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A study of the glass forming ability of some alloys in the Ge–As–Te system by differential scanning calorimetry

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Abstract

The glass formation and devitrification of alloys in the Ge-As-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 temperature at which crystallization begins, 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 stability of some ternary compounds of the $Ge_x\,As_{0.2+y}\,Te_{0.8-(x+y)}$ type has been evaluated experimentally and correlated with the activation energies of crystallization by the kinetic K_r (T) criterion and compared with those evaluated by other criteria. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Glassy alloy; Crystallization kinetics; Heating rate; Glass forming ability

1. Introduction

The glassy alloys of chalcogen elements were an 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. Promising materials with these characteristics have been recently studied [3]. Therefore, it is very important to know the glass forming ability and chemical durability of this type 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 [4–7] 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 [8,9] are based on the reaction rate constant, K. Some of the others [10] are based on crystallization activation energy. These thermal parameters are easily and accurately obtained by differential scanning calorimetry (DSC) during the heating processes of glass samples. Dietzel [4] introduced the first glass criterion, $\Delta T = T_{in} - T_g$ (T_{in} is the temperature at which crystallization begins). By the use of the characteristic temperatures Hruby [6] developed the Hr criterion, $\mathrm{Hr} = \Delta T/(T_m - T_p)$. On the basis of the Hr criterion, Saad and Poulain [7] obtained two other criteria, weighted thermal stability H' and the S criterion, $H' = \Delta T/T_g$, $S = (T_p - T_{in})\Delta T/T_g$, respectively.

In the present work, the above-mentioned criteria have been applied to the alloys $Ge_xAs_{0.2+y}Te_{0.8-(x+y)}$, where $x = 0.05$, $y = 0$ (S1), $x = 0.10$, $y = 0$ (S2) and $x = 0.14$, $y = 0.23$ (S3), and it is found that the parameters ΔT, Hr, H' and S increase with increasing germanium content and with similar contents of arsenic and tellurium. Bearing in mind that the values of these parameters increase with increasing stability, it is possible to suggest that the larger the alloys germanium content, the greater is its glass thermal stability. 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 germanium content. This fact confirm that the S3 alloy is the most stable one.

2. Theoretical basis

The formal theory of transformation kinetics describes the evolution with time, t, of the volume fraction crystallized, x,

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in terms of the crystal growth, u:

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

Here g is a geometric factor and n is an exponent which depends on the mechanism of transformation. In the 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 [11,12].

Taking the derivative of Eq. (1) with respect to time and assuming an Arrhenian temperature dependence for the crystal growth rate [13], the crystallization rate is obtained as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = n(1-x)I_1^{n-1}K_0\exp\left(\frac{-E}{RT}\right) = nK(1-x)I_1^{n-1} \qquad (2)$$

where E is the effective activation energy for crystal growth and K is the reaction rate constant.

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

$$nK_\mathrm{p}\left(I_1^n\right)\big|_\mathrm{p} = \frac{\beta E(I_1^n)|_\mathrm{p}}{RT_\mathrm{p}^2} + (n-1)K_\mathrm{p} \qquad (3)$$

in which $\beta = \mathrm{d}T/\mathrm{d}t$ is the heating rate, 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 [14], 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. (3)) and taking the logarithm of the resulting relationship, one obtains

$$\ln\left(\frac{T_\mathrm{p}^2}{\beta}\right) = \ln\left(\frac{E}{R}\right) - \ln K_0 + \frac{E}{RT_\mathrm{p}} \qquad (4)$$

equation for the 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 stability of glasses, Surinach et al. [8] introduced a $K(T_\mathrm{g})$ criterion and Hu et al. [9] developed the K (T_p) criterion, $K(T_\mathrm{g}) = K_0\exp(-E/\mathrm{R}T_\mathrm{g})$, $K(T_\mathrm{p}) = K_0\exp(-E/RT_\mathrm{p})$, respectively. Thus the values of these two parameters indicate the tendency of glass to devitrify on heating the formation of glass is a kinetic process. It is reasonable to assess the glass stability by a kinetic parameter, $K(T)$. The Hr parameter itself is a stability factor based on characteristic temperatures. Here a stability criterion is defined as K_r (T)

$$K_\mathrm{r}(T) = K_0\exp\left(\frac{-\mathrm{Hr}\,E}{RT}\right)$$

where T is any temperature between T_g and T_p. Just like the $K(T)$ criteria, the smaller the values of $K_\mathrm{r}(T)$, 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 at one temperature such as T_g or T_p.

3. Experimental procedures

The alloys were made in bulk form, from their components of 99.999% purity which were pulverized, mixed in adequate proportions, and introduced into quartz ampoules. The contents were sealed under a vacuum of 10^{-2} Nm^{-2}, heated at 1000°C for 24 h and then quenched in an ice-water bath. The glassy nature of the materials was confirmed 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. For non-isothermal experiments, glass samples were sealed in aluminium pans and scanned at room temperature through their T_g at different heating rates of 2.5, 5, 10, 20 and 40 K min^{-1}. The glass transition temperature was considered as a temperature corresponding to the intersection of two linear portions adjoining the transition elbow in the DSC trace. Fig. 1 shows typical DSC scan patterns corresponding to a heating rate of 10 K min^{-1} for the three studied alloys.

