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Short communication

Utilization of coal fly ash in the glass–ceramic production

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Abstract

Manufacturing the glass–ceramic has been proposed as a useful choice to recycle coal fly ash from power plants. In this work, a glass–ceramic of SiO_2–Al_2O_3–Fe_2O_3–CaO family was synthesized by mixing 90 wt% of coal fly ash, from a power plant in west of China, with Na_2O, and then melted at 1350 °C. The ceramization of the obtained glass was carried out at 770 °C for 2 h. Esseneite and nepheline were found present as major crystal phases. The produced glass–ceramic exhibited good chemical durability as well as good mechanical properties. The toxicity characteristic leaching procedure (TCLP) method found that the glass–ceramic was non-hazardous.

Keywords: Glass–ceramic; Coal fly ash; TCLP; Chemical resistance

1. Introduction

A large amount of coal fly ash is produced in China as well as in the world as a by-product of coal combustion in thermal power plants. Recently, more than 100 million tonnes of coal fly ash is produced annual in China. Disposal of coal fly ash is becoming an increasing economic and environmental burden. As a consequence, there is a growing interest in looking for avenues where the materials can be used as a potential resource for preparation of value added products. In China currently only a small percentage (∼15%) of this waste is utilized, primarily in cementitious products (concrete and cement), remainder being directly discharged into fly ash ponds or landfills, which is regarded as unsightly, environmentally undesirable and a non-productive use of land resources, as well as posing an on-going financial burden through their long-term maintenance. Furthermore, finding disposal sites is becoming increasingly more difficult. These factors have prompted researchers to look for alternative usages for coal fly ash, other than the cement and construction industry [1–5]. Since coal fly ash contains large amount of SiO_2 and Al_2O_3, which are main glass network formers, it is feasible to use coal fly ash as a raw material to develop glass matrices [4,6,7]. One type of the coal fly ashes has been used to vitrify borate waste from nuclear power plants by adding the glass modifier Na_2O in China [6]. Glass–ceramic is fine grained polycrystalline material, with some residual glass matrix, it is prepared by the controlled crystallization of a parent glass. Glass–ceramic usually have superior mechanical and erosion properties to the parent glass and may also exhibit unique thermal and electrical properties. The re-use of silica-rich coal fly ash for the production of glass–ceramic is promising development [4,8,9]. Although a substantial amount of literature is available on the development of a new glass–ceramic by re-use of industrial metallurgical wastes, only minimal work has been reported on producing glass–ceramic from coal fly ash in power plants. On the other hand, the development of new glass materials, made by recycling wastes, is acquiring particular importance in China due to its largest population. However, to the author's knowledge, there is only a limited number of studies on producing glass–ceramic from coal fly ash in China. From the view point of practical application, it is imperative to know the parent glass composition and crystallization route. In the present study, the parent glass composition made of mixture of coal fly ash and Na_2O additives and its crystallization behavior were investigated.

2. Experimental

Although the coal fly ashes have a wide distribution in the composition depending on the coal burned and the burner types,

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the main components are of SiO_2, CaO, Al_2O_3 and Fe_2O_3. A typical coal fly ash obtained from a power plant in west of China was utilized for experimentation. The bulk density of coal fly ash was about 2.4 g/cm^3 according to the producer's report. The optical microscope found that coal fly ash had spheroid morphology with mean particle sizes around 45 μm [10]. The X-ray diffraction (XRD) measurements indicated the presence of mullite ($Al_6Si_2O_{13}$), magnetite (Fe_3O_4), $CaCO_3$, and quartz (SiO_2) [7,10]. The loss on ignition was about 3.9%. The ashes were dried and treated at 1000 °C for 1 h in air to completely remove the unburned coals, then were used to determine the compositions. The chemical compositions of coal fly ash were determined by the means of X-ray fluorescence (XRF) and inductively coupled plasma spectrometry (ICP). The parent glass was made from mixture containing 90 wt% of coal fly ash and additive of Na_2O. Pure sodium carbonate was used to add Na_2O in this experiment. Fusion was carried out in a platinum crucible at 1350 °C for 2 h under an air atmosphere and then annealed at 570 °C for 2 h. The obtained glass was analyzed by the differential thermal analysis (DTA) using a powder sample at the heating rate of 10 °C/min in static air, in order to determine the glass transition temperature and to have an indication of the temperature suitable for the crystallization process. Glass–ceramic was prepared by heating the parent glass monolith for 2 h at the peak temperature of the DTA exotherm. The crystalline phases of glass–ceramic were determined by the XRD (Rigaku) of bulk sample. Microstructural characterization of the obtained glass–ceramic samples was carried out by scanning electron microscopy (SEM) (JEOL-6301F).

