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Study on machinable glass-ceramic containing fluorophlogopite for dental CAD/CAM system

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Abstract The glass-ceramic mainly containing fluorophlogopite is one of widely used dental ceramics. In the K_2O-CaO-MgO-Al_2O_3-SiO_2-F system, a new-type glass-ceramic containing fluorophlogopite Ca-mica has been synthesized. Its crystalline was studied by XRD and EDS. The fluorophlogopite whose formula postulated $K_{1-X}Ca_{X/2}Mg_3AlSi_3O_{10}F_2$ was its main crystalline. The microstructure of the glass-ceramic displayed typical machinable microstructure with lath like crystals isolated and interlocking with different aspect ratio. The material also showed better bending strength (228.11±7.55 MPa). It took less than 12 minutes to fabricate a whole crown by dental CAD/CAM system with the glass-ceramic.

1 Introduction

Dental ceramic materials represent a promising alternative to dental restorative for chemical stability, proper aesthetic and durability. Currently, dental ceramics have two major deficiencies: (1) they require difficult, time-consuming fabrication stages, and (2) they have relatively high clinical failure. CAD/CAM system offers one solution to produce dimensionally accurate ceramic restoratives. It takes much less time to fabricate a restorative than conventional powder-slurry, casting, hot pressing. The materials used for CAD/CAM dental system were relatively low toughness and strength, and limited the scope of restorative procedures, for which they can be safely used, for example, only inlays and onlays were recommended [1]. Mica-based glass-ceramic is one of the most used machinable dental ceramics. Its intrinsic mechanical brittleness leads to high clinic failure. Generally, the bonding strength of interlayer ions are the weakest in mica crystal, so the mechanical properties apparently are depend on the bonding strength of these interlayer ions. It has been reported, fluorophlogopite-type Ca- or Ba-mica [2–4], which Ca^{2+} or Ba^{2+} took place of alkali ions between interlayers, exhibits higher strength.

In the paper, a new fluorophlogopite-type Ca-mica with lath-shaped crystal from glass was formed, which was the main crystalline phase of a mica-based glass ceramic. The composition and microstructure of the glass ceramic were studied with XRD, EDS and SEM. Mechanical properties and machinablity were evaluated.

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2 Experimental

2.1 Materials

A bath mixture of nominal composition of $SiO_2$40%, $Al_2O_3$12%, MgO10%, $MgF_2$24%, CaO5%, K_2O1%, $ZrO_2$8% in weight ratio was melt in a platinum crucible at 1550° C for 2 h. The melt was poured on to a graphite block model. The cast glass nucleated at 660 °C for 1h and heated in a rate of 3∼5 °C /min, then hold at 800, 900, 1050 °C for 4h for precipitation. After heat treatment, the cast glass precipitated to produce glass-ceramic. The nucleate and precipitation temperature were determined by differential thermal analysis (449, Netsch, Germany).

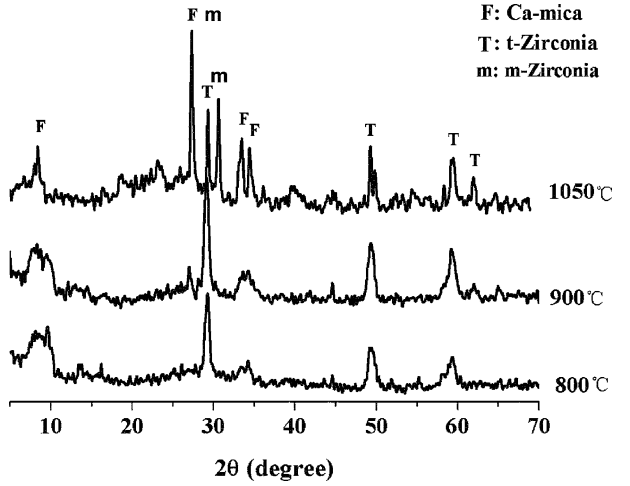

Fig. 1 XRD pattern of the glass ceramic crystallized at 800, 900, 1050 °C for 4h

2.2 Microstructural analysis

The precipitated crystalline phases were identified by X-ray diffraction (D/MAX -II, Rigaku, Japan). Microstructure was characterized using scanning electron microscopy (X-650, Hitachi, Japan and JEOL JSL-5900, Japan) and energy dispersive spectrometry (EDS connected with SEM). The observation surfaces were polished by 400-, 600-, 800-, 1200-grit silicon carbide papers, and then etched with 1% HF. The fracture surfaces kept no treatment besides washing with ultrasound shaking. The crystal aspect ratio was determined from scanning electron micrographs of the polished and etched specimens. The aspect ratio was calculated as the mean ratio of the length along the major axis to that along the minor axis for the all crystals present.

