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Optical, mechanical properties and infiltration rate of spinel/zirconia-glass dental composites prepared by melt infiltration

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Spinel/zirconia-glass dental composites were prepared by melt infiltration to investigate the effect of zirconia addition on mechanical, optical properties and infiltration rate of the composites. The glass infiltration rate decreased with raising the zirconia content having a parabolic dependence of infiltration distance on time described by the Washburn equation due to the reduction in pore size. Although the optimum strength (308 MPa) of the spinel/zirconia-glass dental composite was observed when 20 wt% of zirconia was added, transmittance decreased with further increase in the zirconia content. © *2004 Kluwer Academic Publishers*

1. Introduction
All-ceramic dental crowns consisting of glasses and ceramics have been considered as the method of choice for esthetic restorative treatment in dentistry because of hardness, wear resistance, chemical inertness, non-toxicity and strength [1]. Among them In-Ceram crown that is manufactured by presintering of alumina cores formed by slip casting and subsequent infiltration of glass into the porous cores possesses a superior flexural strength and reasonably high fracture toughness [1–4]. The main aspect of melt infiltrated ceramic-glass dental composites, where molten liquid infiltrates into a consolidated porous structure, involves near-net shape forming process (NNS) having low shrinkage for accurate fit, which is prerequisite for dental crowns [1–4]. NNS includes presintering of alumina at 1120°C to develop a skeleton of fused alumina particles and a subsequent infiltration of the porous structure with lanthanum aluminosilicate glass at 1100°C for the densification. Despite these advantages, the forming process of alumina core by slip casting technique was somewhat troublesome and time consuming in achieving a uniform core thickness [4–6].

Recently, easy shaping was accomplished by using CAD/CAM processs (direct ceramic machining) [1, 7]. DCM may allow the economical rapid prototyping of complex three-dimensional shaped objects like dental bridges [7]. Magnesium aluminate spinel ($MgAl_2O_4$) was also emerging as dental crowns due to the high translucency [1]. Lee *et al.* [8] reported that spinel calcined for 1 h at 1200°C was highly effective to mechanical properties of the spinel-glass dental composites. In the present study, zirconia having a higher fracture toughness of 11 MPa$\sqrt{m}$ [9] was added into spinel to improve the fracture toughness of the spinel/zirconia-glass dental composites because zirconia acted as an inclusion for spinel particles. La_2O_3-Al_2O_3-SiO_2 glass was infiltrated into porous spinel/zirconia preforms to obtain the densified spinel/zirconia-glass dental composites and then the influence of zirconia addition on optical, mechanical properties of the composites and infiltration behavior were examined.

2. Experimental procedure
Powder preparation procedure of zirconia having a composition of 3 mol% Y_2O_3-1.5 mol% Nb_2O_5-95.5 mol% ZrO_2 and spinel (0.94 μm, Sumitomo, Tokyo, Japan) were described elsewhere [9–11]. Spinel/zirconia was prepared by adding zirconia into spinel in 5 wt% intervals in the range of 0–40 wt% using ball milling for 24 h. The milled slurries were dried, sieved through a 100-mesh screen, die-pressed into disks and then isostatically pressed at 140 MPa. The green compacts were presintered for 2 h at 1100°C in air. Disks having a dimension of 20 mm in diameter and 1.7 mm in thickness were used for mechanical property measurements, 25 and 1 mm for transmittance measurements and 10 and 20 mm for glass penetration behavior. The density was measured by the Archimedes method, using distilled water as the immersion medium. The pore size and distribution were measured by a mercury porosimeter (Autopore II 9220, Micrometrics, USA) whose pressure ranged from 0.04 to 400 MPa. The particle size was measured by a laser particle size analyzer. Transmittance of the composites was analyzed by UV spectrometer (UV-2501PC, Shimazu, Japan).

