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Glass-ceramics prepared from sludge generated by a water purification plant

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Abstract

Glass-ceramics were prepared from sludge generated in a water purification process. The main constituents of this sludge were SiO_2 and Al_2O_3, with considerable amounts of Fe_2O_3 and MnO also present. The batch composition of the parent glass was adjusted to be close to the composition of the eutectic point in the CaO–Al_2O_3–SiO_2 system by mixing the sludge with $CaCO_3$ and waste soda-lime glass. The samples were melted at 1300 °C for 2 h and quenched in water. The resulting glass cullet was ground to <100 mesh in a ball mill, uniaxially pressed to form green bodies and fired at 700–1250 °C to densify and crystallize. Crystallization occurred at >850 °C, forming gehlenite ($Ca_2Al_2SiO_7$) and wollastonite ($CaSiO_3$) above 900–950 °C. The color of the sample changed from black to yellow-brown upon crystallization. The average four-point bending strength and Vickers microhardness of the glass-ceramics heated at 1000 °C (99 MPa and 5.2 GPa) was comparable with the values of commercial glass-ceramics. The chemical durability in acid and alkali solutions was 17.7 and 0.23 mg/cm^2, respectively, showing excellent durability in alkali solution.

Keywords: A. Sintering; D. Glass-ceramics; D. Silicate; Waste recycling; Building materials

1. Introduction

The amount of various wastes being re-used to produce various raw materials such as cement [1] is increasing but it is important to develop other applications for waste materials to increase the ratio of their re-use. Since many inorganic wastes mainly consist of SiO_2, Al_2O_3 and CaO, one possible applications is as glass-ceramics. Therefore, various glass-ceramics have been prepared from ashes such as coal fly ash from a thermal power station [2], sewage sludge fly ash [3], municipal waste incinerator fly ash [4], incinerator bottom ash [5] and steel plant fly ash [6], slag from blast furnace [7], silicon manganese and steel furnaces [8], and sludge such as silicate waste [9], refractory waste [10], phosphorous fertilizer production waste [11] and wasted fluorescent glass and shell [12].

We have prepared glass-ceramics using Kira, the waste generated during the benefication of silica sand and plastic clay [13,14], and also paper sludge ash [15]. The resulting glass-ceramics showed high strengths (70–130 MPa), high hardness values (6.6–7.6 GPa) and excellent chemical durability, especially against acid solutions. These properties are even better than those of the commercial glass-ceramics [16]. Their appearances showed shiny white and a smooth surface. All of these properties make them favorable candidate for building materials.

In the preparation of drinking water, a considerable amount of sludge is generated during flocculation, precipitation and filtration of the water. Although this sludge is used as for soil improvement, and in brick and cement, about one-third is still not re-used at Tokyo. The main constituents of the sludge are SiO_2 and Al_2O_3 with a minor component of Fe_2O_3, making it a potential raw material for the preparation of glass-ceramics.

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In this work, glass-ceramics were prepared from water treatment sludge with added $CaCO_3$ and waste soda-lime glass. The mechanical properties, thermal behavior, chemical durability, etc. were determined and compared with the other reported glass-ceramics.

2. Experimental

2.1. Preparation of glass-ceramics

The starting materials were sludge generated during the purification of drinking water from river water at the Asaka plant, Tokyo, Japan, $CaCO_3$ (Wako Chemicals) and waste soda-lime glass. The batch composition, prepared by mixing 36.4 mass% of the sludge with 43.3 mass% of $CaCO_3$ and 20.3 mass% of waste glass, was chosen on the basis of the eutectic composition (CaO 38, Al_2O_3 20 and SiO_2 42 mass%) in the $CaO–Al_2O_3–SiO_2$ system [17]. The starting materials were mixed by wet ball milling for 24 h and dried at 110 °C overnight. The dried powder mixtures were melted at 1300 °C for 2 h in a Pt crucible and water-quenched to obtain granular glass. Glass powder samples were obtained by grinding in an alumina ball mill and sieving to <100 mesh. Pellets (10 mm in diameter) for the crystallization experiments and testpieces (5 mm × 4 mm × 40 mm) for property measurements were formed by uniaxial pressing at 98 MPa. The pellet samples were fired at 700–1200 °C for 1 h by inserting them in a preheated furnace, whereas the testpiece samples were fired at 700° (glass sample) and 1000 °C (glass-ceramic sample) for 1 h at heating and cooling rates of 5 °C/min.

