Kinetic study of selenium used as optical data storage and holographic recording materials

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A kinetic study has been performed on selenium for isothermal and continuous heating processes. The activation energy (E_a) and Avrami exponent (n) have been evaluated in the range 414 to 449 K for the isothermal process and at a heating rate of 5 to 40 K min^{-1} for continuous heating. A new iterative calculation to give exact values of E_a and n for a continuous heating process is also presented.

1. Introduction

The phase transformation of selenium and its alloys can be induced by laser illumination. This property makes them very attractive for optical data storage and holographic recording [1-8]. Many experimental results using selenium and its alloys have been reported, but few cases of phase transformation properties regarding those materials were mentioned. In this paper, some kinetic studies of selenium for both isothermal and continuous heating crystallization are presented. The results reported here support the conclusions reached in earlier optical storage experiments [1].

2. Theory of crystallization kinetics

The Avrami phenomenological equation for solid-to-solid transformation can be used to describe the kinetics of isothermal crystallization [9-11]. This equation is usually written

$$x = 1 - \exp(-Kt^n) \tag{1}$$

where x is the time-dependent crystalline fraction at time t, n is known as the Avrami exponent and K is the reaction rate. This reaction rate is governed over a finite temperature range by the Arrhenius law

$$K = K_0 \exp(-E_a/RT) \tag{2}$$

where T is the temperature in degrees Kelvin, R is the universal gas constant, K_0 is the rate constant and E_a, the apparent activation energy. Both nucleation and growth processes contribute to E_a.

For isothermal crystallization, both E_a and n can be easily obtained. From Equations 1 and 2 we have

$$\ln[-\ln(1 - x)] = \ln K_0 - \frac{E_a}{RT} + n \ln t \tag{3}$$

At constant T, a plot of $\ln[-\ln(1 - x)]$ against $\ln t$ can yield n, and at constant t a plot of $\ln[-\ln(1 - x)]$ against $1/T$ will give E_a. Also a plot of $\ln t_m$ against $1/T$, where t_m represents the time that corresponds to a maximum $(dx/dt)_T$, will yield E_a/n [12] defined as the "effective activation energy" by Henderson [13]. This value could be used to corrobate values of E_a and n obtained from Equation 3.

Many efforts have been made to generalize the Avrami equation to the non-isothermal or continuous heating crystallization case [12-14]. We want to introduce an iterative method to determine more accurately E_a and n values for a continuous heating crystallization process.

We still start with Equation 1 and consider that in a continuous heating process, K is dependent on time and $\phi = dT/dt$ is defined as the heating rate. We must assume, like other authors, that E_a, n and K_0 do not depend on temperature. In fact, it is not necessarily true in all cases, but as we will discuss later, this assumption does not introduce appreciable errors in our case.

From Equation 1 we have

$$\ln(1 - x) = -Kt^n \tag{4}$$

Differentiating Equation 4 with respect to time t and considering K as a time-dependent function, we have

$$\frac{dx}{dt} = (1 - x)\left(\frac{dK}{dt} t^n + Knt^{n-1}\right) \tag{5}$$

It is easy to see that

$$\frac{dK}{dt} t^n = \frac{dK}{dT}\frac{dT}{dt} t^n = -\ln(1 - x)\phi \frac{E_a}{RT^2}$$

and

$$Knt^{n-1} = K^{1/n}n[-\ln(1 - x)]^{(n-1)/n}$$

Assuming that

$$\left| -\ln(1 - x)\phi \frac{E_a}{RT^2} \right| \ll |K^{1/n}n[-\ln(1 - x)]^{(n-1)/n}| \tag{6}$$

we will obtain from Equation 5 the well-known Johnson–Mehl–Avrami–Erofeev equation [14]

