PREPARATION OF GLASS-CERAMICS USING FLY ASH AS A RAW MATERIAL

Waraporn Emem and Shigeki Morimoto[*]

Received: Aug 16, 2005; Revised: Dec 8, 2005; Accepted: Dec 13, 2005

Abstract

The possibility of effective utilization of fly ash originated from a coal burning thermal power plant was investigated as one of the starting materials to synthesize wollastonite-based glass-ceramics. About 35% of fly ash was introduced into a batch as a raw material, and bubble-free and dark green glasses were obtained. The glass free from CaF_2 or spodumene showed surface crystallization; however, glass containing CaF_2 and/or spodumene exhibited bulk crystallization. The crystalline phases were wollastonite for glass with CaF_2, and wollastonite and spodumene for glass with CaF_2 and spodumene. The percent crystallinity was about 50%. The fracture strength of the glass-ceramics was about 220 MPa, which was two times higher than that of the original glass, and the surface hardness might be high, resulting in a scratch-free surface. However, thermal expansion coefficient did not change with crystallization, and hence the thermal shock resistance was presumed to be 2 times higher than that of original glass. Thus, fly ash supplied from a coal burning thermal power plant could be used for glass-ceramics as a raw material.

Keywords: Fly ash, glass, crystallization, glass-ceramics, wollastonite

Introduction

Fly ash (Wesche, 1991), a waste product of coal burning thermal power plants, contains many hazardous substances such as heavy metals and toxic organic compounds and thus is a major source for environmental pollution. Currently, in some countries, a small percentage of this waste has been utilized mainly for the manufacture of concrete, cement and brick products, the remainder being directly buried in fly ash ponds or landfills (Erol *et al.,* 2000; Barbieri, 2001; Erol *et al.,* 2003), which is an unsatisfactory solution both from the ecological and economical points of view. As a consequence, new economical and reliable means have to be found in order to safeguard the environment and provide a useful way for its disposal.

The chemical composition of fly ash is typical of the most common glassy ternary system of SiO_2-Al_2O_3-CaO with a significant amount of metal oxides which are able to act as nucleating agents. Recently, many researches and developments have been conducted in its

---

School of Ceramic Engineering, Institute of Engineering, Suranaree University of Technology 111 University Avenue, Muang District, Nakhon Ratchasima 30000, Thailand. Tel: 66-4422-4475, Fax: 66-4422-4220, E-mail: shigeki@sut.ac.th

[*] *Corresponding author*

Suranaree J. Sci. Technol. 13(2):137-142

utilization as a starting material for glass and glass-ceramics production.

In the present work, the possibility of effective utilization of fly ash originated from a coal burning thermal power plant was investigated as one of the starting materials to synthesize wollastonite-based glass-ceramics.

Materials and Methods

Fly Ash

Fly ash supplied from a Rayong, (Thailand) coal burning thermal power plant was used as a raw material. Its chemical composition was $41.62SiO_2{\cdot}23.11Al_2O_3{\cdot}1.59MgO{\cdot}\ 14.92CaO{\cdot}6.03Fe_2O_3{\cdot}1.15Na_2O{\cdot}1.59{\cdot}K_2O$ (wt%). The raw fly ash comprised some quantity of glassy phase and crystalline phases: α-Quartz (SiO_2), Anorthite ($CaAl_2Si_2O_8$), Ghelenite ($Ca_2Al_2SiO_7$), and the percent crystallinity was evaluated to be about 26%. The average particle size of as-received fly ash was about 33 μm.

Sample Preparation

The batch composition of glasses used is shown in Table 1. The base glass composition (G0) was $60.0SiO_2{\cdot}8.0Al_2O3{\cdot}4.5MgO{\cdot}\ 18.5CaO{\cdot}4.68Fe_2O_3{\cdot}6.0Na_2O{\cdot}1.06{\cdot}K_2O$ (wt%). CaF_2 was added as a nucleating agent and spodumene [$LiAl(SiO_3)_2$] was also added for the reduction of the thermal expansion coefficient by excess wt%.

