Nucleation and crystal growth in a fly ash derived glass

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The devitrification behaviour of a fly ash derived glass, examined by differential thermal analysis (DTA), X-ray diffraction and scanning electron microscopy (SEM), is reported and discussed. The crystallized phases were identified as mullite ($3Al_2O_3 \cdot 2SiO_2$) and anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$). Kinetic parameters for nucleation and crystal growth were estimated from the DTA curves. The temperature of maximum nucleation rate was 790 °C and the activation energy for crystal growth $E = 370$ kJ mol^{-1}. The crystal morphology was investigated by SEM and the crystal shape found to be consistent with the morphological index n calculated by DTA. The glass–ceramic obtained from a previously nucleated glass showed a fine-grained texture.

1. Introduction

Processing of ores and fuels leaves large quantities of waste (ashes, slag, etc.), only part of which can be utilized by cement industry. As regards fly ash, the amount utilized in Italy is about 1% of cement production [1]. As a consequence new uses of fly ash have to be searched for in order to meet requirements arising from the large production and the greater attention of the community towards an adequate disposal in terms of environmental safeguards [2]. Hence there exists a considerable interest in their utilization as starting materials for glass–ceramic production [3, 4]. Moreover, coal fly ashes are much more convenient than steel slag: they are available in a fine powder form, ready for mixing with other ingredients in batches and in greater quantities than slag.

This work is part of a more general study with the ultimate technological objective of maximizing the amount of ashes in the batch; otherwise the production would be unjustified economically. In this paper the devitrification of a fly ash derived glass without the addition of any other ingredient is studied with the aid of differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Experimental procedure

A platinum crucible was charged with approximately 10 g fly ash obtained from coal-burning power plant (ENEL, Porto Marghera, Venezia) whose composition is reported in Table I. The ash was melted in an electric oven at 1600 °C for 4 h. Owing to its high viscosity the melt could not be cast, but it was quenched by plunging the bottom of the crucible into cold water. The as-quenched glass was then fragmented into small pieces suitable for the experimental measurements.

DTA curves were recorded in air at different heating rates (5, 7.5, 10, 15, 20, 25 °C min^{-1}) on bulk specimens of about 60 mg. Powdered Al_2O_3 was added to improve heat transfer between bulk sample and sample holder. A Netzsch thermoanalyser (High Temperature DSC 404) was used with Al_2O_3 as reference material. The nucleation heat treatments were performed in the DTA apparatus to eliminate temperature gradients. Nucleation times were measured on isothermal DTA curves from the time at which the samples, heated at 50 °C min^{-1}, reached the selected temperature.

To investigate the crystalline phases developed during the DTA runs, the thermally processed samples were finely ground. The samples were analysed in a computer-interfaced X-ray (CuK_α) powder diffractometer using a Philips diffractometer (model PW1710) with a scan speed of 1° min^{-1}. Using a built-in computer search program, the X-ray diffraction patterns were matched to JCPDS data and corresponding phases were identified.

TABLE I Coal fly ash composition

Oxide	Composition (wt %)
SiO_2	48.72
Al_2O_3	35.79
Fe_2O_3	3.72
CaO	8.10
MgO	1.40
K_2O	0.57
Na_2O	0.16
TiO_2	1.54

For the investigation of the glass–ceramic texture and crystal morphology, a scanning electron microscope (Cambridge model S-240) was used. Samples were mounted in epoxy and surfaces were ground smooth, then polished with diamond paste. Samples were etched in 1% HF for approximately 60 s. The etched samples were coated with a thin gold film.

3. Results and discussion
3.1. DTA and XRD
As a glass is heated its heat capacity changes abruptly within a narrow temperature range called the glass transition or transformation temperature, which corresponds to the temperature at which the glass network acquires sufficient mobility to change from a rigid to a plastic solid. When a glass heated in a DTA furnace passes through the glass transition temperature range, the slope of the DTA curve changes. As the crystallization takes place, the heat of crystallization is evolved and an exothermic peak appears on the DTA curve. The DTA curves carried out on an as-quenched bulk sample and on a previously nucleated one show a slope change at about 800 °C followed by an exothermic peak at 1195 and 1147 °C, respectively (Fig. 1).

