Production of glass–ceramics from fly ash using arc plasma

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Abstract

Glass–ceramics have been produced from municipal solid waste incinerator (MSWI) fly ash by melting the ash in dc arc plasma reactor and subsequent heat treatment at various temperatures for 2 h. The properties of glass–ceramics have been investigated by differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Microstructure, mechanical properties and chemical resistance of the samples were also determined. Wollastonite and anorthite were found to be the main crystalline phases. Lime addition to fly ash brings forth to gehlenite as a third phase to develop.
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1. Introduction

Municipal solid waste incinerator (MSWI) fly ashes are of actual concern in developed countries. Heavy metals and dioxins condensed on fly ashes during incineration pose serious threat to the environment. These wastes customarily disposed of to landfill in Hungary. To prevent leaching of heavy metals into surrounding groundwater and to comply with strict environmental regulations preliminary construction work on landfill sites that includes the building a thick waterproof concrete basin is required prior to disposal. It increases the cost of landfilling considerably. In order to find a safer solution that stand the test of time the attention has turned to alternative methods. Besides safety considerations fly ashes have lots of utilization fields,[1,2] thereby costs of treatments can be reduced. Among the several ideas arisen for the utilization of fly ashes, vitrification seems to be the most promising[3] due to safety reasons. In the vitrified ash heavy metals are encapsulated in the silicate matrix and leaching becomes hindered.[4] By virtue of mechanical properties vitrified ash may be suitable, e.g. for road base aggregates. In addition, fly ashes belong to the $CaO–SiO_2–Al_2O_3$ system by composition, thereby they can be considered as reliable ceramic raw materials. Vitrified ashes followed by appropriate heat treatment can result in vitroceramics, a product of added value. Degree of

crystallization, proportion and type of crystalline phases can be controlled by adequate heat treatment and suitable additives. Considering that MSWI fly ashes may substantially differ in the chemical composition,[5–9] the suitable vitrification and heat treatment technology should be determined for a particular fly ash specifically.

In this work we carried out vitrification of MSWI fly ashes without additives and with lime additives using dc arc plasma device. Development of crystalline phases after subsequent heat treatment was also investigated. Arc plasmas are reliable device to rapidly melt inorganic wastes due to the extremely high temperatures prevailing inside the plasma combined with effective heat transfer. This technology is extensively used to vitrification of metallurgical wastes.[10–12] Besides, dioxins and other organic contaminants are destroyed owing to the high temperature.

During the trials we followed the conventional technological route, in which vitrified specimens were subjected to heat treatment in bulk as received after vitrification. We compared the products in terms of microstructure, the type of developed phases, the mechanical properties and chemical durability.

2. Experimental

The incinerated fly ash used in this investigation was obtained from the municipal waste incineration plant in Budapest. Incinerator fly ash has wide particle size distribution ranging from 1 to 120 μm with mean particle size of 48.8 μm. The fly ash

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was analyzed by ICP-AES method and had the chemical composition as follows (in wt.%): 56.7% SiO_2, 15.3% CaO, 7.5% Al_2O_3, 1.5% MgO, 1.6% Fe_2O_3, 1.5% Na_2O, 1.8% K_2O, 0.8% Ti_2O, 0.3% ZnO, 6.18% SO_3 and less than a total 0.4% of other metal oxides.

In the tests weighted portion of the fly ash was melted in a lab-scale dc arc plasma furnace under neutral conditions. The temperature of molten bath reached 1600 °C. In the interest of good homogeneity, furnace was slightly tilted and rotated during melting. The melt was cooled down in ambient atmosphere then was annealed at 600 °C for 2 h followed by slow cooling to room temperature to remove residual stresses. Crystallization heat treatments on bulky samples were performed in a chamber furnace at temperatures of 850, 900, 950, 1000 and 1050 °C for 2 h then samples were cooled at a rate of 5 °C/min.

In order to reduce the viscosity of the melt and to facilitate the crystallization at lower temperatures, in some tests lime powder was mixed into the fly ash in a 10:2 ash to lime ratio. Test performed using this feedstock is denoted as m-ash hereinafter.

