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Evaluation of the glass forming ability of some alloys in the Sb–As–Se system by differential scanning calorimetry

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Abstract

The glass formation and devitrification of alloys in the Sb–As–Se 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 $Sb_xAs_{0.52-x}Se_{0.48}$ 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: Amorphous materials; Liquid quenching; Precipitation; Calorimetry; Thermal analysis

1. Introduction

Amorphous materials themselves are nothing new. Man has been making glasses (mainly silica) for centuries, however, it has been only in recent years that ‘glass science’ has emerged as a field of study in its own right. The advances that have been made in the physics and chemistry of these materials have been very appreciated within the research community [1]. Glassy alloys of chalcogen elements were the initial object of study because of their interesting semiconducting properties [2] and more recent importance in optical recording [3]. Recording materials must be stable in the amorphous state at low temperature and have a short crystallization time. Promising materials with these characteristics have recently been studied [4,5]. Therefore it is very important to know the glass forming ability and chemical durability of this type of materials. However, no simple method 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 [6–10] 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 [11,12] are based on the reaction rate constant, K. Some of the others [13–15] are based on crystallization activation energy. These thermal parameters [16] are easily and accurately obtained by differential scanning calorimetry (DSC) during the heating processes of glass samples. The first thorough study on the glass thermal stability of various compounds was done by Sakka and Mackenzie [17], 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, $H_r = \Delta T/(T_m - T_p)$, and compositional dependencies of the Hruby coefficient were survived by Sestak [18]. On the basis of the H_r criterion, Saad and Poulain obtained two other criteria, weighted thermal stability H' and S criterion, $H' = \Delta T/T_g$, $S = (T_p - T_{in})\ \Delta T/T_g$, respectively.

In the present work, the above-mentioned criteria have been applied to the alloys $Sb_xAs_{0.52-x}Se_{0.48}$, where $x = 0.12$ (S1), $x = 0.16$ (S2) and $x = 0.20$ (S3), and it is found that the parameters ΔT, H_r, H' and S increase with decreasing antimony content. Bearing in mind that the

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values of these parameters increase with increasing stability, it is possible to suggest that the lower the antimony content of the alloy, the greater is its glass thermal stability [19]. In addition, a kinetic parameter, $K_r(T)$, with an Arrhenian temperature dependence, is introduced to the stability criteria. Decreasing values of the above-mentioned parameter have been found for the alloys with decreasing antimony content. This fact confirms that the S1 alloy is the most stable one.

2. Theoretical method

The theoretical basis for interpreting DSC results is provided by the formal theory of transformation kinetics. This theory describes the evolution with time, t, of the volume fraction crystallized, x, in terms of the crystal growth rate, u

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

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 in the literature [20–22] as 'site saturation'.

Although, in general, the temperature dependence of the crystal growth rate is not Arrhenian when a broad range of temperature is considered [23], however, over a sufficiently limited range of temperature (such as the range of crystallization peaks in DSC experiments) u may be described in a zeroth-order approximation by

$$u = u_0 \exp(-E/RT) \tag{2}$$

where E is the effective activation energy, u_0 is a pre-exponential factor and R is the ideal gas constant.

Differentiating Eq. (1) with respect to time and substituting Eq. (2) in the resulting expression, the crystallization rate is obtained as

$$\begin{aligned} \mathrm{d}x/\mathrm{d}t &= n(1-x)I_1^{n-1} K_0 \exp(-E/RT) \\ &= nK(1-x)I_1^{n-1} \end{aligned} \tag{3}$$

K being the reaction rate constant.

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

$$nK_p(I_1^n)|_p = \beta E(I_1)|_p / RT_p^2 + (n-1)K_p \tag{4}$$

in which $\beta = \mathrm{d}T/\mathrm{d}t$ is the heating rate and where the quantity 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, according to the literature [23], by the sum of the alternating series

$$S(y') = -e^{-y'} y'^{-2} \sum_{k=0}^{\infty} \frac{(-1)^k (k+1)!}{y'^k}.$$

Considering that in this type of series the error produced is less than the first term neglected and bearing in mind that in most crystallization reactions $y' = E/RT' \gg 1$ (usually $E/RT' \geq 25$), it is possible to use only the two first terms of this series and the error introduced is not greater than 1%. In addition, if it is assumed that $T_0 \ll T$ (T_0 is the starting temperature), so that y_0 can be taken as infinity, the integral I_1 becomes

$$\begin{aligned} I_1 &= K_0 E(\beta R)^{-1} e^{-y} y^{-2} (1 - 2y^{-1}) \\ &= RT^2 K(\beta E)^{-1} (1 - 2RTE^{-1}). \end{aligned} \tag{5}$$