The phases crystallizing during the DTA runs were identified by XRD analysis. Trace (a) of Fig. 2 has broad humps characteristic of the amorphous state of the as-quenched glass. The reflections in the XRD pattern of a glass sample heated in the DTA furnace up to the temperature of 1300 °C (trace (c) of Fig. 2) were attributed to two crystalline phases, mullite ($3Al_2O_3 \cdot 2SiO_2$) and anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$).

3.2. Temperature of maximum nucleation rate
The non-isothermal devitrification of glass is the result of two individual processes: nucleation and crystal growth. The number of nuclei for unit volume N is the sum of surface nuclei N_S, bulk nuclei formed during the DTA run N_h and bulk nuclei formed during a previous heat treatment of nucleation N_n [5]:

$$N = N_S + N_h + N_n$$

The values of N_S, N_h and N_n are respectively proportional to the sample specific surface S, to the reciprocal of DTA heating rate β and to the time t_n of the nucleation heat treatment [5]. Because a glass crystallizes at temperatures well above the temperatures of high nucleation rates, the number of nuclei already present in the glass cannot appreciably increase during the crystallization so that the crystals grow from a nearly fixed number of nuclei [5].

In a glass heated at constant heating rate β, the crystallization degree α at temperature T is expressed by [6]

$$- \ln(1 - \alpha) = A\frac{N}{\beta^n} \exp\left(\frac{-nE}{RT}\right) \quad (1)$$

where α is the volume fraction crystallized at temperature T, E the activation energy for crystal growth, n a parameter related to the crystals shape (rod-like $n = 1$;
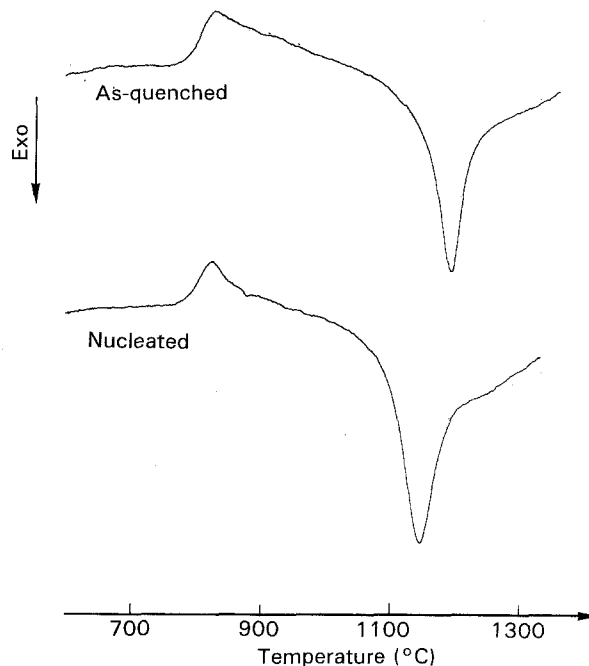

