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Iso-conversional kinetic study of non-isothermal crystallization in glassy $Se_{98}Ag_2$ alloy

C. Dohare · N. Mehta

Abstract The crystallization kinetics of glassy $Se_{98}Ag_2$ alloy is studied at different heating rates (5, 10, 15, and 20 K min^{-1}) using differential scanning calorimetric technique. Endothermic and exothermic peaks are obtained at glass transition (T_g) and crystallization temperature (T_c). Four iso-conversional methods (Kissinger–Akahira–Sunose (KAS), Flynn–Wall–Ozawa (FWO), Tang and Straink) were used to determine the various kinetic parameters (crystallization temperature T_α, activation energy of crystallization E_α, order parameter n) in non-isothermal mode.

Keywords Differential scanning calorimetry · Crystallization kinetics · Chalcogenide glasses

Introduction

Iso-conversional methods are used for non-isothermal analysis, in which the transformation rate at a constant extent of conversion is only a function of temperature as suggested by Vyazovkin et al. [1–4] and other workers. Iso-conversional techniques make it possible to estimate the activation energy of a process as a function of the extent of conversion, α. Analysis of the activation energy dependence on α provides important clues about reaction mechanism. The kinetic parameters, in this case, are considered to be dependent on the degree of transformation at different temperatures and times [5–8]. The use of iso-conversional methods is widespread in the physical chemistry for the determination of the kinetics of the thermally activated solid-state reactions. The physico-chemical changes during an exothermic or endothermic event in DSC are complex and involve multi-step processes occurring simultaneously at different rates. Therefore, the activation energies for such processes can logically not be same, and it may vary with the degree of conversion [9, 10]. While the activation energy of isothermal method is thus constant and independent of the degree of conversion. A strong difference of opinion persists among the researchers in the field of thermal analysis about the concept of variable activation energy. In the metallurgical branch of materials science, most of the thermal phase transformations (like crystallization) are morphological and are considered to be governed by the nucleation and growth processes [11–13]. The transformation mechanisms in these processes are also complex like interface-controlled, diffusion-controlled growth.

The complete kinetic behavior is revealed by iso-conversional method as a variation of the effective energy with the cure progress [14]. El-Oyoun [14] has performed an experiment to study the variation between Avrami exponent n and extent of conversion α. A comparison with other kinetic methods reveals the advantage of iso-conversional method in detecting the complexity of the curing kinetics [15, 16]. Yet another benefit is that iso-conversional methods yield consistent value of activation energy for isothermal and non-isothermal conditions [17]. The lower values of E_α are characteristic of diffusion of small molecules in liquid/solid medium, and the effect can be explained by diffusion control associated with vitrification. A correlation of the decrease in E_α with a decrease in molecular mobility has been established experimentally by temperature-modulated DSC. The correlation of a decrease in the E_α values with vitrification can be demonstrated chemically. A contribution of cross linking becomes

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increasing important so that the E_α value drops quickly to low values of diffusion. The decrease has been reported to correlate with an increase in the shear modulus and a decrease in the complex heat capacity. It is seen that the model free prediction compares very well with actual measurement. Zvetkov [18] has applied an iso-conversion method to cure DGEBA with 1,3 phenylene diamine (m-PDA). Chen and Dollimore [19] have performed an experimental measurement on CaC_2O_4 and mixture of $CaCO_3$ with $Ca(OH)_2$. Recently, Lopez et al. [20] have reported iso-conversional kinetic analysis of resol–clay nanocomposites.

A few crystallization studies of metallic glasses are reported considering the variation of the kinetic parameters with the degree of conversion. Simon et al. [21] have shown the variation of α versus T. Malek [22] has reported a small variation in the value of E_α over $0.3 \leq \alpha \leq 0.7$ range. Recently, Suño and Bonastre [23] reported crystallization kinetics in $Fe_{74}Ni_{3.5}Mo_3B_{16}Si_{3.5}$ and $Fe_{41}Ni_{38}Mo_3B_{18}$ metallic glasses using iso-conversional analysis.