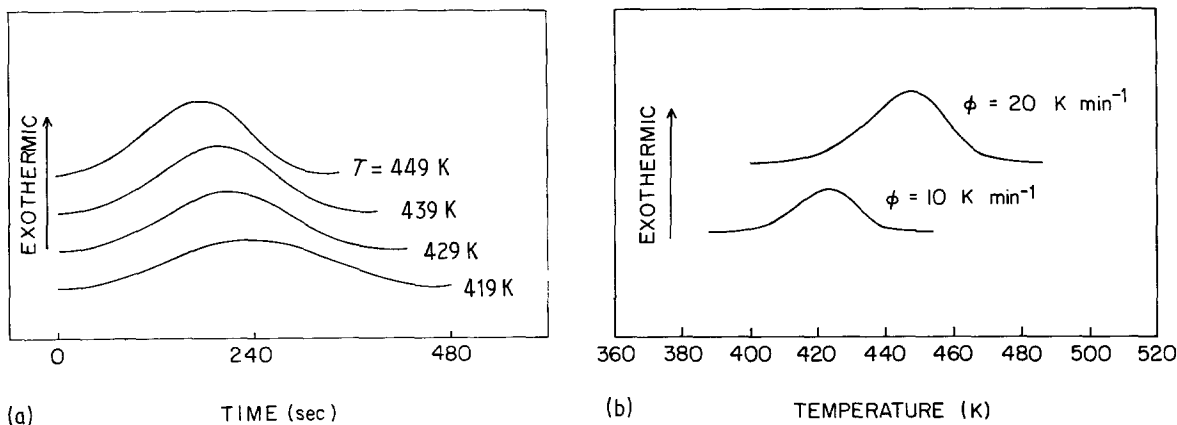$$\frac{dx}{dt} = \frac{dx}{dT}\phi = K^{1/n}n(1 - x)[-\ln(1 - x)]^{(n-1)/n} \tag{7}$$

Figure 1 (a) DSC curves for isothermal crystallization. (b) DSC curves for continuous heating crystallization.

which yields

$$\ln\left(\frac{dx}{dT}\,\phi\right) = \frac{1}{n}\ln K_0 - \frac{E_a}{nRT} + \ln n + \ln(1 - x)$$

$$+ \left(\frac{n-1}{n}\right)\ln\,[-\ln(1 - x)]. \quad (8)$$

A plot of $\ln[(dx/dT)\phi]$ against $1/T$ with fixed x will yield the effective activation energy, E_a/n. Also, a plot of $\{\ln[(dx/dT)\phi] - \ln(1 - x)\}$ against $\ln[-\ln(1 - x)]$ with T fixed will yield $(n - 1)/n$ and so n.

It has been verified with primitive E_a and n values

that in our particular case, the value of the left-hand side of Expression 6 is within the same order of magnitude as the right-hand side, making that assumption invalid.

An iterative method has been developed to give E_a and n values without using the assumption described by Expression 6. Keeping all terms in Equation 5, this equation will be rewritten

$$\phi\left[\frac{dx}{dT} + (1 - x)\ln(1 - x)\frac{E_a}{RT^2}\right]$$
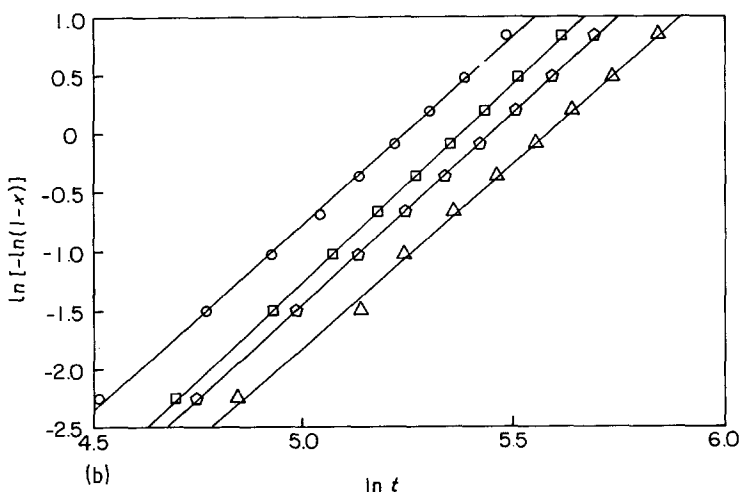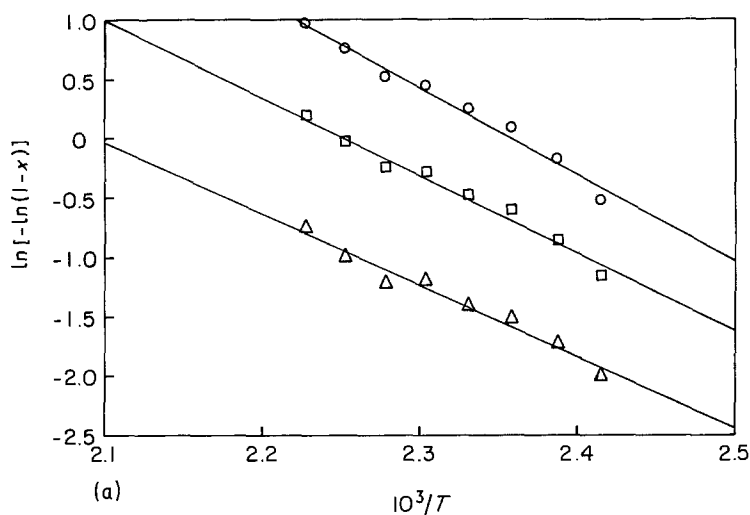
$$= K^{1/n}n(1 - x)[-\ln(1 - x)]^{(n-1)/n} \quad (9)$$

