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นายตุลย์ ศรีอัมพร

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THE ALTERNATIVE METHOD IN SURFACE MODIFICATION OF DENTAL ZIRCONIA USING HYDROFLUORIC ACID

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A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy Program in Prosthodontics
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ปัจจุบันมีการใช้วัสดุเซอร์โคเนียในงานทันตกรรมมากขึ้น เนื่องจากเซอร์โคเนียมีความแข็งแรงเชิงกลสูง ให้ความสวยงามและมีความเข้ากันได้กับเนื้อเยื่อของมนุษย์ มีการศึกษามากมายกล่าวว่าเซอร์โคเนียทางทันตกรรมไม่สามารถกัดด้วยกรดไฮโดรฟลูออริกได้ ดังนั้นวัตถุประสงค์ในการศึกษานี้คือ ศึกษาผลของการปรับสภาพผิวของเซอร์โคเนีย ด้วยกรดไฮโดรฟลูออริก โดยการทดสอบแบ่งออกเป็น 2 ส่วนดังนี้

ส่วนแรก ทดสอบว่ากรดไฮโดรฟูลออริกสามารถกัดผิวของเซอร์โคเนียได้หรือไม่ ผลการศึกษาพบว่าเมื่อแช่ชิ้นทดสอบเซอร์โคเนียในสารละลายกรดไฮโดรฟูลโอริกที่ความเข้มข้น อุณหภูมิ และเวลาที่แตกต่างกัน เมื่อศึกษาด้วยกล้องจุลทรรศน์อิเล็กตรอนชนิดส่องกราดและเทคนิคอีดีเอสพบความขรุขระและการติดอยู่ของหมู่ธาตุฟูลออรีนที่ผิวชิ้นทดสอบ ตามลำดับ รวมถึงพบการหลุดของหมู่ธาตุเซอร์โคเนียมในสารละลายกรดเมื่อทดสอบด้วยเทคนิคไอซีพี

ส่วนที่สอง ทดสอบสมบัติทางกายภาพของเซอร์โคเนียเมื่อกัดด้วยกรดไฮโดรฟูลออริก ผลการศึกษาพบว่า เมื่อทดสอบด้วยเครื่องวัดความหยาบผิวและเทคนิคเอเอฟเอ็ม เซอร์โคเนียที่ถูกกัดด้วยกรดมีค่าความหยาบผิวเพิ่มสูงขึ้นกว่ากลุ่มควบคุม รวมถึงเมื่อทำการทดสอบด้วยเทคนิคเอฟทีไออาร์ เอกซ์อาร์ดี และ เอกซ์พีเอส พบการเปลี่ยนแปลงเฟสโครงสร้างของเซอร์โคเนียจากเททระโกนอลเป็นโมโนคลินิก และพบสารประกอบที่บ่งชี้ถึงการเกิดปฏิกริยาเคมีระหว่างกรดไฮโดรฟูลออริกกับเซอร์โคเนีย

จากผลการศึกษาสามารถสรุปได้ว่า กรดไฮโดรฟลูโอริกสามารถกัดผิวของเซอร์โคเนียทางทันตกรรม สร้างความขรุขระที่ผิว เกิดความเสื่อมของเซอร์โคเนียที่อุณหภูมิต่ำ และสามารถเกิดปฏิกิริยาเคมีกันได้

ภาควิชา ทันตกรรมประดิษฐ์ ลายมือชื่อนิสิต ....

สาขาวิชา ทันตกรรมประดิษฐ์ ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก ....

ปีการศึกษา 2556 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม ....

5276453832 : MAJOR PROSTHODONTICS
KEYWORDS: ACID ETCHING / HYDROFLUORIC ACID / NANO-POROSITY / SURFACE TREATMENT / ZIRCONIA

TOOL SRIAMPORN: THE ALTERNATIVE METHOD IN SURFACE MODIFICATION OF DENTAL ZIRCONIA USING HYDROFLUORIC ACID. ADVISOR: ASST. PROF. NIYOM THAMRONGANANSKUL, Ph.D.,CHUMPHOL BUSABOK, Ph.D., 166 pp.

Recently, the use of dental zirconia has become increasing in dentistry because of its excellent mechanical properties, esthetic appearance and biocompatibility. Most studies reported that dental zirconia cannot be etched with hydrofluoric acid (HF). Therefore, the aim of this study was to evaluate the effect of HF treatment on the dental zirconia surface. The experiment was divided into two parts.

First part, Can HF alter zirconia surface or not? The HF treatment on zirconia surface was done in different acid concentrations, temperatures, and times. The results by using SEM, EDS evaluations showed that treated zirconia appeared to have irregularity surfaces. . In addition, there was the deposition of fluorine element on zirconia surface as well. After using ICP analysis the dislodged zirconium element was found in an immersed HF solution.

Second part, the physical properties of HF treated zirconia were evaluated by using profilometer, AFM, FTIR, XRD, and XPS. The roughness values of the etched specimens as examined by profilometer and AFM increased comparing with control group. By using FTIR, XRD, and XPS analyses, it was found that tetragonal-to-monoclinic phase transformation was induced and the chemical reaction between HF and zirconium oxide occurred.

The results of this study concluded that dental zirconia can be etched by hydrofluoric acid, creating the change of surface morphology. In addition, low temperature degradation was occurred. Furthermore, the chemical reaction between HF and zirconia was confirmed.

Department: Prosthodontics
Field of Study: Prosthodontics
Academic Year: 2013

Student's Signature ....
Advisor's Signature ....
Co-Advisor's Signature ....

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CONTENTS

Page

Page

LIST OF TABLES

Pages

LIST OF FIGURES

Pages

CHAPTER I

INTRODUCTION

BACKGROUND AND RATIONALE

In recent years, the use of high-strength zirconia ceramics has become popular in dentistry. These are suitable for a variety of clinical applications; posts and cores[1, 2], dental implants[3, 4], orthodontic brackets[5, 6], and fixed-partial dentures[7-10] due to their excellent mechanical properties such as high flexural strength and toughness[11], esthetic appearance[12], and biocompatibility[13-15]. Moreover, the zirconia ceramic has a polycrystalline structure, which is acid resistant [15, 16]. The cementation of fixed-partial dentures is important for their clinical success. Silica-based ceramics are bonded using hydrofluoric acid (HF) etching followed by silanization[15]. In contrast, zirconia is a silica-free ceramic, resistant to conventional etching techniques[15, 16]. Airborne abrasion with aluminum oxide particle generates roughness of the zirconia surface and increases bond strength [17]. Other surface treatments of zirconia such as laser treatment[18, 19], selective infiltration technique (SIE)[20], hot etching solution[21, 22], nano-structured alumina coating[23], and slurry–coated ceramic[24] have been developed to improve and enhance the surface roughened area available for mechanical interlocking of ceramic/resin bonds.

The chemical bonding to the zirconia surface can be achieved by a variety of chemical substances. Silane coupling is recommended for use with silica-based material, but is not recommended for zirconia based even if the zirconia surface was coated with silica[25-28]. On the other hand, zirconated coupling agents[29, 30] and primer agents containing phosphate ester monomer such as MDP[31] have been demonstrated an increased bond strength to zirconia.

Hydrofluoric acid treatment is commonly used to react with and remove the glassy matrix of silica based material, so the crystal phase is exposed to surface roughness[32-34]. This process also promotes wettability and surface energy on the ceramic surface, which assists in penetration of the resin cement tags increasing the bond strength value between ceramic and cement[35].

Many studies have reported that hydrofluoric acid etching cannot be used on surface of alumina-and zirconia-based ceramic because of their high crystal phase content[15, 17, 20, 23, 24, 26, 31, 36-46]. Furthermore, most studies have shown hydrofluoric acid etched zirconia in terms of mechanical property, bond strength between the zirconia surface and resin cement, but did not vary the etching times and the concentrations of HF[25, 36-38]. They also did not investigate the surface morphology changes. However, a pilots study has shown that hydrofluoric acid etching can alter the surface of dental zirconia as seen in Figure 70 and 71 of the pilot study data. Therefore, the aims of this study were to investigate whether hydrofluoric acid etching can create surface roughness of dental zirconia (Part I), and investigate the physical property changes of dental zirconia after hydrofluoric acid etching (Part II).

RESEARCH OBJECTIVES

Primary objective

1. To investigate the ability of hydrofluoric acid in etching dental zirconia.

Secondary objectives

1. To evaluate the surface morphology of zirconia after hydrofluoric acid etching.
2. To evaluate the changes of physical properties of dental zirconia after hydrofluoric acid etching.
3. To investigate the etching mechanism of dental zirconia in hydrofluoric acid solution.

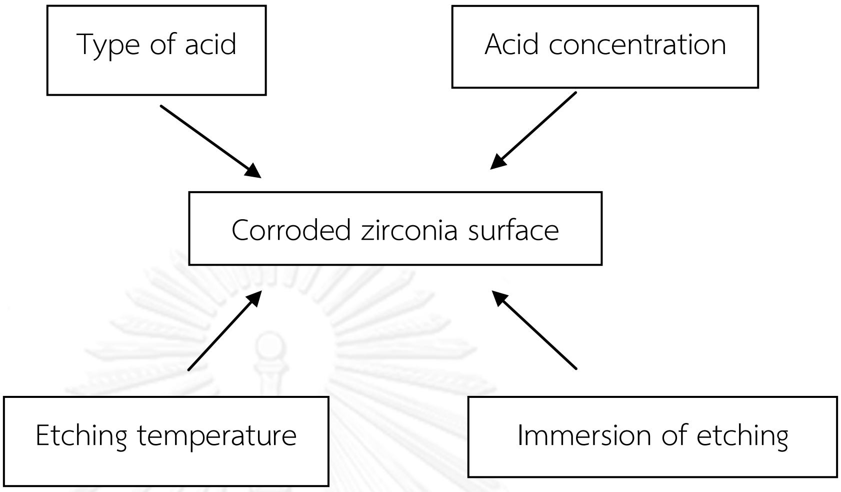
RESEARCH QUESTIONS

1. Can hydrofluoric acid etch the dental zirconia surface?
2. Can hydrofluoric acid etching change the surface morphology of dental zirconia?
3. Can hydrofluoric acid etching change the physical properties of dental zirconia?
4. Can the chemical reaction between hydrofluoric acid and dental zirconia occur?

NULL HYPOTHESES

1. Hydrofluoric acid cannot etch the dental zirconia surface.
2. Hydrofluoric acid etching cannot change the surface morphology of dental zirconia.
3. Hydrofluoric acid etching cannot change the physical properties of dental zirconia.
4. The chemical reaction between hydrofluoric acid and dental zirconia cannot occur.

CONCEPTUAL FRAMEWORK



KEYWORDS

Acid etching, Hydrofluoric acid, Nano-porosity, Surface treatment, Zirconia

RESEARCH DESIGN

Laboratory and experimental research

EXPECTED BENEFITS

1. The concept that dental zirconia cannot be etched by hydrofluoric acid will be changed.
2. The new theory that dental zirconia can be etched by hydrofluoric acid will be advocated.
3. The reaction of dental zirconia and hydrofluoric acid can be explained.
4. Understanding the surface morphology of zirconia after hydrofluoric acid etching.
5. Understanding the physical properties of dental zirconia after hydrofluoric acid etching.

6. Development the dental zirconia surface conditioning with hydrofluoric acid for the biomaterial devices.

CHAPTER II

REVIEW OF RELATED LITERATURE

Zirconia [4, 11, 14]

Zirconia (ZrO_2), sometimes known as zirconia dioxide, is a crystalline oxide of zirconium (Zr). Naturally, the crystal structure of pure zirconia can be changed dependent on the temperature: At temperatures below 1170 °C (2138 °F) zirconia exists in monoclinic form. At the temperature 1170 °C (2138 °F) to 2370 °C (4300 °F) monoclinic structure transforms to tetragonal form while the cubic structure is present at temperature over 2370 °C (4300 °F).

The transformation crystalline structure has an effect on the volume change in each phase. It was found that the volume increased 3.25% as tetragonal transform to monoclinic. In addition form cubic to tetragonal the volume increased 9%.

Additions of some metal oxides such as magnesium oxide (MgO), yttrium oxide (Y_2O_3), calcium oxide (CaO), and cerium oxide (Ce_2O_3) to pure zirconia can inhibit the transformation of crystalline structure, these allow to stabilize either cubic or tetragonal structure of the material at any temperature. The most effective stabilizing additive is yttrium oxide. In common, the zirconia can be obtained into partially stabilized zirconia and fully stabilized zirconia form. For partially stabilized zirconia, it will present in tetragonal phase at room temperature. For the cubic phase at room temperature is indicative of fully stabilized zirconia. The tetragonal zirconia phase of partially stabilized zirconia is stabilized. However, under stress, the phase may change to monoclinic, with a subsequent 3% volumetric size increase. This dimensional change takes energy away from the crack and can stop it in its tracks. This is called "transformation toughening" (Figure 1). Transformation toughening is contributed to zirconia its excellent mechanical properties: flexural strength 900 MPa to 1.2 GPa and toughness 7 to 8 MPa. Other beneficial properties include good biocompatibility and corrosion resistant. However, yttria-stabilized tetragonal zirconia can be transformed from tetragonal to monoclinic structure under moist conditions at low temperature known as "Low Temperature Degradation (LTD)". LTD results in small zirconia grains, roughening of the surface finish (Figure 2).

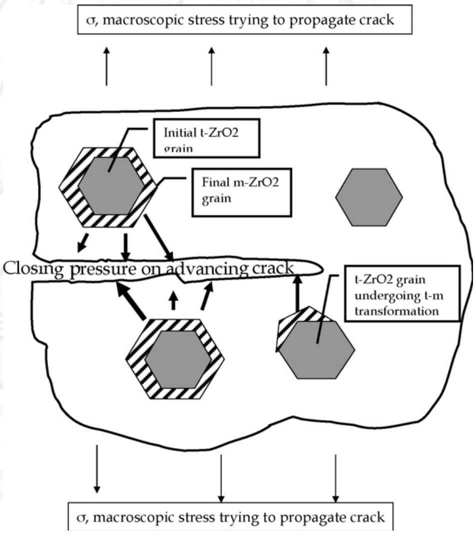


Figure 1 Diagram shows how tetragonal to monoclinic transformation of zirconia increases the fracture toughness. (Kelly and Denry (2008))

(First, metastable tetragonal zirconia changes to monoclinic after initial stress of crack. Following this transformation, the volumetric expansion of the grain and the result is that compressive stresses are present on the surface of the crack. The phenomena is an increasing the toughness of zirconia grain in the face of transformation crack zone, preventing the growth of cracks and improving in the mechanical property of ceramics. (Kelly and Denry (2008)[11], Lughi and Sergo (2010)[47]))

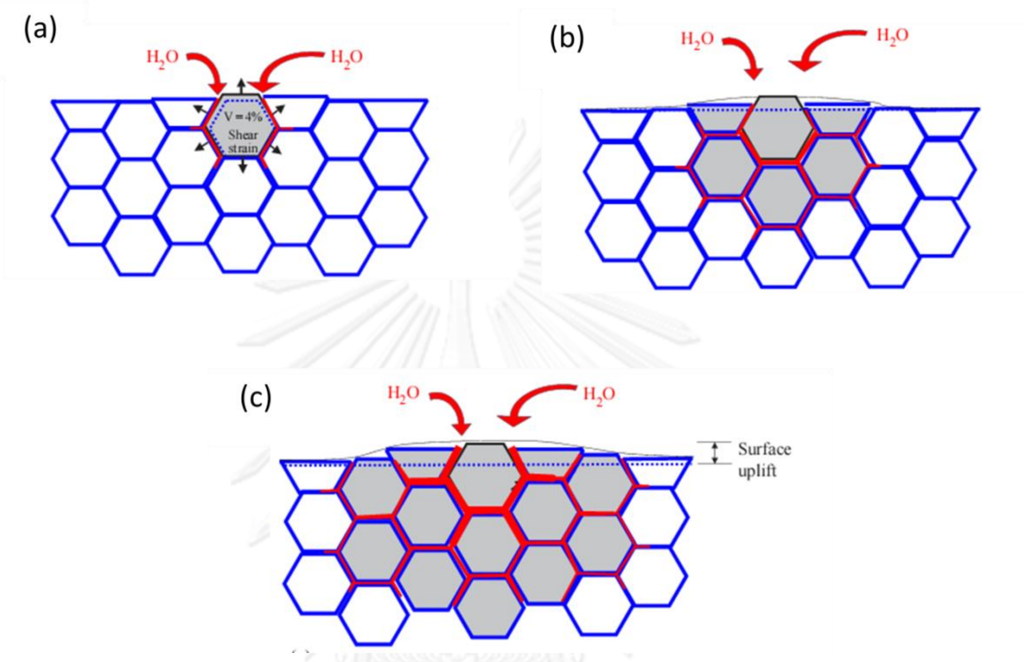


Figure 2 The diagrams of cross section of zirconia grain with LTD process, (Chevalier et al. (2006) [48])

(a) the top of surface exposed to H_2O, One tetragonal grain transformation to monoclinic. It freely expand and then provoking the uplift of surface. This result creates the compressive stress around its grain. (b) The surrounding grain gives tensile stress, leading to transformation to monoclinic and the formation of microcrack. (c) The growth of monoclinic zone, leading to the increasing microcrack and the roughness surface. (Chevalier et al. (2006)[48], Chevalier and Gremillard (2009)[49], and Lughi and Sergo (2010)[47])

Recently, zirconia ceramics available for dental application are only three types.

1. *Single-phase, polycrystalline t-*ZrO_2

The 3Y-TZP is a biomedical grade zirconia that usually contains 3mol% Y_2O_3 (yttria). This material has been used in dentistry for fabrication of fixed partial restorations. The fabrication is processed by using soft machining or milling of pre-sintered blocks followed by sintering method, or by hard milling of full sintered blanks. The grain size of 3Y-TZP depends on tetragonal to monoclinic phenomena and sintering temperature. The grain size less than 1µm has a lower transformation rate but for a very small grain size (~0.2µm), the transformation is not occur, leading to reduced toughness. The examples from the commercial available 3Y-TZP in dental product are Cercon (Dentsply), LAVA (3M ESPE), In-ceram YZ (Vita Zahnfabrik).

2. *Dispersion-toughness ceramics*

These materials are the dispersion of zirconia particle in another matrix such as Al_2O_3 (alumina) and $3Al_2O_3.2SiO_2$ (mullite). Within commercially available dental product is In-ceram zirconia (Vita Zahnfabrik). The main compositions are 30%glass and 70%polycrystlline ceramic that consists of Al_2O_3:ZrO_2 in a volume percent ration of 70:30. In-ceram zirconia can be fabricated by slip-cast technique or milling process followed by sintering method. Final sintering process, approximately 23% of glass phase was presented. The flexural strength for In-Ceram zirconia fabricated by slip-cast method and machining were approximately 630 MPa and 476 MPa, respectively. However, the methods were not significant different in fracture toughness. There materials can be developed tetragonal to monoclinic transformation zone with in crack tip. The increased volume creates microcracks in the alumina matrix surrounding the transformation zone. Therefore, the toughness is increased by micro-cracking.

3. Partially stabilized zirconia (Mg-PSZ)

This material is a magnesia partially stabilized zirconia that contents an amount of MgO in ranges between 8 and 10 mol percent. Mg-PSZ mainly presents porosity, associated with a large grain size (30-60 μm) thus it has not been successful in dental application. The phases of this zirconia consist of tetragonal zirconia within cubic stabilized zirconia matrix. An example of Mg-PSZ ceramic is DenZir-M (Dntronic AB) that was fabricated by hard machining of dental restoration.

Generally used in dentistry the most zirconia ceramic material is yttria-tetragonal zirconia polycrystal (Y-TZP) ceramic, this can provide the highest fracture toughness, esthetic and biocompatibility. It is known that zirconia blasted with Al_2O_3 particle or coated with silica and then applied with silane coupling agent can be enhanced the bond strength between ceramic and resin cement. Therefore, there are many methods for treatment surface of zirconia as follows:

1. Selective infiltration etching (SIE)[20, 39, 50]

The method of selective infiltration etching (SIE) was created by Aboushelib et al. (2007)[20]. This is a novel surface roughening technique. By using a heat-induced maturation (HIM) process, the inter-grain boundaries can be created in zirconia to allow infiltration of molten glass. The glass on zirconia surface was subsequently etched by hydrofluoric acid thus giving surface roughness. The primer and adhesive resin can infiltrate and interlock into this surface. Aboushelib et al.

(2007)[20] also determined the tensile bond strength between zirconia surface after SIE technique and Panavia F2.0 resin cement. They founded that SIE technique treated zirconia surface provided highest tensile bond strength.

Casucci et al. (2009)[21] used atomic force microscopy (AFM) technique to confirm the nano-surface roughness on zirconia surface treated by SIE technique. The results showed significantly greater in surface roughness, when compared to air-abrasive with Al_2O_3 or hydrofluoric acid etching method.

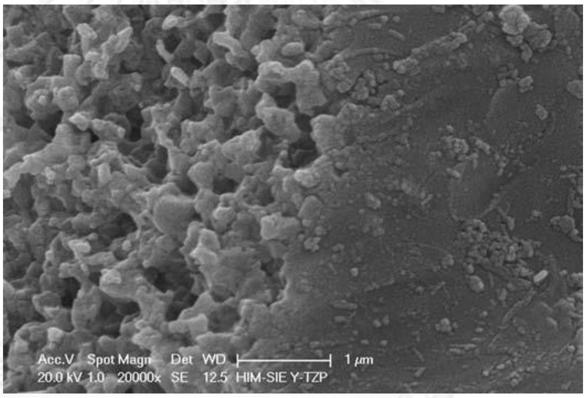


Figure 3 The SEM image of the SIE treated zirconia surface in which left half received SIE treatment, while right half was not treated at 20,000x magnification. (Aboushelib et al. (2007) [20])

The advantage of SIE is that it involves grains only that can control the specific area for etching. However, this process is still under development, because the bond between zirconia and resin cement is mechanically favorable as mentioned above. Yet, it was noted that long-term resistance to microleakage is concerned.

2. Hot etching solution

A hot etching solution has been proposed by Ferrari et al. (1989)[51]. This method is used to etch nickel-chrome-beryllium alloys, create surface roughness and promote the retention of the Maryland bridges. The etching solutions were composed of 800 ml of methanol, 200 ml of 37% HCl acid and 2 gram of ferric chloride. The solutions were then heated to $70^{\circ}C$. The experiment exhibited that a hot etching solution can increase micro-retentive surface area in the metal alloys as it will improve the adhesion between metal and cement.

Casucci et al. (2009)[21] evaluated the surface topography and surface roughness of treated zirconia surface using hot etching solutions, SIE, airborne particle abrasion, hydrofluoric acid treatments and non-treated method. Compared with other treatments, zirconia surface treated with hot etching solution has a higher degree of roughness and surface area. In addition, the observation from hot etching solution treatment found that surface roughness increased with application time.

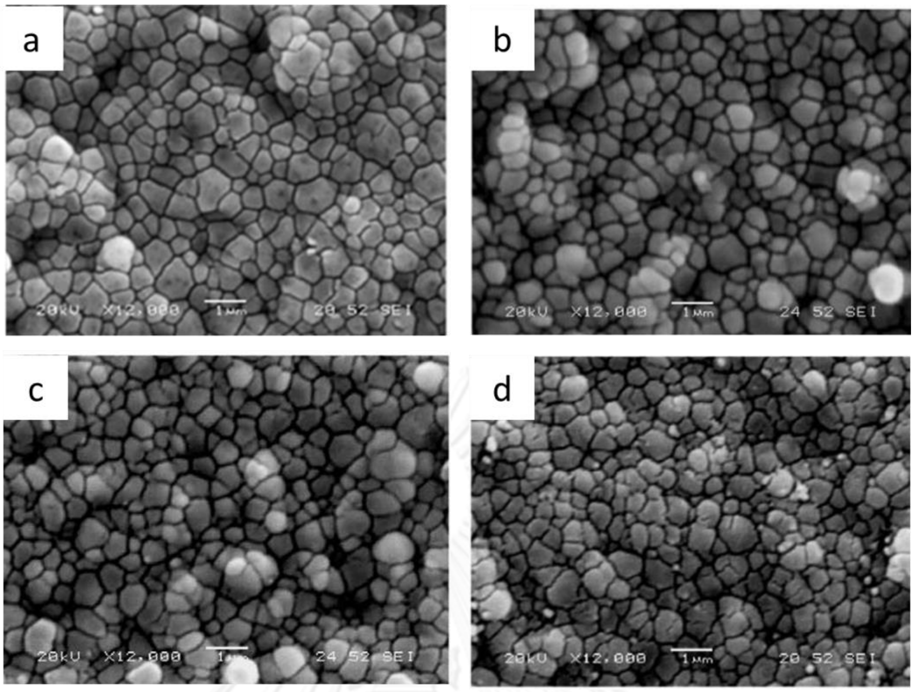


Figure 4 The SEM images of hot etching solution treated zirconia surface at 12,000x magnification: (a) no treatment groups; (b-d) treated with the experimental hot etching solution for 10, 30 and 60 min, respectively. (Casucci et al. (2009) [21])

Later Casucci et al. (2010)[22] studied the effect of hot etching solution technique on three zirconia ceramic brands (Lava, Cercon, and Aadva). The results showed that this process could increase the surface roughness of all zirconia ceramics and improve micromechanical retention of resin cement.

3. *Nano- structured alumina coating*[23]

The zirconia surface was coated with alumina that was generated by the hydrolysis of aluminium nitride (AIN) powder. The SEM/TEM analysis showed that the coating is uniform with the thickness of 240 nm. The nano-structured alumina coating on zirconia ceramic performed a high roughness area resulting in high retention of resin cement. The shear bond strength of treated zirconia was significantly higher than those treated by polishing surface and airborne particle abrasion. The bond strength of nano-structured alumina coating groups did not change during thermocycling process. However, by using polishing surface and air born-particle abrasion the specimens debonded spontaneously during the same process.