Ag-doped chalcogenide glasses and thin films have become attractive materials for fundamental research of their structure, properties, and preparation [24]. They have many current and potential applications in optics, optoelectronics, chemistry, and biology (optical elements, gratings, memories, micro-lenses, waveguides, bio-sensors and chemical-sensors, solid electrolytes, batteries, etc.). Recently, there is an increasing interest on new materials for phase change recording. Usually, these are alloys with silver as dopants. Ag-based phase change materials are characterized by both fast crystallization and high thermal stability of their amorphous recorded mark. Silver containing non-oxide chalcogenide glasses have been extensively studied due to their interesting electronic and optoelectronic properties.

Ag-doped glasses can be used as optical memory materials and materials for holography [24]. Their sensitivity can be increased by the simultaneous application of an electrical field with light. The low free energy of crystallization of Ag (48 kcal mol^{-1}) is a further reason to consider the introduction of Ag in chalcogenide glasses used for phase change optical recording. This enables one for the attainment of the main requirements of good optical recording like high phase transformation rate. Hence, we have selected Ag as chemical modifier with Se as parent element. This study reports the study of crystallization kinetics in glassy $Se_{98}Ag_2$ alloy using iso-conversional methods.

Material preparation

Glassy alloy of $Se_{98}Ag_2$ was prepared by quenching technique. The exact proportions of high purity (99.999%) elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4} g. The materials were then sealed in evacuated ($\sim 10^{-5}$ Torr) quartz ampoules (length ~ 5 cm and internal diameter ~ 8 mm). Each ampoule was kept inside the furnace at 1000 °C (where the temperature was raised at a rate of 3-4 °C min^{-1}). During heating, all the ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules were tucked away in the furnace. This was done to obtain homogeneous glassy alloy.

After rocking for about 12 h, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water rapidly. The ingots of the samples were then taken out by breaking the quartz ampoules.

Experimental

The glass, thus prepared, was ground to make fine powder for DSC studies. 10–20 mg of the powder was heated at constant heating rate, and the changes in heat flow with respect to an empty reference pan were measured. The thermal behavior was investigated using differential scanning calorimeter (Model-DSC plus, Rheometric Scientific Company, UK). The temperature precision of this equipment is ±0.1 K with an average standard error of about ±1 K in the measured values (glass transition and crystallization temperatures). The structure of the annealed sample was verified by a X-ray diffractometer using CuK_α radiation ($\lambda = 1.5405$ A°). The X-ray tube voltage and current were 30 kV and 20 mA, respectively. The scan range was 5°–80° (2θ), and the scan speed was 1°/min. The XRD pattern of annealed sample of $Se_{98}Ag_2$ alloy is shown in Fig. 1. This XRD pattern clearly shows the peaks corresponding to some well-defined crystalline phases. Se, Ag, and Ag_2Se has structural face of hexagonal, cubic (face centered), and cubic (body centered), respectively.

Measurements were made under almost identical conditions at four different heating rates 5, 10, 15, and 20 °C min^{-1} so that a comparison of various kinetic parameters of crystallization could be made to understand the effect of Ag element in binary $Se_{98}Ag_2$ alloy.

Theoretical basis

The kinetics of crystallization in amorphous material can be described by the following rate equation [25]:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \qquad (1)$$

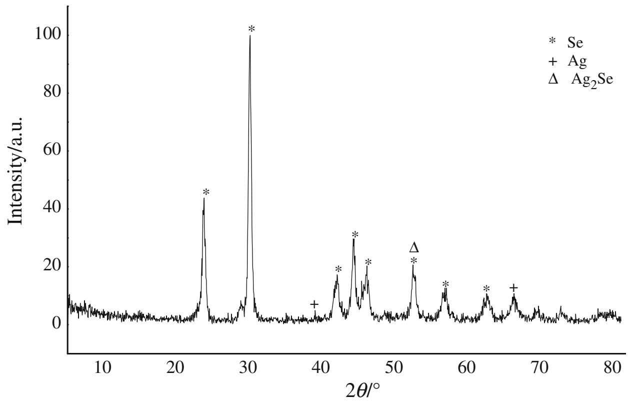

Fig. 1 XRD Scan of $Se_{98}Ag_2$ alloy

where $f(\alpha)$ is the reaction model. Under non-isothermal condition with a constant heating rate $\beta = \frac{dT}{dt}$, Eq. 1 may be written as:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\left(\frac{1}{\beta}\right) = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha). \tag{2}$$

