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CRYSTALLIZATION KINETICS IN THE As–Se–Te SYSTEM

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ABSTRACT

This work consists of a study on the crystallization reaction kinetics of six alloys in the As–Se–Te glassy system, chosen as representatitve of the easy DTA crystallization zone, within the concentration triangle of the system. The study was carried out by differential scanning calorimetry, using continuous heating methods, and the corresponding kinetic parameters were evaluated by an iterative method based on the Johnson–Mehl–Avrami theoretical model. Finally, the glass-forming ability (GFA) of the alloys and of the system are discussed by calculating the rate constant of the crystallization reactions.

INTRODUCTION

The crystallization process in amorphous alloys is generally studied by non-isothermal analysis, because of the great development of calorimetric techniques and the simplicity of performing the experiments performed. The crystallization kinetics of glass-forming materials are controlled by nucleation and growth mechanisms which, with a few exceptions, are characterized by an activation energy, E, and a kinetic exponent, n, according to the Johnson–Mehl–Avrami law [1,2]. These parameters can be determined by differential scanning calorimetry, which also allows an immediate observation of the transformation over a wider temperature range. Although the conclusions derived from the above mentioned Johnson–Mehl–Avrami theoretical model have been deduced strictly for isothermal experiments, they can be applied, under certain restrictions and within a wide temperature range, to the data obtained through non-isothermal experiments, thus obtaining satisfactory kinetic parameters for describing the crystallization reactions studied.

The glass-forming ability (GFA) of the materials can also be evaluated through the deduced kinetic parameters, in agreement with the meaning of the reaction rate constant [3].

Chalcogenide amorphous semiconductors have been extensively studied by many researchers, as they exhibit interesting reversible electrical switching and lock-on (memory) phenomena. Later research has clarified the fact

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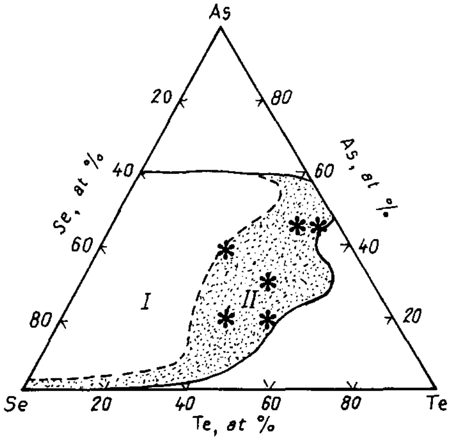

Fig. 1. The As–Se–Te system concentration triangle [4].

that memory phenomena are due to thermally induced phase transformations caused by Joule heating. However, the detailed kinetics of the process are not yet well understood. These electrical properties, as well as others (optical, magnetic, mechanic or thermal), will be well explained only when there is a deep knowledge of the mechanisms which control the structural change that takes place as an amorphous substance becomes crystalline. That is why, during the past few years, such great efforts are being made in the study of crystallization kinetics in glasses.

The As–Se–Te system is one of the most characteristic chalcogenide glasses, which is why it has been chosen for the study of its crystallization kinetics through the analysis of six different alloys that can be considered as representative of the glass possibilities of the system. Figure 1 shows the corresponding concentration triangle [4], where two well-defined areas can be observed. In the first, which has a lower Te content, DTA crystallization does not take place; in the second, the ternary glassy alloys crystallize easily. The points indicated in this figure correspond to the samples analyzed in this work.

BASIC FORMULAE AND ANALYSIS METHOD

The transformation equation for the crystallized fraction, x, as a function of time, t, according to the Johnson–Mehl–Avrami law, is

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

where K is the rate constant, which depends on the temperature as follows

$$K(T) = K_0 \, e^{-E/RT} \tag{2}$$

K_0 being the characteristic frequency factor of the reaction.

Denoting

$$f(x) = n(1-x)[-\ln(1-x)]^{(n-1)/n} \tag{3}$$

the following relationship is found for the crystallization rate, dx/dt

$$\ln(dx/dt) = \ln[K_0 f(x)] - E/RT \tag{4}$$

which, in the constancy interval $\ln[K_0 f(x)]$, makes it possible to construct a straight regression line between experimental values of the temperature and the corresponding crystallization rate, from whose slope, by an iterative method [5], the value of the activation energy, E, is deduced. If we take eqn. (3) into account, the above mentioned condition of constancy leads to the following expression

$$\ln K_0 + \ln n + \ln(1-x) + [(n-1)/n] \ln[-\ln(1-x)] = C \tag{5}$$

C being a constant.

