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Ceramics International 30 (2004) 983–989

CERAMICS INTERNATIONAL

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Preparation and properties of CaO–MgO–Al_2O_3–SiO_2 glass-ceramics from kaolin clay refining waste (Kira) and dolomite

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Received 1 September 2003; received in revised form 17 September 2003; accepted 5 November 2003

Abstract

CaO–MgO–Al_2O_3–SiO_2 glass-ceramics were prepared from mixtures of waste generated from refining of kaolin clay (called Kira) and dolomite ($CaMg(CO_3)_2$). Kira was mixed with dolomite in mass ratios of 65/35 (sample 1) and 75/25 (sample 2). They were melted at 1350 °C and quenched in water to obtain glasses. The quenched glasses were ground to $<$100 mesh and used to prepare glass-ceramics. Crystallization of the parent glass occurred above 900 °C, producing diopside ($CaMgSi_2O_6$) and anorthite ($CaAl_2Si_2O_8$) as major crystalline phases; diopside $>$ anorthite in sample 1 and anorthite $>$ diopside in sample 2. The macroscopic appearance of the samples changed from transparent pale green glass to smooth-textured shiny white upon crystallization. The four point bending strengths of the as-fired glass-ceramics were 130 MPa in sample 1 and 73 MPa in sample 2, which was approximately half of the value for sample 1. Vickers microhardness values were found to be 7.4 and 7.6 GPa in samples 1 and 2, respectively. The thermal expansion coefficients of the glass-ceramics prepared at 1000 °C for 1 h were $6.7 \times 10^{-6}\,°C^{-1}$ (30–380 °C) in sample 1 and $4.7 \times 10^{-6}\,°C^{-1}$ in sample 2. 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: C. Mechanical properties; D. Glass-ceramics; Kaolin clay waste; Dolomite; Chemical durability

1. Introduction

Large amounts of kaolin clay are mined for porcelain raw materials in Seto (Aichi)–Tajimi (Gifu), Japan because this clay shows very good plasticity. However, only the fine fraction is used as a raw material for porcelain; the coarse fraction representing the greater proportion, is wasted during the refining processes. This waste and waste generated from silica sand production are collectively called Kira, the total amount of which is estimated to be about 500,000 t per year in the Seto area alone. No effective uses for Kira have been found, though porous ceramics, bricks, tiles, etc. have been produced from it on a trial basis. Thus, almost all of the Kira is re-buried, consuming a large amount of energy and money. It is, therefore, highly desirable to develop uses for these Kira wastes.

Glass-ceramics are attractive materials used in various applications such as building materials, cooking ceramics, machinable ceramics, bio-ceramics, optical materials, etc. [1,2]. Since the main constituents of glass-ceramics are SiO_2, Al_2O_3, CaO, and/or MgO, many inorganic wastes are potential starting materials. Various wastes have been used, e.g. slags [3,4], coal ash [5,6], incinerator ash [7,8], waste glass, and shell [9], phosphorous fertilizer and oil shale ash [10]. Since these wastes generally contain relatively high contents of Fe_2O_3 and/or TiO_2, the resultant glass-ceramics are colored, limiting their potential applications.

Kira mainly consists of quartz, kaolinite, feldspar and/or mica (sericite), and contains only small amounts of coloring components such as Fe_2O_3 and TiO_2. It is, therefore, considered to be a more suitable raw material for glass-ceramics than other wastes studied to date. We prepared CaO–Al_2O_3–SiO_2 glass-ceramics from mixtures of Kira and $CaCO_3$ by melting at 1400 °C, quenching in water, and sintering and crystallizing the glass powder at 950–1200 °C [11]. Although the glass powder was colored pale green due to the small amounts of Fe_2O_3 and TiO_2 in the raw materials, the glass-ceramics obtained are shiny white in appearance. The glass-ceramics showed a high strength (about 80 MPa), high hardness (about 7 GPa) and

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doi:10.1016/j.ceramint.2003.11.005

good chemical durability, especially against acid solutions. They are, therefore, thought to be good candidates for various applications.