Substituting the last expression of I_1 in Eq. (4), one obtains

$$(I_1)|_p = (1 - 2RT_p/nE)^{1/n}$$

relationship that when it is equated to Eq. (5) gives

$$RT_p^2(\beta E)^{-1} K_0 \exp(-E/RT_p) = (1 - 2RT_p/nE)^{1/n}(1 - 2RT_p/E)^{-1} \tag{6}$$

or in a logarithmic form

$$\ln(T_p^2/\beta) + \ln(K_0 R/E) - E/RT_p = (2RT_p/E)(1 - n^{-2}) \tag{7}$$

where the function $\ln(1-z)$ with $z = 2RT_p/nE$ or $z = 2RT_p/E$ is expanded as a series and only the first term has been taken.

It should be noted that for most crystallization reactions the right hand side (RHS) of Eq. (7) is generally negligible in comparison to the individual terms on the left hand side for common heating rates (≤ 100 K min^{-1}). Therefore, the approximation in Eq. (7) (RHS = 0) might introduce a 3% error in the value of E/R in the worst cases, and Eq. (7) becomes

$$\ln(T_p^2/\beta) = E/RT_p + \ln(E/RK_0). \tag{8}$$

This equation represents a straight line with slope, E/R, and intercept, $\ln(E/RK_0)$. Then, one can obtain E, K_0 and $K(T)$.

In order to evaluate the thermal stability of glassy materials, Surinach et al. [11] introduced a $K(T_g)$ criterion, and Hu et al. [12] 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 $K_r(T)$:

$$K_r(T) = K_0 \exp(-H_r E/RT) \tag{9}$$

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

$$\frac{1}{K_r}\frac{\Delta K_r}{\Delta T} = \frac{H_r E}{RT^2}, \quad \frac{1}{K}\frac{\Delta K}{\Delta T} = \frac{E}{RT^2}.$$

It should be noted that the above-mentioned variation of the parameter $K_r(T)$ 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 at only one temperature such as T_g or T_p.

3. Experimental procedure

High purity (99.999%) antimony, arsenic and selenium in appropriate atomic percent proportions were weighed (total 7 g per batch) into quartz glass ampoules. The contents were sealed under a vacuum of 10^{-2} Pa, heated to 1225 K for about 24 h and continuously rotated in the furnace to homogenize the material. The ampoules were quenched in water, which supplied the necessary cooling rate for obtaining the glass. The amorphous state 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 K. 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 1, 2, 4, 8, 16, 32 and 64 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 provide a constant thermal blanket within the DSC cell, thus eliminating thermal gradients, and ensuring the validity of the applied calibration standard from sample to sample. Moreover, the nitrogen purge allows to expel the gases emitted by the reaction, which are highly corrosive to the sensory 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 glass forming ability 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 the crystallization, Eq. (8) is applied. Fig. 1 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. (8). 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. (9), 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 $K_r(T)$ versus T. It is found that $K_r(T)$ of S1 varies slowly with increasing T and the values are on the 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.

It is known that these existing criteria of glass stability allow to predict the glass forming ability of a material. 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 S1 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 the literature [11,12] ($K(T_g)$ and $K(T_p)$ criteria) the smaller the values of these parameters, the better should be the glass forming ability of the material. So the data for both $K(T_g)$ and $K(T_p)$ in Table 3 indicate that the S1 glass sample is the most stable, and the stability orders at different heating rates are S1>S2>S3. In addition, by using Eq. (9), the data of $K_r(T_g)$ and $K_r(T_p)$ were calculated and given in Table 3, showing that S1 alloy is also the most stable, and the orders of stability are also S1>S2>S3 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

