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Preparation and properties of glass-ceramics from wastes (Kira) of silica sand and kaolin clay refining

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Abstract

Glass-ceramics were prepared from wastes generated from refining of silica sand and kaolin clay, called Kira. Several kinds of Kira were melted at 1300–1550 °C with additions of $CaCO_3$ and quenched in air or water to obtain glasses. The quenched glasses were ground to <48 mesh and used to prepare glass-ceramics. Crystallization of the parent glass occurred above 950 °C, producing wollastonite as a major crystalline phase which gradually transformed to pseudowollastonite above 1150 °C. The macroscopic appearance of the samples changed from transparent pale green glass to smooth-textured shiny white upon crystallization. The thermal expansion coefficient of the glass-ceramics was $5.2\times10^{-6}/°C$ (30–380 °C). The four-point bending strengths of the as-fired glass-ceramics ranged from 76 to 86 MPa. Vickers microhardness was found to be 6.6–7.5 GPa. Since the chemical durability for acid and alkali was excellent in these glass-ceramics, they are considered to be candidates for applications such as building materials, ceramic tiles, etc.

Keywords: Glass-ceramics; Kaolin clay waste; Mechanical properties; Silica sand waste; Waste materials

1. Introduction

Seto (Aichi)-Tajimi (Gifu) has long been one of the famous porcelain production areas in Japan. The development of porcelain industries in that area is related to local availability of good clay resources. Large amounts of silica sand and kaolin clay are mined every year. This production is accompanied by the generation of wastes mainly during the refining processes. These wastes are called Kira and the amount is estimated to be about 500,000 t per year in the Seto area alone. Although porous ceramics, bricks, tiles, etc. have been produced on a trial basis using Kira as the raw material, almost all of the Kira is merely re-buried, consuming a large energy and money. It is therefore highly desirable to develop effective usage of these Kira wastes.

Glass-ceramics are very useful in various applications such as building materials, cooking ceramics, machinable ceramics, bio-ceramics, optical materials, etc.[1,2] Since the main constituents are SiO_2, Al_2O_3, CaO and/or MgO, many inorganic wastes are potential starting materials. Recently, many studies have been reported using various wastes as starting materials for glass-ceramics, e.g. slags,[3] coal ash,[4,5] incinerator ash,[6,7] waste glass and shell,[8] phosphorous fertilizer and oil shale ash,[9] etc. However, these wastes contain relatively high contents of Fe_2O_3 and/or TiO_2. The resultant glass-ceramics are therefore colored, with a resultant decrease in their applications. Kira mainly consists of quartz, kaolinite and/or mica (sericite), and contains only small amounts of coloring components such as Fe_2O_3 and TiO_2. It is therefore considered that Kira is a more suitable raw material for glass-ceramics than the other various wastes studied to date.

In this work, glass ceramics were prepared using Kira as the major raw material with added $CaCO_3$ and their mechanical properties, chemical durability, etc. were determined.

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2. Experimental

2.1. Starting materials

Since Kira is generated during the various refining processes of silica sand and kaolin clay production, five typical samples were collected. Kira samples Nos. 1, 4 and 5 were wastes generated in the refining of kaolin clay. Sample No.1 was the waste generated before elutriation while samples No.4 and 5 were the residues after recovery of the kaolin clay. Sample No.5 was a mixture of the residue with a small amount of cement added to solidify the waste. Samples No.2 and 3 were residues from the refining of silica sand.

2.2. Preparation of glass ceramics

Based on the eutectic composition in $CaO–Al_2O_3–SiO_2$ system,[10] batch compositions were prepared by mixing 62.7 mass% of Kira with 37.3 mass% of $CaCO_3$ (Wako Pure Chemicals), corresponding to 25 mass% CaO. Kira and $CaCO_3$ powders were mixed by wet ball milling for 24 h and dried at 110 °C overnight. The dried powder mixtures were calcined at 900 °C to decompose the $CaCO_3$. They were then fired at 1300–1550 °C for 2 h and air quenched to examine temperature conditions of glass formation. Glass powder samples were prepared from the granular glass by quenching the 1400 °C melt in water.

