1. Introduction

Zirconia ceramics, particularly tetragonal zirconia polycrystalline stabilized with 3 mol% yttria, are the most promising materials for metal-free dental restorations. We mentioned in the previous paper [1] that the precision of fit as a precise occlusal fitting (i.e., high dimensional accuracy) is required for dental restorations to provide a higher restorative quality [2–4]; however, as one of the issues of zirconia-based dental restorations, zirconia ceramics have much less machinability, which is regarded as a key mechanical property for precise fitting [2,3]. Therefore, if zirconia ceramics have high machinability, zirconia-based dental restorations with high dimensional accuracy can be easily fabricated.

As the machinable zirconia ceramics, zirconia/CePO₄ [5,6] and zirconia/LaPO₄ [7] composites have been reported. Also, we fabricated machinable zirconia/mica composites and reported their sintering behavior and mechanical properties in the previous paper [1]. Our composites were drilled using conventional machining tools; however, the bending strength (552 MPa) of the composite containing 30 vol% mica represented a 20% decrease compared with that (687 MPa) of monolithic zirconia ceramics. Hence, the remaining issue of bending strength is one of the remaining issues for the composites.

As the strengthening method for glasses, chemical strengthening by ion-exchange is well known [8–11]. In this method, alkali ions in glasses are exchanged for other cations with a larger size in the molten salts, which induces the compressive stress near surface of the glasses. The compressive stress inhibits the development of cracks near surface of the glasses, resulting in the strengthening of the glasses. Recently, the chemically strengthened glasses have been used as protective covers of smartphones, etc. [11]. This strengthening method is applied to glass ceramics [12–23]. The flexural strength of nepheline glass ceramics was dramatically increased from 58 to 1300 MPa by exchanging Na⁺ ions in nepheline crystals for K⁺ ions [12,13]. Also, stipped β-quartz glass ceramics [14], dental glass ceramics such as lithium disilicate glass ceramics [15–18] and Li₂O-Al₂O₃-SiO₂ (LAS) glass ceramics [19], leucite-reinforced dental glass [20], and dental porcelain [21–23] have been strengthened by the ion-exchange.

Mica used to fabricate machinable zirconia/mica composites in a previous study [1] was fluorlogophite (KMg₃AlSi₃O₁₀F₂) having K⁺ ions as interlayer cations, which is the typical synthetic mica. This mica cannot introduce water molecules in the interlayer space, and so it is called non-swelling mica. On the other hand, micas having smaller interlayer cations such as Li⁺ and Na⁺ ions can introduce water molecules in interlayer
space and are swelled [24,25], and so they are called swelling mica. Another feature of the swelling micas is ion-exchange. Interlayer cations such as Li\(^+\) and Na\(^+\) ions can be easily exchanged for other cations in aqueous solutions [25].

If dense zirconia/swelling mica composites are fabricated and interlayer ions in swelling micas near surface of the dense composites can be exchanged for larger cations, the composites having fracture origin near surface are strengthened by the ion-exchange, like chemically strengthened glasses and glass ceramics.

In this study, zirconia/swelling mica composites were fabricated using Na-fluorphlogopite (NaMg\(_3\) AlSi\(_3\)O\(_{10}\)(F\(_2\) as the swelling mica. Na-fluorphlogopite has Na\(^+\) ions as interlayer ions, which is regarded as fluorphlogopite of which interlayer ions are replaced by Na\(^+\) ions. Then the sintering behavior of the composites was investigated. Next, the ion-exchange of the obtained dense composite was performed, that is, Na\(^+\) ions in the interlayer of Na-fluorphlogopite near surface of the composite were exchanged for K\(^+\) ions in molten potassium salts (KCl, KI, and mixture of KCl and KI). So the ion-exchange behavior of the composite and the mechanical properties of the ion-exchanged composites were investigated.