In this work, $CaO–MgO–Al_2O_3–SiO_2$ glass-ceramics were prepared using Kira as the major raw material with added dolomite ($CaMg(CO_3)_2$). Their mechanical properties, thermal properties, chemical durability, etc were determined.

2. Experimental

2.1. Preparation of glass-ceramics

The starting materials were Kira generated as a residue of kaolin clay refining, corresponding to sample no. 5 in ref. [11], and dolomite obtained from Akasaka, Gifu, Japan.

Based on the eutectic compositions in the $CaO–Al_2O_3–SiO_2$ system [12] and the $MgO–Al_2O_3–SiO_2$ system [12], batch compositions were prepared by mixing 65 mass% of Kira with 35 mass% of dolomite (sample 1) and 75 mass% of Kira with 25 mass% of dolomite (sample 2). The Kira and dolomite powders were mixed by wet ball milling for 16 h and dried at 110 °C overnight. The dried powder mixtures were calcined at 900 °C for 1 h to decompose the dolomite. They were then melted at 1350 °C for 2 h in a Pt crucible and water-quenched to obtain granular glass. Glass powder samples were prepared by dry ball milling and sieved to <100 mesh. Pellets (10 mm in diameter) used in the crystallization experiments and test pieces (5 mm × 4 mm × 40 mm) used for property measurements were formed by uniaxial pressing at 98 MPa. The pellet samples were fired at 850–1200 °C for 1 h by inserting in a preheated furnace while the test piece samples were fired at 1000 °C 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 (Lab X XRD-6100, Shimadzu) to identify and quantitatively analyze the crystalline phases using a conventional calibration method using Si powder as the standard. The glass transition temperature (T_g) and crystallization temperature (T_c) were obtained from DTA analysis (Thermo-plus, Rigaku) at a heating rate of 5 °C/min. The linear thermal expansion coefficients of the glass-ceramics (1000 °C, 1 h) were analyzed using a dilatometer (TMA8310, Rigaku). The sample size was about 4 mm × 5 mm × 13 mm and the measurements were performed at 25–500 °C. The thermal expansion coefficients of the glass-ceramics were calculated based on the temperature range from 30 to 380 °C.

The four point bending strengths of the as-prepared glass-ceramics (1000 °C, 1 h) were measured on unpolished as-produced test pieces using a universal testing machine (AUTOGRAPH DCS-R-10TS, Shimadzu) at a crosshead speed of 0.5 mm/min. The reason for using unpolished test pieces is to obtain the strength data from the as-produced samples such as are actually used as building materials and also to avoid chipping of the glassy-phase-containing samples by polishing. The average bending strength was obtained from measurements of 11 samples. The microhardness of the glass-ceramic was measured using a Vickers tester (MHT2, Matsuzawa Precision Machine) on samples polished using SiC powder (6000 mesh) using 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 sizes of the samples were about 4 mm × 5 mm × 13 mm and the surfaces were polished using SiC powder (8000 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).

3. Results and discussion

3.1. Glass-ceramics

The chemical compositions of the Kira and dolomite samples are listed in Table 1. The major chemical components of the Kira are SiO_2 (67.6 mass%) and Al_2O_3 (25.2 mass%), totaling >92 mass%. The remaining components are K_2O (4.5 mass%), CaO (1.4 mass%) and <1 mass% Fe_2O_3, Na_2O, MgO and TiO_2. Since the Kira is residue of kaolin clay refining, it is richer in Al_2O_3 and K_2O than other Kira wastes [11]. The major mineralogical constituents in the Kira are found by XRD to be quartz (SiO_2), kaolinite ($Al_2Si_2O_5(OH)_4$), microcline ($KAlSi_3O_8$) and muscovite ($KAl_2(Si_3Al)O_{10}(OH)_2$). The dolomite is monophasic according to XRD pattern, though its Ca/Mg molar ratio from the chemical analysis in Table 1 is about 1.9. Although this value is larger than unity it is within the reported composition range of dolomite solid solutions [13].

