

Transformation characteristics of dental  
3Y-TZP by accelerated low temperature  
degradation

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# Transformation characteristics of dental 3Y-TZP by accelerated low temperature degradation

Directed by Professor Kwang-Mahn Kim

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Jong-Suk Lee

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This certifies that the Doctoral  
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June 2011

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실험의 세부적인 과정에 도움을 주신 평가센터 조혜미 선생님, 이채은 선생님 그리고 라만연구소의 최민경 소장님께도 깊이 감사드립니다.

전공의과정에 있는 동안 생체재료공학교실과의 소중한 인연을 만들어주신 고려대학교 신상완 교수님 고맙습니다.

오랜 기간 동안 곁에서 응원해 준 사랑하는 아내에게 이 논문을 드립니다.

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## Abstract

Transformation characteristics of dental 3Y-TZP by accelerated low temperature degradation

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**Purpose:** The purpose of present study is (1) to evaluate difference of t-m transformation between veneered zirconia and unveneered exposed zirconia by accelerated LTD(Low Temperature Degradation) test and (2) to evaluate mechanical change following accelerated LTD test.

**Materials and Methods:** 60 fully sintered 3Y-TZP discs were made. Machined surface was veneered by ZirPress glass ceramic, and the opposite side was highly polished without veneering. By accelerated LTD time, 60 bilayered specimens were divided into three groups. Group A was control, group B and C were undergone accelerated LTD at 134 °C for 5 and 10 hours in distilled water, respectively. Maximum fracture load of bilayered specimens was measured by Piston-on-three-ball test. X-ray diffraction analysis was done to calculate monoclinic fraction( $X_m$ ) on veneered and exposed zirconia surfaces following fracture load test. SEM was taken to survey monoclinic zone in fractured area. To measure Yttrium weight %, energy dispersive X-ray spectroscopy analysis was used on both surfaces. Raman spectroscopy was

taken to identify monoclinic peak at both surfaces and 6  $\mu\text{m}$  below each surfaces in fractured area.

**Results:** There was significant increase of monoclinic fraction at exposed surface compared to veneered surface in group B and C( $p<0.05$ ), but maximum fracture load among three groups was not significantly different( $p>0.05$ ). We could not find clearly identified monoclinic layer by SEM. Yttrium weight % was statistically lower at exposed surface in group C( $p<0.05$ ). Raman spectrum showed monoclinic peak only 6  $\mu\text{m}$  below exposed surface in group C.

**Conclusions:** T-m transformation occurred much more on exposed zirconia, but there was no change on veneered surface following accelerated LTD. And those change did not influence maximum fracture load of veneered zirconia.

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**Key words:** zirconia, dental, 3Y-TZP, low temperature degradation(LTD), t-m transformation

# Transformation characteristics of dental 3Y-TZP by accelerated low temperature degradation

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## I . INTRODUCTION

Dental ceramic materials can reproduce natural optical qualities of human teeth. Until 20th centuries many kinds of dental ceramics have been tried as restorative materials, but their limited mechanical strength restricted their use only on fixed partial denture of short span or single restoration especially anteriors. Ceramic materials are brittle and do not deform plastically until fracture. And they are subject to time-dependent stress failure(Yoshinari, 1994). Moreover the humid condition of oral cavity can weaken ceramic material by stress corrosion(Vult von Steyern, 2001).

Partially Yttria( $Y_2O_3$ )-stabilized Tetragonal Zirconia Polycrystal(Y-TZP) has been used as cosmetic dental material. It has outstandingly high strength and toughness comparable metallic material.

Zirconia has three phases(allotropes). At natural room temperaure, pure zirconia exists as monoclinic phase. Monoclinic phase is very brittle and exists as powder form. Monoclinic phase transforms into tetragonal

intermediate phase at 1170 °C. Above 2370 °C, zirconia transforms to cubic phase, which is stable only at very high temperature. During cooling procedure, pure zirconia transforms to monoclinic phase at 1070 °C with 1 to 5 % volumetric expansion(Hannink et al., 2000). This volumetric expansion causes micro and macro-crack and they break into powder at room temperature. Some metallic oxides, for example Ceria, Magnesia, and Yttria, can be added to stabilize tetragonal zirconia at room temperature.

By adding  $Y_2O_3$  stabilizer zirconia can be made of small metastable tetragonal grains. Other stabilizers such as Magnesia and Calcia also can be added, but phase transformation toughening is less pronounced than Yttria stabilized zirconia(Cales, 2000). Sintered Y-TZP ceramic showed flexural strength ranging from 1000 to 1500 MPa. The reason of high strength of zirconia is so called t-m transformation toughening. Propagation of crack is inhibited by compressive stress field caused by volumetric expansion of monoclinic phase at the end of crack(Garvie et al., 1975).

Development of CAD/CAM technology made it possible to machine zirconia block. Nowadays zirconia is used for inlays, endodontic posts, onlays, veneers, crowns, and framework for fixed partial dentures.

But t-m transformation also can cause negative mechanical result by so called Low Temperature Degradation(LTD, Aging). Zirconia femoral heads have been used for hip joint replacement and several studies reported their failure. In 2001-2002, the failure events of Prozyr<sup>®</sup> femoral heads opened controversial issue. The presence of water at relative low temperature is thought as an important reason of transformation into monoclinic phase. When water is incorporated into zirconia lattice by dissolving Zr-O-Zr bonds

and fill oxygen vacancies, energy barrier for t-m transformation is reduced(Borchers et al., 2010; Kim et al., 1995). This phenomenon is so called Low Temperature Degradation(LTD). By this procedure, LTD is initiated from isolated surface grain and spreads along the surface, and proceeds into the bulk(Chevalier, 2006). LTD can cause micro- and macro-cracks and finally loss of strength. The high strength of zirconia is severely reduced by this transformation procedure.

So, monoclinic transformation of zirconia has double-sidedness; transformation toughening and LTD. The former can seal the cracks by volumetric expansion resulting high mechanical strength, but the latter can cause breakdown of this material.

There are some features of LTD according to investigators(Lawson, 1995). This transformation is related to several factors: mechanical loading, temperature, and exposure time to water. LTD begins from outer surface and spreads into internal part(bulk) of zirconia. Water contact or humid environment enhances the transformation. Stabilizing content and grain size have important effect on LTD process. Higher stabilizing content and smaller grain diameter can increase resistance to LTD. Maximal degradation rate occurs at approximately 250 °C and LTD is time dependent.

Currently proposed models explain the LTD mechanism by water chemisorption that forms zirconium hydroxides( $Zr(OH)_2$ ) at the surface. By this mechanism strain energy accumulates and result in t-m transformation. Yttria also reacts with water and forms Yttrium hydroxides( $Y(OH)_3$ ) and weight % of Yttria is reduced. This procedure also can affect monoclinic transformation.

Laboratory surface treatment procedure also can cause monoclinic transformation of zirconia. Highly localized load, such as grinding, sandblasting, and high temperature(thermal aging) are considered as causing factors of transformation during laboratory procedure.

There are several laboratory methods to evaluate LTD of zirconia(Chevalier, 2006). Because transformation propagates by nucleation and growth process beginning at the surface, if aging time is less than 3 hours at 134 °C, atomic force microscope(AFM) and optical interferometry(OI) can be used. AFM can provide information of the surface at nanometer scale. OI can be used to investigate the surface degradation kinetics at microscopic scale. Lateral resolution of OI is about 2  $\mu\text{m}$  and height resolution is smaller than 1 nm (Deville et al., 2005). OI allows observing the surface relief caused by growth of monoclinic spots. AFM and OI require no sample preparation prior to observation.

X-ray Diffraction(XRD) analysis has been used by other researchers to analyze phase transformation of zirconia surface. Deville et al.(2005) reported that the transformation rate increases progressively up to maximum plateau. They showed that monoclinic fraction does not increase any further after 12 hours at 134 °C. The nucleation and growth mechanism shows curve of sigmoid shape.

But due to large focal size, we cannot analyze small area by XRD. In addition, the XRD signal comes from the surface layer only. So when the transformed layer is deeper than the X-ray penetration depth, XRD data can not exactly represent monoclinic fraction of zirconia.

