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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 cross-head 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, above-mentioned, 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

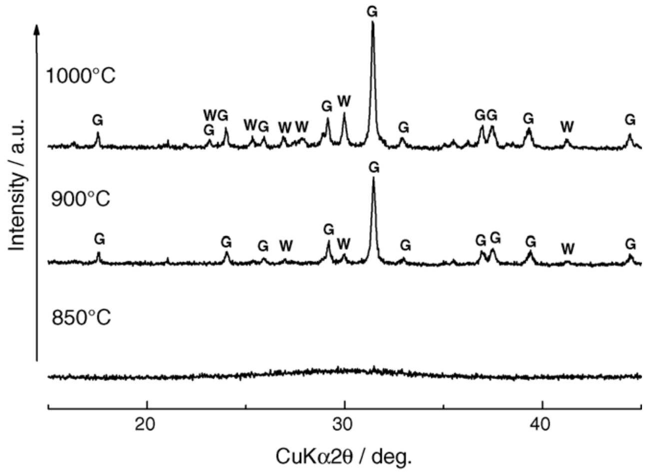

Fig. 1. XRD patterns of samples fired at various temperatures. G: gehlenite, W: wollastonite.

phases is thought to correspond to the two exothermic peaks in the DTA curve. The amounts of the crystalline phases increased up to 1000 °C but gradually decreased above this temperature. The crystallization of the resulting glass cullet was found to involve surface crystallization rather than bulk crystallization even if the glass containing considerable amounts of impurity components and graded the composition as modifier-rich. It is, therefore, necessary to use nucleating agents (e.g. TiO_2, ZrO_2, FeS) to cause bulk crystallization [18].

The photographs of the samples fired at various temperatures are shown in Fig. 2. The color of the samples was dark brown up to 700 °C and this changed to black at 800 °C due to densification of the glass by a viscous flow mechanism. The densification is apparently observed from the shrinkage of the 800 °C sample compared with the 700 °C sample. The black color changed to brown with higher firing temperature $\geq$900 °C. This change is related to crystallization of colorless phases in the black colored glass matrix, which then cause light scattering at the grain boundaries. The sample surface becomes smooth and shiny after densification and its shape becomes rounded at higher firing temperatures.

3.2. Properties of the glass-ceramics

The various properties of the present glass (fired at 700 °C) and glass-ceramics (fired at 1000 °C) are listed in Table 2 together with those reported for Kira-$CaCO_3$ [13], Kira-dolomite [14], Kira-paper sludge [15] and commercial glass-ceramics (NEOPAIRES; [16]). Compared with the data reported for the other materials, the present glass-ceramic sample has a higher bulk density, bending strength and chemical durability for alkali solution. By contrast, the hardness, thermal expansion coefficient and chemical durability for acid solution is poorer.

The bending strength of the present glass-ceramics is 99 MPa and is relatively high compared with those of the other glass-ceramics similarly prepared using glass powders listed in Table 2. The microstructure of the fractured surface of the sample fired at 1000 °C is shown in Fig. 3. Small crystals <5 μm are randomly dispersed in the glassy matrix and this microstructure is quite different from the Kira-$CaCO_3$

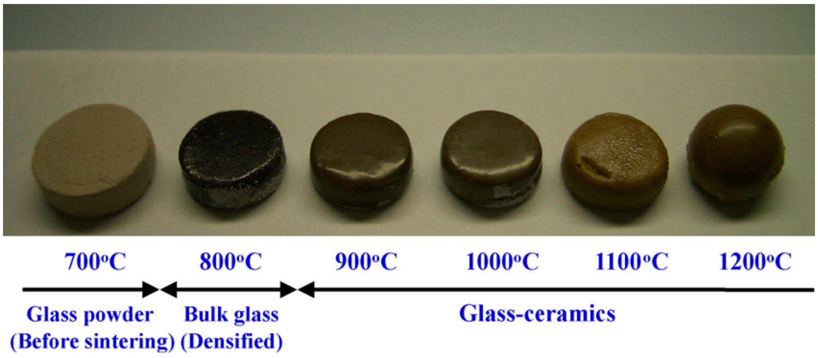

Fig. 2. Photographs of samples fired at various temperatures.

