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A study on the thermal stability of some alloys in the Cu–Ge–Te glassy system by differential scanning calorimetry

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Abstract

The glass formation and devitrification of alloys in the Cu–Ge–Te system were studied by differential scanning calorimetry. A comparison of various simple quantitative methods to assess the level of stability of the glassy materials in the above-mentioned system is presented. All of these methods are based on characteristic temperatures such as the glass transition temperature, T_g, the onset temperature of crystallization, T_{in}, the temperature corresponding to the maximum crystallization rate, T_p, or the melting temperature, T_m. In this work, the parameter $K_r(T)$ is added to the stability criteria. The thermal stability of some ternary compounds of the $Cu_xGe_{0.20-y}Te_{0.80-x+y}$ type has been evaluated experimentally and correlated with the activation energies of crystallization by this kinetic criterion and compared with those evaluated by other criteria.

Keywords: Thermal stability; Differential scanning calorimetry; Volume fraction crystallized; Kinetic parameters; Stability criteria; Reaction rate constant

1. Introduction

Glassy alloys of chalcogen elements were the initial object of study because of their interesting semiconducting properties [1] and more recent importance in optical recording [2]. Recording materials must be stable in the amorphous state at low temperature and have a short crystallization time. Tellurium alloy films, in particular, are used as recording media as they have a low melting temperature and high absorption coefficient for the wavelengths of semiconducting lasers; promising materials with these characteristics have recently been studied [3,4]. Therefore, it is very important to know the glass stability and chemical durability of these types of materials. However, no simple way presently exists to formulate the correlation between the ideal composition and the stability of the glasses.

In order to evaluate the level of stability of the glassy alloys, different simple quantitative methods have been suggested. Most of these methods [5–9] are based on characteristic temperatures such as the glass transition temperature, T_g, the crystallization temperature, T_p, or the melting temperature, T_m. Some of them [10,11] are based on the reaction rate constant, K. Some of the others [12–14] are based on crystallization activation energy. These thermal parameters [15] are easily and accurately obtained by differential scanning calorimetry (DSC) during the heating

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processes of glass samples. The first thorough study on the glass thermal stability of various compounds was done by Sakka and Mackenzie [16] using the ratio T_g/T_m. Dietzel introduced the glass criterion, $\Delta T=T_{in}-T_g$ (T_{in} is the onset temperature of crystallization), which is often an important parameter to evaluate the glass forming ability of the glasses. By the use of the characteristic temperatures, Hruby developed the H_r criterion, $H_r=\Delta T/(T_m-T_{in})$, and compositional dependencies of the Hruby coefficient were survived by Sestak [17]. On the basis of the H_r criterion, Saad and Poulain obtained two other criteria, weighted thermal stability H' and S criterion, $H'=\Delta T/T_g$ and $S=(T_p-T_{in})\Delta T/T_g$, respectively.

In the present work, the above-mentioned criteria have been applied to the alloys $Cu_xGe_{0.20-y}Te_{0.8-x+y}$, where $x=0.03$, $y=0$ (S1), $x=y=0.05$ (S2) and $x=0.08$, $y=0.02$ (S3), and it is found that the parameters ΔT, H_r, H' and S increase with increasing copper content. Bearing in mind that the values of these parameters increase with increasing stability, it is possible to suggest that the bigger the copper content of the alloy, the greater is its glass thermal stability [18]. In addition, a kinetic parameter, $K_r(T)$, with an Arrhenian temperature dependence, is introduced to the stability criteria. Decreasing values of the above parameter have been found for the alloys with increasing copper content. This fact confirms that S3 alloy is the most stable one.

2. Theoretical analysis

The formal theory of transformation kinetics describes the evolution with time, t, of the volume fraction crystallized, x, in terms of the crystal growth rate, u:

$$x=1-\exp\left[-g\left(\int_0^t u\,\mathrm{d}t'\right)^n\right]=1-\exp(-I_1^n). \quad (1)$$

Here g is a geometric factor and n is an exponent, which depends on the mechanism of transformation. In Eq. (1), it is assumed that the nucleation process takes place early in the transformation and the nucleation rate is zero thereafter. This case has been referred to as "site saturation" by Cahn [19,20]. In addition, Arrhenian temperature dependence is also assumed for the crystal growth rate.