Scanning Electron Microscopy(SEM) can be used to observe monoclinic

propagation into the bulk of zirconia. Some authors reported cross sectional SEM images which reveal monoclinic layer. Transformed monoclinic layer is easily removed by polishing, and leaves holes made by microcracking on cross sectional area of samples, and we can observe the transformed layer below the surface by SEM. Thermal or chemical etching procedure can reveal grain boundary more clearly, but these procedure may influence monoclinic phase formation. Although monoclinic fraction by XRD reaches plateau according to increasing aging time, SEM can reveal the monoclinic propagation depth is still increasing continuously into the bulk of zirconia. Ban et al.(2008) reported 3 to 5  $\mu\text{m}$  monoclinic layer after accelerated LTD at 121  $^{\circ}\text{C}$  for 10 days. Kosmac et al.(1999) reported 100  $\mu\text{m}$  on 140  $^{\circ}\text{C}$  for 24 hours. Deville et al.(2005) reported about 4  $\mu\text{m}$  after 11 h, and 11  $\mu\text{m}$  after 16 hour at 134  $^{\circ}\text{C}$ . But, the critical disadvantage of SEM, particularly on cross section, requires specific preparation which could modify the observed surface.

Energy Dispersive X-ray Spectroscopy(EDS) is a method which can identify atomic composition of a material. Each element has unique atomic structure. When charged high energy beam, for example electron, is focused into a sample, excited electron of inner shell of atom is ejected creating an electron hole. An electron from an outer shell fills the hole releasing X-ray which is characteristic from material to material. Papanagiotou et al.(2006) reported that after accelerated LTD yttria concentration decreased from 6.76 to 4.83 weight % when boiled 7 days in water. They suggested that LTD procedure reduced stabilizer concentration which making tetragonal zirconia grains more vulnerable to monoclinic transformation.

Degree of transformation can be evaluated by Raman spectroscopy which uses Raman scattering obtained by a material(Casellas et al., 2001). Because the corresponding characteristic lines are widely separated, monoclinic and tetragonal phases of zirconia can be identified. Casellas et al.(2001) reported that monoclinic doublet appears at 181 and 192  $\text{cm}^{-1}$ . Tetragonal peak appeared at 148 and 264  $\text{cm}^{-1}$ . Raman spectroscopy can be used for small area analysis because it's focal size can be as small as 1  $\mu\text{m}$ . Furthermore, this technique is a non-destructive measuring technique which can discern the phases present. Pittayachawan et al.(2009) studied Raman image of fractured zirconia surface and reported that higher level of monoclinic phase were found near the fractured rough edge, which was located at the center of the specimen. They reported that phase transformation was found only on the lower surface which was tension side, near the fragment tip and fracture origin.

In prosthodontics, zirconia has been used for full-zirconia ceramic restoration or coping for veneer ceramic. Nowadays, zirconia abutment for implant prosthesis is use for restoration of anterior esthetic zone. But in some clinical situations, for example when tooth reduction is insufficient for veneering porcelain, frequently at the preparation margin or occlusal surface of molar area, and when vertical space for ideal connector design is limited, zirconia substructure can be directly exposed at humid oral condition. And at occlusal area those exposed zirconia substructure can be loaded directly by opposing antagonist. In concern of LTD, exposed zirconia can undergo t-m transformation procedure at oral humid condition during long term clinical usage. Ultimately in those situation LTD may result in prosthesis failure.



Laboratory accelerated LTD can be done according to ISO 13356. LTD treatment at 134 °C for 1 hour corresponds to 3 to 4 years in vivo (Cales, 2000; Chevalier et al., 2006; Deville et al., 2005). So we can predict long term behavior of LTD of zirconia by in vitro test. But, there was no research about LTD of veneered vs. exposed zirconia.

The purpose of present study is (1) to evaluate difference of t-m transformation between veneered zirconia and unveneered exposed zirconia by accelerated LTD test and (2) to evaluate mechanical change following accelerated LTD test. The hypothesis (1) is that veneered zirconia will undergo minimal LTD compared to exposed zirconia, and (2) is that mechanical characteristics of zirconia will be affected by accelerated LTD.

## II. MATERIALS AND METHODS

### 1. Materials

Zirconia discs were fabricated using ZirBlank(PS type, Acucera, Korea). Veneering of each zirconia discs was done using e.max<sup>®</sup> ZirPress(Ivoclar vivadent, Liechtenstein)(Table 1).

Table 1. Materials used in this study

Type	Product name & Manufacturer	Composition	Specification
Zirconia	ZirBlank PS Acucera, Korea	ZrO <sub>2</sub> ≥ 94.20 wt% Y <sub>2</sub> O <sub>3</sub> ,HfO <sub>2</sub> ≤ 5.45 wt%	CTE(25~500 °C): 10.5 × 10 <sup>-6</sup> K <sup>-1</sup>
Veneer porcelain	e.max <sup>®</sup> ZirPress (LT A2 shade) Ivoclar vivadent Liechtenstein	fluoroapatite glass ceramic	CTE(10~500 °C): 9.9 × 10 <sup>-6</sup> K <sup>-1</sup> Lot No: LOTL 39116

### 2. Sample Preparation

3Y-TZP powder which has grain size of 0.3 μm was pressed by 47 MPa single direction pressure and sintered at 1500 °C for 2 hours to make fully sintered zirconia cylinder. Cylinder shaped sintered block was sectioned to make disc specimens of 15 mm in diameter and about 1.2 mm in thickness by precision saw. One surface of disc specimen was highly polished using 1 μm diamond suspension and the opposite surface was remained as machined. To remove any monoclinic phase which could be created during machining

procedure all zirconia discs were annealed at 1200 °C for 2 hours(Figure 1).

Totally 60 zirconia disc specimens were made(20 per each group)(Table 2).

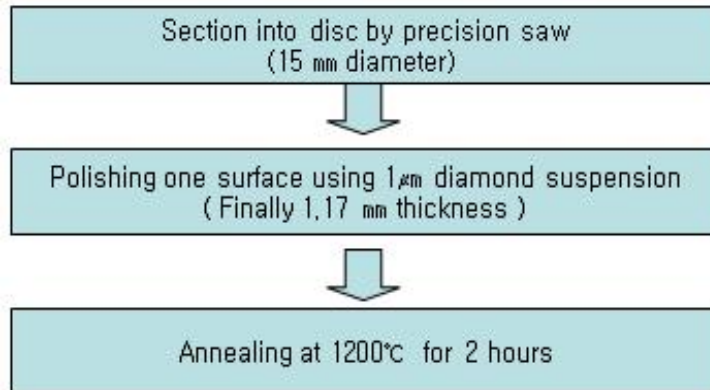


Figure 1. Preparation of zirconia disc after full sintering.

Table 2. Three groups according to accelerated LTD time

Group	Number	Discription
A	20	Stored in dry condition at room temperature
B	20	Stored in water at 134°C for 5 hrs.
C	20	Stored in water at 134°C for 10 hrs.

To facilitate veneering with even thickness of glass ceramic on machined surface, pressing-on technique was used. After waxing up about 2 mm in thickness, wax and zirconia discs were invested and pressed in Programat EP

3000 pressable porcelain furnace(Ivoclar vivadent, Liechtenstein). ZirPress glass ceramic ingot was veneered on machined surface only and the opposite polished surface was untreated(Figure 2).

To enhance bonding of ZirPress to zirconia, ZirLiner was mixed and painted prior to waxing up procedure. ZirLiner was fired at 960 °C for 1 min. After divesting, the total thickness of bilayered specimen was adjusted by grinding ZirPress side until each specimens reach totally 2.8 mm in thickness by grinder (up to #400 sandpaper) with sufficient water cooling.

Group A was stored in dry condition at room temperature. Group B and C were undergone accelerated LTD at 134 °C for 5, and 10 hours, respectively. Specimens were dipped in distilled water during accelerating LTD.

Accelerated LTD equipment manufactured by KODAM engineering(Korea) was used for acceleration procedure(Figure 3).