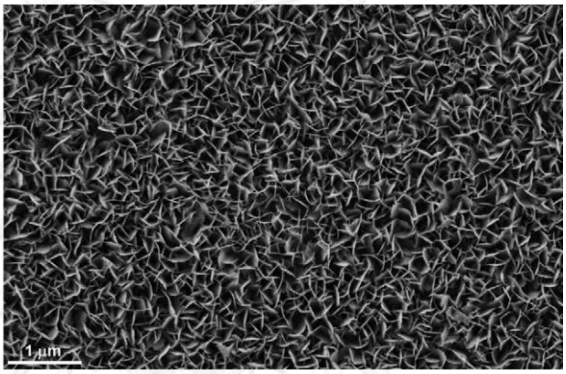


Figure 5 SEM image of zirconia surface after nano-structured alumina coating (Jevnikar (2010)) [23])

4. Chemical vapor deposition (CVD)[52-55]

Chemical vapor deposition (CVD) is a chemical process for depositing thin films of various materials. In a typical CVD process the substrate is exposed to one or more volatile precursors. The volatile precursors will react on the substrate surface to produce the desired deposit. Frequently, volatile by products are also produced, which are removed by gas flow through the reaction chamber. This process is widely used in the production of coatings, powders, fibers and monolithic parts.

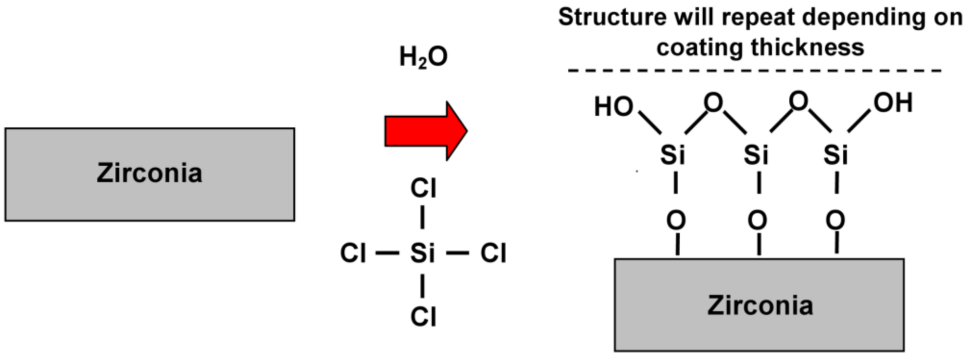


Figure 6 The CVD treated zirconia surface, chemical reaction representative of introducing water and silicon tetrachloride to activate nonsilica-based materials (i.e. zirconia), for subsequent silanation treatment (Piascik et al. (2009)) [56]

Piascik et al. (2009)[56] created a Si_xO_y-functionalized surface (seed layer) on zirconia substrate by CVD process. This technique was performed under the reaction of a chloro-silane gas ($SiCl_4$) and H_20, resulting in the deposition of the Si_xO_y layer on zirconia surface and HCl gas by product. The thin silica-like (seed layer) can be improved adhesion to zirconia by using this technique along with traditional silanization. It was reported that the bond strength of 2.6 nm thickness zirconia treated by CVD process showed the higher value than 23 nm thickness zirconia treated by the same process, tribochemical technique and untreated zirconia, respectively.

5. Slurry coating ceramic

Phark et al. (2009)[24] reported the modified surface of zirconia which is processed by slurry coating ceramic technique. This process employed slurry containing zirconia ceramic powder and pore former. The pore former was burnt off, leaving a porous surface on the zirconia modification surface. They evaluated the shear bond strength of a zirconia treated surface with slurry coating ceramic.

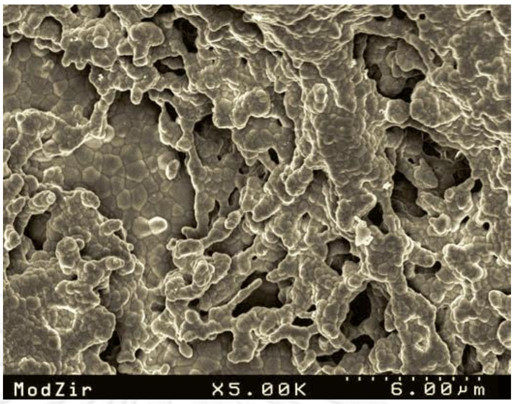


Figure 7 The SEM image of zirconia surface at 5,000x magnification of the modified zirconia surface with slurry coating ceramic technique (Phark et al. (2009)) [24]

The results showed that shear bond strength of the modified surface is higher than that from air-abrasive technique. However, it was not recommended to use airborne particle after modified surface zirconia with this technique because it lead to a decrease value of bond strength.

6. *Tribochemical technique (Rocatec system)*

The tribochemical technique is commonly used to embed silica in the surface. Various researches illustrated that the bond strength value of dental zirconia was increased by tribochemical method as presented in table 1. Because the zirconia is silica free ceramic, traditional silanization is not truly effective with it. Therefore, it is necessary to modify the zirconia surface with the tribochemical method prior to silanization.

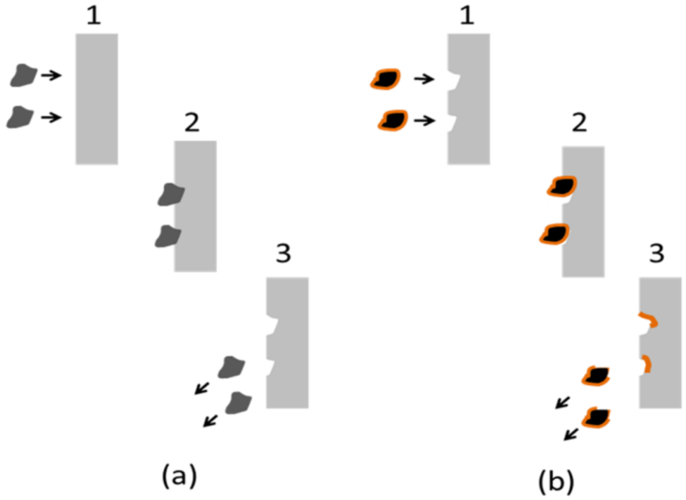


Figure 8 Zirconia surface is modified by tribrochemical tecnique of Rocatec system.

(a) Airborne abrasive with 110 μm Al_2O_3 (Rocatec pre) to create the surface roughness of specimen

(b) Airborne abrasive with 110 μm coating-modified aluminium oxide with silicic acid (Rocatec plus) to embed silica particle on specimen surface

Table 1 The summarization of bond strength values of dental zirconia treated by tribochemical technique

Author	Ceramic	Al_2O_3 blasting (μm)	Resin cement	Testing method	Immersion time	Bond strength (MPa)
Qeblawi 2010[25]	IPS Emax7	50	Mutilink automix	Shear	90 days and thermocycling 6,000 cycle	Control = 10.2 Cojet= 15.3 Cojet+Silane=30.9
Tsukakoshi	Nikkato	50	9 cements	Shear		Rocatec= 31.9-67.1

2008[57]		Sand paper #600grit			24 hrs	Rely-X=5.4
Ozcan 2008[45]	LAVA	50	Panavia F 2.0	Shear	Thermocycling 6,000 cycle	Air abrasive+silane=8.43 Rocatec+silane= 8.23
Valando 2007[28]	Inceram zirconia	_	Panavia F 2.0	μTensile	**1**. 24 hrs+ immediate test = 26.1 **2.** 150 days = 6.5 **3.**150 days+ thermocycling 12,000 = 6.5 **4.**300 days = 4.5 **5.**300 days+ thermocycling 12,000 = 4.3	
Amaral 2006[27]	Inceram-zirconia	_	Panavia F 2.0	μTensile	7 days	**1.** Sand blasting 110 μm=20.5 **2.** Cojet = 24.6 **3.** Rocatec = 26.7
Atsu 2006[26]	Cercon	125	Panavia F 2.0	Shear	24 hrs	**1.** Control =15.7 **2.**Cojet = 21.6 **3.**Cojet+silane = 21.9 **4.**Cojet+MDP = 22.9

7. *Surface fluorination*

The fluorination treatment previously described by Piascik et al. (2011)[58]. The process is using the fluorinated plasma with sulfur hexafluoride (SF_6) precursor gas onto zirconia surface, to create approximately the 2-4 nm conversion of zirconiumfluoride and zirconiumoxyfluoride layers on its surface. After plasma treatment, the surface becomes rich of hydroxyl group, converting layer can react with organo-silane and ester groups in acrylate-based monomers, enabling chemical bonding to the treatment surface. Moreover, the authors used the XPS to evaluated the various stoichiometric of plasma fluorinated treated zirconia, the surface conversion layer had a mixture phases; zirconiumoxyfluoride (ZrO_2F_5 and/or ZrO_3F_4) and zirconiumfluoride(ZrF_4) according to the Zr 3d $_{5/2}$ peak position at ~183.1 eve and ~184.8, respectively. In addition, plasma fluorinated zirconia produced the low contact angle (7.8°), indicating the surface were becoming more hydrophilic, increasing wettability.

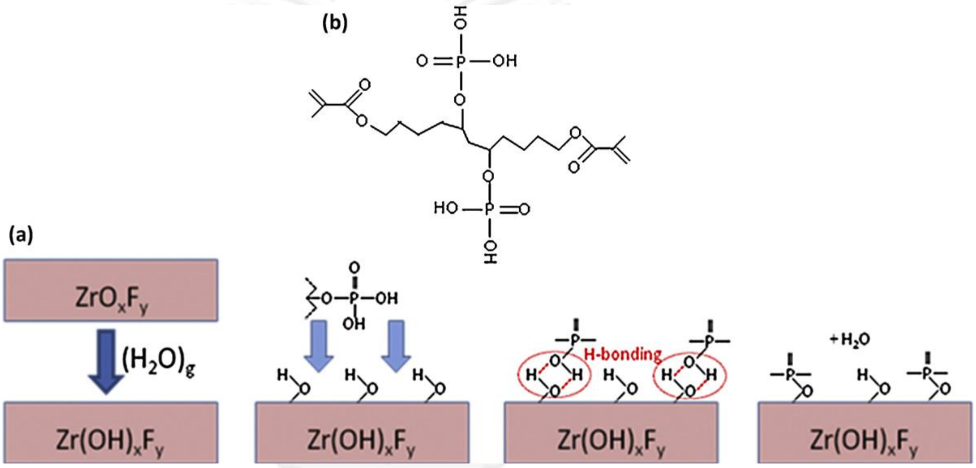


Figure 9 The diagrams of fluorinated plasma treated zirconia and chemical reactions between fluorinated zirconia surface and ester groups in acrylate-based monomers (Piascik et al. (2012) [59])

Generally, hydrofluoric acid treatment can be used to increase micromechanical retention between silica-base ceramic and resin cement. However, many authors exhibited that hydrofluoric acid cannot react on dental alumina and zirconia ceramic surface because it is glass-free, as shown in table below.

Table 2 The reviews showed that hydrofluoric acid treatment was not effective to alumina and zirconia surfaces.

Authors	Journal	Detail	Reference
Kern and Thomson[60]	JPD 1994; 71: 453-61.	HF etching of In-Ceram ceramic could not create a micro retentive surface compared with conventional glass ceramics. On the other hand air abrasion with alumina particle was the best method, creating a micro retentive surface for this material. In addition silane coupling agent application did not significantly increase the resin-to-ceramic bond strength because In-Ceram ceramic consists only a small amount of silica.	Schmid et al.[61] (Dtsch Zahn5rstl Z 1990;45505-a.) Pape et al.[62] (Haftfestigkeit von geatztem In-ceram and Zahnschmelz. Zahnarztl Welt 1991;100:450-453) Kraivixien-Vongphantuset et al.[63] (J Dent Res (IADR Abstracts) 1992;71:533)
Kern and Wegner[64]	Dental material 1998;14:64-71	Following HF etching with silane coupling agent application, which improves the resin-silica based ceramic bond strength, did not influence the resin -alumina or resin-zirconia bond strength.	Salmang and Scholze[65] (1982; Allgemeine Grundlagen Und wichtige Eigenschaften.6th ed. Berlin: Springer) Pape et al.[62] (Haftfestigkeit von geatztem In-ceram and Zahnschmelz. Zahnarztl Welt 1991;100:450-453)
Derand and Derand[37]	(Int J Prosthodont 2000;13:131-135)	In-Ceram (Vita) and Procera AllCeram (Nobel Biocare) are High-strength ceramics. HF etching cannot improve resin bond strength for these materials.	Kern and Thompson[66] (JPD 1995;73:240-249) Awliya et al.[67] (Acta Odontol Scand 1998;56:9-13)

Ozcan et al.[68]	Int J Prosthodont 2001;14:335-339	Neither HF etching nor silane application results in an adequate bond strength of resin- alumina based ceramic.	Kern M, Neikes MJ, Strub JR.[69] Haftfestigkeit des Klebeverbundes auf In-Ceram nach unterschiedlicher Oberflächenkonditionierung. Dtsch Zahnarztl Z 1991;46:758–761.
Ozcan et al.[68]	Int J prosthodont 2001;14:335-339	HF etching did not produce a micro-retentive surface on In-Ceram ceramic because it is a high alumina content, and it was almost ineffective for HF etching of the glass phase for micromechanical interlocking.	No reference
Blatz et al. [16]	JPD 2003;89:268-274	HF acid etching technique has no positive effect on the resin bond to zirconia ceramics. The previous work evaluated different surface treatments and resin cements and reported that Superbond C&B showed the highest bond strength regardless of surface treatment (silica coating, sand blasting, HF etching, or grinding).	Derand and Derand [37] (Int J Prosthodont 2000;13:131-135)
Janda et al.[42]	Dental material 2003;19:567-573	Based on chemical knowledge, HF can corrode SiO_2-based ceramics according to the reaction equation $6H_2F_2 + 2SiO_2 \rightarrow 2H_2SiF_6 + 4H_2O$. This reaction certainly cannot occur with alumina- or zirconia-based ceramic materials.	No reference
Derand et al.[40]	Dent mat 2005;21:1158-1162	HF etching is suitable only for surfaces with a glass component. This acid has no influence on surface of zirconia ceramic because micro grooves cannot be created.	Kern and Wegner[64] (Dental material 1998;14:64-71) Ozcan et al.[68] (Int J Prosthodont 2001;14:335-

			339
Bottino et al.[70]	Int J Prosthodont 2005;18:60–65.	HF or sulfuric acids and silane coupling agent cannot provide a strong bond to alumina based- ceramics because of their low silica content. This inefficiency has been proven by in both the short- and long-term studies, which demonstrate that a compact ceramic surface with high crystalline content resists to degradation by acid etching	Isidor et al.[71] (Eur J Prosthodont Restorative Dent 1995;3:199–202) Awliya et al. [67](Acta Odontol Scand 1998;56:9–13) Madani[72] (J Prosthet Dent 2000;83:644–647) Ozcan et al.[68] (Int J Prosthodont 2001;14:335–339)
Andreatta Filho et al.[73]	J. Appl. Oral Sci 2005;13,53-7	The increase of Al_2O_3 in alumina based-ceramic composition significantly decreases the silica content, making the surface treatment procedures with HF contraindicated, because HF does not create micro-retentions as occurs with the glass ceramic.	Awliya et al. [67](Acta Odontol Scand 1998;56:9–13) Ozcan et al.[68] (Int J Prosthodont 2001;14:335–339) Kraivixien-Vongphantuset et al.[63] (J Dent Res (IADR Abstracts) 1992;71:533)
Yoshida et al.[29]	J Biomed Mater Res Part B: Appl Biomater 2006;77B:28-33	Follow HF etching with silane couping agent application did not provide a good bond strength of resin cement to dental zirconia ceramic as conventional silica-based ceramics.	Derand and Derand[37] (Int J Prosthodont 2000;13:131-135)
Zarone et al.[74]	Int Dent South Africa 2006 ;8:20-6	The researchers found that conventional acid-etch technique had no positive effect on the resin bond to zirconia- based ceramic	Blatz et al.[16] (J Prosthet Dent 2003;89:268-74)
Amaral et al.[27]	Dental Materials 2006;22: 283–	Neither HF etching nor silane application resulted in an adequate bond strength	Rosenstiel et al.[75](Dent Mater 1993;9:274–9)

	290	between resin cement and new high-strength ceramics.	Wolf et al.[76] (Am J Dent 1993;6:155–8)
Atsu et al.[26]	J Prosthet Dent 2006;95:430-6	HF etching and silane application to silica-based ceramics can improve the bond strength between restoration and resin. On the other hand, these procedures did not enhance the bond strength of zirconia- and alumina- based ceramics because their high crystalline content makes them corrosion resistance.	Ozcan and Vallittu [77] (Dent Mater 2003;19:725-31) Derand and Derand[37] (Int J Prosthodont 2000;13:131-5) Yoshida et al.[30](AM J Dent 2004;17:249-52)
Della Bona et al.[38]	Braz Oral Res 2007 ;17:10-15	The study found that HF etching did not produce an effective bonding between resin and alumina- or zirconia-based ceramics. These results agree with the findings of several investigations. .	Della Bona and Anusavice[78] (Int J Prosthodont. 2002;15:159-67) Derand and Derand[37] (Int J Prosthodont 2000;13:131-135)Ozcan and Vallittu[77] (Dental Materials 2003;19:825–31) Ozcan et al.[68] (Int J Prosthodont 2001;14:335-339 Valandro et al.[79] (JPD 2005;93:253-9)
Yoshida et al.[80]	J Prosthodont 2007;16:370-376	HF etching and silane application cannot reliably improve bond strength between zirconia ceramic with no silica content and resin cements, because zirconia is a high acid resistant material.	Borges et al.[33](JPD 2003;89:479-488)
Conrad et al.[7]	(JPD	Tribochemical technique, airborne-particle	Derand and Derand[37]

	2007;98:389-404)	abrasion, airborne-particle abrasion combined with HF etching, or grinding with diamond bur, were shown to have only a minor influence on bond strength to zirconia-based ceramic .	(Int J Prosthodont 2000;13:131-135)
Aboushelib et al.[20]	JPD 2007;98:379-388	It is very difficult to make a strong and stable bond with zirconia-based ceramics because they are acid resistant and do not respond to common etching and silanation procedures used with glass ceramic materials which react to HF and silane coupling agent.	Blatz et al.[16] (JPD 2003;89:268-274)
Ozcan et al.[45]	Dent mat J 2008;27:99-104	The zirconia-based ceramic is a glass-free material, therefore it acts as an acid-resistant or non-etchable material.	Blatz et al.[16] (JPD 2003;89:268-274)
Lu et al.[81]	J Oral rehabilitation 2001;28:805-813	HF cannot create maicro- retention on alumina-based In-Ceram ceramic surface compared with conventional ceramics. Because it contains only a small amount of silica within its glass matrix.	Kraivixien-Vongphantuset et al.[63] (J Dent Res (IADR Abstracts) 1992;71:533)
Aboushelib et al.[39]	Dental materials 2008;24:1268-1272	Zirconia is a silica- free and acid resistant material therefore, HF etching is not effective for surface treatment like other glass ceramic materials	Guazzato et al.[82] (Biomaterials 2004;25:5045-52)*
Duarte Jr et al.[83]	QDT 2009 Vol.32	Owing to the high-resolution SEM evaluations the machined zirconia ceramic surface consists of a lot of crystal grains which evenly distribute throughout the surface. Unlike glass ceramic, zirconia ceramics cannot be etched by HF.	Awliya et al. [67] (Acta Odontol Scand 1998;56:9-13)
Ernst et al.[41]	Am J Dent 2009;22:122-128	In the case of a feldspathic porcelain, surface modification usually consists of HF	Sun et al.[84] (J dent 2000;28:441-445)

		etching with subsequent silane application. In contrast, glass free ceramics cannot be conditioned in this way.	
Piascik et al.[56]	Dent mat 2009;25:1116-1121	The microstructure and chemical reaction of alumina and zirconia ceramics differ from those of conventional glass ceramics. These high strength ceramics are not easily etched by HF or chemically functionalized by silane coupling agent.	No reference
Lehmann and Kern[85]	J adhes dent 2009;11:479-483.	HF etching and silane application are traditional methods used for silica-based ceramics but these methods cannot be used with silica-free ceramics.	Blatz et al.[16] (JPD 2003;89:268-274)
Casucci et al.[21]	Journal of Dentistry 2009;37: 891–897	Several surface modifications have been investigated; similar results showed that HF etching and silanization cannot improve bond strength between resin cement and zirconia ceramic, because of the high crystalline phase and the limited glass phase of this high-strength ceramic.	Oyague et al.[44] (Dental Material 2009;25:392–9.) Sun et al.[86] (Operative Dentistry 2007;32:623–30) Blatz et al.[87] (Quintessence International 2007;38:745–53) Amaral et al.[27] (Dental Material 2006;22:283–90) Della Bona et al.[88] (Inter J Prosthodont 2002;15:248–53) Ozcan and Vallittu [77] (Dental Mater 2003;19:825–31) Matinlinna et al.[89] (Dental Materials 2006;22:824–31) Luthardt et al. [90] (European Journal of

			Prosthodontics and Restorative Dentistry 1999;7:113–9) Derand and Derand[37] (Int J Prosthodont 2000;13:131-135)
Tashkandi[91]	The Saudi Dental Journal 2009;21:113-116	Zirconia core is resistant to aggressive chemical agents such as HF because of its chemical inertness.	Derand and Derand[37] (Int J Prosthodont 2000;13:131-135)
Phark et al.[92]	JPD 2009; 101:29-38.	The technique used to improve micromechanical interlocking to glass ceramics, such as HF etching, does not create an acceptable surface roughness for high-strength ceramics.	Awliya et al.[67] (Acta Odontol Scand 1998;56:9-13)
Oyague et al.[44]	Dental Material 2009; 25:392–9.	Although high-strength zirconia core ceramics have high crystalline content and the very low vitreous phase result in limitation of HF etching and silanization, the luting dental zirconia ceramic still represents a challenge.	Amaral et al.[27] (Dent Mater 2006;22:283–90) Atsu et al.[26] (J Prosthet Dent 2006;95:430–6) Bottino et al.[70](Int J Prosthodont 2005;18:60–5)
Qeblawi et al.[25]	JPD 2010;103:210-220	Silica-based ceramic can be etched by HF that selectively dissolves the glassy components, creating a mico-porosity that allows the penetration of the resin cement. A silane is subsequently applied to the irregular surface to form a siloxane bond. This chemical reaction is not found in dental zirconia ceramic because it is a monolithic ceramic not containing a glass phase.	Wegner and Kern[93] (J Adhes Dent 2000;2:139-47)
Menezes et al.[36]	Braz J Oral Sci 2009;8:9-13	The surface of some ceramics cannot be treated by HF etching. Therefore, dental restorations with usual etching procedures	Atsu et al.[26] (JPD 2006;95(6):430–6)

		and silane application, used for glass ceramics, are not efficient for all types of dental ceramic materials.	
Kitayama et al.[94]	Dental materials 2010;26:426–432	The surface roughness of restoration can improve the micromechanical bonding of the cement and the ceramic surface. Zirconia and alumina ceramics are high crystalline content materials makes them more resistant to roughening by HF etching.	Blatz et al.[16] (JPD 2003;89:268-274) Derand and Derand[37] (Int J Prosthodont 2000;13:131-5) Ozcan et al.[68] (Int J Prosthodont 2001;14:335-339
Yun et al.[17]	Dental materials 2010;26:650–658	Dental zirconia resists to HF because of its glass-free composition structure.	Blatz et al.[16] (JPD 2003;89:268-274)
Jevnikar et al.[23]	Dental materials 2010;26:688–696	In glass ceramic materials, a reliable bond can be achieved with conventional HF etching followed by silane application. While silica-free Y-TZP ceramics are acid etch resistant, and bonding protocols successfully used in glass ceramics cannot be fulfilled.	Blatz et al.[16] (JPD 2003;89:268-274)
Mirmohammadi et al.[95]	Dental materials 2010;26:627-633	Both of HF etching and silanization were unnecessary for dental zirconia surface modification before luting with resin cement.	Atsu et al.[26] (JPD 2006;95(6):430–6) Burke et al.[96] (J Adhes Dent 2002;4(1):7–22)
Magne et al.[43]	Dental Materials 2010;26:345–352	It is well known that highly crystalline ceramics resist conventional etching procedures as they lack glassy phase.	Borges et al.[33] (JPD 2003;89:479–88) Ozcan and Vallittu (Dental Materials 2003;19:825–31) Kim et al. (JPD 2005;94:357–

62) Della Bona et al.

(Braz Oral Res 2007;21:10–5)

Sorensen et al. (1991) [97] studied the effect of 20 % hydrofluoric acid etching for 3 min on the shear bond strength of resin cement to various compositions of dental porcelain. The result reported that the acid etching significantly improved shear bond strength of the low (10% alumina content) and medium alumina content (20% alumina content) but not significantly increased in bond strength of high alumina content (30% alumina content). The authors discussed that the increased alumina content is improvement in strength of ceramic and resistant to acid etching.

Kraivixien-Vongphantuset et al. (1992)[63] who presented in IADR abstract. The objective in this study is to examine shear bond strength of resin cement to In-ceram alumina ceramic after surface treatments; 1) hydrofluoric acid etching 5 min and followed Rocatec-Sil silane 2) hydrofluoric acid etching 5 min and followed Caulk silane 3) tribochemical silanization (Rocatec-Pre, Rocatec-Plus, Rocatec-Sil silane) 4) tribochemical silanization (Rocatec-Pre, Rocatec-Sil silane). The result showed that the mean shear bond strengths were: Gr. 1: 69.9 (27.3); Gr.2 :77.5 (8.5); Gr.3:123.1 (22.9); Gr.4: all specimens failed before testing. They demonstrated that the tribochemical bonding system improves superior bonds of resin cement to alumina core as compared with other methods.

