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Influence of TiO_2 additions on the crystallization kinetics of a coal bottom ash-Li₂O glass system

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The mechanism for the nucleation and crystallization of glass-ceramics fabricated from coal bottom ash discharged at a thermal power plant was studied by examining the activation energy and Avrami constant using a non-isothermal analysis, and the effect of TiO_2 additions on the surface crystallization behavior was investigated. The glass of the coal bottom ash-Li₂O-CaO system had three exothermic peaks in the differential thermal analysis(DTA), and the crystals formed at 946.3 K corresponding to the lowest temperature peak(T_{p1}) had an Avrami constant of 0.94 showing a surface-dominant crystallizing behavior consisting of β -spodumene and magnetite phases identified by X-ray diffraction analysis. Additions of TiO_2 suppressed the surface crystallization, which was observed by SEM, resulting predominantly in bulk crystallization. By altering the crystallizing behavior from a surface to bulk mechanism, the physical properties of the glass-ceramics could be changed, the surface color yellow to silver and the hardness increased.

Key words: surface crystallization, Avrami constant, glass-ceramics, nucleation agent, hardness, coal bottom ash.

Introduction

Thermal power plants produce about 6 million tons of coal ashes annually in South Korea, among which the fly and bottom ash occupies 80% and 20% respectively [1, 2]. In case of fly ashes, there have been steady research since the 1980's and now commercial bricks, blocks, concretes and cement secondary products etc. have been fabricated from these fly ashes. The bottom ashes(BA), however, are limited to a reclamation use due to their inhomogeneous composition and shape [3, 4].

Recently, research for glass-ceramics using a coal bottom ash to apply to artificial marble tiles and construction materials has been done but yet not for successful application [5, 6]. Therefore a comprehensive study on the crystal-lization kinetics, heat treatment schedule, the type and amount of additives should be performed to recycle coal bottom ash effectively.

In this study, glass-ceramics were fabricated by heattreating a glass composed of BA produced at thermal power plants in South Korea with some modifiers. Surface and volume crystallization mechanisms were investigated in terms of Avrami constants, and microstructures and physical properties were analyzed relating to the crystallizing behavior of the glass-ceramics.

Experimental Procedures

The bottom ashes used in this study were obtained from

'Y' power plants in South Korea and preheated at 1000 °C for 3 h for decarbonization. The chemical composition of the decarbonized coal bottom ash (BA) is shown in Table 1 showing that the BA itself could be vitrified due to the high content of glass former, SiO₂ (53.5 wt%), intermediate Al₂O₃(23.9 wt%), and an acid/base oxide ratio of 2.1 which is of suitable basicity [7].

In this study, 10 wt% CaO and 10 wt% Li₂O was added to the coal bottom ash to decrease the melting point of the BA sample and 0-10 wt% TiO₂ was used as a nucleation agent to control the crystallization process. Mixtures of each raw materials were milled using zirconia balls, and melted in an alumina crucible at 1350 °C for 20 minutes then poured into a graphite mold preheated at 20 K higher than the T_g of the mother glass and held for 15 minutes to release the residual stress. The thermal properties of glass samples were measured by TG/DTA(STA 409 C/CD, Netzsch Co.) at a heating rate 5-20 K·minute⁻¹.

Glass-ceramics were produced at 946.3 K for 1 h, the first exothermic peak temperature in the DTA curve. Identification of crystals within samples was done by an X-ray Diffractometer (X'Pert PRO, PANalytical), and microstructural observations and elemental analysis of glass-ceramics fabricated were carried out by a FESEM (field emission scanning electron microscope; JSM-6500F, JEOL Co.) and an EDS (energy dispersive X-ray spectrometer; Oxford EDS 7557, Oxford Co.) respectively.

Table 1. Composition analysis of coal bottom ash(wt%)

SIO ₂ Al ₂ O ₃ Fe ₂ O ₃ CaO) MgO	Na ₂ O	K ₂ O	TiO ₂	ZrO ₂	P ₂ O ₅	Cr ₂ O ₃	MnO
58.53 23.89 10.37 2.79	9 1.00	0.23	0.66	1.71	0.42	0.31	0.01	0.06

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Results and Discussion

DTA curves with various heating rates are shown in Fig. 1 and exothermic peak temperatures and glass transition temperature(T_g) measured from Fig. 1 are listed in Table 2. The glass transition temperature and exothermic peak shift to a higher temperature with an increase in the heating rate. The magnified peaks of the DTA curve obtained at $\beta = 20$ K·minute⁻¹ in (a) is shown in (b) to measure the half-width of the peak precisely.



Fig. 1. DTA curves for glass samples with various heating rates (a), and separation of crystallization peaks for the DTA curve obtained at a heating rate of $20 \text{ K} \cdot \text{minute}^{-1}$ (b).

Table 2. T_g and T_p for various heating rates(β) measured form the DTA curve in Fig 1(a)

$\beta(K \cdot minute^{-1})$	$T_g(K)$	$T_{p1}(K)$	$T_{p2}(K)$	$T_{p3}(K)$
5	805.7	914.9	977.4	1012.1
10	807.5	929.6	990.7	1036.1
15	809.2	938.0	1000.3	1036.4
20	819.8	946.3	1009.2	1046.6

The activation energy (E) for crystal growth was proposed by Kissinger as follows:

$$\ln(T_p^2/\beta) = E/(RT_p) + C$$
(1)

where T_p is the crystallization temperature, β is the heating rate, E is the activation energy for crystallizing, R is the gas constant and C is a constant [7]. Substituting T_p obtained from the DTA data in Fig. 1 into equation (1) and plotting $\ln(T_p^2/\beta)$ vs. $1/T_p$, the activation energies for the crystal growth from the tangent of the plot as shown in Fig. 2, can be calculated as 307.2 and 329.2 kJ/mol for T_{p1} and T_{p3} respectively.