Figure 2 Isothermal crystallization of selenium. (a) Plots of $\ln[-\ln(1 - x)]$ against $1/T$ with t fixed to yield E_a: $t = $ (△) 150 sec, (□) 200 sec, (○) 250 sec (b) Plots of $\ln[-\ln(1 - x)]$ against $\ln t$ with T fixed to yield n: $T = $ (△) 419 K, (○) 429 K, (□) 439 K, (○) 449 K.
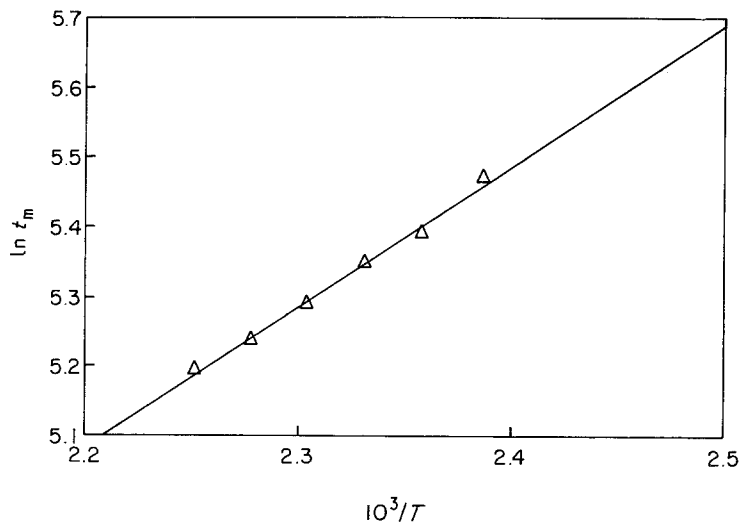
Figure 3 Same isothermal process as in Fig. 2: plot of $\ln t_m$ against $1/T$ to yield E_a/n.

and, in logarithmic form,

$$\ln\left\{\phi\left[\frac{dx}{dT} + (1 - x)\ln(1 - x)\frac{E_a}{RT^2}\right]\right\}$$

$$= \frac{1}{n}\ln K_0 - \frac{E_a}{nRT} + \ln n + \ln(1 - x)$$

$$+ \left(\frac{n - 1}{n}\right)\ln[-\ln(1 - x)]. \tag{10}$$

First of all, the initial values of E_a and n have to be determined. In fact, using Equation 8, these values can be evaluated. From Equation 10 with x fixed, we will have a new E_a/n value from a plot of $\ln\{\phi[(dx/dT) +$

$(1 - x)\ln(1 - x)(E_a/RT^2)]\}$ against $1/T$ and the initial value of n will be used to calculate the new E_a. This new E_a will then be used to determine the new n by means of a plot of $\ln[\phi \ln(\phi\{(dx/dT)[1/(1 - x)] + \ln(1 - x)(E_a/RT^2)\}]$ against $\ln[-\ln(1 - x)]$ with the temperature T fixed. The iteration will be repeated until convergence of E_a and n occurs.

