A CRYSTALLIZATION STUDY OF $Se_{1-x} Bi_x$ (x = 0.05 at) BY CALORIMETRIC METHODS (*)

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ABSTRACT — Crystallization kinetics of the amorphous $Se_{0.95} Bi_{0.05}$ alloy, prepared by quenching of the melt at 850 K, has been studied by calorimetric DSC measurements. The estimated activation energy is 1.18 eV/at. Heterogenous nucleation is found to be preponderant during 80 % of the time taken by the whole crystallization process. The estimated critical cooling rate of 6.2 K/s is much smaller than the experimental one ($\sim 10^8$ K/s) and this produces a high quantity of homogeneity faults.

1 — INTRODUCTION

As is well known pure selenium and selenium alloys have a remarkable ability to amorphize by different methods. The system $Se_{1-x} Bi_x$ takes advantage of such a good ability for amorphization while it introduces a small amount of Bi that improves the transport properties [1].

In this paper some results about the crystallization kinetics of $Se_{1-x} Bi_x$ (x = 0.05 at) are reported. The time dependence of the crystallized fraction is analyzed to estimate the preponderant mechanism in the crystallization process.

The critical cooling rate of amorphization for this alloy is determined and the temperature dependence of viscosity is established from the time-temperature-transformation curve.

Structural and electron-transport studies for this system are in progress.

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2 — EXPERIMENTAL

High purity selenium and bismuth (99.999 %) were mixed and enclosed in an evacuated and sealed glass ampule, then held at 850 K for 5 days to make the mixture homogeneous, and finally quenched into water. X-ray diffraction and DTA preliminary runs showed the amorphous character of the samples.

Calorimetric measurements were carried out using a Perkin-Elmer DSC 1 B Differential Scanning Calorimeter, calibrated with indium standards of melting point 429 K, which needs not a remarkable temperature correction in our range of interest [2]. Five heating rates (2, 4, 8, 16 and 32 K/min) were explored for samples in a weight range 10 to 20 mg. All the experiments gave values of $T_{me}=483\pm3$ K for the melting point and $T_g=305\pm2$ K, for the glass-transition temperature of the alloy and dispersion in these values is within the experimental uncertainty. Nevertheless Larmagnac et al. [3] have recently showed some results about a dependence of T_g on heating rate and ageing for amorphous selenium.

For crystallization kinetics studies, an isothermal annealing run was performed at a temperature slightly below 340 K, which is the lowest crystallization temperature found in continuous heating experiments, i.e., that corresponding to a heating rate of 2 degrees per minute. The total time for the crystallization process to be concluded was 44 min for samples of 15 mg. This is a result to be taken into account in order to disregard annealing at much lower temperatures for thermal analysis purposes, if a precision curve integrator is not available.

3 — RESULTS AND DISCUSSION

Kissinger [4] provides an useful method to evaluate the activation energy involved in the process of crystallization, based in the shift of temperature T_m at the maximum of the crystallization peak with the heating rate. It consists of measuring the function — $\ln(\phi/T_m{}^2)$ versus T_m^{-1}, where ϕ represents the heating rate. Such a function is plotted in Fig. 1 and a fitting coefficient of 0.998 was found. The activation energy calculated turned out to be 1.18 eV/at for this Se-Bi alloy.