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	1	453.1	546.3	566	628.1	93.2	1.501	0.206	4.052
	2	459.4	554.5	579	642.2	95.1	1.505	0.207	5.072
	4	464.3	562.6	587	652.2	98.3	1.508	0.212	5.166
	8	471.6	572.0	601	667.4	100.4	1.512	0.213	6.174
	16	478.0	581.2	610	678.2	103.2	1.513	0.216	6.218
	32	484.3	589.4	626	695.3	105.1	1.517	0.217	7.943
	64	491.8	600.0	641	712.2	108.2	1.520	0.220	9.020
S2	1	484.8	531.3	545.0	590.3	46.5	1.026	0.096	1.314
	2	486.6	534.9	549.5	596.5	48.3	1.028	0.099	1.449
	4	488.3	538.2	555.3	603.7	49.9	1.031	0.102	1.747
	8	493.4	545.2	564.9	614.9	51.8	1.036	0.104	2.068
	16	499.2	552.6	574.3	625.7	53.4	1.039	0.107	2.321
	32	505.5	560.7	583.7	636.7	55.2	1.042	0.109	2.512
	64	513.3	570.3	598.9	653.4	57.0	1.046	0.111	3.176
S3	1	441.7	473.0	491	531.8	31.3	0.767	0.071	1.276
	2	444.5	478.1	496	539.7	33.6	0.769	0.076	1.353
	4	444.8	480.3	500	546.1	35.5	0.770	0.080	1.572
	8	448.8	486.2	509	557.4	37.4	0.773	0.083	1.900
	16	453.8	493.1	516	566.7	39.3	0.775	0.087	1.983
	32	458.4	499.4	526	578.7	41.0	0.778	0.089	2.379
	64	465.1	508.2	536	591.3	43.1	0.779	0.093	2.576

with the literature [19], where it is noted that the crystallizing ability of glassy arsenic selenides increases substantially when antimony is introduced.

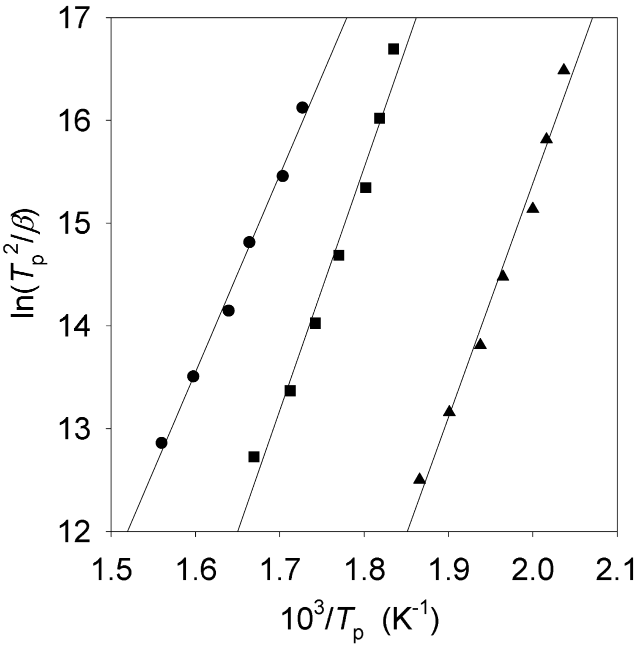

Fig. 1. Plots of ln (T_p^2/β) versus $1/T_p$ and straight regression lines for the three glassy alloys S1 (●), S2 (■), S3 (▲).

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

Alloy	E (kcal mol^{-1})	ln K_0 (K_0 in s^{-1})
S1	38.4±1.1	27.1±0.8
S2	47.1±1.3	37.0±1.1
S3	45.4±1.2	40.1±1.2

5. Conclusion

The glass forming ability of some alloys in the Sb–As–Se system has been evaluated by using various thermal stability criteria, based on characteristic temperatures. Moreover, in the present work, the $K_r(T)$ criterion has been considered for the evaluation of glass stability from DSC data. It includes both the kinetic parameters and the critical temperatures. Therefore, it is reasonable to think that the obtained data from the quoted criterion agree satisfactorily with the values which result from the existing criteria based on characteristic temperatures and $K(T)$ criteria. A high value of $K_r(T)$ means poor stability of the glass. In the present paper, the non-isothermal devitrification of three glassy alloys in the above-mentioned system has been studied at different heating rates and various temperatures. The above quoted 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 the S1 glass sample is smallest, so this glass composition is the most stable. Finally, the stability order of these three glass samples is S1>S2>S3.