The density of the glass–ceramic was determined by the Archimedes method, using water as medium. The bending strength was measured from the 4-points bending strength test on a Universal Testing Machine (DSS-25T). Thermal expansion was evaluated by dilatometric analysis in the range 20–400 °C. The leachability was performed by the toxicity characteristic leaching procedure (TCLP) [6,11]. Glass samples of 2 g were treated at 95 °C for 1 h in 50 ml leaching solutions (0.01 mol/l HCl and 0.01 mol/l NaOH). Weight loss was then measured for the chemical durability evaluation. All these tests were made in duplicate and the error in the average values reported herein is estimated at ±5%.

3. Results and discussion

Development of the glass formulations for coal fly ash is to the constrained multivariant optimization of the following requirements [6,7]: (1) coal fly ash acceptability, (2) melt processability, (3) glass product durability, and (4) overall economics. The acceptability criterion is essential for the product to function as a barrier against the release of heavy metals or other hazardous elements into environment. As a possible industrial material, glass product should have good chemical durability and enough mechanical strength. The glass structure is usually considered as solid at a random network [6,7,12]. The glass components are generally classified into three types: (1) network forming atoms, such as Si, B, P, Ge; (2) network modifiers (or glass fluxes), such as Na, K, Li, Ca, Mg; and (3) intermediates, such as Al, Fe, Zn, Ti, Mo, etc. The glass chemical durability is mainly influenced by the glass composition. The following general rules were applied to develop a suitable glass formulation: (1) the components that form the strongest bonds in glasses result in the greatest improvement of glass and waste durability, whereas those that form the weakest bonds generally prove the greatest detriment to glass and waste glass durability; (2) increasing SiO_2, Al_2O_3, B_2O_3, and ZrO_2 may improve durability; and (3) adding alkali metal oxides may decrease the melt viscosity but also decrease the durability.

Table 1
Chemical composition of tested coal fly ash in terms of oxide contents

Oxides	wt%	Oxides	wt%
SiO_2	49.92	Na_2O	1.15
Al_2O_3	19.80	SO_3	1.46
Fe_2O_3	13.53	ZnO	0.15
CaO	11.85	MnO	0.11
K_2O	0.22	CuO	0.02
MgO	1.78	PbO	0.01

Coal fly ash from a power plant in west of China contains high SiO_2, Al_2O_3, Fe_2O_3 contents, but has very low alkali content, as shown in Table 1. According to current knowledge, the coal fly ash does not contain proper ratios of components for the formation of a glass, additive of glass network modifiers is need in order to achieve full vitrification of coal fly ash. The most effective glass modifier is Na_2O. Therefore, binary compositions were prepared by mixing of coal fly ash with 5–30 wt% of Na_2O in our preliminary studies. A dark brown homogeneous glass contains 90 wt% of coal fly ash and 10 wt% of Na_2O was selected because of its suitable melting property and good chemical durability, which was named as FN-10 hereafter. Higher content of Na_2O (>10 wt%) decreases the chemical durability and compress strength; low content sharply increases melting temperature and makes the processing operations difficult. Since Fe_2O_3 is an effective nucleating agent, the FN-10 glass is possible to produce a glass–ceramic after heat treatment.

The DTA curve of the FN-10 is shown in Fig. 1, where an exothermic peak of crystallization at about 770 °C was found.

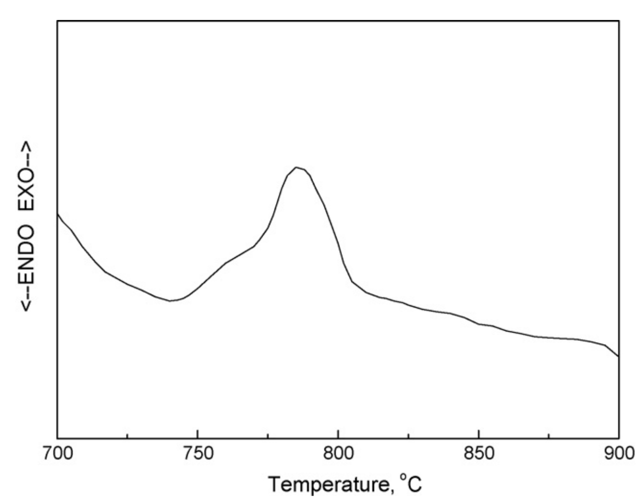

Fig. 1. DTA curve of the glass.

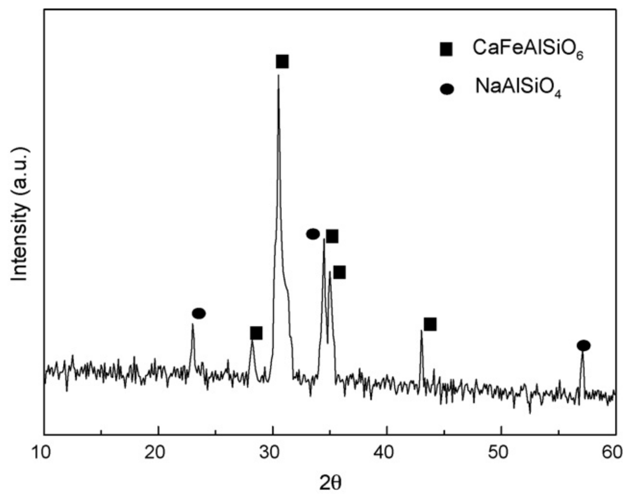

Fig. 2. XRD result of the glass–ceramic prepared at 770 °C for 2 h.

