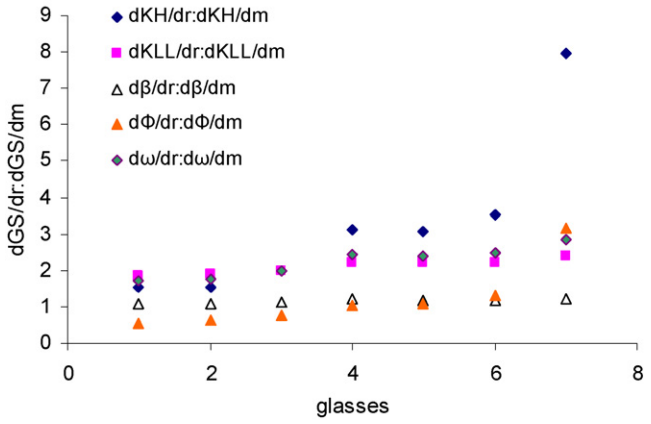

Fig. 1. The ratios $dGS/dr{:}dGS/dm$ ($GS = K_H, K_{LL}, \beta, \Phi, \omega$) for oxide glasses from [9].

3. Testing theoretical results

The results presented in the theoretical part of this study were tested on a series of oxide glasses from the work of Nascimento [9] and BMGs from the works of Long et al. [14] and Yuan et al. [2]. The characteristic temperatures can be found in these works, so that there is no need to list them here. In our tables we presented only the r and m values that were calculated from these temperatures, the values of dGS/dr and dGS/dm, calculated on the basis of expressions from (6) to (15), as well as the ratio $dGS/dr : dGS/dm$. The tables do not show the errors of measurements because the characteristic temperatures that we took over from the mentioned works did not always contain the corresponding measurement errors.

Table 1(a) (see in supplements) lists the values of r, m, dGS/dr and dGS/dm for the oxide glasses from [9], whereas Table 1(b) (see in supplements) gives the ratios $dGS/dr : dGS/dm$ for these glasses. Tables 2(a) and (b) (see in supplements) contain the corresponding values of these quantities for BMGs from [14].

The voluminous results of calculations for the BMGs from [2], which are used to test the outcome of the theoretical part, are not presented in the form of tables but only graphically. Fig. 1 shows the ratios $dGS/dr : dGS/dm$ for the oxide glasses from [9]. The dGS/dr values obtained for 207 BMGs from the work of Yuan et al. [2] are presented in Fig. 2(a), while Fig. 2(b) shows the dGS/dm values for the same glasses. These figures do not show the quantities $d\beta/dr$ and $d\beta/dm$, because their values are much larger than the changes of the other GS parameters. Hence, the $d\beta/dr$ and $d\beta/dm$ for these BMGs are presented in a separate figure (Fig. 2c). Fig. 3 shows the ratio $dGS/dr{:}dGS/dm$ for the BMGs from [2].

4. Discussion

4.1. Oxide glasses

As can be seen from Table 1(a), for all oxide glasses from [9] it holds that $d\beta/dr > dK_H/dr > d\omega/dr > dK_{LL}/dr$. Such relation is in accordance with the prediction of expression (26). The values $d\Phi/dr$ for these glasses except for CAS_2 and LB_2 are smaller even than dK_{LL}/dr. The abrupt change of the value of $d\Phi/dr$ for LB_2 can be explained, using expression (10), by a decrease in the supercooled region and in the value of r. The r value for LB_2 is lower by 10–30% compared to that for the other glasses listed in Table 1(a). As for the sensitivity of GS parameters to m, it can be seen from Table 1(a) that the order is such as predicted by expression (27): $d\beta/dm > d\omega/dm > dK_{LL}/dm$.

