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Nucleation and crystallization kinetics of glass derived from incinerator fly ash waste

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Abstract

Nucleation and crystallization kinetics concerning the conversion of a glass made from municipal solid waste (MSW) incinerator fly ash to glass-ceramics have been investigated. The maximum nucleation rate was found near 720 °C. Activation energies of crystallization were 468–293 kJ/mol and decreased with increasing powder particle size. Avrami exponents for crystallization were 1.5–2.0 which indicates that surface crystallization dominates the overall crystallization. Maximum crystallization can be achieved in a temperature range of 870–980 °C and this temperature increased as the particle size of the specimen increased. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: D. Glass ceramic; Nucleation; Crystallization; Kinetics; Incinerator fly ash waste

1. Introduction

Fly ash from municipal solid waste (MSW) incinerators contains many hazardous substances such as heavy metals and toxic organic compounds. Therefore, the ash needs to be stabilized before burial in landfills [1]. Vitrification has been considered as one of the promising methods for fly ash stabilization. Fly ash from MSW incinerators has a complex chemical composition and in many cases, can be formed into glass through a conventional melt-quenching method [2,3]. Inorganic glasses can incorporate large amount of heavy metal ions inside random network structures. Glasses once formed into solids, also possess high chemical stability against leaching in water [4]. Furthermore, vitrification results in a large reduction in volume and hence can provide considerable benefit to the lifespan of landfill sites.

On the other hand, vitrification is not the most economical way of stabilization due to high energy consumption during melting. Therefore, it is essential to search for new options for recycling vitreous products. These vitrified materials can become useful substances if they can be converted to ceramic materials with good mechanical and thermal properties. Several papers have reported the use of vitrification and crystallization of coal fly ash, sewage sludge ash, and filter dust from waste incinerators [5–7]. Glass-ceramics, prepared by crystallizing glass made of filter dusts, showed an increase of approximately 30% in hardness and Young's modulus. The fracture toughness of the glass-ceramics showed the largest improvement from 0.6 MPa·m$^{1/2}$ for glasses to 1.7 MPa·m$^{1/2}$. However, most of these papers dealt with the properties of glass-ceramics without detailed scientific investigation on the kinetics of crystallization. Recently, there were reports on crystallization kinetics of glasses made from inorganic wastes [8,9]. They were able to find the Avrami parameter (n), but did not provide any further details on the various aspects of the crystallization.

This study reports on the kinetics of the nucleation and crystallization process from glasses made of MSW incinerator ash. Nucleation rates were evaluated using an isothermal method [10,11]. In addition, the crystallization rates were also investigated by use of a non-isothermal method suggested by Cheng [12]. Special attention was paid to the influences of the particle size of the powdered glasses on crystallization kinetics to assess the feasibility of producing glass-ceramics.

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2. Experimental

Parent glass was made from a mixture of 20 SiO_2–5MgO–75fly ash–2TiO_2 (wt.%). SiO_2 powders were added to improve glass formation while MgO and TiO_2 were included to obtain the desired crystalline phase. The glass was prepared by melting the starting powders in an alumina crucible at 1500 °C for 30 min. Melts were poured onto a copper plate, and annealed at 650 °C for 1 h. Final composition of the glass is shown in Table 1.

Nucleation rates were measured by the isothermal nucleation method. Samples (10×10×5 mm^3) were polished and heat-treated, nucleation temperature being set between 650 and 780 °C. All the specimens were subsequently heated at 850 °C for 2 h to enlarge nuclei up to an observable size [10]. The number of nuclei was then manually counted by looking through an optical microscope. The nucleation rate was determined from the slope of the line in Fig. 1 using the following equation.

$$\text{nucleation rate} = \frac{\text{number of nuclei}}{\text{duration for nucleation} - \text{induction time}} \quad (1)$$

Several assumptions are employed. They are, (1) observable crystals grow from a single nucleus, (2) no nucleus larger than the critical size will be re-dissolved or generated during the heat treatment process, and (3) glasses prior to nucleation have no nuclei [10].

Non-isothermal experiments were conducted using a differential scanning calorimeter (DSC) at heating rates of 5, 10, 20, and 30 °C/min. The reference material was alumina powder with a purity of 99.9999%. It is known that derivatives of the DSC signals are proportional to the rate of crystallization [12]. Therefore, the temperature at which the derivative reaches its maximum coincides with the temperature of the highest crystallization rate. In addition, since crystallization kinetics are influenced by the particle size of powders used for measurement [13], experiments were repeated for five sample powders with different particle sizes, i.e. <45, 80–100, 150–180, 300–330 and 500–530 in μm.

