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Conversion to glass-ceramics from glasses made by MSW incinerator fly ash for recycling

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Abstract

Glasses were made using fly ash from municipal solid waste (MSW) incinerators with the addition of SiO_2, MgO and TiO_2. The glasses were then converted to glass-ceramics for further recycling to construction materials. The optimum heat-treatment schedule for the ceramitization of glasses was 720 °C for 90 min for nucleation and 870 °C for 10 h for crystal growth. Diopside ($CaMgSi_2O_6$) was formed as a major crystalline phase. The glass-ceramics showed good mechanical properties with a hardness of 6,730 MPa, fracture toughness of 1.86 Mpa $m^{1/2}$ and bending strength of 127 MPa. Glasses and glass-ceramics with a composition of $20SiO_2$–5MgO–75fly ash–$2TiO_2$ (all given in wt.%) showed an excellent resistance against leaching of heavy metal ions in water. The amount of heavy metal ions leached after 18 h at 23 °C was well below regulation with Cd^{2+} <0.04 ppm, Cr^{3+} <0.004 ppm, Cu^{2+} <0.03 ppm and Pb^{2+} <0.15 ppm, respectively.

Keywords: D. Glasses; D. Glass-ceramics; Waste disposal; Incineration; Fly ash; Vitrification

1. Introduction

Incineration of municipal solid waste (MSW) has advantages over landfilling in terms of volume reduction and sanitary treatment. On the other hand, incineration also has disadvantages such as low economic efficiency due to high energy consumption and generation of hazardous fly ash. Despite these disadvantages, incineration has been considered as a new alternative of MSW treatment in many countries. At present, hazardous fly ash is stabilized by incorporating it into cement-based materials [1]. However cement-based techniques pose problems inside landfills due to weak chemical and physical stability. Particularly, in cases where fly ash with high concentrations of alkali chlorides, it is difficult to apply the cement-based techniques since the alkali chlorides inhibit hydration of cement so that the cement matrix cannot be fully solidified or stabilized. Therefore, it is necessary to search for new techniques for treatment of fly ash. Vitrification is one of the most promising solutions among the various available technologies. Furthermore, toxic organic compounds such as dioxins can be destroyed during the vitrification process.

There are several reports on the vitrification of solid waste [2–4]. It was demonstrated that the addition of bottom ash and glass wastes into fly ash facilitated the formation of glasses upon melting and quenching. However, fly ash used for these studies contains more than 35 wt.% of silica and therefore, vitrification was not difficult to achieve. On the other hand, fly ash from MSW incinerators in Korea contains a significant amount of akali chlorides with <10 wt.% of silica, and as a result, vitrification is not inconsequential. Our previous paper [5] reported the successful vitrification of such fly ash (Table 1) with the addition of 5 wt.% SiO_2. Glasses showed high resistance against the leaching of heavy metal ions in water. The amount of Cd^{2+}, Cr^{3+}, Cu^{2+} and Pb^{2+} leached following the toxicity characteristic leaching procedure (TCLP) was well below international regulations.

It can provide added economical benefits if these glasses can be converted to useful materials and be

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Table 1
Composition of as-recieved fly ash [5]

	Component											
	Na	Mg	Si	S	Al	K	Ca	Cl	P	Zn	Ti	Total
Major compositions												
Conc. (wt.%)	23.1	2.0	5.1	5.7	2.6	13.6	9.8	29.0	1.7	3.0	0.8	96.8
			Cd		Cr		Cu			Mn		Pb
Heavy metals												
Conc. (ppm)			629		332		1653			680		758

recycled. For recycling, it is useful to convert the glasses to glass-ceramics which generally provide an improvement in mechanical and thermal properties. There was a report [6] on the properties of glass-ceramics made of fly ash. However, this work again dealt with fly ash which is relatively easy to vitrify because of its high silica concentration (>35 wt.%) at a low alkaline chloride content (5–15 wt.%). In addition, the previous works did not consider the toxicity of glass-ceramics and the possibility of recycling of glass-ceramics.