Table 2
Various properties of the present glass and glass-ceramics and reported glass-ceramics

Property	Glass (700 °C)	Glass-ceramics (1000 °C)	Kira-$CaCO_3$ [13]	Kira-Dolomite [14]	Kira-Paper sludge [15]	NEOPAIRES [16]
Density (g/cm^3)	2.83	2.81	2.56	–	2.46–2.50	2.7
Bending strength (MPa)	70(11)*	99(13)	81(8)	73(14)–130(14)	63(5)–66(3)	50
Vickers hardness (GPa)	6.5(14)	5.2(7)	6.6(3)	7.4(8)–7.6(5)	6.0(1)–6.4(3)	5.2
Thermal expansion coefficient ($\times10^{-6}$/K)	8.5	7.2	5.2	4.7–6.7	6.3–8.1	6.1
Acid weight loss (mg/cm^2)	41.0(13)	17.7(25)	0.31(2)	0.4–1.3	4.7(4)–8.4(2)	3.4
Alkali weight loss (mg/cm^2)	0.91(5)	0.23(5)	1.60(3)	1.4–2.3	0.71(2)–0.85(4)	1.3

* The numbers in parentheses represent the standard deviation in the last decimal place.

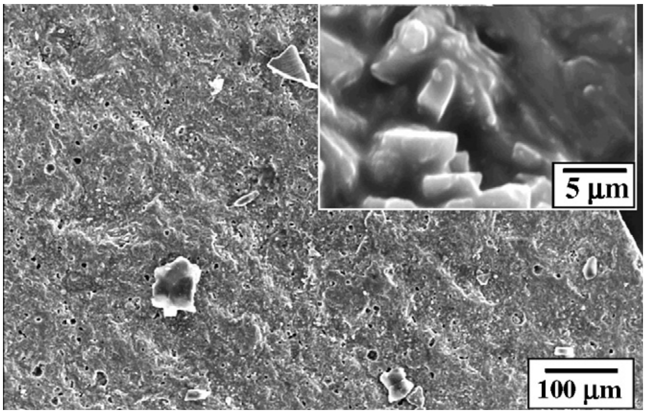

Fig. 3. SEM micrograph of fractured surface of the glass-ceramics.

glass-ceramics [13], radially aligning large needle-like crystals. The difference in the microstructures is suggested to be the reason for difference in their bending strengths. The Vickers microhardness of the present glass-ceramics is 5.2 GPa and is slightly lower than those of the other glass-ceramics listed in Table 2. The reason may be related to the difference of the microstructures because there is little difference in the hardness of the major crystalline phases of gehlenite in the present glass-ceramics and wollastonite in the other glass-ceramics in Table 2.

The thermal expansion coefficient of the present glass-ceramics is 7.2×10^{-6}/K, relatively high compared with the other glass-ceramics listed in Table 2. This is due mainly to higher content of glass modifiers of the present sample, which causes the glassy phase higher thermal expansion. The higher glass modifier content also causes high Ca crystalline phase gehlenite, having high thermal expansion.