2.3 Property tests

The glass-ceramic blocks were cut into $3 \times 4 \times 20$ mm bars for bending strength (in group of six) and fracture toughness measurement (in group of ten). Three-point bending strength and fracture toughness were determinate at Universal Testing Machine (AG-10TA, Shimadza, Japan). The specimens for fracture toughness test were cut a notch 0.28×2 mm at the narrow side, according to the SENB method. The toughness of most dental materials were also studied by IM method [4, 5], so the indention fracture toughness for each specimen was measured as reported [5, 6]. Vickers hardness was measured under a load of 4.9 N for 30s with a diamond tester. The machinability was valued by dental CAD/CAM system (Cerec II, Siemans, Germany) with consuming time fabricated a whole crown.

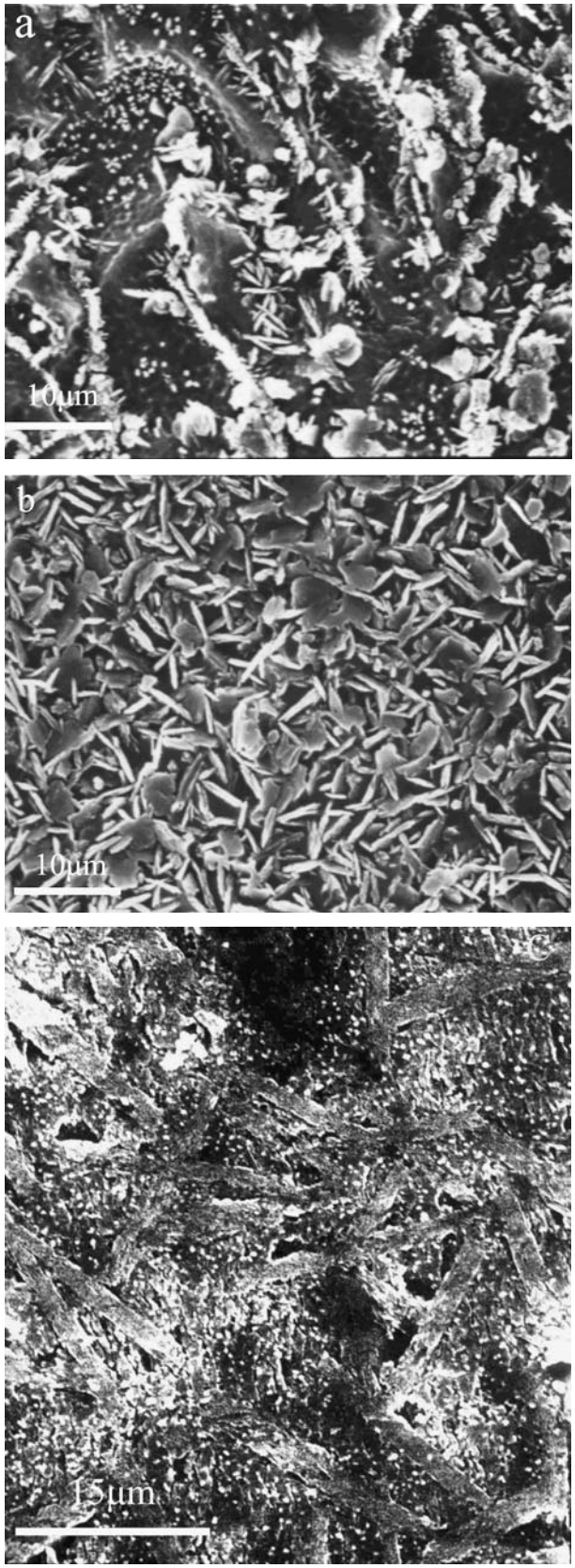

Fig. 2 SEM of the glass ceramics crystallized at different temperature (a. 800 °C, b. 900 °C, c.1050 °C)

Table 1 properties of the glass-ceramics mainly containing fluorophlogopite Ca-mica

Properties	Flexible strength (MPa)	Fracture toughness(SENB) MPa.m$^{1/2}$	Fracture toughness (IM) MPa.m$^{1/2}$	Hardness (Vickers) MPa
KZr-800	135.31 ± 8.25	1.30 ± 0.77	*	*
KZr-900	150.46 ± 10.25	1.98 ± 0.69	2.96 ± 0.37	5.66 ± 0.32
KZr-1050	228.11 ± 7.55	2.17 ± 0.85	3.09 ± 0.45	6.47± 0.56

*Difficult to measure for light transmission.

