Available online at www.sciencedirect.com

Journal of the European Ceramic Society 24 (2004) 2373–2382

www.elsevier.com/locate/jeurceramsoc

Glass-ceramic produced from a municipal waste incinerator fly ash with high Cl content

Jae-Myung Kim, Hyung-Sun Kim*

Department of Materials Science and Metallurgical Engineering, Sunchon National University, Sunchon, 540-742, South Korea

Received 16 March 2003; accepted 18 August 2003

Abstract

This study is concerned with recycling waste materials, focusing on the development of a glass-ceramic from Korean incinerator fly ash with a high Cl content, and the evaluation of its physical properties. In the process, water washing as a pre-treatment before melting the fly ash was used to remove the large amount of Cl in the ash, and to reduce the melting temperature of the fly ash. As a result, glass was obtained at 100 degrees lower than the non-water-washed fly ash. Also, internal crystallization occurred under a single stage heat treatment (at 850–950 °C for 20–240 min) without adding other materials to the ash. It was found that the glass-ceramic was composed of three crystals, gehlenite, augite, and calcium aluminium oxide. Hardness of 8.3 GPa, fracture toughness of 1.7 $MPam^{1/2}$, elastic constant of 145 GPa, and thermal expansion coefficient of $10.5–11.5\times10^{-6}$/K were found in the glass-ceramic, which were high values compared with others reported. Thus, the present process suggests that such glass-ceramic produced from an incinerator ash could be applicable for structural materials in terms of economic and environmental points.

Keywords: Crystallization; Glass-ceramic; Incinerator fly ash; Waste materials

1. Introduction

With the increasing amounts of municipal solid waste (MSW), post incineration problems need to be solved, in particular fly ash that is collected from the flu gas by air pollution control devices. The decreasing amount of land fill space available for fly ash disposal is currently an extremely serious problem in maintaining an environmentally friendly society.[1–3] Recently, existing practices related to the use of MSW fly ash were very well summarized. The potential uses of fly ash are as follows; construction materials, geotechnical uses, agriculture and miscellaneous uses.[4,5] Regarding construction materials, there are several processes for the treatment of fly ash, including solidification for cement, melt-solidification or sintering by firing, and acid leaching by the use of acids and some solvents.[6–9]

Application of glass-ceramics to make construction (structure) materials is a common process, which converts fly ash to a glass by melting at high temperatures and by heat treatments. Using casting or sintering processes, glass-ceramics from MSW fly ash have been developed over many years of study.[10–12] However, the technology in developing glass-ceramics using MSW fly ash cannot be uniformly applied to every country due to differing fly ash characteristics. The composition of MSW fly ash varies according to countries, seasons and regional variations, meaning that the heat treatment condition, nucleation and crystal growth for glass-ceramics are different depending on the sources of the fly ash.

In terms of the characteristic constituent of fly ash in Korea, it has a high chloride content due to the Korean diet. In this study, we report the results of production and properties of a glass-ceramic derived from Korean incinerator fly ash with a high Cl content.

2. Experimental

Glass was prepared by melting fly ash in a Pt crucible at 1450 °C for 3 h after water-washing at room temperature for 48 h to remove the Cl. The melt was poured into a graphite mold and heat-treated at 950–1050 °C

---

* Corresponding author. Tel.: +81-61-750-3555; fax: +81-61-750-3550.

E-mail address: hskim@sunchon.ac.kr (H.-S. Kim).

0955-2219/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2003.08.001

for 0.5–4 h to convert to a glass-ceramic.[13] Differential thermal analysis (DTA, TA-1600, USA) was performed to determine the crystallization behavior and the glass transition temperature (T_g) of the glass using bulk and coarse powder (212–425 °C) samples at a heating rate of 10 °C/min. A particle size analyzer (LS230, Coulter Co., USA) was used for the powder size distribution of fly ash. The crystalline phases of the glass-ceramics were investigated by X-ray powder diffraction (XRD, X'Pert APD system, Philips, Netherlands) and the crystallinity of the glass-ceramics was calculated by a method[14] based on the XRD result. The composition of the fly ash was investigated using an X-ray fluorescence spectrometer (XRF, PW 2400, Philips, Netherlands), and scanning electron microscopy (SEM, S-3500N, Hitachi, Japan) was used to examine the crystalline morphology of the glass-ceramics after etching with 2%HF solution for 1 min and 15% HCl solution for 1 min.

The density of the glass and glass-ceramics was determined by the Archimedes method. Elastic constants of glass and glass-ceramics were assessed on bars ($10\times10\times5$ mm^3) by a pulse reflection tester (Panametrics, USA). Vickers indentation was used to determine the hardness using loads of 300 g for 15 s (Vickers hardness tester, MVK-E3, Akasi, Japan) and fracture toughness was measured using an indentation method. An erosion test was carried out using SiC powder sand (~75 μm) dropped from a height of 1100 mm and impacting on the sample ($3\times3\times3$ mm^3) at an angle of 45°. Mass loss from the sample was measured after every 10 kg of sand dropped, and converted into the weight loss/eroded area, (g/cm^2). Thermal expansion coefficient of the samples ($5\times5\times10$ mm^3) was measured by a thermal mechanical analyzer (Dilatronic, Theta Industrial. Inc., USA) with a heating rate of 5 °C/min in air atmosphere.

3. Result and discussion

3.1. Glass-ceramic production

The effect of the washing process on the powder size of fly ash is represented in Fig. 1 which shows that washed fly ash had smaller particle size of distribution than that of unwashed fly ash, due to the Cl components in NaCl and KCl being removed by washing and thus the volume of powders being reduced. The major components in the fly ash as received were CaO, Cl, and Na_2O, but after water-washing, SiO_2, Al_2O_3, and CaO emerged as major components (Table 1). As shown in Table 1, the major difference in chlorides content between the raw and washed ash, in terms of composition, indicates a typical Korean fly ash from MSW, as compared with others.[1–3, 6–8] The amounts of K_2O, Na_2O and Cl in the fly ash were considerably reduced through the water-washing process as shown in Table 1. It seems that Na and K components exist as NaCl and KCl as a result of water-washing and the high content of CaO in the fly ash affects a decrease in the melting temperature. Adding CaO decreases the ratio of network formers to modifiers and the viscosity of glass becomes low.[13]