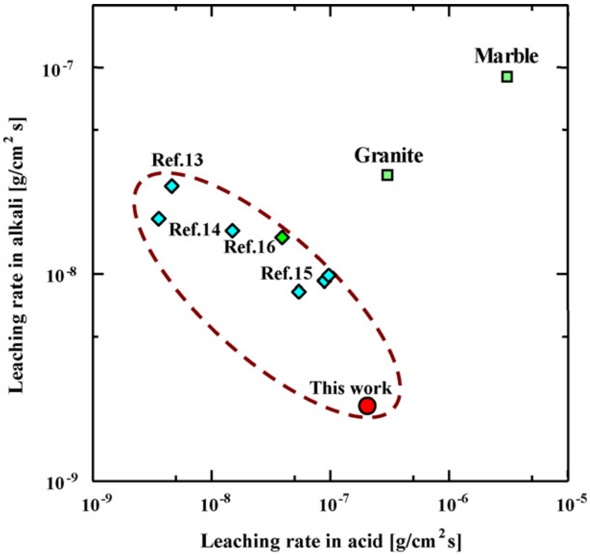

Fig. 5. Relationship between leaching rates of the glass-ceramics and natural stones (granite and marble) in acid and alkali solutions.

The chemical durability of glass-ceramics is evaluated from the weight losses after leaching in acid and alkali solutions. The weight losses of the present glass-ceramics are 17.7 and 0.23 mg/cm^2, respectively. The weight loss in acid is about several tens of that in alkali, indicating lower chemical durability to acid than to alkali. The reported weight losses in commercial NEOPAIRES materials are 3.4 and 1.3 mg/cm^2 for acid and alkali, respectively; the present glass-ceramics thus have apparently lower chemical durability to acid but higher durability to alkali. The microstructures of the samples after the chemical tests are shown in Fig. 4. The acid-treated sample shows formation of a leached layer several micrometers in thickness. This is formed by dissolution of the surface of the sample and precipitation of amorphous silica due to the low solubility in acid. Therefore, the chemical durability of this sample in acid solution should be lower than the evaluation from the weight loss. By contrast to poor chemical durability to acid, the chemical durability to alkali is excellent and the highest durability among the glass-ceramics listed in Table 2. These properties are thought to be due mainly to the chemical composition of the present samples, which are higher in glass modifier components and Fe_2O_3. As shown in Fig. 5 (converted to leaching rate), the chemical durability of the glass-ceramics to acid and alkali is found to be a trade-off relationship.

Comparing the data for the present glass and glass-ceramic samples in Table 2, some unique results are observed; the glass-ceramic sample shows a lower bulk density, hardness and thermal expansion than the glass sample. The slightly lower bulk density and thermal expansion coefficient is due mainly to the generation of closed pores in the microstructure by expanding of the closed pores. The lower hardness is thought to be due to the lower hardness of the resulting crystalline phases. On the other hand, crystallization produces better mechanical strength and chemical durability. Especially this last result makes the glass-ceramic a more suitable material than the glass for applications as building materials.

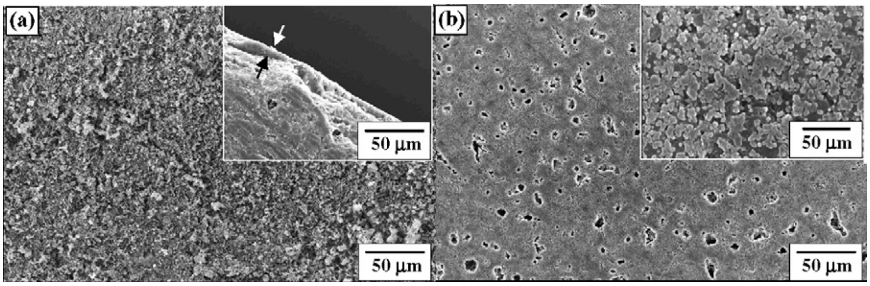

Fig. 4. SEM micrographs of the surfaces of the samples after leaching in acid (a) and alkali (b) solutions.

4. Conclusions

Glass-ceramics were prepared from water-treatment sludge mixed with $CaCO_3$ and waste glass. The following results were obtained:

1. The glass-ceramics could be prepared by melting the powder mixture at 1300 °C and re-firing the resulting powdered sample above 900 °C.
2. The resulting glass-ceramics showed a brown color due to the significant Fe_2O_3 content and also the presence of a small amount of MnO.
3. The glass-ceramics prepared at 1000 °C showed good mechanical strength (about 100 MPa) and excellent chemical durability in alkali solution.

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