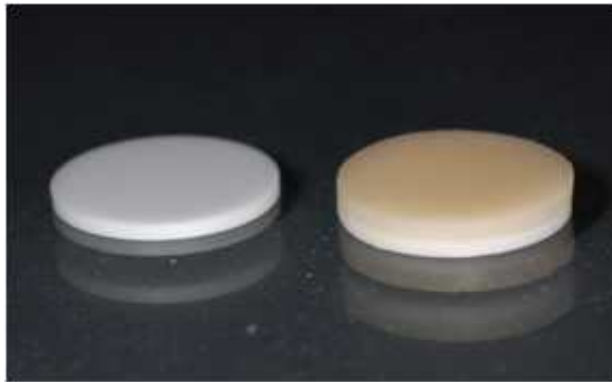


Figure 2. Zirconia disc and Bilayered specimen.



Figure 3. Accelerated LTD equipment.

### 3. Methods

#### A. Fracture Load measurement

Fracture load of bilayered specimen was measured by universal testing machine(Instron 3366, Instron Corporation, U.S.A., Figure 4).

Piston-on-three-ball test was carried out(ISO 6872:2008). Crosshead speed was 1 mm/min. Veneered surface was upward facing to the loading rod. Loading was stopped automatically when sudden drop of load-displacement curve happens.

By fracture load measurement each specimen was broken into several parts. Veneering material was delaminated from zirconia disc and destroyed into more small particles(Figure 5).



Figure 4. Universal Testing Machine for fracture load measurement (Instron Corporation, U.S.A.).

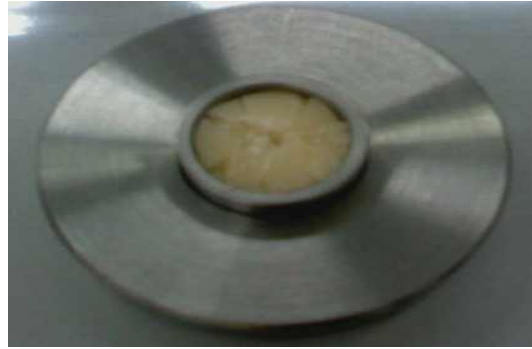


Figure 5. The specimen after fracture load measurement.

## B. XRD measurement

The crystalline phases of veneered and exposed surface of each group were analyzed (n=10/group) using X-ray Diffraction analysis (XRD) by Ultima IV X-ray diffractometer (Rigaku Co., Japan, Figure 6).

The scans were conducted at 40 kV and 120 mA for  $2\theta$  angles between  $20.0^\circ$  and  $40^\circ$  at  $1^\circ/\text{min}$  scan speed using Cu-K $\alpha$  radiation. And the step size was  $0.02^\circ$ . The monoclinic phase fraction was calculated using Garvie and Nicholson's equation (Garvie et al., 1975)(1), where  $I_m$  and  $I_t$  are the integrated intensities of monoclinic and tetragonal diffraction peaks.

$$X_m = \frac{I_{m(\bar{1}11)} + I_{m(111)}}{I_{m(\bar{1}11)} + I_{m(111)} + I_{t(111)}} \text{ ----- (1)}$$



Figure 6. X-ray diffractometer (Ultima IV, Rigaku Co., Japan).



### C. Scanning Electronic Microscope(SEM) and Energy Dispersive X-ray Spectroscopy(EDS) analysis

To evaluate existence of monoclinic layer, a zirconia fragment of each group following fracture load measurement was gold sputter-coated, and examined under SEM(S-3000N, HITACHI, Japan). Veneered and exposed side of fractured surface was examined at various magnification to observe monoclinic zirconia grains which could be detached by micro- and macro-crack without any surface treatment.

EDS(EX-250, HORIBA, Kyoto, Japan) was used to evaluate chemical composition at both surfaces. Information about atomic peak was gained especially Yttrium. Weight % of each component was surveyed. Electron beam was shot to randomly selected 5 areas per sample.

### D. Raman Spectroscopy

Raman spectrum was taken to identify monoclinic and tetragonal intensity peak with fractured fragment of zirconia. Randomly selected sample of each group is used for Raman spectroscopy. On veneered surface, 6  $\mu\text{m}$  below veneer/zirconia interface, 6  $\mu\text{m}$  below exposed surface and on exposed surface was shot by Raman laser. Measurements were made in backscattering geometry with a JY LabRam HR fitted with a liquid nitrogen cooled CCD detector(Figure 7). The spectra were collected under ambient conditions using 633 nm line of a He-Ne laser. Focal size of laser was about 1  $\mu\text{m}$ .

### E. Statistical Method

To analyze statistical difference of maximum fracture load, and weight % of Yttrium among groups, one-way ANOVA was carried out by SPSS Statistics(ver. 19, IBM, U.S.A.). Levene's equal variance test and Tukey's Post-Hoc test was done. Within each group,  $X_m$  of veneered and exposed surface were compared by T-test.



Figure 7. Equipment for Raman spectroscopy: LabRam HR(High Resolution), Jovin Yvon, France.

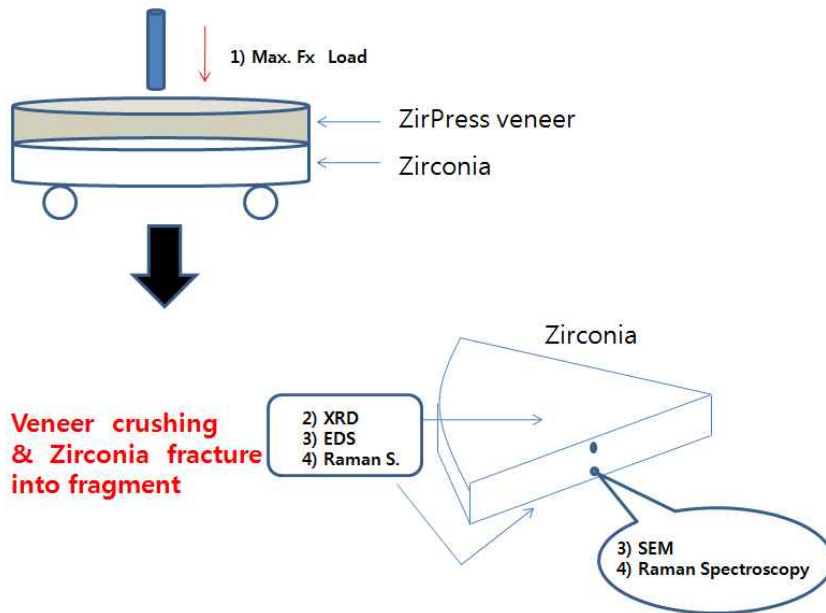


Figure 8. Mimetic diagram of analytic methods.

### III. RESULTS

#### 1. Maximum Fracture Load

Mean and standard deviation of maximum fracture load is shown as Table 3. Levene's test showed equal variance in all samples( $p>0.05$ ). According to one way ANOVA, there was no statistical differences among three groups( $p>0.05$ )(Table 3 and Figure 9). In group A, zirconia core of 5 specimens were not broken during loading test. These unbroken samples were excluded for statistics. In group B and C, 2 and 1 zirconia specimen were not broken respectively and they also discarded.

Table 3. Mean and standard deviation of maximum fracture load measured

Group	n	Max. Load(N)	S.D.
A	15	2771.6	347.6
B	18	2950.7	378.9
C	19	2932.2	372.3

n: number of specimen

N: Newton

S.D.: Standard Deviation

| : Vertical line indicates no statistical difference( $p>0.05$ ).

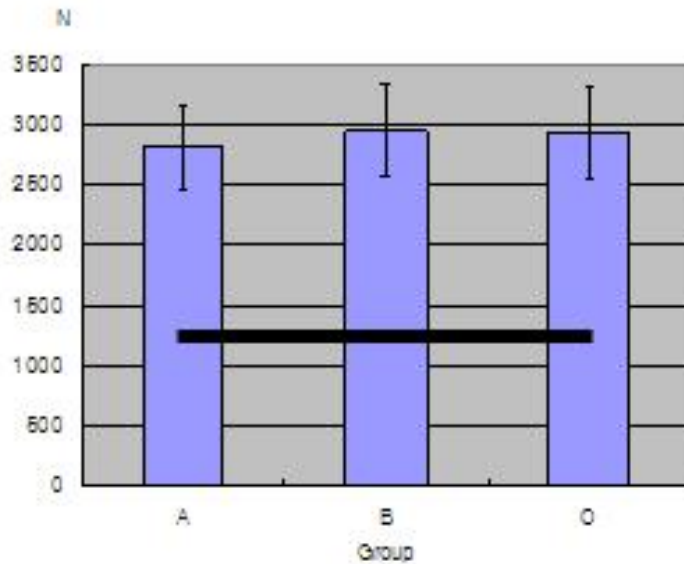


Figure 9. Maximum fracture load.