From the same table it is also seen that for these glasses holds: $d\beta/dm > dK_H/dm > d\phi/dm > d\omega/dm > dK_{LL}/dm$, the exception being again LB_2. The data in Table 1(a) indicate that the parameter

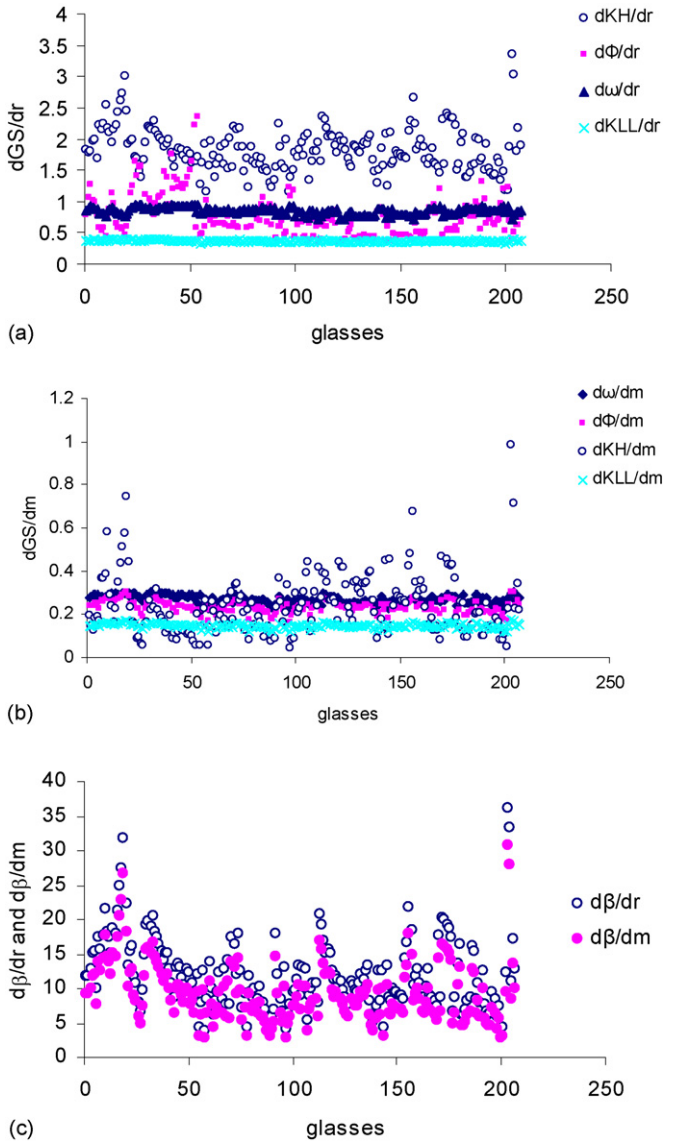

Fig. 2. (a) The changes of GS parameters (K_H, Φ, ω, K_{LL}) with r for BMGs from [2]. (b) The changes of GS parameters (K_H, Φ, ω, K_{LL}) with m for BMGs from [2]. (c) The changes of $d\beta/dr$ and $d\beta/dm$ for BMGs from [2].

β is in some cases even by several hundreds time more sensitive to the changes of both m and r than the other GS parameters.

4.1.1. Correlation with GFA

Based on data from [9], for the glasses from Table 1, we calculated the coefficients of correlation (R^2) of GS parameters with GFA, and obtained the following values K_{LL}—0.984, K_H—0.957, ω—0.969, Φ—0.828, β—0.755, r—0.922, whereas m did not correlate with GFA.

It is evident that r correlates well with GFA of these glasses. From expression (26) it follows that β is more sensitive to the change in r than K_H, K_{LL} and ω, which is also corroborated by the values from Table 1(a). However, as can be seen, the value of R^2 for β is smaller than for the other GS parameters. Thus, the correlation of β with GFA is not, obviously, related to its partial sensitivity to r. On the other hand, with these glasses m does not correlate with R_c. Of all the parameters, β is also most sensitive to m, and $d\beta/dm$ has the largest value. The somewhat smaller value of the R^2 coefficient for β can be explained by its great dependence on m. However, it seems that the correlation of GS and GFA is not influenced by the extent to which some of the GS parameters is partially sensitive to m. Namely, when K_H is concerned, the next value in the order $d\beta/dm > dK_H/dm > d\phi/dm > d\omega/dm > dK_{LL}/dm$ is dK_H/dm, but the parameter K_H correlates very well with R_c.