The 150 g samples of each glass was prepared by mixing and melting the batch in air using a 100 cc Pt/Rh10 crucible in an electric furnace at 1,450°C for 2 h. The melt was poured onto an iron plate, then crushed and remelted under the same conditions. This refined melt was again poured onto an iron plate. Bubble-free and dark green glass was obtained.

A rod about 5 mm in diameter was freshly drawn and cut into piece, each about a 7 cm length. The samples were then annealed at just above T_g for 30 min and cooled to room temperature in the furnace. They were then heat-treated for nucleation and crystallization under various conditions. The densities of the glasses and glass-ceramics were measured by the He-gas substitution method using an Accupic 1,330 (Micromeritics).

DTA, TDA, XRD and SEM

A differential thermal analysis (DTA) and a thermo-dilatometric analysis (TDA) were routinely carried out using a Perkin-Elmer DTA-7 and a Netzsch DIL 402EP at the heating rates of 10°K/min and 5°K/min, respectively.

The crystalline phases and percent crystallinity (Ohlberg and Stricker, 1962) were determined by powder X-ray diffraction analysis (XRD, Bruker, AXS Model D5,005) using Cu-Kα radiation under the condition of 40KV-30 mA and 2°/min. The fracture surfaces of the glasses and glass-ceramics were etched in a 1% HF solution and observed by a scanning electron microscope (SEM, JEOL JSM6,400).

Fracture Strength

The fracture strengths of the glasses and glass-ceramics were measured using an Instron 5569 in accordance with ASTM-C-158. The three point bending method was employed and the surfaces of the specimens were abraded with #320 SiC abrasive papers before measurement, and the strengths of non-abraded specimens were also measured. The span length and loading rate were 50 mm and 10 mm/min, respectively.

Chemical Durability

Glass and glass-ceramics were ground and sieved to -18 mesh and +30 mesh. The density gram specimens were immersed in 100 cc. of 1N of HCl and 1N of NaOH at 90°C for 5 h, and then calculated the percent of weight loss.

Results and Discussion

Properties of Glasses

The properties of the glasses are summarized in Table 2. The glass transition temperature (T_g) and dilatometric softening point (Y_p) were decreased by adding CaF_2 and spodumene. The thermal expansion coefficient was also decreased slightly by adding CaF_2 and spodumene. The density was increased by adding CaF_2, but decreased markedly by adding spodumene. The acid durability was increased by adding CaF$_2$ and spodumene, but the alkaline durability showed a complicated feature independence on composition.

The fracture strengths of the glass were about 124 MPa for non-abraded specimens and 98 MPa for abraded specimens; these values were reasonable.

The crystallization exothermic peaks appeared at 970°C for G0 glass and 900°C for G3 and G5 glasses. It was clear that the addition of CaF$_2$ and spodumene reduced the crystallization temperature. All glasses were heat treated at 750°C for 10 h and further at 950°C for 5 h for crystallization, and the crystallization behavior was examined by the naked eye; G0 glass showed only surface crystallization, whilst the other glasses exhibited bulk crystallization. This indicated that CaF$_2$ and spodumene affected the crystallization.

Nucleation and Crystallization

Figure 1 shows SEM micrographs of glasses heat-treated at 750°C for 10 h. Though the structural change was not observed clearly, the small particles were formed in G0 and G3 glasses. However, the XRD detected no exact diffraction peak. On the contrary for G5 glass, the three dimensional interconnected structure was observed clearly, and this structure was due to the phase separation.

Figure 2 shows the XRD patterns of glass-ceramics heat-treated at 750°C for 10 h and followed by further heat treatment at 950°C for 5 h. Only wollastonite [CaSiO$_3$] crystal was detected in G0 and G3 glass-ceramics; however, wollastonite and spodumene [LiAl(SiO$_3$)$_2$] crystals were also observed in G5 glass-ceramics. Hence, the crystallization behaviors of G3 and G5 glasses were investigated in detail.