4. Results and discussion

The characteristic temperatures from DSC scans are given in Table 1. The glass forming ability of the three

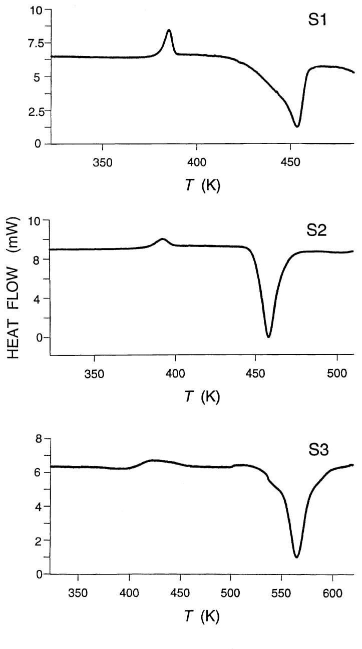

Fig. 1. Thermograms, at $\beta = 10$ K min^{-1} for the three alloys S1 - S3.

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)	Hr	H'	S
	2.5	376	440	442	475	64	1.929	0.170	0.340
	5	378	446	448	483	68	1.953	0.180	0.360
S1	10	380	451	453	489	71	1.972	0.187	0.374
	20	381	456	458	496	75	1.992	0.197	0.394
	40	384	462	464	503	78	2.018	0.203	0.406
	2.5	377	445	447	480	68	2.054	0.180	0.361
	5	379	451	453	488	72	2.057	0.190	0.380
S2	10	380	456	458	495	76	2.055	0.200	0.400
	20	382	462	464	502	80	2.105	0.209	0.419
	40	384	468	470	510	84	2.107	0.219	0.438
	2.5	416	520	542	577	104	2.971	0.250	5.500
	5	418	525	554	590	107	2.972	0.256	7.423
S3	10	419	529	565	602	110	2.973	0.263	9.451
	20	420	533	578	616	113	2.974	0.269	12.107
	40	421	537	591	630	116	2.981	0.276	14.879

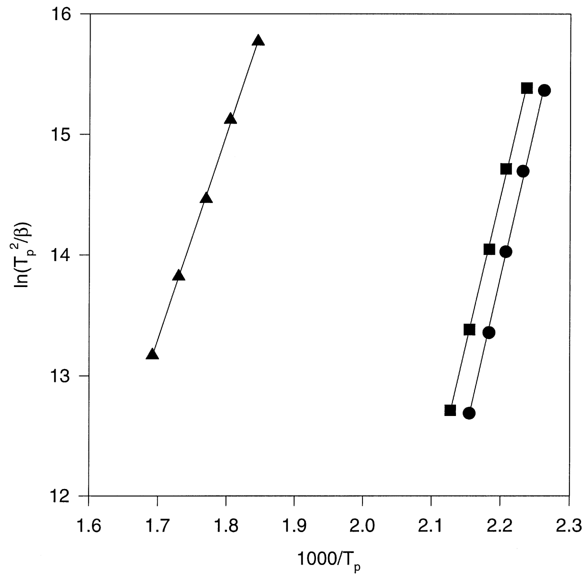

Fig. 2. Plots of $\ln(T_p^2/\beta)$ vs. $1/T_p$ and straight regression lines for the three glassy alloys S1(●), S2(■) and S3(▲).

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 on Table 1.

To obtain the kinetic parameters of the crystallization, Eq. (4) is applied. Fig. 2 represents the evolution of ln (T_p^2/β) versus $1/T_p$ for the three alloys. The plots were found to be straight lines in accordance with (Eq. (4)). The activation energy, E, and frequency factor, K_0, are then valuated 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 are calculated and listed in Table 3. Fig. 3 represents the plots of $K_r(T)$ versus T. It is found that $K_r(T)$ of S3 varies slowly with increasing of T and the values are on T axis, while K_r(T) of S1 varies rapidly with increasing of T. They verify the thermal stability order of the above mentioned glassy alloys.

It is known that these existing criteria of glass stability allow the prediction of the glass forming ability. 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, Hr, H' and S, in Table 1 show that S3 glass sample is more stable than the other two samples. However, it is difficult to obtain the consistent stable order for these glasses by these criteria based on characteristic temperatures especially at different heating rates. According to literature [8,9] ($K(T_g)$ and $K(T_p)$ criteria) the smaller the values of these parameters the better should be the glass forming ability of material. 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, according to the preceding theory, the data of $K_r(T_g)$ and $K_r(T_p)$ in Table 3 show that S3 alloy is also the most stable, and the orders 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.

