J. Gifu Dent. Soc.
Vol.46, No.1, 9 ~ 16
June, 2019



ORIGINAL ARTICLES

# Reinforcement of dental porcelain by a newly developed potassium-containing paste

UNO MITSUNORI[1)], KAWAKI HARUMI[2)], NONOGAKI RYUGO[1)], HONDA AYUMU[1)],
SAWANO MIKU[1)], SAWADA TOSHIKO[1)], OKA TOSHIO[1)], KONDOH NOBUO[2)],
KURACHI MASAKAZU[3)], ISHIGAMI HAJIME[1)], DOI YUTAKA[3)]

*We investigated porcelain reinforcement achieved through ion exchange using newly developed potassium-containing of 3 types pastes. The surface of dental porcelain was first covered by the paste and then fired to promote ion exchange of sodium in the porcelain with potassium in the paste. The ion exchange significantly suppressed crack extension on the porcelain surface but did not alter the Vickers hardness. This is likely because residual compressive stress was successfully created on the porcelain surface after the ion exchange of* $Na^+$ *with* $K^+$*. More important from an aesthetic standpoint is that the ion exchange showed no essential influence on the porcelain color. The results of the present study showed that enhancement of the physical properties of dental porcelain by ion exchange using a potassium-containing paste is effective. As a result, the extension of porcelain cracks induced by stress caused by daily occlusal contacts could be successfully suppressed, allowing the dental porcelain to maintain its quality over a long period.*

Key words : Dental ceramics, Ion exchange, Potassium-containing paste

## Introduction

The goal of prosthodontics is to recover the form, function, and aesthetics of teeth using artificial materials that are resistant to discoloration, chipping of the dental crown (partially or wholly), or loss of teeth[1-4)]. Regeneration of organs and tissues in regenerative medicine emphasizes functional factors, whereas prosthetic treatment emphasizes aesthetics. For this reason, ceramics such as porcelain have been frequently used as a dental material to solve the problem of aesthetics and metal allergies, satisfy the aesthetic desires of patients, and improve their quality of life[5)]. The development of the CAD/CAM system has also enabled the manufacture of prostheses with a stable level of quality. The development of materials applicable to the CAD/CAM system, such as porcelain and zirconia, has gained significant attention in recent years. Several all-ceramic restoration systems, in which strong ceramics are applied and covered with enamel-colored porcelain, have recently entered the market[6, 7)]. However, both metal and zirconia ceramic prostheses covered with porcelain suffer from small cracks and fractures of the porcelain. This damage occurs more frequently in zirconia ceramics. Previous studies have reported that such damage is typically caused by aggregated fracture that takes place inside the porcelain, rather than at the interface between the porcelain and zirconia frame [8)]. Therefore, the establishment of a method that enhances the strength of porcelain is crucial to improving porcelain-based dental prostheses, allowing them to maintain their quality over a long period. In order to enhance the physical properties of a porcelain, a dispersing material that prevents the propagation of porcelain cracks can be effective. Another approach to reinforcing porcelain materials is the introduction

[1)] *Department of Prosthodontics, Division of Oral Functional Science and Rehabilitation, Asahi University School of Dentistry*
[2)] *Department of Oral Biochemistry, Division of Oral Structure, Function, and Development, Asahi University School of Dentistry*
[3)] *Asahi University*
*1851 Hozumi Mizuho-city Gifu Prefecture 501-0296*
*(Accepted April 5, 2019)*

of residual compressive stresses to their surfaces. The effectiveness of introducing residual stress for enhancement of the physical properties of porcelain has been demonstrated in several reports[9-13]). In one method, residual stress was introduced by "hot quenching". This process generates a temperature difference between the surface of the porcelain and its interior, creating a compressive stress on the surface. In another method, residual stress was introduced by ion exchange, in which sodium ion was replaced by a larger alkali metal ion, such as potassium [9-13]. Porcelain reinforcement by ion exchange can be achieved irrespective of the shape or thickness of the manufactured prostheses. In a previous study [14], silver and potassium ions were introduced into a commercial staining slurry. Treatment by the staining slurry increased the Vickers hardness of the surface of IPS blocks and inhibited crack propagation. Compared to silver ions, the effect was more greatly affected by potassium ions.

