ELSEVIER

May 1998

Materials Letters 35 (1998) 151–156

MATERIALS LETTERS

Evaluation of the stability of some alloys in the Cu–As–Te glassy system by differential scanning calorimetry

J. Vázquez [a,*], P.L. López-Alemany [a], P. Villares [b], R. Jiménez-Garay [a]

[a] *Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad de Cádiz, Apartado 40, 11510 Puerto Real, Cádiz, Spain*

[b] *Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Cádiz, Apartado 40, 11510 Puerto Real, Cádiz, Spain*

Received 9 September 1997; accepted 16 September 1997

Abstract

The glass formation and devitrification of alloys in the Cu–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 a new parameter $K_r(T)$ is added to the stability criteria. The stability of some ternary compounds of $Cu_xAs_{0.55-x}Te_{0.45}$ type has been evaluated experimentally and correlated with the activation energies of crystallization by this new kinetic criterion and compared with those evaluated by other criteria. © 1998 Elsevier Science B.V. All rights reserved

PACS: 81.05.Ge; 81.05.Kf

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

1. Introduction

Traditionally solid state physics has meant crystal physics. Solidity and crystallinity are considered as synonymous in the texts on condensed matter. Yet, one of the most active fields of solid state research in recent years has been the study of solids that are not crystals, solids in which the arrangement of the atoms lacks the slightest vestige of long-range order. The advances that have been made in the physics and chemistry of these materials, which are known as amorphous solids or as glasses, have been widely appreciated within the research community. 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

---

[*] Corresponding author. Fax: +34-56-834924.

PII S0167-577X(97)00241-3

recently been studied [3,4]. Therefore it is very important to know the glass stability and chemical durability of this type 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 are easily and accurately obtained by differential scanning calorimetry (DSC) during the heating processes of glass samples. Dietzel introduced the first glass criterion, $\Delta T = T_{in} - T_g$ (T_{in} is the temperature at which crystallization begins), which is often an important parameter to evaluate the glass forming ability of the glasses. By the use of characteristic temperatures, Hruby developed the Hr criterion, $\mathrm{Hr} = \Delta T/(T_m - T_p)$. On the basis of the Hr 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 $Cu_xAs_{0.55-x}Te_{0.45}$, where $x = 0.10$ (S1), $x = 0.20$ (S2) and $x = 0.25$ (S3), and it is found that the parameters ΔT, Hr, 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 [15]. 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, u

$$x = 1 - \exp\left[-g\left(\int_0^t u\,\mathrm{d}t'\right)^n\right] = 1 - \exp(-gI_1^n). \tag{1}$$

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 as 'site saturation' by Cahn [16,17].

Although, in general, the temperature dependence of the crystal growth rate is not Arrhenian when a broad range of temperature is considered [18], 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 for crystal growth 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

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

K being the reaction rate constant.

The maximum crystallization rate 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 for a non-isothermal process 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 the alternating series

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

where it is possible to use only the first term, without making any appreciable error, and to obtain $I_1 =$

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
S1	2	405	443	466	517	38	0.745	0.094	2.158
	4	410	449	472	524	39	0.750	0.095	2.188
	8	413	453	478	531	40	0.755	0.097	2.421
	16	417	458	483	537	41	0.759	0.098	2.458
	32	422	464	489	544	42	0.764	0.100	2.488
S2	2	413	460	482	533	47	0.922	0.114	2.504
	4	417	465	488	540	48	0.923	0.115	2.647
	8	420	469	494	547	49	0.925	0.117	2.917
	16	424	474	501	555	50	0.926	0.118	3.184
	32	427	478	508	563	51	0.927	0.119	3.583
S3	2	416	466	490	537	50	1.064	0.120	2.885
	4	420	472	497	545	52	1.074	0.124	3.095
	8	423	476	504	553	53	1.081	0.125	3.508
	16	425	479	511	561	54	1.085	0.127	4.066
	32	428	483	519	569	55	1.092	0.129	4.626

$RT^2K(\beta E)^{-1}$, 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. (4), one obtains