3. Experimental results and discussion
3.1. Experimental details
The data for the crystallization process were obtained by differential scanning calorimetry (DSC). It was performed on a Perkin-Elmer DSC2. About 2.4 mg
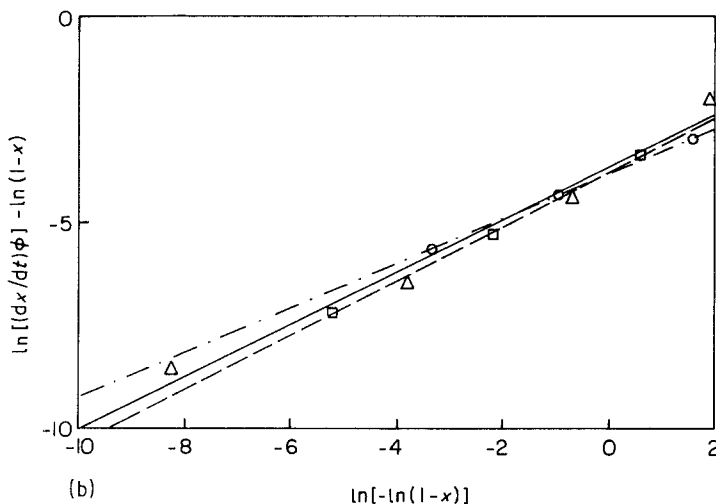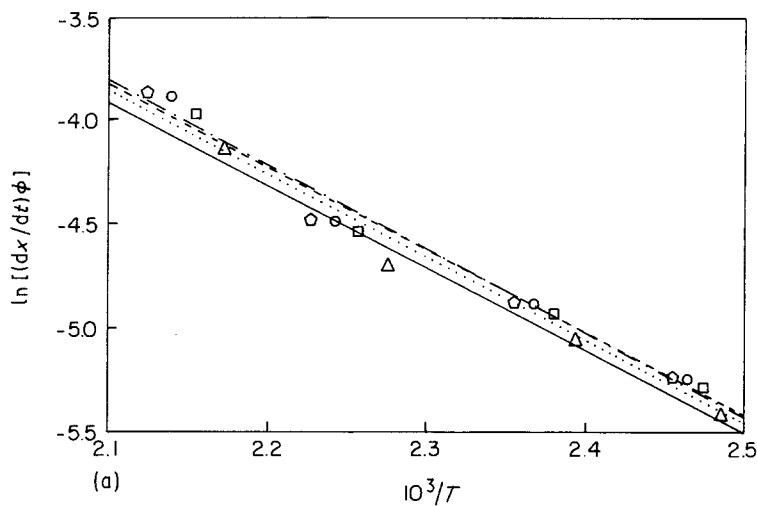

(a)

(b)