Figure 1 DTA curves of the investigated glass recorded at 20 °C min^{-1}: upper curve, as-quenched sample; lower curve, sample nucleated 12 h at 790 °C.
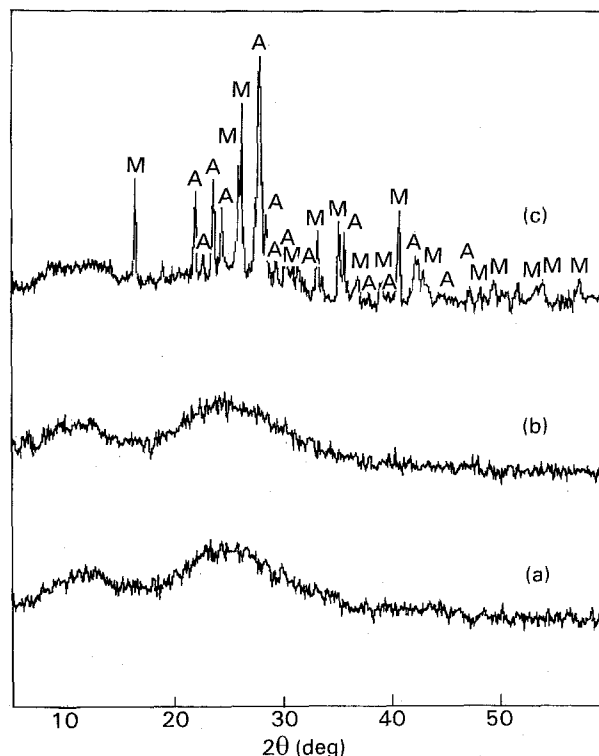

Figure 2 X-ray diffraction patterns: (a) as-quenched glass, (b) glass sample nucleated 12 h at 790 °C, (c) sample heated in DTA furnace up to 1300 °C. (A) anorthite, (M) mullite.

plate-like $n = 2$; three-dimensional $n = 3$), β the DTA heating rate and A a constant. Assuming that at the temperature T_p of the DTA crystallization peak the crystallization degree reaches the same specific value independent of the DTA heating rate [7], Equation 1 becomes

$$n \ln \beta - \ln N = \frac{-nE}{R}\left(\frac{1}{T_p}\right) + \text{const.} \quad (2)$$

A nucleation rate–temperature-like curve can be obtained from DTA curves by the following method [8]. If the DTA runs are carried out on samples of the same specific surface S at the same heating rate β, the sum N_0 of surface nuclei (N_S) and bulk nuclei formed during the DTA run (N_h) is constant and Equation 2 becomes, for a previously nucleated sample,

$$\ln(N_0 + N_n) = \frac{nE}{R}\left(\frac{1}{T_p}\right) + \text{const.} \qquad (3)$$

and for an as-quenched sample $(N_n = 0)$

$$\ln N_0 = \frac{nE}{R}\left(\frac{1}{T_p^\circ}\right) + \text{const.} \qquad (4)$$

From Equations 3 and 4 the following equation can be derived:

$$\ln\left(\frac{N_0 - N_n}{N_0}\right) = \frac{nE}{R}\left(\frac{1}{T_p} - \frac{1}{T_p^\circ}\right) \qquad (5)$$

If bulk samples (low specific surface) are used, the DTA runs are carried out at a high heating rate $(10\,^{\circ}\text{C min}^{-1})$ and the samples are nucleated for a long time $(t_n = 2\,\text{h})$, then

$$N_n \gg N_0$$

If the samples are held for the same time t_n at each temperature T_n of the heat treatment, a plot of $(1/T_p)$ $-(1/T_p^\circ)$ against the temperature T_n of the nucleation heat treatment (Fig. 3) gives a nucleation rate–temperature-like curve that exhibits a maximum at a temperature $790\,^{\circ}\text{C}$ very close to T_g ($800\,^{\circ}\text{C}$).