The integral form of reaction model can be obtained by integrating Eq. 2 as:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^{t} \exp\left(-\frac{E}{RT}\right)dT = \frac{A}{\beta}I(E,T). \tag{3}$$

Using an advanced iso-conversional method, n experiments are carried out at different heating rates. And the effective activation energy can be determined at any particular value of α.where the integral $I(E,T)$ is given by

$$I(E,T) = \int_0^{t} \exp\left(-\frac{E}{RT}\right)dt. \tag{4}$$

Kissinger–Akahira–Sunose (KAS) method

Iso-conversion methods require the determination of the temperature $T_{\alpha i}$ at which a fixed fraction of α of the total amount is transformed. In KAS method, the relation between the temperature $T_{\alpha i}$ and heating rate β is given by [26, 27]:

$$\ln\left(\frac{\beta}{T_{\alpha i}^2}\right) = -\frac{E_\alpha}{RT_{\alpha i}} + \text{const.} \tag{5}$$

The subscript i denotes different heating rate. For each degree of conversion, corresponding $T_{\alpha i}$ and heating rate are used.

Flynn–Wall–Ozawa (FWO) method

Flynn–Wall–Ozawa method [28–30] has been used for the determination of non-isothermal analysis of crystallization in which the temperature integral in Eq. 3 is simplified using the Doyle's approximation [31, 32] and the relation is estimated as follow:

$$\ln \beta_i = -1.052\left(\frac{E_\alpha}{RT_{\alpha i}}\right) + \text{const.} \tag{6}$$

Tang method

Temperature integral relation has been suggested by Tang and given as [33]:

$$\ln\left(\frac{\beta_i}{T_{\alpha i}^{1.895}}\right) = -1.00145\left(\frac{E_\alpha}{RT_{\alpha i}}\right) + \text{const.} \tag{7}$$

Straink method

The method proposed by Straink is given as [34, 35]:

$$\ln\left(\frac{\beta_i}{T_{\alpha i}^{1.92}}\right) = -1.0008\left(\frac{E_\alpha}{RT_{\alpha i}}\right) + \text{const.} \tag{8}$$

Results and discussion

The glass crystallization kinetics is generally well characterized from the data of DSC experiment at different heating rates. Figure 2 shows typical DSC scans at heating rate of 5, 10, 15, and 20 K min^{-1} for glassy $Se_{98}Ag_2$ alloy. Each DSC scan showed a well-defined endothermic peak at the glass transition temperature T_g and an exothermic peak at the crystallization temperature T_c

Variation of α with temperature T

In DSC scan, the crystallization temperature is exhibited as a temperature corresponding to the crystallized fraction (α) due to a sudden change in specific heat. The plot of α against T at four different heating rates is shown in Fig. 3. The values of T corresponding to α are given in Table 1. From this table, we notice a systematic shift in T to higher temperatures with an increase in heating rate β. Figure 3 shows the extent of crystallization α as a function of temperature at different heating rates.

Evaluation of activation energy of crystallization

Recent studies in iso-conversional method, the activation energy of crystallization is not constant but shows variation in different stages of the transformations. The activation energy of the crystallization process is obtained using Kissinger–Akahira–Sunose method (Eq. 5), Flynn–Wall–Ozawa method (Eq. 6), Tang method (Eq. 7), and Straink method (Eq. 8). Straight lines are obtained by plotting $\ln(\beta_i/T_{\alpha i})$ versus $1000/T$ (Eq. 5), $\ln(\beta_i)$ versus $1000/T$ (Eq. 6),