The maximum crystallization rate in a non-isothermal process is found by making $\mathrm{d}^2x/\mathrm{d}t^2=0$, thus obtaining the relationship

$$nK_p(I_1^n)|_p=\beta E(I_1)|_p/(RT_p^2)+(n-1)K_p, \quad (2)$$

in which $\beta=\mathrm{d}T/\mathrm{d}t$ is the heating rate, E the effective activation energy, K the reaction rate constant and where the magnitude values which correspond to the maximum crystallization rate are denoted by subscript p.

By using the substitution $y'=E/(RT')$, the integral I_1 can be represented by an alternating series [21], resulting in

$$I_1=[K_0E/(\beta R)]\left[\mathrm{e}^{-y'}y'^{-2}\sum_{k=0}^{\infty}\frac{(-1)^k(k+1)!}{y'^k}\right]_{y_0}^{y},$$

where it is possible to use only the first term, without making any appreciable error, and to obtain $I_1=RT^2K(\beta E)^{-1}$, if it is assumed that $T_0\ll T$ (T_0 is the starting temperature), so that y_0 can be taken as infinity.

Substituting the last expression of I_1 in Eq. (2), one obtains

$$RT_p^2(\beta E)^{-1}K_0\exp[-E/(RT_p)]=1,$$

or in a logarithmic form

$$\ln(T_p^2/\beta)=\ln(E/R)-\ln K_0+E/(RT_p). \quad (3)$$

This equation represents a straight line, with slope, E/R, and intercept, $\ln(E/R)-\ln K_0$. Then, one can obtain E, K_0 and $K(T)$.

In order to evaluate the thermal stability of glassy materials, Surinach et al. [10] introduced a $K(T_g)$ criterion, and Hu and Jiang [11] developed the $K(T_p)$ criterion, $K(T_g)=K_0\exp[-E/(RT_g)]$ and $K(T_p)=K_0\exp[-E/(RT_p)]$, respectively. Thus, the values of these two parameters indicate the tendency of glass to devitrify on heating. The larger their values, the greater is the tendency to devitrify. The formation of glass is a kinetic process. It is reasonable to assess the glass stability by a kinetic parameter, $K(T)$. The H_r parameter itself is a stability factor based on characteristic temperatures. Here a stability criterion is defined as $K_r(T)$:

$$K_r(T) = K_0 \exp[-H_r E/(RT)], \qquad (4)$$

where T is any temperature between T_g and T_p. The theoretical background for the definition of the new parameter $K_r(T)$ would be based on the analysis of the relation between the parameters $K(T)$ and $K_r(T)$. Differentiating the expressions of both parameters results in

$$\mathrm{d}K_r = H_r E K_r (RT^2)^{-1}\,\mathrm{d}T, \quad \mathrm{d}K = EK(RT^2)^{-1}\,\mathrm{d}T,$$

and the relative variation in each parameter per Kelvin is

$$\frac{\Delta K_r}{K_r T} = \frac{H_r E}{RT^2}, \quad \frac{\Delta K}{KT} = \frac{E}{RT^2}.$$

It should be noted that the above-mentioned variation of the parameters $K_r(T)$ is H_r times the variation in parameter $K(T)$, which could justify the accuracy of this new parameter.

Just like the $K(T)$ criteria, the smaller the values of $K_r(T)$, the greater is the thermal stability of the glass. The obvious advantage of this method is that it can evaluate the glass stability over a broad temperature range other than that at one temperature such as T_g or T_p.

3. Experimental details

The alloys were prepared in bulk form by the standard melt quenching method. High purity (99.999%) copper, germanium and tellurium in appropriate atomic per cent proportions were weighed (total 7 g per batch) into quartz glass ampoules. The contents were sealed under a vacuum of 10^{-4} Torr (10^{-2} N m^{-2}), heated to 1373 K for about 72 h and continuously rotated in the furnace to homogenize the material. The ampoules were quenched in a continuous-flow liquid nitrogen bath in order to avoid the vapour thermal isolating envelope around the ampoules, therefore increasing the efficiency and reproducibility of the fabrication process. The amorphous nature of the material was checked through a diffractometric X-ray scan in a Siemens D500 diffractometer. The calorimetric measurements were carried out in a Perkin-Elmer DSC7 calorimeter with an accuracy of ±0.1°C. Temperature and energy calibrations of the instrument were performed using the well-known melting temperatures and melting enthalpies of high-purity indium and zinc supplied with the instrument. For non-isothermal experiments, glass samples weighing about 20 mg were sealed in aluminium pans and scanned at room temperature through their T_g at different heating rates of 2, 4, 8, 16 and 32 K min^{-1}. An empty aluminium pan was used as reference, and in all cases, a constant 60 ml min^{-1} flow of nitrogen was maintained in order to drag the gases emitted by the reaction, which are highly corrosive to the sensor equipment installed in the DSC furnace. The glass transition temperature was considered as a temperature corresponding to the inflection point of the lambda-like trace on the DSC scan.