Table 2
Straight regression lines (SRL) fitted to values of ln (T_p^2/β) and kinetic parameters of the analyzed alloys.

Alloy	SRL	E (kcal mol^{-1})	K_0 (s^{-1})	r^a
S1	$25.3415 \times 10^3/T_p - 41.9389$	50.7	4.02×10^{22}	0.997
S2	$24.5856 \times 10^3/T_p - 39.6044$	49.2	3.90×10^{21}	0.998
S3	$17.0425 \times 10^3/T_p - 15.6698$	34.1	1.09×10^{11}	0.998

[a] r is the correlation coefficient.

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

Alloy	β(K min^{-1})	$K(T_g)$	$K(T_p)$	$K_r(T_g)$	$K_r(T_p)$
	2.5	2.11×10^{-7}	4.97×10^{-3}	1.33×10^{-34}	3.60×10^{-26}
	5	3.01×10^{-7}	1.07×10^{-2}	5.28×10^{-35}	4.31×10^{-26}
S1	10	4.28×10^{-7}	2.00×10^{-2}	2.96×10^{-35}	4.77×10^{-26}
	20	5.11×10^{-7}	3.68×10^{-2}	1.11×10^{-35}	5.26×10^{-26}
	40	8.59×10^{-7}	7.54×10^{-2}	5.59×10^{-36}	5.28×10^{-26}
	2.5	1.79×10^{-7}	4.90×10^{-3}	2.42×10^{-37}	3.15×10^{-28}
	5	2.52×10^{-7}	1.02×10^{-2}	4.04×10^{-37}	1.20×10^{-27}
S2	10	2.99×10^{-7}	1.84×10^{-2}	6.53×10^{-37}	4.51×10^{-27}
	20	4.20×10^{-7}	3.68×10^{-2}	5.24×10^{-38}	1.33×10^{-27}
	40	5.88×10^{-7}	7.24×10^{-2}	9.34×10^{-38}	4.97×10^{-27}
	2.5	1.73×10^{-7}	2.37×10^{-3}	1.43×10^{-42}	2.81×10^{-30}
	5	2.10×10^{-7}	4.69×10^{-3}	2.45×10^{-42}	2.06×10^{-29}
S3	10	2.32×10^{-7}	8.54×10^{-3}	3.14×10^{-42}	1.19×10^{-28}
	20	2.55×10^{-7}	16.85×10^{-3}	4.03×10^{-42}	8.66×10^{-28}
	40	2.81×10^{-7}	32.23×10^{-3}	4.04×10^{-42}	4.88×10^{-27}

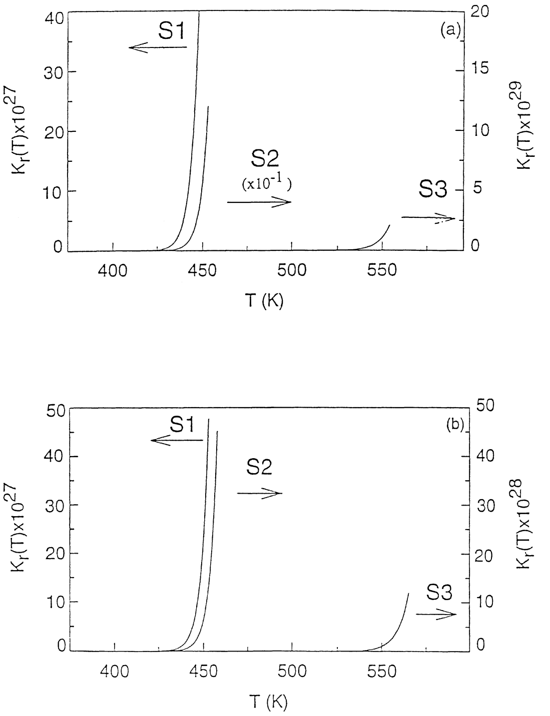

Fig. 3. Plots of $K_r(T)$ vs. T for the three glassy alloys to verify the stability order, (a) $\beta = 5$ K min^{-1}, (b) $\beta = 10$ K min^{-1}.

The above-mentioned stability orders agree satisfactorily with literature [15], where it is noted that the compositions in the middle of the glass formation region (case of S3 alloy) have the highest glass-forming ability.

5. Conclusions

The $K_r(T)$ criterion has been considered in this work for the evaluation of glass forming ability from DSC data. It includes both the kinetic parameters and characteristic temperatures. The above criterion is more accurate and reasonable than the existing criteria based on critical temperatures, and $K(T)$ criteria. High values of $K_r(T)$ means poor stability of the glass. In the present work, the non-isothermal devitrification of three glassy alloys in the Ge–As–Te system has been studied at different heating rates. 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 others criteria show a bigger variation with the heating rate and the temperature. Among the three glassy alloys, $K_r(T)$ of S3 sample is smallest, so this glass composition is the most stable. Finally, the stability order of these three glassy alloys is S3 > S2 > S1.

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