Differential thermal analysis (DTA) were carried out to evaluate the crystallization properties of as-received glass samples and to determine the characteristic glass transition temperature and peak crystallization temperature using a Setaram DTA-DSC Analyzer. Measurements were performed by heating some 50 mg preliminarily ground glass powders in a Pt-crucible up to a temperature of 1100 °C at a heating rate of 10 °C/min. Al_2O_3 was used as reference material.

Microstructure of vitrified and crystallized samples was investigated by XRD technique and scanning electron microscope. X-ray diffraction measurements were carried out by a Philips Xpert XRD apparatus using Cu K_α radiations generated at 40 kV and 30 mA.

SEM investigations were performed by a Philips XL30 ESEM apparatus linked with an energy dispersive attachment (EDX). For SEM investigations, specimens were polished followed by etching in HF solution (5%) for 1.5 min and in HCl solution (5%) for additional 5 min.

During the Vickers microhardness tests a constant load of 400 g were used to indent the surface. Mean values were calculated from seven measurements.

Chemical resistance of vitrified ash and heat-treated glass–ceramic samples were tested by measuring the weight loss after etching in acidic and alkali solutions. Specimens grounded below 0.5–1 mm were placed in HCl (20 wt.%) and NaOH (20 wt.%) solutions and boiled at 95 °C for 20 min at elevated pressure.

3. Results and discussion

DTA thermograms of the vitrified materials show similar run (Fig. 1). Endothermic peaks refer to glass transition temperature range. Lowest peak value of ash samples is twice of the m-ash samples that probably associated with the much stronger softening of ash samples experienced in heat treatments at the same temperatures. Peak crystallization temperature of m-ash samples ($T_{cr} = 918$ °C) indicated by the exothermic peak is much lower than that of the ash samples ($T_{cr} = 987$ °C). The second
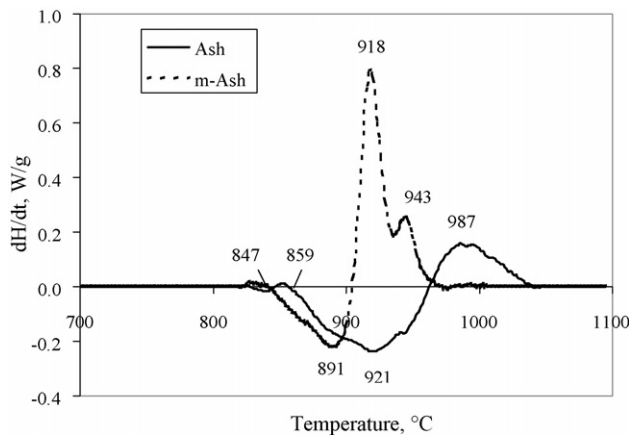

Fig. 1. DTA plots of ash and m-ash glasses.

exothermic peak on the DTA line of m-ash samples suggests a second crystallization process.

3.1. Microstructure of glass-ceramics

Fig. 2 represents the XRD peaks of vitrified ash samples after heat treatment of 2 h at different temperatures. The relatively short heat treatment period was insufficient for the samples to be crystallized at temperatures of 850 and 900 °C that actually are well below the peak crystallization temperature of 987 °C and the material remained virtually glassy. Even prolonged heat treatment period of 5 h resulted in a weakly crystallized structure. Raising the temperature up to 1000 °C led to the development of crystallites. Diffraction peaks became more intensive at still higher temperatures, such as 1050 °C presumably due to the greater degree of crystallization. This is in sharp contrast with the findings of Cheng et al.[13,14] who conducted similar heat treatment procedure, however, using a finely ground and compacted glass powders. This suggests the significance of fine particles on the rate of crystallization. The main crystal phases comprise wollastonite ($CaSiO_3$) in a greatest amount and anorthite ($CaAl_2Si_2O_8$) as it was expected from the chemical composition considering the well-known $CaO–SiO_2–Al_2O_3$ ternary diagram.