The vitrified product is composed of the main ternary compounds (13–33 wt.%), SiO_2, Al_2O_3, and CaO and includes MgO, P_2O_5, TiO_2, Fe_2O_3, and ZnO as minor

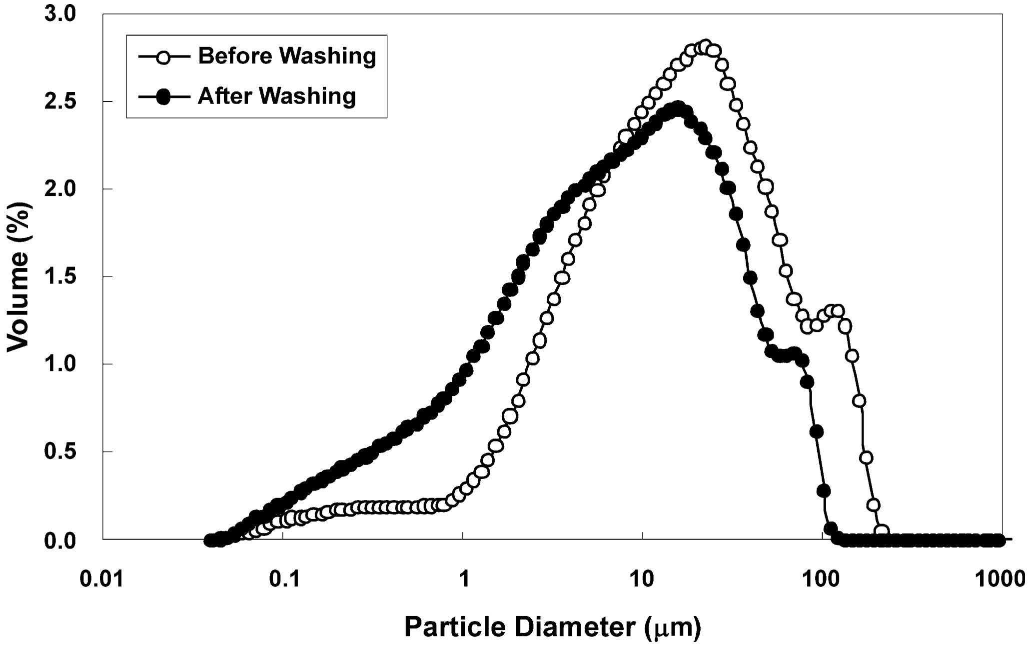

Fig. 1. Powder size distribution of fly ash before and after water washing.

components (3–7 wt.%). Thus the composition of fly ash is favorable for glass-melting and formation of glass-ceramics due to the presence of glass forming oxides (SiO_2, Al_2O_3, and CaO) and nucleating agents (P_2O_5, TiO_2, and Fe_2O_3). The result of XRD analysis on the fly ash suggests that the major species, NaCl, KCl, and $CaCl_2$, $CaCl_2Ca(OH)_2H_2O$), and $CaSO_4$ as minor crystalline phases in the ash were removed by the water-washing process (Fig. 2b). In contrast, the major phases in the as-received fly ash appear to be NaCl, KCl, and $CaSO_4$ (Fig.2a).

Table 1
Comparison of composition of fly ash (as received/after water-washing) and glass (vitrified) (in wt.%)

Composition	Sample		
	As received	After water washing,	Vitrified product
SiO_2	7.30	21.94	25.77
Al_2O_3	3.20	9.97	13.02
CaO	19.50	26.23	33.04
MgO	2.61	8.32	6.86
TiO_2	2.77	3.80	5.68
P_2O_5	1.72	5.76	5.24
ZnO	3.02	4.72	3.57
Fe_2O_3	1.39	2.08	2.89
Na_2O	13.07	2.11	1.95
K_2O	11.21	0.84	0.29
PbO	–	1.13	0.20
Cl	21.98	0.77	0.05
SO_3	9.76	11.93	0.05
Total	100	100	100

The ash was unstable at high temperature, showing a weight reduction of 35% when heated to 1000 °C with a significant loss at around 800 °C (Fig. 3a). However, thermal degradation (decomposition) of fly ash treated by water-washing was more stable than non-water washed fly ash. There was a 5 wt.% reduction up to 1000 °C, increasing sharply until reaching a 20% loss at 1200 °C, then remaining relatively stable until reaching 1400 °C. In case of fly ash as received, the significant reduction in weight at around 800 °C resulted from sudden evaporation after melting at 804 and 779 °C for NaCl and KCl, respectively (Fig. 3, Table 1). However, the stable reaction of only 5% reduction during heating up to 1000 °C is related to the removal of chlorides in the fly ash as shown in Fig. 3b. With or without the water-washing process, the fly ash follows the same reaction in the heating process; dissociation of $Ca(OH)_2$ at 485 °C and $CaCl_2Ca(OH)_2H_2O$ at 689 °C resulting in the 5% reduction up to 1000 °C.

Based on the result of Fig. 3, the glass melting, which was higher than the liquidus temperature ($T_l = 1280$ °C), was performed at 1450 °C for 3 h to produce a clear and uniform melt. Thermal analysis on the coarse glass powder showed two exothermal peaks, irrespective of whether the fly ash underwent the washing process prior