Glass-ceramics were prepared using the glass powder from the Kira sample No.3 and $CaCO_3$. The glass powder was ground in a ball mill and sieved <100 mesh for determination of the crystallization conditions and to <48 mesh for preparation of test pieces to determine the properties of the glass-ceramics. Pellets (10 mm in diameter) used in the crystallization experiments and test pieces ($5\times4\times40$ mm^3) used for property measurements were formed by uniaxial pressing at 98 MPa. The pellet samples were fired at 900–1250 °C for 1 h by inserting in a pre-heated furnace while the test piece samples were fired at 950° and 1000 °C for 1, 2 and 4 h at heating and cooling rates of 5 °C/min.

2.3. 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 (Lab X XRD-6100, Shimadzu) to identify and quantitatively analyze the crystalline phases using a conventional calibration method. The glass transition temperature and crystallization temperature were obtained from DTA analysis (Thermoplus, Rigaku) at a heating rate of 10 °C/min. The linear thermal expansion coefficient of the glass-ceramics (1000 °C for 1 h) was analyzed using a dilatometer (TMA8310, Rigaku). The sample size was $4.1\times5.3\times12.9$ mm^3 and the measurement was performed at 25–450 °C. The density of the glass-ceramics (fired at 1000 °C for 1 h) was measured by the Archimedes method using water.

The four point bending strengths of the as-prepared glass-ceramics 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 reasons to use unpolished testpieces are to avoid chipping by the polishing because the samples contain high content of glassy phase and to obtain strength data of as-produced samples considering actual use as building materials. The average bending strength was obtained from measurements of 11 samples. The microhardness of the glass-ceramics was measured using a Vickers tester (MHT2, Matsuzawa Precision Machine) on samples polished using SiC powder (6000 mesh) with an indention of 9.8 N for 15 s. The average value was obtained from 11 indentations.

The chemical resistance of the glass-ceramics (1000 °C, 1 h) was examined in acid and alkali solutions. The size of the samples was $3.5\times4.5\times13$ mm^3 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. The samples were washed with de-ionized water, dried at 110 °C overnight and weighed. The chemical durability of the glass-ceramics was determined as the weight difference before and after the chemical leaching.

The microstructure of the glass-ceramics was observed using a SEM (JSM-5310, JEOL) at an accelerating voltage of 15 kV. The samples were polished using SiC powder (8000 mesh) and chemically etched for 1 min in 1 mass% HF (0.5 mol/l). The microstructures of the samples after the chemical tests were also observed by SEM.

3. Results and discussion

3.1. Starting materials

The chemical compositions of the five Kira samples are listed in Table 1. The chemical compositions of the

Table 1
Chemical compositions of Kira samples (dry weight basis, mass%)

Sample	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O
Kira 1	88.8	7.4	0.1	0.2	tr	0.1	3.2	0.1
Kira 2	82.4	13.4	Tr	0.3	Tr	Tr	3.5	0.3
Kira 3	79.0	16.7	Tr	0.5	0.1	0.2	3.3	0.1
Kira 4	69.1	24.7	0.5	0.5	0.1	Tr	4.6	0.2
Kira 5	67.6	25.2	0.2	0.5	1.4	0.2	4.5	0.3

samples vary considerably according to their origin, but the composition variation in each Kira type is relatively small. In all the Kiras, the major components are SiO_2 (67.6–88.8 mass%) and Al_2O_3 (7.4–25.2 mass%), totaling >95 mass%. The remaining components are K_2O and <1 mass% Fe_2O_3 and TiO_2. Variations in the compositions of the five Kiras occur only in SiO_2/Al_2O_3 mole ratio which varied from 4.6 in sample No.5 to 20.4 in sample No.1. A slightly higher CaO content in sample No.5 results from the addition of cement to the waste, as in sample No. 4, but the effect on the overall chemical composition is relatively small.

The XRD patterns of the Kira samples are shown in Fig. 1. The crystalline phases are similar in all the samples, being mainly quartz with minor amounts of kaolinite, feldspar and mica. The increase in Al_2O_3 content from Nos.1 to 5 corresponds to an increase in the kaolinite XRD peaks and a decrease in the quartz peaks.