A glass sample nucleated for a long time (12 h) at the temperature of maximum nucleation rate is still an amorphous material (see trace (b) of Fig. 2). No significant difference was observed between the XRD patterns of an as-quenched glass and of a nucleated one when both were devitrified at $1200\,^{\circ}\text{C}$ for 4 h. This result indicates that the nucleation heat treatment does not change the nature of the crystallizing phases. On the other hand, there exists a remarkable differ-
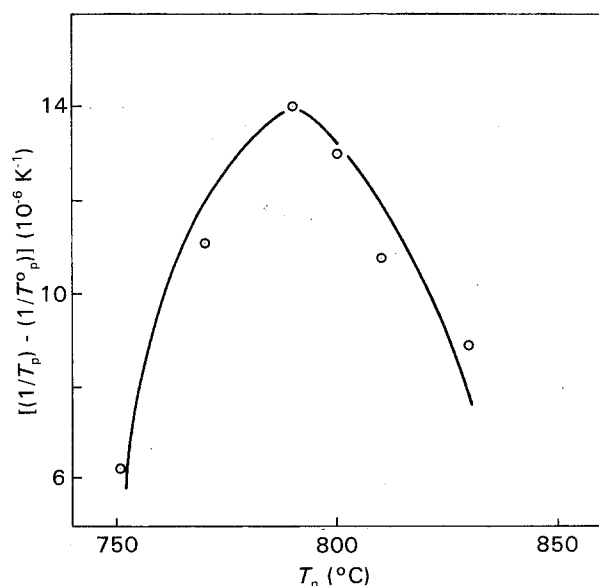
ence in the glass–ceramic texture as can be observed by comparing Fig. 4 and Fig. 5. The previously nucleated sample exhibits a finer-grained texture than the non-nucleated sample.

3.3. Kinetic parameters of crystal growth

If the DTA runs are carried out on bulk (low specific surface area) samples previously nucleated for a long time at a temperature of high nucleation rate $(N \simeq N_n)$ the crystals grow at each heating rate from the same number of nuclei, i.e. the number of nuclei formed during the DTA run can be regarded as negligible.

Samples of the studied glass were nucleated for 12 h at the temperature of the maximum nucleation rate as detected on the nucleation rate temperature-like curve. Therefore Equation 2 becomes

$$\ln\beta = \frac{E}{R}\left(\frac{1}{T_p}\right) + \text{const.} \qquad (6)$$

A value of activation energy, $E = 370\,\text{kJ mol}^{-1}$, for the crystal growth was calculated from the slope of the straight line obtained by plotting $\ln\beta$ against $1/T_p$ (Fig. 6).

The morphological index n can be evaluated from the following equation [9, 10]:

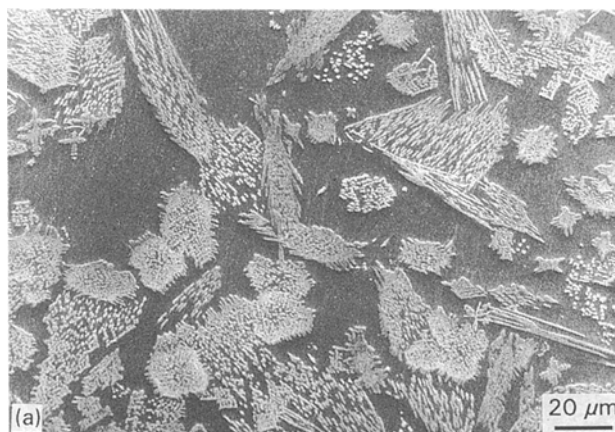$$\ln\dot{\Delta T} = \frac{-nE}{R}\left(\frac{1}{T}\right) + \text{const.} \qquad (7)$$

Figure 4 SEM photomicrographs of as-quenched glasses: (a) after a DTA run up to $1200\,^{\circ}\text{C}$, (b) heated 4 h at $1200\,^{\circ}\text{C}$.

Figure 3 Nucleation rate–temperature-like curve.