Horizontal bar indicates no significant difference( $p > 0.05$ ).

## 2. XRD and $X_m$

XRD of each group are shown in Figure 11 to 13. Monoclinic peaks appeared at  $2\theta = 28.2^\circ$  and  $31.3^\circ$ . Tetragonal peak was at  $2\theta = 30.2^\circ$ .

In group A, veneered and exposed surface showed similar monoclinic intensity peak(Figure 10). But, at exposed surface in group B and C, monoclinic peaks increased and tetragonal peak decreased(Figure 11 and 12). Within each group, monoclinic fraction( $X_m$ ) between veneered and exposed surface was compared by T-test. Group A has similar  $X_m$  at both surfaces( $p > 0.05$ ). In group B and C,  $X_m$  of each surfaces were statistically different( $p < 0.05$ )(Table 4 and Figure 13).

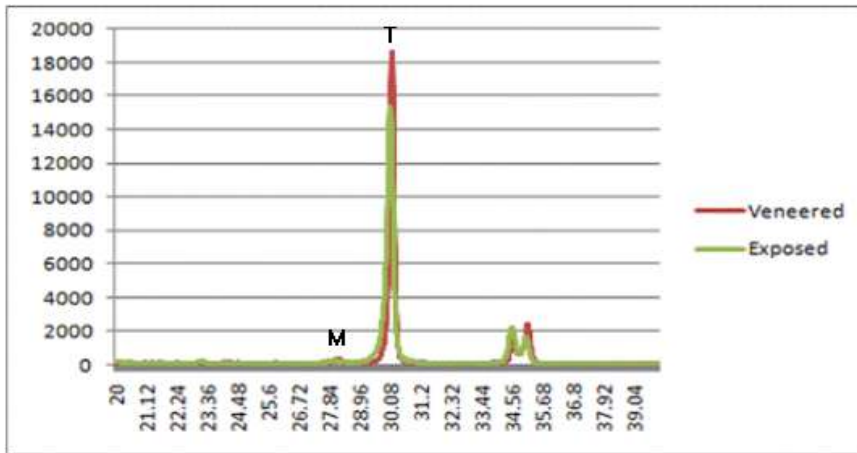


Figure 10. XRD of a sample in group A.

T : tetragonal peak

M : monoclinic peak

Table 4. Monoclinic fraction( $X_m$ ) of each surface

Group ( n=10 )	$X_m$ (S.D.) %	
	veneered	exposed
A	2.195 (0.812)	1.527 (0.979)
B	1.090 (0.830) <sup>a</sup>	17.141 (9.535) <sup>b</sup>
C	1.638 (1.706) <sup>a</sup>	30.565 (10.357) <sup>b</sup>

<sup>a,b</sup>: significant difference with different characters by t-test( $p < 0.05$ ).

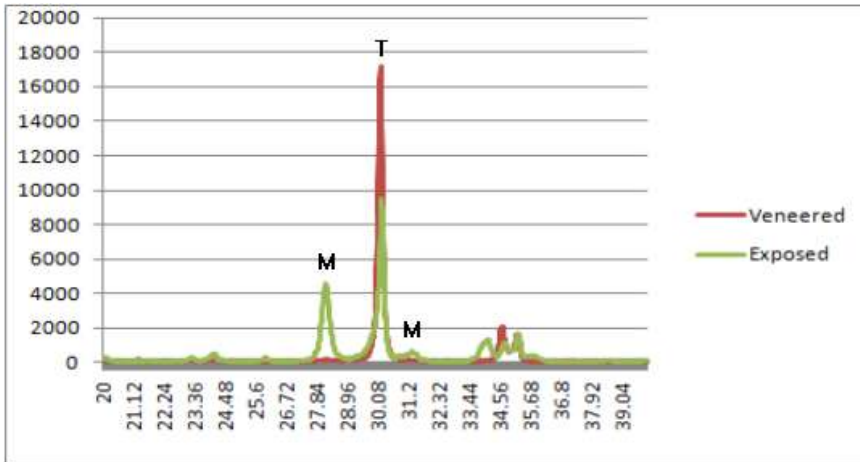


Figure 11. XRD of a sample in group B.

T : tetragonal peak

M : monoclinic peak

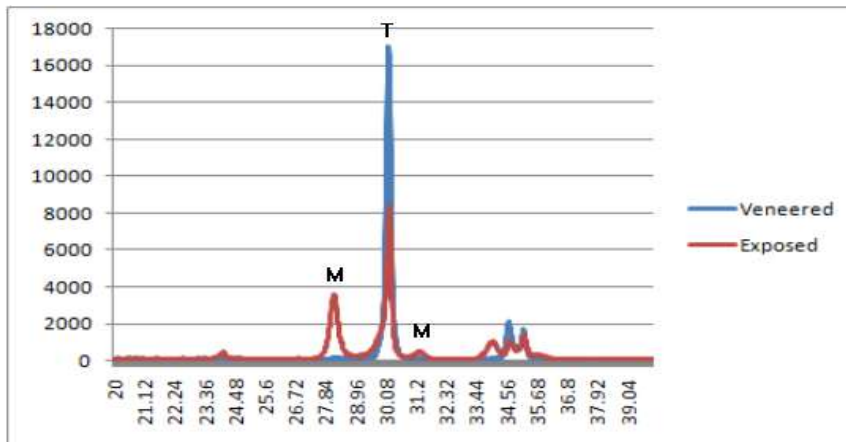


Figure 12. XRD of a sample in group C.

T : tetragonal peak

M : monoclinic peak

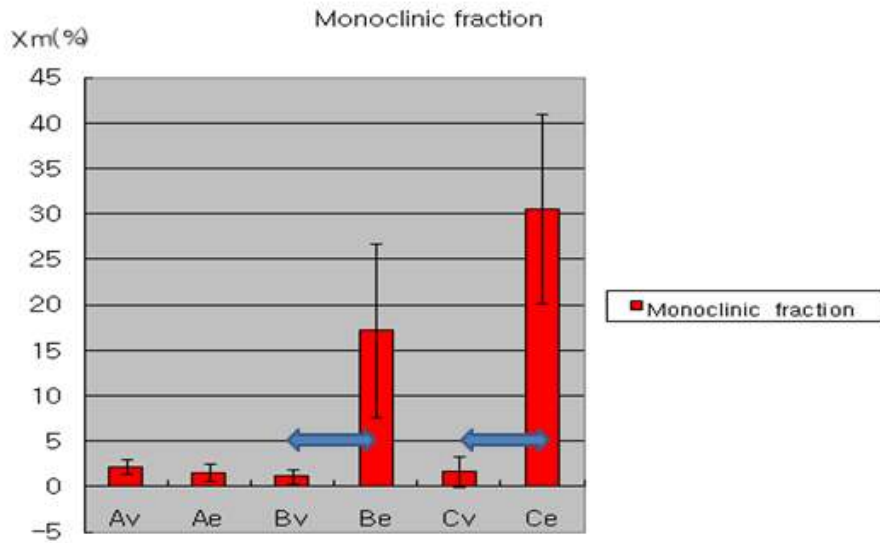


Figure 13.  $X_m(\%)$  of each group.

Blue arrow indicates statistically significant difference ( $p < 0.05$ ).

Av : Group A, veneered surface

Ae : Group A, exposed surface

Bv : Group B, veneered surface

Be : Group B, exposed surface

Cv : Group C, veneered surface

Ce : Group C, exposed surface



### 3. SEM & EDS

We could not find any swollen monoclinic layer distinguished from tetragonal zirconia(Figure 14).

Following T-test, Yttrium weight % was significantly different between exposed and veneered surface only in group C( $p < 0.05$ )(Table 5).

Table 5. Elemental Analysis from EDS

Group	Mean Yttrium weight % (S.D.)	
	veneered	exposed
A	2.37 (0.374)	1.62(0.740)
B	2.634(0.488)	1.918(0.926)
C	2.966(0.633) <sup>a</sup>	1.846(0.750) <sup>b</sup>

<sup>a,b</sup>: significant difference with different characters by t-test( $p < 0.05$ ).