Figure 4 Continuous heating crystallization of selenium. (a) Plot of $\ln[(dx/dT)\phi]$ against $1/T$ with x fixed to yield E_a/n (primitive): (——, $\triangle$) $x = 0.3$; (- - -, $\square$) $x = 0.4$; (— · —, $\bigcirc$) $x = 0.5$; (· · · ·, $\bigcirc$) $x = 0.6$. (b) Plot of $\{\ln[(dx/dT)\phi] - \ln(1 - x)\}$ against $\ln[-\ln(1 - x)]$ with T fixed to yield n (primitive); (——, $\triangle$) $T = 420$ K; (- - -, $\square$) $T = 430$ K; (— · —, $\bigcirc$) $T = 440$ K.
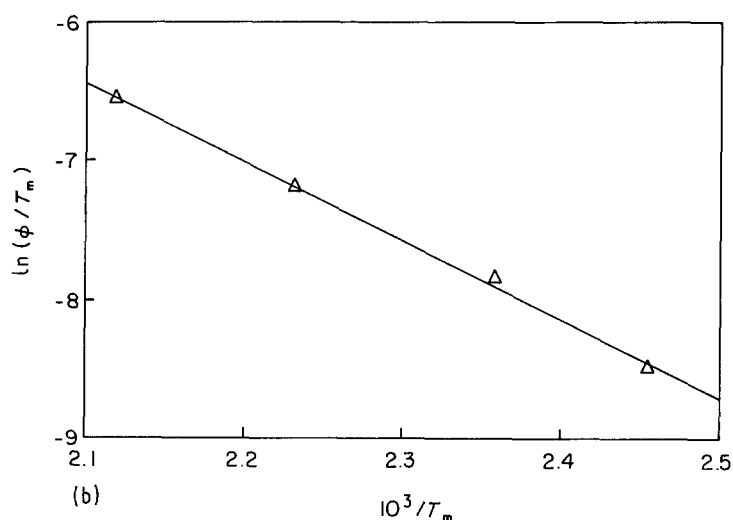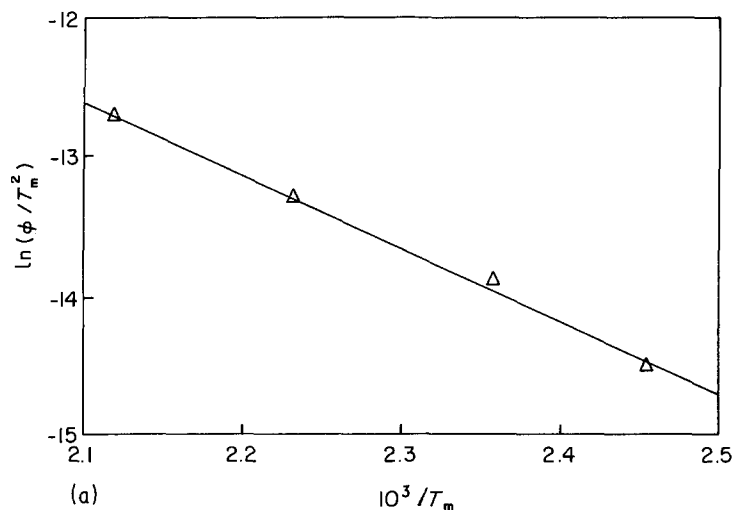
Figure 5 (a) Kissinger's plot, $\ln(\phi/T_m^2) = -(E_a/nRT) + \text{const.}$ (b) Marseglia's plot, $\ln(\phi/T_m) = -(E_a/nRT) + \text{const.}$

of powdered selenium specimen were used in our experiments and each specimen was treated to get an amorphous phase before an isothermal or continuous heating experiment. Isothermal annealing was performed at a heating rate of $320\,\text{K}\,\text{min}^{-1}$ until the annealing temperature was reached, and isothermal measurements were taken between 414 and 449 K. Continuous heating experiments were conducted at heating rates of 5 to $40\,\text{K}\,\text{min}^{-1}$, from $0°\,\text{C}$ (273 K) to the melting point. Typical exothermic curves are shown in Fig. 1.

3.2. Experimental results

Fig. 2a shows the plots of $\ln[-\ln(1 - x)]$ against $1/T$ for the isothermal process from which the activation energy E_a can be determined. Fig. 2b shows the plots of $\ln[-\ln(1 - x)]$ against $\ln t$ of the same isothermal process from which the Avrami exponent n is evaluated. The plot of $\ln t_m$ against $1/T$ is shown in Fig. 3 and the slope of this straight line gives the effective activation energy as indicated above.

Figs 4a and b show the plots of $\ln[(\mathrm{d}x/\mathrm{d}T)\phi]$ against $1/T$ and $\{\ln[(\mathrm{d}x/\mathrm{d}T)\phi] - \ln(1 - x)\}$ against $\ln[-\ln(1 - x)]$, respectively, for the continuous heating process. From these curves we obtained the values of effective activation energy E_a/n, activation energy E_a and Avrami exponent n under the approximation assumed in Expression 6.

For the sake of comparison, the Kissinger [15] and

Marseglia [12] continuous heating process plots were also carried out and are shown respectively in Figs 5a and b. The effective activation energies corresponding to these two methods were evaluated.

For more accurate E_a and n values, the iterative calculation described earlier was performed. E_a and n obtained from the plots of Fig. 4 were used as initial values for this calculation.

Table I includes all experimental and calculated results for both isothermal and continuous heating processes.