2. Materials and methods

2.1. Preparation of swelling mica

The reagents of MgO (Wako Pure Chemical Industries, Ltd, Osaka, Japan, purity: >98%), Al\(_2\)O\(_3\) (Wako Pure Chemical Industries, Ltd, Osaka, Japan, Wako Special Grade, purity: >98%), SiO\(_2\) (Wako Pure Chemical Industries, Ltd, Osaka, Japan, purity: >98.9% containing loss on ignition of <6%), NaF (Wako Pure Chemical Industries, Ltd, Osaka, Japan, purity: >99%), and MgF\(_2\) (Wako Pure Chemical Industries, Ltd, Osaka, Japan, purity: >99%) were mixed in a chemical composition corresponding to that of Na-fluorphlogopite (Na-mica), dried at 60°C for 24 h, melted in a sealed platinum container at 1350°C for 2 h and then cooled outside of the furnace. The obtained lump of mica (as-prepared Na-mica) was crushed using a mortar and then was pulverized in deionized water by ball milling for 48 h using zirconia pot and zirconia balls with a size of 3 mm. After the obtained slurry was ultrasonically treated, it was quietly kept for 3 days to allow large mica particles sediment in the bottom layer of the slurry. Then, the upper layer of the slurry was elutriated to collect fine mica particles. In this way, the fine Na-mica particles (fine Na-mica) were obtained in the elutriated slurry. The crystalline phases, microstructures, particle size distributions, and thermal properties of as-prepared Na-mica and fine Na-mica were determined using an XRD analyzer (MiniFrelx II, Rigaku Corp., Japan), observed through field emission-scanning electron microscopy (FE-SEM; S-4100, Hitachi High-Technologies Corp., Japan), measured using a particle size analyzer (Partica LA-950, Horiba Ltd., Japan), and were analyzed using thermogravimetry (TG)–differential thermal analyzer (DTA) (ThermoPlus2, Rigaku Corp., Japan), respectively.

2.2. Preparation of zirconia/swelling mica composite

The elutriated slurry containing fine Na-mica was mixed with 3 mol\% Y\(_2\)O\(_3\) containing zirconia powder (HSY-3 F-J-LA, Daichi Kigenso Kagaku Kogyo Co., Ltd., Japan, particle size: 0.43 μm) by ball milling for 24 h using zirconia pot and zirconia beads with a size of 0.5 mm. The ball-milled slurry was freeze-dried and the obtained powder mixture was passed through a 100-mesh sieve. The powder mixture contained 20 wt% (35 vol%) swelling mica (fine Na-mica). The powder mixture was compacted by cold isostatic pressing at 190 MPa, calcined at 400°C for 0.5 h to eliminate water containing in swelling mica, and then fired in a sealed platinum container at 1100–1250°C for 1 min to 2 h. Both heating and cooling rates of the firing were 10°C/min. In this way, zirconia/swelling mica composites were prepared. Monolithic zirconia-sintered bodies were also prepared by cold isostatic pressing zirconia powder at 190 MPa and then firing the powder compacts in air.

The crystalline phases of the prepared composites were determined using an XRD analyzer. The bulk and true densities were measured by the Archimedes and pycnometer methods, respectively. The relative densities were determined from the bulk and true densities. The microstructures were observed through FE-SEM and scanning transmission electron microscopy (STEM; HD2300A, Hitachi High-Technologies, Corp., Japan).

2.3. Ion-exchange of zirconia/swelling mica composites

The cylindrical dense composite with a size of φ 7 mm × 2 mm, which was prepared by sintering at 1200°C for 1 min, was used for ion-exchange. The top and bottom surfaces of the cylindrical dense composite were polished to a mirror finish and then the composite was ion-exchanged in molten salts at 800°C for 0.5 h to 16 h. As the salts, KCl, KI, and mixture of KCl (50 mol %)–KI (50 mol%) were used. According to the phase diagram of the KCl–KI system [26], the melting points of KCl and KI are 771and 681°C, respectively, and the eutectic composition and eutectic temperature of the KCl–KI system are KCl (50 mol%) – KI (50 mol%) and 598°C, respectively. Also, all of KCl, KI, and mixture of KCl (50 mol %) – KI (50 mol%) are completely melted at
800°C. The ion-exchanged composites were washed using water and dried.

The crystalline phases, microstructures, and elemental analysis of near surface of the composite and ion-exchanged composites were determined using an XRD analyzer, observed through FE-SEM and STEM, and performed using an electron probe micro analyzer (EPMA; EPMA-1610, Shimadzu Corp., Japan), respectively.

2.4. Estimation of mechanical properties

Vickers hardness and Young’s modulus of the composite and ion-exchanged composites were measured by the Vickers indentation fracture method using a hardness tester (VMT-7, Matsuzawa Co. Ltd., Japan) and the pulse-echo method using an ultrasonic thickness meter (PANAMETRICS-NDT 35, Olympus Corp., Japan), respectively. For the Vickers indentation, a 98.07 N load was applied on the surface for 10 s.