The relationship between time (t) and crystal volume fraction (X) when a glass is heated was proposed by Johnson-Mehl-Avrami(JMA) as follows [8-10]:

$$X = 1 - \exp(-(Kt)^n)$$
⁽²⁾

where X is the volume fraction of crystallized phase at time t, and n is the Avrami constant, normally ranging from 1 to 4. The crystallization of n close to 4 is known as favoring a volume nucleation while a surface nucleation is for close to 1 [11]. The Avrami constant can be calculated from a half-width of peak of the DTA curve and activation energy for crystallization as proposed by Augis-Bennett as follows:

$$n = (2.5/\Delta T_{FWHM})(RT_p^2/E)$$
(3)

where ΔT_{FWHM} is the half-width in terms of temperature of the crystallization peak in the DTA curve and E is an activation energy for crystallization [12]. The Avrami constant for T_{p1} and T_{p3} was calculated from equation (3) as 0.94 and 1.35 respectively. So, the crystallization corresponding to T_{p1} and T_{p3} showed a surface-dominant behavior [13].

The XRD results for the surfaces of glass-ceramics heat treated at 946.3 K (T_{p1}) for 1 h are shown as a function of the amount of nucleation agent TiO₂ in Fig. 3. A low angle at glancing incidence diffraction ($\alpha = 1^{\circ}$) was used for the surface crystal analysis to eliminate the diffracted rays caused by the interior crystals. The surface of the



Fig. 2. Plots of $\ln(T_p^2/\beta)$ vs. $1/T_p$ for glasses.



Fig. 3. XRD patterns for the surfaces of glass-ceramics with various TiO_2 contents.

glass-ceramics is composed of a β -spodumene solid solution, magnetite and unknown crystal phases whether TiO₂ is added or not, and the relative ratio between crystals is not much changed.

The XRD patterns for the interior parts of glass-ceramics with varying TiO₂ contents are shown in Fig. 4. No crystal was found in the interior of glass-ceramics containing TiO₂ 0-2 wt%, but some crystal traces were found in the specimen with 4 wt% TiO₂. Increasing the TiO₂ content above 6 wt% increases the peak intensities of the XRD patterns and this could be confirmed in the micrographs of Fig. 5 showing that the area occupied by the crystals against glassy matrix increase with an increase in the TiO₂ content. The crystals in the interior was composed of a major phase of β -



Fig. 4. XRD patterns for interiors of glass-ceramics with various TiO_2 contents.

spodumene solid solution, a minor phases of magnetite and some unknown phases.

It is certain that the glass-ceramics without TiO₂ additions had a well-grown surface crystal layer and amorphous interior from the pictures obtained by optical microscopy as shown in Fig. 5. The thickness of the surface crystal layer is about 257 μ m for the specimen with no TiO₂ addition and decreases to 143 μ m for 6 wt% TiO₂, and 29 μ m for the 10 wt% TiO₂ showing that addition of TiO₂ suppressed the surface crystallization. Also addition of TiO₂ above 6 wt% induced bulk crystallization and most of the interior part was filled with crystals for the glass-ceramics containing TiO₂ 10 wt%.

The microstructure of the interior part of a glass-ceramics



Fig. 5. Optical microscopic images for the cross sections of glass-ceramics with various TiO_2 contents; (a) 0, (b) 2, (c) 4, (d) 6, (e) 8 and (f) 10 wt%. The capital 'S' and 'I' means a surface and an interior part of the specimen respectively.

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Fig. 6. SEM micrograph for the interior part of a glass-ceramics containing 4 wt% TiO₂.



Fig. 7. Surface hardness for glass and glass-ceramics as a fraction of TiO_2 content.

containing TiO_2 analyzed by a SEM is shown in Fig. 6, showing hexagonal crystals spread in the matrix.

The surface of glass-ceramics shows various colors at different TiO_2 contents. The glass-ceramics containing TiO_2 0-4 wt% are tinged with yellow, and dark yellow and silver for 6-8 wt% and 10 wt% TiO_2 respectively.

The Vickers hardness for the glass-ceramics is presented in Fig. 7. Adding TiO_2 up to 8 wt% increases the surface hardness of glass-ceramics. The glass-ceramics without TiO_2 , in which only surface crystallization occurred, showed a lower hardness than that of the glass which means the surface crystallization lowered the mechanical properties of glass-ceramics. But the hardness of glass ceramics increased with the TiO₂ content due to enhanced internal crystal growth. The glass-ceramics containing 8 wt% TiO₂ had a hardness of 650 MPa, 1.3 times higher than that of the glass. When the content of TiO₂, however, is above 8 wt%, the hardness of glass-ceramics decreased because the excess TiO₂ might not act as an effective nucleation agent.

Conclusions

The crystallization behavior of a coal bottom ash-Li₂O-CaO system glass was surface-dominated as confirmed by the calculation of activation energy(E) and Avrami constant from Kissinger and Augis-Bennett equations respectively. Addition of TiO₂ depressed the surface crystallization and induced the bulk crystallization which was clearly observed in the microstructure. So, surface/volume crystallization control by the addition of TiO₂ could be useful to change the physical properties such as surface color and hardness.

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