It is clear that the magnitude of the particular partial sensitivity to r, or m, of the given GS parameter is not related to the degree of its correlation with GFA. It is more probable that this correlation is influenced by the ratio $dGS/dr : dGS/dm$. Such reasoning has also been suggested by the conclusions from [20].

As can be seen from Table 1(b) and Fig. 1, the values of the ratios $dK_{LL}/dr : dK_{LL}/dm$, $d\omega/dr : d\omega/dm$ and $d\beta/dr : d\beta/dm$ are greater than unity. The values of $dK_H/dr : dK_H/dm$ have somewhat larger variations, but they are also greater than one. This means that K_H, K_{LL}, ω and β are more sensitive to the change in r than to the change in m. For K_H, K_{LL} and β this has been predicted in the theoretical part by expressions (21)–(23). As far as the parameter ω is concerned, it is easy to see from Table 1(a) that for all the glasses the condition $m > r\sqrt{2} - 1$, which results from our theoretical derivation, is satisfied. Because of that the change in ω with r is greater than with m. Since only r (and not m) correlates well, it can be supposed that for these GS parameters the R^2 coefficient will be larger because the value of r has a greater influence than m. If we consider the R^2 coefficients, they are larger for K_H, K_{LL} and ω. From Fig. 1 and Table 1(b), we can see that $d\beta/dr : d\beta/dm \approx 1$, which means that β is similar sensitive to the changes in relation to m and r.

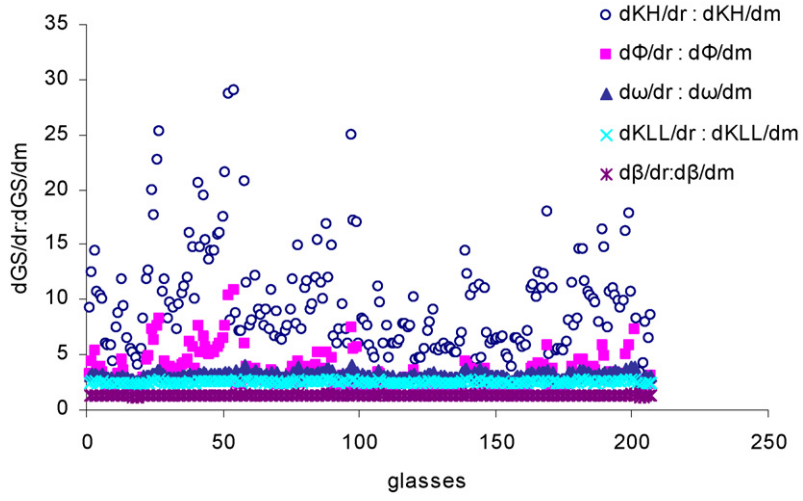

Fig. 3. The ratios $dGS/dr{:}dGS/dm$ ($GS = K_H$, K_{LL}, β, Φ, ω) for BMGs from [2].

The fact that m correlates poorly with GFA, affects also on the correlation of β and its values of R^2.

Similar situation is also with the ratio of the sensitivity of Φ. Its values vary, but for the first three glasses from Table 1(b) it holds that $d\phi/dr : d\phi/dm < 1$. Thus, here too, the influence of m, which does not correlate with GFA, is significant. Hence, one can expect that R^2 for Φ is also smaller than for K_{LL}, K_H and ω, which was also confirmed by our calculation of R^2.

It is a little bit strange that the value of R^2 is smaller for β than for Φ, because the parameter β is always more sensitive to the changes in relation to r than in relation to m (which does not correlate). This topic will be discussed once more, when we will take into account BMGs, too.

4.2. BMGs

From Table 2(a), giving the data for the glasses from [14], as well as from Fig. 2(a) and (c), showing the dGS/dr values for 207 glasses from [2], one can see that the order $d\beta/dr > dK_H/dr > d\omega/dr > dK_{LL}/dr$ always holds. This is in agreement with our theoretical result given by expression (26).