In addition, the fracture toughness was determined by the indentation-fracture (IF) method. The lengths of the impression diagonals 2a and the surface cracks 2c were measured immediately after the indentation, and the crack-to-indentant ratios (c/a) was 2.2 for the composite and 1.4–2.1 for the ion-exchanged composites. Therefore, their crack geometry was estimated to be the Palmqvist type, and so the fracture toughness (KIC) was calculated using the following formula derived by Niihara et al. [27,28]:

\[
(KIC \phi/\text{Ha}^{1/2}) (H/E\phi)^{2/5} = 0.035(l/a)^{-1/2}
\]

where \( \phi \) is the constraint factor (≈3), \( H \) is the hardness, \( E \) is Young’s modulus, \( l \) is the Palmqvist crack length, and \( a \) is the indent half-diagonal. When calculating \( KIC \) of the ion-exchanged composites, Young’s modulus of the composite was used as \( E \) because Young’s modulus of the surface of the ion-exchanged composites cannot be measured by the pulse-echo method.

The mechanical strengths of the composite and ion-exchanged composite with the size of 3 mm × 1.8 mm × 20 mm were measured using a three-point bending tester (Autograph AG-300kNXplus, Shimadzu Corp., Japan), with a crosshead speed of 0.5 mm/min and a span length of 20 mm.

The machinability was qualitatively evaluated using a bench-drilling machine (TB-1131 K, Ryobi Ltd., Japan). The drill with a 3 mm diameter was used. The rotational frequency was 620 rpm.

3. Results and discussion

3.1. Characterization of prepared swelling mica

XRD patterns of as-prepared Na-mica and fine Na-mica are shown in Figure 1. Mica was obtained as a single crystalline phase in the XRD pattern of as-prepared Na-mica and amorphous phase as halo pattern was not observed. Crystallinity of the mica was lowered by ball milling as shown in the XRD pattern of fine Na-mica. In addition, diffraction peaks of (00 l) planes of mica were remarkably weakened by finer and thinner of mica crystals while other diffraction peaks at 19°, 33–35°, and 60° were strengthened relatively. SEM image of fine Na-mica is shown in Figure 2. Mica particles were flake-like shape and their size was less than 1 µm. The particle size distribution of fine Na-mica, which is shown in Fig. S1 as supporting information, indicates that the particle size range was 0.08 µm to 0.7 µm and the average particle size was 0.15 µm. DTA and TG curves of fine Na-mica are shown in Figure 3. The specimen was analyzed in air while the composites were fired in a sealed container. From approximately 950°C, the endothermic transformation started in the DTA curve during the elevation temperature and simultaneously the weight loss also started in the TG curve. They resulted from the melting of fine Na-mica with volatilization of fluoride or fluorine [29,30].

The fine Na-mica powder was ion-exchanged in molten KCl and KI salts at 800°C for 0.5–8 h. XRD patterns of the ion-exchangers are shown in Figure 4. The diffraction peaks of (001) and (003) planes of mica were shifted to low diffraction angle side by the ion-exchange while that of (060) plane was not shifted. Then, the basal spacing (c sinβ) and lattice constant b of mica were precisely determined from (003) and (060) planes, respectively. The results are shown in Table 1. The size of basal spacing depends on the size of the interlayer cation in mica and increases with an increase in the size of the interlayer cation. Table 1 shows that the size of basal spacing was increased by the ion-exchange, that is, Na+ ions in the interlayer of mica were exchanged for K+ ions having a larger size in such molten salts. These results demonstrate that interlayer cations in Na-mica can be exchanged for other cations having a larger size in molten salts. In addition, Figure 4 shows that mica reacted with such molten salts to form forsterite (Mg2SiO4), kaiophilitie (KAl2Si2O8), etc. After ion-exchanging at 800°C for 8 h, a large amount of mica remained in KCl molten salt (Figure 4(b)) while most mica disappeared in KI molten salt and the reaction products between mica and molten KI, such as forsterite, kaiophilitie, etc., appeared (Figure 4(f)). These results suggest that KI had higher reactivity with mica than KCl.

3.2. Densification and microstructure

The relative densities of the prepared zirconia/swelling mica composites and monolithic zirconia are shown in Figure 5. While the monolithic zirconia reached a relative density of 94.7% at 1200°C for 2 h, the composite did an approximately full density
at 1200°C for 1 min. And the relative density of the composite fired at 1200°C for 30 min became lower than that of the composite fired at 1200°C for 1 min due to over-firing. The swelling mica having a composition of NaMg₃AlSi₉O₂₈F₂ enhanced the densification of zirconia as well as the non-swelling mica having a composition of KMg₃AlSi₉O₁₉F₂, which was added to zirconia powder in a previous study [1]. However, while the relative density of the monolithic zirconia increased at higher temperatures up to 1350°C, that of the composites was lowered at 1250°C.