4. Results and discussion

The characteristic temperatures from DSC scans are given in Table 1. The thermal stability of the three alloys studied can be estimated by using these characteristic temperatures, T_g, T_{in}, T_p, and T_m. The existing stability criterion parameters based on these characteristic temperatures are also listed in Table 1.

To obtain the kinetic parameters of crystallization, Eq. (3) is applied. Fig. 1 represents the evolution of

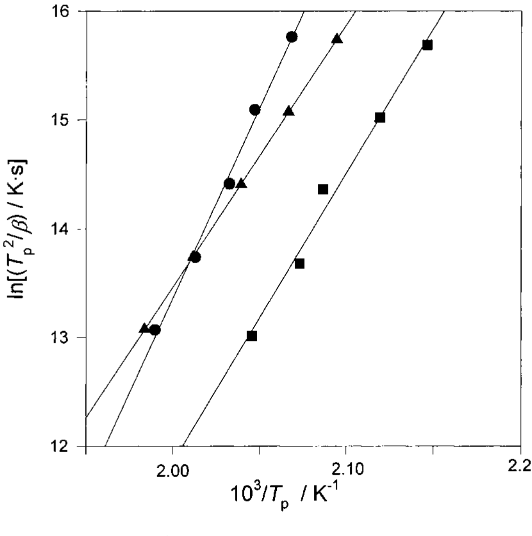

Fig. 1. Plots of $\ln(T_p^2/\beta)$ vs. $1/T_p$ and straight regression lines for the three glassy alloys S1 (●), S2 (■), and S3 (▲).

Table 1
Characteristic parameters of the alloys S1, S2 and S3

Alloy	β (K min^{-1})	T_g (K)	T_{in} (K)	T_p (K)	T_m (K)	ΔT (K)	H_r	H'	S (K)
S1	2	428.7	474.7	483.5	517.5	46.0	1.353	0.107	0.944
	4	432.5	479.5	488.5	523.0	47.0	1.362	0.109	0.978
	8	434.0	482.4	492.0	527.5	48.4	1.363	0.112	1.071
	16	435.2	484.4	496.8	532.8	49.2	1.366	0.113	1.402
	32	435.8	485.3	502.6	538.8	49.5	1.367	0.114	1.965
S2	2	401.3	453.6	465.9	497.1	52.3	1.676	0.130	1.603
	4	405.7	459.2	471.9	503.5	53.5	1.693	0.132	1.675
	8	407.4	462.1	479.3	511.5	54.7	1.699	0.134	2.309
	16	409.3	465.3	482.4	515.3	56.0	1.702	0.137	2.340
	32	410.5	467.5	488.9	522.3	57.0	1.706	0.139	2.971
S3	2	404.6	462.7	477.5	509.3	58.1	1.827	0.144	2.125
	4	408.1	467.1	483.9	516.1	59.0	1.832	0.145	2.429
	8	411.4	471.6	490.4	523.1	60.2	1.841	0.146	2.751
	16	413.9	474.9	497.1	530.2	61.0	1.843	0.147	3.272
	32	416.3	478.3	504.1	537.6	62.0	1.851	0.149	3.842

Table 2
Kinetic parameters of the analysed alloys obtained from the straight regression lines fitted to values of $\ln(T_p^2/\beta)$ vs. $1/T_p$

Alloy	E (kcal mol^{-1})	$\ln K_0$ (K_0 in s^{-1})
S1	69.9±1.8	67.1±1.1
S2	53.2±1.5	51.5±1.5
S3	48.3±1.1	44.8±1.3