The La_2O_3-Al_2O_3-SiO_2 glass [11] was prepared by melting the desired oxides in a platinum crucible at 1400°C, quenching the melt in water and then grinding into a powder using a disc mill (Pulverisett 13, Fritsch

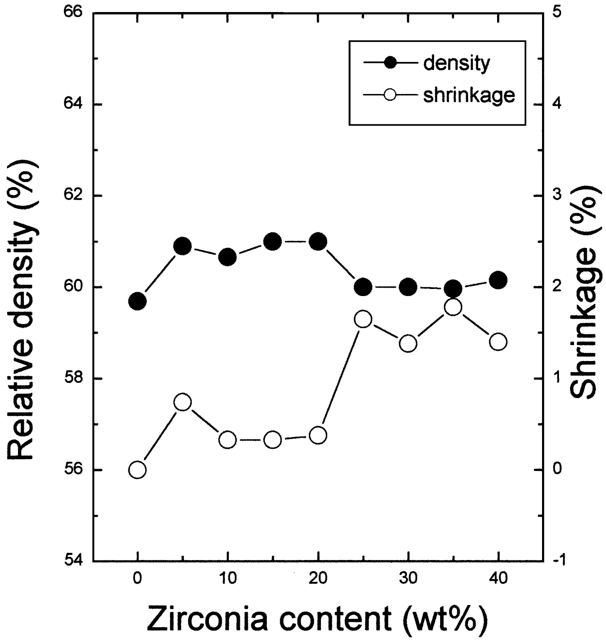

Figure 1 Shrinkage and relative density of spinel/zirconia preforms as a function of zirconia content.

GmbH, Germany). The glass powder-water slurry was placed on the presintered spinel/zirconia preforms (for 2 h at 1100°C) and infiltrated for up to 4 h at 1080°C with a rate of 30°C/min and then furnace cooled. The disk-type composites were polished to a 1 μm finish. For the measurement of the penetration behavior, the glass was infiltrated into the spinel/zirconia preform at 1080°C for 0.1 to 2 h in the interval of 10 min and sectioned along the diameter using a diamond saw and then penetration distance of the composites was determined by an optical microscopy (Kanscope, Sometech, Korea).

The strength of the composites was evaluated by a flat-on-three-ball biaxial flexure testing. The specimens were broken using a biaxial strength fixture at a stress rate of 23 $MPas^{-1}$ [12]. A Vickers indentation of 196 N was placed on the center of the tensile faces of the five test specimens to measure fracture toughness [13]. A drop of silicon oil was applied to minimize moisture assisted subcritical crack growth. For the calculation of the fracture toughness, the hardness to modulus ratio was estimated from the measurements of the diagonal dimensions of Knoop indentations after Marshall *et al.* [14].

3. Results and discussion

Mean particle size of spinel and zirconia powders having a bimodal particle size distribution was 3.0 and 0.49 μm, respectively, indicating that fine zirconia particles may fill the voids of skeletal structure formed by coarse spinel particles. Taruta *et al.* [15] reported that zirconia retarded the densification among alumina particles and the grain growth of alumina because zirconia may act as an inclusion for alumina particles. It was expected that fine zirconia particles having a narrow size distribution width may fill the voids easily formed by the coarse spinel particles, resulting in poor densification