This paper reports the conversion of glass to glass-ceramics and the characteristics of glass-ceramics thus prepared. The chemical stability was evaluated to examine the environmental influence. In addition, recycling possibilities of these glass-ceramics were proposed based on the properties examined.

2. Materials and methods

2.1. Materials

Glasses were prepared from fly ash from a stoker-type incinerator at the Da-Dae MSW disposal site (Busan, Korea). Detailed information on the characteristics of fly ash and the vitrification process can be found in our previous paper [5]. SiO_2 was added to facilitate the formation of glasses. In addition, 5 wt.% of MgO was added to the total starting powders to obtain the target crystalline phase, diopside ($CaMgSi_2O_6$). TiO_2 (2 wt.%) was also added as a nucleating agent following the conventional glass-ceramic processing method [7].

2.2. Crystallization

For the conversion of glasses to glass-ceramics, temperature and duration of heat treatment for the nucleation and crystal growth must be determined. For the determination of the nucleation temperature, a differential thermal analyzer (DTA) was used at a heating rate of 10 °C/min. First, glass samples were heated in the DTA apparatus to different nucleation temperatures in the range 700–750 °C and held for 30 min. This temperature range was selected since the optimum nucleation temperature usually lies at 50–100 °C above the glass transition temperature (Tg), which is 665 °C for glass used in the present work [7]. After nucleation at each temperature, specimens were heated again to 870 °C inside a DTA to complete the crystallization. A plot between the height of the exothermic crystallization peak (δT_p) and the nucleation temperature was obtained. The temperature where δT_p shows the maximum was selected as an optimum nucleation temperature. A similar method was used to determine the optimum nucleation time except that the glass powder was held at the specified optimum nucleation temperature for a different duration, generally 30–150 min.

The optimum crystallization temperature could not be determined by the general method because the difference between crystallization temperature (Tx) and softening point (Tsp) was only 25 °C. Therefore, an optimum crystal growth temperature of 870 °C was selected as the temperature immediately below the softening point (Tsp). The optimum duration of heat-treatment for crystallization was determined from the maximum in the plot of the intensity of the highest XRD peak (I_n) versus the total intensity of peaks in the XRD patterns (I_{total}) for different durations of crystallization, 1–16 h.

2.3. Properties

Several techniques were used to assess the mechanical and physical properties of the glass-ceramics. The density was measured by the Archimedes method using water as a medium. Hardness and fracture toughness were analyzed by the Vickers indentation method [8]. Vickers hardness was measured with a load of 200 g and loading time of 10 s. The fracture toughness values, K_{IC}, were calculated using the equation suggested by Evans and Charles [9]. Loads of 1 kg with loading times of 10 s were used. To determine rupture modulus, four-point bending strength was measured with spans of 20 and 40 mm at a cross-head speed of 100 μm/min, as designated by the American Society of Testing Materials (ASTM) [10]. For the measurement of mechanical properties, the specimens were polished with No. 2000-sand paper and 1 micron-diamond polishing paste.

Table 2
Actual composition of parent glass

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

Thermal expansion coefficients (α) were measured by a thermomechanical analyzer (TMA) for the temperature range of room temperature to 600 °C. Glass transition (Tg) and crystallization (Tx) temperatures were determined from differential scanning calorimetry (DSC) thermograms. Thermal analyses were performed at a heating rate of 10 °C/min in air atmosphere. Leaching of heavy metal ions from glass-ceramics in water was estimated by the toxicity characteristic leaching procedure (TCLP) method of the US Environmental Protection Agency (EPA). Samples for the leaching tests were ground and sieved to a particle size <50 μm, similar to the size of fly ash, so that a direct comparison becomes possible. Powders were immersed into acidic water (pH 4.93) at 22 ± 3 °C for 18 ± 2 h. For analysis of the heavy metal concentration in the leached solution, inductively coupled plasma–atomic emission spectroscopy (ICP–AES) was used.