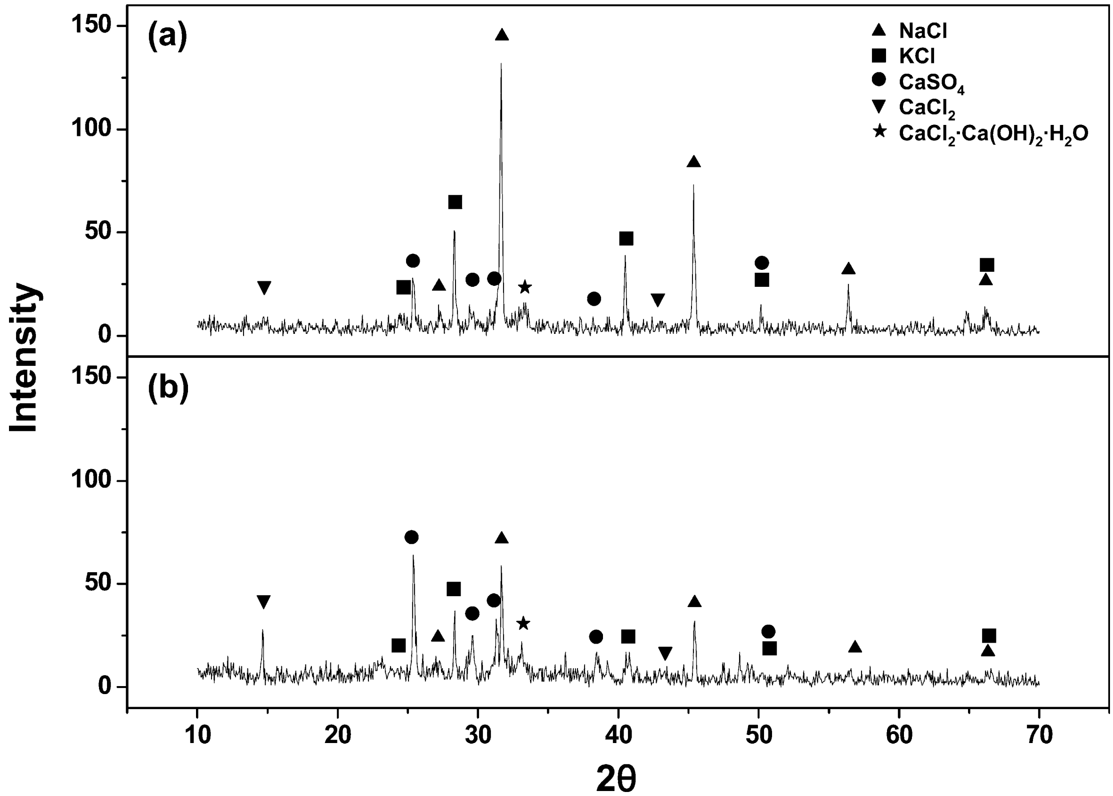

Fig. 2. Crystalline phases of fly ash (a) before (as received) and (b) after water washing.

to melting (Fig. 4). The first exothermal peak was related to bulk crystallization and the second to crystal transformation or a new crystal formation. The first exothermal reaction, representing bulk crystallization, started at 885 °C. On the other hand, when analyzing the crystallization mechanism of fly ash glass, the same exothermal peak temperature, 895 °C as shown in Fig. 4(b) and (c) suggested that internal crystallization occurred during heat treatment. Irrespective of coarse and fine glass powder sizes, crystallization occurred with the same T_g, namely 700 °C.

Observation of the samples by the naked eye noted that with increasing heat treatment temperature and time, the color of the glass-ceramic changed from black to light yellow, which is a result of the formation of crystallines. Fig. 5 shows the result of XRD analysis for the glass-ceramic after heat treatment at different temperatures for 1h. At 850 °C, calcium aluminium oxide

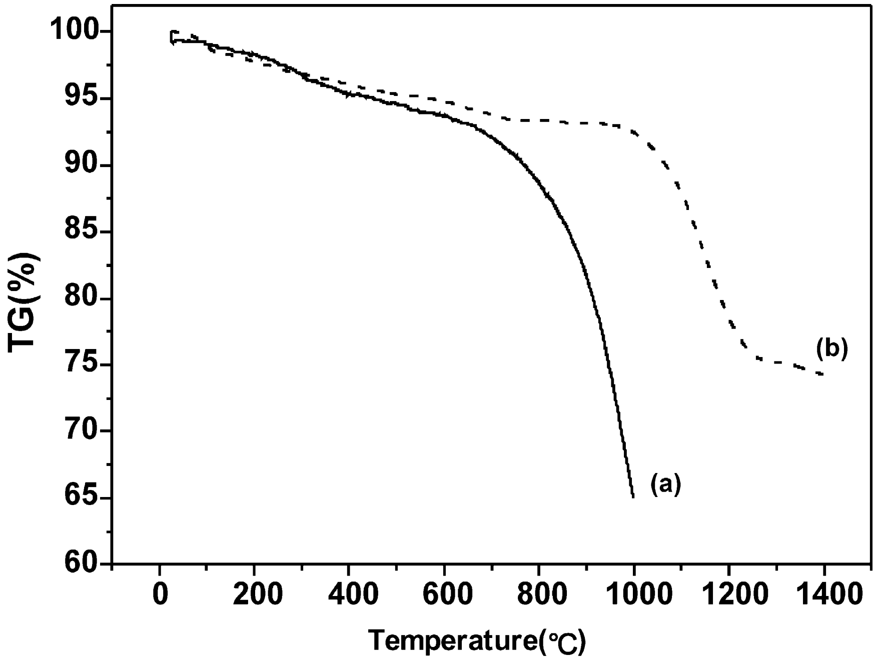

Fig. 3. TG of fly ash (a) before and (b) after water washing.

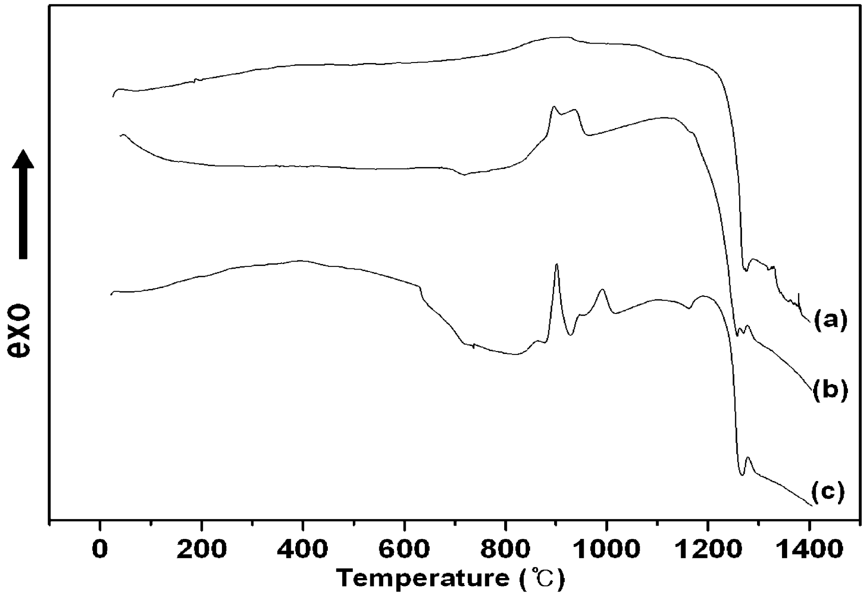

Fig. 4. Result of DTA on (a) fly ash after water-washing (as-received), (b) coarse powder of glass (glass powder: 212–425 μm powder) and (c) fine powder of glass (glass powder: <38 μm).

