Academician of the Academy of Sciences of the Uzbek SSR S. V. STARODUBTSEV, T. S. PUGACHEVA, V. M. MIKHAELYAN,

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Abstract

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Academician of the Academy of Sciences of the Uzbek SSR S. V. STARODUBTSEV, T. S. PUGACHEVA, V. M. MIKHAELYAN,
V. M. LENCHENKO

ON THE KINETICS OF THE FORMATION OF CRYSTALLIZATION NUCLEI IN GLASSY SELENIUM

One of the possible phenomenological descriptions of the kinetics of the formation and growth of crystallization nuclei in glassy selenium is considered. It is known that, under the action of X-rays and other ionizing radiations, the crystallization process of amorphous selenium is considerably accelerated.

In work (^{1}) it was found that preliminary irradiation of glassy selenium leads to an increase in the number N of crystallization grains in it. In this case a complex dependence of N on the irradiation dose D is observed. At small doses a law of the type of first-order reactions is obeyed; at larger doses the curves correspond to reactions of higher order and are approximated by a formula of the form

$$N = aD^n, \tag{1}$$

where $n = (4—5)$, $a = a(p)$, is the dose rate. An increase in the linear growth rate of crystallization grains with increasing dose rate was also found. We shall show that the facts listed can be qualitatively explained by making certain very general assumptions.

Glassy selenium is a thermodynamically unstable modification. Nevertheless it is known (^{2}) that at room temperature this modification can be preserved indefinitely long without noticeable signs of crystallization. This feature is connected with the polymeric nature of the structure of selenium. According to the data of work (^{3}), glassy selenium consists of a mixture of ring polymer molecules containing from 8 to 10^3 atoms. Crystallization of such a system is greatly hindered; molecules of different sizes and shapes, under conditions of low mobility, cannot rearrange into a regular crystal lattice consisting of elongated and parallel helical chains. For crystallization, preliminary destruction of the polymer molecules is necessary, which facilitates the spatial regrouping of the chains. Usually this is achieved by heat treatment. In our case the initiator of destruction is ionizing radiation.

The crystallization process consists in the formation of nuclei of the crystalline phase and their subsequent growth. Let us assume that, for a nucleus to form, it is necessary that in a volume of the order of the critical* one there occur some minimum (at the given temperature) number of ruptures of polymer molecules. In this case there arises a corresponding number of fragments of the molecule, or "mobile" segments, which can, as a result of rearrangement, form a stable nucleus. The further growth of subcritical nuclei is accomplished by the successive attachment of "mobile" segments, consisting on average of the same number of atoms, to the surface of the nucleus. The system of kinetic equations describing the process of nucleus formation at all stages of growth has the following general structure:

$$\frac{\partial \nu_i}{\partial t} = \nu_{i-1}\gamma_{i-1} - \nu_i\gamma_i; \tag{2}$$

Here v_i is the number of nuclei consisting of i segments; the term $v_{i-1}\gamma_{i-1}$ denotes the increase of this number due to the attachment of one segment to a nucleus consisting of $(i-1)$ segments; the term $v_i\gamma_i$ denotes the decrease of v_i due to the formation of nuclei containing $(i+1)$ segments; γ_i and γ_{i-1} are, respectively, the rates of these processes. The quantity γ_i will be determined by the probability of formation of a "mobile" segment near the nucleus, α_i, and by the probability of its attachment to the nucleus, f_i:

$$\gamma_i = \alpha_i f_i. \tag{3}$$

We shall consider the solution of equation (2) separately for the stages of formation and growth of nuclei.

Let us adopt the following assumptions. The formation of a single "mobile" segment, or broken bond, is apparently still insufficient for rearrangement into the configuration of the surrounding molecules. Such a defect has a short lifetime, so that over a comparatively short time interval (shorter than the duration of the experiments) an equilibrium concentration of them is established, $v_i = g \cdot \tau$, where g is the rate of generation of "mobile" segments and τ is their lifetime. Aggregates consisting of a large number of segments will be more stable, and their lifetime increases with increasing size of the aggregate. We shall assume that, beginning with $i = 2$, the aggregates are stable with respect to the duration of the experiments, provided that the distance between the segments being formed is of the order of the dimensions of the critical volume. At the first stage, the quantity α_i is determined by the rate of generation of "mobile" segments g and by the magnitude of that critical volume within which the interaction of the segments with one another leads to the formation of a nucleus stable at the given temperature.