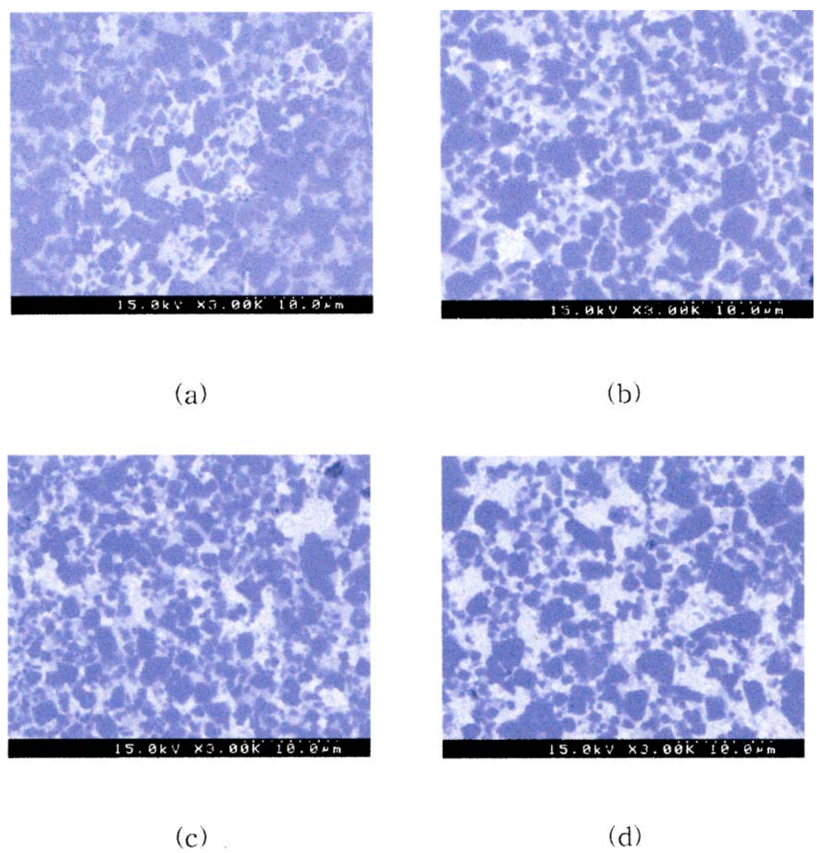

Figure 2 SEM micrographs of imaged with backscattered electrons of the spinel/zirconia-glass dental composites. The zirconia content is: (a) 0%, (b) 10%, (c) 20% and (d) 40%, respectively.

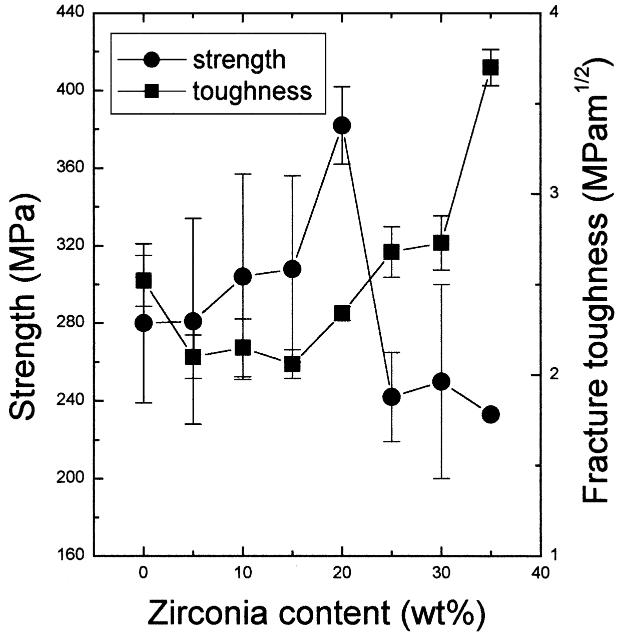

Figure 3 Flexural strength and fracture toughness of spinel/zirconia-glass dental composites as a function of zirconia content.

and higher shrinkage of spinel/zirconia powder mixtures. It was observed that shrinkage and relative density, as shown in Fig. 1, increased and decreased, respectively, when the zirconia was added more than 25 wt%, indicating that higher zirconia addition was not effective to the densification of the spinel powders containing zirconia. Zirconia (small white circles in Fig. 2) may hinder the grain growth of spinel because of the zirconia migration on grain boundaries [15], resulting in smaller pore size (less than 1 μm).

Strength and fracture toughness of the spinel/zirconia-glass dental composites having different amount of zirconia are shown in Fig. 3. The optimum mechanical properties were observed for the dental composites containing 20 wt% of zirconia. Strength and toughness increased and decreased, respectively, with further increase in the zirconia content. Guazzato *et al.* [16] reported that greater strength and toughness of the glass-infiltrated alumina/zirconia over the glass-infiltrated alumina may be due to synergic combination of the phase transformation of the zirconia grains and the crack deflection related to the alumina grains. The crack was deflected by the high strength spinel grains, whereas it propagated through the transformed zirconia grains as depicted in Fig. 4. Phase transformation of highly transformable zirconia [9] occurred at the crack tip caused compressive stresses, which was effective to crack shielding. Such benefits were likely to be counteracted by the presence of the greater porosity [16, 17]. However, strength started to decrease when 25 wt% of zirconia was added probably due to the difficulty in densification of the composites caused by the smaller pore size of 0.03 μm [5] and the higher porosity. This dependence of submicrometer pore size on strength was also demonstrated in the alumina-glass composite system [5, 6, 17]. The infusion of liquid of glass into the gap between the skeleton of fused spinel/zirconia particles may be hampered.