Table 1. Batch compositions of glasses studied

Glass No.	Fly ash	Silica sand	Folomite	Linestone	Soda ash	CaF$_2$*	Spodumene*
G0	35	45.5	15	14	8	0	0
G3	35	45.5	15	14	8	3	0
G5	35	45.5	15	14	8	3	20

* Excess wt%

** Base glass; 100 g of glass (G0)

Table 2. Properties of glasses studied

No.	Thermal properties			DTA	Density	Chemical durability		Fracture
	Tg (°C)	Yp (°C)	α* (x10^{-7}/K)	T$_{peak}$ (°C)	(g/cm^3)	Acid Δ(%)	Alkali Δ(%)	strength Mpa**
G0	655	702	95	970	2.6594	-1.45	0.96	-
G3	630	691	85	900	2.6917	-1.21	-0.13	124.5 ± 48.5 98.5 ± 40.3
G5	615	690	80	900	2.6049	-0.91	-0.87	-

* 100 - 300°C,

** upper: non-abraded, lower: abraded (#320)

Figure 3 shows the relation between the percent crystallinity and the heating temperature. The percent crystallinity of G3 glass increased with an increase in temperature, reached the maximum at about 1,000°C and then decreased again. On the other hand, in G5 glass, it decreased monotonically with an increase in temperature. This indicated that the maximum crystallization temperature might be below 900°C.

Generally, small amounts of additives have been widely used in glass-ceramics processing. These additives are called nucleating agents, which result in fine-grained glass-ceramic articles without deformation of the original glass. Their role is believed to be: 1) promotion of phase separation, and 2) provision of the interface for a heterogeneous nucleating site. It is well known that F^- acts as an optimum nucleating agent for the Li_2O-Al_2O_3-SiO_2 and Na_2O-CaO-MgO-SiO_2 systems of glass. In these glasses, F^- promotes phase separation of parent glasses, and the composition of one phase is similar to certain crystals, and such crystals start to precipitate in that phase.

Although an apparent phase separation was not observed in CaF_2 containing glass (G3), isolated droplet-like particles could be detected by SEM observation. A DTA curves also showed a remarkable decrease in the crystallization

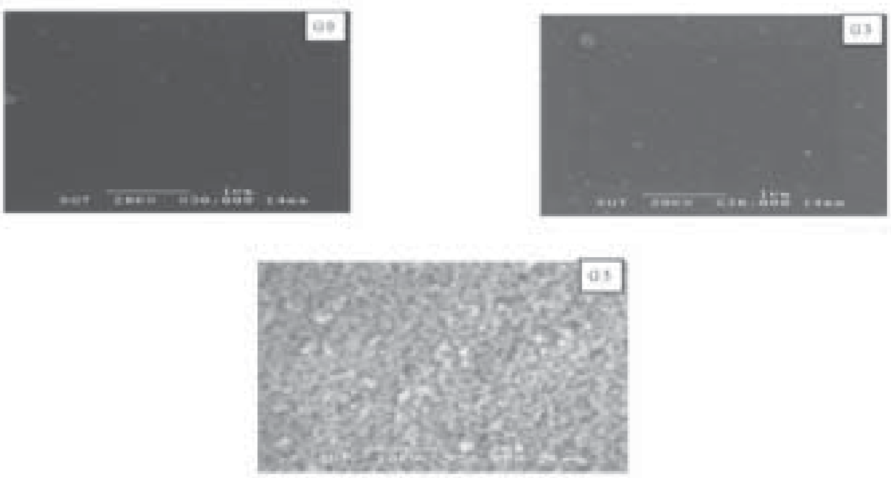

Figure 1. SEM micrographs of glasses treated at 750°C for 10 h

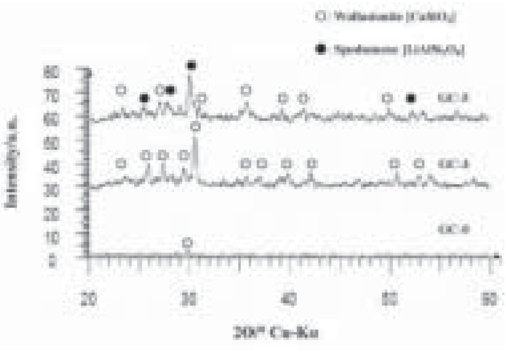

Figure 2. XRD patterns of glass-ceramics heat treated at 750°C for10 h and 950°C for 5 h