3.2. Glass-ceramics

The appearance of the mixed powder samples fired at various temperatures is listed in Table 2. Samples No. 2–4 melt to form glass above 1300 °C but the sample No.1 did not melt even at 1550 °C. This indicates that all the samples except No.1 are suitable as raw materials for glass–ceramics. The DTA curves of the glass powder samples No. 2–4 are shown in Fig. 2. The glass transition (T_g) temperatures of these samples were 739, 739, 745 and 745 °C, respectively. The base lines of the DTA curves decrease steeply at about 870–900 °C, thought to be caused by shrinkage of the samples due to sintering by a viscous flow mechanism. Exothermic peaks due to crystallization are observed at 1011, 1020, 1036 and 1027 °C in samples Nos. 2–5, respectively. The exothermic peaks of samples No. 2–4 are relatively broad while that of the sample No. 5 is sharp and intense. Crystallization treatments were therefore performed at $\geqslant 850$ °C, chosen on the basis of these DTA results.

Sample No. 3 was selected as the raw material for glass-ceramics preparation. The glass powders were pressed into pellets and fired at various temperatures. The photographs and XRD patterns of the samples are shown in Figs. 3 and 4, respectively. The sample fired at 850 °C did not densify well and it is amorphous according to its XRD pattern. By contrast, many peaks are observed in the XRD patterns of the samples fired above 950 °C indicating the formation of crystalline phases. The surface of these pellets has also become shinny and smooth. The shape of the glass-ceramics samples deforms to become more rounded at higher firing temperature. This may be relating to the lowering of the viscosity of the glassy phase in the matrix and the samples deformed to sphere shape to minimize surface area of the samples. The surfaces of these fired samples are very smooth. The crystalline phase formed at 950–1100 °C is wollastonite (the low temperature phase of $CaSiO_3$), gradually transforming to pseudowollastonite (the high temperature phase of $CaSiO_3$) at $\geqslant 1150$ °C, the vicinity of the phase transition temperature.[11] The

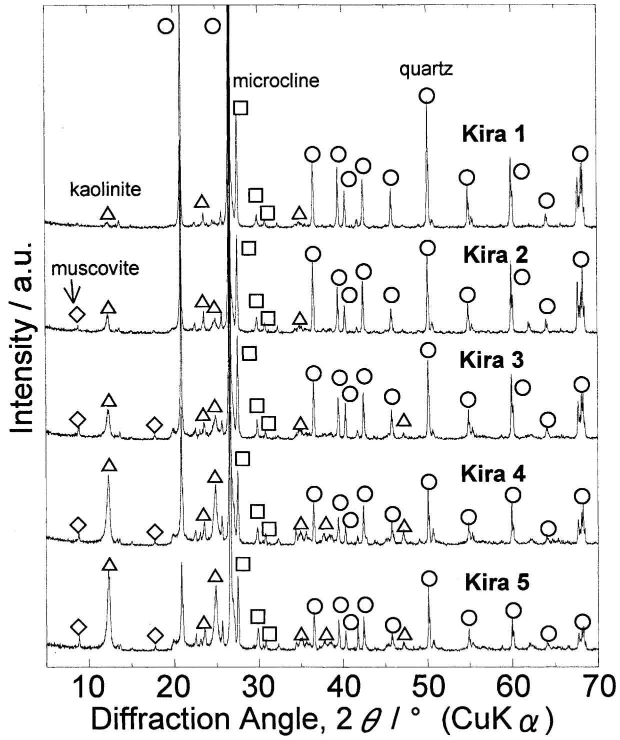

Fig. 1. XRD patterns of the five Kira samples.

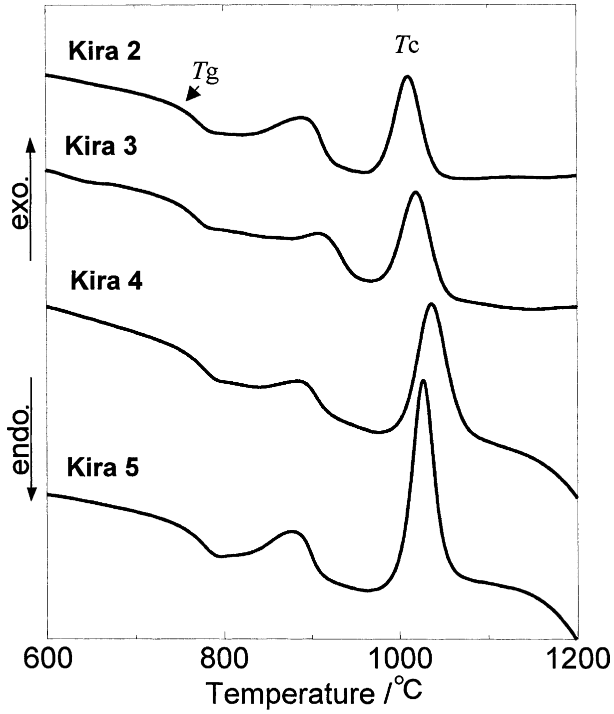

Fig. 2. DTA curves of the glass powder samples.

chemical composition of this sample suggests that anorthite ($CaAl_2Si_2O_8$) should be formed, but this is not detected under the present firing conditions.

