Journal of Non-Crystalline Solids 355 (2009) 569–576

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

The application of differential thermal analysis to the study of isothermal and non-isothermal crystallization kinetics of coal fly ash based glasses

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ARTICLE INFO

Article history:
Received 5 July 2007
Received in revised form 22 September 2008
Available online 2 March 2009

PACS:
81.05.Kf
81.10.Aj
81.70.Pg
82.20.Pm

Keywords:
Crystallization
Crystal growth
Glass ceramics
Glasses

ABSTRACT

The crystallization kinetics of glasses obtained from coal fly ash was investigated by both isothermal and non-isothermal methods using differential thermal analysis (DTA) data. In DTA experiments, glass samples having coarse (800–1000 μm) and fine (<180 μm) particle sizes were used and the results were compared. The Avrami exponent (n) was calculated by means of Johnson–Mehl–Avrami (JMA) and Ozawa equations. Calculated kinetic parameters indicated that the appropriate crystallization mechanisms were bulk and surface crystallization for coarse and fine particles, respectively. Isothermal and non-isothermal DTA experiments showed that the crystallization activation energies of coarse glasses are changed in the range of 444–578 kJ/mol, while the crystallization activation energies of fine glasses are changed in the range of 610–662 kJ/mol. It was found that crystallization activation energies of fine glasses are higher than those of the coarse glasses. Results showed that isothermal and non-isothermal crystallization kinetics of glasses produced from coal fly ash is in agreement within the experimental error.

1. Introduction

Knowledge of nucleation and crystallization kinetic parameters such as, activation energy for crystal growth and crystal growth mechanism is important in the preparation of glass–ceramics with desired microstructure and properties. DTA is widely used in investigating the crystallization kinetics of glasses [1–5]. Two methods, namely isothermal and non-isothermal methods, are applied for the differential thermal analysis of glass samples. JMA equation is generally used for the kinetic analyses of isothermal DTA data [6–8]. In the JMA method, glass samples are quickly heated up and held at a temperature above the glass transition temperature. In this case, crystallization occurs at constant temperature. In the non-isothermal method, glass samples are heated up at a fixed heating rate and crystallized during the thermal analysis scan [1]. The non-isothermal method is more simple and quicker than the isothermal method. Activation energy and crystallization mechanisms are the most important kinetic parameters for the crystallization of glasses. These parameters can be obtained by experimental DTA results using the equations that are proposed to interpret non-isothermal data [5,9,10]. However, most of these equations assume that the variation of peak crystallization temperature is directly related to the heating rate [1,5,9,10]. These equations shed important light on understanding the nature of the crystallization mechanisms of different glass forming systems. Recently, there were reports on examining the crystallization behavior of glasses produced from industrial wastes (such as incinerator fly ash, slag) by using isothermal and non-isothermal methods [11–14]. However, only a few researchers have done investigations on glasses produced from coal fly ash [15–17]. In this study, JMA [6–8], Kissinger [9], Matusita and Sakka [5] and Ozawa [10] equations were used to determine the crystallization mechanism and the activation energy values for crystallization. The main aims of this study are to determine more accurate value for the Avrami exponent and activation energy for crystallization; to examine the effect of particle size on crystallization mechanism and to compare the results of kinetic data as determined by isothermal and non-isothermal methods.

2. Experimental procedure

2.1. Starting material and glass preparation

Coal fly ash sample was obtained from Tunçbilek Thermal Power Plant in Turkey and used as a raw material source. The chemical analysis showed that the coal fly ash consists of the following oxides (in wt%): 54.08% SiO_2, 25.58% Al_2O_3, 3.10% CaO,

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doi:10.1016/j.jnoncrysol.2009.01.023

3.03% MgO, 9.82% Fe_2O_3, 0.58% Na_2O and 1.51% K_2O [18]. Fly ash was melted in a platinum crucible for 2 h in an electrically heated furnace (Protherm PLF 1600 Model) at 1773 K. No additives or nucleating agents were added to the fly ash batch. To ensure homogeneity, the melt was poured into water. The cast glasses were crushed, pulverized and remelted at the same temperature for 3 h to remove the air bubbles from the melt. Following this procedure, the refined melt was cast in a preheated graphite mould and the glass samples were obtained.

2.2. Differential thermal analysis (DTA)

DTA scans of glass specimens were carried out using a Perkin Elmer (Model TAC7/DX) thermal analyzer. The glasses were ground to a coarse particle size (800–1000 μm) to be a representative of a bulk sample and to a fine particle size (<180 μm) to be a representative of powder samples. DTA experiments were performed by heating 20 mg glass samples in a Pt-crucible and using Al_2O_3 as a reference material in the temperature range between 293 and 1373 K at the heating rates of 5, 10, 15 and 20 K/min.