By imposing condition (5) for any two values of the crystallized fraction, x_1 and x_2, within the said interval, it is possible to obtain the following for the kinetic exponent of the reaction

$$n = \frac{\ln[\ln(1-x_2)/\ln(1-x_1)]}{\ln[(1-x_2)\ln(1-x_2)/(1-x_1)\ln(1-x_1)]} \tag{6}$$

Expressions (5) and (6) make it possible to find the kinetic parameters n and K_0 from the data derived from the records obtained during the DSC experiments.

EXPERIMENTAL PROCEDURE

All the alloys were made in bulk form, from 99.999% pure components, homogeneously mixed in adequate proportions after being pulverized to grains of diameter under 64 μm. The mixture thus obtained was subjected to melting (600 °C) and quenching in cold water (0 °C) in order to avoid crystallization.

In all cases, the amorphous nature of the alloy obtained was checked by X-ray diffraction in a Siemens D-500 diffractometer. With part of the material obtained in each case, reduced to powder, the calorimetric experiments were carried out in a DSC Thermoflex (Rigaku Co.) previously calibrated with Sn, Pb and In standards. The samples used were kept in the mass range 7.00–30.00 mg, and were crimped in aluminium pans. An empty aluminium pan was used as reference in all the measurements, during which an inert gas (He-55) flowed through the heating furnace at 60 ml min^{-1}. The experiments were carried out using the continuous heating method, at rates of 2, 4, 8, 16 and 32 K min^{-1}.

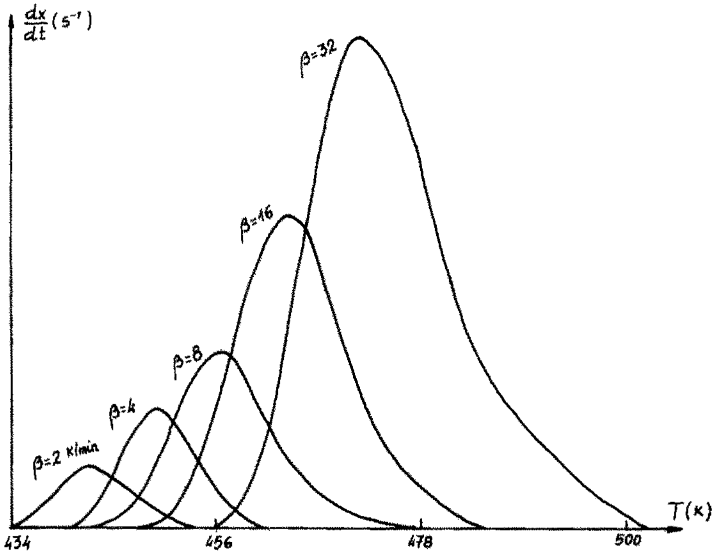

Fig. 2. dx/dt versus T curves for the different experimental β values for alloy $As_{0.45}Se_{0.10}Te_{0.45}$.

All the alloys studied exhibited one crystallization peak except $As_{0.45}Se_{0.05}Te_{0.50}$, which exhibits two perfectly defined crystallization stages. Figure 2 shows, as an example, the curves of dx/dt versus temperature obtained for the different heating rates, β, corresponding to alloy $As_{0.45}Se_{0.10}Te_{0.45}$.

The areas under the peaks, as well as the partial areas corresponding to the different crystallized fractions, were evaluated by a numerical procedure, similar to Simpson's method, which makes it possible to work with errors under 5%, the maximum value of the experimental error.

RESULTS

The first property supplied by inspection of the thermograms obtained for the analyzed alloys is that their characteristic temperatures, such as the glass transition temperature, T_g, and crystallization temperature, T_c (which has been identified in this work with the temperature corresponding to the maximum crystallization rate), increase as the experimental heating rate, β, increases. That is why Table 1 shows, for these magnitudes, the extreme values for $\beta = 2$ and $\beta = 32$ K min^{-1}, the remaining values being within the interval so defined. It is also observed that the maximum crystallization rate, $[dx/dt]_p$, for the different values of β for each alloy increases in a proportion similar to the increase in the heating rate, as has been pointed out by other authors for different alloys [6]. The table also shows the extreme values of this parameter for each compound.