Awliya et al. (1998)[67] determined shear bond strength and surface morphology of the densely sintered high-purity alumina (Procera All Ceram coping) using difference surface treatments as following 1) 9.6% hydrofluoric acid etching for 2 min, 2) airborne particle with 50 µm Al_2O_3 for 15 sec, 3) Roughening with a diamond and etching with 37% phosphoric acid for 2 min, and 4) No treatment (control). By using SEM, it was found that surface morphology of the alumina core treated by 9.6% hydrofluoric acid etching was not different compared with control. Shear bond strength of the surface treatment with 9.6% hydrofluoric acid (5.38±1.28 MPa) were lower than the bond strength of specimen treated with sandblasting (11.99±3.12 MPa). The authors reported that hydrofluoric acid was improved bond strength value of most feldspathic ceramics but did not increase the bond strength of the high alumina content. They suggest that the difference of ceramic materials is the important factor of surface morphology after etching.

Derand and Derand (2000)[37] determined the shear bond strength of zirconia ceramic after five surface treatments; 1) control 2) air abrasion with Al_2O_3 250 µm 3) air abrasion with Al_2O_3 50 µm 4) air abrasion with Al_2O_3 50 µm followed etching with 38% hydrofluoric acid for 12 mins and 5) ground with diamond bur. The testing was using 3 resin cements; Panavia 21, Twinlook and Superbond C&B. The result showed that Superbond C&B was the highest bond strength and hydrofluoric acid etching demonstrated weak tendency to improve shear bond strength. In addition, they reported that the used of hydrofluoric acid for high-density core material is not improvement of micromechanical retention of resin cements.

Ozcan et al. (2001)[68] determined the effect of three surface treatment; 5% hydrofluoric acid for 90 sec, airborne abrasion with 110 µm Al_2O_3, and tribochemical silica coating on the shear bond strength of luting cement to In-Ceram ceramic (each of specimen were treated by that of surface treatments prior to silanization). The result showed that bond strength for luting cements treated by hydrofluoric acid etching was less than that treated by other techniques. In addition, a surface roughness on In-Ceram ceramic cannot be created by hydrofluoric acid etching. This is because of its high alumina content.

Della Bona and Anusavice (2002)[78] investigated ceramic surface topography (feldspathic porcelain, alumina and zirconia containing ceramic) after treatment with ammonium bifluoride for 1 min, 9.6% hydrofluoric acid for 2 min, and 4% acidulated phosphate fluoride for 2 min. By treatment with 9.6% hydrofluoric acid, it could build up an irregular etching pattern on porcelain in which pores were the characteristic topographic feature. The surface etched by ammonium bifluoride showed plenty of grooves. Using 4% acidulated phosphate fluoride etching solution caused the precipitation of crystal on to surface. The authors concluded that hydrofluoric acid treatment can create the most prominent etching pattern on dental porcelain. The high alumina core ceramics exhibited less topographic change after those of etching treatment because of their high alumina crystal content and chemical resistance. They suggested that the differences in ceramic microstructure and its composition have an influence on etching pattern on ceramic surface.

Borges et al. (2003)[33] investigated the microstructure and surface topography of 6 different ceramics (IPS Empress, IPS EmpressII, Cergogold, In-Ceram Alumina, In-Ceram Zirconia, and Procera) after treatment with 10% hydrofluoric acid etching and airborne abrasion with 50 μm Al_2O_3 using SEM analysis. The results revealed that airborne particle abrasion did not change the morphologic characteristics of both In-Ceram Alumina and In-Ceram Zirconia ceramics. Treatment with 10 % hydrofluoric acid could produce elongated crystals scattered shallow irregularities on IPS Empress II surface. Furthermore, it could create honeycomb-like on the IPS Empress and Cergogold surface as well. An observation showed that 10% hydrofluoric acid treatment did not change superficial surface of In-Ceram Alumina, In-Ceram Zirconia and Procera. However, the authors concluded that the hydrofluoric acid and airborne particle with 50 µm Al_2O_3 did not change morphogenic microstructure on In-Ceram Alumina, In-Ceram Zirconia and Procera.

Dell Bona et al. (2006)[38] determined the tensile and shear bond strength of a glass-infiltrated alumina-based zirconia–reinforced ceramic to a resin composite with following surface treatments: 1) 9.5 % HF acid for 1 min 2) sand blasting with 25 µm Al_2O_3 particles for 10 sec 3) silica coating for 1 min following silanization. The results showed that hydrofluoric acid treatment exhibited lower value in the tensile and shear bond strength than other treatments. This was because hydrofluoric acid etching did not produce effective retention in alumina and zirconia base ceramics.

The micro shear bond strength of different dental ceramics (IPS Empress II, Cergogold, In-Ceram Alumina, and Cercon) and surface treatments (control, 9.5% hydrofluoric acid and airborne particle) was studied by Menezes et al. (2009)[36] It was found that the Cergogold and Empress II ceramics can be etched by both 9.5% hydrofluoric acid and abraded by airborne particle surface treatment resulting high micro shear bond strength compared with control. However, there were no differences on morphography of the In-Ceram Alumina and Cercon after surface treatment with either 9.5% hydrofluoric acid or airborne particle. However, they reported that the acid etching treatment had not an impact on bond strength of both Cercon and In-Ceram ceramic. This was probably due to the absence of glass phase (SiO_2) in these ceramics, as explained by Borges et al.[33]

Hydrofluoric acid (HF) [98-102]

Hydrofluoric acid (HF) is an inorganic acid of hydrogen fluoride in water. It is known to dissolve silica base materials such as glass, quartz, porcelain as well as various metals, natural rubber, leather, and most organic materials including human and animal tissue. Industrially, hydrofluoric acid is used to etch glass material, clean metal surface before electroplating, and etch silicon wafers in electronic semiconductor materials. In the home, HF can be found in household cleaners, rust removers, aluminum brighteners and heavy duty cleaners.

Generally, hydrofluoric acid is a colorless. They range in concentration from less than 1% to as much as 70% (for safety). Hydrofluoric acid is miscible in water and in solution has virtually no odor whereas; the gaseous form of hydrofluoric acid has a very strong and irritating odor. Hydrofluoric acid (HF) is manufactured from calcium fluoride (commonly called “fluorspar”), which is reacted with sulfuric acid to form HF gas as the following reaction.

$$CaF_2\ (s) + H_2SO_4\ (l) \leftrightarrow 2\ HF\ (g) + CaSO_4\ (s)$$

Where CaF_2 = fluorspar and H_2SO_4 = sulfuric acid.

The gas of HF is then cooled and stored as an anhydrous HF liquid, which by definition refers to concentrations greater than 99%. For acid solution, HF ionizes in aqueous solution in a similar way to other common acids.

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$

Hydrofluoric acid and additional free fluoride ions are also generated when ammonium bifluoride dissociates in aqueous solution as the following chemical reaction.

$$NH_4HF_2 \longrightarrow HF + F^{-} + NH_4^{+}$$

Where NH_4HF_2 = ammonium bifluoride.

Generally, in dental applications, concentrations of 4% to 10% HF are typically used in dental clinic and dental laboratory. This concentration range is safely for dental procedures application, including intra oral repair porcelain (in case of chipping or fracture of ceramic restorations). From the chemical property of hydrofluoric acid that it can dissolve silica base materials and we know that dental porcelain consists of two phases, a crystalline phase and an amorphous glassy phase. The main crystalline component is leucite ($K_2O.Al_2O_3.4SiO_2$)[103] while the glassy phase is an amorphous structure of SiO_2. Therefore, etching porcelain with hydrofluoric acid is selectively dissolve the glassy phase, resulting in a micro-porous, high-surface energy.[104] In principle, this is similar to what happens to enamel surfaces after etching with 37% phosphoric acid.

The surface modification of porcelain by hydrofluoric acid is also dependent on many factors. Calamia (1985)[105] recommended adjusting the etching times and concentration of hydrofluoric acid depending on the type of porcelain being treated. For example, feldspathic porcelains mainly consist of metal oxides such as SiO_2, Al_2O_3, and K_2O that they are in the part of glassy phase and crystal phase. For the alumina content, crystalline microstructure and size can all influence the concentration and etching time of hydrofluoric acid.[97, 106, 107]

Besides hydrofluoric acid, there are some etchants, such as 1.23% APF (acidulate phosphate fluoride) and NaF (sodium fluoride) gels have been shown the ability to etch porcelain, though the time of application was considerably longer than for HF etching.[103, 108, 109] There were many studies reported that etching with hydrofluoric acid resulted in a very definitive microscopic etching pattern, while etching with other etchants showed heterogeneous shallow pattern.[33, 110-112]

The etching time of hydrofluoric acid has been suggested to range from 60 seconds to 20 minutes.[34, 103, 113-115] Zarone et al. (2006)[74] demonstrated that etching with 40% HF acid for 2 minutes can be produced micro-retentions on the feldspathic porcelain surface, but did not achieve proper surface roughness on both alumina and zirconia surfaces. Phoenix and Shen (1995)[110] suggested that feldspathic porcelain was treated with 9.5% HF acid etching resulted in changing of surface topography and the lowest contact angle values when compared with other etchants or after alumina air abrasion. Borges et al. (2003)[33] used low concentration of HF (10 %) with an extended etching time (20 seconds) created the surface roughness of porcelain. In addition, Chen et al.(1998)[34] found 10% HF acid etching porcelain for 2 minutes enhanced shear bond strength between etched porcelain surface and resin cement.

Pisani-Proenca et al. (2006)[104] suggested that lithium disilicate-based ceramic treated with 5% HF acid for 20 seconds and followed a silane coupling agent increased microtensile bond strength when compared with control group (untreated group). For the zirconia surface treatment, Blatz et al.(2003)[16] reported the conventional acid etching had no effect on the resin bond to zirconia ceramic.

Similar to other reports have stated that dental zirconia cannot be etched by HF acid as shown in table 2.

CHAPTER III
RESEARCH METHODOLOGY

The materials and methods of this study were divided into 2 parts: 1) Hypothesis testing and 2) Physical properties testing.

Part I: Hypothesis testing

The aims of this study were 1) to investigate the effect of hydrofluoric acid treatment on the surface topography by using a scanning electron microscope (SEM), 2) to determine elementals occurring on zirconia surface after etching with hydrofluoric acid by using energy-dispersive X-ray spectroscopy (EDS), and 3) to measure the dislodged elements in hydrofluoric acid solution after etching dental zirconia by using inductively coupled plasma (ICP) technique.

Therefore, hypothesis testing in part I was to prove if hydrofluoric acid can etch zirconia or not.

The null hypotheses tested were 1) hydrofluoric acid cannot alter the zirconia surface topography, 2) no elemental changes will be presented on the etched zirconia surface, and 3) no dislodged zirconium element will be observed in the hydrofluoric acid solution after etching dental zirconia

Three commercially available zirconia disk brands were evaluated in this study: KATANA Pre-Sintered Zirconia Block (Kuraray Noritake Dental Inc., Aichi, Japan), Cercon base (DeguDent, GmbH, Hanau, Germany), and ZENOTEC Zr Bridge (Wieland, Copenhagen, Denmark). The pre-sintered zirconia disks of each brand were cut into square-shaped specimens (10x10x2 mm). Next, each sample was polished to a flat surface using dry 1200-and 2000-grit silicon carbide abrasive paper and blown with clean dry air for 30 seconds. The samples were sintered at temperatures according to the manufacturers' instructions. Table 3 shows the brand names, compositions, batch numbers, and manufacturers of the material used in this study.

The specimens prepared from each brand were randomly divided into four groups. For groups 2 and 3, the specimens were divided into four subgroups and the group 4 specimens were divided into two subgroups according to the surface treatment performed. No treatment was performed for Group 1, which served as the control group. Group 2: immersion in 9.5% HF at 25 $^{\circ}$C for 1, 2, 3, or 24 hours. Group 3: immersion in 9.5% HF at 80°C for 1, 3, 5, or 30 minutes. Group 4: immersion in 48% HF at 25 $^{\circ}$C for 30 or 60 minutes. Flowchart of specimen preparation is shown in Figure 10.

Table 3 Materials used in this study

Material	Main composition	Lot number	Manufacturer
KATANA Pre-Sintered Zirconia Block	Zirconium dioxide	KT11BGKLP	Kuraray Noritake Dental Inc., Aichi, Japan
Cercon base	Zirconium dioxide	18010880	DeguDent GmbH, Hanau, Germany
ZENOTEC Zr Bridge	Zirconium dioxide	6901001140	Wieland, Copenhagen, Denmark
Hydrofluoric acid solution	Hydrofluoric acid in water	B0346834 909	Merck KGaA, Darmstadt, Germany

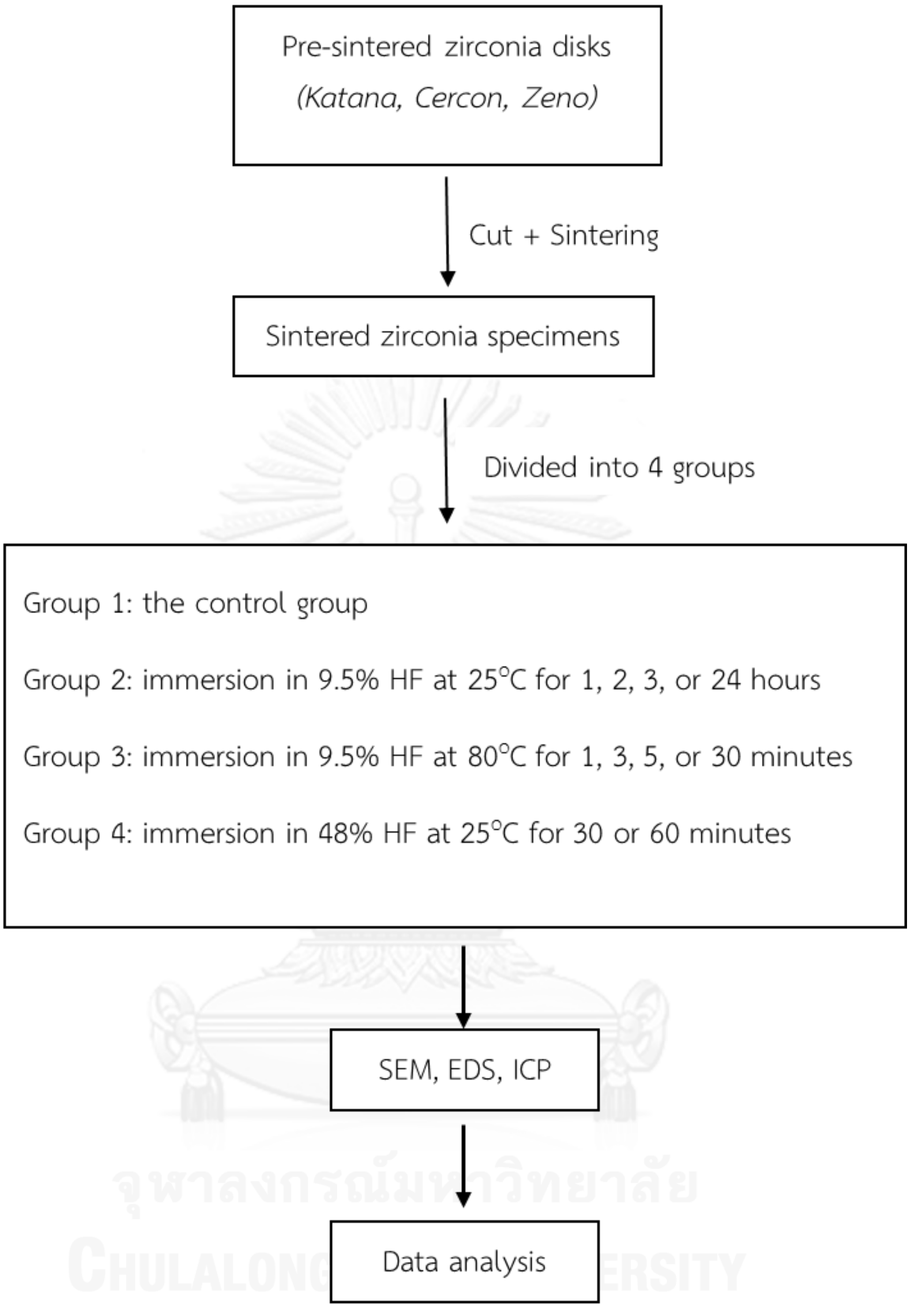


Figure 10 Flowchart of specimen preparation for the hypothesis testing

For the immersion procedure, the specimens were immersed in the HF solution contained in a polytetrafluoroethylene beaker and all processing was carried out in a fume hood (Figure 11). After achieving the indicated immersion time, specimens were subjected to analysis. SEM was used to evaluate the effect of hydrofluoric acid treatment on the surface topography. The elements occurring on the surface of etched zirconia were examined by EDS. ICP was carried out to determine dislodged element released after immersion in HF solution.

Figure 11 Zirconia specimens were immersed in 9.5% HF at 80°C and all processing was carried out in a fume hood

1.1 Scanning electron microscopy (SEM) evaluation

The SEM evaluation was to investigate the effect of hydrofluoric acid treatment on the surface topography. After achieving the indicated immersion time, the zirconia specimen (10x10x2 mm) (Figure 12) from each experiment were randomly selected and were rinsed with deionized water for 1 minute, followed by ultrasonically cleaned in deionized water for 10 minutes, and then gently air-dried. The samples were mounted on a metallic stub, and gold sputter coated. Five surface topography areas were randomly selected and photographed using an electron microscope (JSM-5410LV, JEOL, Japan) at 10,000x magnification and 15 kV accelerating voltage.

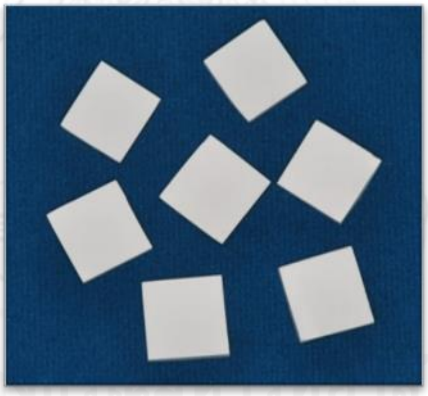


Figure 12 The sintered zirconia specimens (10x10x2 mm)

Ultrasonic and non-ultrasonic cleaning of HF-treated zirconia

The aim of this study was to evaluate the effect of ultrasonic cleaning on the surface of HF-etched zirconia using SEM analysis at 500x, 2,000x and 10,000x magnification. The surface topography was characterized in order to compare between ultrasonic cleaning and non-ultrasonic cleaning. Ten specimens (10x10x2 mm) of Katana sintered zirconia were used in this study. The specimens were immersed in 9.5%HF at 80°C for 10 minutes followed by being picked up and cooled down at room temperature. Then, the immersed zirconia specimens were divided into two groups:

Group1: ultrasonic cleaning in deionized water for 10 minutes and then gently air-dried

Group2: non-ultrasonic cleaning

The specimens from each experiment were randomly selected to evaluate under SEM analysis.

1.2 Energy-dispersive X-ray spectroscopy (EDS) analysis

Energy-dispersive X-ray spectroscopy (EDS) is an analytical technique for the elemental analysis of the surface sample. The purpose of this study was to evaluate the element on zirconia surface after etching with hydrofluoric acid. The null hypothesis tested was hydrofluoric acid cannot alter the elemental of zirconia surface.

Three band sintered zirconias (Katana, Cercon and Zeno) were used in this study. All specimens were ultrasonically cleaned in deionized water for 10 minutes, and then gently air-dried prior to apply with HF treatment. The zirconia specimens form each band were divided into 4 groups by surface treatment condition as same as SEM experiment. For group 2, 3 and 4, the specimens were divided into two subgroups according to the ultrasonic cleaning performed. Flowchart of specimen preparation for EDS testing is shown in Figure 13.

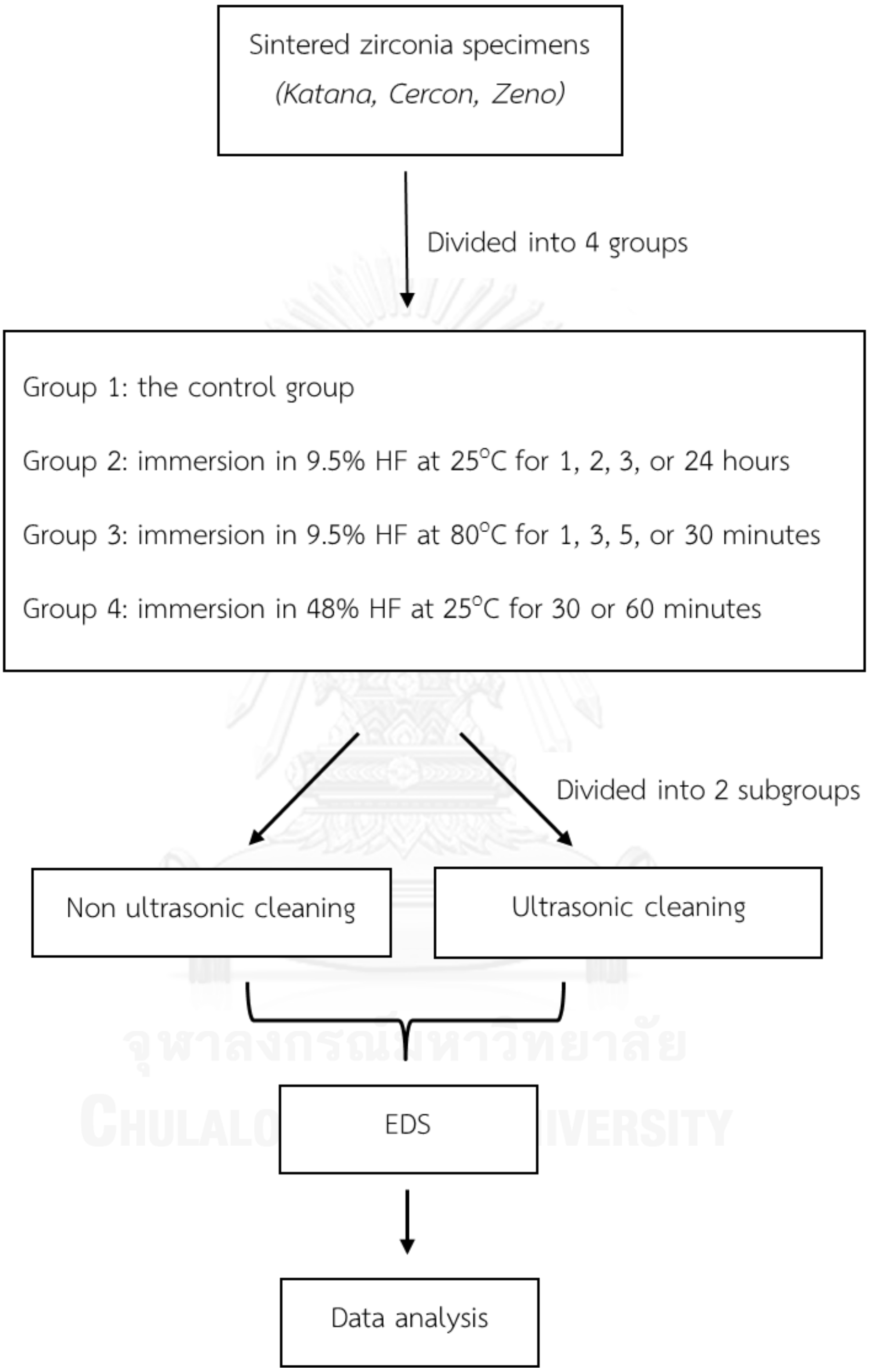


Figure 13 Diagram of EDS testing

The zirconia specimens from each condition were analyzed for elemental compositions using EDS. The data were obtained by a SEM (JSM-5800LV, JEOL, Japan and ISIS Series 300, Oxford, England) fitted with an energy dispersive X-ray spectrometer. The primary electron energy used was varying from 5 to 20 keV. The testing parameters were set to WD=15 mm, process time=5 sec, live time=60 sec, dead time=30-40%. Three different areas were selected from each sample, and each area was scanned five times.

1.3 Inductively coupled plasma (ICP) evaluation

Inductively Coupled Plasma (ICP) is an analytical technique used for determination of elements in liquid. The aims of this study were to evaluate the dislodged elements in hydrofluoric acid solution after etching dental zirconia and to measure the quantitative dislodged zirconia per surface area. The hypothesis tested was that the zirconia element cannot be dislodged by hydrofluoric acid treatment. The ICP (ICP-Plasma-2000, Perkin Elmer, UK) testing in this study was divided into 3 parts as followed: 1) Finding the ICP peak of zirconia element, 2) Quantification of dislodged zirconium element and 3) Identifying zirconium ion per surface area from each condition, respectively.