The granular glasses were transparent but pale green due to the small amount of Fe_2O_3 present. The chemical compositions of these glass samples are listed in Table 2 together with the data for $CaO–Al_2O_3–SiO_2$ glass prepared from mixtures of Kira and $CaCO_3$ [11]. Compared with the chemical composition of $CaO–Al_2O_3–SiO_2$ glass, the Al_2O_3 contents of the present glasses are higher while the SiO_2 contents are lower in sample 1 but higher in sample 2.

Table 1
Chemical compositions of starting materials Kira and dolomite (mass%)

Sample	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Ig. loss
Kira	67.6	25.2	0.2	0.5	1.4	0.2	4.5	0.3	0.2
Dolomite	0.4	0.1	Trace	0.1	36.9	16.2	Trace	Trace	46.3

Table 2
Chemical compositions of glass samples (mass%)

Sample	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O
Sample 1	52.9	16.2	Trace	0.4	17.7	9.5	3.1	0.2
Sample 2	60.4	17.9	Trace	0.5	11.6	5.3	4.1	0.2
Reference [11]	57.9	12.3	Trace	0.4	26.8	0.1	2.4	Trace

The DTA curves of the glass powder samples 1 and 2 are shown in Fig. 1. The glass transition (T_g) temperatures of these samples were 693 and 720 °C, respectively. The base line of the DTA curve of sample 1 decreases steeply at about 850 °C, thought to be caused by shrinkage of the samples due to sintering by a viscous flow mechanism, but this behavior is not observed in sample 2. Exothermic peaks due to crystallization are observed at 930 and 905 °C in samples 1 and 2, respectively. Endothermic peaks observed at 1220 and 1195 °C in these samples are attributed to melting of the samples. Crystallization treatments were, therefore, performed at 850–1200 °C, chosen on the basis of these DTA results.

The glass powders were pressed into pellets and fired at various temperatures. The photographs (sample 1) and XRD pattern of the sample are shown in Figs. 2 and 3, respectively. The sample fired at 850 °C showed sintering due to viscous flow of the compacted glass powder which had a glassy appearance, with a pale green color. The XRD of this sample shows a halo pattern (Fig. 3). By contrast, many peaks are observed in the XRD patterns of the samples fired at 1000 °C indicating the formation of crystalline phases. The appearance of this sample in Fig. 2 because shiny white with a smooth surface. The shape of these glass-ceramic samples becomes more rounded at higher firing temperatures due to the lowering of the viscosity of the glassy matrix phase. However, this deformation is apparently smaller than observed in $CaO–Al_2O_3–SiO_2$ glass-ceramics [11], which deformed to almost spherical shape to minimize the sample surface area. The crystalline phases formed in both samples are diopside ($CaMgSi_2O_6$) and anorthite ($CaAl_2Si_2O_8$). The amount of diopside is higher than anorthite in sample 1 but opposite in sample 2.

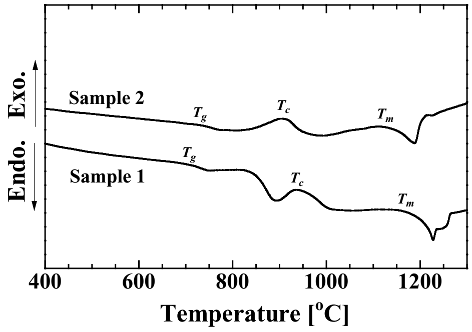

Fig. 1. DTA curves of glass samples 1 and 2.