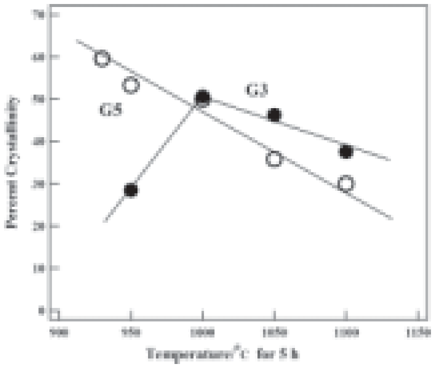

Figure 3. Relation between percent crystallinity and heating temperature for G3 and G5 glass. 1st heat treatment: 750°C for 10 h

temperature. Furthermore the three-dimensional interconnected structure due to phase separation was observed clearly in G5 glass. It was considered that CaF_2 provided a heterogeneous nucleating site in G3 by the precipitation of small particles, and also promoted phase separation in G5 glass, respectively. Thus these observations suggested that CaF_2 affect the crystallization process and acted as a nucleating agent, and provided fine-grained glass-ceramic.

The properties of glass-ceramics are summarized in Table 3. The thermal expansion coefficient of glass-ceramics did not change. The fracture strength of glass-ceramics increased by about two times compared with that of glass, and the abraded strength did not decrease so much. This suggested that the surface hardness increase with the crystallization.

Figure 4 shows the microstructure of these glass-ceramics. The rod-like crystal was observed clearly in G3 and G5 glass-ceramics, and it grew from all directions. The aspect ratio of this crystal might be 5 - 10, and this crystal seemed to be wollastonite.

In this study, the crystalline phases precipitated were wollastonite in G3 glass-ceramics, and wollastonite and spodumene in G5 glass-ceramics. Their percent crystallinity was about 50%. Spodumene has a low thermal expansion coefficient; however, the thermal expansion coefficient of glass-ceramics containing spodumene (G5) was not low. It was similar to that of G3 glass-ceramics (without spodumene). If all spodumene would precipitate in G5 glass-ceramics, its amount would have been about 20%, which was not enough to reduce the thermal expansion coefficient. Therefore, the thermal shock resistance of these glass-ceramics strongly depended on the fracture strength. The fracture strength of these glass-ceramics was about 220 MPa, which was two times higher than that of glass. Thus, the thermal shock resistance should be about two times higher than that of glass (Kingery *et al*., 1991), but the surface hardness might be much higher than that of glass, and hence it could be expected to be a scratch-free surface.

Conclusion

The possibility of effective utilization of fly ash originated from a coal burning thermal power plant was investigated as one of the starting materials to synthesize wollastonite-based glass-ceramics. About 35% of fly ash was introduced into a batch as a raw material, and bubble-free and dark green glasses were obtained. The glass free from CaF_2 or spodumene showed surface crystallization; however, glass containing CaF_2 and/or spodumene exhibited bulk crystallization. The crystalline phases were wollastonite for glass

Table 3. Properties of glass-ceramics (750°C for 10 h, 950°C for 5 h) studied

No.	Crystalline[*] phases	α[**] (10^{-7}/K)	Density (g/cm^3)	Chemical durability		Fracture Strength Mpa[***]	Remarks
				Acid Δ(%)	Alkali Δ(%)		
G0	W	90	2.710	-1.29	-0.54	135.1 ± 58.6 134.7 ± 51.4	Surface crystallization
G3	W	85	2.718	-1.51	-0.53	206.2 ± 58.6 193.6 ± 37.0	Bulk crystallization
G5	W, Sp	85	2.657	-1.67	-0.32	230.4 ± 39.6 211.4 ± 46.7	Bulk crystallization

[*] W = Wollastonite, Sp = Spodynene

[**] 100 - 300°C

[***] upper: non-abraded, lower: abraded (#320)