XRD patterns of the surface and pulverized powder of the composite fired at 1200°C for 1 min are shown in Figure 6. The main crystal phase near surface of the composite was tetragonal zirconia, and mica was observed as a trace phase in its XRD pattern. The mica in the composite was melted above 950°C during heating and was recrystallized during cooling. The pulverized powder contained not only tetragonal zirconia but also a small amount of monoclinic zirconia, which indicates that slight tetragonal zirconia was transferred to monoclinic zirconia by pulverizing.

FE-SEM and STEM images of the composite fired at 1200°C for 1 min are shown in Figure 7. In the FE-SEM image of the polished surface of the composite (Figure 7(a)), the dark grains are mica and the bright grains are zirconia. The mica grains were uniformly distributed in the composite. Their sizes were less than 1 µm, but they seem to slightly grow in the composite after melting, compared with fine Na-mica shown in Figure 2. On the other hand, in the STEM image of the composite (Figure 7(b)), the dark grains are zirconia and the bright grains are mica. The zirconia grains were less than 0.5 µm, which only a little grew, compared with the raw zirconia powder with a particle size of 0.43 µm. The boundaries between the zirconia grains were flat and smooth, which was caused by grain shape accommodation [31]. That is, as a result of melting of swelling mica during heating, the densification of zirconia in zirconia/swelling mica composite was promoted through the solution-precipitation mechanism of the liquid phase sintering as well as that of zirconia in zirconia/non-swelling mica composites reported in a previous paper [1].
3.3. Ion-exchange of composite in molten salts

The dense composite sintered at 1200°C for 1 min was ion-exchanged in molten KCl, KI, and mixture of KCl and KI at 800°C for 0.5–16 h. Potassium and sodium mappings of cross section of the composite ion-exchanged in a molten mixture of KCl and KI for 2 h, which were analyzed using EPMA, are shown in Figure 8. Potassium was detected near the surface of the ion-exchanged composite while sodium was not almost detected near the surface. Other elements such as Zr, Y, Si, Mg, and Al were distributed uniformly over the cross section. These results indicate that Na⁺ ions in the interlayer of mica near surface were exchanged for K⁺ ions in the molten salt. Potassium mappings of cross sections of the composites ion-exchanged in molten KCl and KI at 800°C are shown in Figure 9. The mappings (Figure 9(a,b)) of the composites ion-exchanged

![Figure 4](image-url) XRD patterns of (a) fine Na-mica and ion-exchanged fine Na-micas in molten KCl at 800°C for (b) 8 h and (c) 16 h and in molten KI at 800°C for (d) 0.5 h and (f) 8 h.

![Figure 5](image-url) Relative densities of monolithic zirconia (○) and zirconia/swelling mica composites (□).
in molten KCl for 2 h and 16 h indicate that as ion-exchanging time was longer, potassium penetrated deeper inside from the surface. Comparing Figure 9 (c) with Figures 8(a) and 9(a), it is clear that potassium penetrated deeper inside by the ion-exchange using KI, which suggests that KI interacted with mica more rapidly than KCl.

FE-SEM images of near surfaces of the composites ion-exchanged in molten KCl for 16 h, in a molten mixture of KCl and KI for 4 h, and in molten KI for 2 h are shown in Figure 10. Although the surfaces of composites were polished to a mirror finish before ion-exchanging, the surface was coarsened by ion-exchange in a molten mixture of KCl and KI for 4 h and in molten KI for 2 h, and the particulate products were observed on the surface (Figure 10(b,c)). However, even for the composite ion-exchanged for 16 h using KCl, only a few products were observed on the surface (Figure 10(a)). These results also suggest that KI reacted with mica more rapidly than KCl, corresponding with the results of ion-exchange of mica powder (Figure 4).