To determine various properties of the glass-ceramics, samples were prepared by firing the glass powder ($\leqslant$48 mesh) at 950 and 1000 °C for 1, 2 and 4 h. The amounts of crystalline phases in these samples are listed in Table 3. The main crystalline phase is wollastonite but a small amount of pseudowollastonite is also present. This result is inconsistent with the crystalline phase observed in the glass-ceramics prepared from <100 mesh glass powder. This result may be related to the difference of particle size and distribution between the two samples but the reason is not clear at present. More detailed examination using samples with different particle sizes is necessary to clear this unusual result. With longer firing times, the amount of wollastonite increased but pseudowollastonite decreased. This is because the former is the stable phase but the latter is a metastable phase at these firing temperatures. The total amount of crystalline phases increases slightly at longer firing times from 42 to 61 mass% in the 950 °C samples and from 55 to 64 mass% in the 1000 °C samples.

The SEM micrograph of the surface of the glass-ceramics (1000C for 1 h) polished and chemically etched with HF is shown in Fig. 5. The many needle-like pores observed in the surface are thought to correspond to selectively leached crystals of wollastonite which occur in a characteristic needle-like habit reflecting the character of their crystal structure.[12] These needle-like pores are aligned radially and this texture is thought to result from crystal growth from the surface to the center of the glass particles. Careful inspection of the SEM micrograph allows the pseudomorphs of the original glass particles to be identified in the microstructure.

3.3. Properties of the glass-ceramics

The various properties of the resultant glass-ceramics are listed in Table 3 and compared with the commercial NEOPARIE glass-ceramics.[13] The bending strengths of the present glass-ceramics range from 76 to 86 MPa but these strengths show no apparent relationship with the sample preparation conditions. Although these bending strengths are lower than those of glass-ceramics prepared by bulk crystallization method (>100 MPa),[6,13] they are relatively high compared with other glass-ceramics similarly prepared from glass powder (mostly >50 MPa).[4,7,13–15] Summarizing these reported data, a trend is observed between the bending strength and chemical composition of these materials, i.e. the strength increases with higher SiO_2 content. Even though the present strengths were measured on unpolished samples, (expected to be of lower strength than for polished samples), the bending strengths of the present glass-ceramics are considerably higher than expected from the relationship between strength and SiO_2 content observed for the reported glass-ceramics. One possible

Table 2
Appearance of samples after firing at various temperatures[a]

Sample	Temperature (°C)				
	1300	1350	1400	1500	1550
1	–	–	–	x	x
2	x	O	O	O	–
3	Δ	O	O	O	–
4	O	O	O	O	–

[a] O: transparent, Δ: translucent, x: not melt, –: no data.

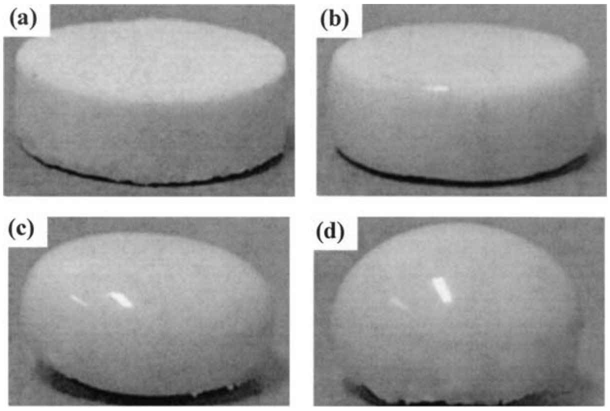

Fig. 3. Photograph of the samples fired at 850 (a), 1000 (b), 1150 (c) and 1250 °C (d) for 1 h.