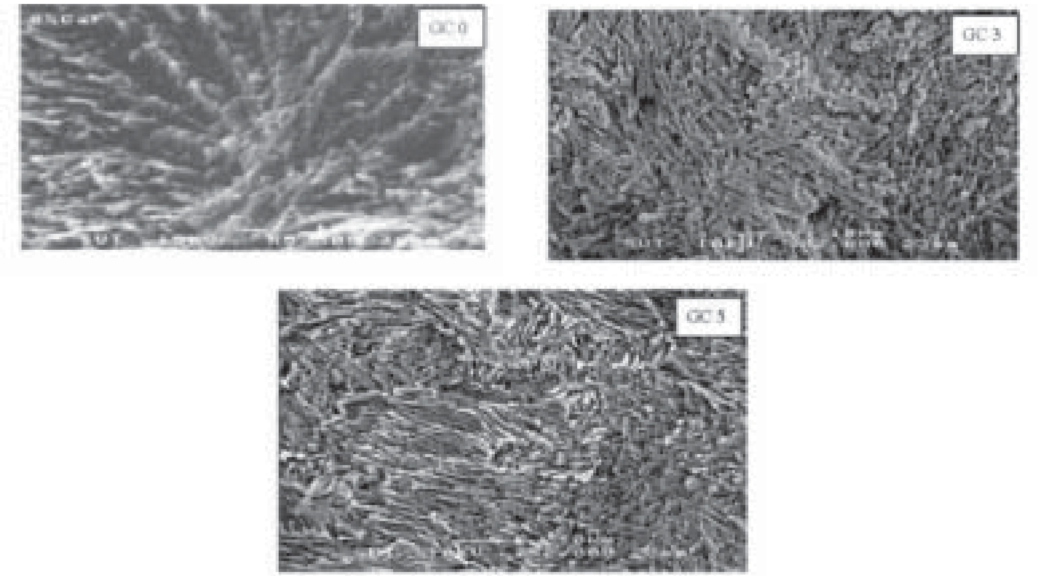

Figure 4. SEM micrographs of glass - ceramics heat treated at 750°C for 10 h and 950°C for 5 h

with CaF_2, and wollastonite and spodumene for glass with CaF_2 and spodumene. The percent crystallinity was about 50%.

The fracture strength of the glass-ceramics was about 220 MPa, which was two times higher than that of the glasses, and the surface hardness might be high, resulting in a scratch-free surface. However, the thermal expansion coefficient did not change with the crystallization, and hence the thermal shock resistance was expected to be 2 times higher than that of glass. Thus, fly ash supplied from a coal burning thermal power plant could be used for glass industry as a raw material.

Acknowledgement

This study was supported by Special Coordination Funds of Suranaree University of Technology, to which the authors are indebted.

References

Barbieri, L., Lancellotti, I., Manfredini, T., Pellacani, G.C.,Rincon, J.M., and Romero, M. (2001). Nucleation and crystallization of new glasses from fly ash originating from thermal power plant. J. Am. Ceram. Soc., 84:1,851-1,858.

Erol, M., Demirler, U., Kucukbayrak, S., Ersoy-Mericboyu, A., and Ovecoglu, M.L. (2003). Characterization investigations of glass-ceramics developed from Seyitomer thermal power plant fly ash. J. Euro. Ceram. Soc., 23:757-763.

Erol, M., Genc, A., Ovecoglu, M.L., Yucelen, E., Kucukbayrak, S., and Taptik, Y. (2000). Characterization of a glass-ceramic produced from thermal power plant fly ashes. J. Euro. Ceram. Soc., 20:2,209-2,214.

Kingery, W.D., Bowen, H.K., and Uhlmann, D.R. (1991). Introduction to Ceramics. 2nd ed. John Wiley & Sons, NY, p. 818-823.

Ohlberg, S.M., and Strickler, D.W. (1962). Determination of percent crystallinity of partly devitrified glass by X-ray diffraction. J. Am. Ceram. Soc., 45:170-171.

Wesche, K. (1991). Fly Ash in Concrete Properties and Performance. E&FN Spon, London and Chapman & Hall, NY.