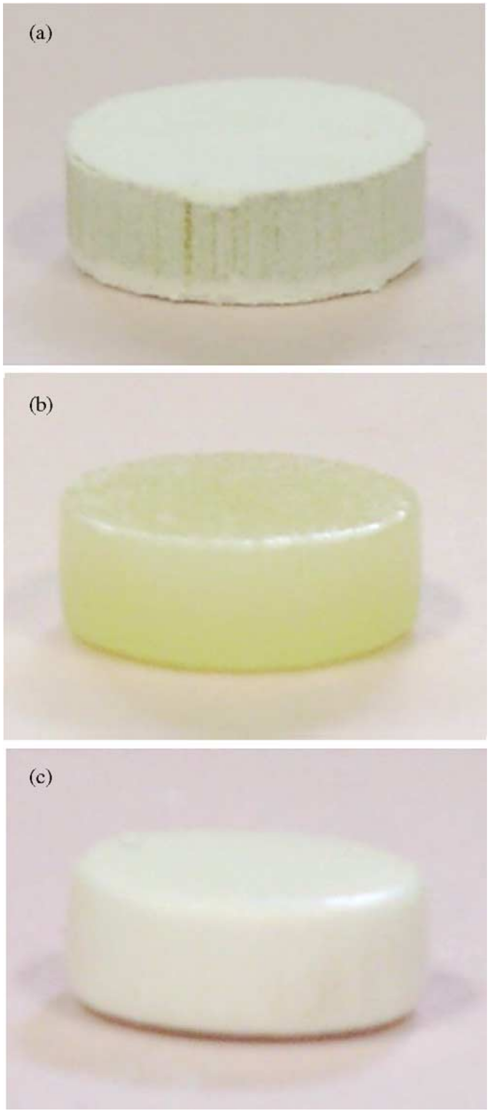

Fig. 2. Appearance of as-pressed sample 1 (a), those fired at 850 °C (b), and 1000 °C (c).

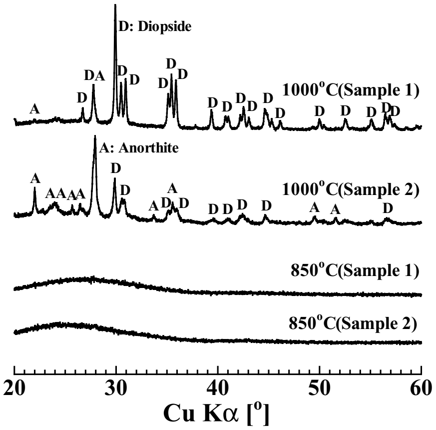

Fig. 3. XRD patterns of samples 1 and 2 fired at 850 and 1000 °C for 1 h.

Changes of the crystalline phase contents in the two samples fired for 1 h are shown in Fig. 4 as a function of firing temperature. Sample 1 starts to crystallize between 850 and 900 °C, with the amounts of diopside and anorthite increasing steeply up to 975 °C, becoming stable between 975 and 1100 °C, and decreasing above this temperature. The amounts of diopside and anorthite in sample 1 fired at 1000 °C for 1 h are 66 and 15 mass%, respectively. The total amount of crystalline phase in this sample (81 mass%) is apparently higher than that in CaO–Al_2O_3–SiO_2 glass-ceramics (55 mass%) [11]. This difference is the reason for the smaller deformation of this glass-ceramic compared with the CaO–Al_2O_3–SiO_2 glass-ceramics [11]. The crystallization temperature of sample 2 is slightly higher than that of sample 1 though the exothermic peak temperature of crystallization was higher in sample 1. The amounts of the two crystalline phases similarly increase steeply up to 975 °C and remain stable between 975 and 1100 °C. The amounts of diopside and anorthite in this sample fired at 1000 °C for 1 h are 24 and 51 mass%, respectively. The total amount of crystalline phase (75 mass%) is thus slightly lower than that of sample 1 but is still higher than that of CaO–Al_2O_3–SiO_2 glass-ceramics [11]. The higher total amount of crystalline phases in the present CaO–MgO–Al_2O_3–SiO_2 glass-ceramics compared with CaO–Al_2O_3–SiO_2 glass-ceramics [11] may be related to the content of MgO, which is believed to decrease the viscosity of the melt and enhance crystallization [14,15].