Lime addition to the fly ash has substantial effect on the crystallization. The diffraction peaks after heat treatment are
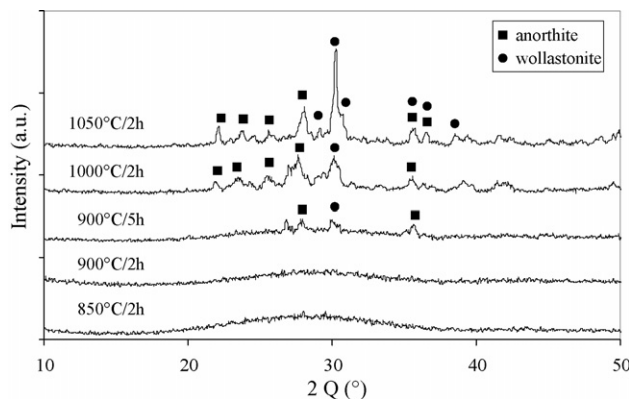

Fig. 2. XRD patterns of ash samples after heat treatment at various temperatures.
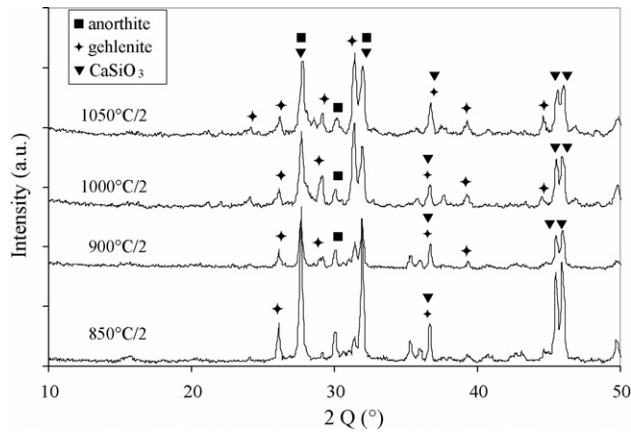
Fig. 3. XRD patterns of m-ash samples after heat treatment at various temperatures.

presented in Fig. 3. In contrast to vitrified ash samples, crystallization occurred even at the lowest heat treatment temperature of 850 °C that is below its peak crystallization temperature of 917 °C. With increased lime content the composition theoretically shifted to the eutectic point of the wollastonite, anorthite and gehlenite region in the CaO–SiO_2–Al_2O_3 ternary approaching the area of acidic blast furnace slag. Sure enough $CaSiO_3$, anorthite and gehlenite ($Ca_2Al_2SiO_7$) make up the main crystalline phases on the XDR patterns. On increasing the temperature, not any new crystal could be observed, but diffraction peaks became more intensive. No diopside can be observed in contrast to other papers[15,16] presumably due to the low MgO content.

Scanning electron microscope images (Figs. 4 and 5.) are in accordance with XRD results. In ash samples heat-treated at lower temperature of 850 and 900 °C the bulk is apparently remained glassy. Micropores homogenously dispersed in the material tend to coalesce as temperature increases. At higher temperatures (1000 °C) crystals developed and tend to grow with the temperature.

Scanning micrographs of m-ash samples (Figs. 6 and 7.) show crystalline structure even at the lowest temperature. Grain growth with increasing heat treatment temperature is also apparent.
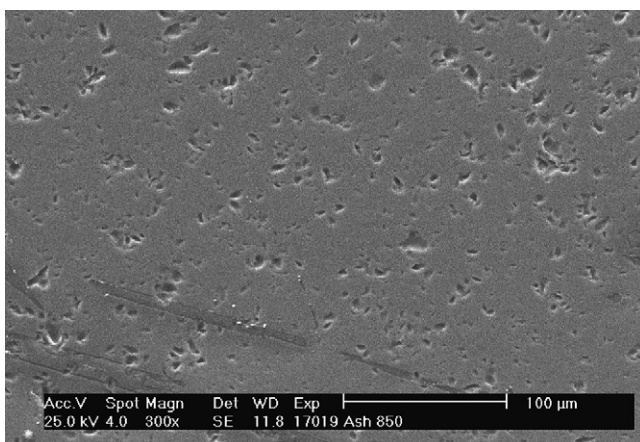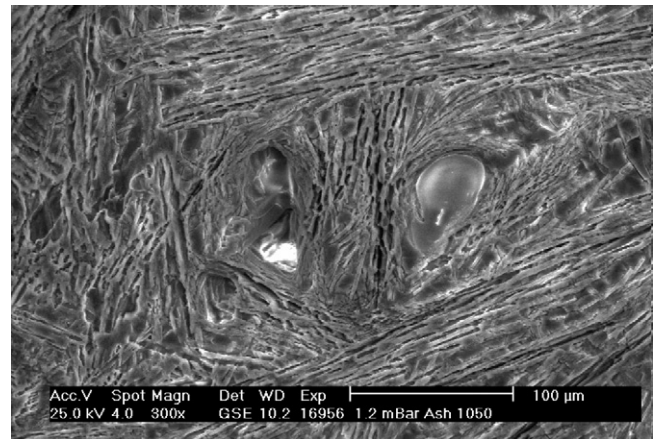

