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A study on the non-isothermal transformation kinetics of glassy alloys when the nucleation frequency and crystal growth rate depend on time as a power law
Application to the crystallization of the $Ag_{0.16}As_{0.42}Se_{0.42}$ semiconductor glass

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ABSTRACT

A procedure has been developed to obtain an evolution equation with the temperature for the actual transformed volume fraction under non-isothermal regime and to calculate the kinetic parameters in glassy solids. Once an extended volume of transformed material has been defined and spatially random transformed regions have been assumed, a general expression of the extended volume fraction has been obtained as a function of the temperature, bearing in mind the case presented in the practice of a kinetic exponent with a larger value than 4. This unexpected value is justified assuming that both the nucleation frequency and the crystal growth rate depend on time as a power law. Moreover, considering impingement effect and from the quoted expression, the actual volume fraction transformed has been deduced. The kinetic parameters have been obtained, by assuming that the reaction rate constant is a temperature function of Arrhenius type and using the following considerations: the condition of maximum crystallization rate and the quoted maximum rate. The theoretical model developed and the Johnson–Mehl–Avrami model have been applied to the crystallization kinetics of the $Ag_{0.16}As_{0.42}Se_{0.42}$ glassy alloy, which presents two exothermic peaks. The second peak gives for the kinetic exponent values enough larger than 4 in both models. The quoted values do not fulfil the assumptions of the Avrami model and it is necessary to resort to the hypotheses of the developed model to justify the unexpectedly high value of the kinetic exponent. Moreover, the experimental curve of the transformed fraction shows a better agreement with the theoretical curve of the developed model than with the corresponding curve of the Avrami model, confirming the reliability of the theoretical model developed in order to analyze the transformation kinetics of the above-mentioned glassy alloy.

1. Introduction

Although glass has been used as an artistic medium and industrial material for centuries, it has been only in relatively recent years when the “glass science” has emerged as a field of study in its own right. Yet one of the most active fields of solid-state research in the last decades has been the study of solids that are not crystals, solids in which the arrangement of the atoms lacks the slightest vestige of long-range order.

The advances that have been made in physics and chemistry of these materials, which are known as amorphous solids or non-crystalline, have been widely appreciated within the research community. Solid-state phase transformations play an important role in the production of many materials. Therefore, a great impulse has been given at the study of a general description of the kinetics of phase transformations [1], and accordingly, the last 50 years have seen a theoretical and practical interest in the application of calorimetric analysis techniques to the study of the quoted transformations [2–4]. Thus, the classical theory of nucleation and crystal growth has been developed over the last 60 years. A full development of the theory is given by Christian [5] and a relatively recent review published by Kelton [6].

The calorimetric analysis techniques are very quick and need very small quantities of glass samples to obtain the kinetic parameters of a transformation. There are two thermal analysis regimes: one is the isothermal regime [4–7], in which glass samples are quickly heated up and held at a temperature above glass transition temperature, and the other is so-called non-isothermal regime

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[8–12], in which glass samples are heated up at a fixed heating rate. In general, an isothermal experiment takes longer times than a non-isothermal experiment, but isothermal experimental data can be interpreted by the well-established Johnson–Mehl–Avrami kinetic equation [13–16]. On the contrary, non-isothermal experiments have as an advantage, the rapidity that makes this type of experiments more attractive. The use of non-isothermal techniques to study solid-state transformations and to determine the kinetic parameters of the rate controlling processes has been increasingly widespread. Therefore, the use of the non-isothermal regime has produced a large number of mathematical treatments to analyze thermal process data.

The quoted techniques have become particularly prevalent for the investigation of the processes of nucleation and growth that occur during transformation of the metastable phases in a glassy alloy as it is heated. These techniques provide fast information on such parameters as: glass transition temperature, transformation enthalpy and activation energy over a wide range of temperature [17]. In addition, the physical form and the high thermal conductivity as well as the temperature at which transformations occur in most amorphous alloys make these transformations particularly suited to be analyzed by a differential scanning calorimeter (DSC).

The study of crystallization kinetics in amorphous materials by means of differential scanning calorimetry methods have been widely discussed in the literature [6–18]. There is a large variety of theoretical models and theoretical functions proposed to explain the crystallization kinetics. The application of each of them depends on the type of amorphous material studied and how it has been made.

In the present work, a theoretical procedure has been developed to obtain an evolution equation with temperature for the actual transformed volume fraction. This equation has been obtained bearing in mind the mutual interference of regions growing from separated nuclei and the case in which the kinetic exponent takes a larger value than 4, which is presented in the practice, according to the literature [19]. We justify the quoted case assuming that both the nucleation frequency and the crystal growth rate depend on time as a power law [19–21]. The kinetic parameters and the glass–crystal transformation mechanism have been deduced from DSC experiments, using the above-mentioned equation and assuming a non-isothermal regime.