The time to achieve a given penetration depth is believed to be directly proportional to the pore radius

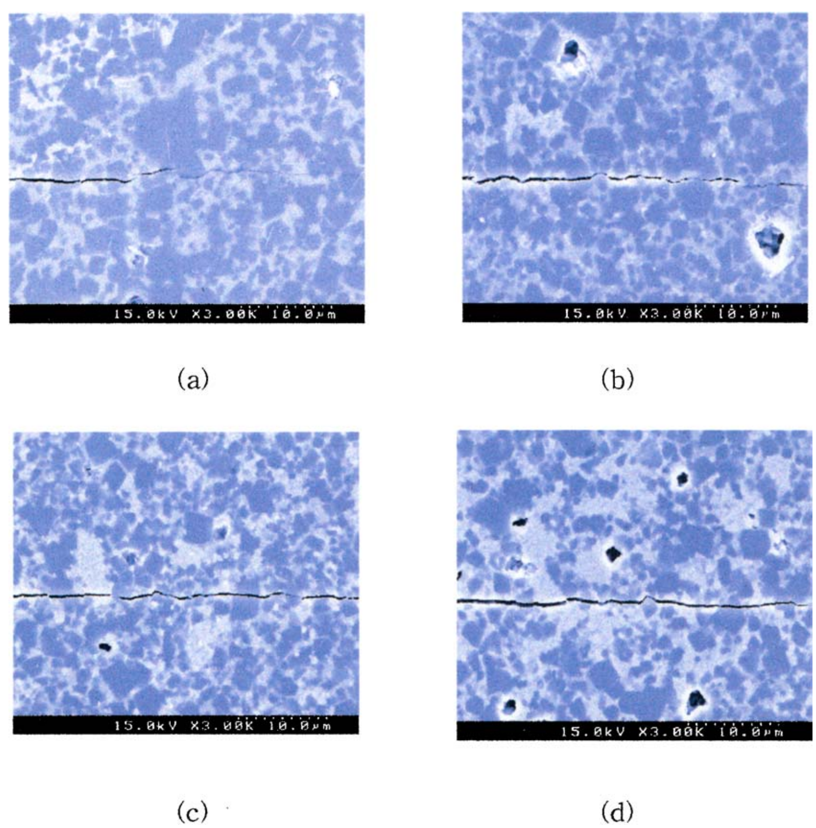

Figure 4 SEM micrographs of imaged with backscattered electrons of the indented spinel/zirconia-glass dental composites. The zirconia content is: (a) 0%, (b) 10%, (c) 20% and (d) 40%, respectively.

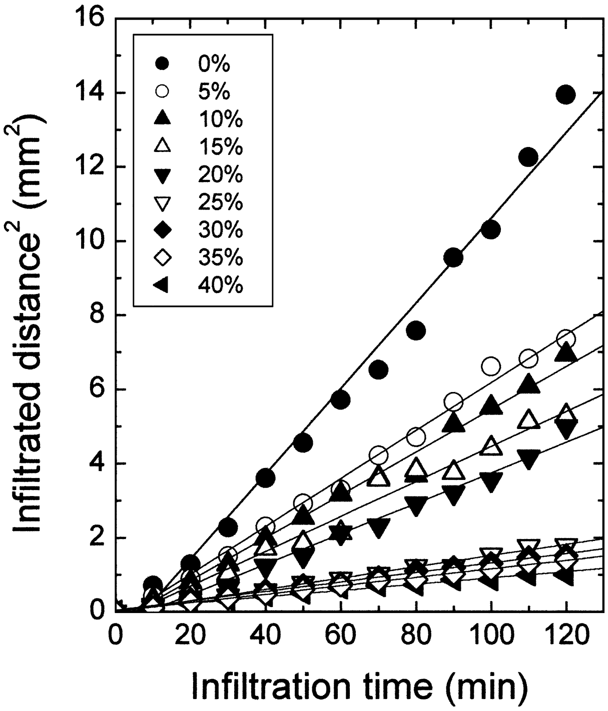

Figure 5 (Infiltrated distance)^2 as a function of infiltration time for the spinel/zirconia preforms having different zirconia content.

[18, 19]. Therefore, the extent of infiltration of the glass may be a function of pore size because infiltration was driven by capillarity [18–20]. Fig. 5 indicated that the infiltration distance was parabolic in time as described by the Washburn equation and the penetration rate constant, K, increased with decreasing the zirconia content due to the increase in pore size. Especially, the infiltration rate of the spinel/zirconia preforms containing more than 25 wt% of zirconia was retarded significantly as expected due to the smaller pore size.