In general, potassium-containing staining slurries are much easier to handle and are less dangerous than slurries with molten potassium nitrate when performing ion exchange. Staining slurries, however, have some drawbacks and have been known to drip from the specimen surface when applied in greater than recommended amounts. In the present study, a porcelain surface was coated with potassium-containing paste, and the material was fired in order to promote ion exchange of sodium ions with potassium ions on the surface of the porcelain. The Vickers hardness and fracture toughness of the resulting porcelain were subsequently investigated. Influences of the paste on the porcelain color were also investigated.

## Materials and Methods

### 1. Preparation of porcelain specimens

Porcelain blocks (IPS Empress CAD) were purchased from Ivoclar vivadent (Tokyo, Japan). The porcelain blocks were cut into smaller, 3-mm-thick blocks, which have overall dimensions of 12 mm x 14 mm x 3 mm. These specimens were polished by an automatic polisher (Abramin, Struers, Denmark) to #250 to 4,000 using water resistant SiC polishing paper.

### 2. Ion exchange of the porcelain surface using potassium nitrate

Paste that contains potassium nitrate at a concentration of 0.1, 0.2, or 0.3 mol/l (Okuno Chemical Industries, Osaka, Japan) was used for ion exchange on the porcelain surface. These pastes were painted on the surface of polished porcelain specimens to prepare three types of samples (K01, K02, and K03). The specimens were fired (dried for 1 hr, rate of temperature increase: 50° C/min, vacuum: 730 mmHg, final firing temperature: 500℃, rapid cooling) in a porcelain furnace (KDF Master Summit J100, Denken Co., Oita, Japan). Figure 1 shows the procedure for sample preparation and all three types of samples.

### 3. Vickers hardness

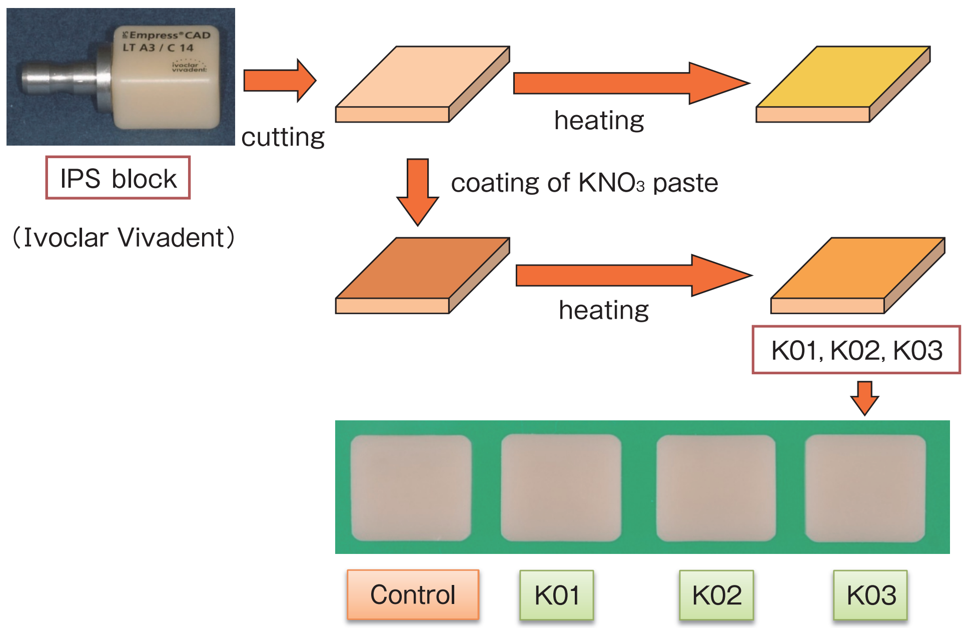
Using a micro-hardness tester (HMV, Shimadzu Co. Kyoto, Japan), a Vickers indenter was pressed into five areas on each specimen for 15 s at a load of 1.961 N (Load 1), 2.942 N (Load 2), 4.903 N (Load 3), 9.807 N (Load 4), or 19.614 N (Load 5), and the Vickers hardness (HV) was calculated based on the length of the diagonal line of the pressure impression.