Table 3
Various properties of the present glass-ceramics

Properties	950 °C 1 h	950 °C 2 h	950 °C 4 h	1000 °C 1 h	1000 °C 2 h	1000 °C 4 h
Wollastonite content [mass%]	31	50	52	43	51	55
Pseudowollastonite content [mass%]	11	11	7	12	9	9
Bending strength [MPa]	84(8)[a]	80(10)	76(11)	81(8)	80(11)	86(10)
Vickers hardness [GPa]	6.9(5)	7.5(3)	7.5(2)	6.6(3)	6.7(2)	6.8(3)
Weight loss in acid [mg/cm^2]	–	–	–	0.31(2)	–	–
Weight loss in alkali [mg/cm^2]	–	–	–	1.60(3)	–	–
Linear thermal expansion [$\times10^{-6}$/°C]	–	–	–	5.2	–	–
Density [g/cm^3]	–	–	–	2.56	–	–

[a] The numbers in the parentheses represent standard deviation in the last decimal place.

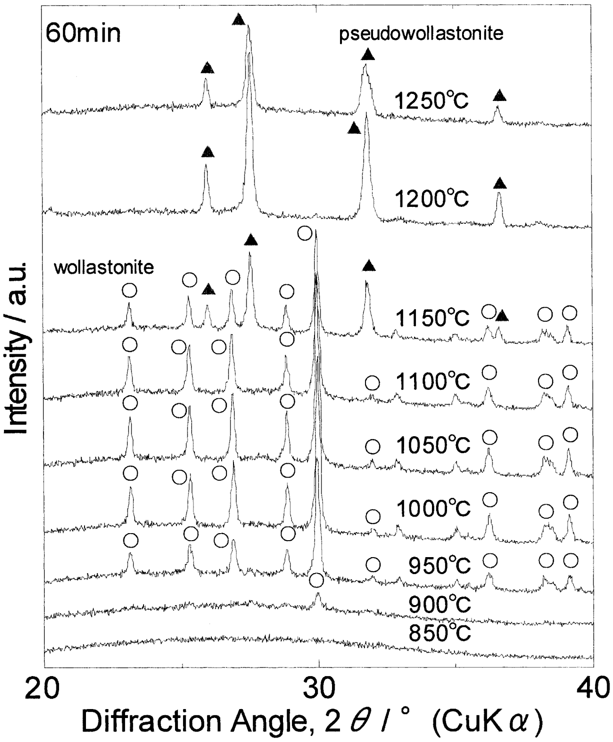

Fig. 4. XRD patterns of the pellet samples after firing at various temperatures for 1 h.

reason for this enhancement of strength is the effect of particle size of the glass powder used for the preparation of the glass-ceramics. In the present study the glass powder was ground by ball mill to <48 mesh and contained a relatively high content of small particles, providing a particle size distribution with decreases the defect size in the glass-ceramics. The other possible reason is the difference of the contents of minor components (Fe_2O_3, B_2O_3, Na_2O etc) in the samples because these components are considered to work to lower the strength.

The Vickers microhardness values of the present glass-ceramics range from 6.6 to 7.5 GPa and show little variation with different preparation conditions. The microhardness values of the 950 °C samples are a little higher than those of the 1000 °C samples. Since the total amount of crystalline phases does not vary greatly between these samples, smaller crystalline grains as well as finer microstructure may be the explanation for this observation. The microhardness of the present glass-ceramics is somewhat higher than previously reported[4,7,13] for reasons similar to those advanced for bending strength differences.

The chemical durability of glass-ceramics, especially in acid conditions, is important if the materials are to be considered as potential building materials because acid rain is becoming an increasing serious problem in a number of countries. The weight losses of the present glass-ceramics after leaching in acid and alkali solutions are 0.3 and 1.6 mg/cm^2, respectively. The weight loss in acid is about 1/5 of that in alkali, indicating higher chemical durability to acid than to alkali. The reported weight losses in NEOPAIRE materials are 3.4 and 1.3 mg/cm^2 for acid and alkali respectively; the present glass-ceramics thus have significantly higher chemical durability to acid but slightly lower durability to alkali. The microstructures of the samples after the chemical tests are shown in Fig. 6. The acid-leached sample contains needle-like pores distributed nonuniformly and concentrated in some regions. These pores are thought to be generated by selective leaching of the crystalline $CaSiO_3$ phases which are more soluble in acid than the glassy matrix. Since this matrix consists of a glassy phase with high durability in acid, the degree of leaching is low and results in excellent chemical durability to acid. On the other hand, the glassy phase is more soluble in alkali than in acid. The greater weight loss in alkali is therefore attributed to dissolution of the glassy phase. In the alkali-treated sample, shallow dimples were observed in some regions rather than the needle-like small pores found in the acid-treated sample. These dimples were formed only under alkali treatment and were not uniformly distributed in the sample. Leaching occurs in the glassy matrix rather than in the crystalline phases in this case. Thus, once preferential leaching starts in one region, it enhances leaching of the surrounding area to form a dimple. The leaching continues preferentially in the matrix. Increased durability to alkalis may be achieved by lowering the solubility of glassy phase by changing the chemical composition of the system.

