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Effect of crystallization time on behaviors of glass-ceramic produced from sludge incineration ash

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Abstract

Incineration has become a significant treatment method for municipal sewage sludge because of the rising difficulty to find suitable sites for traditional landfill. However, a large amount of sludge incineration ash containing high levels of heavy metals is remained. In order to achieve resource utilization, glass–ceramics have been produced using sludge incineration ash. The optimum heat treatment was identified as T_n = 837°C for 1.0 h and T_c = 977°C for 2.0 h, respectively. The major crystalline phase identified from X-ray diffraction (XRD) and scanning electron microscopy (SEM) was wollastonite ($CaSiO_3$) and the products displayed good performances. The results indicated that it was a feasible attempt to produce glass-ceramics from sludge incineration ash as decorative materials.

Keywords: Heavy metal; Glass-ceramic; Sludge incineration ash

1. Introduction

The high efficient incineration technology has become increasingly important in solid waste treatment, which meets ecological and environmental requirements. However, the large amount of sludge incineration ash (SIA) containing high levels of heavy metals needs further treatment because of increased environmental awareness and pressing need for precious land resources [1]. Sludge incineration ash contains large amount of SiO_2, Al_2O_3, CaO, P_2O_5 and Fe_2O_3, which are suitable raw material for glass-ceramics production [2-4]. Vitrification has been proven to be efficient method to solidify many types of hazardous wastes, which the heavy metals can be stabilized in the glass matrix. The glass-like slag could be used for backfill and civil engineering. For further value-added utilization, sintering technology could even convert the glass-like material into glass–ceramic product for significant economic

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benefits [5]. The performance indexes of glass-ceramics, such as the features of crystals, their numbers and final sizes, were highly dependent on the initial composition and heat treatment. The glass network obtained in the process is an environmentally friendly and new competitive decorative material [6, 7].

The present research emphasized on the production of glass-ceramics from SIA. The products were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM) for crystal composition and microstructure. In addition, the density and water absorption were also investigated. This research will provide some useful information about the optimized parameters in glass-ceramics preparation from SIA. Research is beneficial to establish the theoretic and technical foundation for the development and exploitation of glass-ceramics using SIA, which will have significant ecological and economic impact.

2. Experimental

2.1. Raw material and glass-ceramics production

The sludge used in this research was obtained from a wastewater treatment plant (WWTP) located in Dalian, China. The dry sludge was incinerated at 900^{o}C in a laboratory scale tubular furnace, and the obtained SIA was ground into size below 75 μm for experiment. The chemical composition of experimental sample **(**Table 1**)** was determined by X-ray fluorescence (PDA-5500II, Shimadzu, Japan).

Table 1. Chemical composition and content of the experiment sample.

Component	
Substance	Content (wt %)
SiO_2	35.1731
P_2O_5	13.6982
Al_2O_3	6.1682
Fe_2O_3	5.7022
CaO	28.1385
K_2O	2.6981
MgO	2.2599
SO_3	1.6587
CuO	1.5747
Others	2.9284

The heavy metals containing in the experiment **(**Table 2**)** were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 2000DV, PerkinElmer, USA).

Table 2. Contents of heavy metals in the experiment sample.

Heavy metals	Content (μg/g)				
Element	Cr	Cu	Ni	Pb	Zn
SIA	702	11890	393	117	3531

The experimental sample was prepared by mixing SIA with analytic reagent CaO according to CaO-

Al_2O_3-SiO_2 (CAS) ternary phase diagram. The sample was mixed in agate pot by ball mill for 120 min. Well-mixed powder sample was kept at 1500°C for 2 h in corundum crucible in an electrically heated furnace to ensure complete melting. The melt was rapidly poured into water to form parent glass. For further studies on microstructures and properties of glass-ceramics at different crystallization time, the parent glass powder was filled in corundum crucible to obtain cylindrical sample. Prepared samples were heat treated to the nucleation temperature at a rate of 3°C/min and held for 1.0 h. Being heated at the rate of 5°C/min to T_c, the samples were crystallized at crystallization temperature (T_c) for 1.0 h, 2.0 h and 3.0 h, respectively, and then cooled naturally in the furnace.