3. Results

3.1. Vitrification

In this research, 20 wt.% SiO_2 and 5 wt.% MgO were added into fly ash in consideration of glass formation and the crystalline phase, respectively. Specifically, addition of 5 wt.% MgO facilitates the formation of diopside ($CaMgSi_2O_6$) during the crystallization process. Diopside was selected as the target crystalline phase because of its excellent thermal and mechanical properties [11]. In addition, 2wt.% TiO_2 was added as a nucleating agent. Therefore, glasses prepared were made from a mixture of 75 wt.% fly ash–20wt.% SiO_2–5wt.% MgO–2wt.% TiO_2. Table 2 shows the actual composition of glass analyzed by X-ray fluorescence (XRF) spectroscopy.

3.2. Conversion to glass-ceramics

The optimum nucleation conditions were determined as explained previously. The plot of crystallization peak height against nucleation temperatures (Fig. 1) showed that the optimum nucleation temperature is 720 °C. Fig. 2 is a plot of the crystallization peak height versus nucleation time at 720 °C. The plot demonstrated that the curve reached a plateau after heat treatment for 90 min. Therefore, the optimum nucleation time was approximately 90 min.

A crystal growth temperature of 870 °C was determined between the crystallization temperature (Tx: 850 °C) and softening point (Tsp:875 °C). To investigate the optimum duration of crystal growth, heat treatments were carried out at 870 °C from 1 to 16 h. Fig. 3 shows the X-ray diffractogram after each heat treatment. It was clear that diopside ($CaMgSi_2O_6$) was formed by heat treatment in accordance with expectations. The plot of I_n/I_{total} versus crystal growth time demonstrated that the optimum crystal growth time appeared to be 10 h (Fig. 4).

The morphology of diopside crystal was investigated for specimens prepared by nucleating at 720 °C (1.5 h) and crystallizing at 870 °C (10 h) (Fig. 5). Chemical analysis of the packed columnar structure by energy dispersive X-ray spectroscopy (EDS) also suggested that the crystalline phase was diopside (Table 3).

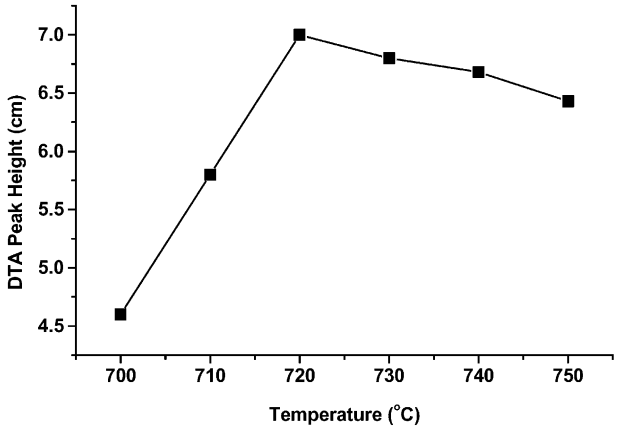

Fig. 1. Determination of nucleation temperature for $20SiO_2$–5MgO–75fly ash–$2TiO_2$ glass.

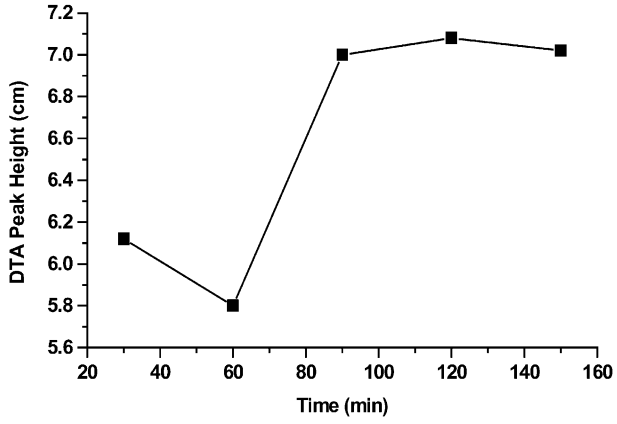

Fig. 2. Determination of nucleation time for $20SiO_2$–5MgO–75fly ash–$2TiO_2$ glass.