### 4. Crack length by the indentation fracture method

The lengths of median cracks ($2a_1$, $2a_2$) that extended from the edge of the impression were measured in each pressure impression following JSMS-SD-4-01[15], and the mean value, 2a, was calculated. Where "a" is half the crack length (m), and "d" is the diagonal length of the pressure impression (m) (Figures 2A and 2B). Before the measurements, an appropriate load for measuring the Vickers hardness of the samples was selected from the aforementioned loads (loads 1-5) under JSMS-SD-4-01[15].

The load of 9.807 N was selected from 3 condition based on the standards by the Society of Materials Science, Japan (JSMS-SD-4-01[15]). The first condition, the 5 points (Load1 to Load5) are out of from the dotted line of Proportional relationship (Figure 2c). Second condition, the 5 points (Load1 to Load5) are proportional relation (Figure 2c). And thirdly condition, mean of 2a / mean of d is 1.6 or more. Using this 9.807 N, the Vickers hardness and the crack length of the samples was measured.

A




B

| Sample Name | | K01 | K02 | K03 |
|---|---|---|---|---|
| $KNO_3$ concentration | (mol/l) | 0.1 | 0.2 | 0.3 |

Figure 1
A: Overview of the procedure for preparation of the porcelain specimen.
B: List of porcelain samples

5. Color measurements

Color was measured using 4-mm-thick sintered specimens that were polished in the manner described above. The color was determined as previously described[16], according to the CIE $L^*a^*b^*$ color scale relative to a standard white barium sulfate tile (CIE $L^* = 100$, $a^* = 0$, $b^* = 0$) on a spectrophotometer (UV-3600, Shimadzu Co.) in the range of 200 to 780 nm with an attached integrating sphere. Here, $L^*$ represents the lightness, $a^*$ represents the red-green chromaticity coordinate, and $b^*$ represents the yellow-blue chromaticity coordinate.

6. Statistical analysis

Data on Vickers hardness, crack length development and color change were collected from each 5 sites on three types of samples. All statistical analyses were carried out using one-way analysis of variance (ANOVA) followed by Bonferroni post-test to assess differences among groups. All data are expressed as the group mean ± standard deviation. A probability level of 0.01 or less was accepted as significant.

## Results

1. Vickers hardness

Regardless of ion exchange treatment using a potassium nitrate, no significant difference was observed in the Vickers hardness of the porcelain specimens (Figure 3).