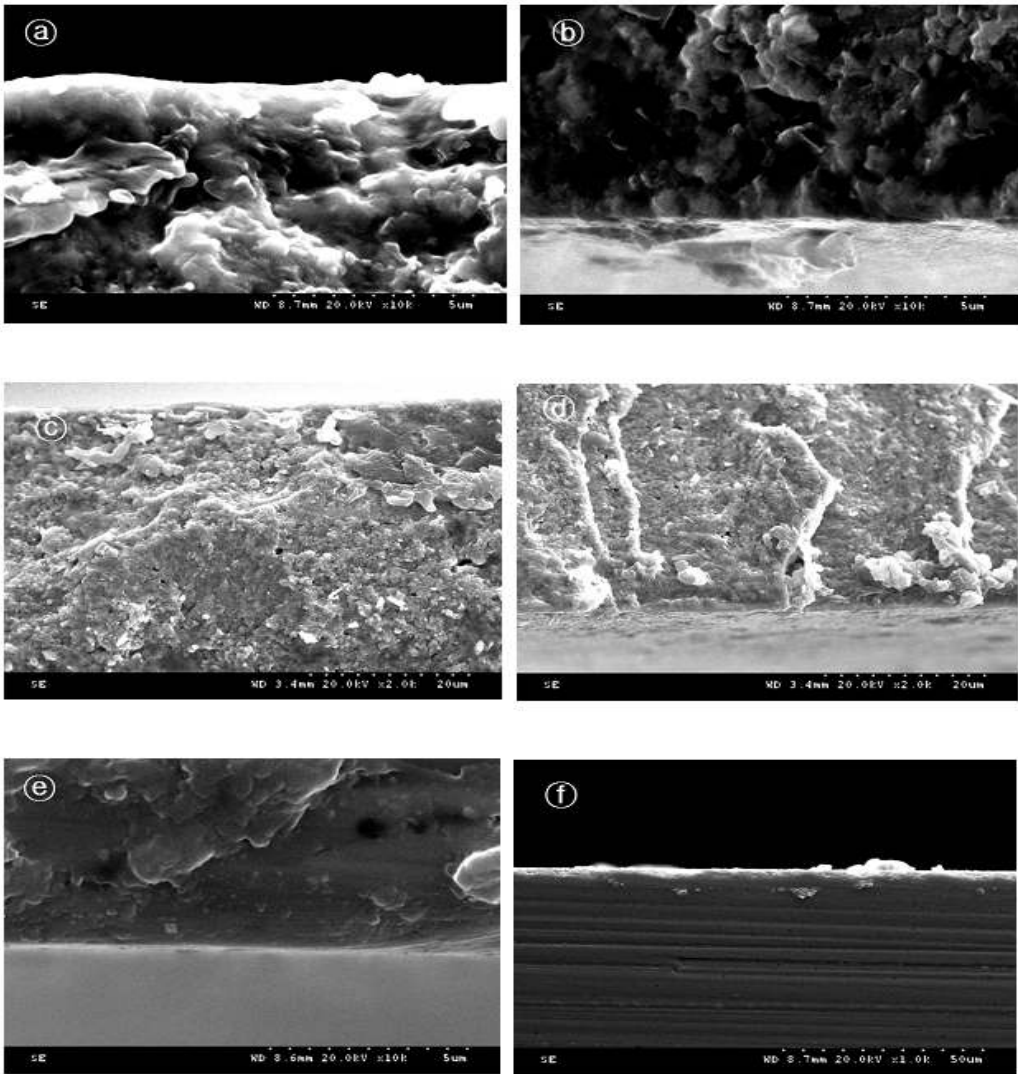


Figure 14. SEM of fractured surface of zirconia.

- ①: Group A, veneered side of fractured surface
- ②: Group A, exposed side of fractured surface
- ③: Group B, veneered side of fractured surface
- ④: Group B, exposed side of fractured surface
- ⑤: Group C, veneered side of fractured surface
- ⑥: Group C, exposed side of fractured surface

#### 4. Raman spectroscopy

Raman spectroscopy of randomly selected specimen of each group showed there was no monoclinic peak except group C at 6  $\mu\text{m}$  below exposed surface(Figure 15 to 17).

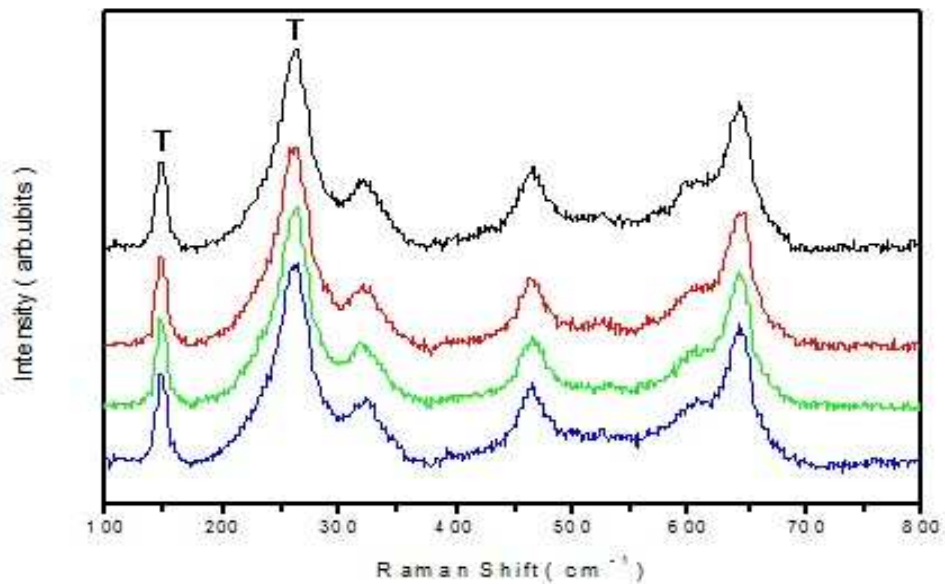


Figure 15. Raman spectra of group A.

■ : 6 $\mu\text{m}$  below veneer/zirconia interface

■ : Veneered surface of zirconia

■ : 6 $\mu\text{m}$  below exposed surface

■ : Exposed surface of zirconia

T: tetragonal peak

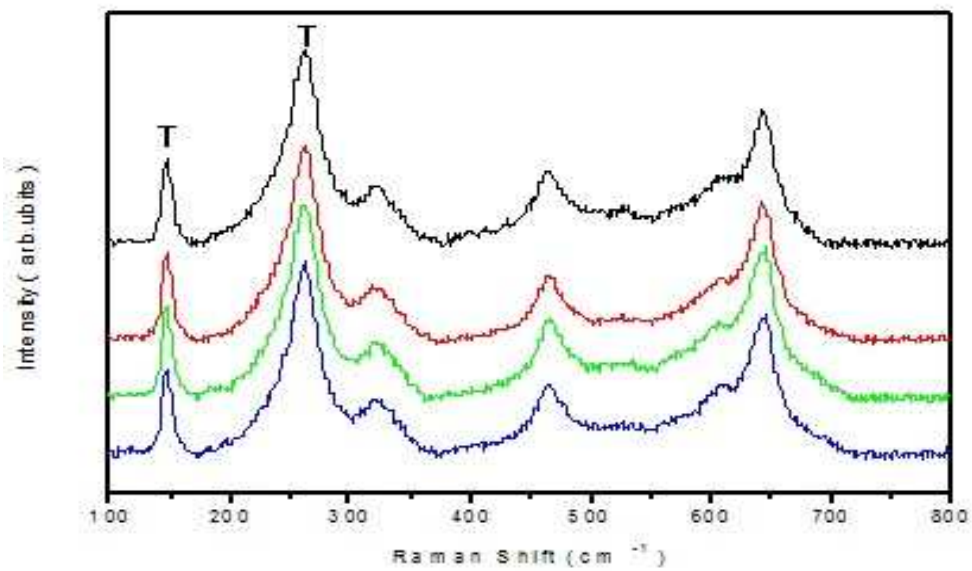


Figure 16. Raman spectra of group B.