Part II: Physical properties testing

In this part the physical properties of etched zirconia specimens from each treatment were evaluated. The testing included: 1) SEM to investigate the surface topography at the low magnification and to compare with the surface morphology of ceramic at given surface treatment such as alumina blasted zirconia, as-sintered zirconia, polished zirconia, as-sintered porcelain, alumina blasted porcelain and HF treated porcelain, 2) Profilometer and AFM to evaluate the surface roughness (R_a) of HF treated zirconia in term of micro-roughness and nano-roughness, respectively, 3) FTIR to investigate the functional groups on the HF acid treated zironia, 4) XRD to observe the crystal structure of dental zirconia after HF etching, and 5) XPS to determine the chemical structure and stoichiometry on the etched zirconia surface

KATANA Pre-Sintered Zirconia Block (Kuraray Noritake Dental Inc., Aichi, Japan) were chosen in this study. The disks were milled into cylinder-shaped (Ø ~19 mm, height ~21 mm) using milling machine and then the cylinder zirconia shapes were mounted and cut with sectional cutting machine into the dimensions of ~19 mm diameter (Ø) and ~1.5 mm height. The samples were sintered at temperatures recommended in the manufacturers' instructions and then allowed the furnace to cool down slowly to room temperature. Finally, the sintered zirconia specimens had Ø ~15 mm and height ~1.2 mm. After cooling down of specimens, they were kept in well closed plastic containers to protect any contaminations. The modification of sintered zirconia disks surface was applied before performing physical-property experiment.

Figure 14 KATANA Pre-Sintered Zirconia Block

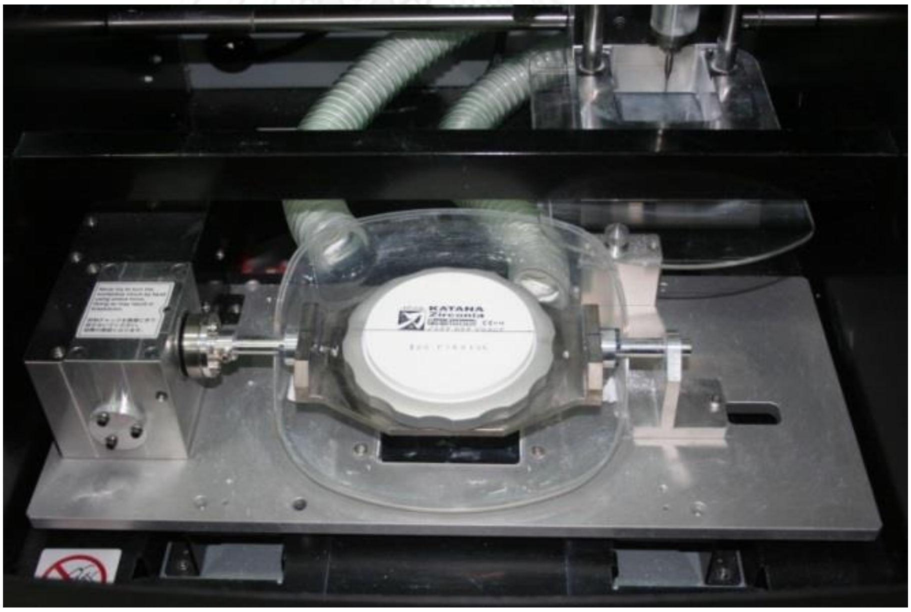


Figure 15 The pre-sintered zirconia block was milled into cylinder-shaped (Ø ~19 mm, height ~21 mm) by using a milling machine.

Figure 16 The cylinder-shaped of the pre-sintered zirconia (Ø ~19 mm, height ~21 mm).

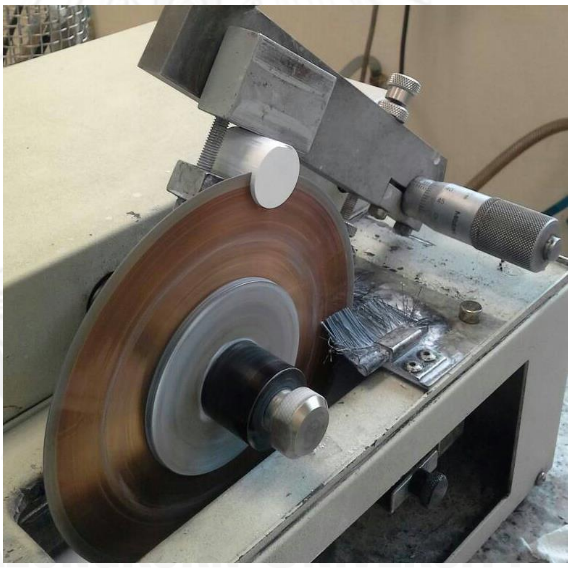


Figure 17 The cylinder-shaped of the pre-sintered zirconia was cut by a sectional cutting machine.

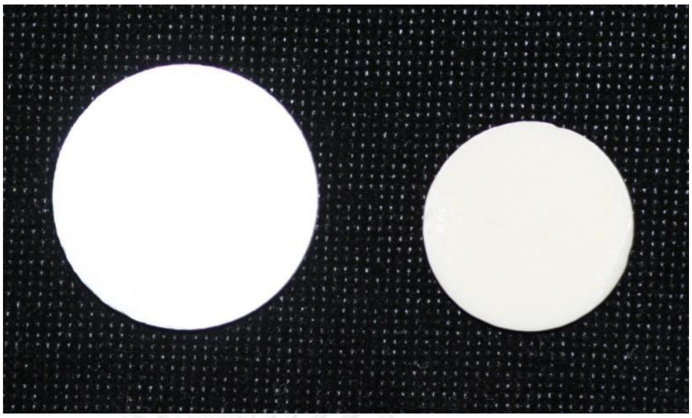


Figure 18 Pre-sintered zirconia specimen before sintering process (Ø ~19 mm, height~1.5 mm) (left), and after sintering process (Ø ~15 mm, height ~1.2 mm) (right)

2.1 The SEM evaluation at 200x, 500x, 2,000x magnifications

The SEM analysis was used to investigate the surface morphology of sintered zirconia specimens compared with sintered porcelain specimens (CERABIEN ZR, Kuraray Noritake Dental Inc., Aichi, Japan). The specimens from each material were divided into five groups according to the surface treatment performed.

Group 1: the control group of zirconia includes *as-sintered zirconia*, *polished sintered zirconia* (using dry 1200-and 2000-grit silicon carbide abrasive paper), and *airborne-particle abraded* (with 1 µm Al_2O_3 at 2.5 bars pressure for 15 sec at a 10 mm distance).

Group 2: the zirconia specimen immersion in 9.5% HF at 25 °C for 1, 2, or 3 hours

Group 3: the zirconia specimen immersion in 9.5% HF at 80°C for 1, 3, 5, or 30 minutes

Group 4: the zirconia specimen immersion in 48% HF at 25 °C for 30 or 60 minutes

Group 5: the porcelain group includes as-sintered porcelain, HF treated porcelain (9.5% HF at 25°C for 1 minute), and airborne-particle abraded (with 110 µm Al_2O_3 at 2.5 bars pressure for 15 sec at a 10 mm distance).

After achieving the surface treatment conditions, the specimens were rinsed with deionized water for 1 minute and ultrasonically cleaned in deionized water for 10 minutes, and then gently air-dried. The samples were analyzed under a scanning electron microscope (SEM) for surface topography analysis at 200x, 500x and 2,000x magnifications.

The 2D SEM images form each condition at 200x, 500x, and 2,000x magnification were converted in 3D images by using the ImageJ software ver.1.47 (National Institutes of Health, USA), based on relative grayscale value for evaluated the height variation of treated specimen.

2.2 Surface roughness evaluation of HF treated zirconia

Surface roughness is a calculation of surface texture. Roughness value is often described as smooth, uneven or irregular surface. It is quantified by the vertical spacing of the real surface from its ideal form. The average roughness value (R_a) is the most commonly used parameter for expressing measurements of surface contour. R_a is the arithmetic average of the absolute values of the profile height deviations from the mean line, recorded within the evaluation length. In brief, R_a is the average of a set of individual measurements of a surfaces peaks and valleys. The surface roughness testing in this study consisted of 2 techniques: 1) profiometer technique and 2) AFM technique.

2.2.1 Surface roughness value by using profilometer technique

The aim of this part was to evaluate the zirconia surface roughness value after treated with hydrofluoric acid in any conditions. The null hypothesis tested in this study was that there is no significant difference in surface roughness among the different zirconia surface treatment procedures.

KATANA Pre-Sintered Zirconia Block (Kuraray Noritake Dental Inc., Aichi, Japan) was evaluated in this study. The zirconia specimens (Ø ~ 15 mm and height ~1.2 mm) were prepared as the same method that was descried in the topic of physical properties testing.

After sintering process, 240 cylinder-shaped zirconia specimens were used in this study. The zirconia surfaces were subjected to the polishing machine (DPS 3200, IMTECH, South Africa) by using SiC papers in sequence (grit 1,000, 1,200 and 2,000) for 30 minutes under water irrigation at 150 rotations per minutes (rpm) to obtain standardized flat surfaces before applying the surface treatments. After polishing procedure, all specimens were ultrasonically cleaned in distilled water for 10 minutes to remove any surface residues, and then air dried.

The zirconia specimens were randomly divided into four groups according to surface treatment conditions (n=20);

Group 1: the control group as the polishing zirconia

Group 2: the blasting zirconia (airborne-particle abraded with 110 μm Al_2O_3 at 2.5 bars pressure for 15 seconds at a 10 mm distance)

Group 3: the zirconia specimen immersion in 9.5% HF at 25 $^{\circ}$C for 1, 2, or 3 hours

Group 4: the zirconia specimen immersion in 9.5% HF at 80°C for 1, 3, 5, or 30 minutes

Group 5: the zirconia specimen immersion in 48% HF at 25 $^{\circ}$C for 30 or 60 minutes

After surface treatment, all specimens were rinsed under the water spray, ultrasonically cleaned in deionized water for 10 minutes and air-dried.

After surface treatment process, surface roughness value was measured by using a profilometer (Handysurf E- 35B, Tokyo Seimitsu, Tokyo, Japan), with a standard cutoff of 0.8 mm, using a Gaussian filter, measurement length of 4.00 mm. The surface roughness value was measured five times for each sample, and then the average value obtained was calculated as R_a (roughness average) of each specimen.

2.2.2 Surface roughness value using Atomic force microscopy (AFM) evaluation

The objective of this study was to evaluate the surface changes in average surface roughness (Ra) at the nano-scale provided by different dental zirconia surface treatments using Atomic force microscopy (AFM) evaluation. The hypothesis tested was that the HF treatments cannot change the zirconia surface roughness and morphology at the nano-scale.

Twenty sintered Katana zirconia specimens (10x10x2 mm) have been selected for the study. All specimens were polished to a flat surface by using SiC abrasive paper (grit# 800, 1200 and 2000) for 30 minutes and ultrasonically cleaned in deionized water for 10 minutes, and then gently air-dried. The specimens were randomly divided into 4 groups according to surface treatment conditions; No treatment was performed for Group 1, which served as the polishing group, Group 2: immersion in 9.5% HF at 80 $^{\circ}$C for 1 minutes, Group 3: immersion in 9.5% HF at 80 $^{\circ}$C for 5 minutes, and Group 4: immersion in 9.5% HF at 80 $^{\circ}$C for 30 minutes.

Five Katana zirconia specimens from each experiment were evaluated under an Atomic Force Microscope (AFM, SPM Nanoscpe IV, Digital Instruments, Veeco Metrology group, Santa Barbara, CA, USA). Five measurements were performed for each zirconia specimen after different surface treatment conditions using a 3 µm x 3 µm scan size, recorded with a 0.1 Hz scan rate and analyzed the surface roughness (R_a) using specific software (Nanoscope V530R35R, and the mean value were calculated.

2.3 Fourier Transform Infrared (FTIR) evaluation

The FTIR is a method of obtaining an infrared spectrum to detect the functional group of samples. The aim of the this study was to investigate the alterations of functional groups on the HF acid treated zironia surface by using infrared spectroscopy. The proposed hypothesis was that HF treated zirconia cannot be changed the functional groups of dental zirconia surface. The samples of this study were divided into 2 groups: Group1 was the sintered Katana zirconia powder and Group 2 was the powder of HF treated zirconia obtianed by very gently scrathing the specimens surface with a clean blade No.11.

The powder from specimen surfaces of group 1 and 2 was examined by Fourier transform infra-red spectroscopy with IR Prestige-21 spectrometer (Shimadzu Scientific Instruments, Columbia,MD, USA) (Figure 3.10). For IR analysis, first, 1 mg of the powder sample was carefully mixed with 300 mg of KBr (infrared grade) and pelletized under vacuum. The samples were carried on in the dessicator to protect chemicals or that protected with H_2O from humidity. Then the pellet was analyzed with IR spectrometer in the range of 250 to 4,000 cm^{-1} at scan speed of 40 scan/min with 4 cm^{-1} resolution.

Figure 19 Fourier Transform Infrared (FTIR) spectrometer

2.4 The X-ray diffraction (XRD) evaluation

The aim of XRD test was to investigate the effect of hydrofluoric acid treatment on the crystal structure change of Y-TZP zirconia ceramics. The conventional 2θ–θ method and the grazing angle method of XRD analysis were performed in this study.

2.4.1 XRD conventional 2θ–θ method of HF treated zirconia specimens

Twenty-one cylinder-shaped sintered Katana zirconia specimens were divided into 4 groups according to surface treatment methods (n=3):

Group 1: control group

Group 2: immersion in 9.5% HF at 25°C for 3 hours under non-ultrasonic and ultrasonic condition

Group 3: immersion in 9.5% HF at 80°C for 30 minutes under non-ultrasonic and ultrasonic condition

Group 4: immersion in 48% HF at 25°C for 60 minutes under non-ultrasonic and ultrasonic condition

All of the specimens were kept in desiccator to avoid any possible contaminations. The specimens from each group were performed with a diffractometer (XRD, D8, discover, Bruker AXS GmbH, Germany) using conventional 2θ-θ method (Figure 20). The Cu radiation at 40 kV and 405 mA was performed to identify the crystalline composition phases on the zirconia specimen surface.

Diffraction patterns were collected within 10-65 2θ at a scan speed of 0.5°/min, covering the area of highest peaks of tetragonal and monoclinic phases of zirconia.

Figure 20 The diffractometer for XRD analysis

2.4.2 XRD the grazing angle method of HF treated zirconia specimens

The nine cylinder-shaped sintered Katana zirconia specimens were used in this study and divided randomly into 3 groups according to surface treatment methods (n=3):

Group 1: control group

Group 2: immersion in 9.5% HF at 80°C for 30 minutes, without ultrasonic cleaning

Group 3: immersion in 9.5% HF at 80°C for 30 minutes and then ultrasonic cleaning

All of the specimens were kept in desiccator to avoid any possible contaminations.

The grazing angle method at incident angle $\theta = 3^\circ$ method was chosen to identify the crystalline composition phases on the zirconia specimen at the penetration depth of 3 µm. Diffraction patterns were obtained from 10-65 2θ at a scan speed of 0.5°/min, covering the area of highest peaks of tetragonal and monoclinic phases of zirconia.

2.4.3 Conventional XRD on scratched white powder

The subject of this study was to evaluate the white powder that prepared by gently scracthed on the specimens surface with a clean blade No.11. The crystal structure and chemical compound of white powder were investigated by using a diffractometer (XRD, D8, discover, Bruker AXS GmbH, Germany). The XRD analysis was described elsewhere previously.

2.5 The X-ray photoelectron spectroscopy (XPS) analysis

X-ray photoelectron spectroscopy is the surface-sensitive characterization technique that analyses the elemental composition, compound formula, electronic state and chemical state of the elements which exist within materials. The objective of XPS evaluation was to investigate the effect of hydrofluoric acid treatment on the chemical composition change of zirconia ceramics.

The fifteen specimens were divided into 5 groups by surface treatment conditions (n=3);

Group 1: control group or un-treated zirconia specimen,

Group 2: zirconia treated with 9.5%HF at 80°C for 10 minutes and then ultrasonic cleaned,

Group 3: zirconia treated with 9.5%HF at 80°C for 10 minutes,

Group 4: zirconia treated with 48%HF at 25°C for 3 hours, and

Group 5: zirconia treated with 9.5%HF at 25°C for 3 hours

After surface treatment, all of zirconia specimens were kept in well-closed plastic container to avoid any possible contaminations. X-ray photoelectron spectroscopy (XPS; AXIS ULTRADLD, Kratos Analytical Ltd., Manchester, UK) was used to determine surface chemistry and stoichiometry of the changes in the zirconia specimen surfaces. In brief, for the procedure, the base pressure in the XPS analysis chamber was about $5x10^{-9}$ torr. Akratos Analytical Axis Ultra XPS system with a monochromatic Alkα source operated at 15 kV 10mA 150W and pass energy of 1.4 eV was used to obtain Zr 3d core level spectra. The photoelectrons were detected with a hemispherical analyzer positioned at an angle of 45° with respect to the normal to the sample surface. The spectra were then deconvoluted using CasaXPSTM software employing a Shirley background subtraction and mixed Gaussian-Lorentzian (G-L) peaks associated with the oxide, oxy-fluoride or other components. For XPS analysis, the commonly reported peak position for tetragonal ZrO_2 ($Zr3d_{5/2}$) at 182.2 was referenced for all spectra.

CHAPTER IV

RESULTS

Results of Part I: Hypothesis testing

1.1 Scanning electron microscopy (SEM) evaluation

SEM images of the zirconia surfaces from each brand are shown in Figures 21-24. The unetched zirconia surface of the control specimens (Figure 21 a.1-c.1) had a homogenous fine grain structure and closed inter-grain space.

Figure 22 shows the zirconia specimen surface from each brand after immersion in 9.5% HF at 25°C for 1, 2, 3, or 24 hours. After 1 hour of treatment, data regarding the dislodgment of superficial grains, irregular grain structure, decrease in grain size, and enlargement of the inter-grain space compared with the control is shown in Figures 21 (a.1, b.1, and c.1). In addition, with longer treatment times, the images of zirconia HF-treated for 2, 3, or 24 hours (Figs. 22 (a.2-a.4), (b.2-b.4) and (c.2-c.4) revealed a further increase in the dislodgment of superficial grains, smaller grains and increased inter-grain space with longer treatment times. Immersion for 24 hours resulted in the development of large holes on the zirconia surfaces (Figs. 22 (a.4, b.4 and c.4)).

The zirconia specimens from each brand immersed in 9.5% HF at 80°C for 1, 3, 5 or 30 minutes are illustrated in Figure 23 (a.1-a.4, b.1-b.4, and c.1-c.4). The dislodgment of superficial grains, irregular grain shape, decrease in grain size, and enlargement of inter-grain space was again present as immersion time increased. In addition, large holes were evident after an immersion time of 30 minutes (Figs. 23 (a.4, b.4 and c.4)).

For group 4, images of the zirconia specimens from each brand immersed in 48% HF at 25°C for 30 and 60 minutes are shown in Figures 24 (a.1-a.2, b.1-b.2 and c.1-c.2). The SEM images revealed irregular morphology similar to that seen in groups 2 and 3. The surface irregularities observed on the specimen surfaces increased with increasing immersion time and higher concentration of the etching solution.

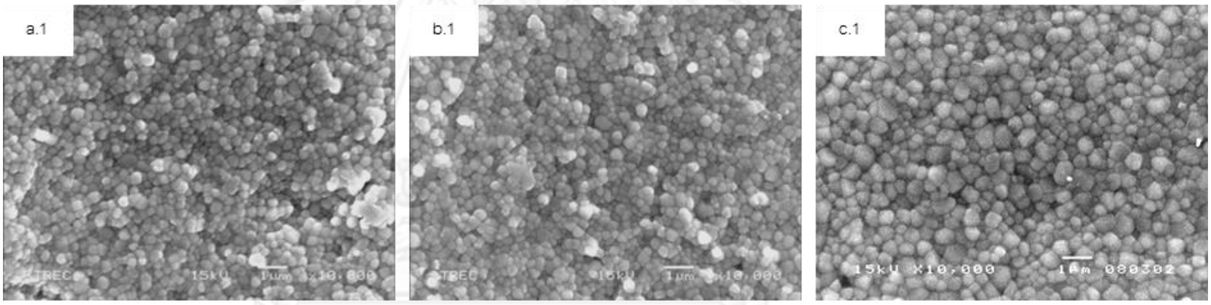


Figure 21 SEM images at 10,000x magnification of control zirconia specimens from each brand: (a.1) KATANA Pre-Sintered Zirconia Block, (b.1) Cercon base and (c.1) ZENOTEC Zr Bridge.

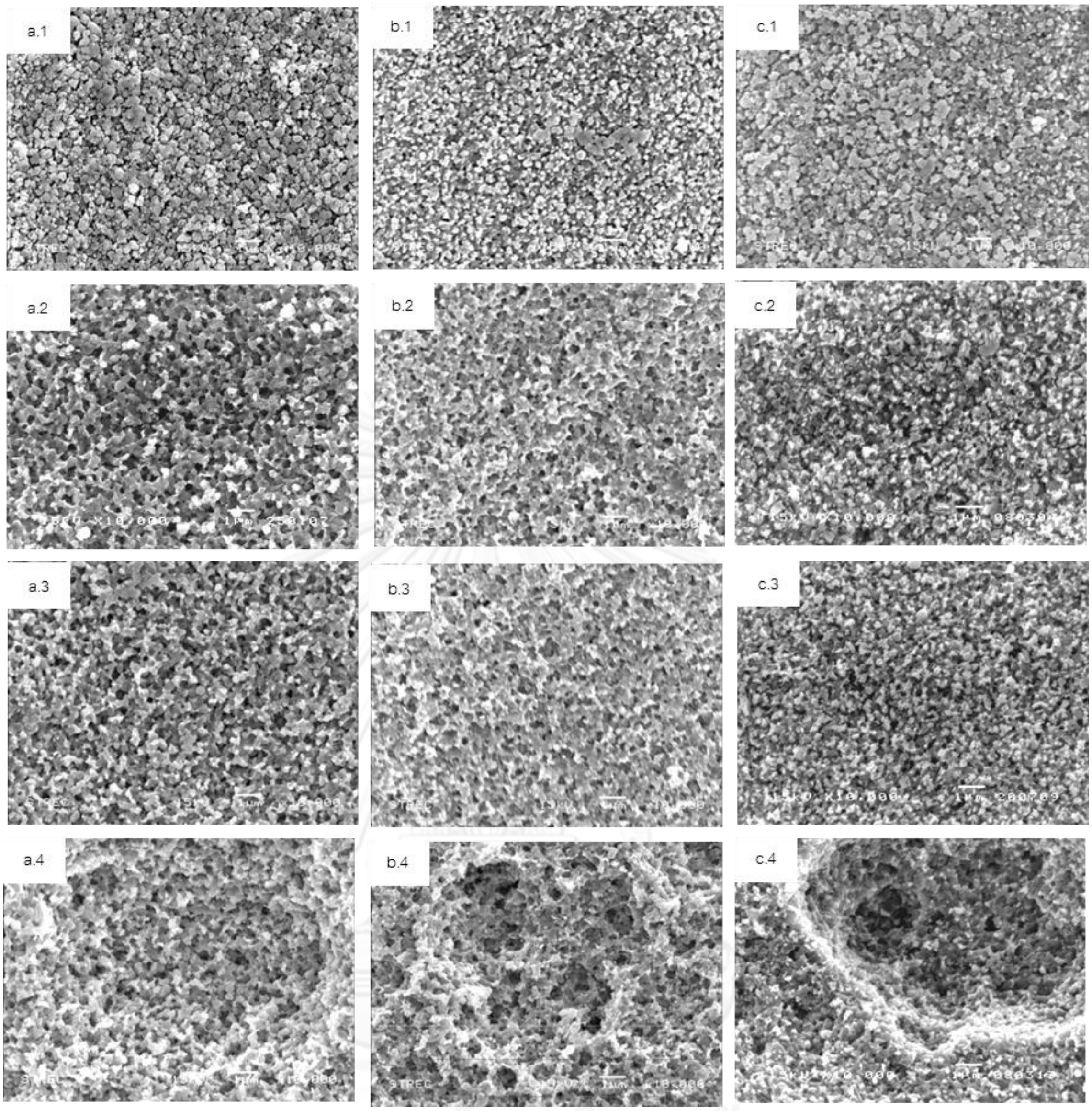


Figure 22 SEM images at 10,000x magnification of zirconia specimen surface from each brand after immersion in 9.5% HF at 25°C for 1, 2, 3 or 24 h, respectively: (a.1-a.4) KATANA Pre-Sintered Zirconia Block, (b.1-b.4) Cercon base and (c.1-c.4) ZENOTEC Zr Bridge.

