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Preparation of low melting temperature glass-ceramics from municipal waste incineration fly ash

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ABSTRACT

Glass-ceramics have been prepared from air pollution control residues (fly ash) of a municipal solid waste incineration (MSWI) plant in southern China. The use of additives was investigated in order to decrease the melting temperature of the waste and thus to reduce the costs of production of glass-ceramics from the vitrified waste. Results showed that the melting temperature can be decreased significantly from 1500 to 1200 °C, which was achieved by combining the MSWI fly ash with silica sand powder and a Fe₂O₃-rich and CaO-rich iron slag to form a glass in the SiO₂-CaO-Al₂O₃-Fe₂O₃ quaternary phase system. Sodium carbonate and borax were used as fluxing agents and TiO₂ of chemical grade was added as a nucleation agent. The main crystalline phase in both high and low melting temperatures glass-ceramics of size in the range 100–200 nm which developed at crystallization temperatures in the range 800–900 °C for 1–2 h. The leaching behaviour of the glass-ceramic materials was tested, and it was found to be lower than that of a cement-stabilized body that was fabricated using the same waste for comparison. The results demonstrate the feasibility of reusing MSWI fly ash for glass-ceramic production at relatively low melting temperature, e.g. in a less energy-intensive process, as a viable approach for tackling the problem of hazardous MSWI residues.

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1. Introduction

Municipal solid waste incineration (MSWI) is a high efficient domiciliary waste management technique because of the reduction of volume, reduction of weight and recovery of energy. In the 1970-1980s, at the time of the early developments of MSWI, control of dioxins/furans and control of incineration fume gases were identified as a major environmental problem derived from the use of MSWI. Currently advanced air pollution control (APC) systems have been developed for MSWI, and the solidification/stabilization of the APC residues becomes a new problem since most of organic pollutants and heavy metals have been transferred from fume gases into these residues [1-2]. Cement solidification is a common method for treatment of hazardous wastes, however the long-term risk of cement solidification of MSWI APC residues is being debated since the leaching concentration of heavy metals would increase in the acid environment of landfill especially after the fifth year of landfilling [3,4].

Vitrification of hazardous waste has been demonstrated to be an attractive method for the long-term and safe immobilization of heavy metals in a host glass matrix [5–7]. However a disadvantage of vitrification is that it is an energy-intensive process involving relatively high costs [8]. There are two approaches to improve the economics of the vitrification technique. The first option is to decrease the melting temperature, as a direct approach, leading to reduced energy consumption and costs. The second option is the fabrication of added value produced from vitrified material. Preparation of glass-ceramics from the vitrified waste, having enhanced physical and mechanical properties and potential application in industry (e.g. as building materials), is thus an indirect approach to improve the economics of waste vitrification technology. Normally the melting temperature of APC residues and other solid wastes is in the range 1400-1500 °C, which is required to obtain the parent glass [9,10]. The melting point of the parent glass can be decreased using additives or fluxes, such as sodium carbonate and boron compounds. Li et al. [11] have revealed for example that Fe₂O₃ and CaO in coal could decrease the melting temperature of fly ash while Dimech et al. [12] have investigated the use of boron containing compounds to reduce the melting and sintering temperature of powder mixtures containing high concentrations of MSWI residues. In this paper, the production of low melting temperature glass-ceramics from MSWI fly ash has been investigated using different additives and the new materials are compared to glass-ceramics produced by the conventional process (no additives).





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2. Experimental

2.1. Raw materials and the parent glass samples

MSWI fly ash samples were obtained from a plant with rotary kiln process in Guangdong province of China. The chemical composition of fly ash is shown in Table 1, indicating that this is in the $SiO_2-CaO-Al_2O_3$ ternary phase system. Silica sand powder was used to increase the glass-forming ability of the mixture. As a low-cost Fe_2O_3 -rich and CaO-rich additive, steel slag was introduced to form a $SiO_2-CaO-Al_2O_3-Fe_2O_3$ quaternary phase system with lower melting point. Sodium carbonate and borax (Tian Jin No. 3 Chemical Reagents, China) were used as fluxing agents, and TiO_2 of chemical grade was added as a nucleation agent. The chemical compositions of steel slag, silica sand powder and borax used are also reported in Table 1.

After several preliminary experiments, two kinds of mixtures of the starting powders were selected for further investigation. One mixture is a representative sample with high melting temperature, namely 90 wt% MSWI fly ash, 5 wt% silica sand, and 5 wt% TiO₂ (designated HIGH). The other mixture is a representative sample with relatively low melting temperature, namely 72 wt% MSWI fly ash, 4 wt% silica sand, 10 wt% steel slag, 5 wt% sodium carbonate, 8 wt% borax and 1 wt% TiO₂ (designated LOW).