■ : 6µm below veneer/zirconia interface

■ : Veneered surface of zirconia

■ : 6µm below exposed surface

■ : Exposed surface of zirconia

T: tetragonal peak

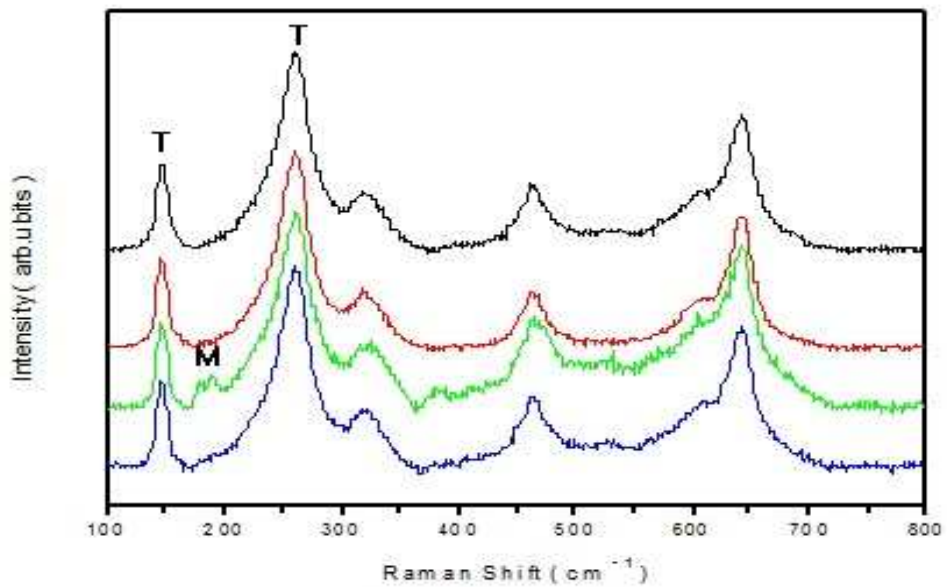


Figure 17. Raman spectra of group C.

■ : 6 $\mu$ m below veneer/zirconia interface

■ : Veneered surface of zirconia

■ : 6 $\mu$ m below exposed surface

■ : Exposed surface of zirconia

T: tetragonal peak

M: monoclinic peak

## IV. DISCUSSION

LTD is an important factor for long-term life of zirconia prosthesis in human body. The accelerated LTD is regarded as accelerating test method for LTD study. So we don't need to observe for long period in vivo in order to study LTD. According to ISO 13356(2008(E)), test environment for accelerated LTD is  $(134 \pm 2) \text{ }^\circ\text{C}$  under a pressure of 0.2 MPa for a period of 5 hours. This period corresponds to 15 years in living body. In this study, we tried to evaluate up to 10 hours(group C), which corresponds to 30 years at intraoral humid condition.

Sectioning and finishing process of zirconia disc from zirconia cylinder can induce monoclinic transformation. Lee and Kim(1991) have shown that transformation is reversible by annealing above  $1200 \text{ }^\circ\text{C}$ . In this study, machined zirconia discs were annealed at  $1200 \text{ }^\circ\text{C}$  for 2 hours before ZirPress veneering procedure. And it could be assumed that all monoclinic phase was reversed into tetragonal phase before veneering. But after veneering, we could not do annealing procedure, because firing temperature of ZirPress is far below annealing temperature.

Veneering process of ZirPress also would have caused monoclinic transformation of tetragonal zirconia core by thermal stimulation during pressing-on procedure. In group A, we kept specimens at dry condition. Monoclinic fraction( $X_m$ ) of the veneered surface and exposed surface in group A was  $(1.882 \pm 0.998) \%$  and  $(1.078 \pm 0.826) \%$  respectively. Statistical significance was not found between  $X_m$  of two opposing surfaces in group A( $p > 0.05$ ). There can be two reason of these monoclinic fraction in group A. One is thermal stimulation during pressing ZirPress veneer, the other is tensional stress during fracture test procedure.

Exposed(tension) side following loading test did not show more monoclinic fraction than veneered(compressed) side in Group A( $p>0.05$ ). Therefore we can deduce that fracture process induced by loading is not critical factor of  $X_m$  at the tensional side of zirconia. In group B and C,  $X_m$  was significantly different between veneered and exposed surface( $p<0.05$ ). The influence of tensional load on  $X_m$  by loading test in group B and C could be considered ignorable as above mentioned. So the difference of  $X_m$  between exposed surface and veneered surface can be regarded caused by accelerated LTD test.

To evaluate LTD at zirconia core surface of bilayered specimen, we should eliminate surface veneering ceramic without any damage to core zirconia. But there is no method to remove veneer material without mechanical damage to core zirconia. Grinding out veneering material from the surface can produce heat and mechanical damage which can induce t-m transformation of core zirconia, and it is impossible to grind specimen until the interface of two materials appears.

Following measurement of maximum fracture load, veneered ZirPress crushed and clearly broken away from zirconia surface prior to core fracture. So, we could proceed with XRD to evaluate monoclinic fraction of veneered side of zirconia from fractured fragment. Manufacturer of ZirPress recommends zirconia that has CTE ranging  $10.5-11.0 \times 10^{-6}K^{-1}$  to use with. The CTE of Zirconia disc used in this study was  $10.5 \times 10^{-6}K^{-1}$  and satisfies CTE range recommended by manufacturer(Ivoclar vivadent, Liechtenstein).

Guazzato et al.(2004) studied mode of fracture of bilayered porcelain/Y-TZP, and concluded that ultimate strength of bilayered specimen was dictated by the properties of the layer on the bottom(facing the three balls). Kim et al.(2007) examined crack propagation kinetics of bilayered specimens and mentioned that crack did not tend to propagate from low modulus and low fracture toughness ceramic to high modulus and high fracture toughness ceramic. Therefore, in this

study the maximum fracture load dictates not the properties of veneering material but the properties of zirconia core because veneered surface was upward facing to the loading pin of universal testing machine. According to Guazzato et al.(2004), when top side compressive load increases and reach compressive strength of veneer material, veneer undergo Herzian cone cracks just beneath the loading pin. These cone cracks are hindered by core material and spread laterally along the interface between core and veneer. As a result of these crack propagation procedure, delamination of veneering ZirPress might be taken place in our study. If load increase thereafter, zirconia core undergo radial cracking process on tension side, and eventually result in bulk fracture. Although it was not displayed in the result, force-displacement curve showed this process. There was small peak which indicates crushing of ZirPress veneer before core fracture. This small peak sometimes did not clearly identified. During loading process at UTM, there was sharp cracking sound of veneer(ZirPress) prior to core fracture. Finally core was broken and displacement curve dropped to almost zero. This point, the last peak at the force-displacement curve, was regarded as core fracture.

At some samples, veneers crushed without core fracture. These samples showed remaining veneer material adhering to zirconia core just below loading pin area, like vulcano shape. At these samples, other parts of veneer was crushed out along the interface without zirconia core fracture. Sudden drop of load/displacement curve were not happen on those specimens, so these samples were discarded. Wakabayashi and Anusavice(2000) suggested that the thickness ratio of the core to the veneer is the dominant factor that control failure initiation site in bilayered ceramic disks. At those discarded samples, fracture initiated at veneer surface just underneath loading pin, but there was no radial crack of core zirconia. Guazzato et al.(2004) also described this phenomenon on



their study. This might be owing to the core to veneer thickness ratio smaller than 1:1 in our study. If we had made bilayered specimen with more thicker zirconia veneered by more thinner ZirPress, we could have induced zirconia fracture at all specimens.

Surface defects and flaw distribution can affect mechanical strength of ceramic materials. In this study, highly polished zirconia surface was at tension during fracture load test to minimize influence by those factors. Although there was no statistical significance, some increase of maximum fracture load in group B and C was observed. This might be due to more monoclinic transformation which makes compressive stress field at the exposed surface in group B and C. This may increase fracture load during fracture test.

XRD is frequently used to evaluate transformation kinetics in many studies. But its disadvantage is that XRD signal is only from the surface layer no more than the surface few microns. So, if we want to know phase transformation of subsurface area we should cross-section or fracture zirconia specimen. And the focal size of X-ray beam is a few millimeters, and we can not get accurate information of localized small area less than a few micrometers. We tried XRD to investigate veneered and unveneered(exposed) wide surface of each disc specimen after fracture load test. According to Deville et al.(2005), the curve of monoclinic fraction by XRD shows sigmoidal shape and transformation rate increases up to plateau value and does not increase after 12 hours at 134 °C. This can be considered as saturation point on the zirconia surface. In this study we designed test group up to 10 hours(group C), and this is under the surface saturation point mentioned by Develle et al.(2005). Because low temperature degradation proceeds into the bulk(inner part) of zirconia following surface saturation of monoclinic phase, we could predict that exposed surface in group C would undergo surface monoclinic transformation which might not proceed into

the bulk.