2. Crack length development

The crack length developed on the porcelain

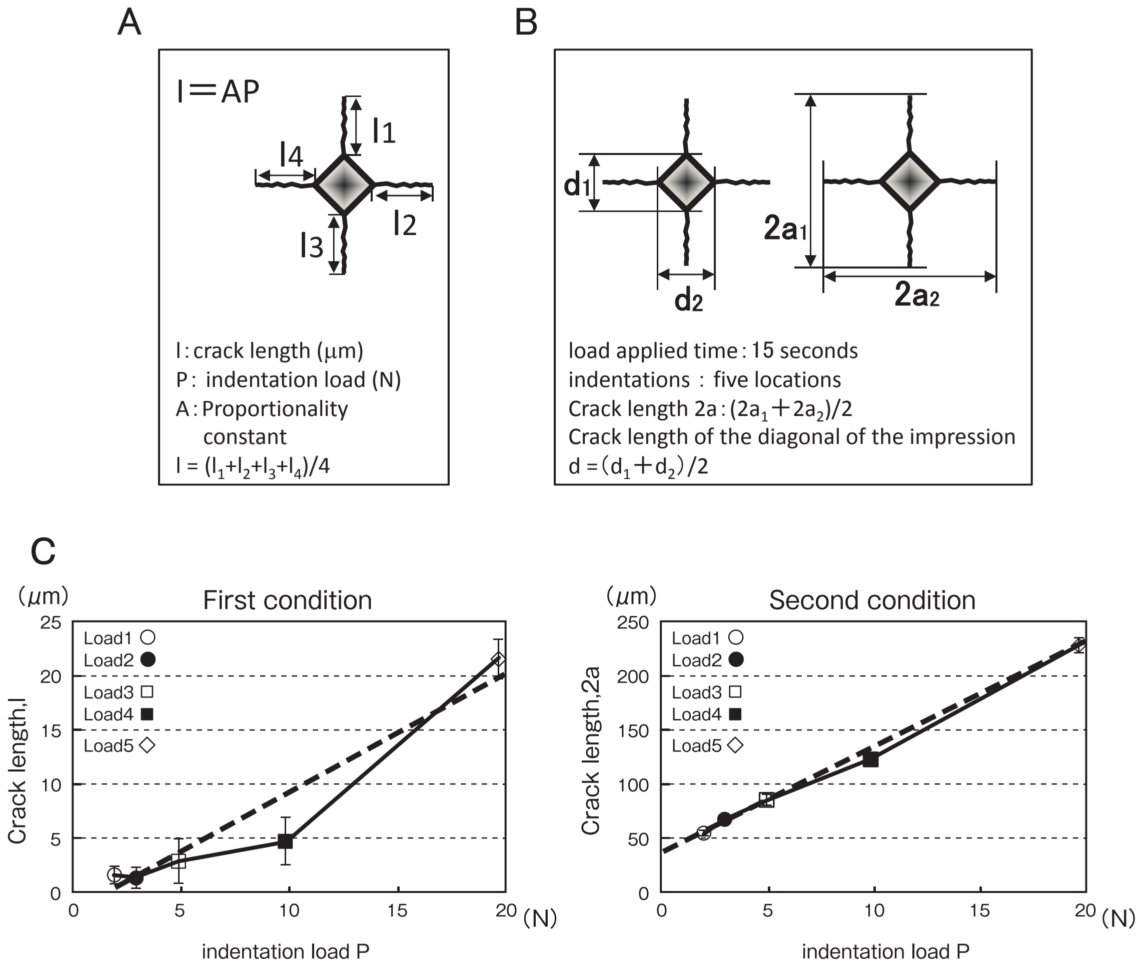



Figure 2

A: Schematic diagram of the cracks created on the porcelain by the diamond indenter and the index (I, P, A) used to measure the crack length.

B: Schematic diagram of the cracks created on the porcelain by the diamond indenter and the index (d, a) used to measure the crack length.

C: Both 4L (left panel) and 2a (right panel) for each load were calculated in order to determine the load for the indentation fracture test.

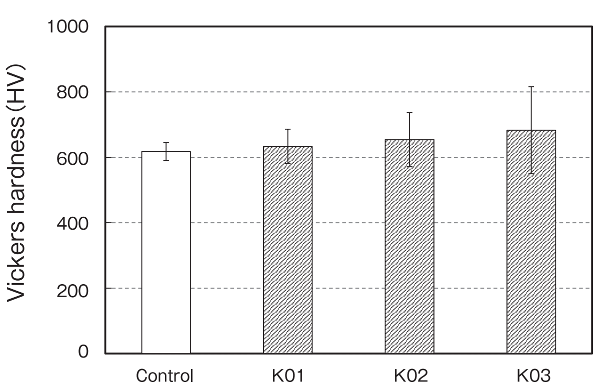



Figure 3 Effect of ion exchange using potassium-containing paste on the Vickers hardness of the porcelain surface.

material by a diamond indenter became significantly shorter with potassium nitrate ion exchange treatment (Figure 4). Among the three concentrations of potassium nitrate used in the present study, 0.2 M was found to be the most effective concentration to suppress the crack extension.