After grinding, the mixed starting powders were melted in Al_2O_3 crucibles in air, then the melt was cast in preheated steel moulds. For the HIGH composition mixture, the samples were held at 1500 °C for 2 h; and for the LOW composition sample, these were held at 1200 °C for 2 h. To remove thermal residual stresses, the as-cast glass samples were annealed in all cases in a muffle at 550 °C for 2 h followed by slow cooling to room temperature.

2.2. Thermal characterization of the parent glass

The crystallization process was investigated by Differential Thermal Analysis (DTA) technique (Perkin–Elmer 7 Series Thermal Analyzer) using 30.300 mg of glass powder (mean particle size <45 μ m) heated commonly from 20 to 1300 °C at a rate of 10 °Cmin⁻¹ in helium atmosphere. DTA was carried out to determine the glass transition temperature (T_g) and crystallization peak temperature (T_p).

2.3. Heat-treatments and characterization of glass-ceramics

On the basis of DTA analyses, the heat-treatment of the parent glass was carried out in a two-step process. Nucleation and crystallisation temperatures were determined corresponding to T_g and T_p , respectively.

Powder X-ray diffraction (XRD) investigations were carried out with a D/Max-3B diffractometer using Cu K α radiation, operated at 30 kV and 30 mA in the 2 θ range from 10° to 70° at the rate of 4° min⁻¹. The crystalline phases were identified by comparing the peak intensities and positions in the spectrum with those in the Joint Committee on Powder Diffraction Standards data files.

The microstructure characterization of glass-ceramics produced at the different heat-treatment conditions was performed by Scanning Electron Microscopy (SEM) (JSM-35C) on gold coated samples. The glass–ceramic specimens were prepared using standard metallographic techniques followed by chemical etching in a 15 vol % HF solution for 10 s. They were then washed with water and dried in air at room temperature.

2.4. Leaching tests

Leaching tests of as-received MSWI fly ash samples, the parent glasses and glass-ceramics were investigated by the toxicity characteristic leaching procedure (TCLP) method according to the US Environmental Protection Agency [13]. At the same time, for comparison, ordinary Portland cement (No. 425) solidification of MSWI fly ash was investigated after curing for 28 d. MSWI fly ash samples were directly tested after drying. Glass, glass-ceramic, and cement-solidified specimens were crushed to a powder with a particle size of less than 50 μ m for the leaching tests. The concentration of heavy metals in the leaching solution was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a TraceScan AdvantageTM equipment (Thermo Jarrell Ash Corp).

2.5. Properties tests

Physical properties such as density and water adsorption were evaluated according to Archimedes method. The samples were ground and polished prior to the conduction of Vickers indentation-hardness, H_{v} , measurements using a microhardness device (HV-1000, Laizhou Weiyi Experiment Machine Manufacturing Co. Ltd., China) with a load of 200 g for 10 s. Five indentations were made for each value reported. Bending strength tests of rectangular samples with dimensions of 4.0 mm × 4.0 mm × 35.0 mm were



Fig. 1. DTA curves of the parent glasses of HIGH and LOW compositions.

Table 1
Compositions of main raw materials (wt%).

Raw materials	SiO ₂	CaO	Al_2O_3	Fe ₂ O ₃	MgO	$Na_2O + K_2O$	TiO ₂	MnO	B_2O_3	Cl-	SO_4^-	LOI
MSWI fly ash	27.52	16.60	11.00	5.04	3.14	8.24	1.88	-	-	10.32	8.34	13.36
Silica sand	93.42	1.02	1.44	0.83	0.07	0	0.47	0	-	-	-	2.75
Steel slag	14.59	43.19	0.15	25.06	10.98	-	-	1.53	-	-	-	1.05
Borax	10.39	10.96	0.26	0.18	15.26	8.15	-	-	12.50	-	-	39.78



Fig. 2. XRD patterns of glass-ceramics (a) HIGH composition samples nucleated at 700 °C for 2 h followed by heat-treatment at different crystallization temperatures for 2 h; (b) LOW composition samples nucleated at 620 °C for 40 min followed by heat-treatment at different crystallization temperatures for 60 min.

carried out with MTS 858 Material Testing System (MTS Systems Corporation, USA).