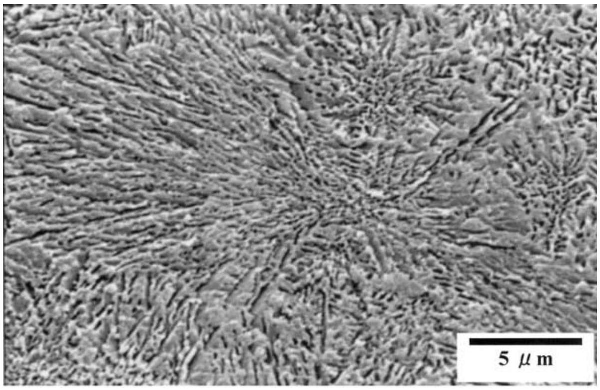

Fig. 5. SEM micrograph of surface of the glass-ceramics (1000C for 1 h) polished and chemically etched in HF.

The thermal expansion coefficient of the present glass-ceramics is 5.2×10^{-6}/°C, a little lower than that of NEOPARIE materials (6.2×10^{-6}/°C).[13] This difference may be due to differences in Al_2O_3 content of the glasses; this component is well known to decrease the thermal expansion and grain size of the crystallized wollastonite, which has a higher thermal expansion than glass. The present thermal expansion is also low compared to the values reported for various glass-ceramics,

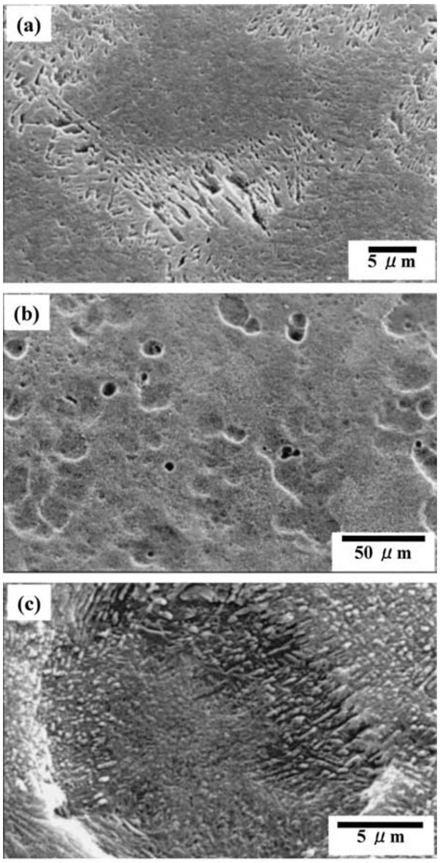

Fig. 6. SEM micrographs of surfaces of the glass-ceramics after chemical treatment in H_2SO_4 (a) and NaOH (b and c).

giving the present materials an enhanced ability to suppress thermal stress in applications involving repeated temperature variations as with building materials.

4. Conclusion

Glass-ceramics were prepared from wastes generated from silica sand and kaolin clay refining (so-called Kira) with added $CaCO_3$ as a fluxing agent. The following results were obtained.

1. Mixtures of Kira and $CaCO_3$ can be melted at <1500 °C, from which glass powder can be prepared by quenching the melt in water.
2. The glass transition temperatures of these melted samples range from 740 to 770 °C and wollastonite crystallizes at $\geqslant 950$ °C. The amounts of crystalline phase in the samples range from 40 to 60 mass%.
3. The resulting glass-ceramics were white in color and of smooth surface with a density of 2.56 g/cm^{-3}.
4. The four point bending strengths of the glass-ceramics range from 76 to 86 MPa and the Vickers microhardness ranges from 6.6 to 7.5 GPa.
5. The chemical durability of the glass-ceramics was higher for acid than for alkali.
6. The thermal expansion coefficient determined between 30 and 380 °C was 5.2×10^{-6}/°C and was relatively low compared with values reported for other glass-ceramics.

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