2.2. Characterization methods

The thermal behaviour of parent glass was investigated by differential scanning calorimetry (DSC) (449 F3, Netzsch, Germany). About 15 mg powder was ground to powder with particle size below 75 μm, put into a alumina crucible and then heated from room temperature to 1300°C at the rate of 10°C/min in nitrogen atmosphere. The crystalline phases in glass-ceramics were identified by XRD (D/MAX-2400, Rigaku, Japan) analysis. The samples were analyzed over a range of 2θ angles from 5° to 90° using Cu Kα radiation. The obtained phases were confirmed according to the Joint Committee on Powder Diffraction Standard data. SEM (Quanta 450, FEI, USA) analysis was carried out to reveal the microstructure of produced glass-ceramics. The products were grounded flat by sandpaper, polished with diamond paste to achieve a mirror-smooth surface, etched with HF solution (20 vol. %) for 90 s, and then rinsed with distilled water. The density and water absorption were tested using the procedure outlined in GB/T 9966.3-2001.

3. Results and discussion

3.1. Differential scanning calorimetry (DSC)

It is important to determine nucleation and crystallization temperatures precisely for effective conversion of glass to glass-ceramics. The DSC curve shown in Fig. 1 reveals important features of the parent glass, including nucleation temperature (T_n), crystallization temperature (T_c) and melting temperature (T_m).

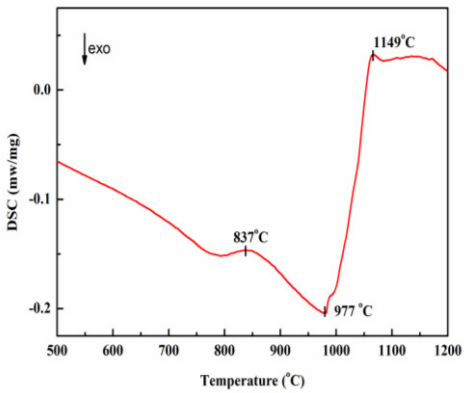

Fig. 1. DSC curve of the parent glass.

The endothermic peak at T_n = 837°C was attributed to the beginning of crystal nucleus growth. The

nucleation temperature was an important factor on crystal nucleus formation. The exothermal peak at T_c = 977°C was identified as crystallization temperature, which was important to crystal growth. The independent peak showed that only one kind of main crystalline phase would emerge within the glass-ceramic at this temperature. As the temperature rose, the melting temperature of parent glass appeared at T_m = 1149°C.

3.2. Microstructural characterization of glass-ceramics

The X-ray diffraction patterns of glass–ceramics at different crystallization time are shown in Fig. 2. The major crystalline phase was identified as wollastonite ($CaSiO_3$), of which the peak intensity changed regularly along with crystallization time, indicating a time dependence of wollastonite crystallization. It can be found that an increase of crystallization time was associated with an increase in peak intensity compared with Fig. 2a and Fig. 2b. However, the intensity of diffraction peak decreased when crystallization time was up to 3.0 h. The diffraction peak intensity of wollastonite phase was the maximum in Fig. 2b. It can be concluded that the condition crystallized at T_c for 2.0 h was optimal for glass-ceramic production because of higher crystallization degree. Additionally, a small amount of anorthite ($[Ca,Na][Al,Si]_2Si_2O_8$) was existed as minor crystalline phase in the products. Similar crystalline phases existing in the glass-ceramics prepared from other municipal waste were also reported elsewhere [8-10].