Transmittance spectra of the spinel/zirconia-glass dental composites in the visible region (360–700 nm) are shown in Fig. 6. No discontinuous spectra (Fig. 6a) were observed, indicating that no particular absorption edge was occurred in the visible region. Transparency of the spinel-glass composites (17.1%) was two times higher than that of the alumina-glass composites (7.9%) [20]. Although the transmittance decreased as the extent of zirconia rose, the transmittance of the spinel/zirconia-glass dental composites (Fig. 6b) was always higher than that of the alumina/zirconia-glass dental composites throughout the visible region.

4. Conclusions

Spinel/zirconia-glass dental composites were prepared by die-pressing and melt infiltration to investigate the effect of zirconia addition on mechanical, optical properties and infiltration rate of the composites. The infiltration distance was parabolic in time as described by the Washburn equation and the penetration rate constant, K, decreased due to the reduction in pore size as the zirconia content rose. The optimum strength of the spinel/zirconia-glass dental composite was observed when 20 wt% of zirconia was added. Although K and transmittance decreased with increasing the zirconia content, transmittance of the spinel(/zirconia)-glass dental composites was always higher than that of the alumina(/zirconia)-glass dental composites.

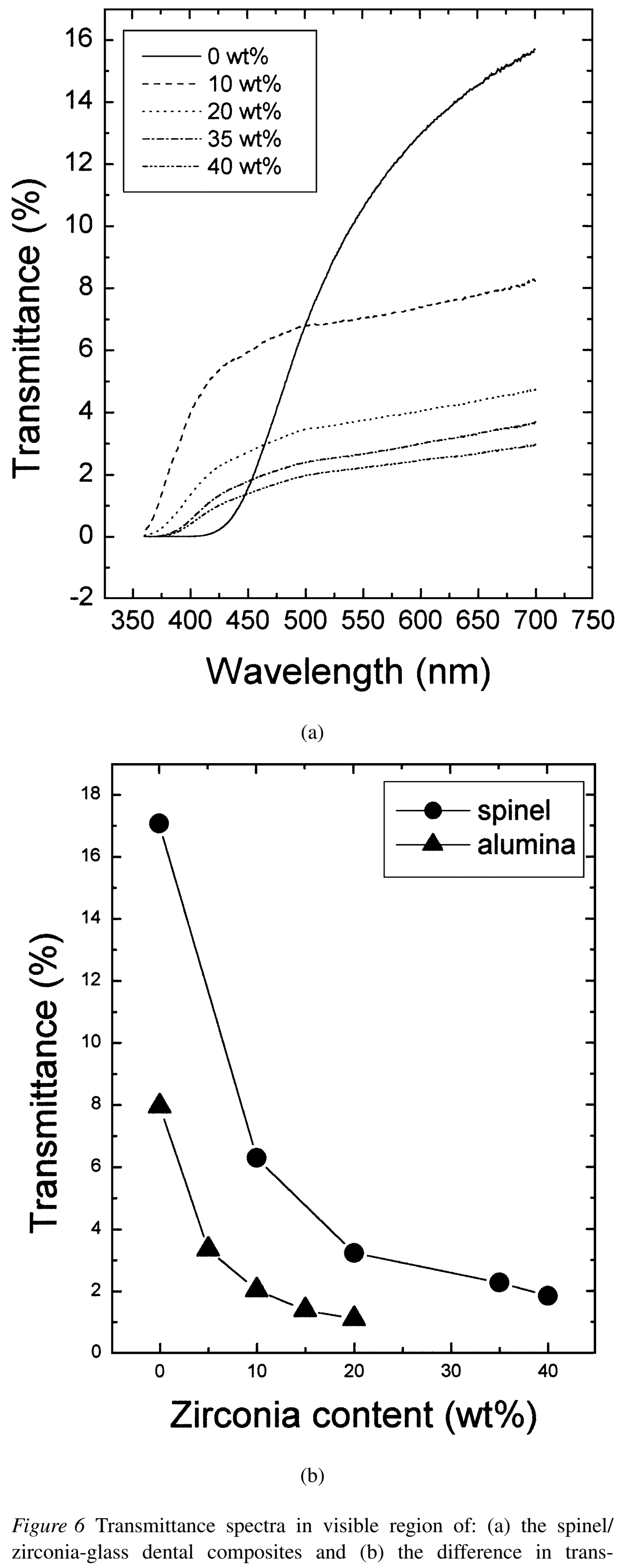

Figure 6 Transmittance spectra in visible region of: (a) the spinel/zirconia-glass dental composites and (b) the difference in transmittance rate between the spinel/zirconia-glass composites and the alumina/zirconia-glass composites.

Acknowledgements

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