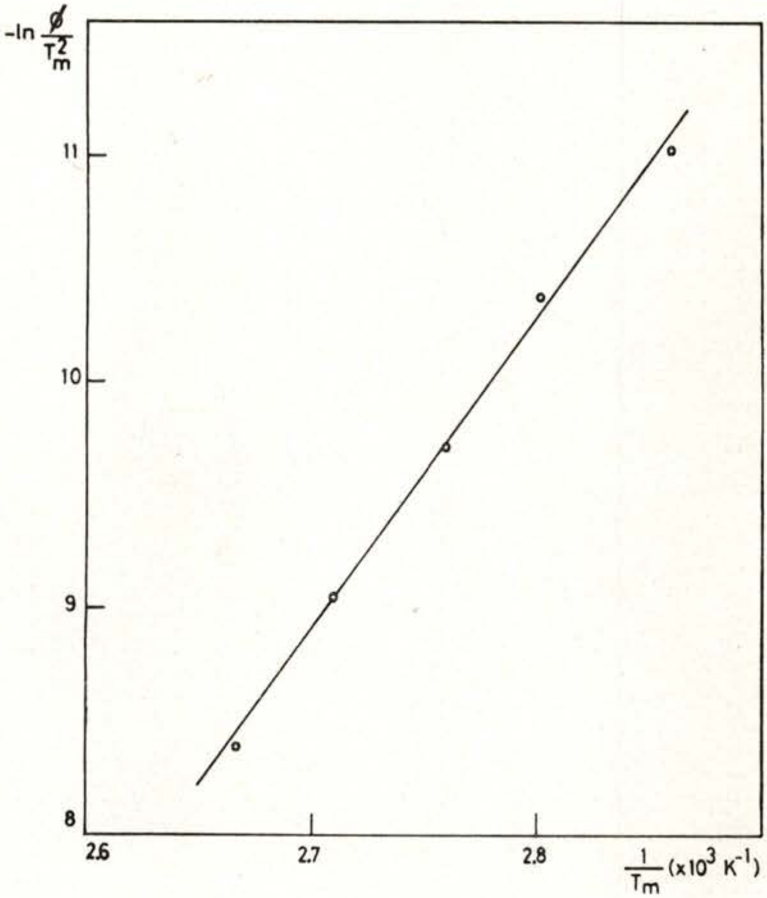

Fig. 1—Evaluation of activation energy by the Kissinger method. E=1.18 eV/at.

The isothermal annealing at a temperature close to the lowest crystallization temperature allows to determine the time evolution of the crystallized fraction α (t), as is plotted in Fig. 2. It is a standard sigmoidal curve, the three characteristic stages in crystallization being present. There is a very short period of germination, due to the initial existence of a great amount of defects and homogeneity faults that become centres of heterogeneous nucleation in crystallization processes. It is followed by a much longer period of acceleration of the process, and then by a final decay until the crystallization is completed. Following

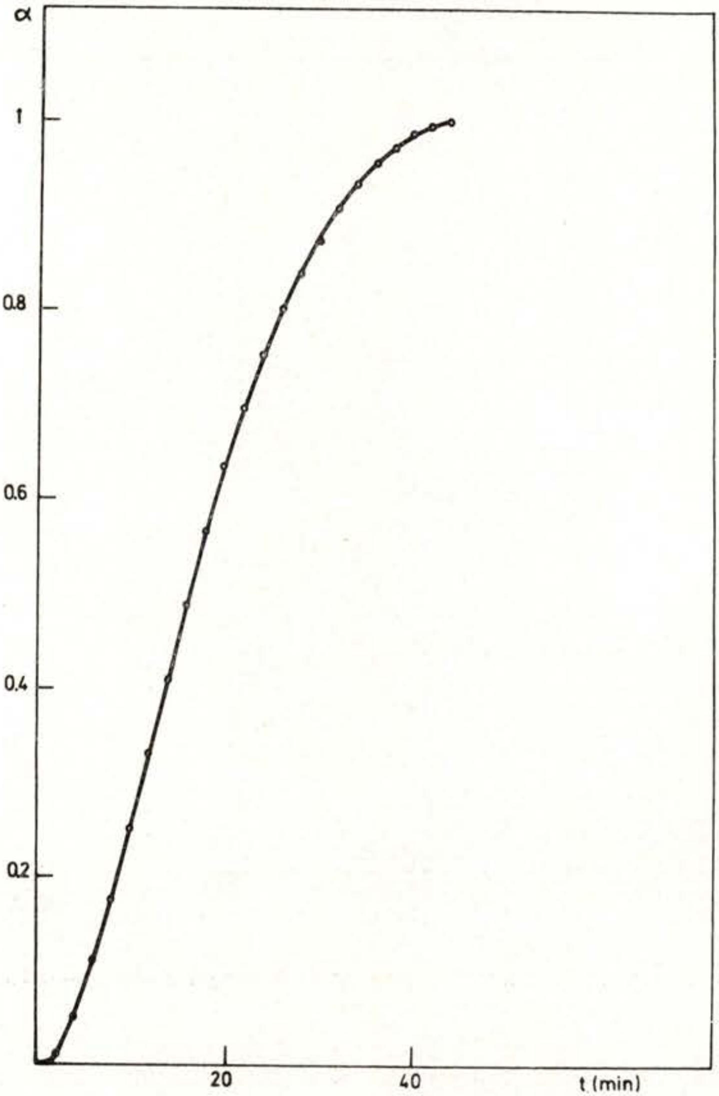

Fig. 2 — Time evolution of crystallized fraction.