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

or in a logarithmic form

$$\ln\left(T_p^2/\beta\right) = \ln(E/R) - \ln K_0 + E/RT_p \qquad (5)$$

An equation for 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 stability of glassy materials, Surinach et al. [10] introduced a $K(T_g)$ criterion, and Hu et al. [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 Hr parameter itself is a stability factor based on characteristic temperatures. Here a stability criterion is defined as $K_r(T)$:

$$K_r(T) = K_0\exp(-\mathrm{Hr}E/RT)$$

where T is any temperature between T_g and T_p. 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 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

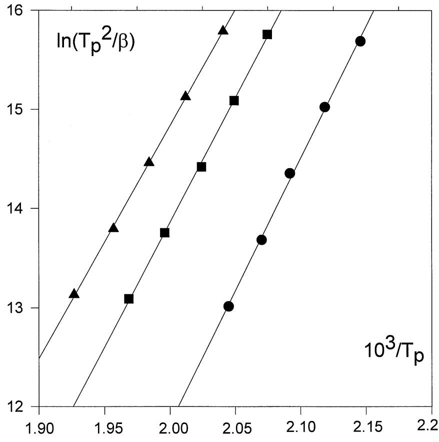

Fig. 1. Plots of $\ln(T_p^2/\beta)$ versus $1/T_p$ and straight regression lines for the three glassy alloys. S1 (●), S2 (■), S3 (▲).

Table 2
Straight regression lines (SRL) fitted to values of $\ln(T_p^2/\beta)$ and kinetics parameters of the analyzed alloys

Alloy	SRL	E (kcal mol^{-1})	K_0 (s^{-1})	r
S1	$26.6674 \times 10^3/T_p - 41.5018$	53.3	2.82×10^{22}	0.9992
S2	$25.0692 \times 10^3/T_p - 36.2790$	50.1	1.43×10^{20}	0.9996
S3	$23.4295 \times 10^3/T_p - 32.0283$	46.9	1.90×10^{18}	0.9998

r is the correlation coefficient.

(99.999%) copper, arsenic and tellurium 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^{-4} Torr, heated to 900°C for about 5 h and then quenched in ice water, which supplied the necessary cooling rate for obtaining the glass. The ampoules were continuously rotated in the furnace to homogenize the contents. 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 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 intersection of the two linear portions adjoining the transition elbow in the DSC trace.

4. Results and discussion

The characteristic temperatures from DSC scans are given a Table 1. The stability of the three alloys studied can be estimated by using these characteristic

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	7.46×10^{-7}	4.11×10^{-3}	14.45	8.85×10^3
	4	1.66×10^{-6}	8.50×10^{-3}	18.98	11.47×10^3
	8	2.67×10^{-6}	1.73×10^{-2}	19.59	14.76×10^3
	16	4.95×10^{-6}	3.07×10^{-2}	24.21	18.31×10^3
	32	1.06×10^{-5}	6.05×10^{-2}	31.37	23.30×10^3
S2	2	6.51×10^{-7}	3.84×10^{-3}	7.39×10^{-5}	0.221
	4	1.17×10^{-6}	7.28×10^{-3}	1.19×10^{-4}	0.379
	8	1.79×10^{-6}	1.36×10^{-2}	1.57×10^{-4}	0.609
	16	3.14×10^{-6}	2.76×10^{-2}	2.49×10^{-4}	1.116
	32	4.76×10^{-6}	5.49×10^{-2}	3.45×10^{-4}	2.010
S3	2	6.27×10^{-7}	3.12×10^{-3}	1.70×10^{-8}	1.46×10^{-4}
	4	1.07×10^{-6}	6.13×10^{-3}	1.72×10^{-8}	1.87×10^{-4}
	8	1.59×10^{-6}	1.18×10^{-2}	1.79×10^{-8}	2.72×10^{-4}
	16	2.07×10^{-6}	2.23×10^{-2}	1.90×10^{-8}	4.52×10^{-4}
	32	3.05×10^{-6}	4.53×10^{-2}	1.97×10^{-8}	7.09×10^{-4}

temperatures, T_g, T_{in}, T_p, and T_m. The existing stability criterion parameters based on these characteristic temperatures are also listed an Table 1.