Figure 7 SEM of crystal structure in a glass matrix.
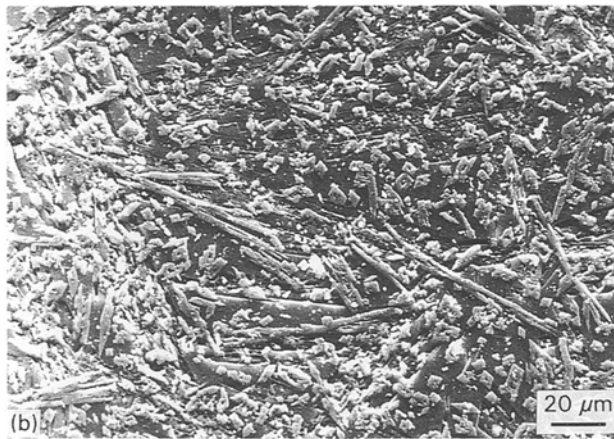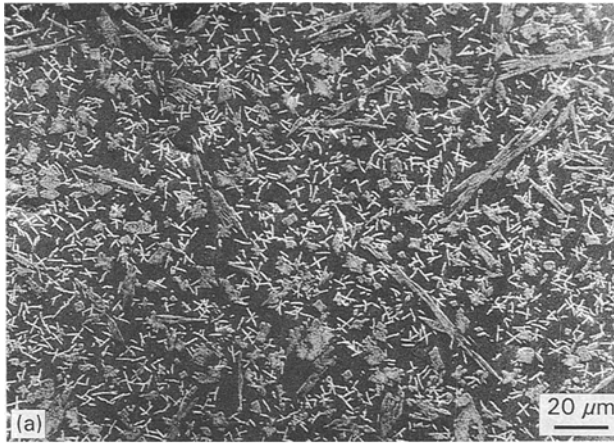

Figure 5 SEM photomicrographs of glasses nucleated 12 h at 790 °C: (a) after a DTA run up to 1200 °C, (b) heated 4 h at 1200 °C.
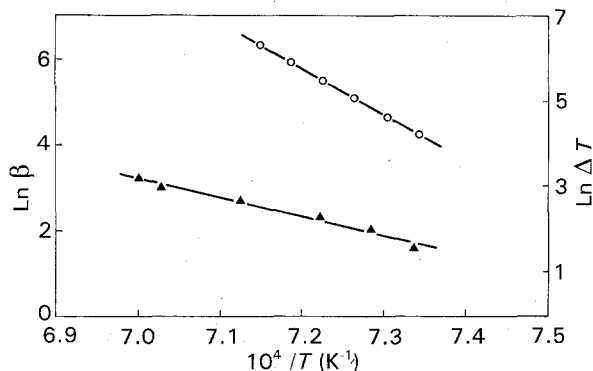

Figure 6 Plots of (▲) ln β versus $1/T_p$ and (○) ln ΔT versus $1/T$.

based on the assumption that in the initial part of the DTA crystallization peak the change in temperature T has a much larger effect on the baseline deflection ΔT compared with the change in α [9]. A value of $n \simeq 2$ was calculated from the slope of the straight line obtained by plotting ln ΔT against $1/T$ (see Fig. 6) and using the value of E previously calculated. The value
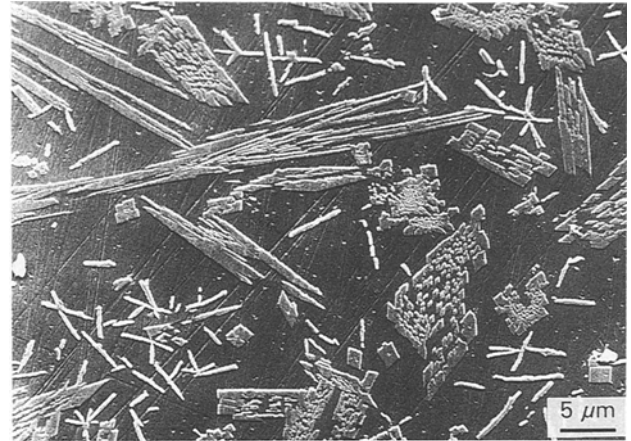
of n is an average one consistent with the morphology of the acicular ($n = 1$) mullite crystals and the three-dimensional ($n = 3$) anorthite crystals as shown in Fig. 7.

4. Conclusions

From the experimental results the following conclusions can be drawn:

(a) The investigated glass exhibits internal crystal nucleation with a maximum nucleation rate at 790 °C.

(b) The crystallizing phases, mullite and anorthite, grow with an average activation energy $E = 370 \text{ kJ mol}^{-1}$.

(c) A nucleation heat treatment leads to a fine-grained glass–ceramic material.

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