The activation energy (E) of the crystallization was obtained from the relationship between heating rate (ϕ) and the temperature of the maximum (T_p) in the exothermic peak of the DSC curve using Kissinger equation [14];

$$\ln\frac{\phi}{T_p^2} = -\frac{E}{RT_p} + C \quad (2)$$

where, C is a constant and R is the gas constant. From the value of the activation energy, the Avrami parameter (n) was calculated by the Augis-Bennett equation [15];

$$n = \frac{2.5}{\Delta T} \times \frac{RT_p^2}{E} \quad (3)$$

where, ΔT is the full width of the exothermic peak at the half maximum intensity. The value of n close to one means that surface crystallization dominates overall crystallization while the value of three implies a significant contribution of the bulk crystallization process. The n value of four indicates homogeneous crystallization [16].

Table 1
Composition of the parent glass

Component (wt.%)	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	K_2O	Na_2O	P_2O_5	TiO_2
	46.38	9.22	1.20	0.13	13.09	12.05	1.85	7.18	2.71	4.69

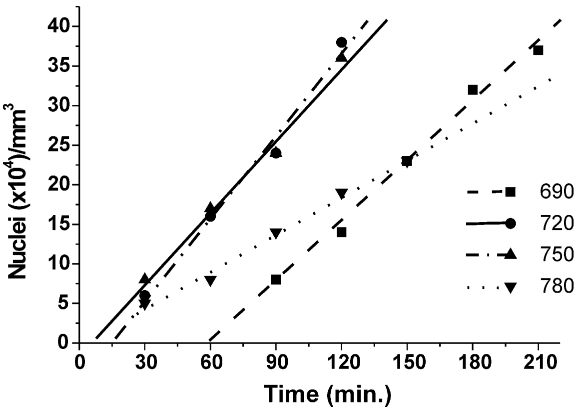

Fig. 1. Number of nuclei produced per unit volume as a function of time.

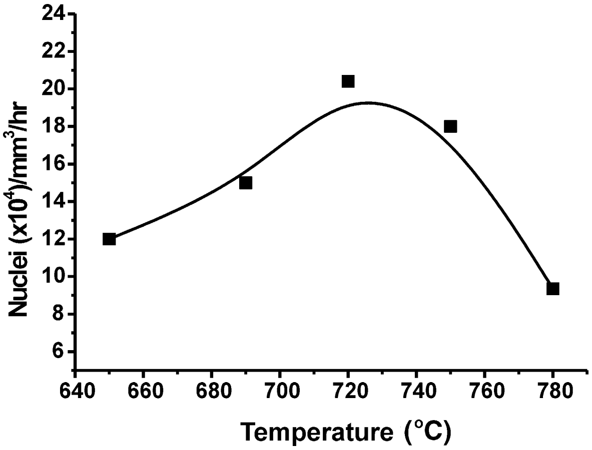

Fig. 2. Changes in nucleation rate with temperature.

Table 2
Kinetic parameters of crystallization for specimens with dfferent particle sizes

Kinetic parameters	45 μm under	80–100 μm	150–180 μm	300–330 μm	500–530 μm
Activation energy (kJ/mol)	468 ± 14	326 ± 6	310 ± 8	294 ± 8	293 ± 10
Avrami exponent (*n*)	1.09 ± 0.04	1.70 ± 0.05	1.79 ± 0.10	1.58 ± 0.11	1.55 ± 0.15

Table 3
Shifts in peak temperature (T_f in °C) in derivatives of DSC thermograms with changes in the heating rate and particle size of specimens

Heating rate (°C)	Sample size				
	45 μm under	80–100 μm	150–180 μm	300–330 μm	500–530 μm
5	880	884	908	913	929
10	889	903	922	933	939
20	905	929	947	958	961
30	916	947	964	977	981

DSC, differential scanning calorimeter.

3. Results and discussion

Nucleation, in principle, can occur within a wide temperature range. However, nucleation at low temperatures requires a long induction time and therefore, becomes meaningless in practice [17]. In this study, nucleation was monitored from the annealing temperature (650 °C) to 780 °C. Fig. 1 shows the number of nuclei produced per unit volume as a function of time. Nucleation rates, obtained from the slope of the straight lines, showed the maximum at around 720 °C (Fig. 2). At temperatures higher than 720 °C, the nucleation rate decreased due to the decrease in thermodynamic driving force [10]. On the other hand, induction time increased as nucleation temperature decreased as shown in Fig. 1.