3. Color change in porcelain after ion exchange by $KNO_3$

No significant differences were observed across the parameters of $L^*$, $a^*$, and $b^*$ for any of the pastes containing different concentrations of potassium nitrate (Figure 5A). In addition, no significant

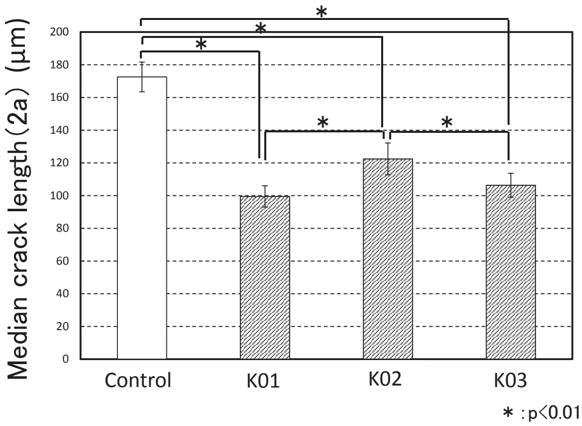



Figure 4 Effect of ion exchange using potassium-containing paste on the extension of the cracks on the porcelain surface

differences were observed in the color difference (ΔE*ab) between the control and treated porcelains for K01, K02, or K03 (Figure 5B).

## Discussion

Dental porcelain has long been used as a material for dental repair due to its aesthetic value, biological affinity, and material stability[1-6]. However, the fracture toughness of dental porcelain is only 1 $MPam^{1/2}$ [17]. Therefore, the material is fragile, and cracks and fractures induced by daily mastication-induced stress are often observed on dental porcelain. This has encouraged a number of researchers to make efforts toward strengthening