Germain et al. [5] an order of magnitude for the different crystal growth mechanisms can be derived by determining the power *r* that affects the time *t* in the most significant terms of the polynomy $\ln\,[1/(1\text{-}\alpha)] = \lambda\ t^r$.

Fig. 3 shows a plot of $\ln \{ \ln\,[1/(1\text{-}\alpha)] \}$ *vs* ln t. The first straight stage gives values $r = 1.81$ and $\lambda = 4.38 \times 10^{-3}\ \text{min}^{-2}$,

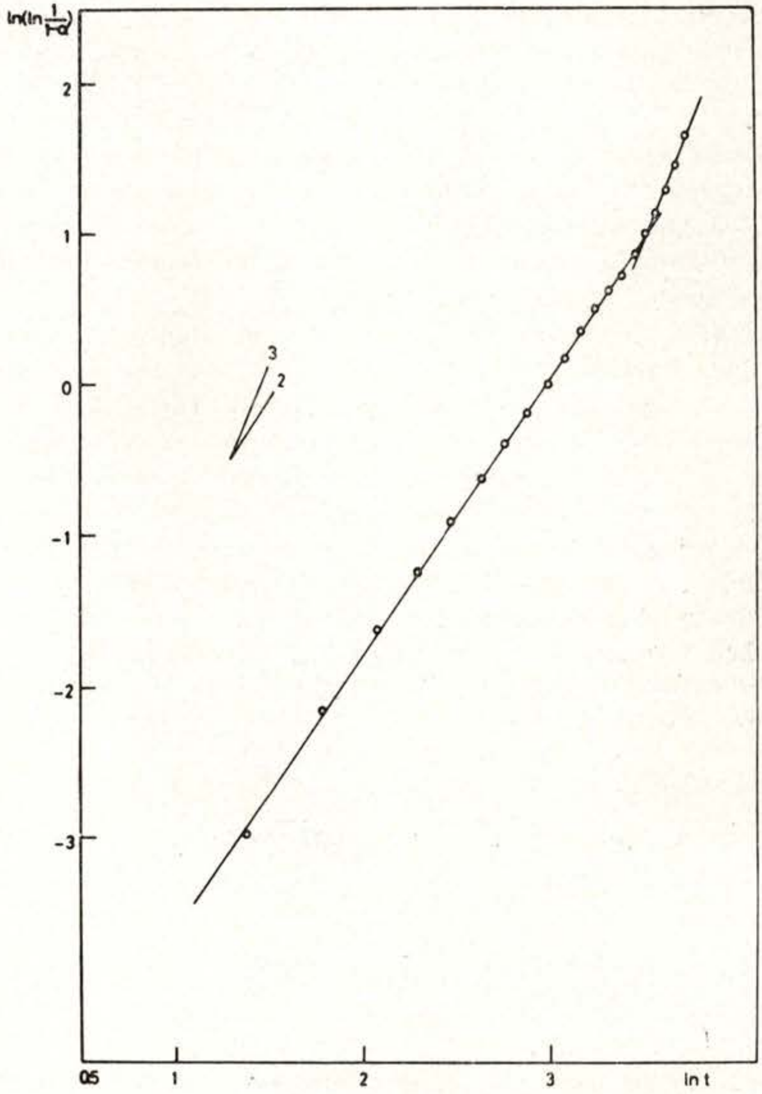

Fig. 3 — Kinetics of amorphous-crystal transformation.

with a fitting coefficient of 0.999. Such a power $r \sim 2$, for a bulk induced crystallization, allows λ to be $\lambda = (p/S)\ \pi\ V_g^2$, where V_g is the crystal growth rate and p/S is the initial number of crystallites per unit area, that will contribute to heterogeneous growth. Assuming a typical value of $V_g = 10$ Å s^{-1}, we obtain a crystallite concentration $p/S = 3.9 \times 10^7\ cm^{-2}$.

The second stage in Fig. 3 gives $r = 3.14$, $\lambda = 4 \times 10^{-5}\ min^{-2}$ (fitting coefficient 0.996) and a power $r \sim 3$ leads to describe $\lambda = (\pi/3)\, n\, V_g^2$, where n is the homogeneous nucleation rate per unit area. So the resulting nucleation rate is $n = 1.1 \times 10^6\ cm^{-2}\ min^{-1}$.