To obtain the kinetic parameters of the crystallization, Eq. (5) is applied. Fig. 1 represents the evolution of $\ln(T_p^2/\beta)$ versus $1/T_p$ for the three alloys. The plots were found to be straight lines in accordance with Eq. (5). 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 are listed in Table 3. Fig. 2 represents the plots of $K_r(T)$ versus T. It is found that $K_r(T)$ of S3 varies slowly with increasing T and the values are on T axis, while $K_r(T)$ of S1 varies rapidly with increasing 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 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, Hr, H' and S, in Table 1 show that the 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 [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 the S3 glass sample is the most

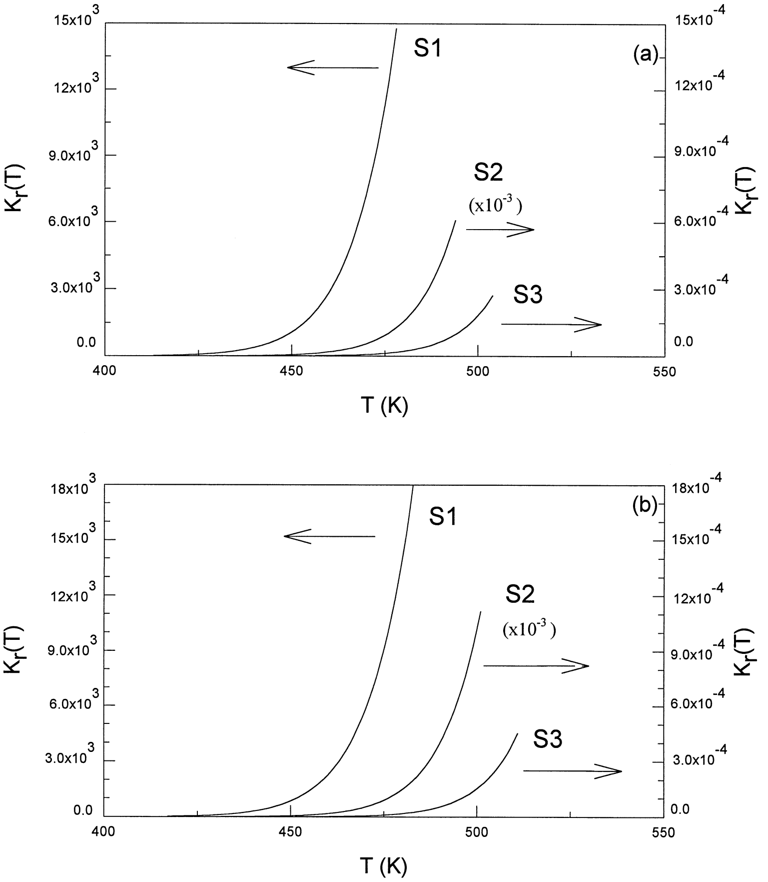

Fig. 2. Plots of $K_r(T)$ versus T for the three glassy alloys to verify the stable order. (a) $\beta = 8$ K min^{-1}, (b) $\beta = 16$ K min^{-1}.

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 alloys are also the most stable, and the order 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 [15], where it is noted that when copper is introduced into glassy arsenic tellurides their thermal stability is increased, since one produces a substantial strengthening of glass structure.

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. 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 Cu–As–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 and temperature. Among the three glassy alloys, $K_r(T)$ of the 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.

Acknowledgements

The authors are grateful to the Junta de Andalucía for their financial support.

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, D. 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] Z.U. Borisova, Glassy Semiconductors, Plenum, New York, 1981.
[16] J.W. Cahn, Acta Metall. 4 (1956) 573.
[17] J.W. Cahn, Acta Metall. 4 (1956) 449.
[18] H. Yinnon, D.R. Uhlmann, J. Non-Cryst. Solids 54 (1983) 253.