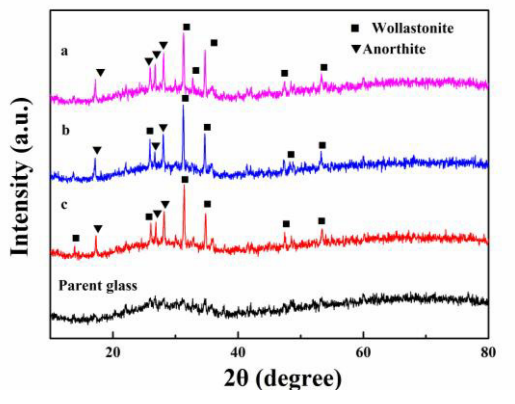

Fig. 2. XRD patterns of parent glass and glass-ceramics at different crystallization time. (a—1.0 h, b—2.0 h, c—3.0 h).

This crystallization behavior could be explained by the theory of stable energy of glass structure unit, in which the structure units of CAS system glass are $[SiO_4]$ and $[AlO_4]Ca[AlO_4]$. When it comes to nucleation temperature, the structure unit $[AlO_4]Ca[AlO_4]$ begin to be broken apart. The free Ca^{2+} is apt to unite $[SiO_4]$ and thus wollastonite is first formed. After wollastonite deposits, the structure unit $[AlO_4]Ca[AlO_4]$ is forced to rearrange and unite $[SiO_4]$. Thus anorthite deposits from the parent glass after wollastonite deposits [3, 11, 12].

SEM micrographs of glass–ceramics shown in Fig. 3 revealed the microstructure of glass-ceramics. In Fig. 3a the microstructure was composed of flake shape crystals, exhibiting an irregular structure distribution. With the increase of crystallization time up to 2.0 h, the quantity of crystals was increased, and the morphology of crystals was prone to compact granular shape crystals of length 1–3 μm, as shown in Fig. 3b. The non-directional interlaced distribution structure is beneficial to physical and mechanical properties [13]. When it came to the heat treatment of T_c = 943°C for 3.0 h, crystals continued to grow and secondary recrystallization happened. The better microstructure of glass-ceramic was broken. This

phenomenon indicated that the characteristic of crystals in the glass-ceramics changed with crystallization time, and the appropriate crystallization time was necessary for more crystal quantity and better crystal microstructure.

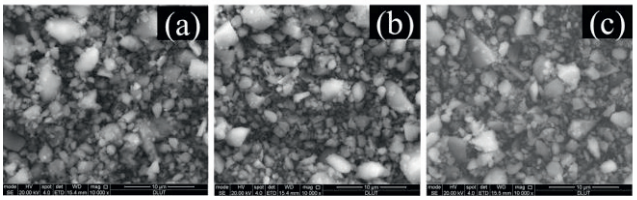

Fig. 3.SEM micrographs of glass-ceramics at different crystallization time. (a—1.0 h, b—2.0 h, c—3.0 h).

The density and water absorption are summarized in Table 3. The density values of glass-ceramics were in the range of 2.19-2.30 g/cm^3. When it was crystallization for 2.0 h, the maximum density value implied optimal crystallization condition.

Table 3. Physical properties of prepared glass-ceramics.

Crystallization time	1.0 h	2.0 h	3.0 h
Density (g/cm^3)	2.19	2.30	2.26
Water absorption (wt.%)	2.03	1.55	1.81

Previous studies indicated that the density of glass-ceramics increased with the enhancement of crystallization degree [9, 14, 15]. The high crystallization degree caused a reduction of the open porosity so that the glass-ceramics material showed a good water resistance [16]. The optimum heat treatment was nucleated at $T_n = 837^oC$ for 1.0 h and crystallized at $T_c = 977^oC$ for 2.0 h.

4. Conclusion

This research shows the feasibility of producing value-added glass-ceramics from sludge incineration ash (SIA). XRD and SEM analysis revealed that crystallization time influenced the quantity and microstructure of crystals, but did not change the type of main crystalline phase. The optimum heat treatment was identified as $T_n = 837^oC$ for 1.0 h and $T_c = 977^oC$ for 2.0 h, respectively. Attractive properties of glass-ceramics were observed based on the optimum parameter. Therefore, it was a good way to produce value-added glass-ceramics from SIA as environmentally friendly decorative materials.

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