3 Results and discussion

3.1 Analysis on crystalline phase

Figure 1 shows XRD of the glass ceramics reheated at 800,900,1050°C for 4 hrs. Zirconia initially precipitated at 800°C. The diffraction peaks ascribed to fluorophlogopite can be observed and their intensities increase as the reheated temperature increased. Fluorophlogopite (mica), t-ZrO_2 and m-ZrO_2 are main crystalline phase at the specimen crystallized at 1050 °C as shown in Fig. 1.

The microstructure of the glass-ceramic(Fig. 2(c)) displays typical feature of the machinable glass ceramic with lath like crystals isolated and interlocking. These lath-like crystals are 1–3 μm thick and more than 10μm long, whose composition were analyzed by EDS(Fig. 3). The atom concentration ratio of the lath like crystals is Mg/Al/Si/O/F≈2.5/1.2/3/10/2 according to the EDS result, which is similar to that of fluophlogopite. The formula of typical fluorophlogopite and fluorophlogopite Ca-mica is $KMg_3AlSi_3O_{10}F_2$, $Ca_{1/2}Mg_3AlSi_3O_{10}F_2$ respectively. According to EDS pattern (Fig.3), it is seen that not only Ca but also K was detected in lath like crystals. Therefore, we think that K^+ and Ca^{2+} act as bonding ion between the double layers of Al-Si tetrahedral at the structural network of fluorophlogopite. The formula of the fluorophlogopite postulates $K_{1-X}Ca_{X/2}Mg_3AlSi_3O_{10}F_2$ in our study. As we know, the ion field intensity of Ca^{2+} is much larger than that of K^+, so its shield from electron field has a more effective influence on oxygen. This effect made the formation of [$AlO_{4/2}$] Ca difficult. Even if [$AlO_{4/2}$] Ca was formed, it has bad miscibility with [$SiO_{4/2}$]. Therefore it is deduced that Ca^{2+} has an unfavorably effect on the formation of the basic unit [$AlSiO_{4/2}$] in the system. It means that it is difficult to precipitate fluorophlogopite Ca-mica. The introduction to low content K_2O led to different result. The content of non-bridge oxygen increases with the introduction to K_2O, and so Al^{3+} tends to form [$AlO_{4/2}$] which carries excess negative charge. Potassium neighbors to [$AlO_{4/2}$] form K [$AlO_{4/2}$] compound [7]. This compound possesses good miscibility with [$SiO_{4/2}$] tetrahedral. Then this effect results in formation of [$AlSiO_{4/2}$], which is the basic structure of fluoromica. After the [$AlSiO_{4/2}$] groups were formed, Ca^{2+} works as bonding ion for its high electrovalence. At the same time, K^+ still remains in the compound, and also acts as bonding ion. As a result, a new-type fluorophlogopite precipitates from glass matrix.

ZrO_2 are most commonly used as nucleating agent in glass ceramic procedure. Some of ZrO_2 dissolve in the glass system and Zr^{4+} substitutes one of Si^{4+} in [SiO_4] tetrahedral, therefore EDS can detect in the lath like crystal (Fig. 3). The others precipitate as t- or m-ZrO_2 particles showed by XRD pattern (Fig. 1).

3.2 Microstructure

The glass ceramics were produced with multiple aspect ratios under different crystallization temperature according to SEM as shown in Fig. 2. At 800°C, a crystallized specimen with a low degree of crystallinity and needle crystals with the aspect ratios over 5.0 and the width of 1μm were produced. At 900°C, the lath like crystals mean crystal aspect ratios over 7 and the width of 2–3μm were occurred with a higher degree of crystallinity. At 1050°C, the mean width of 4 μm for the lath crystals are showed in Fig. 2 (c), and the aspect ratios for the lath crystals are over 10. The microstructure was a typical structure with interlocked lath crystals as shown in Fig. 2 (c). The last heat treatment highly crystallized and