The diffraction peak of the (003) plane of mica near surfaces of the original composite and composites ion-exchanged in molten KCl and KI are shown in Figure 11. The diffraction peak appeared at 27.6° before ion-exchanging (Figure 11(a)). However, that of the composite ion-exchanged in molten KI disappeared (Figure 11(c–e)). And when the composite was ion-exchanged in molten KI for 8 and 16 h, diffraction peaks of other crystals appeared at 26–29° (Figure 11(d,e)). It is reported [32,33] that kaolinite (Al₂Si₂O₅(OH)₃), which is a layered silicate compound as well as mica reacted with molten potassium salts (KF, KCl, KBr, K₂CO₃, etc.) to form kaliophilite (KAlSiO₄) through the amorphous phase. This suggests that a similar reaction occurred in the zirconia/swelling mica composites during ion-exchanging. That is, Na-mica in the composite reacted with molten KI to form kaliophilite, forsterite (Mg₂SiO₄), and other crystals through an amorphous phase.
Simultaneously, Na\(^+\) ions in the interlayer of Na-mica were exchanged for K\(^+\) ions in molten KI. On the other hand, the diffraction peak of the (003) plane of mica in the composite ion-exchanged in molten KCl for 16 h remained (Figure 11(b)) but became weaker. It was not almost shifted by the ion-exchange and other peaks did not appear at 26–29\(^\circ\), which suggest that K\(^+\) ions were not inserted in the interlayer of Na-mica and Na-

**Figure 7.** (a) FE-SEM image of polished surface of zirconia/swelling mica composite fired 1200\(^\circ\)C for 1 min and (b) STEM image of the composite.

**Figure 8.** (a) K and (b) Na mappings of cross section of composite ion-exchanged in molten mixture of KCl and KI at 800\(^\circ\)C for 2 h.

**Figure 9.** K mappings of cross sections of composites ion-exchanged in molten KCl at 800\(^\circ\)C for (a) 2 h and (b) 16 h and (c) in molten KI at 800\(^\circ\)C for 2 h.

mica reacted with molten KCl to form the amorphous phase together with ion-exchange. Probably, if the composite preserves in molten KCl for a longer time, the reaction between Na-mica and molten KCl will proceed and other materials such as kaliophilite, forsterite, etc. will be formed.

The above results suggest that Na-mica near surface of the composites transformed in molten potassium salts such as KCl, KI, and their mixture as follows. First, Na-mica reacted with molten potassium salts to form the amorphous phase. Simultaneously with the reaction, Na\(^+\) ions in mica were discharged into molten salts and K\(^+\) ions in molten salts were penetrated into the amorphous phase. Next, as the reaction between Na-mica and molten KCl proceeded, the amorphous phase increased and then other crystalline phases such as kaliophilite, forsterite, etc., were formed.

**3.4. Mechanical properties**

FE-SEM images of the Vickers indentations of the original composite and composite ion-exchanged in molten KCl at 800\(^\circ\)C for 16 h are shown in Figure 12. The cracks developed from the indentation corners were obviously shortened by the ion-exchange, which is one of the evidence that the compressive stress was generated near surface by the ion-exchange [15,22]. The change in the crack length of the ion-exchanged composites with a soaking time of ion-exchange is shown in Figure 13. The crack length of all the ion-exchanged composites was shorter than that of the original composite. So the crack length of the composites ion-exchanged in a molten mixture of KCl and KI and molten KI became shorter in short soaking time but increased after a certain fixed soaking time. As shown in Figure 10, many particulate products, which were formed by the
reaction between molten salt and mica in the composite, appeared on the surface of the composite ion-exchanged in a molten mixture of KCl and KI for 4 h and in molten KI for 2 h while such products were slightly observed on the surface of the composite ion-exchanged in molten KCl for 16 h. These results indicate that the compressive stress generated by the ion-exchange was relaxed by the ejection of the reaction products on the surface. So the crack length of the composite ion-exchanged in a molten mixture of KCl and KI and molten KI was increased by the relaxation of compressive stress after a certain fixed soaking time. On the other hand, the crack length of the composite ion-exchanged in molten KCl was not varied during the soaking time of 4–16 h because the compressive stress was not almost relaxed even at 16 h. As shown in Figure 10(a), a few particulate products that were formed by the reaction between molten KCl and mica in the composite were observed near surface of the composite ion-exchanged in molten KCl for 16 h. This result indicates that the compressive stress was not almost relaxed in the composite. As the result, the crack length of the composite ion-exchanged in molten KCl was not varied during the soaking time of 4–16 h. So if the soaking time of the ion-exchange is prolonged, many reaction products are ejected on the surface of the composite and then the compressive stress is relaxed, resulting in the increase in the crack length.