Like with oxide glasses, with BMGs too, the β parameter is more sensitive to the change in r, in some cases by several hundreds times more than the other GS parameters. Then follows K_H, whereas the sensitivities of ω, Φ and K_{LL} are smaller (and with smaller variations of K_{LL} values). The position of the change of Φ with respect to the other parameters is different for the glasses from [14] and [2]. With the former ones, in the majority of cases $d\omega/dr > d\phi/dr > dK_{LL}/dr$, and for the latter ones, the relation $d\phi/dr > d\omega/dr > dK_{LL}/dr$ is more frequent. By comparing expressions (10) and (14) we obtain that the condition $ar^2(r-1)^{a-1}/m < 1$ should be fulfilled in order to have that $d\omega/dr > d\phi/dr$. Knowing that $a = 0.143$, this requirement will be generally fulfilled for large values of m (for a lower T_{rg}) and large values of r (large values of the supercooled region).

As is evident from Table 2(a), this is always fulfilled when $r > 1.064$ for the glasses from [14], whereas for the BMGs from [2] it is fulfilled for $r > 1.072$. However, among the glasses from [2] are often found the glasses with a small value for r, e.g. the majority of glasses with Cu, for which data were taken over from [23,26,27], and for them it holds that $d\omega/dr < d\phi/dr$.

When considering the sensitivity of GS parameters to the change of m, it is evident from Fig. 2(b) and (c), and Table 2(a) that our prediction given by expression (27) is always fulfilled for BMGs too, in the same way as for the oxide glasses, and it holds that $d\beta/dm > d\omega/dm > dK_{LL}/dm$. Again, it can be seen that the values $d\beta/dm$ are in some cases even several hundreds times higher than the changes of the other parameters with m.

As can be seen from Fig. 2(b) and Table 2(a), the values of dK_H/dm show great variations. On the other hand, for the glasses from both [2] and [14], the values for $d\Phi/dm$ and $d\omega/dm$ are very similar.

4.2.1. Correlation with GFA

In the Long's paper [14], one can find values of R^2 coefficients for the correlation between the $T_{rg}(1/m)$, $K_{LL}(\gamma)$, β, ω and Φ parameters and critical cooling rate R_c for the BMGs presented there. For these glasses, we calculated R^2 for both r and K_H. The R^2 values for the glasses from [14] are:

$$T_{rg}(1/m) : 0.753, r : 0.613, K_{LL}(\gamma) : 0.909, \beta : 0.504, \omega : 0.922,$$

$$\Phi : 0.888, K_H : 0.630.$$

Yuan gave, for BMGs in [2], the R^2 coefficients for T_{rg} $(1/m)$, $K_{LL}(\gamma)$, β, Φ, whereas Long et al. [14] calculated the R^2 coefficients for the glasses from [2], among them for $1/\omega$ too. For these glasses we additionally calculated R^2 for r and K_H. In summary, the R^2 values for the glasses from [2] are:

$$T_{rg}(1/m) : 0.380, r : 0.273, K_{LL}(\gamma) : 0.629, \beta : 0.751, 1/\omega : 0.797,$$

$$\Phi : 0.624, K_H : 0.44.$$

As can be seen, for the BMGs considered, r and m show approximately similar correlation with GFA, which is unlike to the oxide glasses, where one of these quantities correlates and the other not. However, neither with BMGs nor with analyzed oxide glasses there is a connection between the partial sensitivity of the GS parameter to r (that is m) and its correlation with GFA. For example, for the parameter K_{LL}, which is (except in some cases), least sensitive to both r and m, the R^2 coefficient is not lowest for either of groups of BMGs.

Like with oxide glasses, the ratio of the parameter sensitivity to r and m, is also indicative for the degree of its correlation with GFA.