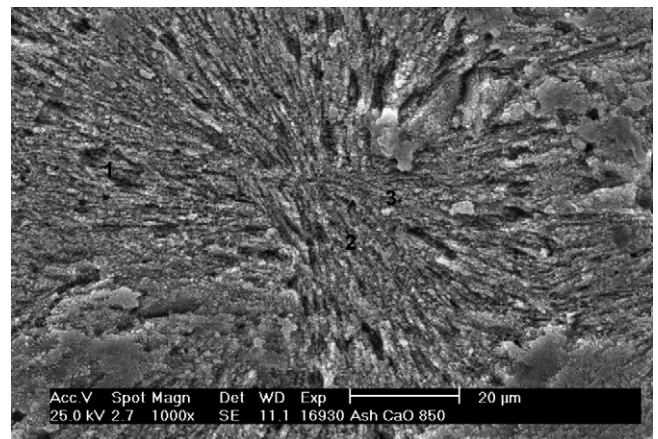Fig. 5. SEM image of ash sample heat treated for 2 h at 1050 °C.

Fig. 6. SEM image of m-ash sample heat-treated for 2 h at 850 °C.

Specimens were analyzed by EDX in several points on the surface to check chemical homogeneity. Results of analysis are presented in Table 1. ash sample was completely homogenous and segregation did not occur at higher temperatures. Conversely, m-ash samples show considerable difference in the chemical composition at different spots that could be attributed to bigger size of the different kinds of crystallites. The difference

Fig. 4. SEM image of ash sample heat treated for 2 h at 850 °C.
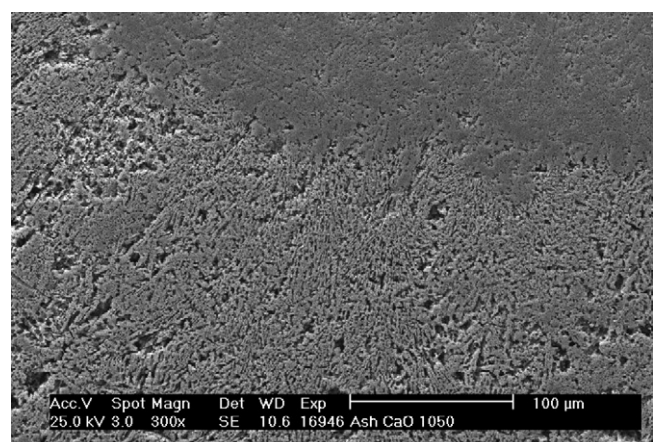

Fig. 7. SEM image of m-ash sample heat-treated for 2 h at 1050 °C.

Table 1
EDX results of vitrified specimens after heat treatment at various temperatures