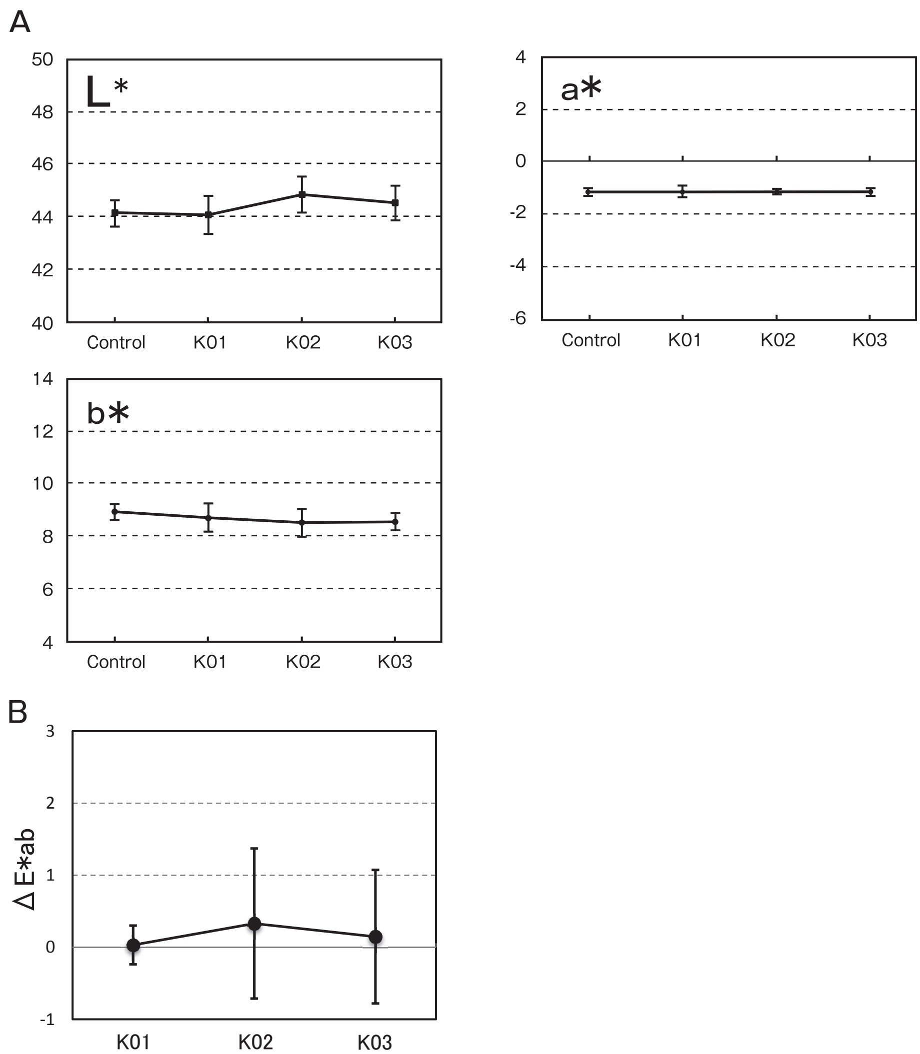



Figure 5 Effect of ion exchange using potassium-containing paste on the color of the porcelain surface
A: L* (brightness), a* (color scale coordinates for red and green), and b* (color scale coordinates for yellow) of the porcelain surface after ion exchange with the potassium-containing paste.
B: ΔE* (color difference) of the porcelain surface before and after ion exchange with the potassium-containing paste.

dental porcelain materials[18-20]. One method to enhance physical properties of a porcelain is to disperse metal particles in the material in order to prevent the extension of cracks. In a previous study, the fracture toughness was evaluated with porcelain materials containing nanoparticles of silver and platinum[16, 21]. The metal particles were found to absorb the crack energy and fracture toughness was found to increase in proportion to the amount of nanoparticles added. In general, metals have much greater toughness than porcelain. Studies on glass reinforcement, in which Ni[22], Al[23], and W[24], as well as metal alloys, such as FeNiC[25], FeCr[26], and stainless steel[27], were added to the specimens have suggested that metal dispersion is effective to reinforce glass. However, although the physical properties of the porcelain were improved by metal addition, a change in color was observed, somewhat compromising the aesthetics. Previously, the addition of rare metal nanoparticles to the porcelain was attempted, and the physical properties of the resulting materials were evaluated[16]. Upon addition of metal particles to porcelain, the crack energy is believed to be absorbed by dispersed metal particles. However, the addition of metal particles can be sometimes problematic because such particles may compromise the aesthetics of enamel-colored porcelain.

A chemical process of ion exchange is another method to strengthen porcelain materials, in which large alkaline ions, such as potassium, are substituted into porcelain surface sites that are occupied by smaller ions, such as sodium[7, 8]. The introduction of silver ions into glass by a silver compound slurry was reported to strengthen the material[28, 29]. In a previous study, we compared the effects of introducing silver and potassium ions by a commercial staining slurry on the Vickers hardness and fracture toughness of CAD/CAM blocks[14]. The staining slurry containing silver or potassium nitrate generated compressive residual stress and consequently increased the fracture toughness. Compared to silver ion, potassium ion was found to exert much greater effects on toughening the materials.