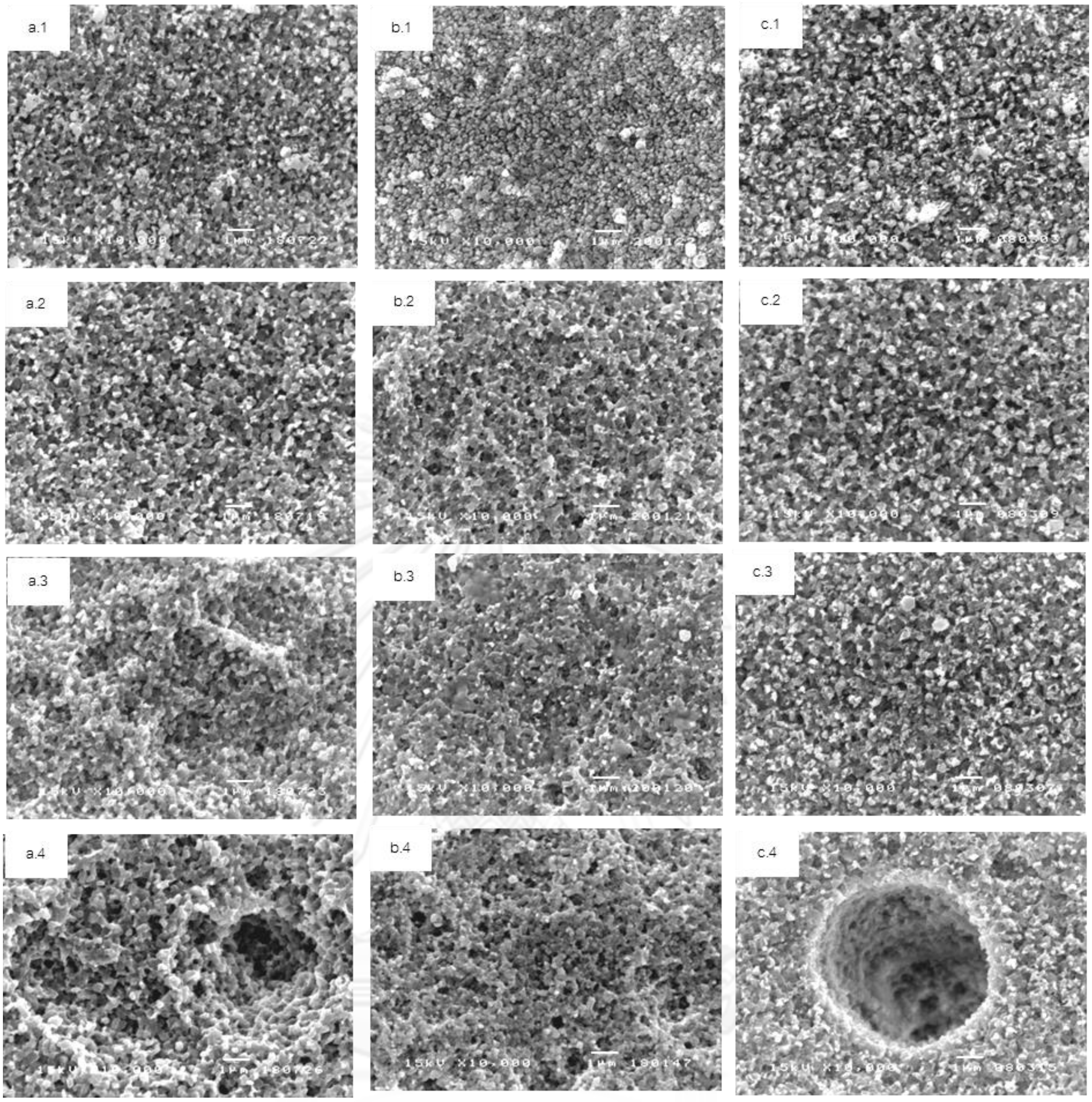


Figure 23 SEM images at 10,000x magnification of zirconia specimen surface from each brand after immersion in 9.5% HF at 80°C for 1, 3, 5 or 30 min, respectively: (a.1-a.4) KATANA Pre-Sintered Zirconia Block, (b.1-b.4) Cercon base and (c.1-c.4) ZENOTEC Zr Bridge.

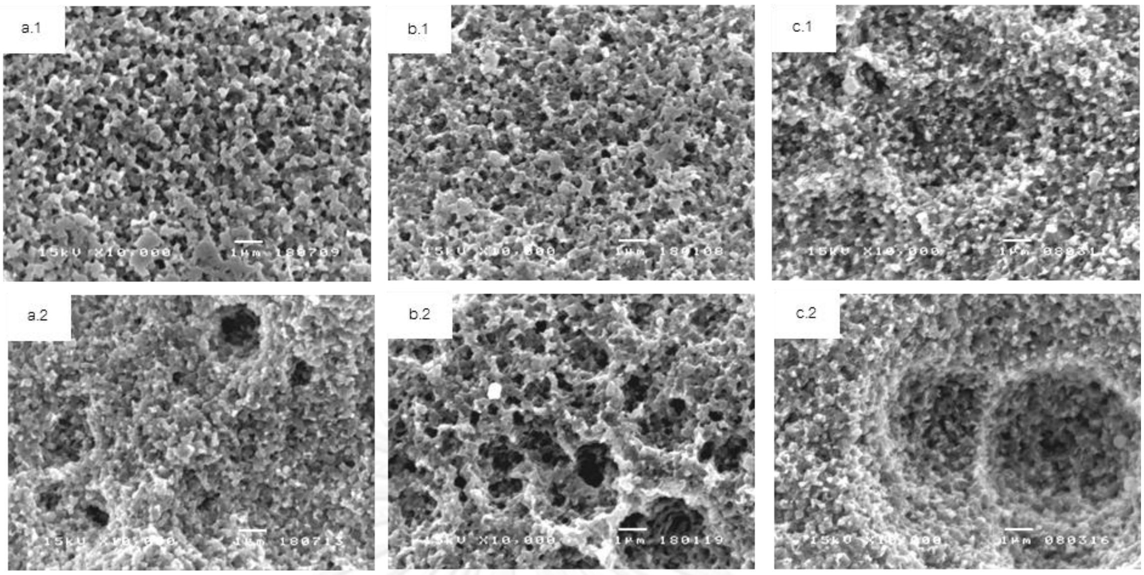


Figure 24 SEM images at 10,000x magnification of zirconia specimen surface from each brand after immersion in 48% HF at 25°C for 30 or 60 min, respectively: (a.1-a.2) KATANA Pre-Sintered Zirconia Block, (b.1-b.2) Cercon base and (c.1-c.2) ZENOTEC Zr Bridge.

The results by using SEM evaluation showed that hydrofluoric acid treatment was able to etch the zirconia ceramic, causing variation in surface topography. Based on these results the null hypotheses were rejected.

After the surface treatment with HF, it can be observed that a thin layer of white powder was deposited on the surface of non-ultrasonic cleaned specimens. In addition, this layer can be removed and scratched off by the cleaned blade no.11 (as shown in Figure 25). Therefore, the next experiment was performed to evaluate the effect of ultrasonic cleaning of dental zirconia surface after hydrofluoric acid treatment in term of surface topography by using SEM evaluation.

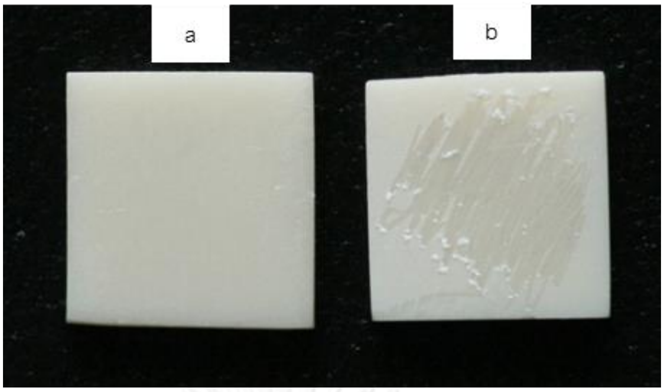


Figure 25 HF-treated zirconia specimen surface (a) with a powder layer (b) after removing a white layer by cleaned blade no.11

SEM evaluation of ultrasonic and non-ultrasonic cleaning of HF-treated zirconia

SEM images of HF-treated zirconia revealed structural differences from the samples that were ultrasonic cleaned in comparison with those without non-ultrasonic cleaned (Figure 26). At the 2,000x magnification, Group 1 sample displayed small porosity whereas an enlargement of inter-grain space, an irregular grain shape and a decrease in grain size were observed at the10,000x magnification as illustrated in this previous study. However, non-ultrasonic treated zirconia surface (group 2) showed various cracks and grooves morphologies of the thin layer at 500x and 2,000x magnification (Figure 27a and b). At the large magnification (10,000x), the thin layer appeared to form a newly formed crystal that looked like “Pine leaf appearance” (Figures 27c and 28a).

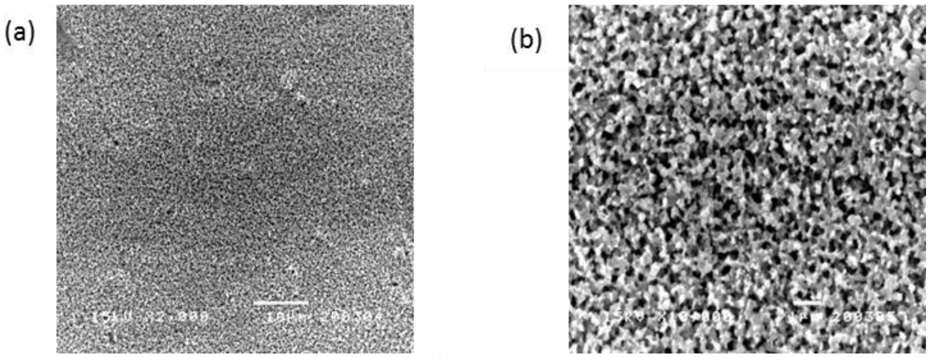


Figure 26 SEM images of zirconia surface after immersion in 9.5%HF at 80°C for 10 minutes and then ultrasonic cleaning at 2,000x(a) and 10,000x(b) magnification.

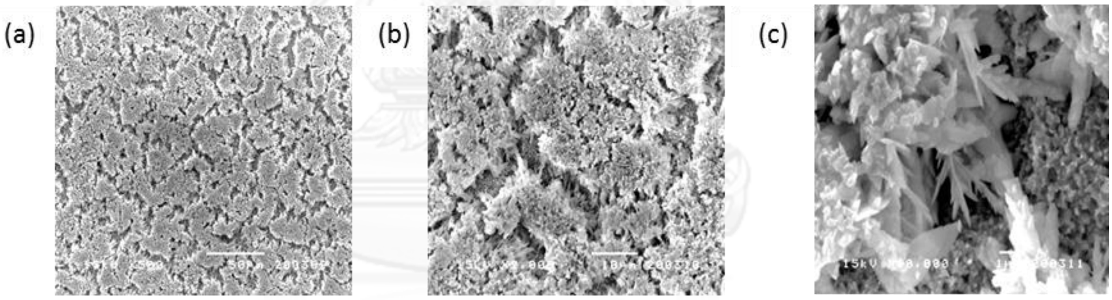


Figure 27 SEM images of zirconia surface after immersion in 9.5%HF at 80°C for 10 minutes without ultrasonic cleaning at 500x (a), 2,000x (b) and 10,000x (c) magnification.

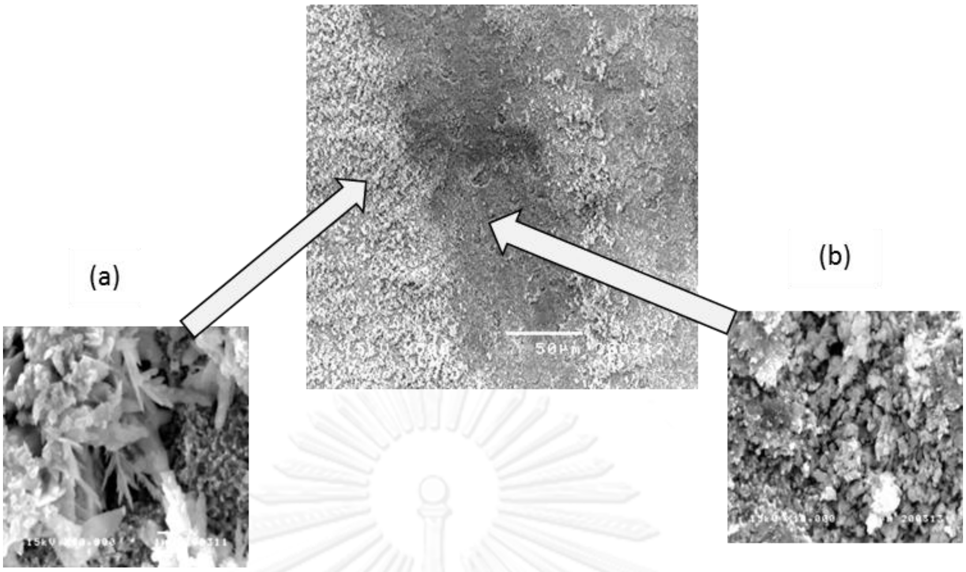


Figure 28 SEM image at 10,000x magnification of zirconia surface after immersion in 9.5%HF at 80°C for 10 minutes (a) without ultrasonic cleaning and (b) after removing white powder layer with blade No.11

The SEM images only provided a surface topography on the HF-treated zirconia surface. However, the white layer formation was considered to be a potential source of interests. More details in this layer need to be extended to support hypothesis testing. Therefore, the next study in part II would be the analysis of the physical properties of white powder layer covered HF-treated zirconia specimens by using special equipments.

1.2 Energy-dispersive X-ray spectroscopy (EDS) analysis

Energy dispersive spectroscopic (EDS) analyses of zirconia surface from each brands are shown in Figures 29. The surface element of control group from all brands (Figure 4.9) showed the same Zr and O peak of EDS spectra at 2.042(Lα) and 0.525(Kα) keV, respectively. In addition, the surface of HF treated zirconia with ultrasonic cleaning showed Zr and O spectra at the same position with the control group (Figure 30(a), 31(a) and 32(a)). However, additional peak of fluorine at 0.677(Kα) keV were presented on the surface of HF treated zirconia without ultrasonic cleaning (Figure 30(b), 31(b) and 32(b)). The presence of fluoride is possibly from the white layer covered on HF-etched zirconia.

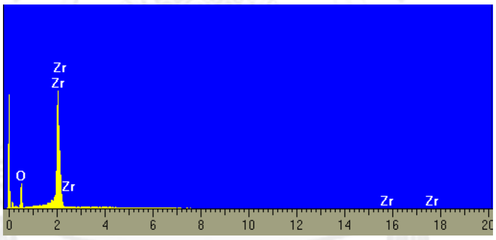


Figure 29 EDS spectra of control zirconia

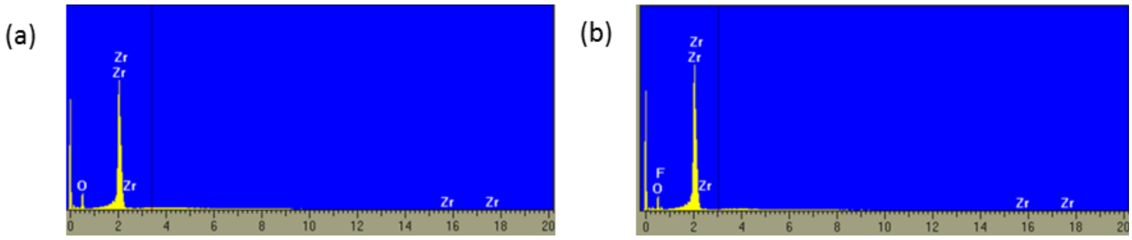


Figure 30 EDS spectra of Group 2 (immersion in 9.5% HF at 25°C for 1, 2, 3, or 24 hours) (a) with ultrasonic cleaning, (b) without ultrasonic cleaning

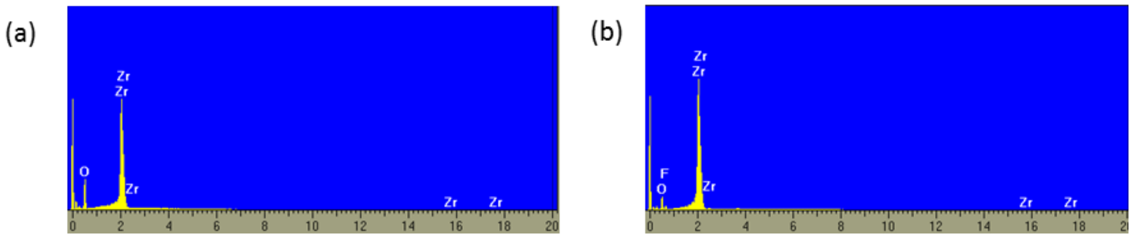


Figure 31 EDS spectra of Group 3 (immersion in 9.5% HF at 80°C for 1, 3, 5, or 30 minutes) (a) with ultrasonic cleaning, (b) without ultrasonic cleaning

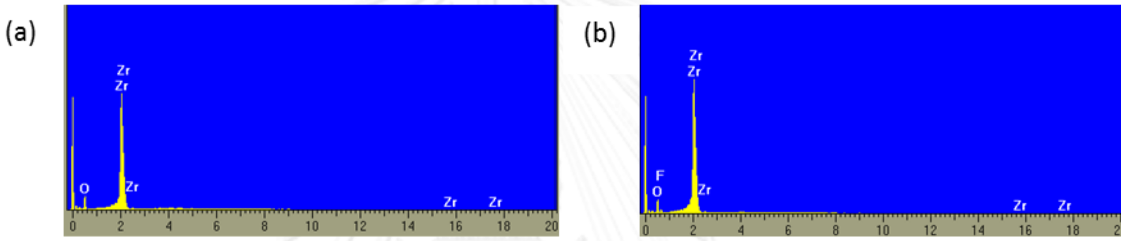


Figure 32 EDS spectra of Group 4 (immersion in 48% HF at 25°C for 30 or 60 minutes) (a) with ultrasonic cleaning, (b) without ultrasonic cleaning

Table 4 Summary of elemental compositions of dental zirconia specimens using EDS technique

Groups (Katana, Cercon, Zeno)		Elemental analysis	
		Ultrasonic cleaning	Non-ultrasonic cleaning
Group 1: the control group		Zr, O	Zr, O
Group 2: immersion in 9.5% HF at 25°C	1hr	Zr, O	Zr, O, F
	2hrs	Zr, O	Zr, O, F
	3hrs	Zr, O	Zr, O, F
	24hrs	Zr, O	Zr, O, F
Group 3: immersion in 9.5% HF at 80°C	1min	Zr, O	Zr, O, F
	3mins	Zr, O	Zr, O, F
	5mins	Zr, O	Zr, O, F
	30mins	Zr, O	Zr, O, F
Group 4: immersion in 48% HF at 25°C	30mins	Zr, O	Zr, O, F
	60mins	Zr, O	Zr, O, F

1.3 Inductively coupled plasma (ICP) evaluation

1.3.1 Finding the ICP peak of zirconia element

A high purity zirconia oxide (99.99 % ZrO_2) 1 mg was dissolved in 30 ml deionized water. This solution was then analyzed by inductively coupled plasma (ICP-Plasma-2000, Perkin Elmer, UK) for examining the ICP peak of zirconium element (Zr). The peak shown at 343.823 nm can be identified as zirconium element (Zr) (Figure 33)

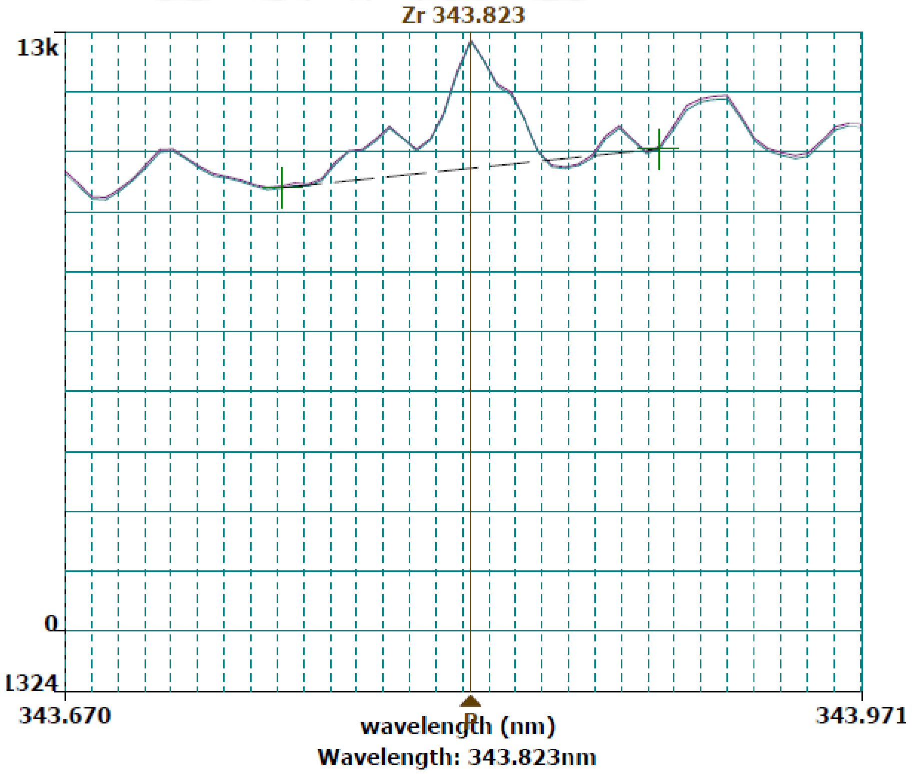


Figure 33 ICP spectra of Zirconium

1.3.2 Quantification of dislodged zirconium element

The aims of this experiment were to quantify the amount of zirconia in acid solution using calibration curve that correlated between intensity of dislodged wavelength and known concentration of standard zirconium solution.

The stock zirconia standard solution was prepared from a high purity zirconia oxide (99.99 % ZrO_2). The stock standard solutions were diluted with deionized water to concentration of 0, 1, 3, 5 and 10 ppm. Zirconia peak from each concentration was collected and analyzed by using ICP method. The intensity of zirconium peak at 343.823 nm wavelength from each concentration was measured and three replications were performed. Next, the data of intensity of zirconia peak at different concentration of zirconia solution are summarized in Table 5 and plotted in a diagram. The linear calibration curve was determined: $y = mx+c$; “y” is the signal intensity and “x” is the known concentration of the zirconia in the calibration solution.

Table 5 Concentration and mean intensity of zirconium standard solution

Concentration of standard Zr (ppm)	Mean intensity (n=3)	SD	RSD (%)
0	4745.9	33.83	0.71
1	784833.9	14908.79	1.90
3	2112774.6	11523.83	0.55
5	3411039.2	123094.27	3.61
10	7045896.7	158271.27	2.25

The results revealed that the mean intensities of zirconia concentration were; 0 ppm: 4745.9 (±33.83), 1 ppm: 784833.9 (±14908.79), 3 ppm: 2112774.6 (±11523.83), 5 ppm: 3411039.2 (±123094.27) and 10 ppm: 7045896.7(±158271.27), respectively. The data were to calculate a linear regression analysis using Excel program. The linear regression analysis of the data showed that there was a linear correlation (R^2 = 0.9993) between the zirconia concentration and mean intensities. The equation relation between intensity and concentration of Zr standard solution was y = 697,278.9899x + 26,560.8978 (y = intensity, x= concentration) (Figure 34)

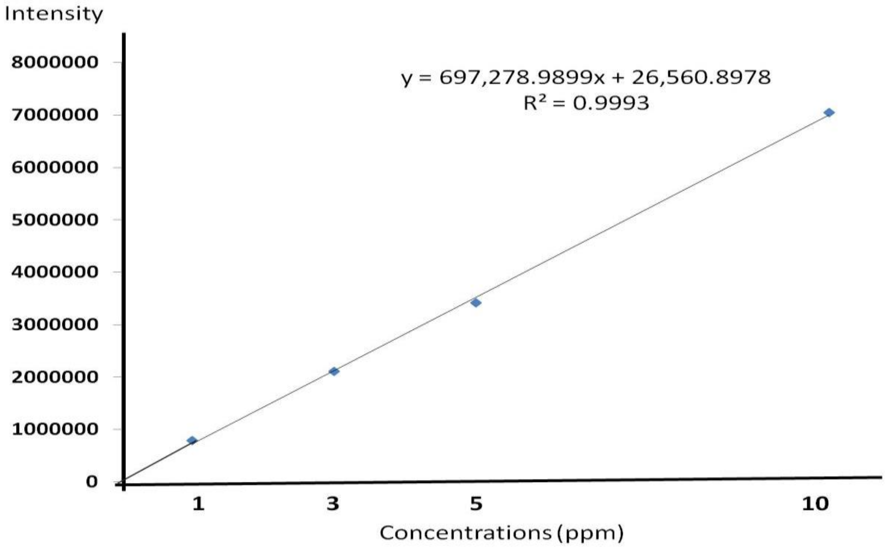


Figure 34 Plot of the line correlation between the concentration (ppm) and intensity of zirconium solution standard

1.3.3 Quantification of zirconium ion per surface area from each condition.

The square-shaped specimens from three commercially sintered Y-TZP zirconia disk brands (2x2x2 mm) were evaluated in this study: Katana, Cercon and

Zeno. The specimens were cleaned with deionized water for 10 minutes by using a sonicator before the application of surface treatment. The samples from each brand were divided into 3 groups according to the surface treatment methods. (Surface area from each sample about 24 mm^2)

Group 1: immersion in 9.5%HF 30 ml at 25°C for 1, 2 or 3 hours

Group 2: immersion 48%HF 30 ml at 25°C for 1, 2 or 3 hours

Group 3: immersion 9.5%HF 30 ml at 80°C for 5, 10, 15, 30 or 60 minutes

After treating dental zirconia, the specimens were sonicated about 10 seconds in room temperature in order to ensure that all dislodged zirconia element were removed from those of specimens. The HF solution form each condition was analyzed with inductively coupled plasma (ICP-Plasma-2000, Perkin Elmer, UK). The solution was diluted and neutralized the active hydrofluoric acid with boric acid (added to induce the complex of fluoride to protect the quartz plasma torch of ICP). Inductively coupled plasma spectrometric analysis was performed on a flow-capillary nebulizer with a solution uptake rate of <1 mL/min. The data were analyzed and compared between among each experiment condition groups. The amount of dislodged zirconium element per unit area was calculated using the equation given in experiment 4.3.2. Table 6-8 and Figure 35 show ICP results of dislodged zirconia after immersion in hydrofluoric acid form each condition.