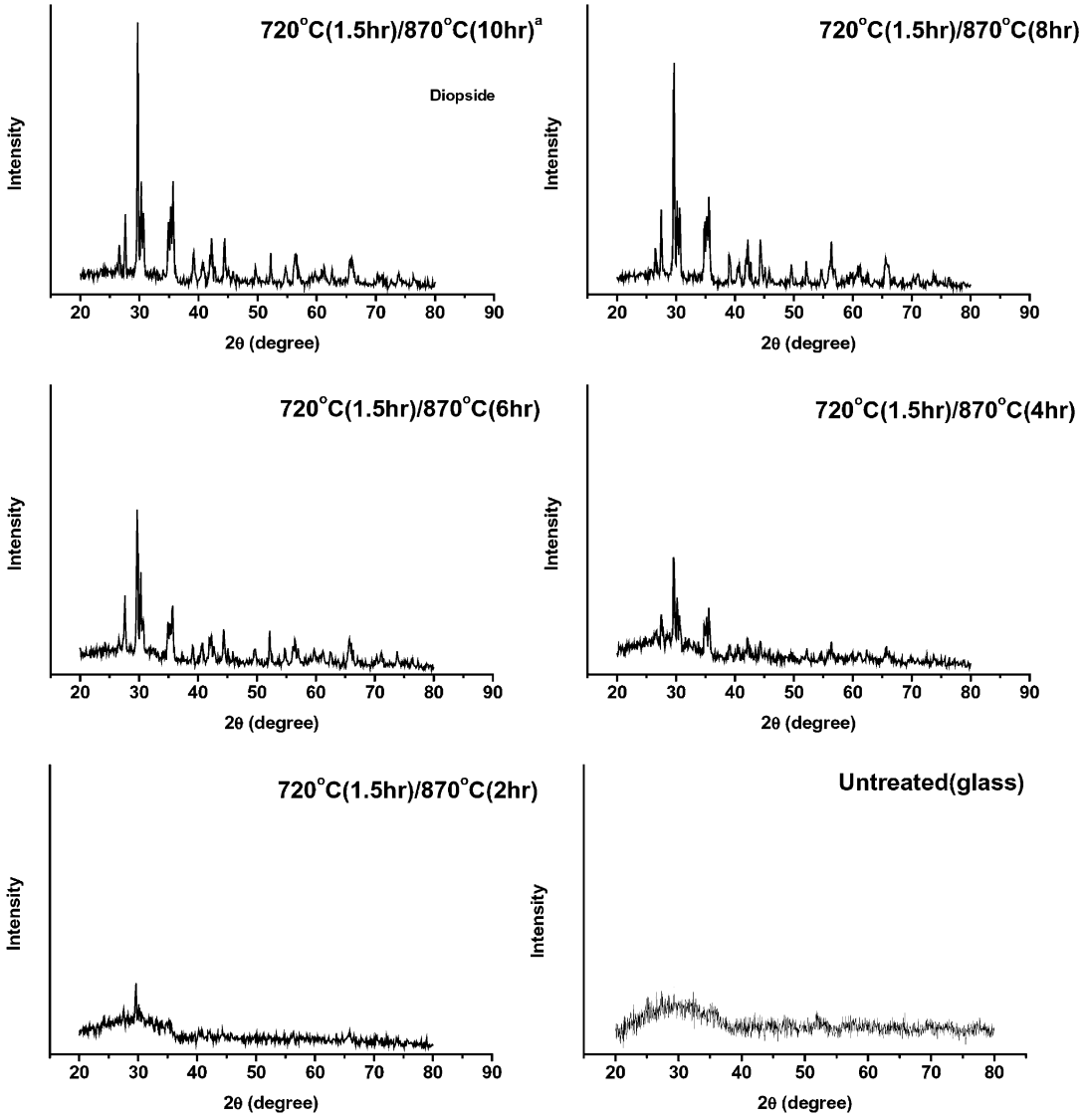

Fig. 3. X-ray diffractogram of glass-ceramics after heat treatment at 870 °C during various times.

3.3. Glass and glass-ceramics properties

Table 4 compares properties of glass and glass-ceramics prepared in this study. The properties of glass-ceramic are better than these of glass. In particular, mechanical properties such as hardness, toughness, and bending strength improved considerably upon crystallization.