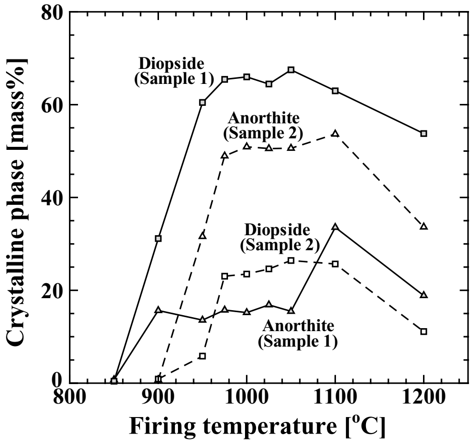

Fig. 4. Changes of the amounts of diopside (squares) and anorthite (triangles) in sample 1 (solid lines) and sample 2 (broken lines) as a function of firing temperature (for 1 h).

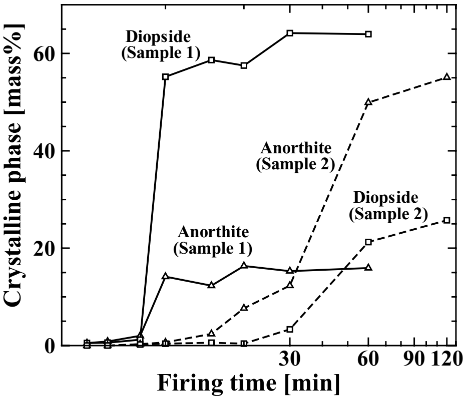

Fig. 5. Changes of the amounts of diopside (squares) and anorthite (triangles) in sample 1 (solid lines) and sample 2 (broken lines) as a function of firing time (at 1000 °C).

The samples were also fired at 1000 °C for various times to examine the dependence of crystallinity on firing time. Changes of the amounts of crystalline phases in these samples are shown in Fig. 5 as a function of firing time. An apparent difference in the crystallization rates is found between the two samples. Crystallization of sample 1 starts after a firing time of between 8 and 10 min, and the amounts of the two crystalline phases increase very steeply up to 10 min. By contrast, the crystallization of sample 2 starts similarly after firing for 10 min but the increase in the crystalline phases is very slow. Steep increases in the amounts of the two crystalline phases are observed between 30 and 60 min. The total amount of crystalline phase becomes almost constant after firing for only 10 min in sample 1 but a firing time of at least 1 h is necessary in sample 2. This difference is suggested to correspond to the difference in the crystallization rates of the major crystalline phases in these samples, i.e. diopside in sample 1 and anorthite in sample 2. A similar tendency was found in the crystallization of CaO–Al_2O_3–SiO_2 glass [11], i.e. a fast crystallization rate of wollastonite, which is of similar structure group to diopside but a slow crystallization rate of anorthite.

From the examination of the crystallization behavior of samples 1 and 2 as a function of temperature and firing time, the firing conditions to convert them to glass-ceramics were decided on, namely, a temperature of 1000 °C for 1 h.

The SEM micrographs of the surfaces of the glass-ceramics polished and chemically etched with HF are shown in Fig. 6. Many needle-like pores are observed in the surfaces. At first, these pores were thought to correspond to selectively leached crystals of diopside and/or anorthite as was