phase and at 900 °C both gehlenite and calcium aluminium oxide crystals were found to be major crystals (relatively the largest proportion of the phase) in the glass-ceramic. However, above 950 °C, the amount of augite appearing at lower temperature was reduced and gehlenite was detected as a major phase. Additionally, a small portion of augite was present within the range of 850–950 °C. The change of major crystals (from $Ca_9Al_6O_{18}$ to gehlenite) in the glass-ceramic appears to be related to the result of DTA (Fig. 4b), namely the two exothermal peaks ($T_p = 895$, 960 °C). From the result of XRD analysis (Fig. 5), the crystallinity of glass-ceramics was obtained. With increasing heat treatment temperature and time, the crystallinity of glass-ceramics increased and reached 70–80% under a single stage heat treatment. Above 60 min of heat treatment time however, the effect on the crystallinity at above 850 °C was not noticeable, as shown in Fig. 6.

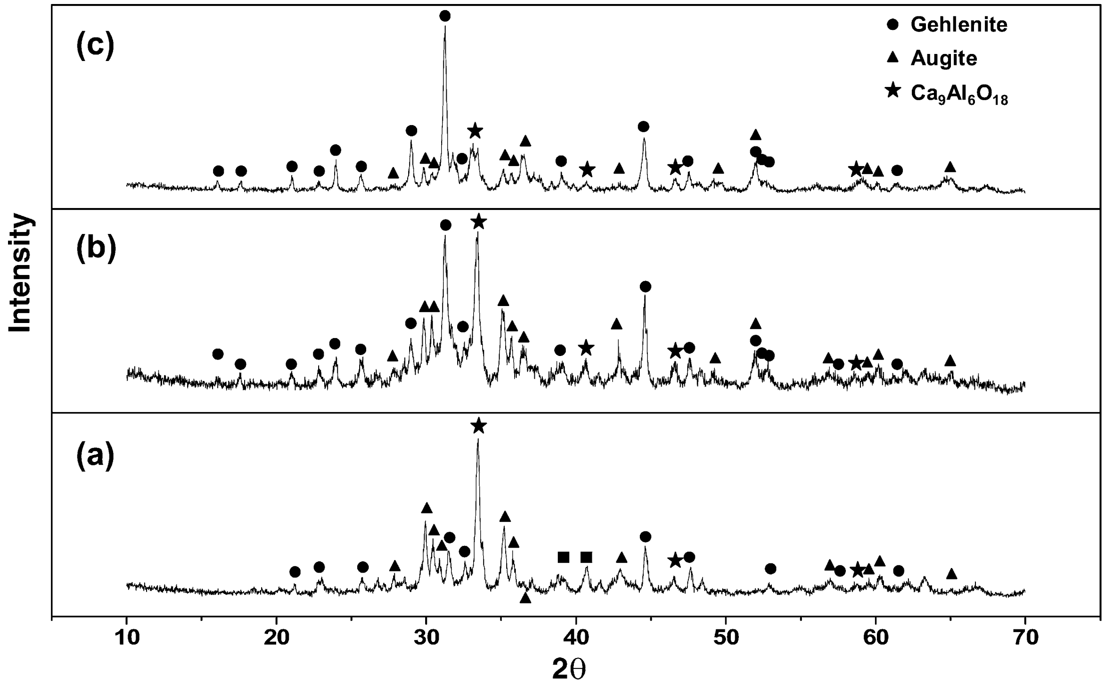

Fig. 5. XRD result of glass-ceramic as a function of heat treatment temperature (a) 850, (b) 900 (c) 950 °C for 60 min.

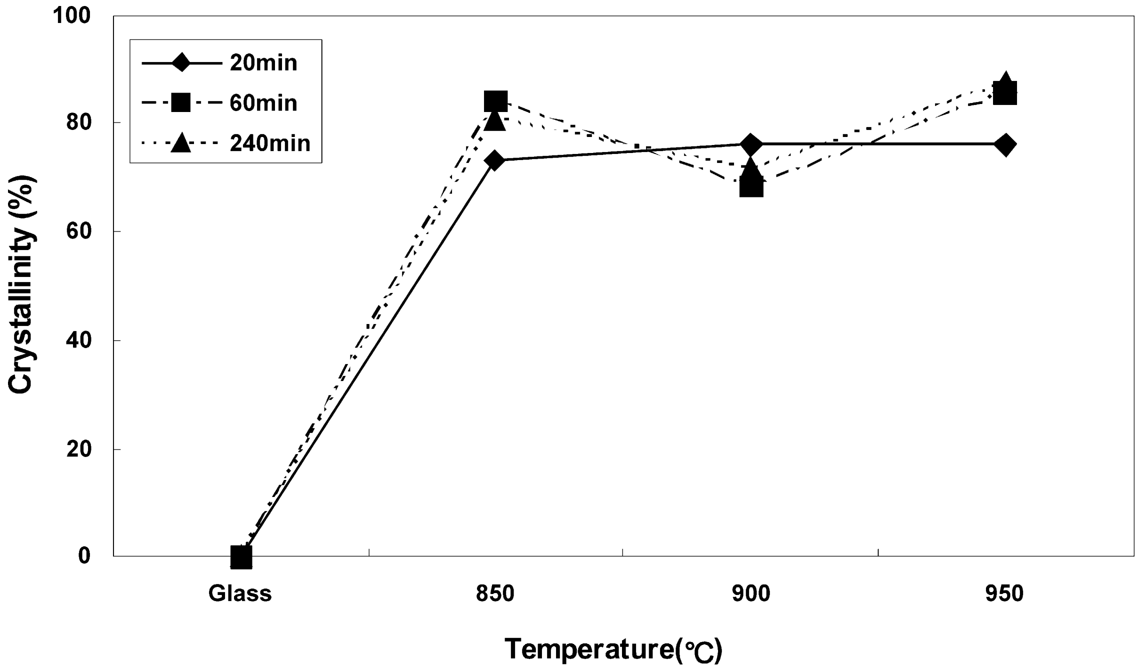

Fig. 6. Crystallinity of glass-ceramics heat treated at different heat treatment condition (temperature and time).