4. Discussion

4.1. Crystallization

The activation energy for crystallization (E) can be calculated from the relationship between the temperature of the maximum in the exothermic peak (T_p) and the heating rate (ϕ) using the equation;

$$\ln \frac{\phi}{T_p{}^2} = -\frac{E}{RT_p} + C \tag{1}$$

where, C is a constant and R is the gas constant. In Fig. 6, a linear relationship was obtained between $\ln(\phi/T_p^2)$ and $1/T_p$ in accordance with the Kissinger equation [12]. The value of E, determined from the slope of the line in this plot, was 499 kJ mol^{-1}.

From the value of the activation energy, the Avrami exponent (n) was calculated by using the equation:

$$n = \frac{2.5}{\Delta T} \times \frac{RT_p^2}{E} \tag{2}$$

where, ΔT is the width of the exotherm at half maximum [13]. The value of n for this glass is 1.09 which indicates that the formation of diopside crystals was

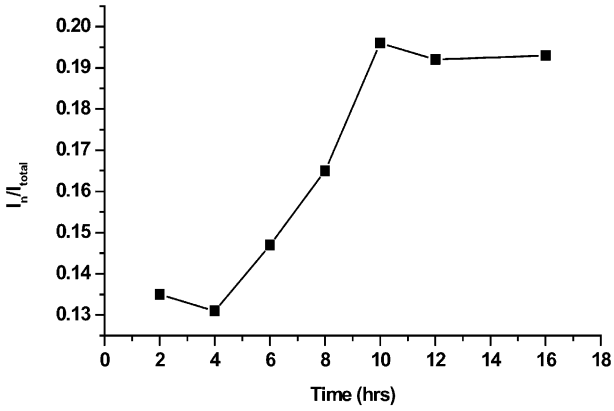

Fig. 4. Determination of optimum duration of crystal growth.

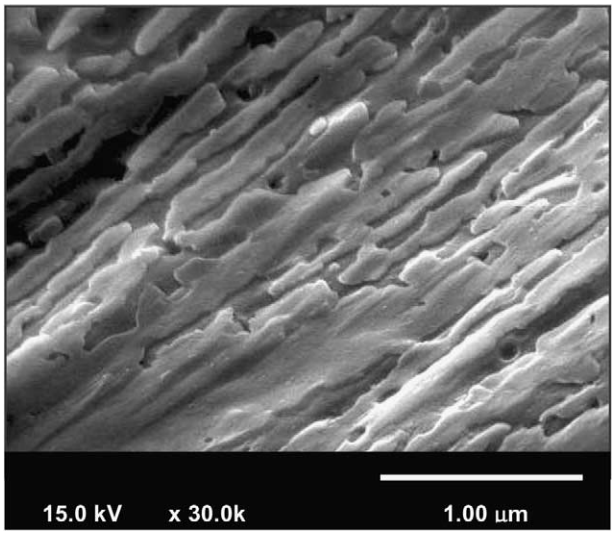

Fig. 5. Scanning electron micrograph of glass-ceramics. Heat treatment schedules were 1.5 h/720 °C for nucleation and 10 h/870 °C for crystal growth.

Table 3
EDS analysis of the crystalline phase

Element	O	Mg	Si	Ca	Ti
At.%	44.2	12.31	29.01	10.71	2.70

Table 4
Properties of glasses and glass-ceramics (nominal composition of the starting mixture was $20SiO_2$–5MgO–75Fly ash–$2TiO_2$ in wt.%)

	Glass	Glass-ceramic
Density (g/cm^3)	2.76	2.78
Hardness (MPa)	5235	6730
Fracture toughness (MPa m$^{1/2}$)	0.92	1.86
Bending strength (MPa)	78	127
Thermal expansion coefficient (α) (K^{-1})	95.4×10^{-7}	89.5×10^{-7}