As can be seen from Table 2(b), for the BMGs from [14], the highest value of the sensitivity ratio is for the Hruby parameter. The values of $dK_H/dr{:}dK_H/dm$ vary in the interval from 2.5 to 57. From Fig. 3, showing the ratio $dGS/dr{:}dGS/dm$ for the glasses from [2], we can see that the highest value of this ratio is again for K_H, which also exhibits high variations (from 4 to 30). Compared to the other parameters, K_H is in all cases much more sensitive to the changes in r than to the changes in m. Because of that, with these BMGs K_H behaves similarly to r, whereas the influence of m is much weaker. Hence, because of the influence of one parameter, it can be expected that the values of R^2 coefficient for K_H should be lower, and possibly close to the values observed for r itself. If we look at the R^2 values for the glasses from [14] we can see a good agreement between them (r: 0.613, K_H: 0.63). For the glasses from [2], the R^2 for K_H is again the lowest, although somewhat higher than for r. However, here too, the ratios $dK_H/dr{:}dK_H/dm$ are somewhat smaller, that is m participates more in the ratio of sensitivities. Based on Fig. 3 and Table 2(b) we can establish the following relation:

$$dK_H/dr : dK_H/dm > d\omega/dr : d\omega/dm > dK_{LL}/dr : dK_{LL}/dm > d\beta/dr : d\beta/dm \quad (28)$$

As can be seen from the figure and the table, the values of the ratios $d\Phi/dr{:}d\Phi/dm$ also vary.

They are often greater even than $d\omega/dr{:}d\omega/dm$, sometimes smaller than $dK_{LL}/dr{:}dK_{LL}/dm$, never smaller than $d\beta/dr{:}d\beta/dm$, and mainly three times smaller than $dK_H/dr{:}dK_H/dm$.

The all GS parameters are more sensitive in relation to changes of r than of m.

It should be borne in mind that the difference in the correlation of r and m with GFA for both groups of BMGs is not so high. This is different from the situation observed with oxide glasses, for which one parameter (r) correlates well, and the other (m) does not correlate at all. Hence the R^2 values for the correlation of ω, K_{LL}, and even of Φ, cannot reflect the difference in the sensitivity of the ratios $dGS/dr : dGS/dm$, which is not so high for these GS parameters. It is evident from Table 2b and Fig. 3 that the ratios $d\omega/dr{:}d\omega/dm$ and $dK_{LL}/dr{:}dK_{LL}/dm$ are not much different from each other. This means that ω and K_{LL} behave similarly in respect of their combination of sensitivities to r and m. As for the parameter Φ, the values of the ratio $d\Phi/dr{:}d\Phi/dm$ oscillate between the corresponding values observed for ω and K_{LL}. It may be also noted that the values of the R^2 coefficients for Φ are close to those observed for ω and K_{LL}.

As far as the parameter β is concerned, it is similar sensitive to m and to r, and the values for $d\beta/dr{:}d\beta/dm$ are two to three times smaller than the corresponding ratios of ω and K_{LL}. However, this difference in sensitivity is not as large as in the case of K_H. Here, both m and r correlate in a similar way, but it is essential that for the GS

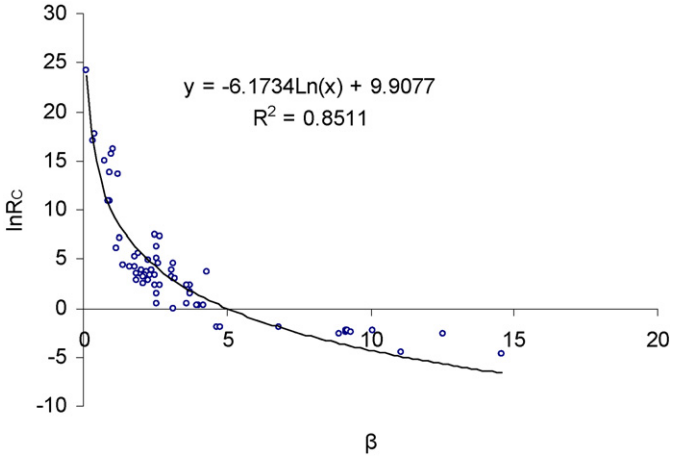

Fig. 4. The logarithmic (ln) correlation between $\ln R_c$ and β for BMGs from [14].