In the field of ionizing radiation, the formation of broken bonds proceeds mainly in two ways (for X-rays and soft γ-rays): 1) through recombination of ions, in

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* By critical we mean the volume possessed by a nucleus that is in thermodynamic equilibrium with the initial phase.

which energy sufficient for rupture of the –Se–Se–bond is released, and 2) upon excitation of molecules by secondary electrons and their subsequent dissociation. It can be shown that in both cases the generation rate is proportional to the dose rate; consequently,

$$\gamma_i \sim \alpha_i \sim g \sim P. \tag{4}$$

The solution of the system of equations (2) may approximately be written in the following form:

$$\gamma_i = \frac{1}{(i-1)!}\gamma_1\gamma_2 \cdots \gamma_{i-1} g t^{i-1} \tag{5}$$

under the condition $\gamma_i t \ll 1$, which is satisfied in the experiments (^{1}). Taking (4) into account, we obtain the dependence of the number of critical nuclei on irradiation time:

$$v_{i_0} = AP^i t^{i-1}, \tag{6}$$

where the subscript "0" refers to a nucleus of critical dimensions, and A is a constant (in our approximation).

Nuclei with dimensions above the critical size ($i > i_0$) grow monotonically with a constant linear velocity. The quantity α_i is now proportional to the surface of the nucleus s_i, in accordance with our adopted ideas concerning the mechanism of growth of supercritical nuclei. The structure of the equations for the kinetics of nucleus growth in this case is of the same type as (2); however, taking into account that we are interested in the solution for large i ($i > i_0$), the difference equations (2) may, in the first approximation, be replaced by the equivalent first-order differential equations

$$\frac{\partial v_i}{\partial t} = -\frac{\partial}{\partial i}\left(\gamma_i v_i\right). \tag{7}$$

Using the boundary and initial conditions

$$v_i\big|_{i=i_0} = v_{i_0} = AP^i t^{i-1}, \qquad v_i\big|_{t=0} = \varphi(i),$$

where $\varphi(i)$ is the distribution function of the nuclei present in the specimen before irradiation, the solution of system (7) will be found as the sum of two terms

$$v_i(t) = v_i^{(1)}(t) + v_i^{(2)}(t),$$

where the term

$$v_i^{(1)}(t) = \left(\frac{S_0}{S}\right) v_{i_0} \left(t - \frac{S^{1/2} - S_0^{1/2}}{b}\right), \tag{8}$$

determines the dependence of the number of nuclei created by irradiation on the irradiation time, while the term

$$v_i^{(2)}(t) = S^{-1}(S^{1/2} - bt)^2 \varphi\left[(S^{1/2} - bt)^3\right] \tag{9}$$

determines the dependence of the number of nuclei that have grown on centers of nonradiation origin. Here

$$b = \frac{1}{t}\int_0^t C(P,T)\,dt, \tag{10}$$

where $C(P,T)$ is a quantity proportional to the linear growth rate of the nuclei. Carrying out the integration of expression (8), taking (4) into account, we obtain for the number of manifested nuclei formed under irradiation

$$N^{(1)}(t) = Bb(T,P)(D - D_k)^{i_0};$$

here $B = \text{const}$ (in our approximation), $D = Pt$ is the irradiation dose, and $D_k = Pt_k$ is the dose corresponding to a certain induction period during which nuclei with $i = i_0$ reach sizes corresponding to the value $i = i_k$. As for the value $N^2(t)$, as is readily seen with the aid of (9), it is a monotonically increasing function up to doses of the order of $S_k^{1/2}P/b$, at which saturation is reached. From comparison of formula (11) with the experimental formula (1), we find for i_0 the value 4–5. In accordance with the idea adopted above concerning the formation of crystallization nuclei, this means that, for the emergence of a nucleus of critical dimensions (at the irradiation temperature), it is necessary that at least 4–5 "mobile" segments accumulate. This conclusion is in full agreement with the known literature data[4] that, at temperatures sufficiently far from the polymer melting point, the critical nucleus must have dimensions of the order of the elementary cell, which for hexagonal selenium consists of four chains.

Institute of Nuclear Physics
Academy of Sciences of the Uzbek SSR

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.