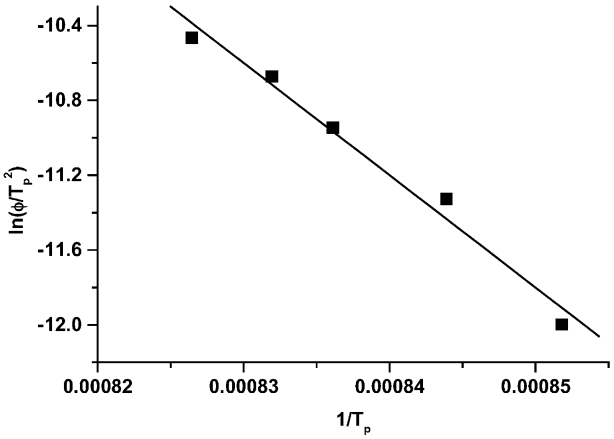

Fig. 6. Calculation of activation energy (E) for crystallization from Kissinger's equation [13].

from the heterogeneous crystallization on the surface [14].

4.2. Recycling

Fly ash from MSW incinerators contains high concentrations of heavy metals and dioxins. Dioxins can be destroyed by a high-temperature melting process, but heavy metal ions still remain in the vitrified materials. Therefore, the chemical stability of the glasses and glass-ceramics must be evaluated to access the environmental safety of these recycled substances.

The American EPA's toxicity characteristic leaching procedure (TCLP) was used to examine the chemical stability of these materials in terms of leaching of heavy metal ions (Table 5). The amount of heavy metal ions leached from the as-received fly ash was well above the regulatory standard [15]. However, when fly ash was converted to glasses and glass-ceramics, the degree of leaching decreased substantially to below the regulation amount. In particular, the amount of Cd^{2+} leached decreased from 25 ppm for as-received fly ash to a negligible amount after conversion to glasses and glass-ceramics. All other heavy metal ions were also incorporated inside these materials which proves that these new recycled materials are environmentally sustainable.

In addition, mechanical properties must be considered for recycling. The Vickers microhardness of glass was 5235 MPa and increased up to 6730 MPa after the conversion to glass-ceramics. These microhardness values are high in comparison to window glass (4100 MPa) [16] or granite (5500 MPa) [17]. Fracture toughnesses of glass and glass-ceramics were 0.92 and 1.86 MPa m$^{1/2}$, respectively, which are comparable to those of general silicate glasses (0.4∼0.8 MPa m$^{1/2}$) [9, 18] and canasite glass-ceramics (0.9∼1.6 MPa m$^{1/2}$) [18]. In terms of bending strength, values of 78 MPa for glass and 127 MPa for glass-ceramic were obtained, which are again similar to those for silicate glass (60–70 MPa) [18]

Table 5
Results of leaching tests by the toxicity characteristic leaching procedure (TCLP)—ppm in wt

Heavy metals	Fly ash (as received)	Glass	Glass-ceramic	Korean regulatory standard (leachate)
Cd	25.490	N.D.[a]	0.035	0.1
Cr	0.030	N.D.[a]	0.004	2.0
Cu	24.020	0.009	0.030	3.0
Mn	1.630	0.129	0.040	10.0
Pb	9.740	0.068	0.151	1.0
Zn	362.100	2.150	0.847	5.0

[a] Not detected (detection limit: Cd and Cr 0.003 ppm, Pb 0.009).

and granite (130–150 MPa) [17]. These glass and glass-ceramics have good chemical and mechanical properties and can therefore be applied for various facets of the construction materials.

5. Conclusions

Glasses and glass-ceramics were prepared using fly ash from the MSW incinerator with the addition of SiO_2, MgO and TiO_2. Glass-ceramic was prepared most effectively by nucleating at 720 °C for 90 min and by crystallizing at 870 °C for 10 h. The glass-ceramics showed good mechanical properties with a hardness of 6730 MPa, fracture toughness of 1.86 MPa $m^{1/2}$, and bending strength of 127 MPa. Diopside ($CaMgSi_2O_6$) was formed as a main crystalline phase. The chemical stability estimated by the toxicity characteristic leaching procedure (TCLP) proved that heavy metal ions formed chemically stable bonds with glasses and glass-ceramics structures.

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