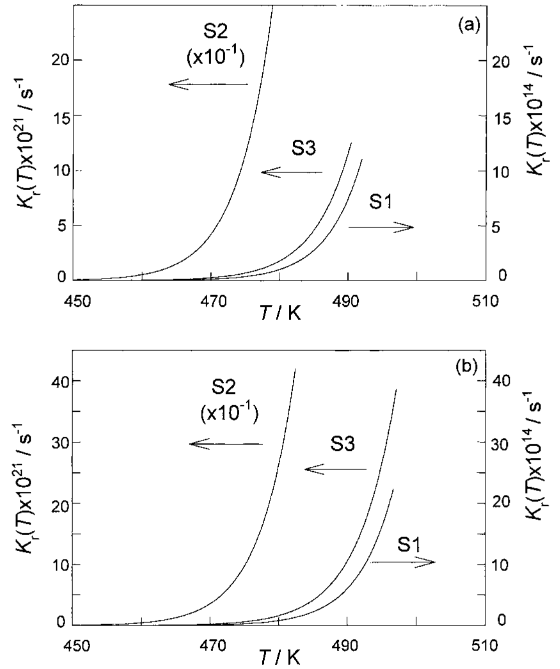

Fig. 2. Plots of $K_r(T)$ vs. T for the three glassy alloys to verify the stable order: (a) β=8 K min^{-1}, and (b) β=16 K min^{-1}.

$\ln(T_p^2/\beta)$ vs. $1/T_p$ for the three alloys. The plots were found to be straight lines in accordance with Eq. (3). The activation energy, E, and frequency factor, K_0, are then evaluated by least-squares fitting method. Table 2 summarizes the values determined by these calculations. After knowing the values of E and K_0, the kinetic parameters $K(T)$ and $K_r(T)$ of studied alloys were calculated by using the relationship $K(T)=K_0 \exp[-E/(RT)]$ and Eq. (4), respectively. These calculations were carried out in order to compare the stability sequence of the studied materials from the quoted parameters with the corresponding sequence deduced from stability criteria based on characteristic temperatures. The values of $K(T)$ and $K_r(T)$ for the temperatures T_g and T_p are listed in Table 3. Fig. 2 represents the plots of $K_r(T)$ vs. T. It is found that $K_r(T)$ of S3 varies slowly with increasing T and the values are on T axis, indicating a relatively high stability, while $K_r(T)$ of the other two samples varies more rapidly with increasing T, which signifies a minor stability. These considerations verify the thermal stability order of the above-mentioned glassy alloys.

Table 3
Kinetic parameters $K(T)$ and $K_r(T)$ for the three alloys

Alloy	β (K min^{-1})	$K(T_g)$ (s^{-1})	$K(T_p)$ (s^{-1})	$K_r(T_g)$ (s^{-1})	$K_r(T_p)$ (s^{-1})
S1	2	4.87×10^{-7}	5.01×10^{-3}	1.55×10^{-19}	4.15×10^{-14}
	4	9.96×10^{-7}	1.05×10^{-2}	1.97×10^{-19}	5.94×10^{-14}
	8	1.32×10^{-6}	1.75×10^{-2}	2.66×10^{-19}	1.11×10^{-13}
	16	1.64×10^{-6}	3.47×10^{-2}	2.83×10^{-19}	2.28×10^{-13}
	32	1.84×10^{-6}	7.82×10^{-2}	3.03×10^{-19}	6.45×10^{-13}
S2	2	3.94×10^{-7}	3.86×10^{-3}	1.36×10^{-26}	6.68×10^{-20}
	4	8.08×10^{-7}	7.98×10^{-3}	1.49×10^{-26}	8.65×10^{-20}
	8	1.06×10^{-6}	1.90×10^{-2}	1.60×10^{-26}	2.71×10^{-19}
	16	1.44×10^{-6}	2.72×10^{-2}	2.21×10^{-26}	4.20×10^{-19}
	32	1.74×10^{-6}	5.66×10^{-2}	2.36×10^{-26}	1.18×10^{-18}
S3	2	3.54×10^{-7}	3.21×10^{-3}	1.29×10^{-28}	2.20×10^{-21}
	4	5.90×10^{-7}	6.27×10^{-3}	2.45×10^{-28}	5.81×10^{-21}
	8	9.49×10^{-7}	1.21×10^{-2}	3.44×10^{-28}	1.25×10^{-20}
	16	1.35×10^{-6}	2.36×10^{-2}	5.88×10^{-28}	3.86×10^{-20}
	32	1.65×10^{-6}	4.63×10^{-2}	6.88×10^{-28}	9.11×10^{-20}