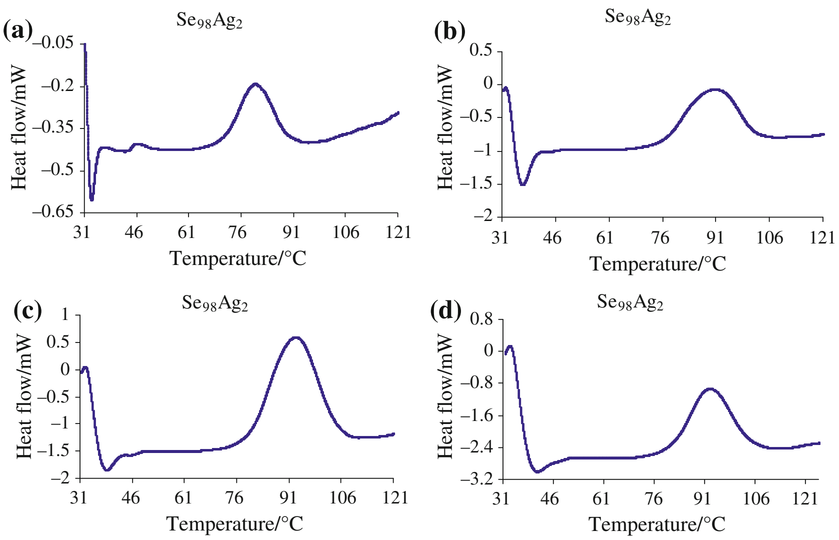

Fig. 2 DSC scans of $Se_{98}Ag_2$ alloy at heating rate of **a** 5/K min^{-1}, **b** 10/K min^{-1}, **c** 15/K min^{-1}, and **d** 20/K min^{-1}

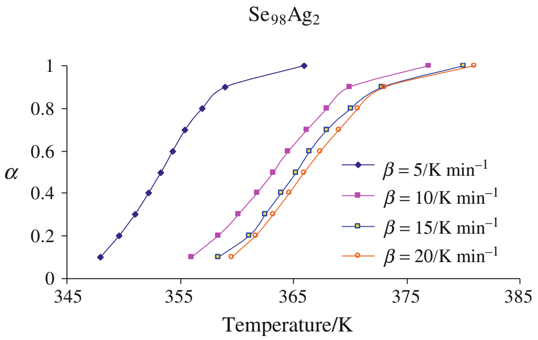

Fig. 3 Plot of α versus temperature T for glassy $Se_{98}Ag_2$ alloy

$\ln(\beta_i/T_{\alpha i}^{1.895})$ versus $1000/T$ (Eq. 7), and $\ln(\beta_i/T_{\alpha i}^{1.895})$ versus $1000/T$ and shown in Fig. 4. From the slope of the straight line, it is possible to derive the value of the activation energy of the crystallization. The calculated activation energy of crystallization at four different methods is given in Table 2.

Activation energy with variation of α and crystallization temperature T

In order to investigate the variation of activation energies with extent of conversion and hence with temperature, four isoconversional methods were used. Experimental data of above mentioned four methods were used to evaluate the activation energies at different values of α. Figure 5 shows a pronounced variation in the effective activation energy, E, as a function of the degree of conversion α. As indicated in Fig. 5, all the methods show a gradual decrease in E as α increase.

Figure 6 shows the variation in the effective activation energy, E, as a function of crystallization temperature T. The observed decrease of the activation energy with temperature demonstrates that the rate constant of crystallization is in fact determined by the rates of two processes, nucleation and diffusion. This interpretation is based on the nucleation theory proposed by Fisher and Turnbull [36].

Table 1 Values of temperature in crystallization region for fixed extent of conversion (α) glassy $Se_{98}Ag_2$ alloys at different heating rates

Crystallized fraction (α)	Temperature/K			
	5/K min^{-1}	10/K min^{-1}	15/K min^{-1}	20/K min^{-1}
0.1	348.0	356.0	358.4	359.5
0.2	349.6	358.4	361.1	361.7
0.3	351.0	360.2	362.5	363.2
0.4	352.2	361.8	363.9	364.6
0.5	353.3	363.2	365.2	366.0
0.6	354.3	364.5	366.4	367.4
0.7	355.4	366.2	368.0	369.0
0.8	357.0	368.0	370.1	370.7
0.9	359.0	370.0	372.8	373.0
1.0	366.0	377.0	380.0	381.0