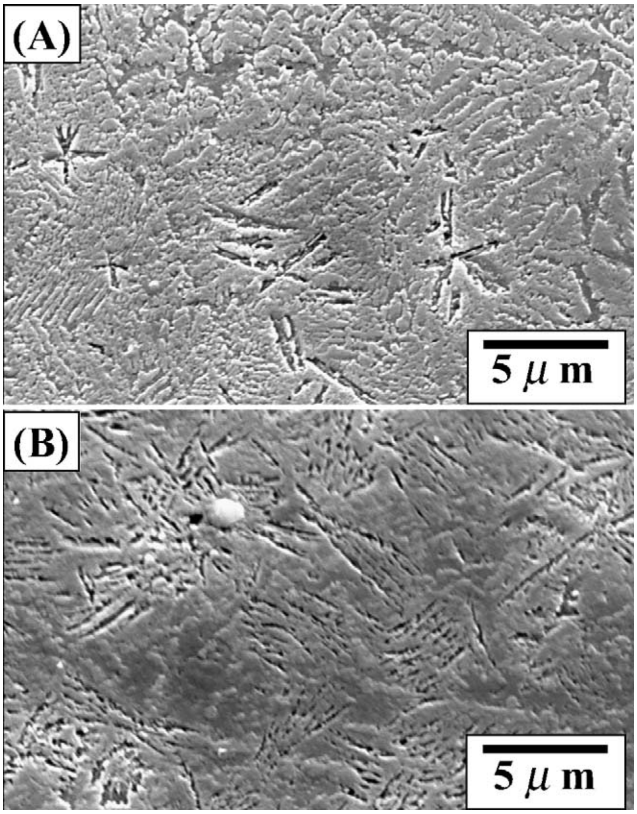

Fig. 6. SEM photographs of samples 1 and 2 fired at 1000 °C for 1 h chemically etched by 1 mass% HF.

found for wollastonite in $CaO–Al_2O_3–SiO_2$ glass-ceramics [11]. However, the areas of these pores appear to be lower than expected from the amounts of crystalline phases in the two samples (about 70–80 mass%). Since the chemical durability of diopside and anorthite is higher than that of wollastonite [16], the glassy phase in the grain boundaries may correspond to these pores in the present glass-ceramics.

3.2. Properties of the glass-ceramics

The various properties of the resultant glass-ceramics are listed in Table 3 together with the corresponding data for $CaO–Al_2O_3–SiO_2$ glass-ceramics [11]. The bending strengths of the present glass-ceramics are 130 MPa in sample 1 and 73 MPa in sample 2. The strength of sample 1 is approximately twice that of sample 2, which has a similar strength to the $CaO–Al_2O_3–SiO_2$ glass-ceramics [11]. Since there is only a slight difference in the total amounts of crystalline phases in samples 1 and 2 but the major crystalline phase is diopside in sample 1 and anorthite in sample 2, the difference in strength may be attributed to the different major crystalline phases. It is, therefore, found that diopside is a more preferable crystalline phase than anorthite from the viewpoint of the strength of these glass-ceramics. A similar tendency was also reported by Park et al. [17] in glass-ceramics prepared from sewage sludge fly ash. They prepared two glass-ceramics with diopside > anorthite and anorthite > diopside, and found that the bending strength of the former glass-ceramic (92 MPa) was higher than that of the latter (75 MPa). Diopside is also suggested to be a more preferable crystalline phase in glass-ceramics compared with the strength of the wollastonite in $CaO–Al_2O_3–SiO_2$ glass-ceramics [11] (Table 3) though the amount of wollastonite is less than diopside. Superior mechanical properties were also reported for glass-ceramics with Mg-containing crystalline phases such as cordierite ($Mg_2Al_4Si_5O_{18}$) [18] and akermanite ($Ca_2MgSi_2O_7$) [19]. By contrast with the apparent difference in the strengths of two glass-ceramics, their hardness values show no significant difference. The hardness values obtained in the present glass-ceramics are relatively high compared with those of various other glass-ceramics [11,17].

The thermal expansion coefficients of the present glass-ceramics are 6.7×10^{-6} and $4.7 \times 10^{-6}\,^{\circ}C^{-1}$ in samples 1 and 2, respectively. This difference is attributed to the differences in CaO and MgO contents of samples 1 and 2 because those components are known to increase the thermal expansion. The thermal expansion coefficient of the commercial glass-ceramics (NEOPARIES) which are used as building materials, is reported to be $6.2 \times 10^{-6}\,^{\circ}C^{-1}$ [20]; the coefficient of sample 1 is of a similar order and that of sample 2 is lower than in these commercial glass-ceramics. The present thermal expansion is relatively low compared with values reported for various other glass-ceramics, indicating that the present materials have an enhanced ability to avoid thermal stress in applications such as building materials involving repeated temperature variations.