3. Results and discussion

3.1. Thermal analysis of the parent glass

Fig. 1 shows the DTA traces of the two parent glasses. For the HIGH composition sample, T_g was at about 700 °C, and crystallization temperatures T_p were detected at 920 °C and 1094 °C. Generally, the nucleation temperature is near T_{g} and the crystallization temperature is near $T_{\rm p}$. Thus, the heat-treatment schedule for the HIGH composition parent glass included a nucleation stage at 700 °C for 2 h followed by a crystal growth stage at different crystallization temperatures (800 °C, 900 °C, and 1000 °C) for 2 h. For the LOW composition parent glass, $T_{\rm g}$ was about 631 °C, and $T_{\rm p}$, corresponding to crystallization, was observed at 805 °C. Then, the heat-treatment schedule of the LOW composition parent glass included a nucleation stage at 620 °C for 40 min followed by a stage at different crystallization temperatures (750 °C, 875 °C, and 900 °C) for 60 min. The additives in the LOW composition can have a significant effect in decreasing the viscosity of these glass samples, therefore atoms are able to diffuse easily in the glass structure in this material, leading to the observed reduction of the nucleation and crystallization temperatures. There was a melting endothermic peak (T_m) after the crystallization peak for both HIGH and LOW composition samples. However, the melting endothermic peak for the HIGH composition was at about 1254 °C while for the LOW composition, it was at 1066 °C. This result was consistent with the melting temperature of these two parent glasses.

3.2. Crystalline phases at different heat-treatment conditions

The XRD patterns of the glass-ceramics and the parent glass of HIGH composition are shown in Fig. 2a. For the parent glass, XRD



Fig. 3. SEM images of HIGH composition glass-ceramics nucleated at 700 °C for 2 h followed by heat-treatment at different crystallization temperatures for 2 h. (a) 800 °C; (b) 900 °C; (c) 1000 °C.



Fig. 4. SEM images of LOW composition glass-ceramics nucleated at 620 °C for 40 min followed by heat-treatment at different crystallization temperatures for 60 min. (a) 750 °C; (b) 875 °C; (c) 900 °C.

confirmed the amorphous glass structure. The crystalline phase was identified as diopside (Fe-bearing) in the XRD patterns of the glass–ceramics nucleated at 700 °C for 2 h followed by different crystallization temperatures (800 °C, 900 °C, and 1000 °C). The influence of the crystallization temperature from 800 °C to 1000 °C on the crystalline phase is not seen to be significant since the relative intensity and 20 position of the peaks did not change. For the LOW composition sample, the XRD pattern (shown in Fig. 2b) is almost consistent with that of the HIGH composition

material. However, an impurity peak is apparent at about 37° in Fig. 2a, but no peak could be found at the same position in Fig. 2b. This result indicates that other crystalline phases could be present in the HIGH composition sample. Nevertheless, the change of composition to decrease the melting point did not affect significantly the type of crystalline phases formed. It is inferred that the additives in the LOW concentration sample only have an effect on the glassy phase of the glass–ceramic structure, however they might have some effect on the ability of the glass to crystallize with the shifting of the nucleation and crystallization temperatures to lower values.

Results of the leaching tests on fly ash	, vitrified waste,	glass-ceramic	and	cement-
solidified bodies (mg L^{-1}).				

Table 2

Samples	Cr	Zn	Pb	Cu	Cd
Fly ash powder	1.201	0.453	0.645	0.372	0.993
HIGH parent glass	0.003	N.D.	N.D.	N.D.	N.D.
HIGH glass-ceramic	N.D.	N.D.	N.D.	N.D.	N.D.
LOW parent glass	N.D.	N.D.	N.D.	N.D.	N.D.
LOW glass-ceramic	N.D.	N.D.	N.D.	N.D.	N.D.
Cement-stabilized body	0.075	0.010	0.009	0.010	0.011
Chinese regulatory standard	1.5	50	3.0	50	0.3

Table 3

Properties of LOW composition glass-ceramics nucleated at $620\,^\circ\text{C}$ for $40\,\text{min}$ followed by heat-treatment at different crystallization temperatures for $60\,\text{min}$.

750 °C	850 °C	875 °C	950 °C
3.007	3.046	3.076	2.993
0.11	0.04	0.03	0.08
7.978	7.724	8.650	7.396
65.307	70.212	70.957	68.561
	750 °C 3.007 0.11 7.978 65.307	750 °C 850 °C 3.007 3.046 0.11 0.04 7.978 7.724 65.307 70.212	750 °C 850 °C 875 °C 3.007 3.046 3.076 0.11 0.04 0.03 7.978 7.724 8.650 65.307 70.212 70.957

 Table 4

 Summary of thermal characteristics and energy consumption in glass-ceramic production process.