All-ceramic crowns have been fabricated by carving the crowns out of IPS blocks or porous, hypodense sintered blocks using a CAD/CAM system, allowing glass to infiltrate the pores after processing to produce a glass-infiltrated ceramic[30], and then re-sintering to increase their density and strength[31]. This is a much more efficient fabrication technique than the conventional method, which involves a technician manually aggregating and burning powder to reproduce the form. A common ion exchange method is performed by immersing glass in molten salt for a certain time. In contrast, the paste can be applied with a brush to all-ceramic crowns, and the dental technician can choose the location that he/she wants to enhance. Furthermore, the remaining paste can be saved for later application. In addition, the potassium nitrate paste prepared in the present study has better flow than the previous staining slurry[14]. Moreover, the thickness of the coated surface can be made more uniform.

In the present study, porcelain reinforcement by ion exchange using potassium-containing paste was successfully achieved without reducing the aesthetic appeal. Ion exchange with potassium nitrate did not affect the Vickers hardness but significantly suppressed crack extension on the porcelain surface. This is likely because residual compressive stress was created on the porcelain surface by replacing $Na^+$ in the porcelain with $K^+$ in the paste[32], where a concentration of $KNO_3$ of 0.2 M was found to be the most effective. Ion exchange using potassium-containing paste, however, showed no significant influence on the porcelain color. The color difference between the control and the treated materials was less than $\Delta E$ 0.15 on average for all samples. Chang et al.[29] reported that humans barely notice changes in color less than 2.69, indicating that ion exchange with potassium-containing paste and subsequent heat treatment does not affect the porcelain color.

## Conclusion

The potassium-containing paste developed in the present study is easy to handle and is effective in promoting ion exchange of sodium with potassium. The ion exchange resulted in reinforcing dental porcelain. As a result, the extension of porcelain cracks caused by stress induces by daily occlusal contacts could be successfully suppressed, and the porcelain can maintain its quality over a long period.