It is known that these existing criteria of glass stability allow the prediction of the tendency to devitrify. It is possible to suggest that the larger their values, the greater should be the glass thermal stability. According to these suggestions, the parameters, ΔT, H_r, H' and S, in Table 1 show that the S3 glass sample is more stable than the other two samples. Also, it is possible to obtain a consistent stable order for these glasses by the reaction rate constant. According to literature [10,11] ($K(T_g)$ and $K(T_p)$ criteria), the smaller the values of these parameters, the better should be the thermal stability of glass. So the data for both $K(T_g)$ and $K(T_p)$ in Table 3 indicate that S3 glass sample is the most stable, and the stability orders at different heating rates are S3>S2>S1. In addition, by using Eq. (4), the data of $K_r(T_g)$ and $K_r(T_p)$ were calculated and given in Table 3, showing that S3 alloy is also the most stable, and the orders of stability is also S3>S2>S1 at various heating rates. This stability result agrees with that of the $K(T_g)$ and $K(T_p)$ criteria.

The above-mentioned stability orders agree satisfactorily with literature [18], where it is noted that when copper is introduced into glassy germanium tellurides, their thermal stability is increased, since one produces a substantial strengthening of glass structure. It is possible to suggest that the excess chain-like tellurium is transformed into three-dimensional structural species as a result of interaction with the germanium and copper. The weak Van der Waals bonds between the chains are replaced in this case by rigid covalent bonds, and the glass structure becomes stronger.

5. Conclusion

The $K_r(T)$ criterion has been considered in this work for the evaluation of glass stability from DSC data. It includes both the kinetic parameters and characteristic temperatures. Therefore, it is reasonable to think that the obtained data from the above criterion agree satisfactorily with the values which result from the existing criteria based on critical temperatures and $K(T)$ criteria. High value of $K_r(T)$ means poor stability of the glass. In the present work, the non-isothermal devitrification of three glassy alloys in the Cu–Ge–Te system has been studied at different heating rates and various temperatures. The above-mentioned study has verified that the $K_r(T)$ criterion is slightly affected both by the heating rate and by the temperature, while the other criteria show a bigger variation with the heating rate. Among the three glassy alloys, $K_r(T)$ of S3 glass sample is smallest, so this glass composition is the most stable. Finally, the stability order of these three glass samples is S3>S2>S1.

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References

[1] K. Tanaka, Y. Osaka, M. Sugi, S. Iizima, M. Kikuchi, J. Non-Cryst. Solids 12 (1973) 100.

[2] Y. Sugiyama, R. Chiba, S. Fugimori, N. Funakoski, J. Non-Cryst. Solids 122 (1990) 83.

[3] S. Fugimori, S. Sagi, H. Yamazaki, N. Funakoski, J. Appl. Phys. 64 (1988) 100.

[4] Y. Maeda, H. Andoh, I. Ikuta, M. Magai, Y. Katoh, H. Minemura, N. Tsuboi, Y. Satoh, Appl. Phys. Lett. 54 (1989) 893.

[5] A. Dietzel, Glasstech. Ber. 22 (1968) 41.

[6] D.R. Uhlmann, J. Non-Cryst. Solids 7 (1972) 337.

[7] D.R. Uhlmann, J. Non-Cryst. Solids 25 (1977) 43.

[8] A. Hruby, Czech. J. Phys. B 22 (1972) 1187.

[9] M. Saad, M. Poulain, Mater. Sci. Forum 19 20 (1987) 11.

[10] S. Surinach, M.D. Baro, M.T. Clavaguera-Mora, N. Clavaguera, J. Mater. Sci. 19 (1984) 3005.

[11] L. Hu, Z. Jiang, J. Chin. Ceram. Soc. 18 (1990) 315.

[12] A. Marotta, A. Buri, F. Branda, J. Non-Cryst. Solids 95 96 (1987) 593.

[13] X. Zhao, S. Sakka, J. Non-Cryst. Solids 95 96 (1987) 487.

[14] F. Branda, A. Marotta, A. Buri, J. Non-Cryst. Solids 134 (1991) 123.

[15] J. Málek, J. Non-Cryst. Solids 107 (1988) 323.

[16] S. Sakka, J.D. Mackenzie, J. Non-Cryst. Solids 6 (1971) 145.

[17] J. Sestak, J. Therm. Anal. 33 (1988) 75.

[18] Z.U. Borisova, Glassy Semiconductors, Plenum Press, New York, 1981.

[19] J.W. Cahn, Acta Metall. 4 (1956) 573.

[20] J.W. Cahn, Acta Metall. 4 (1956) 449.

[21] J. Vázquez, C. Wagner, P. Villares, R. Jiménez-Garay, Acta Mater. 44 (1996) 4807.