Moreover, this work applies the theoretical model developed (TMD) and the Johnson–Mehl–Avrami (JMA) model for the analysis of the crystallization kinetics of the $Ag_{0.16}As_{0.42}Se_{0.42}$ glassy semiconductor, which presents two exothermic peaks. The values of the kinetic exponent obtained for the second peak in both models are enough larger than 4. It should be noted that the quoted TMD allows to justify the obtained value, whereas a value of the kinetic exponent cannot be larger than 4, according to JMA model.

Besides, the experimental and theoretical curves of the transformed volume fraction, x, vs. temperature, T have been compared for every model considered. The mentioned curves show a better agreement in the case of the TMD than the curves corresponding to the JMA model, confirming the reliability of the theoretical model developed to describe the glass–crystal transformation of the studied alloy.

2. Theoretical basis

2.1. Nucleation, crystal growth and volume fraction transformed

The theoretical basis to interpret DSC results is provided by the formal theory of transformation kinetics [14–16,22–24]. This formal theory supposes that the crystal growth rate, in general, is anisotropic, and therefore, the volume of a region originating at time $t=(1-\alpha)\tau$ (τ being the nucleation period and where α is a parameter equal to zero in the case of continuous nucleation, and equal to the unit in the case of "site saturation"[25]) is then.

$$\upsilon_\tau = g\prod_i \int_{(1-\alpha)\tau}^{t} u_i(t')\mathrm{d}t' \tag{1}$$

where $u_i(t')$ ($i=1, 2, 3$) represents the principal growth velocities in the three mutually perpendicular directions, the expression $\prod_i \int_{(1-\alpha)\tau}^{t} u_i(t')\mathrm{d}t'$ condenses the product of the integrals corresponding to the values of the above quoted subscript i and finally g is a geometric factor, which depends on the dimensionality and shape of the crystal growth, and therefore, its dimension equation can be expressed as

$$[g] = [L]^{3-i} \quad ([L] \text{ is the length})$$

Defining an extended volume of transformed material and assuming spatially random transformed regions [26–28], the elemental extended volume fraction, $\mathrm{d}x_e$, in terms of nucleation frequency per unit volume, $I_V(\tau)$, is expressed as

$$\begin{aligned}\mathrm{d}x_e &= [\alpha \mathrm{d}N + (1-\alpha)I_V(\tau)\mathrm{d}\tau]\upsilon_\tau \\ &= g[\alpha dN + (1-\alpha)I_V(\tau)\mathrm{d}\tau]\prod_i \int_{(1-\alpha)\tau}^{t} u_i(t')\mathrm{d}t' \end{aligned} \tag{2}$$

where $\mathrm{d}N$ is the elemental number of nuclei existing per unit volume.

When the crystal growth rate is isotropic, $u_i=u$, an assumption, which is in agreement with the experimental evidence, since in many transformations the reaction product grows approximately as spherical nodules [5], Eq. (2) can be written as

$$\mathrm{d}x_e = g\,[\alpha \mathrm{d}N + (1-\alpha)I_V(\tau)\mathrm{d}\tau]\left[\int_{(1-\alpha)\tau}^{t} u(t')\mathrm{d}t'\right]^m \tag{3}$$

where m is an exponent related to the dimensionality of the crystal growth.

It should be noted that over a sufficiently limited range of temperature (such as the range of transformation peaks in DSC experiments) the quantities $I_V(\tau)$ and $u(t)$ may be considered to have an Arrhenian temperature dependence [28]. In this case, the kinetic exponent is $n=m+1$ in continuous nucleation processes and $n=m$ in "site saturation" processes. Accordingly, the maximum values of the quoted exponent are 4 and 3, respectively [29]. Nevertheless, in the practice major values are obtained, which according to the literature [30,31] suggest a very high nucleation rate with three-dimensional growth. Besides, these high values of kinetic exponent can be justified in accordance with the literature [19–21] if $I_V(\tau)$ and $u(t)$ depend on time as a power law.

It is interesting to denote that, according to the literature [19], there are two major competing ideas, dating back over 60 years, that try to provide overall models to describe the origin of crystallization textures. The quoted ideas are known as oriented nucleation and oriented growth, and were proposed by Burgers and Louwerse [32] in 1931 and by Barret [33] in 1940, respectively. The essential basis of oriented nucleation is that new grains with the orientation of the major component of the crystallization texture nucleate at a much higher frequency than do grains of all other orientations. In the case of oriented growth, the nuclei already produced with the required orientation for the crystallization grow faster than nuclei of other orientations [19].

With the aim to explain the probable physical nature of the quoted time-dependence for the nucleation frequency and the crys-