Crystallization activation energies (*E*) for specimens of different particle sizes were determined from the slope of the lines in Fig. 3 using Eq. (1). Activation energies decreased from 468 to 293 kJ/mol as particle sizes increased (Table 2). Using activation energy values, the Avrami parameter (*n*) was also determined, and it was ascertained that it followed a trend similar as the changes in activation energy. When particle size was small (<45 μm), the value of *n* was 1.09, which indicates that primary crystallization started from the surface [13]. For the specimens with larger particle size, the values of *n* increased to 1.5–2.0. In all cases, crystallization of the glasses is largely heterogeneous and a major portion of nucleation started from the surface.

Fig. 4 is a collection of differentials of the exothermic peak in DSC curves recorded at various heating rates. Overall differentials of the whole exothermic peak are similar to the one in Fig. 4(a). But only low-temperature half was shown in Fig. 4(b)–(e). The temperature where the crystallization peak in the DSC curve shows inflection (T_f) was determined from the peak maximum at the differential DSC curve. The T_f value lies in the range of 870–980 °C depending on the heating rate and particle size of the sample. Table 3 shows the changes in T_f at different heating rates and particle sizes. First, T_f values increased as particle size increased. In other words maximum crystallization occurs at higher temperatures when the particle size increases. In addition, crystallization rates decreased with increasing particle size as evidenced from the intensity of the differentials in Fig. 4. This is due to the decrease in the amount of surface crystallization as the particle size of the specimen increased [13]. However, the Avrami exponent remained below two which indicates the dominance of surface crystallization.

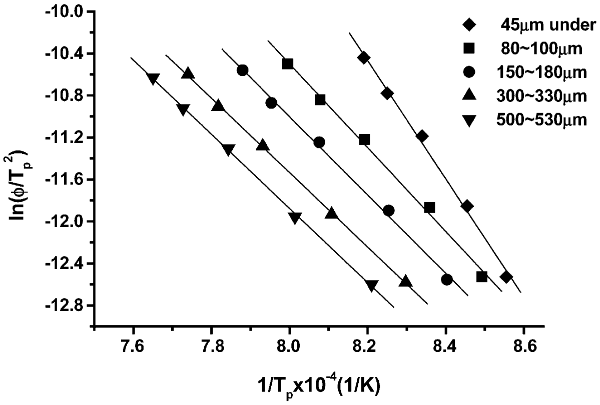

Fig. 3. Plots used for the determination of activation energy (*E*) of crystallization using Kissinger equation.

The progress of crystallization was identified from the optical micrograph (Fig. 5). Both specimens were heat-treated for 1.5 h at 720 °C first after which crystallization was attempted for 2 and 6 h at 870 °C, respectively. Heating rate was 5 °C/min for both samples. Crystallization started from the surface of the glass and