SEM can be used to evaluate monoclinic propagation into the material. Monoclinic transformation of zirconia accompanies extensive microcracking, and when polishing the surface monoclinic phases easily taken away leaving holes (Deville et al. 2005). So, they explained that on cross sectional area one can observe transformed area distinguished from tetragonal area. Ban et al. reported 3 to 5  $\mu\text{m}$  thickness swollen monoclinic layer after accelerated LTD at 121  $^{\circ}\text{C}$  for 10 days. They polished using 1  $\mu\text{m}$  diamond suspension and thermally etched at temperature 150  $^{\circ}\text{C}$  below each sintering temperature for 1 hour to reveal grain boundary. Deville et al. reported about 4  $\mu\text{m}$  after 11 hours at 134  $^{\circ}\text{C}$  in accelerated LTD. In our study SEM image of fractured surface showed no transformed area in all groups. SEM image of group C highly polished specimen also showed no monoclinic zone. Because thermal etching could influence monoclinic transformation, in this study fractured cross sectional area was observed without thermal etching. In this study, the SEM result implies that monoclinic transformation did not proceed into the deeper part of zirconia on exposed and veneered surfaces in all groups.

Yttrium concentration was lower at exposed surface than that of veneered surface in all groups. But in group A and B there was no statistical difference between two surfaces ( $p > 0.05$ ). Only in group C, there was significant decrease of yttrium at exposed surface ( $p < 0.05$ ). Those decrease of yttrium is thought to be caused by monoclinic transformation at exposed surface. This result corresponds to the study of Papanagiotou et al. (2006). They mentioned that yttrium depletion could decrease the tetragonal phase stability over time although LTD did not degrade strength in their study.

Raman spectroscopy of randomly selected samples showed only tetragonal peaks except at 6  $\mu\text{m}$  below exposed surface in group C. This distance of 6  $\mu\text{m}$

from the surface area was decided according to Borchers et al.(2010). They suggested that depth of transformation zone could influence strength of zirconia if crack length reaches certain value decided by equation of stress intensity factor (2).

$$K_{IC} = \sigma_c \sqrt{(\pi a Y)} \quad \text{----- (2)}$$

$K_{IC}$  is stress intensity factor,  $\sigma_c$  is the critical stress which lead to propagation of a crack with initial length 'a' and Y a geometry factor taken as 1.12 for a surface crack. According to manufacturer, critical stress of zirconia specimen in this study is 1300 MPa, and  $K_{IC}$  is 6.0 MPa • m<sup>1/2</sup>. From equation (2) about 6 μm can be considered as minimum depth of the transformation zone which can affect zirconia strength.

Although monoclinic phase can be generated by fracture process itself, it concentrates on fracture margin and tensional surface (Pittayachawan et al., 2008). In this study, Raman laser focused only on halfway between corner edge, so this focusing spot can be regarded not influenced by fracture induced t-m transformation but represents result of LTD process. Raman spectroscopy showed that there was no monoclinic peak except a point in group C. There was no monoclinic peaks at veneered and exposed surface in all groups. If monoclinic phase did not spread all over the surface by accelerated LTD, and Raman laser was focused on remaining tetragonal area, we could not find monoclinic peaks on Raman spectrum. Maybe this could be due to small focal size (about 1 μm) of Raman spectroscopy. If more wide area could be scanned, for example Raman scanning image, we could detect more monoclinic area corresponding to XRD results.

There should be more well established and acceptable experimental method to evaluate monoclinic transformation of zirconia under veneering ceramic in the future. If there are monoclinic phase under veneer ceramic, it can influence bond strength between zirconia and veneer material. Because coefficient of thermal expansion of monoclinic phase is far lower than that of tetragonal phase, tensional stress could be developed on veneer at veneer/zirconia interface. And this could result in early failure of zirconia bilayered prosthesis by veneer chipping. There should be further research on bond strength of bilayered zirconia by accelerated LTD.

From the results of this study we can conclude that LTD happened at exposed surface in group B and C, but it did not spread into inner portion of zirconia core which could be detected by SEM and Raman spectroscopy. And, mechanical property of exposed zirconia core was not influenced by accelerated LTD procedure.

In clinical environment, exposed zirconia core can undergo low temperature degradation. But, within limitation of this study, it may not influence clinical performance and prosthesis longevity concerning zirconia core. Moreover, if we can veneer 3Y-TZP core by appropriate ceramic, low temperature degradation of zirconia could be prevented.

## V. CONCLUSION

The following results were drawn from measurement of fracture load, X-ray diffraction analysis, scanning electron microscopy, energy dispersive X-ray spectroscopy, and Raman spectroscopy of veneered and exposed zirconia to accelerated low temperature degradation.

1. Fracture load of each group did not show statistical difference among three groups( $p>0.05$ ).
2. In group A, monoclinic fractions( $X_m$ ) of veneered and exposed zirconia surface were not statistically different( $p>0.05$ ). In group B and C, exposed zirconia surface has higher  $X_m$  than veneered surface( $p<0.05$ ).
3. SEM of fractured surface did not show clearly identified monoclinic zone.
4. EDS showed decrease of yttria concentration at exposed surface in all groups, but there was statistical difference only in group C( $p<0.05$ ).
5. Raman spectra showed monoclinic peak only at 6  $\mu\text{m}$  below exposed surface in group C. Other points of group C and other groups showed only tetragonal peaks.

In the limitation of this study, monoclinic phase transformation occurs much more on exposed zirconia surface, but it can be detected only by

XRD, SEM/EDS and Raman spectroscopy did not show distinct evidence of monoclinic phase. Veneered portion of zirconia did not transformed to monoclinic phase after accelerated LTD. Hypothesis (1) is accepted, and (2) was denied. So, in this study we can conclude that accelerated LTD procedure corresponding to 30 years in vivo has no negative effect on mechanical characteristic of bilayered dental 3Y-TZP.

## REFERENCES

- Aboushelib MN, Kleverlaan CJ, Feilzer AJ: Evaluation of a high fracture toughness composite ceramic for dental applications. *J Prosthodont* 17: 538-544, 2008a.
- Aboushelib MN, Kleverlaan CJ, Feilzer AJ: Microtensile bond strength of different components of core veneered all-ceramic restorations. Part 3: Double veneer technique. *J Prosthodont* 17: 9-13, 2008b.
- Al-Dohan HM, Yaman P, Dennison JB: Shear strength of core-veneer interface in bi-layered ceramics. *J Prosthet Dent* 91: 349-355, 2004.
- Anusavice KJ: Crack initiation modes in bilyered alumina/porcelain disks as a function of core/veneer thickness ratio and supporting substructure stiffness. *J Dent Res* 79: 1398-1404, 2000.
- Ardlin BI: Transformation-toughened zirconia for dental inlays, crowns and bridges: chemical stability and effect of low-temperature aging on flexural strength and surface structure. *Dent Mater* 18: 590-595, 2002.
- Ban S, Sato H, Suehiro Y, Nakanishi H, Nawa M: Biaxial flexure strength and low temperature degradation of Ce-TZP/ $\text{Al}_2\text{O}_3$  nanocomposite and Y-TZP as dental restoratives. *J Biomed Mater Res Part B: Appl Biomater* 87B: 492-498, 2008.

Borchers L, Stiesch M, Bach FW, Buhl JC, Hubsch C, Kellner T, Kohorst P, Jendras M: Influence of hydrothermal and mechanical conditions on the strength of zirconia. *Acta Biomaterialia* 6: 4547-4552, 2010.

Cales B: Zirconia as a sliding material: histologic, laboratory, and clinical data. *Clin Orthop Relat Res* 379: 94-112, 2000.