## References


1 ) Schmitter M, Mussotter K, Rammelsberg P, Gabbert O, Ohlmann B. Clinical performance of long-span zirconia frameworks for fixed dental prostheses: 5-year results. *J Oral Rehabil* 2012; 39: 552–557.
2 ) Contrepois M, Soenen A, Bartala M and Laviole O. Marginal adaptation of ceramic crowns: a systematic review. *J Prosthet Dent*. 2013; 110: 447-454.
3 ) Larsson C and Wennerberg A. The clinical success of zirconia-based crowns: a systematic review. *Int J Prosthodont*. 2014; 27: 33-43
4 ) Sailer I, Makarov NA, Thoma DS, Zwahlen M and Pjetursson BE. All-ceramic or metal-ceramic tooth-supported fixed dental prostheses (FDPs)? A systematic review of the survival and complication rates. Part I: Single crowns (SCs). *Dent Mater*. 2015; 31: 603-23.
5 ) Donovan TE. Factors essential for successful all ceramic restorations. *J Am Dent Assoc*. 2008; 139: 14–18.
6 ) Sherill CA, O'Brien WJ. Transverse strength of alminous and feldspatic porcelain. *J Dent Res* 1974; 53: 683-690.
7 ) Shoher I and Whiteman AE. Reinforced porcelain system, A new concept in ceramo metal Restorations. *J Prosthet Dent* 1983; 50: 489-496.
8 ) Coelho PG1, Silva NR, Bonfante EA, Guess PC, Rekow ED and Thompson VP. Fatigue testing of two porcelain-zirconia all-ceramic crown systems. *Dent Mater*. 2009; 25: 1122-1127.
9 ) Seghi RR, Crispin BJ and Wito W. The effect of ion exchange on flexural strength of feldspathic porcelains. *Int J Prosthodont*. 1990; 3: 130-134.
10) Piddock V, Quaktrough AJE and Brough I. An investigation of an ion strengthening paste for dental porcelains. *Int J Prosthodont*. 1991; 4: 132-137.
11) Brajevic F and Seghi RR. Effect of ion exchange reinforcement on surface indentation properties of dental ceramics. *J Dent Res*. 1991; 70: 290.
12) Seghi RR, Denry I and Brajevic F. Effect of ion Exchange on hardness and fracture toughness of dental ceramics. *Int J Prosthodont*. 1992; 5: 309-314.
13) Anusavice KJ, Hojjatie B and Chang TC. Effect of grainding and fluoride-gel exposure on strength of ion-exchanged porcelain. *J Dent Res*. 1994; 73: 1444-1449.
14) Uno M, Nonogaki R, Fujieda T, Ishigami H, Kurachi M, Kamemizu H, Wakamatsu N, Doi Y. Toughening of CAD/CAM all-ceramic crowns by staining slurry. *Dent Mater J*. 2012; 31: 828-834.
15) JSMS Committee on Fatigue of Materials (2001). Residual stress measurement for engineering ceramics by indentation fracture method. JSMS-SD-4-01.
16) Uno M, Kurachi M, Wakamatsu N and Doi Y. Effects of adding silver nanoparticles on the toughening of dental porcelain. *J Prosthet Dent*. 2013; 109: 241-247.
17) Cesar PF, Yoshimura HN, Miranda Júnior WG and Okada CY. Correlation between fracture toughness and leucite content in dental porcelains. *J Dent*. 2005; 33: 721-729.
18) Dunn B, Levy MN and Reisbick MH. Improve the fracture resistance of dental ceramic. *J Dent Res*. 1977; 56: 1209-1213.
19) Brajevic F and Seghi RR. Effect of ion exchange reinforcement on surface indentation properties of dental ceramics. *J Dent Res*. 1991; 70: 290.
20) Maehara S, Fujishima A, Hotta Y and Miyazaki T. Fracture toughness measurement of dentalceramics using the indentation fracture method with different formulas. *Dent Mater J*. 2005; 24:328-334.
21) Fujieda T, Uno M, Ishigami H, Kurachi M, Wakamatsu N and Doi Y. Addition of platinum and silver nanoparticles to toughen dental porcelain. *Dental Materials J*. 2012; 31: 711-716.
22) Biswas DR. Strength and fracture toughness of indented glass-nickel compacts. *J. Mat. Sci*. 1980; 15: 1696-1700.
23) Krstic VK, Nicholson PS and Hoagland RG. Toughening glasses by metallic particles. *J.Am. Ceram. SOC*. 1981; 64: 499-504.
24) Hasselman DPH and Fulrath RM. Effect of spherical tungsten dispersions on Young's modulus of glass. *J. Am. Ceram. SOC*. 1965; 48: 548-549.
25) Moore RH and Kunz SC. Metal particle-toughened borosilicate sealing glass. *Ceram. Eng. Sci. Proc*. 1987; 8: 839-847.
26) Boccaccini AR, Ondracek G and Syhre C. Borosilicate glass matrix composites reinforced with short metal fibres. Glasstech. Ber. 1994; 67: 16-20.
27) Pernot F and Rogier R. Mechanical properties of phosphate glass-ceramics-3161 stainless steel composites. *J. Mat. Sci*. 1993; 28: 6676-6682.
28) Zhang AY, Suetsugu T, Kadono K. Incorporation of silver into soda-lime silicate glass by a classical staining process. *J Non-Cryst Solids*. 2007; 353: 44-50.
29) Chang J, Da Silva JD, Sakai M, Kristiansen J and Ishikawa-Nagai S. The optical effect of composite luting cement on all ceramic crowns. *J Dent*. 2009; 37: 937-943.
30) Piconi C, Maccauro G. Zirconia as a ceramic biomaterial. *Biomaterials* 1999;20: 1-25.
31) Vultvon SP, Carlson P, Nilner K. All-ceramic

fixed partial dentures designed according to the DC-Zirkon technique. A 2-year clinical study. *J Oral Rehabil* 2005; 32: 180-187.

32) Seghi RR, Denry I and Brajevic F. Effect of ion Exchange on hardness and fracture toughness of dental ceramics. *Int J Prosthodont*. 1992; 5: 309-314.