Table 3
Various properties of the present glass-ceramics and comparison with ref. [11]

Properties	Sample 1	Sample 2	Reference [11]
Crystalline phase (mass%)	81	75	55
Bending strength (MPa)	130 (14)[a]	73 (14)	81(8)
Vickers hardness (GPa)	7.4 (8)	7.6 (5)	6.6 (3)
Weight loss in acid (mg/cm^2)	0.4	1.3	0.31(2)
Weight loss in alkali (mg/cm^2)	2.3	1.4	1.60 (3)
Linear thermal expansion ($\times 10^{-6}\,^{\circ}C^{-1}$)	6.7	4.7	5.2

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

The chemical durability of glass-ceramics, especially for acid solution, is important if the materials are to be considered as potential building materials, because acid rain is becoming an increasingly serious problem in a number of countries. The weight losses of the present glass-ceramics after leaching in acid and alkali solutions are 0.4 and 2.3 mg/cm^2 in sample 1, and 1.3 and 1.4 mg/cm^2 in sample 2, respectively. The weight loss in acid is apparently lower than that in alkali in sample 1 but the loses are almost same in sample 2. Since the reported weight losses in commercial glass-ceramics (NEOPARIES) are 3.4 and 1.3 mg/cm^2 for acid and alkali, respectively [20], the present glass-ceramics have significantly higher chemical durability to acid but slightly lower durability to alkali.

4. Conclusion

Glass-ceramics were prepared from wastes generated from kaolin clay refining (so-called Kira) with added dolomite ($CaMg(CO_3)_2$) as a fluxing agent. The following results were obtained.

(1) Mixtures of Kira and dolomite in mass ratios of 65/35 and 75/25 can be melted at $<1350\,^\circ C$, from which glass powder can be prepared by quenching the melt in water.

(2) The glass transition temperatures of the two melted samples are 693 and 720 °C, and diopside and anorthite crystallize at $\geq 900\,^\circ C$. The relative amounts of the crystalline phases are diopside $>$ anorthite in sample 1 and anorthite $>$ diopside in sample 2. The total amounts of crystalline phase as much as 80 mass% in sample 1 and about 75 mass% in sample 2. The crystallization ratios of the present glass-ceramics were apparently higher than that of $CaO–Al_2O_3–SiO_2$ glass ceramics [11], probably due to the effect of MgO in the former.

(3) The present glass-ceramics were white in color with smooth surfaces. The shape of the glass-ceramics becomes to rounded on firing, but the deformation is smaller than in $CaO–Al_2O_3–SiO_2$ glass ceramics [11].

(4) The four point bending strengths of the glass-ceramics are 130 MPa in sample 1 and 73 MPa in sample 2. The strength of sample 1 is clearly higher than reported for $CaO–Al_2O_3–SiO_2$ glass ceramics [11].

(5) The Vickers microhardness values are 7.4 and 7.6 GPa in samples 1 and 2, respectively, slightly higher than those of $CaO–Al_2O_3–SiO_2$ glass ceramics [11].

(6) The thermal expansion coefficients determined between 30 and 380 °C were 6.7×10^{-6} and $4.7 \times 10^{-6}\,^\circ C^{-1}$ for samples 1 and 2, respectively, and were relatively low compared with values reported for other glass-ceramics.

(7) The chemical durability of the glass-ceramics was excellent, especially to acid.

Acknowledgements

We are grateful to Maruishi Ceramic Raw Materials Co., Shimizu Industry and Dr. K. Shimosaka for help of collecting Kira and dolomite samples. We are also grateful to Professor K.J.D. MacKenzie of Victoria University of Wellington for critical reading and editing of this manuscript.

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