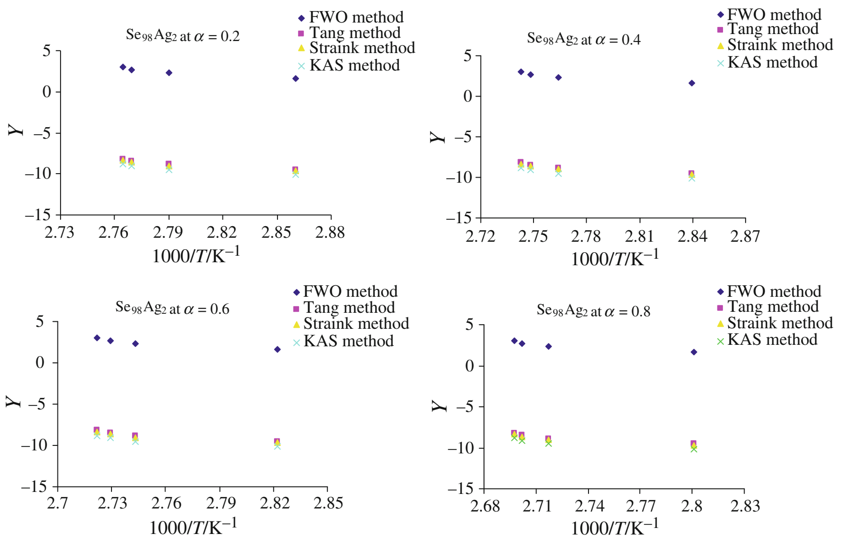

Fig. 4 Plots of ln ($\beta_i/T_{\alpha i}^2$) versus $10^3/T_{\alpha i}$, ln (β) versus $10^3/T_{\alpha i}$, ln ($\beta_i/T_{\alpha i}^{1.895}$) versus $10^3/T_{\alpha i}$, and ln ($\beta_i/T_{\alpha i}^{1.92}$) versus $10^3/T_{\alpha i}$ for glassy $Se_{98}Ag_2$ alloy

Table 2 Activation energy of crystallization of glassy $Se_{98}Ag_2$ alloys at different extent of conversion (α) for different iso-conversional methods

Crystallized fraction (α)	E/kJmol^{-1}			
	KAS method	FWO method	Tang method	Straink method
0.1	111.4	111.4	111.4	111.4
0.2	103.2	103.8	103.4	103.4
0.3	102.6	103.1	102.7	102.7
0.4	100.6	101.3	100.8	100.8
0.5	98.9	99.7	99.0	99.0
0.6	96.9	97.8	97.1	97.1
0.7	92.9	94.1	93.2	93.2
0.8	91.6	92.8	91.8	91.7
0.9	90.0	91.4	90.6	90.2

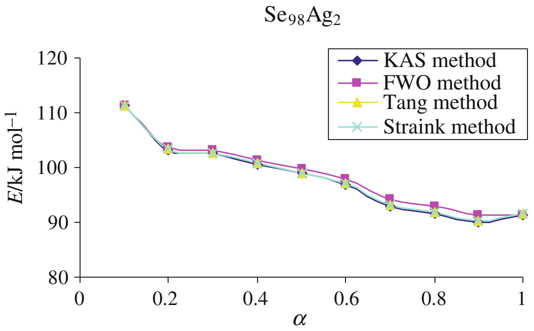

Fig. 5 Plot of activation energy E versus crystallized fraction α for glassy $Se_{98}Ag_2$ alloy

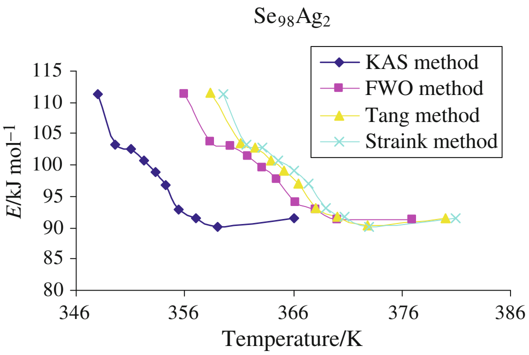

Fig. 6 Plot of activation energy E versus temperature T for glassy $Se_{98}Ag_2$ alloy