3.3. Discussion

The activation energy $(68.4\,\text{kJ}\,\text{mol}^{-1})$ given in Table I and obtained for a continuous heating process by using the iterative method is in good agreement with the value $(55.1\,\text{kJ}\,\text{mol}^{-1})$ obtained from an isothermal process. The difference between the Avrami exponents of an isothermal process and a continuous heating process is due to the difference in the saturation degree of the nucleation sites. Since in a continuous heating process the temperature increases constantly and the transformation takes place at low temperature, partial or complete nucleation site saturation is produced before reaching the growth part of the transformation. A decrease of n for a transformation with saturated nucleation sites (corresponding to the continuous heating process in our case) was indicated by Christian [16] and by

TABLE I Summary of results

Process	E_a/nR (× 10³)	E_a/R (× 10³)	E_a (kJ mol⁻¹)	n	$E_e = E_a/n$ (kJ mol⁻¹)
Isothermic		6.629*	55.1	3.24†	17.0
Isothermic, t_m method	2.011				16.7
Continuous heating, from Equation 8	3.996‡		86.9	2.62§	33.2
Continuous heating, from Equation 10	3.170¶		68.4	2.60ᵃ	26.4
Continuous heating, Kissinger's method		5.235	43.5		
Continuous heating, Marseglia's method	5.674				47.2

*Calculated from average of data obtained for t = 150, 200 and 250 sec.
†Calculated from average of data obtained for T = 419, 429, 439 and 449 K.
‡Calculated from average of data obtained for x = 0.3, 0.4, 0.5, and 0.6.
§Calculated from average of data obtained for T = 420, 430, and 440 K.
¶x = 0.4.
ᵃT = 430 K.

Ranganathan and Vonheimendahl [17]. The iterative calculation of E_a and n for a continuous heating process improves the calculation accuracy, especially for determining the E_a value.

The activation energy of selenium obtained here is lower than the value already published [18]. This could be due to the difference of purity of the selenium powder used in the experiments. In fact, the kinetic study of material used in the present work is done with material commonly used in optical recording experiments, making the results more relevant to this area.

In the isothermal experiments, an increase of Avrami exponent n with annealing temperature was observed but in the finite temperature range fom 419 to 449 K. The maximum variation with respect to the average value was lower than 4%. Thus this variation can be regarded as negligible. Since the activation energy is contributed to by the activation energy of nucleation and growth, and the activation energy of nucleation is dependent on temperature, thus a dependence of activation energy on temperature for the isothermal process should be observed. In fact, one can see this from the variance of linear regression in the determination of E_a. As can be seen, this dependence can also be regarded as negligible.

The activation energy E_a and Avrami exponent n seem to be more stable for a continuous heating process, which could be due to the nucleation saturation in this process [16].

Finally, we see that the activation energy of selenium is relatively small, and hence the crystallization of selenium can easily occur. This property allows us to quicken the crystallization process during the erasure process with selenium and its alloys used as optical data storage materials, and to decrease the optical recording energy for holographic recording. In our early optical recording experiment, an erasure time of 15 nsec for a pure selenium thin film was observed by using a frequency-doubled Nd⁺ : YAG laser (λ = 532 nm) with 15 nsec pulse duration [1]. Although these erasures with 15 nsec pulse duration were sometimes imcomplete due to laser power fluctuation, it allows us to hope for an erasure time lower than 100 nsec with selenium and its alloys. Since the

amorphous phase of pure selenium is rather unstable at room temperature the binary data written in a pure selenium thin film cannot last a long time. According to our isothermic process calculation, an amorphous spot in a thin film of pure selenium will be erased in a few hours at room temperature, thus making the alloys of selenium essential for practical utilization of this material for optical recording.

4. Conclusion
From a kinetic study of selenium, we conclude that a short erasure time in optical data storage applications and a low optical recording energy in holographic recording applications of thin films of selenium and its alloys can be expected because of its low activation energy.

The agreement between the isothermal process and the continuous heating process is satisfactory in our kinetic study of selenium. An iterative calculation for the continuous heating case can increase the accuracy of the results. More kinetic studies of selenium alloys are intended to be realized soon.

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