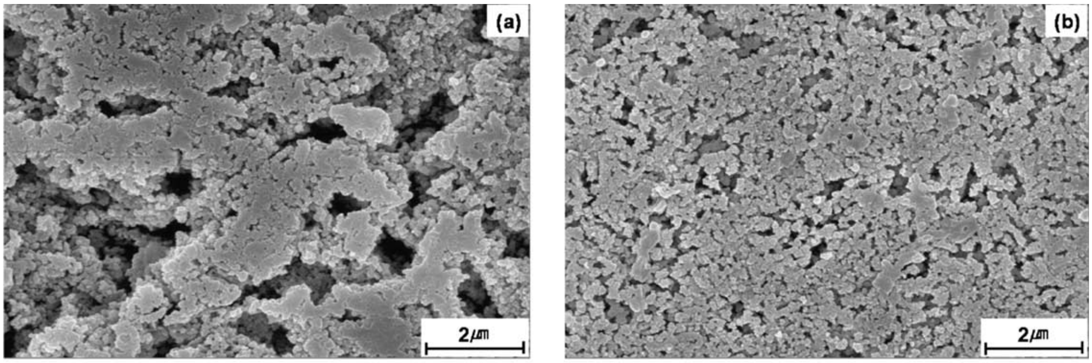

Fig. 7. Microstructure of glass-ceramic produced using pre-treatment (a) without washing and (b) after water washing (heat treatment condition: at 900 °C for 60 min).

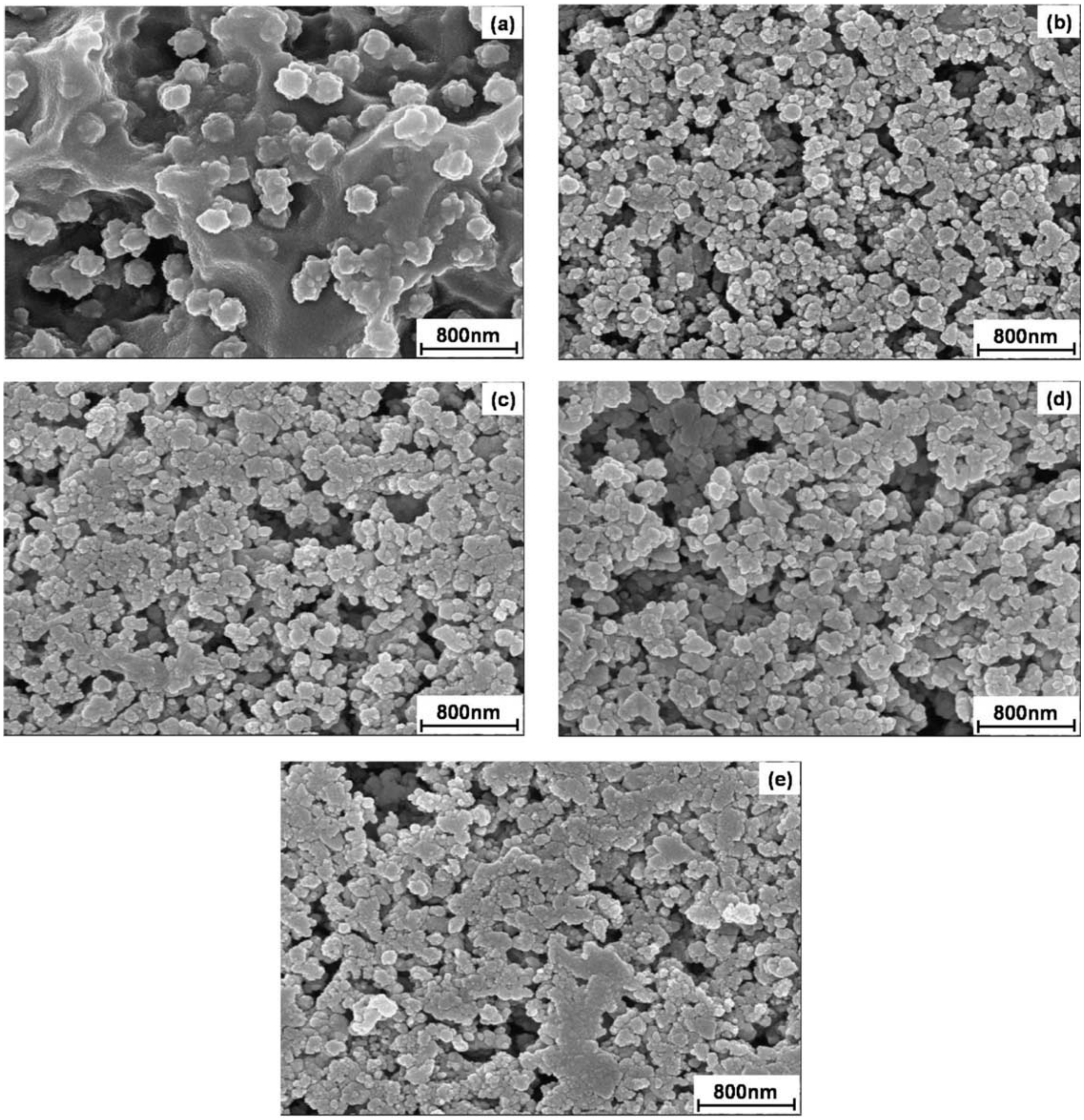

Fig. 8. Microstructure (etched surface) of glass-ceramic heat treated at different temperature (a) 820, (b) 850, (c) 880, (d) 900, and (e) 920 °C for 60 min.

The effect of water washing of fly ash on the microstructure of glass-ceramics is clear in Fig. 7, which shows the comparison of different microstructure of glass-ceramic produced at 900 °C. The dense surface of glass-ceramic with high crystallinity is detected only on the pre-treatment of fly ash before melting (Fig. 7b). The microstructure of glass-ceramic heat treated at 820 °C contained small amounts of glass phase (dark region, Fig. 8a) whereas the structure changed to a dense glass-ceramic with high crystallinity and small size crystals as the heat treatment temperature increased up to 950 °C. Unfortunately the different crystal phases are not distinguished in the microstructure shown in Fig. 8.