TABLE 1

Alloys	T_g (K)	T_c (K)	$dx/dt \times 10^{-3}$ (s^{-1})	N	r	E (kcal mol^{-1})	Δx	n	K_0 (s^{-1})	$\langle K_p \rangle$ (s^{-1})
$As_{0.20}Se_{0.40}Te_{0.40}$	378–384	459–485	2.16–23.18	368	0.984	34.21	0.20–0.60	1.94	9.7×10^{13}	0.018
$As_{0.20}Se_{0.30}Te_{0.50}$	365–381	424–458	4.06–28.19	367	0.992	27.21	0.20–0.70	2.10	5.3×10^{11}	0.021
$As_{0.45}Se_{0.05}Te_{0.50}$(I)	401–421	458–486	1.84–20.44	249	0.986	39.50	0.20–0.60	1.96	1.7×10^{16}	0.010
$As_{0.45}Se_{0.05}Te_{0.50}$(II)		511–546	2.16–40.65	184	0.981	47.76	0.20–0.60	1.80	8.5×10^{17}	0.020
$As_{0.45}Se_{0.10}Te_{0.45}$	386–411	442–468	3.97–31.87	219	0.989	32.16	0.15–0.60	1.75	5.1×10^{13}	0.019
$As_{0.30}Se_{0.25}Te_{0.45}$	382–408	450–496	3.30–26.16	184	0.996	20.08	0.20–0.65	2.05	$2.4–10^{7}$	0.014
$As_{0.35}Se_{0.30}Te_{0.35}$	399–409	478–528	2.0–26.12	227	0.976	25.01	0.20–0.60	1.91	6.6×10^{8}	0.012

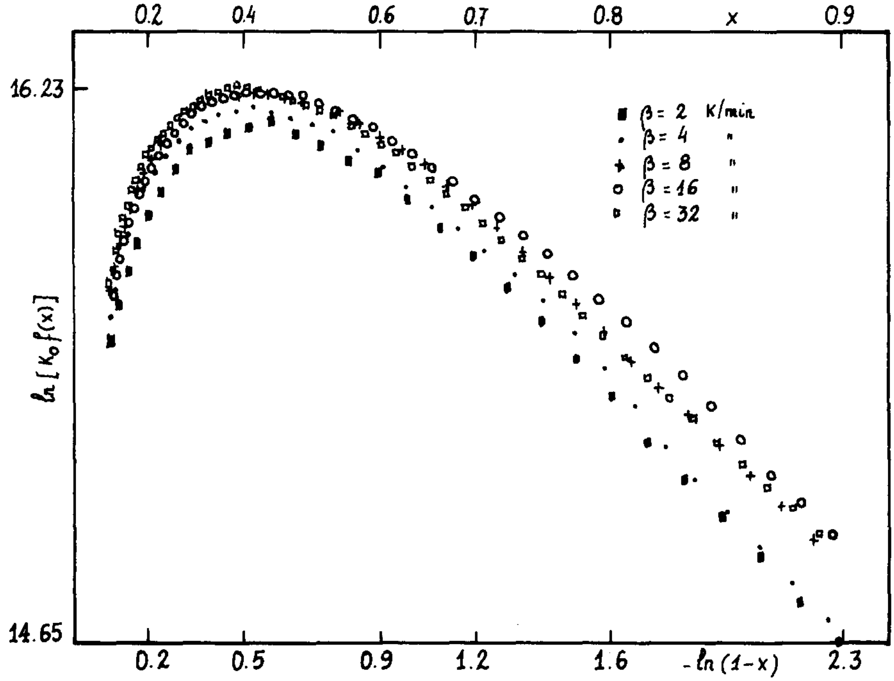

Fig. 3. Plot of $\ln[K_0 f(x)]$ versus x for alloy $As_{0.30}Se_{0.25}Te_{0.45}$.