	Thermal characteristics of the parent glass			Melting schedule	Heat-treatment schedule		
	Tg	Tp	T _m		Nucleation	Crystallization	
HIGH sample LOW sample	700 °C 631 °C	920 and 1094 °C 805 °C	1254 °C 1066 °C	1500 °C for 2 h 1200 °C for 2 h	700 °C for 2 h 620 °C for 40 min	800, 900, or 1000 °C for 2 h 750, 875, or 900 °C for 1 h	

3.3. Microstructure of glass-ceramics at different heat-treatment conditions

SEM images of glass-ceramics of HIGH composition at different crystallization temperatures are shown in Fig. 3. In Fig. 3a the microstructure is seen to be composed of fine crystal particles of \sim 100 nm in size exhibiting uniform distribution in the glass-ceramic microstructure nucleated at 700 °C for 2 h followed by crystallization at 800 °C for 2 h. With the increase of crystallization temperature up to 900-1000 °C, the morphology of the crystals was observed to change to short columnar shape of length 200-400 nm, as shown in Fig. 3b and c. SEM images of glass-ceramics of LOW composition at different heat-treatment conditions are shown in Fig. 4. In Fig. 4a, for glass-ceramics nucleated at 620 °C for 40 min followed by a crystallization stage at 750 °C for 60 min, spherical crystals are seen to be distributed in the glass matrix. This glass matrix exhibits a porous structure indicating that the glass phase was easily etched by HF acid during the preparation of SEM samples. With the increase of crystallization temperature to 875 °C, the microstructure seemed to be more compact, as shown in Fig. 4b, compared to that of glass-ceramics crystallized at 750 °C. When the crystallization temperature rose up to 900 °C, the microstructure was seen to be formed by high concentration of columnar crystals of length of about 500 nm, as shown in Fig. 4c. This observation indicates that crystals can grow quickly at the crystallization temperature of 900 °C. Generally, a microstructure consisting of uniformly distributed fine crystals of size 100-200 nm was observed at crystallization temperatures of 800-900 °C and heat-treatment time of 1–2 h for both HIGH and LOW compositions.

3.4. Leaching characteristics of glass-ceramics and cement-stabilised bodies

TCLP results on parent glass, glass–ceramics, cement-stabilized specimens and on as-received MSWI fly ash are summarized in Table 2. It is noted that the amount of Cd²⁺ leached from as-received fly ash was three times higher than the regulatory standard accepted in China. However, the concentration of other heavy metals, such as Cr, Zn, Pb, Cu, leached from the vitrified glass and glass–ceramics were too low to be detected, except for Cr from the HIGH composition parent glass. The concentrations of heavy metals leached from the cement-stabilized body were also lower than the regulatory limits accepted in China. The reason for the lower leachability characteristics of the vitrified materials is suggested to be the heavy metal ions being incorporated in the silicate glass framework of the vitrified structure [14].

3.5. Properties

Physical and mechanical properties of glass–ceramics of LOW composition nucleated at 620 °C for 40 min followed by heat-treatment at different crystallization temperatures for 60 min were summarized in Table 3. Properties of LOW composition glass–ceramics were consistent with reported properties in previous literatures [15,16]. From Table 3, physical and mechanical properties of glass–ceramics crystallized at 875 °C were optimum, which indicated that 875 °C was the optimum crystallization temperature for glass devitrification.

3.6. Feasibility of lower energy heat-treatment for vitrification of MSWI fly ash

The thermal characteristics of the parent glass and the heattreatment schedules for production of glass-ceramics are summarized in Table 4. With the change of chemical composition of the parent glass from HIGH to LOW composition, the thermal characteristics change leading to lower processing temperatures. Especially the melting temperature can decrease significantly, from 1500 to 1200 °C. Moreover, both nucleation and crystallization temperatures decrease to some extent. It is therefore confirmed that the objective of developing a lower energy consumption process for vitrification of MSWI fly ash can be achieved with the optimum design of the starting batch composition formed by smart mixture of several waste and additives. It should be noted that emission of greenhouse gas (CO₂) will be reduced in correlation with the decrease of energy consumption. Therefore, vitrification of combination of silicate waste at relatively low melting temperatures coupled with glass-ceramic production should be regarded as competitive and environmental friendly technologies for hazardous waste management strategies.

4. Conclusions

By carefully choosing the composition of starting materials (parent glasses), glass-ceramics with melting temperature of 1200 °C have been prepared from a mixture of silicate wastes, including MSWI fly ash and additives. The crystalline phase of the glass-ceramics with lower melting temperature was found to be diopside (Fe-bearing). The microstructure was composed of fine crystals of size in the range 100–200 nm which developed at the crystallization temperature of 800–900 °C for a 1–2 h heat-treatment. The decrease of melting temperature had no significant influence on the type of crystalline phase formed and on the microstructure development. The leaching characteristics of glass-ceramics from vitrified MSWI fly ash containing waste were shown to be comparable for the different glass-ceramics produced and the leaching values were lower than those of a cement-stabilized MSWI fly ash body.

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