parameters both components are taken in a fairly balanced ratio, that is that none of them is dominant, as is the case, e.g. for K_H. For this reason, the R^2 coefficient for β might be within the limits of the values observed for ω, K_{LL} and Φ. If one considers the R^2 values for the glasses from [2], this is satisfied. However, the corresponding values for BMGs from [14] indicate that the correlation of β is much weaker. Here, something else should be taken into account. The partial sensitivity of β to both r and m is by several hundreds times higher compared to that of the other parameters. When plotting the dependence between R_c and GS parameter, because of the large range of R_c values, it is necessary to present the logarithm of this quantity. The same holds for the parameter β—because of its very high sensitivity, it is also better to present logarithmic (ln) dependence between $\ln R_c$ and β. Fig. 4 shows that correlation between $\ln R_c$ and β for the glasses from [14], with the corresponding R^2 being 0.851. This is a better result than for K_H, and only somewhat worse than for Φ. Let us notice that for the same reasons for the mentioned oxide glasses the logarithmic correlation between $\ln Rc$ and β gives also a higher correlation coefficient (R^2 −0.885). This value is still smaller than the value of R^2 coefficients for K_H, K_{LL} and ω, the parameters which are more dependent on r. In spite of it, R^2 −0.885 is the more significant value than the value of R^2 for the parameter Φ. As we already know for oxide glasses, the following equation $d\beta/dr : d\beta/dm > d\phi/dr : d\phi/dm$ is almost always true and the parameter Φ is more sensitive in relation to m, which does not correlate with GFA. Therefore, this is the result, which can be expected for oxide glasses.

5. Conclusion

- The analyzed GS parameters (K_H, K_{LL}, β, ω, Φ) can be expressed via $r = T_x/T_g$, or $r = T_c/T_g$ and $m = T_m/T_g$, r being related to the supercooled region, and m to the reduced glass transition temperature.
- The GS parameters differ in their sensitivity to r and m. Theoretical derivation showed that the dependence of β on both r and m is most pronounced compared to all the other GS parameters. We showed theoretically that the following relation always holds:
- $d\beta/dr > dK_H/dr > dK_{LL}/dr$, and, bearing in mind the value of r, probably, the following relation too $d\beta/dr > dK_H/dr > d\omega/dr > dK_{LL}/dr$.
- For the sensitivity of GS parameters to m it holds that:

$$d\beta/dm > d\omega/dm > dK_{LL}/dm.$$

- The positions of Φ in the above orders and of K_H in the order of sensitivity to m, depend on both r and m.
- Testing of one series of oxide glasses and two series of BMGs agrees entirely with our theoretical derivation, and corroborates the above order.
- The values obtained in the testing show that β is much more sensitive to the changes in r and m than the other analyzed GS parameters. With the exception of several samples, the least sensitive is K_{LL}. This is important for the application of these parameters in the estimation of GS. For the possibility of a practical application, of essential importance is a sufficient sensitivity of the GS parameter to the change of supercooled region, and reduced glass transition temperature in order to be able to discern the difference between one glass and another.
- The individual partial sensitivity of a GS parameter to r and m is not related to the R^2 coefficient for the correlation of the GS parameter and GFA. The balance of sensitivity of the GS parameter to r and m (the ratio $dGS/dr{:}dGS/dm$) implies the magnitude of the R^2 coefficient. At the same time, the degree of correlation of values r and m with the GFA is significant.
- With the analyzed oxide glasses, r correlates well ($R^2 = 0.922$), whereas m does not correlate with GFA. The R^2 coefficients for the parameters K_H, K_{LL} and ω, which depend most on r, have also the highest value.
- For BMGs, we can establish the following order of sensitivity ratios

$$dK_H/dr : dK_H/dm > d\omega/dr : d\omega/dm > dK_{LL}/dr : dK_{LL}/dm > d\beta/dr : d\beta/dm.$$

- The all parameters are more sensitive to the change of r than of m. For the parameter K_H it often holds that $dK_H/dr{:}dK_H/dm \gg 1$. K_H is much more sensitive to the change of one parameter (r) than is the case with ω, Φ, β and K_{LL}. Because of that, the R^2 for the correlation of K_H with GFA is smaller, and it is being close to that for r itself. For BMGs, the difference in the correlation of the particular r and m values is not as large as for the tested oxide glasses. Thus, the difference in sensitivity for the parameters ω, Φ, K_{LL} and β is not sufficient to be reflected on R^2.
- For the parameter β, because of its very high sensitivity, the correlation with the critical cooling rate is better expressed as a logarithmic than the linear dependence.