According to the above mentioned iterative method, which has been expounded in detail in previous work [5], the experimental data were fitted linearly by least squares, in order to calculate the value of the activation energy for the alloys studied, by selecting the interval of the crystallized fraction in which the constancy of the function $\ln[K_0 \mathrm{f}(x)]$ is assumed, and in which the approximation of the method can be applied, in the Johnson–Mehl–Avrami theoretical model, to the data obtained through linear heating experiments. The table shows the number of experimental data, N, used with each alloy in this adjustment, the corresponding linear correlation coefficient, r, the constancy interval, Δx, for the crystallized fraction, and the calculated activation energy, E. In all cases, the constancy of the function $\ln[K_0 f(x)]$ was accepted when its variation in the interval under consideration was below 3% of the variation that such a function suffers in the total interval for the crystallized fraction ($0 \leqslant x \leqslant 1$), if this fact does not mean an excessive restriction of Δx. Figure 3 shows, as an example, the plots of $\ln[K_0 f(x)]$ versus x for the five heating rates at which alloy $As_{0.35}Se_{0.25}Te_{0.45}$ was analyzed, corresponding to the first approximation of the method ($0.1 \leqslant x \leqslant 0.9$); in the plots, the crystallized fraction interval in which the procedure will be repeated can be seen. Also, the experimental points are seen to correspond very well to the function associated to the chosen theoretical model [7].

The correctness of the adjustment carried out, and so of the calculated activation energy, depends on the width of the temperature interval for which experimental data are available, that is, on the range of heating rates that the DSC equipment used allows. In this sense, it has been observed that the use of experimental data which widen the thermal intervals most leads to better results, even if the instrumental limits are reached, than if the intervals are restricted to the heating rates best controlled by the DSC furnace.

Through expressions (5) and (6), by using a high enough number of values of the crystallized fraction, and by averaging the results for all of them, we can determine the other two kinetic parameters, Avrami's index, n, and the frequency factor, K_0, which are also shown in Table 1.

The values obtained for the activation energies of the analyzed samples may be considered analogous in order, except for the second crystallization phase of the alloy $As_{0.45}Se_{0.05}Te_{0.50}$. The value for this is higher, as demonstrated by the fact that the reaction takes place at a higher temperature because the formation of the activated complex requires a greater amount of energy. This fact may be interpreted in the sense that the energy barriers that separate the glassy states from the corresponding crystalline ones are similar for the six alloys studied, and that, as these are representative of the easy crystallization zone of the As–Se–Te glassy system, the reasoning could be extended to the whole system. It does not seem reasonable to expect very different behaviour in the crystallization reactions, at least in those with a single crystallization peak, within this zone, in contrast to what happens with other glassy system, in which the difference in concentration of one of the elements can be decisive, not only in terms of the kinetic parameters, but even in the resulting crystallization phases.

The calculated kinetic exponents also reinforce the previous conclusion, as they all have values close to 2, which, in the commonly accepted interpretation for this index [8], is representative of one-dimensional crystalline growth.

As to the glass-forming ability of these amorphous materials, the rate constant of the reaction corresponding to the maximum crystallization rate has been calculated for each compound and for each heating rate, according to eqn. (2), and, by averaging the value obtained, $\langle K_p \rangle$ has been determined for all the alloys studied. The results, which are also shown in Table 1, make it possible to establish an order of the compounds studied according to their GFA (which increases as the reaction rate constant decreases), but this order does not totally agree with what might be expected from their composition. This anomaly arises because these alloys contain two chalcogenide elements, Se and Te, which have a strong influence on glass-forming, the former favouring and the latter inhibiting it; their simultaneous presence leads to effects which are not very well understood, at least when it comes to evaluating them a priori.

Nonetheless, the order of magnitude found for the rate constant of these alloys, in relation to that found for compounds of other systems [5,9], makes it possible to state that the As–Se–Te system has a high glass-forming ability, which is also similar to that found for alloys of the Ge–As–Te system [3].

CONCLUSIONS

The constancy interval method has been proved effective for calculating the kinetic parameters of the crystallization reactions in the As–Se–Te system, and also for verifying the descriptive validity of the theoretical function derived from the Johnson–Mehl–Avrami model, through the good agreement with the experimental data.

The values obtained for the activation energy, as well as the rate constants, make it possible to classify the system as having a high glass-forming ability, in line with other ternary glasses.

All the alloys analyzed exhibit nucleation and one-dimensional crystalline growth, a fact which may be extended to all the alloys in the system, as those studied are considered representative, at least in the easy DTA crystallization zone.

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