Table 6 ICP results of dislodged Katana zirconia after hydrofluoric acid treatment

						Zirconia concentration			Surface Area	Dislodged zirconia	
		Time	Intensity (y)	m	b	x (mg/l)	Volume (ml)	mg/30 ml	mm^2	mg/100 (mm)^2	ug/mm^2
	Group 1	1 hr	185093.7	697278.99	26560.90	0.23	30	0.007	24	0.028	0.28
		2 hrs	377628.1	697278.99	26560.90	0.50	30	0.015	24	0.063	0.63
		3 hrs	555035.5	697278.99	26560.90	0.76	30	0.023	24	0.095	0.95
Katana	Group 2	1 hr	2025479.1	697278.99	26560.90	2.87	30	0.086	24	0.358	3.58
		2 hrs	6775812.1	697278.99	26560.90	9.68	30	0.290	24	1.210	12.10
		3 hrs	8835395.7	697278.99	26560.90	12.63	30	0.379	24	1.579	15.79
	Group 3	5 mins	419161	697278.99	26560.90	0.56	30	0.017	24	0.070	0.70
		10 mins	1088684.3	697278.99	26560.90	1.52	30	0.046	24	0.190	1.90
		15 mins	1550528.1	697278.99	26560.90	2.19	30	0.066	24	0.273	2.73
		30 mins	2394855.3	697278.99	26560.90	3.40	30	0.102	24	0.425	4.25
		60 mins	6417537.7	697278.99	26560.90	9.17	30	0.275	24	1.146	11.46

Table 7 ICP results of dislodged Cercon zirconia after hydrofluoric acid treatment

						Zirconia concentration			Surface Area	Dislodged zirconia	
		Time	Intensity (y)	m	B	x (mg/l)	Volume (ml)	mg/30 ml	mm^2	mg/100 (mm)^2	ug/mm^2
Cercon	Group 1	1 hr	98230.4	697278.99	26560.90	0.10	30	0.003	24	0.013	0.13
		2 hrs	232632.5	697278.99	26560.90	0.30	30	0.009	24	0.037	0.37
		3 hrs	443771.9	697278.99	26560.90	0.60	30	0.018	24	0.075	0.75
	Group 2	1 hr	3800282.7	697278.99	26560.90	5.41	30	0.162	24	0.677	6.77
		2 hrs	6528656.0	697278.99	26560.90	9.32	30	0.280	24	1.166	11.66
		3 hrs	8705063.4	697278.99	26560.90	12.45	30	0.373	24	1.556	15.56
	Group 3	5 mins	212455.3	697278.99	26560.90	0.27	30	0.008	24	0.033	0.33
		10 mins	741495.1	697278.99	26560.90	1.03	30	0.031	24	0.128	1.28
		15 mins	1661465.5	697278.99	26560.90	2.34	30	0.070	24	0.293	2.93
		30 mins	2221676.5	697278.99	26560.90	3.15	30	0.094	24	0.394	3.94
		60 mins	4861343.3	697278.99	26560.90	6.93	30	0.208	24	0.867	8.67

Table 8 ICP results of dislodged Zeno zirconia after hydrofluoric acid treatment

						Zirconia concentration			Surface Area	Dislodged zirconia	
		Time	Intensity (y)	m	B	x (mg/l)	Volume (ml)	mg/30 ml	mm^2	mg/100 (mm)^2	ug/mm^2
Zeno	Group 1	1 hr	162281.2	697278.99	26560.90	0.19	30	0.006	24	0.024	0.24
		2 hrs	213404.4	697278.99	26560.90	0.27	30	0.008	24	0.033	0.33
		3 hrs	645394.7	697278.99	26560.90	0.89	30	0.027	24	0.111	1.11
	Group 2	1 hr	5508399.6	697278.99	26560.90	7.86	30	0.236	24	0.983	9.83
		2 hrs	10426456.4	697278.99	26560.90	14.91	30	0.447	24	1.864	18.64
		3 hrs	13318278.8	697278.99	26560.90	19.06	30	0.572	24	2.383	23.83
	Group 3	5 mins	350492.7	697278.99	26560.90	0.46	30	0.014	24	0.058	0.58
		10 mins	1166853.5	697278.99	26560.90	1.64	30	0.049	24	0.204	2.04
		15 mins	1559199.7	697278.99	26560.90	2.20	30	0.066	24	0.275	2.75
		30 mins	3960533.1	697278.99	26560.90	5.64	30	0.169	24	0.705	7.05
		60 mins	6469459.2	697278.99	26560.90	9.24	30	0.277	24	1.155	11.55

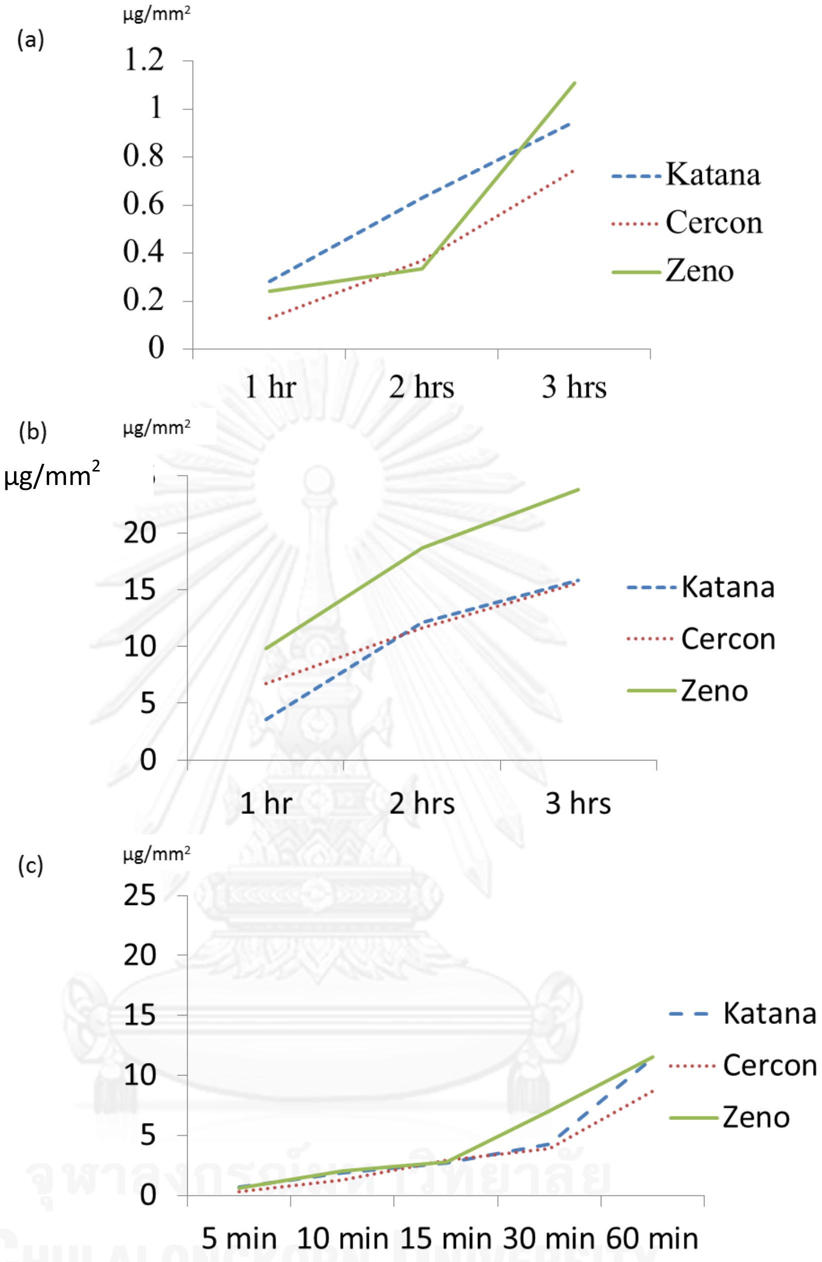


Figure 35 Graphs presenting the relation between rates of dislodged zirconia form each bands and time of immersion zirconia for Group1(a): Group 1: immersion in 9.5%HF 30 ml at 25°C for 1, 2 or 3 hours, Group 2(b): immersion 48%HF 30 ml at 25°C for 1, 2 or 3 hours and Group 3(c): immersion 9.5%HF 30 ml at 80°C for 5, 10, 15, 30 or 60 minutes.

In Figure 35 (a), it can observed dislodged zirconia element in group 1 after treatment with HF from all brands. Different treatment in group 2 and 3 also show the same trend (Figure 35 (b-c)). At short times HF can extract zirconium ion in small amount. The concentration of dislodged zirconia increases as times increase. At the same time, the higher amount of dislodged zirconia in group 2 was observed in comparison with group 1 (Figure 35). This result displayed that HF concentration had an influence on the rate of etching. A large amount of dislodge zirconium ion at 60 minutes from group 3 was presented compared with group 1. According to this, temperature could affect the rate of etching.

Summary in Part I

The results by using SEM, EDS and ICP evaluation showed that hydrofluoric acid treatment was able to etch the zirconia ceramic, providing fluorine element on the etched zirconia surface, and dislodged zirconium element in the HF solution. Based on these results all null hypotheses in Part I were rejected.

Results of Part II: Physical properties testing

2.1 The SEM evaluation at 200x, 500x, 2,000x magnifications

SEM images of the group 1 zirconia surface are shown in Figures 36 and 41. The surface of as-sintered zirconia demonstrated a mild irregular appearance (Fig. 36a.1-a.3 and 41a.1-41a.3). Figure 36b.1-b.3 and 41b.1-b.3 display the polishing zirconia surface that shows a smooth flat surface. For the blasting condition, the specimens show a very irregular rough surface (Fig. 36c.1-c.3 and 41c.1-c.3).

For group 2-4, all of HF treated zirconia surface resulted in the development of irregular rough surface with small porosities (Figs 37-39 and Figs 42-44). In addition, different sizes of the hole that we can observe both of the large and small holes appear all the surface of the specimen after immersion in the strong condition such as 9.5% HF at 80°C for 30 minutes (Figs 38d.1-d.3 and Figs 43d.1-d.3) and 48% HF at 25°C for 60 minutes (Figs 39b.1-b.3 and Figs 44b.1-b.3).

Porcelain surface groups are shown in Figure 40a-c and Figure 45a-c. The as-sintered porcelain had smooth-flattened surface (Figs 40a.1-a.3 and Figs 45a.1-a.3). When the specimen was etched with 9.5% HF for 1 minute, it showed crystals with shallow irregularities and produced morphological honeycomb-like surfaces (Figs 40b.1-b.3 and Fig 45b.1-b.3). Blasting porcelain showed a surface irregular rough appearance that look like the blasting zirconia surface (Figs 40c.1-c.3 and Fig 45c.1-c.3).

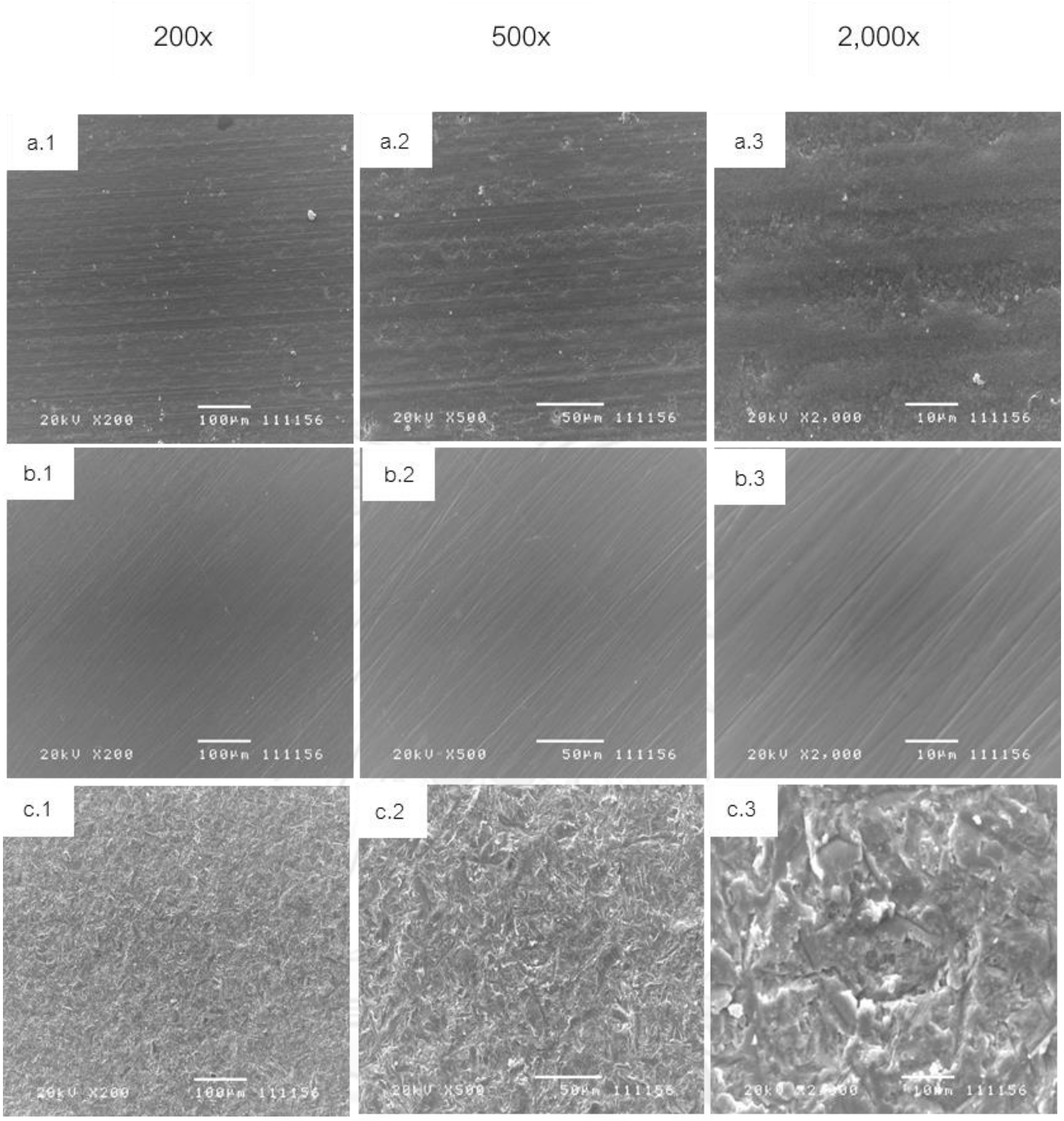


Figure 36 The SEM images of the specimen surfaces from each condition at 200x, 500x, 2,000x magnifications, respectively: (a.1-a.3) as-sintering zirconia, (b.1-b.3) polishing zirconia and (c.1-c.3) blasting zirconia

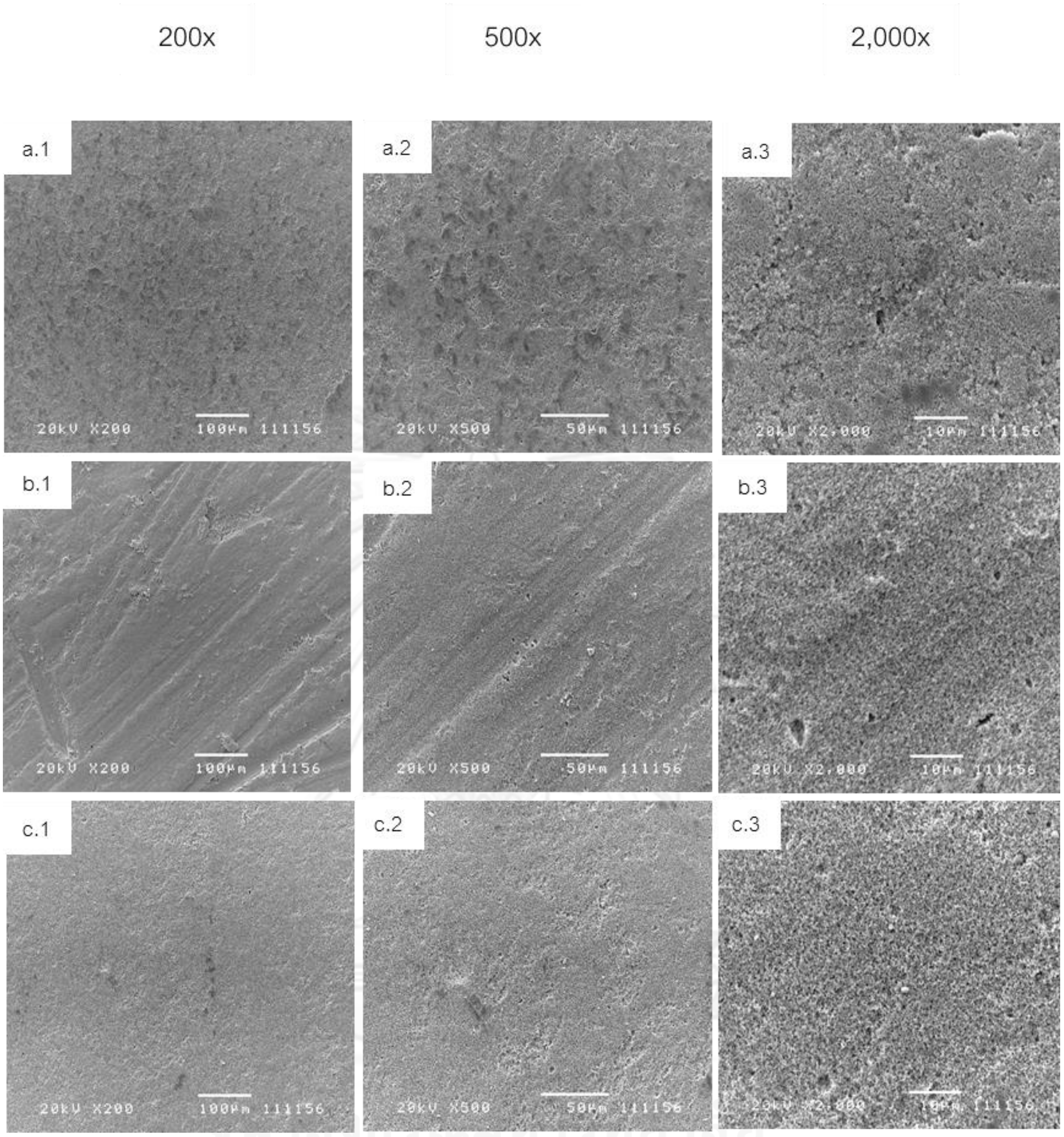


Figure 37 The SEM images of the zirconia specimen surfaces after immersion in 9.5% HF at 25°C at 200x, 500x, 2,000x magnifications, respectively: (a.1-a.3) 1 hour, (b.1-b.3) 2 hours, and (c.1-c.3) 3 hours

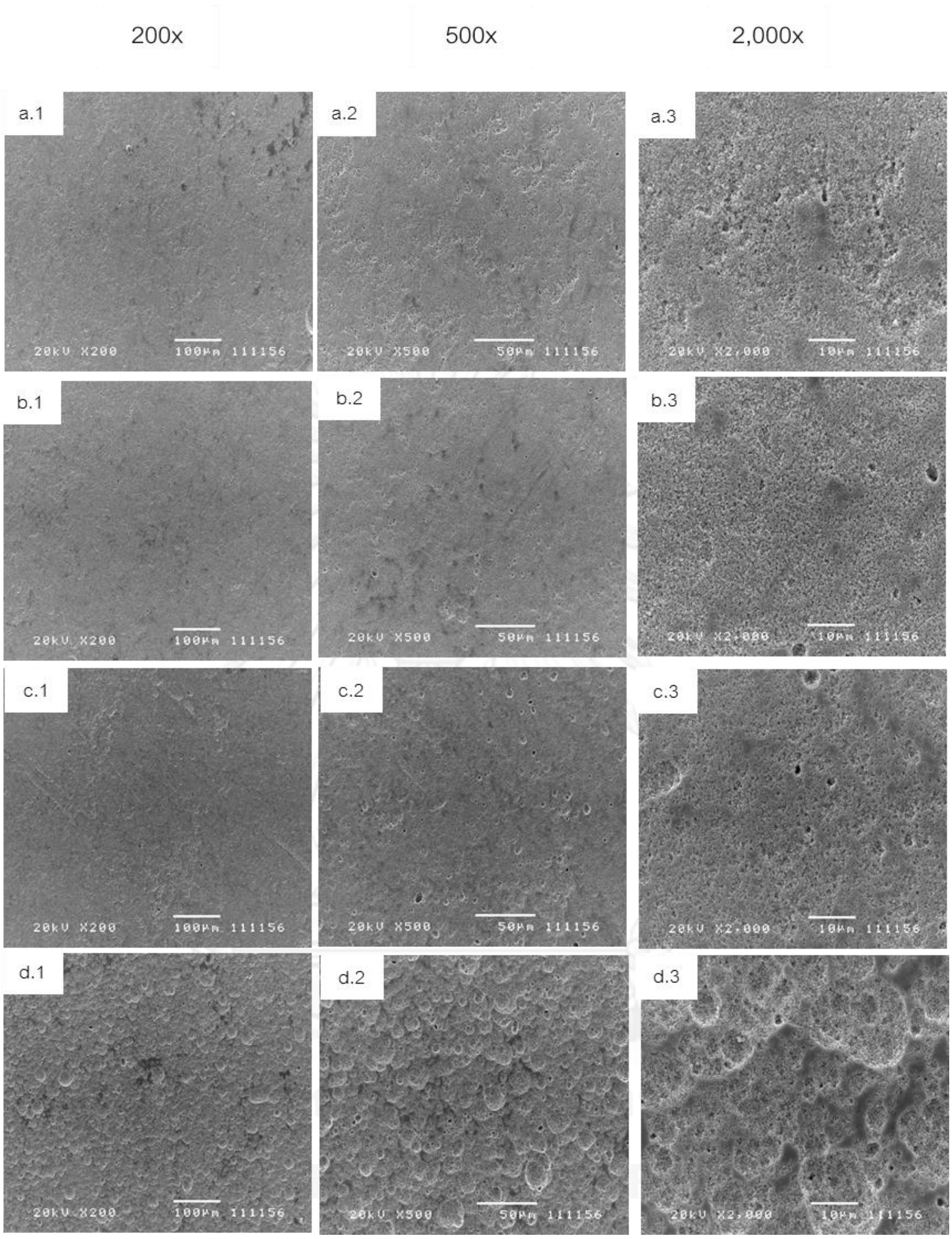


Figure 38 The SEM images of the zirconia specimen surfaces after immersion in 9.5% HF at 80°C at 200x, 500x, 2,000x magnifications, respectively: (a.1-a.3) 1 minute, (b.1-b.3) 3 minutes, (c.1-c.3) 5 minutes and (d.1-d.4) 30 minutes

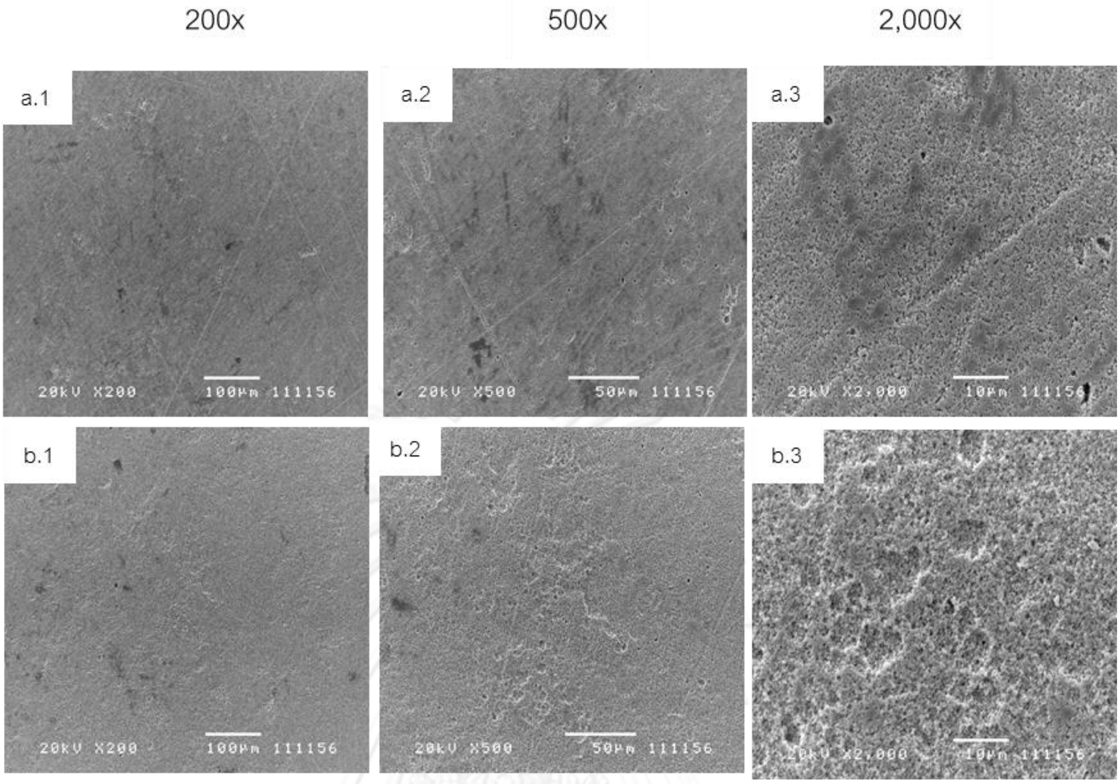


Figure 39 The SEM images of the zirconia specimen surface after immersion in 48% HF at 25°C at 200x, 500x, 2,000x magnification, respectively: (a.1-a.3) 30 minutes, and (b.1-b.3) 60 minutes

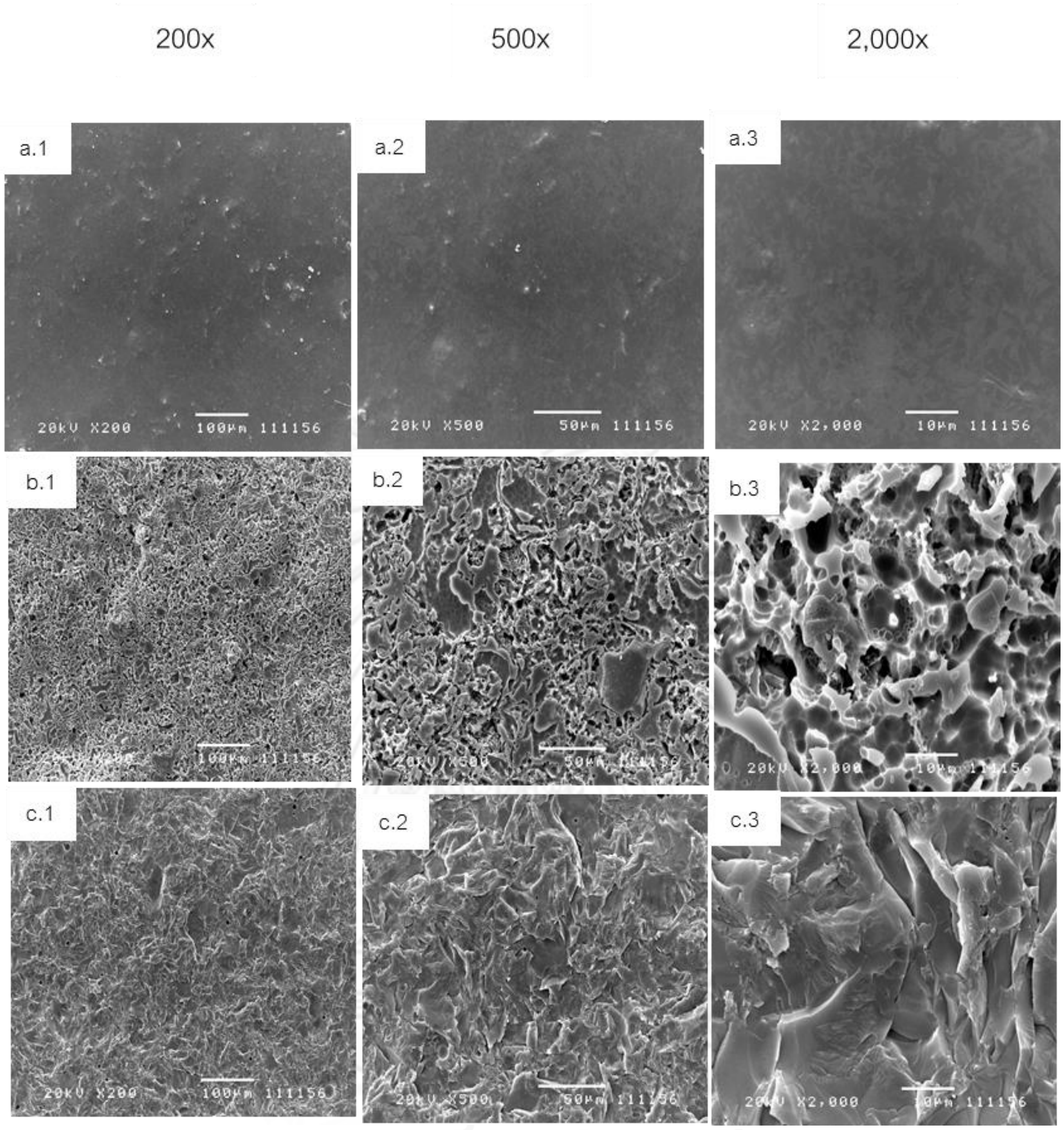


Figure 40 The SEM images of the porcelain specimen surfaces from each condition at 200x, 500x, 2,000x magnifications, respectively: (a.1-a.3) control porcelain, (b.1-b.3) porcelain treated with 9.5% HF for 1 minute and (c.1-c.3) blasting porcelain.