Acknowledgements

This work has been carried out with the financial support of the Serbian Ministry of Science and Technological Development, within the project "*Amorphous and Nanostructural Chalcogenides*", No. 141026.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2010.07.007.

References

[1] I. Avramov, E.D. Zanotto, M.O. Prado, J. Non-Cryst. Solids 320 (2003) 9–20.
[2] Z.Z. Yuan, S.L. Bao, Y. Lu, D.P. Zhang, L. Yao, J. Alloys Compd. 459 (2008) 251–260.
[3] W.B. Sheng, J. Non-Cryst. Solids 351 (2005) 3081–3086.
[4] O.N. Senkov, J.M. Scott, J. Non-Cryst. Solids 351 (2005) 3087–3094.
[5] A.A. Cabral, C. Fredericci, E.D. Zanotto, J. Non-Cryst. Solids 219 (1997) 182–186.
[6] Z.P. Lu, C.T. Liu, Acta Mater. 50 (2002) 3501–3512.
[7] A.A. Cabral, A.A.D. Cardoso, E.D. Zanotto, J. Non-Cryst. Solids 320 (2003) 1–8.
[8] M.L.F. Nascimento, N.O. Dantas, Mater. Lett. 61 (2007) 912–916.
[9] M.L.F. Nascimento, L.A. Souza, E.B. Ferreira, E.D. Zanotto, J. Non-Cryst. Solids 351 (2005) 3296–3308.
[10] D. Turnbull, Contem. Phys. 10 (1969) 473–488.
[11] A. Hruby, Czech. J. Phys. B 22 (1972) 1187–1193.
[12] Z.P. Lu, C.T. Liu, Phys. Rev. Lett. 91 (2003) 115505.
[13] G.J. Fan, H. Choo, P.K. Liaw, J. Non-Cryst. Solids 353 (2007) 102–107.

[14] Z. Long, G. Xie, H. Wei, X. Su, J. Peng, P. Zhang, A. Inoue, Mater. Sci. Eng. A 509 (2009) 23–29.
[15] A.F. Kozmidis-Petrovic, Thermochim. Acta 499 (2010) 54–60.
[16] P. Zhang, H. Wei, X. Wei, Z. Long, X. Su, J. Non-Cryst. Solids 355 (2009) 2183–2189.
[17] M.C. Weinberg, Phys. Chem. Glasses 35 (1994) 119–123.
[18] Z.P. Lu, C.T. Liu, Intermetallics 12 (2004) 1035–1043.
[19] A. Inoue, T. Zhang, T. Masumoto, J. Non-Cryst. Solids 156–158 (1993) 473–480.
[20] C. Suryanarayana, I. Seki, A. Inoue, J. Non-Cryst. Solids 355 (2009) 355–360.
[21] T.A. Waniuk, J. Schroers, W.I. Johnson, Appl. Phys. Lett. 78 (2001) 1213–1215.
[22] A. Inoue, W. Zhang, T. Zhang, K. Kurosaka, Acta Mater. 49 (2001) 2645–2652.
[23] Q. Chen, J. Shen, D. Zhang, H. Fan, J. Sun, D.G. McCarney, Mater. Sci. Eng. A 433 (2006) 155–160.
[24] X.H. Du, J.C. Huang, C.T. Liu, Z.P. Lu, J. Appl. Phys. 101 (2007) 086108.
[25] K. Mondal, B.S. Murty, J. Non-Cryst. Solids 351 (2005) 1366–1371.
[26] E.S. Park, H.J. Chang, D.H. Kim, T. Ohkubo, K. Hono, Scripta Mater. 54 (2006) 1569–1573.
[27] I.A. Figueroa, R. Rawal, P. Stewart, P.A. Carroll, H.A. Davies, H. Jones, I. Todd, J. Non-Cryst. Solids 353 (2007) 839–841.