Those results show that, if the same V_g is still assumed, the homogeneous nucleation does not become preponderant until about 35 min after the beginning of crystallization, which is about 80 % of full time, and it is due to the presence of such a large number of nucleation centres.

In order to determine the glass-forming ability, a suitable crystalline fraction of 3.10^{-2} was measured from the total area of thermograms. A time-temperature-transformation (TTT) curve is drawn in Fig. 4, where the lower part (points o) is experimental and the rest (points +) is extrapolated by the use of the kinetics expression for the crystallization fraction $\alpha \sim (\pi/3)\ I\ u^3\ t^4$, I and u being the homogeneous nucleation rate and the crystal growth rate respectively [6]. Such an extrapolation may be done through the calculation of another interesting parameter: the liquid quenched viscosity η in the range T_{me} (melting point) to T_g (glass-transition temperature). Viscosity is evaluated from the experimental data using Uhlmann theory [7] through the expressions

$$I = \frac{N_v^o\ K\ T}{3\ \pi\ a_o^3\ \eta} \exp\left[-\frac{16\ \pi}{3}\ \frac{\sigma^3\ T_{me}{}^4}{(\Delta H_{me})^2\ (\Delta T)^2\ RT^3} \right]$$

and

$$n = \frac{f\ K\ T}{3\ \pi\ a_o^2\ \eta} \left[1 - \exp\left(-\frac{\Delta H_{me}\ \Delta T}{R\ T\ T_{me}} \right) \right]$$

where N_v^o is the mean volume concentration of atoms, a_o is the atomic diameter, σ is the molar free interface enthalpy between

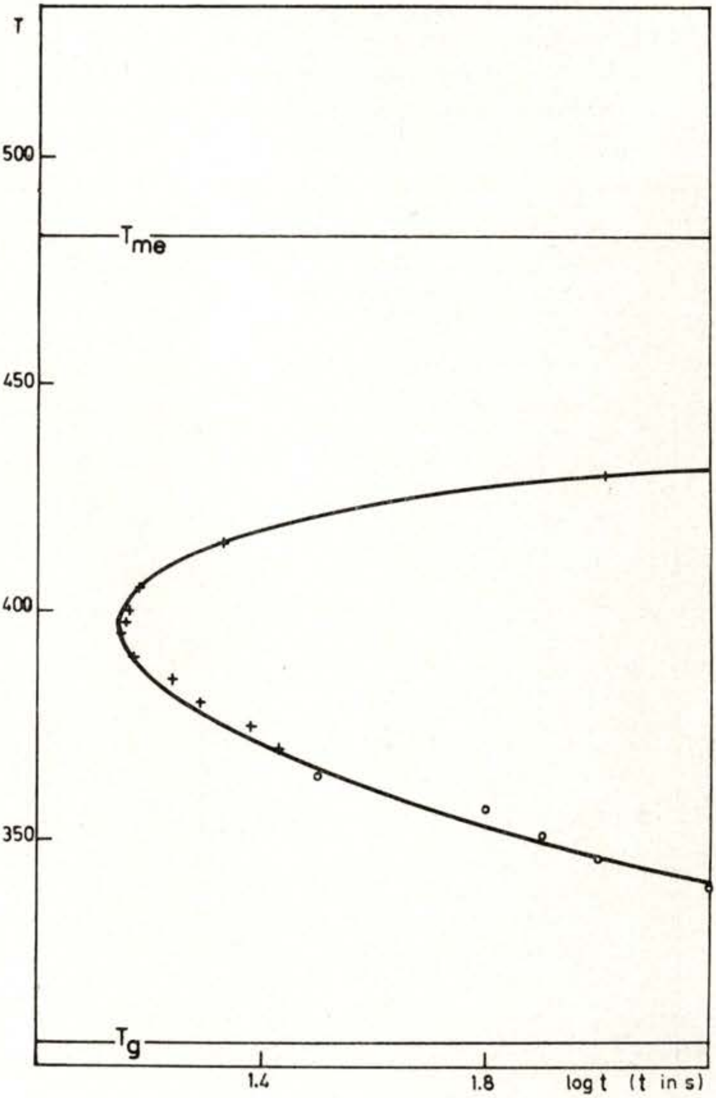

Fig. 4 — Time-Temperature-Transformation (TTT) curve between T_{me} and T_g. (o: experimental; +: calculated).