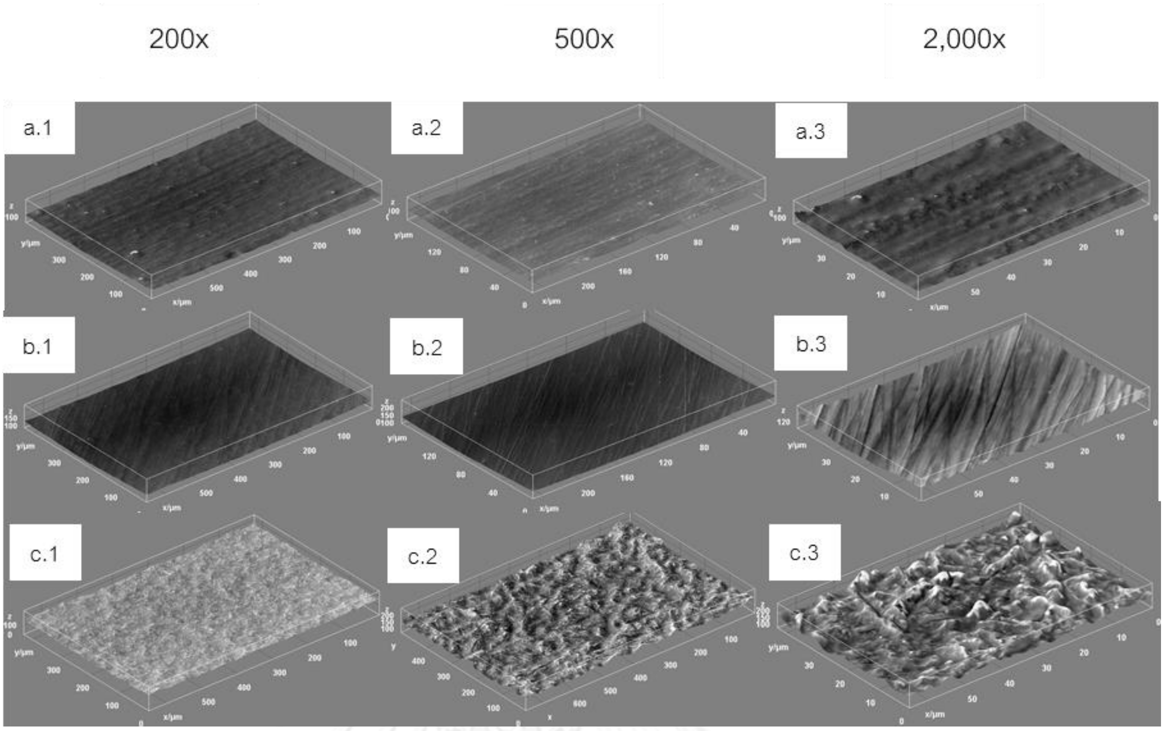


Figure 41 The 3D images of the specimen surfaces from each condition at 200x, 500x, 2,000x magnifications, respectively: (a.1-a.3) as-sintering zirconia, (b.1-b.3) polishing zirconia and (c.1-c.3) blasting zirconia

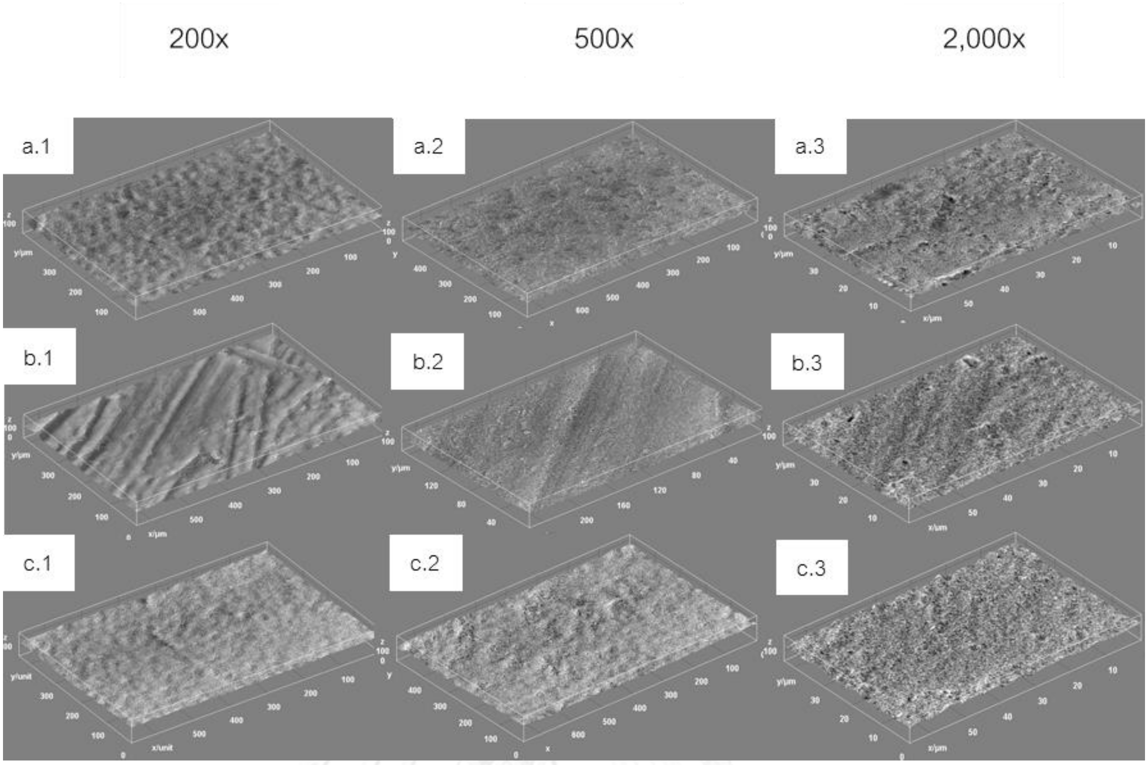


Figure 42 The 3D images of the zirconia specimen surfaces after immersion in 9.5% HF at 25°C at 200x, 500x, 2,000x magnifications, respectively: (a.1-a.3) 1 hour, (b.1-b.3) 2 hours, and (c.1-c.3) 3 hours

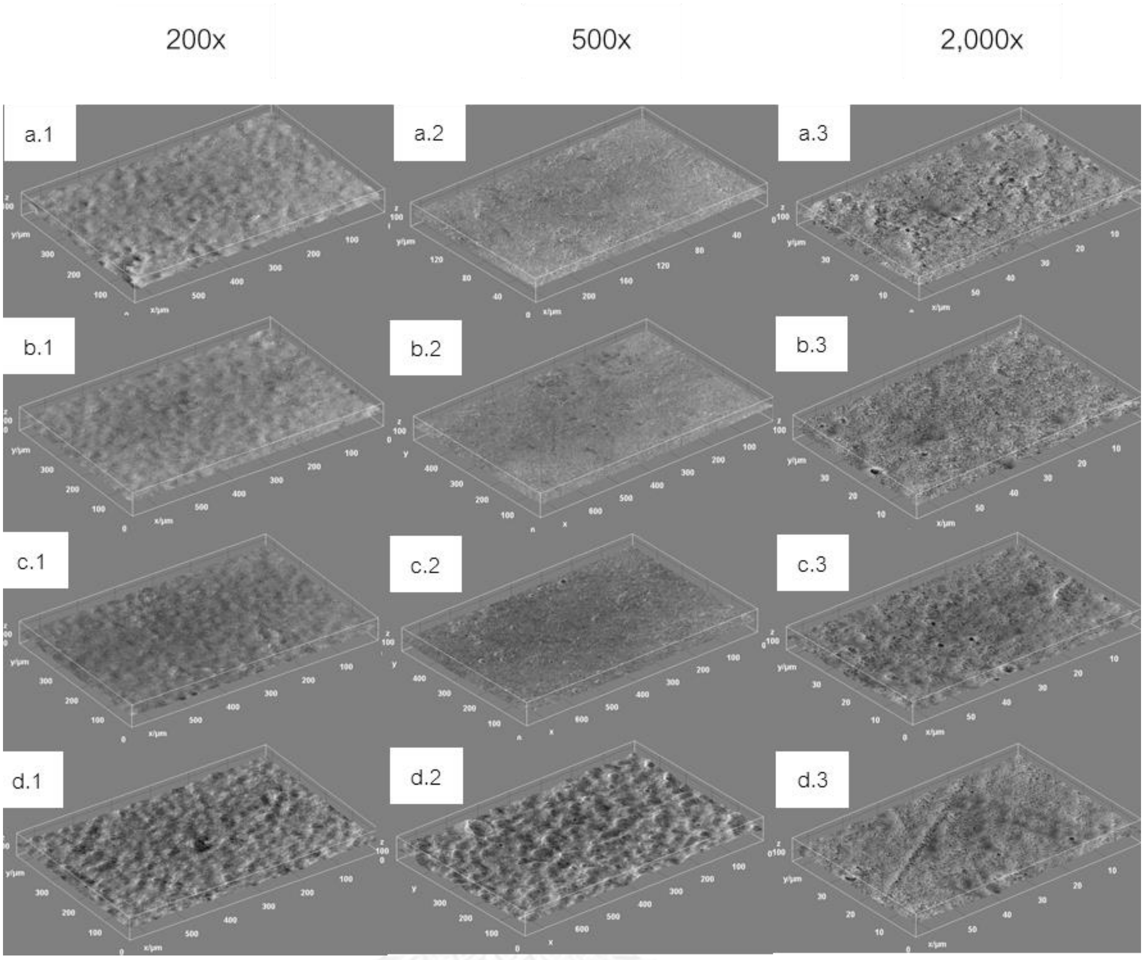


Figure 43 The 3D images of the zirconia specimen surfaces after immersion in 9.5% HF at $80^{\circ}C$ at 200x, 500x, 2,000x magnifications, respectively: (a.1-a.3) 1 minutes, (b.1-b.3) 3 minutes, (c.1-c.3) 5 minutes and (d.1-d.4) 30 minutes

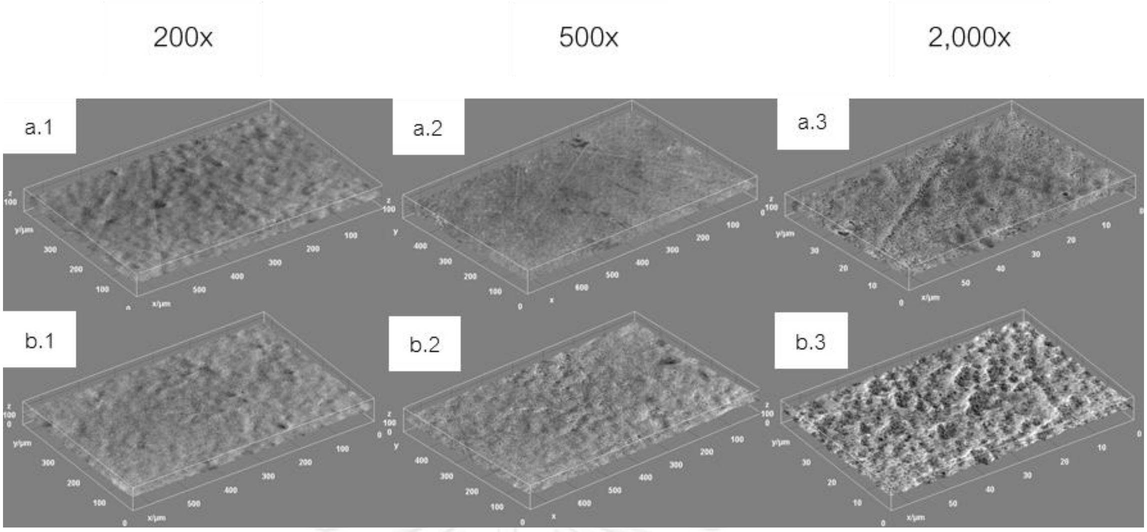


Figure 44 The 3D images of the zirconia specimen surfaces after immersion in 48% HF at 25°C at 200x, 500x, 2,000x magnifications, respectively: (a.1-a.3) 30 minutes, and (b.1-b.3) 60 minutes

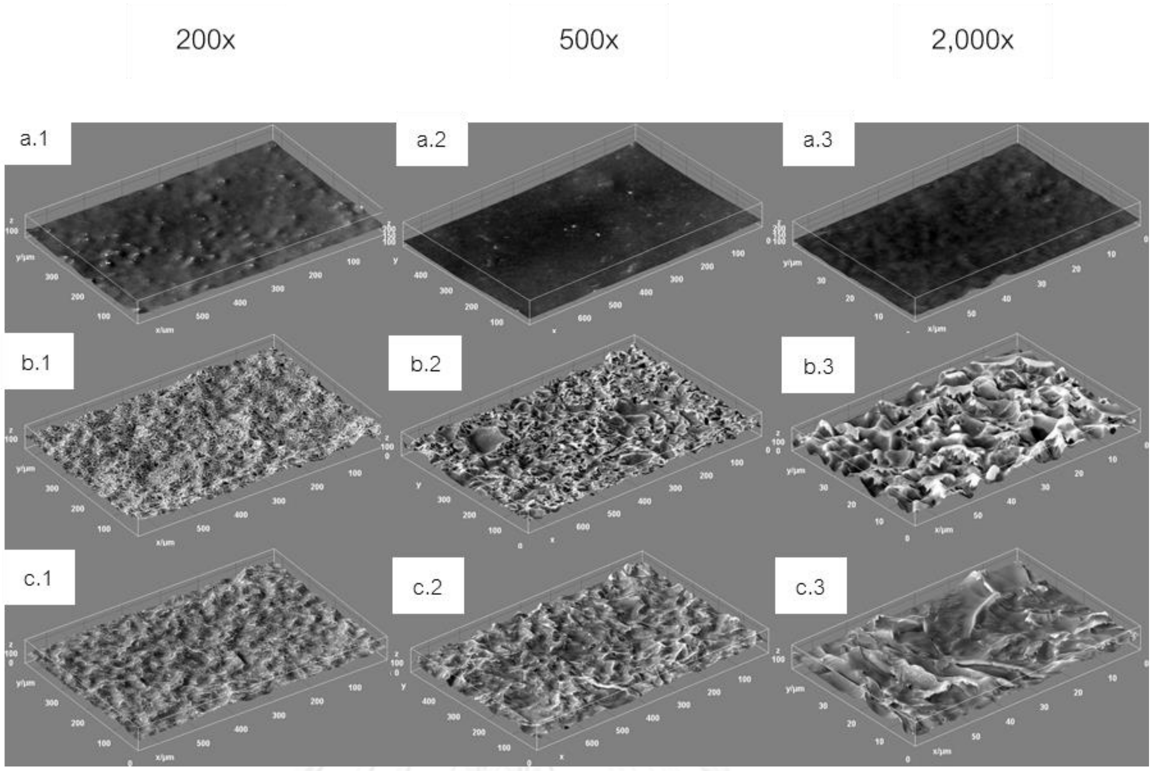


Figure 45 The 3D images of the porcelain specimen surfaces from each condition at 200x, 500x, 2,000x magnifications, respectively: (a.1-a.3) control porcelain, (b.1-b.3) porcelain treated with 9.5% HF 1 min and (c.1-c.3) blasting porcelain

2.2 Surface roughness evaluation of HF treated zirconia

2.2.1 Surface roughness value by using profilometer technique

All R_a data were performed using SPSS 16.0 for windows (SPSS Inc., Chicago, IL, USA). The means and standard deviations of surface roughness value were calculated for each group. The data of surface roughness were subjected to statistical analysis by one-way ANOVA and Tukey's multiple comparison test at a significance level of $\alpha = 0.05$.

Means and standard deviations of the zirconia surface roughness from each surface treatment condition are shown in Table 9. The airborne-particle abraded zirconia group (0.52 ±0.09 μm) exhibited the highest R_a values, whereas the polished zirconia group (0.18 ±0.03 μm) displayed the lowest R_a values. For the HF etched zirconia groups (Group 3-5), the mean roughness values were approximately 0.19-0.29 μm. The surface roughness data were not significantly increased after HF treatment by compared with control group ($p>0.05$). However, the difference among Group 3, Group 4 (except: subgroup immersion in 9.5%HF 80°C 30 minutes) and Group 5 were not significant ($p > 0.05$). For subgroup, zirconia immersed in 9.5%HF 80°C 30 minutes the mean roughness value was 0.29 ±0.05 μm which was significantly lower than blasting zirconia ($p < 0.01$).

Table 9 Means (±SD) of R_a values (μm) and the statistical significances

Group	Surface treatment conditions	Surface average roughness (SD) μm
1	Control group (Polishing zirconia)	0.18 (±0.03) ^{a}
2	Blasting zirconia	0.52 (±0.09) ^{d}
3	immersion in 9.5% HF at 25 °C for 1 hour	0.19 (±0.04) $^{a, b}$
	2 hours	0.22 (±0.03) $^{a, b}$
	3 hours	0.22 (±0.03) $^{a ,b}$
4	immersion in 9.5% HF at 80 °C for 1 minute	0.21 (±0.06) $^{a, b}$
	3 minutes	0.23 (±0.04) ^{b}
	5 minutes	0.23 (±0.04) ^{b}
	30 minutes	0.29 (±0.05) ^{c}
5	immersion in 48% HF at 25 °C for 30 minutes	0.19 (±0.04) $^{a, b}$
	60 minutes	0.22 (±0.07) $^{a, b}$

*The same letters indicate that no significant difference in respective line.

For the micro-roughness testing, it was determined that the R_a values were not significantly increased in hydrofluoric acid treated zirconia compared with control group. Furthermore, there was not statistically difference among HF-treated zirconia groups. However, HF provided roughness on zirconia surface less than did airborne-particle abraded zirconia.

However, the results of micro-surface roughness value are contrary to previous studies. The images of SEM showed that the irregularities on the zirconia surface increased as immersion times were increased and at higher etching solution temperatures. Furthermore, the results in surface roughness values by using digital profilometor were only on micro-scale. The next study was to evaluate the nano-scale surface roughness value by using AFM technique. Therefore, the AFM technique was required to evaluate the nano-porosities because this equipment is more precise for detecting the nano-scale surface roughness than did digital profilometer.

2.2.2 Surface roughness value using Atomic force microscopy (AFM) evaluation

First, the average roughness values were checked for normal by using Kolmogorov–Smirnov test. As the data were normally distributed, one way ANOVA analysis of variance was used to assess significant differences among the experimental groups. The multiple post hoc comparisons were applied using Tukey's $p < 0.05$. The statistical analysis was performed with SPSS version16.0 (SPSS Inc., Chigaco, IL, USA).

The means and standard deviations of zirconia surface roughness (R_a) using AFM method are reported in Table 10. The statistical analysis revealed a significant difference in the surface average roughness values. As expected, the control group demonstrated a low roughness values (6.84 ± 0.92 nm). Furthermore, the HF treated zirconia groups significantly improved the average surface roughness of dental zirconia ($p<0.05$), achieving comparable results. However, the zirconia immersed in 9.5%HF at 80°C for 30 min group showed the highest surface roughness value of 132.07 ± 17.53 nm and the group 2 and 3 displayed the roughness value of 45.61±5.04 nm and 85.54±14.84 nm, respectively.

Table 10 Means and standard deviations of surface average roughness values (R_a) analyzed with AFM after different zirconia surface treatments

Surface treatments	Surface average roughness (S.D.) nm
Polished zirconia	6.84 (0.92) ^{a}
Immersion in 9.5%HF at 80°C for 1 minute	45.61 (5.04) ^{b}
Immersion in 9.5%HF at 80°C for 5 minutes	85.54 (14.84) ^{c}
Immersion in 9.5%HF at 80°C for 30 minutes	132.07 (17.53) ^{d}

*Different alphabetical letters indicate groups, are statistically different at $p < 0.05$

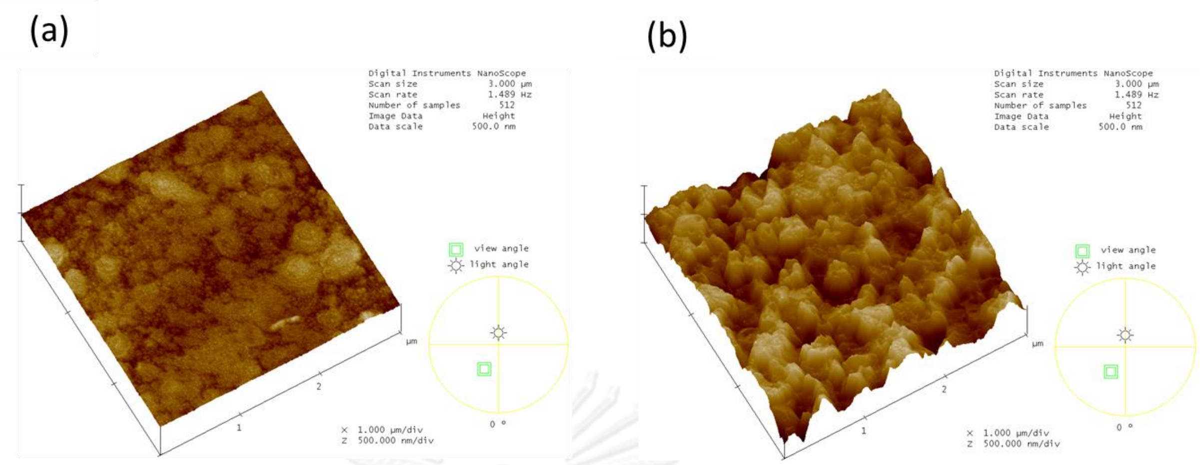


Figure 46 The AFM images of control group surface (a), and AFM picture of Group 3 surface: immersion in 9.5% HF at 80°C for 5 minutes

Summary of surface roughness evaluation

1. The airborne-particle abraded zirconia group showed the highest micro-R_a values.
2. The polishing zirconia group exhibited the lowest micro-R_a values.
3. Using profilometer analysis, the micro-surface roughness data were not significantly increased after HF treatment by compared with control group.
4. The nano-scale surface roughness values by using AFM technique of HF etched zirconia were significantly increased after HF treatment and there were statistically differences among HF-treated zirconia groups.