Mechanical properties are shown in Table 2. Those of the monolithic zirconia were the values determined in the previous study [1]. The fracture toughness became larger by the ion-exchange. The composite ion-exchanged in a molten mixture of KCl and KI for 1 h showed the largest fracture toughness of 5.6 MPa·m^{0.5}, which was a little larger than the fracture toughness (5.1 MPa·m^{0.5}) of monolithic zirconia. These results indicate that the fracture toughness on the surface of the composite was improved by the compressive stress induced by the ion-exchange. The bending strengths of the monolithic zirconia, original composite, and composite

**Figure 10.** FE-SEM images of near surfaces of composites ion-exchanged (a) in molten KCl at 800°C for 16 h, (b) in molten mixture of KCl and KI at 800°C for 4 h and (c) in molten KI at 800°C for 2 h.

**Figure 11.** Diffraction peak of (003) plane of mica near surfaces of (a) original composite and composites ion-exchanged (b) in molten KCl at 800°C for 16 h and in molten KI at 800°C for (c) 2 h, (d) 8 h, and (e) 16 h.
These original ened swelling.

Figure 606

Figure 12. FE-SEM images of the Vickers indentations of (a) original composite and (b) composite ion-exchanged in molten KCl at 800°C for 16 h.

Figure 13. Crack length of (●) original composite and composites ion-exchanged in molten (▲) KI, (■) mixture of KCl and KI and (♦) KCl at 800°C for 0.5–16 h.

ion-exchanged in molten KCl for 16 h were 687 ± 37 MPa, 322 ± 37 MPa, and 447 ± 69 MPa, respectively. These results indicate that the bending strength of zirconia ceramics was lowered by the combination with swelling mica and that of the composite was strengthened by the compressive stress induced by the ion-exchange in molten KCl at 800°C for 16 h. The bending strength (322 ± 37 MPa) of the zirconia/swelling mica composite in this study was lower than that (470 ± 49 MPa) of the zirconia/non-swelling mica composite containing 36 vol% mica in a previous study [1]. Probably it will be heightened by a more uniform disperse of finer Na-mica in the composite.

The composite sintered at 1200°C for 1 min was sufficiently machined with a drill made of hard metal, but the machinability was degraded by the ion-exchange because the mica content near the surface of the composite was decreased and the hardness of the surface was a little increased by the ion-exchange.

4. Conclusions

In this study, zirconia/swelling mica composite, which contained 35 vol% mica, were fabricated using Na-fluorphlogopite (NaMg$_3$Al$_2$Si$_3$O$_{10}$F$_2$) as the swelling mica. Na$^+$ ions in the interlayer of mica near surface of the composites were exchanged for K$^+$ ions in molten potassium salts (KCl, KI, and mixture of KCl and KI). The obtained results were summarized as follows.

(1) The densification of zirconia in the composite was accelerated by the liquid phase formed by melting of mica during firing, and the composite reached an approximately full density at 1200°C for 1 min. The melting mica recrystallized during cooling. Both zirconia and mica grains grew slightly during sintering. So the composite consisted of zirconia grains with a size of less than 0.5 µm and uniform dispersed mica grains with a size of less than 1 µm.

(2) Na$^+$ ions in the interlayer of mica near surface of the composites were exchanged for K$^+$ ions in the molten potassium salts at 800°C. However, K$^+$ ions were not inserted in the interlayer of mica in the composite although they were inserted in the interlayer of powderized mica. Interaction between Na-mica near surface of the composites and molten potassium salts progressed as follows. First, Na-mica reacted with molten salts to form an amorphous phase in the composite. Simultaneously with the reaction, Na$^+$ ions in mica were discharged into molten salts and K$^+$ ions in molten salts were penetrated into the amorphous phase. Next, the amorphous phase increased and then crystalline phases such as kaliophilite, forsterite, etc., were formed.

(3) The crack developed from the Vickers indentation corners was obviously shortened by the ion-exchange, which is one of the evidence that the compressive stress was generated near surface of the composite by the ion-exchange. However, the crack length was lengthened after a certain fixed soaking time of ion-exchange, which resulted from the relaxation of compressive
stress due to the ejection of the reaction products on the surface of the composite.

(4) The fracture toughness on the surface of the composite, which was determined by the IF method, became larger by the compressive stress induced by the ion-exchange. The largest fracture toughness was 5.6 MPa√m0.5, which was a little larger than the fracture toughness (5.1 MPa√m0.5) of monolithic zirconia. Also, the bending strength of the original composite was 322 ± 37 MPa, which was lower than that of the monolithic zirconia (687 ± 37 MPa), and was increased to 447 ± 69 MPa by the compressive stress induced by the ion-exchange in molten KCl at 800°C for 16 h.

Disclosure statement

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