2.2. Characterization

The chemical compositions of the samples were determined by X-ray fluorescence (RIX2000, Rigaku). X-ray measurements were performed using monochromated Cu Kα radiation (LaX XRD-6100, Shimadzu) to identify the crystalline phases. The glass transition temperatures and crystallization temperatures were determined by DTA (Thermoplus, Rigaku) at a heating rate of 10 °C/min. The linear thermal expansion coefficients of the samples were measured using a dilatometer (TMA8310, Rigaku). The sample sizes were 5 mm × 4 mm × 12 mm and the measurements were performed at 25–600 °C. The bulk densities of the samples were measured by the Archimedes method using water.

The four-point bending strengths of the as-prepared samples were measured on unpolished testpieces using a universal testing machine (AUTOGRAPH DCS-R-10TS, Shimadzu) at a crosshead speed of 0.5 mm/min. The average bending strength was obtained from measurements of 11 samples. The microhardness of the samples was measured using a Vickers tester (MHT2, Matsuzawa Precision Machine) on samples polished using SiC powder (6000 mesh) with an indentation of 9.8 N for 15 s. The average value was obtained from 14 indentations.

The chemical resistance of the samples was examined in acid and alkali solutions. The size of the samples was about 4.5 mm × 3.5 mm × 14 mm and the surfaces were polished using SiC powder (6000 mesh). Five pieces of sample were immersed in 100 ml of 1 mass% H_2SO_4 (about 0.1 mol/l) or 1 mass% NaOH (0.25 mol/l) at 90 °C for 24 h [16]. The samples were washed with de-ionized water, dried at 110 °C overnight and weighed. The chemical durability of the samples was determined as the weight difference before and after the chemical leaching. The microstructures of the samples were observed using a SEM (JSM-5310, JEOL) at an accelerating voltage of 15 kV. The microstructures of the samples after the chemical tests were also observed by SEM.

3. Results and discussion

3.1. Glass-ceramics

The chemical compositions of the raw materials of sludge and waste glass are listed in Table 1. The major components of the sludge are SiO_2 and Al_2O_3, totaling about 85 mass%. The remaining components are Fe_2O_3 and 1–2 mass% MgO, P_2O_5, MnO, CaO, K_2O and Na_2O. The chemical composition of the sludge is known to show considerable seasonal changes towards more SiO_2 rich compositions. Since the sludge cannot be melted at <1500 °C, it was mixed with additives to lower the melting temperature. $CaCO_3$ and waste glass were selected as the additives. As listed in Table 1, the waste glass contains not only CaO but also Na_2O, which is effective in lowering the melting temperature. The mixing ratio of these starting materials, abovementioned, was chosen to bring the chemical composition to one of the eutectic temperatures (1265 °C) of the $CaO–Al_2O_3–SiO_2$ system [17]. This eutectic point was chosen rather than the other eutectic point (CaO 23, Al_2O_3 15 and SiO_2 62 mass%) with a lower melting temperature of 1170 °C to facilitate bulk crystallization and produce more crystalline phases.

The mixture was fired at 1200–1500 °C to check for melting. Complete melting was observed from 1300 °C but the melt could not be cast even from 1500 °C due to its high viscosity. Therefore, glass cullet was produced by water quenching. The chemical composition of the resulting glass is listed in Table 1 showing good agreement with the calculated value. The DTA curve of the glass sample showed a glass transition temperature at 615 °C, two exothermic peaks at 930 and 986 °C corresponding to crystallization, and endothermic peaks at 1210 and 1228 °C corresponding to melting. These temperatures are lower than those found for the Kira based glass-ceramics [13–15]. The glass samples heated at various temperatures gave the partial XRD patterns shown in Fig. 1. Crystallization was observed from 900 °C, producing crystalline gehlenite ($Ca_2Al_2SiO_7$) as the major phase and wollastonite ($CaSiO_3$) as the minor phase. The formation of these crystalline

Table 1
Chemical compositions of raw materials and resulting glass-ceramics

Sample	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	MnO	P_2O_5
Sludge	45.0	39.6	1.5	1.8	1.1	1.5	6.1	1.6	1.7
Waste glass	73.3	2.1	11.0	0.04	13.5	–	0.02	–	–
Glass-ceramics	38.9	16.2	35.6	0.9	3.6	0.7	2.9	0.7	0.7