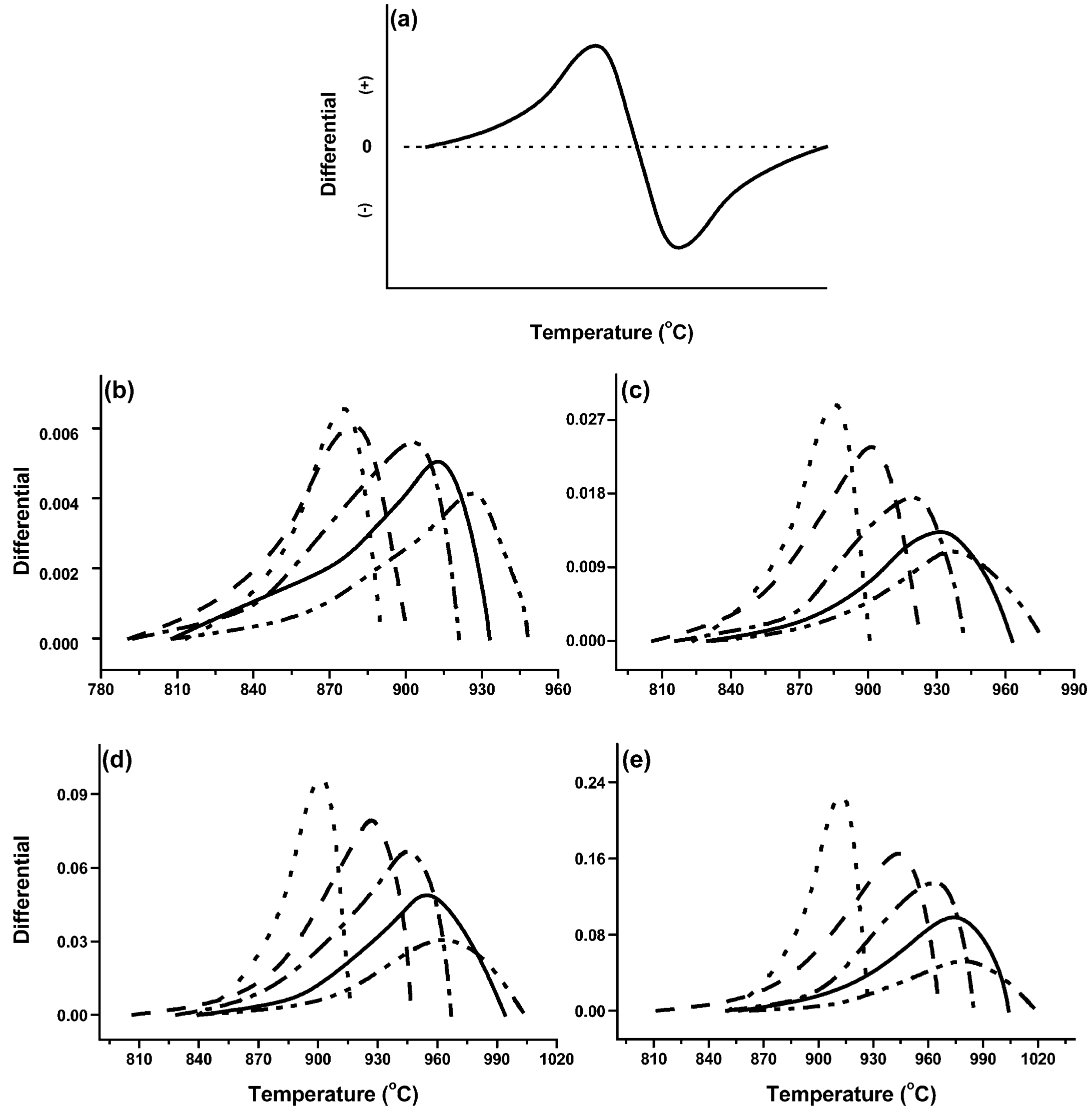

Fig. 4. Derivatives of exothermic peaks at differential scanning calorimeter (DSC) thermograms at a heating rate of (b) 5, (c) 10, (d) 20, and (e) 30 °C/min, respectively. Particle sizes of samples used for the experiments were (· · ··· ·) < 45, (- - - -) 80–100, (-·-·-) 150–180, (——) 300–330 and (–··–) 500–530 in µm.

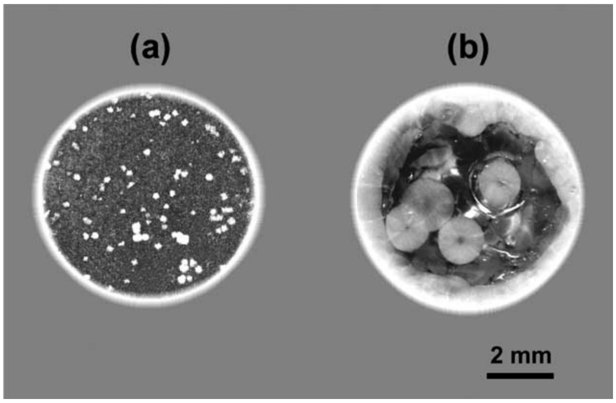

Fig. 5. Optical micrograph of glasses after heat treatment of 1.5 h at 720 °C for nucleation and (a) 2 h and (b) 6 h at 870 °C for crystallization, respectively.

proceeded inward as expected from the analysis of the crystallization kinetics. In addition, a few crystals grew simultaneously from inside these glasses. These micrographs indicate that the glasses crystallized heterogeneously and that crystallization occurs mainly on the surface with a small portion doing so from the inside.

4. Conclusions

Nucleation and crystallization kinetics of glass made of MSW incinerator fly ash were investigated. The maximum nucleation rate was found near 720 °C. Activation energies of crystallization were 468–293 kJ/mol and decreased by increasing the particle size of the powders. Avrami exponents associated with crystallization were 1.5–2.0. This indicates that crystallization began mainly from the surface with a minor portion initiating from inside. Maximum crystallization temperatures were located in the range of 870–980 °C and increased as the particle sizes of the specimen increased.

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