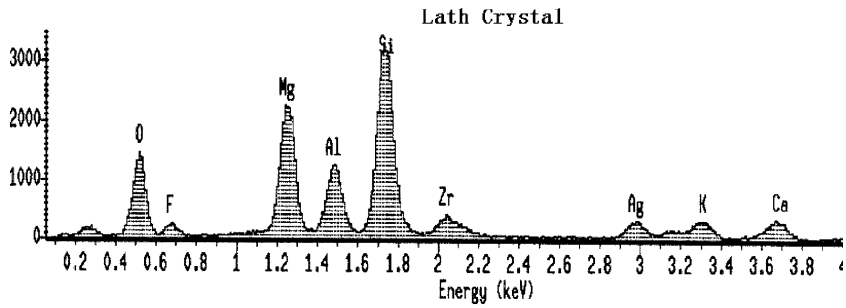

Fig. 3 EDS pattern of the rod like crystal in Fig. 2 (c). (Ag is the coating material for SEM observation)

produced lath crystals with larger aspect ratio and width. The white dot crystals of ZrO_2 also occurred at 800 °C, and kept no obvious change with the crystallization temperature increased.

According to the study results about mica crystal growth [8, 9], the growth index of mica was 2, which meant the mica crystal grew along two dimensions, Therefore most mica based glass ceramics possessed lath like or plate like crystals [2, 3, 10]. The aspect ratios and size of mica crystals were considerably much depends on the viscidity of melt. As the crystallization temperature increased, the viscidity of melt decreased. Then the diffusion of ions from glass matrix to crystal was easy to realize, the size of mica crystals increased.

3.3 Mechanical properties

Properties of the glass-ceramics are shown inTable 1, and the glass-ceramics in our study is designated KZr-???, ??? represents the crystallizing temperature. It can be seen that strength and fracture toughness are considerably higher than most of mica-based glass-ceramics in dental restorative. The higher the crystallization temperature was, the better the mechanical. As Crossman's study [10], in the mica based glass ceramic system, strength in creased with the size for mica crystal increases. For the larger the mica crystals were, the higher the crystallite volume, and then the strength increased.

Faber and Evans [11, 12] had reported that toughness increased monotonically with aspect ratio. Baik [13] also determined by SEM that crack deflecting and bridging effect enhance the toughness in mica system.Figure 4 is SEM of fracture surface for the each glass-ceramic obtained at 800, 900, 1050°C respectively. Figure 4(a) shows the fracture surface of the mica crystals with the aspect ratio over 5 and a low degree crystallinity, a "dimple" fracture surface almost without deflect is present. To produce this pattern surface, the crack propagated through the glass matrix with little deflecting, and implying the crystal particles having less contribution to toughen. Figure 4 (b) exhibits a much more tortuous crack path than the fracture surface for an aspect ratio of 7 of the mica crystals, an indication for higher fracture toughness. For the propagating crack was deflected by the crystals. In Fig. 4(c), the surface appears extremely tortuous, but with sharp deflection angles instead of smooth curves as seen in the Fig. 4(b). The occurrence of house of cards structure is present in the all micrograph, which implies the fracture path was trangranular [14] and pass through the fluorophlogopite crystals with a aspect ratio over 10. Therefore, the increment of fracture toughness was partially due to crack deflection both trangranular and intergranular. The other increment of fracture toughness contributes to the transformation of t -ZrO_2[15].