As shown in Table 2, the relatively higher content of Mg, Al, Ti, Fe, and Zn in the crystal compared with the glass region (Fig. 9) is related to the formation of crystals of augite ($Ca(Fe,Mg)Si_2O_6$), gehlenite ($Ca_2Al_2SiO_7$), and calcium aluminum oxide ($Ca_9Al_6O_{18}$) comprising of Ca, Mg, Si and O with some specified ions for the nuclei. In other processes, oxides such as SiO_2, MgO and TiO_2 are mixed with fly ash in order to reduce the melting temperature and intentionally induce crystalline formations in glass-ceramics,[8,9] and a two stage heat treatment resulting in nucleation and crystal growth or long time heat treatment is used to produce crystals. In the present study however, an economical process using a one stage heat treatment, without changing the composition of the fly ash was applied to the production of glass-ceramics.

Table 2
Chemical analysis of crystal and glass in the glass-ceramic by EDX (in wt.%) in Fig. 9

Oxides	Crystal (a)	Residual glass (b)
Na_2O	7.2	6.4
MgO	15.5	12.2
Al_2O_3	17.3	15.4
SiO_2	31.9	36.0
CaO	14.4	18.9
TiO_2	4.6	3.7
Fe_2O_3	3.4	3.0
ZnO	5.7	4.3
Total	100	100

3.2. Properties of glass-ceramics

The density of the glass-ceramic decreased after 60 min holding time above 900 °C as shown in Table 3. The reason is related to the formation of crystallines with different densities (gehlenite = 3.042, augite = 3.510 and calcium aluminium oxide = 3.028g/cm^3) as a function of temperature (Fig.5). The elastic constants of the glass and the glass-ceramics were 105 GPa and ~140 GPa, respectively, as shown in Table 3. Though the increasing trend of elastic constant with time at 850 °C was evident, the trend decreased above 900 °C and with more than 1h holding time. Specifically, the elastic constant of materials produced at 950 °C for more than 20 min rapidly decreased and was not able to be determined, because the long holding time at a high temperature

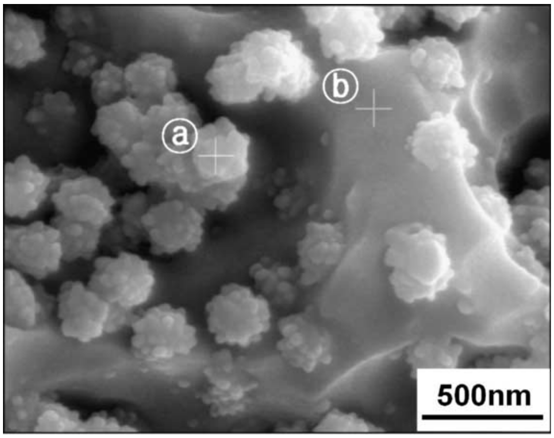

Fig. 9. Crystalline (a) and residual glass (b) in the glass-ceramic produced at 820 °C for 60 min.

Table 3
Physical properties of glass and glass-ceramic prepared at different heat treatment conditions

Materials	Density (g/cm^3)	Elastic constant (GPa)	Vickers Hardness (GPa)	Fracture toughness (MPam$^{1/2}$)
Glass	3.0184±0.002	104	6.27±0.066	0.84±0.029
850 °C 20 min	3.3125±0.015	139	7.47±0.028	1.36±0.104
60 min	3.2962±0.003	145	8.13±0.032	1.42±0.089
240 min	3.2937±0.001	147	8.03±0.025	1.27±0.011
900 °C 20 min	3.3056±0.007	142	8.23±0.065	1.71±0.045
60 min	3.3274±0.02	143	7.76±0.154	1.64±0.079
240 min	3.1187±0.003	126	7.44±0.159	1.56±0.047
950 °C 20 min	3.3340±0.005	146	8.07±0.137	1.39±0.063
60 min	3.2964±0.003	–[a]	7.64±0.174	–
240 min	3.2356±0.002	–	6.81±0.137	–

[a] Not determined due to micro cracks in the samples with high crystallinity

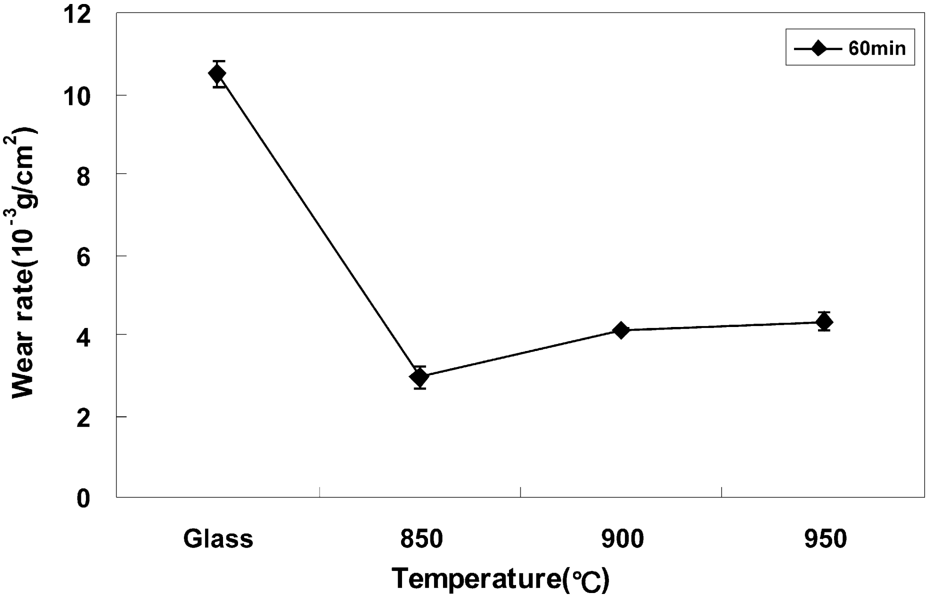

Fig. 10. Wear resistance of samples before and after crystallization at (a) 850 (b) 900 and (c) 950 °C for 60 min.