Casellas D, Cumbre FL, Sanchez-Bajo F, Forsling W, Llanes L, Anglada M: On the transformation toughening of Y-ZrO<sub>2</sub> ceramics with mixed Y-TZP/PSZ microstructures. *J Euro Ceram Soc* 21: 765-777, 2001

Chevalier J: What future for zirconia as a biomaterial? *Biomaterials* 27: 535-543, 2006.

Chevalier J, Cales B, Drouin JM: Low temperature aging of 3Y-TZP. *J Am Ceram Soc* 82: 2150-2154, 1999.

Curtis AR, Wright AJ, Fleming GJ: The influence of surface modification techniques on the performance of a Y-TZP dental ceramic. *J Dent* 34: 195-206, 2006.

Deville S, Gremillard L, Chevalier J, Fantozzi G: A critical comparison of methods for the determination of the aging sensitivity in biomedical grade yttria-stabilized zirconia. *J Biomed Mater Res Part B: Appl Biomater* 72B: 239-245, 2005.

Dundar M, Ozcan M, Comlekoglu E: Bond strengths of veneering ceramics to



reinforced ceramic core materials. *Int J Prosthodont* 18: 71-72, 2005.

Garvie RC, Hannink RH, Pascoe RT: Ceramic steel? *Nature* 258: 703-704, 1975.

Gremillard L, Chevalier J, Deville S, Epicier T, Fantozzi G: Modeling the aging kinetics of zirconia ceramics. *J Eur Ceram Soc* 24: 3483-3489, 2004.

Guazzato M, Proos K, Quach L: Strength, reliability and mode of fracture of bilayered porcelain/zirconia (Y-TZP) dental ceramics. *Biomaterials* 25: 5045-5052, 2004.

Guazzato M, Quach L, Albakry M, Swain MV: Influence of surface and heat treatments on the flexural strength of Y-TZP dental ceramic. *J Dent* 33: 9-18, 2005.

Hannink RHJ, Kelly PM, Muddle BC: Transformation toughening in zirconia-containing ceramics. *J Am Ceram Soc* 83: 461-487, 2000.

Kim B, Zhang Y, Pines M, Thompson VP: Fracture of porcelain-veneered structures in fatigue. *J Dent Res* 86: 142-146, 2007.

Kim DJ, Jung HJ, Cho DH: Phase transformation of  $Y_2O_3$  and  $Nb_2O_3$  doped tetragonal zirconia during low temperature aging in air. *Solid State Ionics* 80: 67-73, 1995.

Kim JW, Covell NS, Guess PC, Rekow ED, Zhang Y: Concerns of hydrothermal degradation in CAD/CAM Zirconia. *J Dent Res* 89: 91-95, 2010.

Kosmac T, Oblak C, Jevnikar P, Funduk N, Marion L: Strength and reliability of surface treated Y-TZP dental ceramics. *J Biomed Mater Res* 53: 304-313, 2000.

Kosmac T, Oblak C, Jevnikar P, Funduk N, Marion L: The effect of surface grinding and sandblasting on flexural strength and reliability of Y-TZP zirconia ceramic. *Dent Mater* 15: 426-433, 1999.

Lawson S: Environmental degradation of zirconia ceramics. *J Eur Ceram Soc* 15: 485-502, 1995.

Lee JK, Kim H: Monoclinic-to-tetragonal transformation and crack healing by annealing in aged 2Y-TZP ceramics. *J Mat Sci Lett* 22: 1765-1767, 1991.

Oh GJ, Yun KD, Lee KM, Lim HP, Park SW: Sintering behavior and mechanical properties of zirconia compacts fabricated by uniaxial press forming. *J Adv Prosthodont* 2: 81-87, 2010.

Papanagiotou HP, Morgano SM, Giordano RA, Pober R: In vitro evaluation of low-temperature aging effects and finishing procedures on flexural strength and structural stability of Y-TZP dental ceramics. *J Prosthet Dent* 96: 154-164, 2006.

Pittayachawan P, McDonald A, Young A, Knowles JC: Flexural strength, fatigue life, and load-induced phase transformation study of Y-TZP dental ceramic. *J Biomed Mater Res Part B: Appl Biomater* 88B: 366-377, 2009.

Stuart AR, Filser F, Kocher P, Gauckler LJ: In vitro lifetime of dental

ceramics under cyclic loading in water. *Biomaterials* 28: 2695-2705, 2007.

Sundh A, Sjögren G: A comparison of fracture strength of yttrium-oxide-partially-stabilized zirconia ceramic crowns with varying core thickness, shapes and veneer ceramics. *J Oral Rehabil* 31: 682-688, 2004.

Taskonak B, Mecholsky JJ Jr, Anusavice KJ: Residual load in bilayer dental ceramics. *Biomaterials* 26: 3235-3241, 2005.

Ruiz L, Readey MJ: Effect of heat treatment on grain size, phase assemblage, and mechanical properties of 3-mol % Y-TZP. *J Am Ceram Soc* 79: 2331-2340, 1996.

Vult von Steyern P: Five-year evaluation of posterior all-ceramic three-unit(In-Ceram) FPDs. *Int J Prosthodont* 14: 379-384, 2001.

Wakabayashi N, Anusavice KJ: Crack initiation modes in bilayered alumina/porcelain disks as a function of core/veneer thickness ratio and supporting substructure stiffness. *J Dent Res* 79: 1398-1404, 2000

Wakabayashi N, Papanagiotou HP, Morgano SM, Giordano RA, Pober R: In vitro evaluation of low-temperature aging effects and finishing procedures on the flexural strength and structural stability of Y-TZP dental ceramics. *J Prosthet Dent* 96: 154-164, 2006.

Yoshinari M: Fracture strength of all-ceramic crowns. *Int J Prosthodont* 7: 329-338, 1994.

## 국문요약

가속화된 저온열화에 따른 치과용 3Y-TZP의 상전이 특성

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본 연구는 3Y-Tetragonal Zirconia Polycrystal(3Y-TZP)을 재료로 하여 수분에 직접 노출된 경우와 비니어도재에 의해 피개된 경우에 있어서의 가속화된 저온열화처리에 따른 t-m 상전이 차이를 알아보고 이러한 상전이가 기계적 특성에 영향을 주는지 알아보려고 하였다. 총 60개의 완전소결된 원판형 3Y-TZP를 제작하고 각각의 가공면에 ZirPress를 Press-on 기법으로 비니어 하였고, 그 반대쪽은 경면연마하였다. 군당 20개 씩, 가속화 조건에 따라 대조군(A군)과 증류수 침적조건하의 134℃에서 5시간(B군), 10시간(C군) 처리군으로 각각 나누었다. 비니어된 3Y-TZP시편의 최대파절하중을 측정하였고, 그 뒤 비니어가 분리된 파절된 시편을 X-Ray Diffraction analysis(XRD), Scanning Electronic Microscope(SEM), Energy Dispersive X-ray Spectroscopy(EDS), Raman spectroscopy의 방법으로 분석하였다. B군과 C군에 있어서 XRD를 통해 얻은 단사정상 분률( $X_m$ )은 비니어 되었던 면 보다 노출된 면에서 유의차 있게 높게 나타났지만( $p < 0.05$ ), 최대파절하중은 대조군을 포함한 세 군간에 차이를 나타내지 않았다( $p > 0.05$ ). 파절단면의 SEM 결과 세

군 모두에서 명확히 분리된 단사정상 층을 관찰할 수 없었고, EDS 측정 결과 C군에서만 노출된 면의 Yttrium의 무게백분율이 비니어되었던 면보다 유의차 있게 감소했다( $p < 0.05$ ). 라만분석에서는 C군의 파절단면에 있어서 노출되었던 면으로부터 6  $\mu\text{m}$  하방에서만 단사정상 피크가 관찰되었고, C군의 나머지 측정부위와 A군과 B군의 모든 측정부위에서는 정방정상 피크만 관찰되었다.

이상의 결과로부터, 구강내 환경으로는 각각 15년과 30년에 해당하는 가속화된 저온열화 조건에서 수분에 직접 노출된 3Y-TZP는 비니어도재에 의해 피개된 3Y-TZP보다 유의차 있게 높은 t-m 상전이를 보이지만, 이는 표층에 국한된 것으로 여겨지며, 저온열화에 의한 보철물의 실패에 영향을 주지 않는 것으로 생각된다.

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핵심 되는 말: 치과용 지르코니아, 3Y-TZP, 저온열화, t-m 상전이