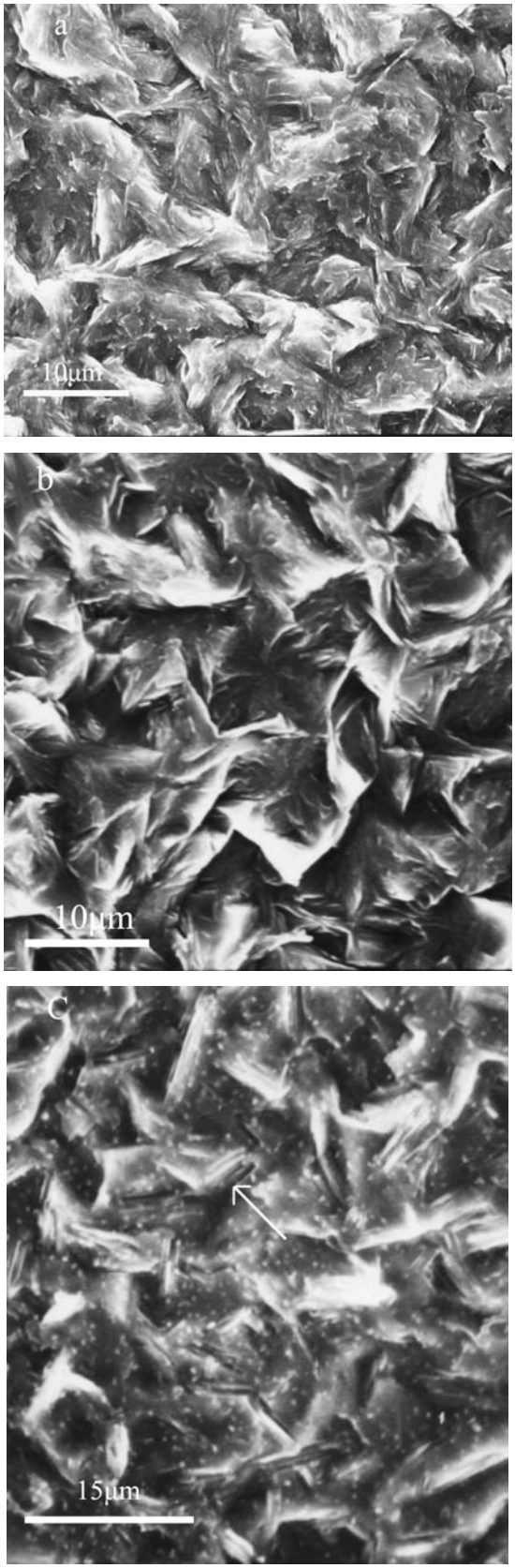

Fig. 4 SEM of the fracture surface of the glass ceramics crystallized at different temperature (a. 800°C, b: 900°C, c: 1050°C), and the arrow in Fig. 4(c) indicates the occurrence of house of cards structure

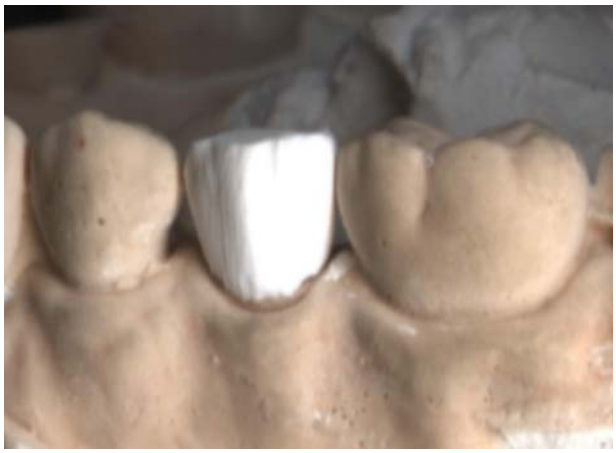

Fig. 5 The crown fabricated by dental CAD/CAM system with the glass-ceramic KZr-1050

3.4 Machinablity

A whole crown(Fig. 5) fabricated by dental CAD/CAM system with the glass-ceramic KZr-1050. The glass-ceramic block $10 \times 10 \times 14$ was applied for CAD/CAM fabrication. The expected time defined by the machine was 652s, while the actual consuming time was 646s. The size of the fabricated crown consisted in the model in the dental CAD/CAM system.

4 Summary

In the K_2O-CaO-MgO-Al_2O_3-SiO_2-F system, the glass-ceramic containing fluorophlogopite Ca-mica has been synthesized. Its crystalline phases were studied by XRD and EDS. The fluorophlogopite whose formula postulated $K_{1-X}Ca_{X/2}Mg_3AlSi_3O_{10}F_2$ was its main crystalline. The microstructure of the glass-ceramics displayed typical machinable microstructure with lath like crystals isolated and interlocking with different aspect ratios. The material also showed better bending strength and fracture toughness as crystallization temperature increased. The strength increase was attributed to crystallinity. The enhancement of toughness was due to crack deflecting by crystals with larger aspect ratios. Therefore the glass-ceramic crystallized at 1050°C showed better mechanical properties, which with a high degree crystallinity and a larger aspect ratio. It took less than 12 minutes to fabricate a whole crown by dental CAD/CAM system with the glass-ceramics**.** The glass-ceramics are expected to be a promising machinable material for CAD/CAM dental system.

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