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

Alloy	β (K/min)	$K(T_g)$ (s^{-1})	$K(T_p)$ (s^{-1})	$K_r(T_g)$ (s^{-1})	$K_r(T_p)$ (s^{-1})
S1	1	2.24×10^{-7}	1.05×10^{-3}	1.35×10^{-16}	4.36×10^{-11}
	2	4.00×10^{-7}	2.25×10^{-3}	2.73×10^{-16}	1.20×10^{-10}
	4	6.22×10^{-7}	3.53×10^{-3}	4.68×10^{-16}	2.14×10^{-10}
	8	1.18×10^{-6}	7.56×10^{-3}	1.04×10^{-15}	5.95×10^{-10}
	16	2.03×10^{-6}	1.21×10^{-2}	2.29×10^{-15}	1.18×10^{-9}
	32	3.43×10^{-6}	2.71×10^{-2}	4.30×10^{-15}	3.52×10^{-9}
	64	6.28×10^{-6}	5.55×10^{-2}	9.58×10^{-15}	9.55×10^{-9}
S2	1	9.37×10^{-6}	2.00×10^{-3}	2.65×10^{-6}	6.52×10^{-4}
	2	1.12×10^{-5}	2.85×10^{-3}	2.89×10^{-6}	8.60×10^{-4}
	4	1.33×10^{-5}	4.47×10^{-3}	2.97×10^{-6}	1.20×10^{-3}
	8	2.18×10^{-5}	9.18×10^{-3}	3.92×10^{-6}	2.05×10^{-3}
	16	3.80×10^{-5}	1.82×10^{-2}	6.04×10^{-6}	3.67×10^{-3}
	32	6.85×10^{-5}	3.52×10^{-2}	9.68×10^{-6}	6.46×10^{-3}
	64	1.39×10^{-4}	9.79×10^{-2}	1.68×10^{-5}	1.60×10^{-2}
S3	1	1.20×10^{-5}	2.09×10^{-3}	1.901	1.00×10^{2}
	2	1.66×10^{-5}	3.33×10^{-3}	2.200	1.30×10^{2}
	4	1.71×10^{-5}	4.80×10^{-3}	2.201	1.64×10^{2}
	8	2.70×10^{-5}	1.07×10^{-2}	2.618	2.67×10^{2}
	16	4.72×10^{-5}	1.96×10^{-2}	3.644	3.90×10^{2}
	32	7.79×10^{-5}	4.52×10^{-2}	4.635	6.55×10^{2}
	64	1.59×10^{-4}	1.01×10^{-1}	7.689	1.17×10^{3}

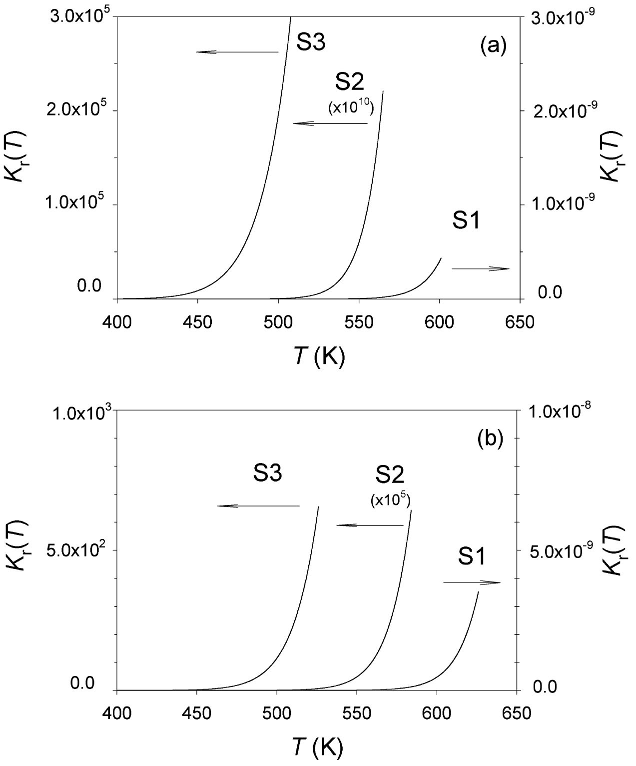

Fig. 2. Plots of $K_r(T)$ versus T for the three glassy alloys to verify the stable order: (a) $\beta=8$ K/min, and (b) $\beta=32$ K/min.

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