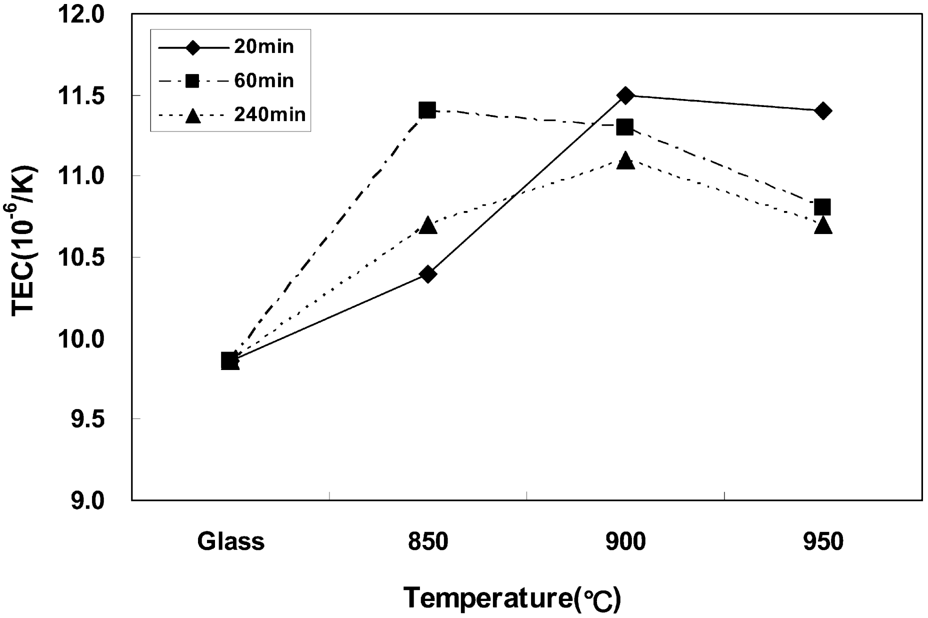

Fig. 11. Thermal expansion coefficient (TEC) of glass and glass-ceramics as a function of heat treatment time and temperature.

induced high crystallinity in the microstructure with micro cracks.

Table 3 summarizes the result of the hardness of the glass and the glass-ceramics as a function of heat treatment time and temperature. The glass-ceramics comprised of crystalline, gehlenite, augite, and calcium aluminium oxide have higher hardness (7.4–8.2 GPa) than glass (6.3 GPa). The effect of holding time and heat treatment temperature on the hardness is limited to a small range: over 1 h and beyond the limit a negative effect was apparent in the microstructure. The fracture toughness of glass-ceramics remained unchanged after 20 min heat treatment as shown in Table 3. The highest toughness (1.7 MPam$^{1/2}$) was found at 900 °C for 20 min.

The wear rate of glass and glass-ceramics produced at 850–950 °C for 1 h, measured by erosion testing are shown in Fig. 10. The glass-ceramic (at 850 °C for 60 min) (2.23×10^{-3}g/cm^2) showed high wear resistance compared to the glass (10.6×10^{-3}g/cm^2) because of the formation of crystalline phases with higher elastic constant. The trend of wear rate change was similar to the hardness and the elastic constant of the materials

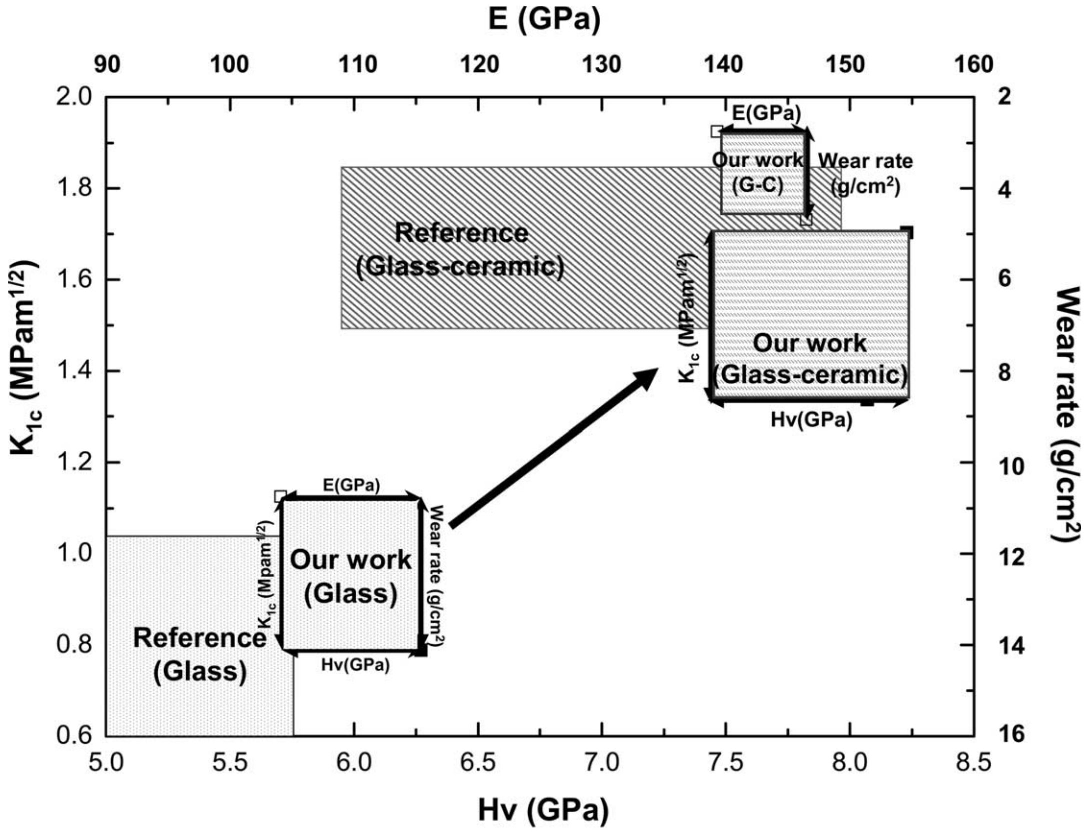

Fig. 12. Relationship between toughness (K_{Ic}), hardness (Hv) and elastic constant (E) of glass-ceramic can be predicted for wear resistance.