Then heat treatment of the FN-10 at 770 °C for 2 h was performed to synthesis the glass–ceramic. The XRD analysis result of produced glass–ceramic is presented in Fig. 2. A calcium iron aluminum silicate, esseneite, $CaFeAlSiO_6$, was identified as a major phase. A second phase, a sodium aluminum silicate, nepheline, $NaAlSiO_4$, has also precipitated. The crystallization was also observed by SEM micrographs, as shown in Fig. 3. Glass–ceramics with spherical crystals of size below 500 nm and that are homogeneously dispersed within parent glass matrix, have been obtained via suitable heat treatments. The density of the glass–ceramic was around 2.67 g/cm^3. The bending strength of the glass–ceramic was about 53.68 MPa, and the linear thermal expansion coefficient between 20 and 400 °C was 93.7×10^{-7} K^{-1}. Reference [9] gives that the glass–ceramics M-PC800 and M-PC870 had bending strength of 47.59 MPa and 67.02 MPa, respectively, which showed similar properties with our results.

The dissolution of the silica matrix can release heavy metals from the glass structure. The TCLP test was conducted to study the heavy metals migration. In this study, the TCLP analyses were limited to the main hazardous heavy metals of Pb, Zn, Cu and Mn. The TCLP performance of the parent glass and produced glass–ceramic is listed in Table 2. The results were compared with the United States Environmental Protection Agency (US EPA) limits [7]. It was found that all the tested element concentrations are within the US EPA limits, which means that the heavy metals were successfully solidified into the glass matrix. Therefore, the glasses or glass–ceramic produced from the coal fly ash can be taken as non-hazardous, which showed the potential application as useful materials.

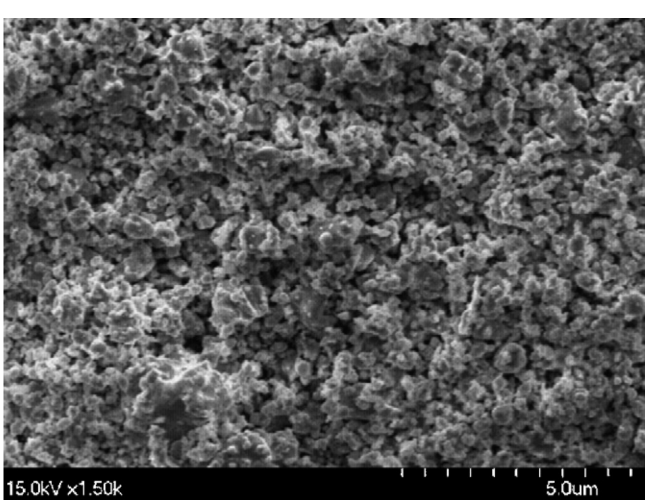

Fig. 3. SEM micrograph of the glass–ceramic.

Table 2
TCLP data of heavy metals

Samples	TCLP tests (μg/ml)			
	Pb	Zn	Cu	Mn
FN-10	0.009	0.770	0.007	0.052
Glass–ceramic	0.003	0.337	<0.001	0.018
US EPA limit	0.50	500.00	5.00	5.00

The reaction of glass or glass–ceramic with water is usually dominated by two primary reactions: ion exchange to release alkali metals and glass network hydrolysis break down the glass network to release silicon or other network formers [12–14]. In general, ion exchange processes between the hydrogen and the most mobile network modifier ions, such as Na, dominate the glass or glass–ceramic dissolution in 0.01 mol/l HCl solution; while network hydrolysis reactions dominate the dissolution in 0.01mol/l NaOH solution. The weight losses of the glass–ceramic were 1.36 and 1.12 wt% in 0.01 mol HCl and 0.01 mol/l NaOH solution, respectively. Although the literature does not exactly specify chemical resistance values for commercial bricks and tiles or for natural marbles and granites, it should be noticed that the chemical durability of the obtained glass–ceramic corresponds to that of glasses and glass–ceramics of high chemical resistance [15].

4. Conclusions

The coal fly ash from thermal power station was successfully vitrified by adding 10 wt% of Na_2O as glass flux. After heating of glass at 770 °C for 2 h, a glass–ceramic was obtained. The main crystal phases were $CaFeAlSiO_6$ and $NaAlSiO_4$. The produced glass–ceramic was non-hazardous and had good chemical resistance and mechanical property. From the practical point view, such glass–ceramic may be viable as an engineering material.

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