The variation of the crystallization peaks with different heating rates can be used to estimate the activation energy for crystallization and to determine the crystallization mechanism. The crystallization behavior of glasses was determined by using the both isothermal and non-isothermal methods. DTA was performed on both coarse and fine glass samples in each method to determine the particle size effect on the crystallization mechanism. Johnson–Mehl–Avrami (JMA) method has been widely used as an isothermal method for the interpretation of the crystallization experiments and for the determination of the crystallization mechanisms from the results of DTA curves. In the JMA method, the as-quenched glass samples were heated to the maximum nucleation temperature at a heating rate of 20 K/min and nucleated at this temperature for the maximum nucleation time. Fully nucleated samples were then heated to the selected temperature at a heating rate of 20 K/min and held at this temperature for 15, 30 and 60 min. Then the temperature was raised to the crystallization temperature without being removed the samples from the DTA.

Kissinger, Matusita–Sakka and Ozawa methods were used to determine the kinetic parameters from the non-isothermal methods. Crystallization mechanisms and activation energies were calculated in each method from the heating rate dependence of the crystallization peak temperature. In order to investigate the crystallization behavior of glass samples by using the Kissinger equation, the glass samples were heated to the maximum nucleation temperature and held at this temperature for the maximum nucleation time for complete nucleation to prevent the increase in the number of nuclei during the DTA scans. The temperature was then raised to the maximum working temperature of DTA. DTA scans of fully nucleated glass samples were obtained at the heating rates of 5, 10, 15 and 20 K/min at which, the number of nuclei is independent of the heating rate. Assuming that the nucleation had occurred in glass samples during the DTA measurements, DTA data were also analyzed by Matusita–Sakka and Ozawa methods. For this purpose, the glass samples were heated to 1373 K at the heating rates of 5, 10, 15 and 20 K/min without being removed from the DTA equipment. In these conditions, the number of nuclei is inversely proportional to the heating rate. The reason that all of these methods were used in the present study is to obtain more accurate kinetic parameters for the glasses produced from coal fly ash.

2.3. Theoretical analysis

2.3.1. Isothermal method

Isothermal methods are generally based on the Johnson–Mehl–Avrami (JMA) transformation kinetic equation given below [6–8]:

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

where x is the fraction crystallized at a given temperature in time t; k is the reaction rate constant and n, the Avrami exponent, which is a dimensionless constant and related with the nucleation and growth mechanisms. The reaction rate constant, k, can be related to the activation energy for the process, E, through the Arhenius temperature dependence:

$$k = \nu \exp(-E/RT) \tag{2}$$

where ν is frequency factor, R is the ideal gas constant and T is the (isothermal) absolute temperature. By taking logarithms, Eq. (2) may be rewritten as:

$$\ln(k) = \ln(\nu) - E/RT. \tag{3}$$

Appropriate values of k are found experimentally by plotting the fraction crystallized, x, against the isothermal hold time for different temperatures. From these plots, the time to reach a given x can then be found for a range of x values. Values for k and n are then determined using the following relationship (derived from Eq. (1) by taking logs and rearranging):

$$\ln[-\ln(1-x)] = n\ln k + n\ln t. \tag{4}$$

The above equation indicates that a plot of $\ln[-\ln(1-x)]$ against $\ln t$ for different temperatures is expected to be linear and gives the values of n and k. A plot of $\ln k$ against $1/T$ for different isothermal temperatures is also expected to be linear according to the Eq. (3). From these plots, the values of E and ν can be easily obtained [3].

2.3.2. Non-isothermal methods

Several equations have been proposed, attempting to interpret crystallization behavior from the non-isothermal data [5,9,10]. Most of these equations assume that the variation of peak crystallization temperature, T_p, is directly related to the heating rate, α. For example, in the Kissinger method [9], the crystallization peak temperature is monitored as a function of the heating rate and the following relationship is given:

$$\ln\left(\frac{\alpha}{T_p^2}\right) = \left(\frac{-E_{\mathrm{ck}}}{RT_p}\right) + \text{constant} \tag{5}$$

where E_{ck} is activation energy for crystallization, determined by the Kissinger method. A plot of $\ln(\alpha/T_p^2)$ vs $1/T_p$ should be straight line, from the slope of which E_{ck} can be determined. Matusita and Sakka [5,19] has stated that Eq. (5) is valid only when crystal growth occurs on a fixed number of nuclei. Incorrect values for the activation energy are obtained if a majority of the nuclei are formed during the DTA measurement, due to the number of nuclei continuously varies with α. They have proposed a modified form of the Kissinger equation as given below:

$$\ln\left(\frac{\alpha^n}{T_p^2}\right) = \left(\frac{-mE_c}{RT_p}\right) + \text{constant} \tag{6}$$

where E_c is the correct activation energy for crystallization and m is the numerical factor which depends on the dimensionality of crystal growth. When surface crystallization predominates, $m = 1$ and when the crystallization is predominantly bulk, $m = 3$ (Table 1) [20]. The value of m is related to n as $m = n$ when crystallization at different heating rates occurs on a fixed number of nuclei (i.e. the number of nuclei is constant during DTA runs at different values of α), and $m = n - 1$ when nucleation occurs during DTA and the number of nuclei in the glass is inversely proportional to α [4]. In addition, when surface crystallization predominates, $m = n = 1$ and Eq. (6) essentially reduces to the Kissinger equation E_{ck} equals to E_c.