Element (wt.%)	O	Ca	Si	Al	Mg	Fe	Ti	Na	S
Ash (°C)									
850	42.6	17.2	26.6	6.7	1.9	2.2	1.0	0.8	0.1
900	43.1	15.1	25.7	7.5	2.0	1.9	1.2	1.3	0.4
1000	44.5	14.8	25.2	8.6	1.6	1.8	0.8	1.2	0.2
1050	44.6	14.6	24.3	8.7	2.0	2.4	1.2	1.3	0.2
m-ash									
850	40.1	27.6	17.9	6.0	1.9	2.5	1.1	0.9	0.3
	38.7	26.7	20.8	6.1	1.8	1.9	1.0	1.0	0.3
900	32.8	24.0	20.9	10.0	2.9	3.6	1.9	0.7	0.3
	48.0	15.7	17.0	10.0	4.4	1.8	1.4	0.6	–
1000	40.7	25.1	18.2	7.8	2.4	1.9	1.1	1.3	0.1
	48.1	16.8	18.0	9.2	2.4	1.3	0.8	1.5	0.2
1050	46.7	15.8	17.9	11.1	2.6	2.4	1.3	1.1	0.2
	38.9	24.5	19.0	8.8	1.7	3.4	1.1	1.1	0.4

Table 2
Chemical resistance of vitrified ash and glass–ceramics after heat treatment at various temperatures

Chemical 20 (wt.%)	Type of sample	Loss (wt.%)			
		Glassy	850 °C	1000 °C	1050 °C
HCl	ash	0.60	0.15	0.32	0.45
	m-ash		0.25	0.08	0.52
NaOH	ash	4.49	2.15	1.44	2.67
	m-ash		38.77	26.54	17.85

measured in the weight ratio of Ca to Si is in agreement with the Ca to Si ratio in the gehlenite and anorthite.

3.2. Physical and technical properties of glass-ceramics

Vitrification entailed a substantial degree of volumetric reduction as much as 60% and a moderate weight reduction of 10%, as well. Density of the vitrified ashes was measured to 2.75–2.9 g/cm^3 by picnometry.

Microhardness of the vitrified samples was 7 GPa regardless whether the starting material contained additional lime or not. Comparison of the microhardness values of the heat-treated specimens at various temperatures is presented in Fig. 8. On the effect of heat-treatment ash samples exhibited some minor decrease in the microhardness values. Considerable changes did not occur even on the formation of crystallites. Conversely, heat treatment of m-ash samples had adverse effect on the micro-hardness that decreased with increasing temperature. Notable, that crystallization of this material takes place even at the lower temperatures. Heat treatment conducting at higher temperatures
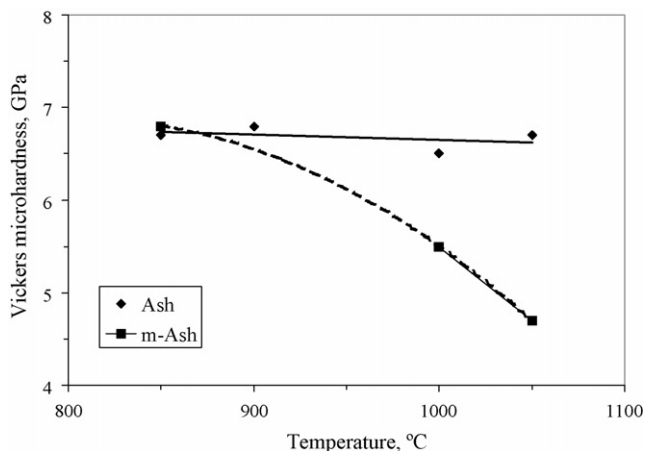
leads to grain growth that eventually accounts for the decrease in the microhardness.

Chemical durability of vitrified ashes and glass–ceramics is of importance in terms of potential application of the product and environmental aspect, as well. Weight loss of samples on chemical attacks is given in Table 2. ash samples are outstanding in respect of chemical durability that is still improved on the effect of heat-treatment. However, m-ash samples are unable to withstand harsh basic attack owing to the presence of gehlenite as reported in other papers.[6]

4. Summary

Vitrification of MSWI fly ash in dc arc plasma furnace and subsequent heat-treatment in one-step yields a glass–ceramic product having outstanding properties in terms of mechanical properties and chemical durability. For the interest of extensive crystallization, heat-treatment must be carried out at temperatures above 950 °C and/or holding time must be increased. Addition of lime to fly ash prior to any treatment enables a crystal structure to be developed at much lower temperatures, but has an adverse effect on its technical properties.

Fig. 8. Vickers microhardness of vitrified ash and m-ash specimens after heat treatment at various temperatures.

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