Table 4
Comparison of properties of glass and glass-ceramics produced by fly ash

Properties	Ash (75%) + SiO_2, MgO, TiO_2 [13]		Ash1 (100%) [11]		Ash2 (100%) [12]	Ash3 (100%) [10]		Ash (100%) Our work	
	Glass	Glass-ceramic	Glass	Glass-ceramic	Glass-ceramic	Glass	Glass-ceramic	Glass	Glass-ceramic
Density (g/cm^3)	2.76	2.78	2.80	2.89	2.95	2.95	3.02	3.1	3.33
Hardness (GPa)	5.2	6.7	5.5	7.9	5.9	5.1	6.6	6.3	8.3
Fracture toughness ($MPam^{1/2}$)	0.92	1.86	0.6	1.7	1.5	0.8	1.7	0.8	1.6
Bending strength (MPa)	78	127	90	240	–	–	–	90[15]	180[15]
TEC (10^{-6}/K)	9.54	8.95	5.9	6.5	9.0	9.7	8.7	9.8	10–11
Young's modulus(GPa)	–	–	93	124	134	90	115	105	140

(Table 3) . The small decrease of wear resistance above 850 °C was attributed to the crystallinity of glass-ceramics with a lower content of the residual glass (Fig. 6).

The thermal expansion coefficient (TEC) of glass-ceramics are in the range of 10.5–11.5×10^{-6}/K, which are slightly higher than that of glass (9.8×10^{-6}/K) in Fig. 11. With increasing time at high temperature (at 900, 950 °C) the TEC's decreased. Considering that the softening point (T_d, dilatometric point) of glass is 756 °C and the T_d of glass-ceramic was not detected until 800 °C, the glass-ceramic proved to have a high thermal stability.

Fig. 12 shows that the wear (erosion) resistance of glass-ceramics derived from the incinerator fly ash is related to the elastic constants, hardness, and fracture toughness. The higher erosion resistance is due to higher toughness, hardness and elastic constant. Thus, it is our main intention to produce a high wear resistance glass-ceramic for structural materials with the characteristics of high hardness and fracture toughness as suggested in Table 3. As shown in Fig. 12, it is a reasonable approach to set up the heat treatment conditions (time and temperature) towards the upper right-hand quadrant of the table for high E, K_{Ic}, Hv and low wear rate.

Other glass-ceramics derived from incinerator fly ash waste are compared with the current result (Table 4).

4. Conclusions

In the current process, water washing as a pre-treatment before melting the fly ash was used to remove the high Cl content and to reduce the melting temperature of the fly ash. The fly ash contained transition elements so enabling it to induce internal crystallization during the making of glass-ceramics without the addition of other oxides into the ash as nucleating agents. As a result, internal crystallization occurred under a single stage heat treatment stage and developed glass-ceramics that had good mechanical properties.

References

1. Scarinci, G., Brusatin, G., Barbieri, L., Corradi, A., Lancellotti, I., Colombo, P., Herglich, S. and Dall'Igna, R., Vitrification of industrial and natural wastes with production of glass fibres. *J. Eur. Ceram. Soc.*, 2000, **20**, 2485–2490.
2. Romero, M., Rincon, J. M., Rawlings, R. D. and Boccaccini, A. R., Use of vitrified urban incinerator waste as raw material for production of sintered glass-ceramics. *Mater. Res. Bull.*, 2001, **36**, 383–395.
3. Park, Y. Z. and Heo, J., Vitrification of fly ash from municipal solid waste incinerator. *J. Hazard. Mater.*, 2001, **2783**, 1–11.
4. Barbieri, L., Bonamartini, A. C. and Lancellotti, I., Alkaline and alkaline-earth silicate glasses and glass-ceramics from municipal and industrial wastes. *J. Eur. Ceram. Soc.*, 2000, **20**, 2477–2483.
5. Ferreira, C., Ribeiro, A. and Ottosen, L., Possible applications for municipal solid waste fly ash. *J. Hazard. Mater.*, 2002, **3920**, 1–16.
6. Boccacini, A. R., Schawohl, J., Kern, H., Schunck, B., Rincon, J. M. and Romero, M., Sintered glass ceramics from municipal incinerator fly ash. *Glass Technology*, 2000, **41**, 99–105.
7. Barbieri, L., Corradi, A. and Lancellotti, I., Bulk and sintered glass-ceramics by recycling municipal incinerator bottom ash. *J. Eur. Ceram. Soc.*, 2000, **20**, 1637–1643.
8. Karamanov, A., Pelino, M. and Hreglich, A., Sintered glass-ceramics from municipal solid waste-incinerator fly ashes-part I: the influence of the heating rate on the sinter-crystallisation. *J. Eur. Ceram. Soc.*, 2003, **23**, 827–832.
9. Leroy, C., Ferro, M. C., Monteiro, R. C. C. and Fernandes, M. H. V., Production of glass-ceramics from coal ashes. *J. Eur. Ceram. Soc.*, 2001, **21**, 195–202.
10. Romero, M., Rawlings, R. D. and Rincon, J. M., Crystal nucleation and growth in glasses from inorganic wastes from urban incineration. *J. Non-Cryst. Solids*, 2000, **271**, 106–118.
11. Boccaccini, A. R., Kopf, M. and Stumpfe, W., Glass-ceramics from filter dust from waste incinerators. *Ceram. Int.*, 1995, **21**, 231–235.
12. Romero, M., Rawlings, R. D. and Rincon, J.Ma., Development of a new glass ceramic by means of controlled vitrification and crystallization of inorganic wastes from urban incineration. *J. Eur. Ceram. Soc.*, 1999, **19**, 2049–2058.
13. Kim, J. M. and Kim, H. S., Crystallization phenomena and vetrification from a fly ash with large content of Cl. *Kor. J. Mater. Res.*, 2002, **12**, 924–929.
14. Kim, H. S., Rawlings, R. D. and Rogers, P. S., Quantitative determination of crystal and amorphous phase in glass-ceramics by X-ray diffraction analysis. *Br. Ceram. Trans. J.*, 1989, **88**, 21–25.
15. Kim, H. S., Kim, J. M., Oshikawa, T. and Ikeda, K., Production and properties of glass-ceramic from incinerator fly ash. *Mat. Sci. Forum*, 2003, **439**, 180–185.