nucleus and liquid, ΔH_{me} the molar enthalpy of fusion, $\Delta T = T_{me} - T$ and f the fraction of sites at the crystal-liquid interface. To calculate η, N_v^o is known from the alloy density ($\rho = 4.6$ g.cm^{-3}),

ΔH_{me} measured is 1700 J/at.g, and assumptions made in [8] remain valid so that $a_o = 4$ Å, $f = 1$ and $\sigma = 0.32\ \Delta H_{me}$.

Fig. 5 shows the temperature dependence of viscosity where the full line is experimental and the dashed portion is calculated

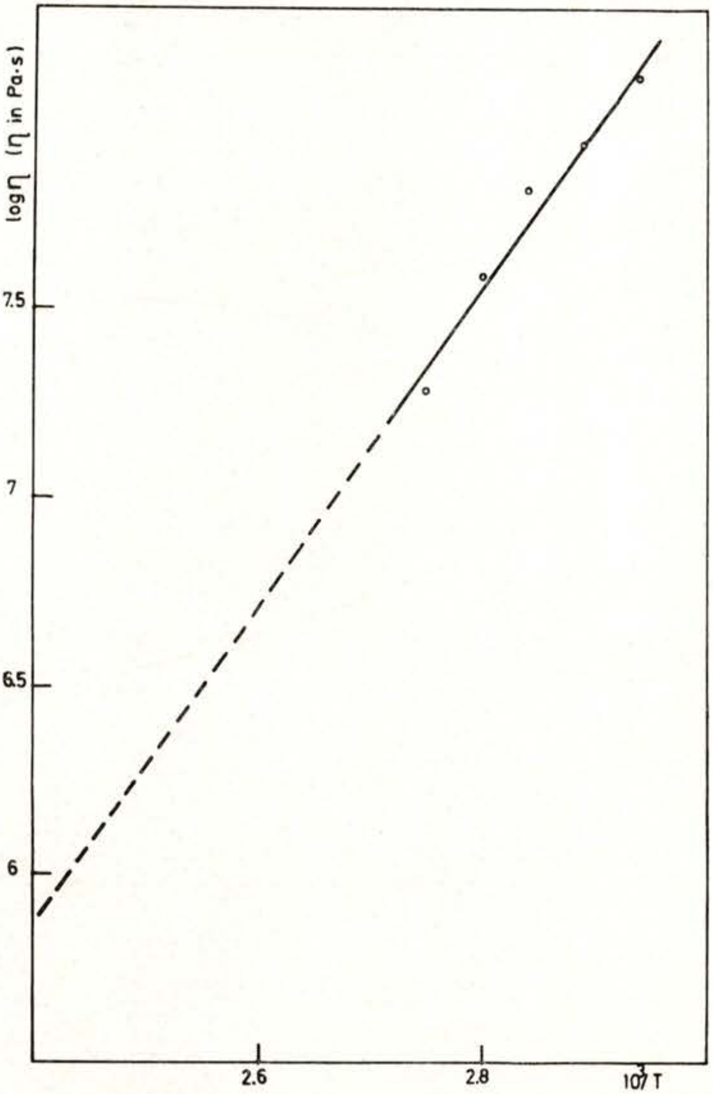

Fig. 5 — Temperature dependence of viscosity η (Full line: experimental; dashed line: calculated).

from an Arrhenius equation $\eta = A \exp(a/T)$, with $A = 4.2 \times 10^{-5}$ Pa.s and $a = 4260$ K.

Temperature T_n and time t_n being 395 K and 14.1 s, respectively, at the nose of the TTT curve, the corresponding value for the critical cooling rate R_c, to get the alloy amorphous is: $R_c = (T_{me} - T_n)/t_n = 6.2\ K\ s^{-1}$, which is well below what is achieved with a quenching technique. This value of the critical cooling rate is consistent with the known ability of amorphization of selenium alloys, but is more restricting than the estimated for ternary alloys [8].

The experimental cooling rate ($\sim 10^3\ K.s^{-1}$) is much higher than the critical value; this could explain the high amount of homogeneity faults and, therefore, the preponderance of an heterogeneous nucleation mechanism along the crystallization process.

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