Estimation of local Avrami exponent n with α

The Avrami exponent can be calculated from the following equation [37]:

$$n(\alpha) = -\frac{R}{E(\alpha)} \frac{\partial \ln[-\ln(1-\alpha)]}{\partial\left(\frac{1}{T}\right)}. \tag{9}$$

The calculated values of the Avrami exponent n for different heating rates are plotted as a function of α in Fig. 7. The results of Avrami exponent n with respect to α are given in Table 3. The Avrami exponent n shows strong dependence on (α) for heating rate 5°C min^{-1}, whereas the variation of n is very small in the range of $0.3 < \alpha < 0.6$

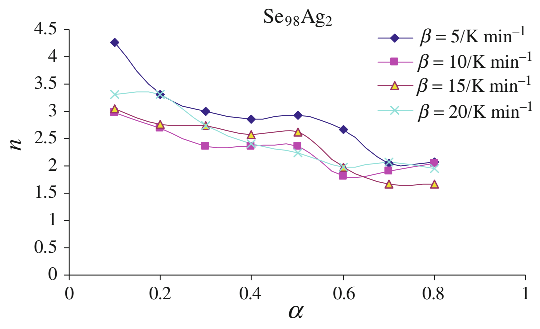

Fig. 7 Plot of local Avrami exponent n versus crystallized fraction α for glassy $Se_{98}Ag_2$ alloy

Table 3 Local Avrami exponent n of glassy $Se_{98}Ag_2$ alloys at different extent of conversion (α) for different heating rates

Crystallized fraction (α)	n			
	$5/K\ min^{-1}$	$10/K\ min^{-1}$	$15/K\ min^{-1}$	$20/K\ min^{-1}$
0.1	4.3	2.9	3.0	3.3
0.2	3.3	2.7	2.8	3.3
0.3	3.0	2.4	2.7	2.8
0.4	2.9	2.3	2.6	2.4
0.5	2.9	2.4	2.6	2.2
0.6	2.7	2.1	1.9	2.1
0.7	2.1	1.9	1.7	1.9
0.8	2.1	1.8	1.6	1.9

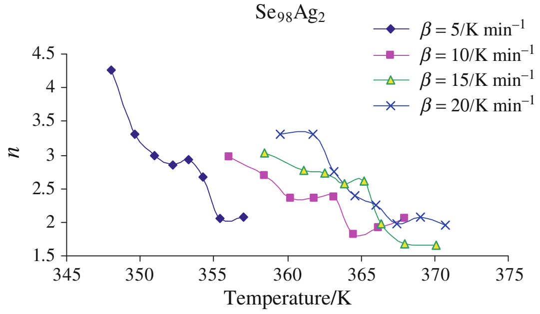

Fig. 8 Plot of local Avrami exponent n versus temperature T for glassy $Se_{98}Ag_2$ alloy

for the heating rate 10, 15, and 20°C min^{-1}. The local Avrami exponent for the more reliable higher heating rate 10, 15, and 20°C min^{-1} is about 2.5. This is consistent with a reaction dominated by continuous nucleation and interface-controlled growth. Figure 8 shows the variation of local Avrami exponent n, with temperature T. It is clear from Fig. 8 that n decreases with increase in temperature. It is well known that crystallization of chalcogenide glasses is associated with nucleation and growth process and the extent of crystallization α increases with increase in temperature. In other words it tends to its maximum value 1. The decreasing trend of n, therefore, shows the decrease in the nucleation rate due to nucleation saturation.

Conclusions

The crystallization kinetics of amorphous to crystalline phase transformation in glassy $Se_{98}Ag_2$ alloy is studied by DSC technique using iso-conversional methods. The major conclusions are listed below:

(1) The activation energy as determined from four iso-conversional methods was found to vary with the extent of conversion.
(2) All the four iso-conversional methods showed that the activation energy decreases with increase of temperature.
(3) Order parameter n was found to vary with the extent of conversion at all heating rates.
(4) Order parameter n was found to be decrease as the temperature increases.

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