2.3 Fourier Transform Infrared (FTIR) evaluation

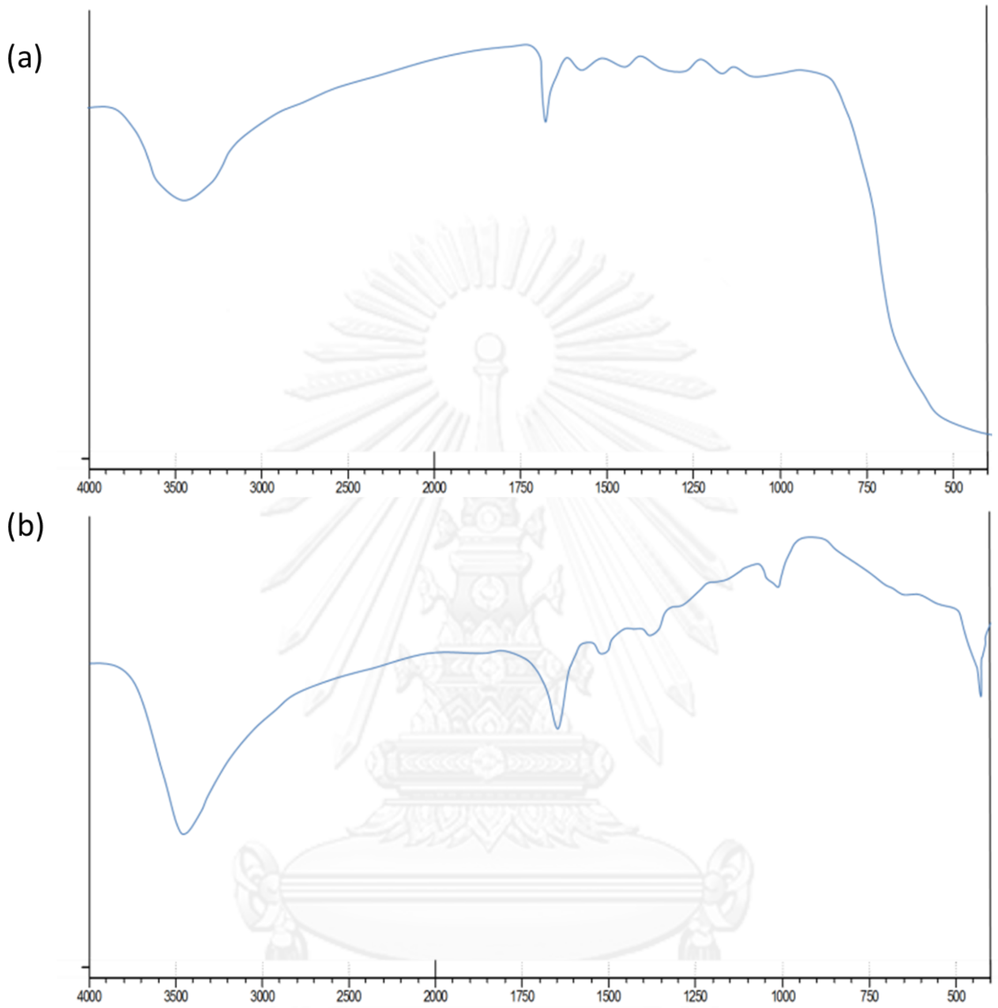


Figure 47 The FTIR spectra of (a) control zirconia group and (b) treated zirconia with HF group

The FTIR spectra of control group and HF treated zirconia are presented in Figure 47(a) and (b), respectively. Broad absorption peaks at 3000-3600 cm^{-1}, and peaks at 1630 cm^{-1} showed for both diagrams. The former were assigned to the stretching pattern of -OH bands, and the latter were due to the bending mode of H-

O-H band. Furthermore, the bending vibration of Zr–OH groups at 1353 cm^{-1} showed for both diagrams. In contrast, a main peak of Zr-F and F-Zr-F at approximately 250-500 cm^{-1} presented in the powder coating on the HF-treated specimen.

Summary of FTIR evaluation

The functional groups such as -OH, Zr-OH, Zr-F and F-Zr-F were presented on the HF treated zirconia specimens.

2.4 The X-ray diffraction (XRD) evaluation

2.4.1 XRD conventional 2θ–θ method of HF treated zirconia

The XRD analysis by using conventional method (control group) demonstrated that a tetragonal phase peak at approximately 30.24 2θ (Figure 48a) was observed on an un-etched zirconia surfaces. An additional monoclinic phase peak at approximately 28.27 2θ was present in all of the HF treated specimens (Figure 48b and 48c). However, HF treated zirconia specimens with non-ultrasonic cleaning displayed higher intensity levels than those with ultrasonic.

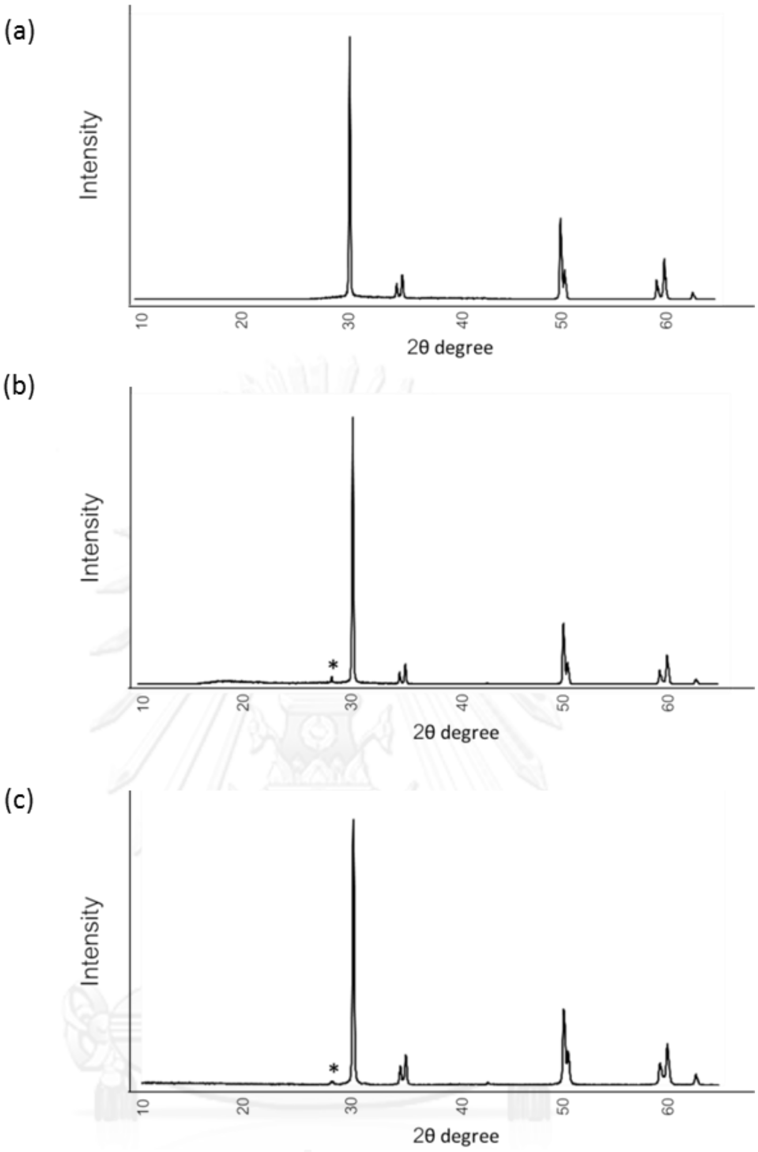


Figure 48 The XRD conventional method analysis of zirconia-oxide ceramic surface, a) control specimen presenting only tetragonal peaks, b) etched zirconia with non-ultrasonic cleaning specimen presenting both tetragonal and monoclinic (*) peaks, and c) etched zirconia with ultrasonic cleaning specimen presenting both tetragonal and monoclinic (*)

Table 11 Summary of XRD peaks using conventional 2θ-θ method of treated

Group	Surface treatments	XRD peaks after etched with HF	
		Non-ultrasonic cleaning	Ultrasonic cleaning
1	control group**	T	
2	immersion in 9.5% HF at 25°C for 3 hours	T, M	T, M
3	immersion in 9.5% HF at 80°C for 30 minutes	T, M	T, M
4	immersion in 48% HF at 25°C for 60 minutes	T, M	T, M

* Where T is tetragonal phase, and M is monoclinic phase.

** The control group, the specimens did not immerse in HF.

2.4.2 XRD the grazing angle method of HF treated zirconia

Glazing angle method (at incident angle θ = 3°) was carried out in order to examine XRD peaks on zirconia specimens at the penetration depth of ~3 μm. The results showed that only tetragonal phase peak at approximately 30.24 2θ was observed in a control group (Figure 49a). However, an additional peak of monoclinic at approximately 28.27 2θ was presented in all of the HF treated specimens (Figure 49b-c). To compare between non ultrasonic and ultrasonic cleaning, non-ultrasonic cleaning of HF treated zirconia specimen display the unknown small peaks at approximately 22-28 2θ which was needed to identify.

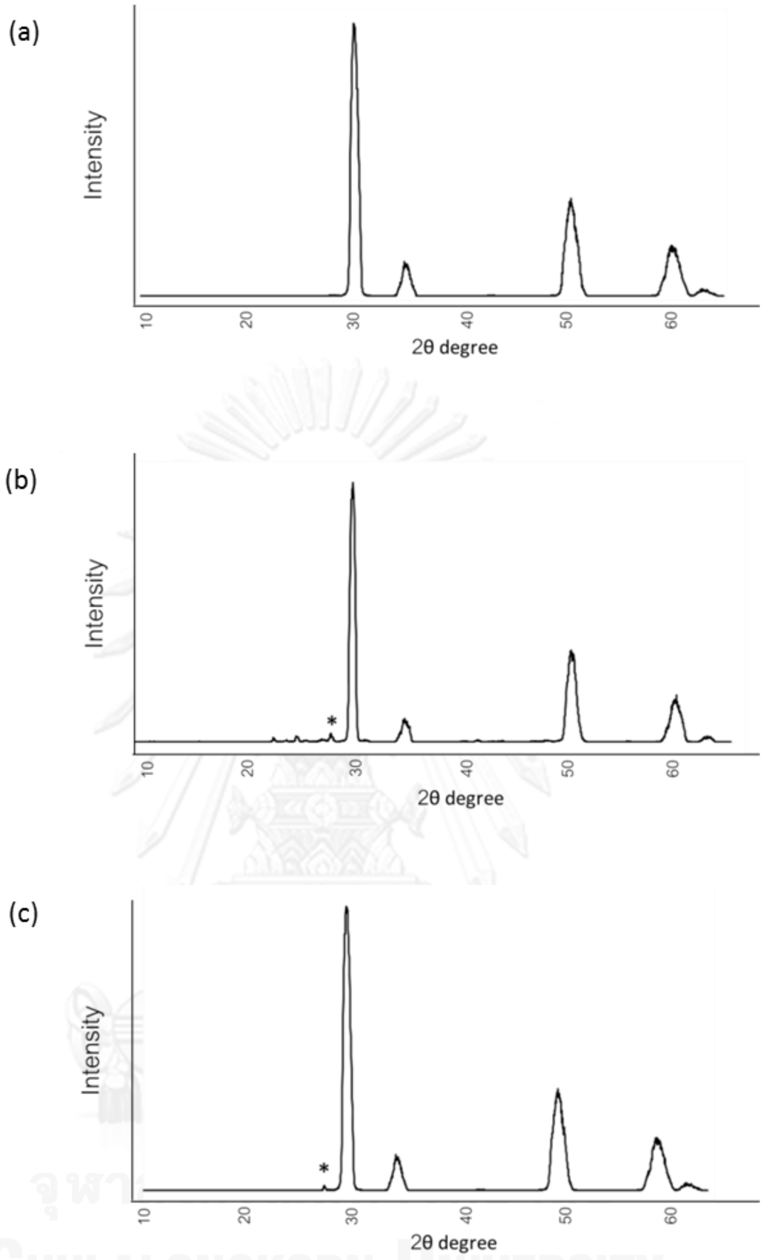


Figure 49 The XRD the glazing angle method (at incident angle $\boldsymbol{\theta} = 3^{\circ}$) analysis of zirconia-oxide ceramic surface, a) control specimen presenting only tetragonal peaks, b) etched zirconia with non-ultrasonic presenting both tetragonal and monoclinic (*) peaks and displaying the small peaks at approximately 22-28 $2\boldsymbol{\theta}$, and c) etched zirconia with ultrasonic cleaning specimen presenting both tetragonal and monoclinic (*) peaks

From the results as described above, the occurrence of small peaks could probably come from the white powder deposited on the treated zirconia surface (Figure 50). Therefore, the deposited white powder was needed to remove in order to further investigate by using XRD analysis.

Figure 50 The white powder coated on HF-treated zirconia surface without ultrasonic cleaning

2.4.3 Conventional XRD on scratched white powder

Figure 51 displays the X-ray diffraction pattern of white powder deposited onto HF- treated zirconia surface. XRD pattern at intensity higher than 60% showed the peaks at around 22.97, 23.34, 23.65, 24.17, 24.47, 24.89, 25.55, 25.90, 26.53, 27.43, 28.28, 31.30, and 31.43 2θ. A tetragonal phase peak at approximately 30.24 2θ was not presented. This can confirm that the white powder did not include tetragonal zirconia phase.

The XRD peak appearing at around 28.28 and 31.43 2θ was specific of the zirconia monoclinic phase. It was possible that monoclinic zirconia exist on both white powder and HF-treated surface. Furthermore, a zirconia-fluoride (ZrF_4) peak at approximately 22.9, 25.90 and 27.43 2θ was presented. There peaks were possibly indicative to the unknown small peak in the XRD glazing analysis. The rest peaks were too difficult to identify thus requiring a special technique for detecting.

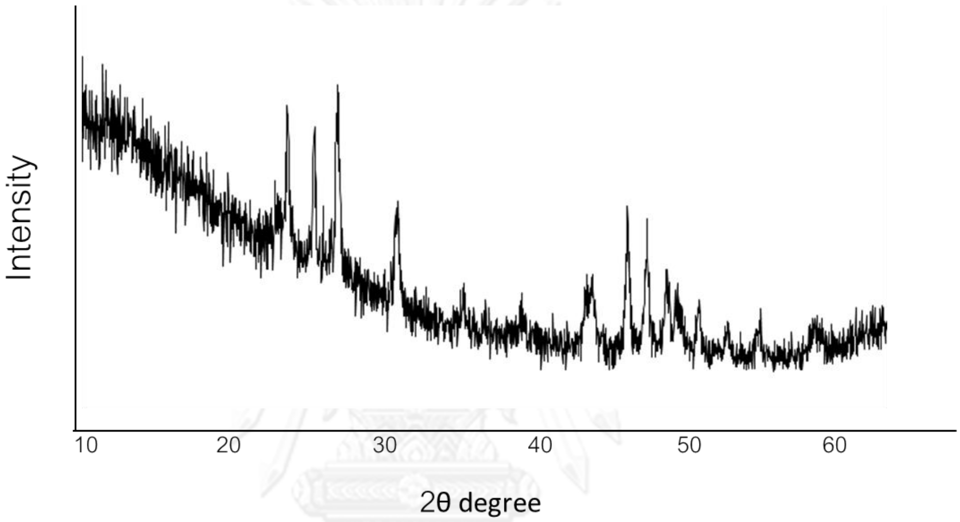


Figure 51 XRD peak analysis of white powder of HF- treated zirconia

Summary of XRD evaluation

Zirconia surfaces etched with hydrofluoric acid presented the tetragonal-to-monoclinic phase transformation. The white powder on the etched zirconia surface had many chemical compounds such as zirconia oxide that was monoclinic phase form, zirconium fluoride compound that was ZrF_4 and many new chemical compounds.

2.5 The X-ray photoelectron spectroscopy (XPS) analysis

The XPS survey spectra of dental zirconia and HF-treated zirconia are showed in Figure 52. The XPS spectra of control zirconia displayed O, C, Zr, and Y peak of binding energy at about 530, 285, 182 and 159 eV, respectively. The major components of zirconia surface were Zr, O and Y. The carbon signal occurred at 285 eV results from carbon contamination during specimen preparation and treatment application. However, after surface treatment with HF, an additional F1s peak was presented at about 685 eV (Figure 53 a-d).

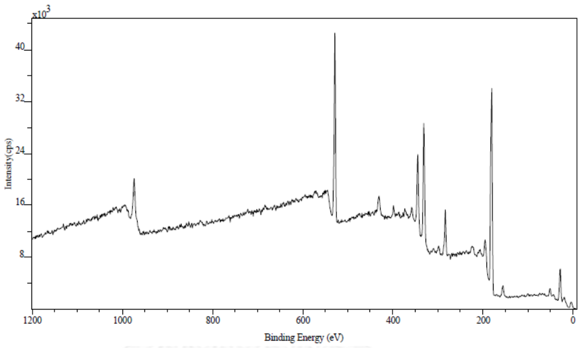


Figure 52 Survey scan of XPS of control zirconia surface

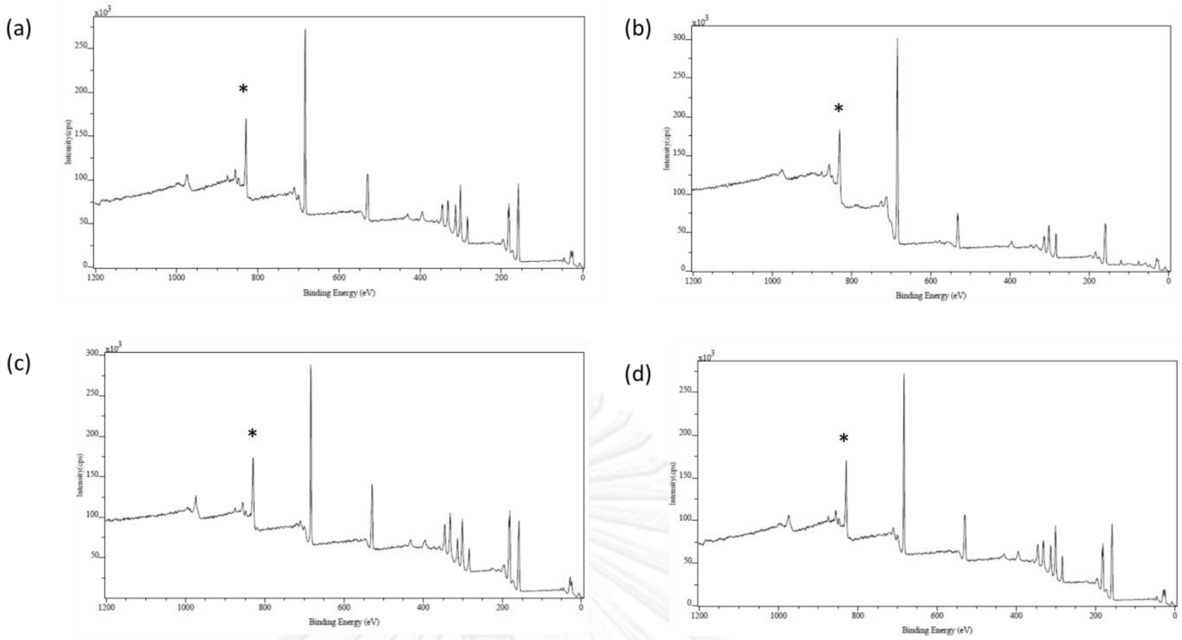


Figure 53 Survey scan of XPS of sample groups 2-5 (a-d), “ * ” is F1s peak

The change in atomic concentration of F1s in treated zirconia surface under various treatments as shown in Table 12.

Table 12 Atomic concentration % of zirconia surface after various surface treatments

	Atomic concentration (%)				
Sample	O 1s	C 1s	Zr 3d	Y 3d	F 1s
Group 1	46.64	32.61	18.07	2.68	-
Group 2	50.15	27.32	19.35	1.00	2.19
Group 3	15.69	22.41	0.70	7.74	53.46
Group 4	23.47	20.86	7.76	9.85	38.07
Group 5	37.45	24.79	5.55	10.56	37.45

The narrow scan XPS spectra of control zirconia specimens revealed the zirconia-oxide spectra peaks at about 182.2 and 184.5 binding energy for Zr3d$_{5/2}$ and Zr3d$_{3/2}$ as shown in Figure 54. However, it could observe four subpeaks of Zr3d$_{5/2}$ and Zr3d$_{3/2}$ in all HF-etched zirconia surfaces. At about 183.1 and 186.1 binding energy, the peaks were corresponding to zirconia oxyfluoride. The other subpeaks at approximately 184.8 and 187.2 binding energy were an indicative of zirconia-fluoride (Figure 55 and Table 13).

In addition, the narrow scan of F1s present the peaks at about 685 and 686 eV corresponding to zirconia-oxyfluoride and zirconia-fluoride, respectively (Figure 56 and Table 13).

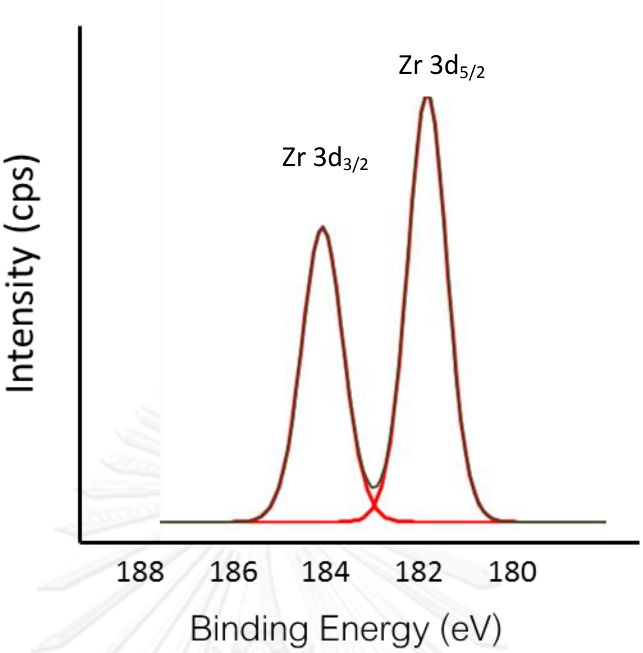


Figure 54 Narrow scan peak of Zr 3d spectra from control zirconia surface

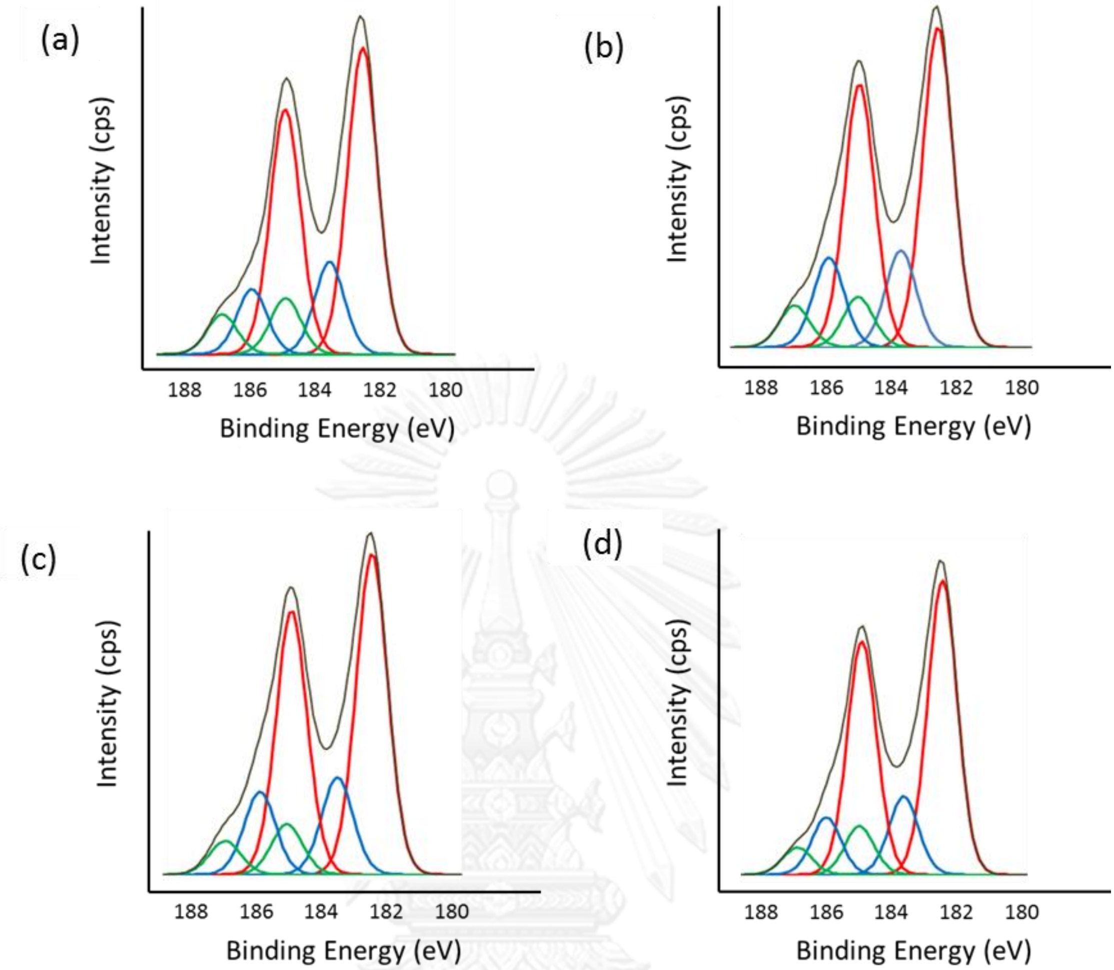


Figure 55 Narrow scan peak of Zr 3d spectra from all-HF treated zirconia surface of group 2-5 (a-d)

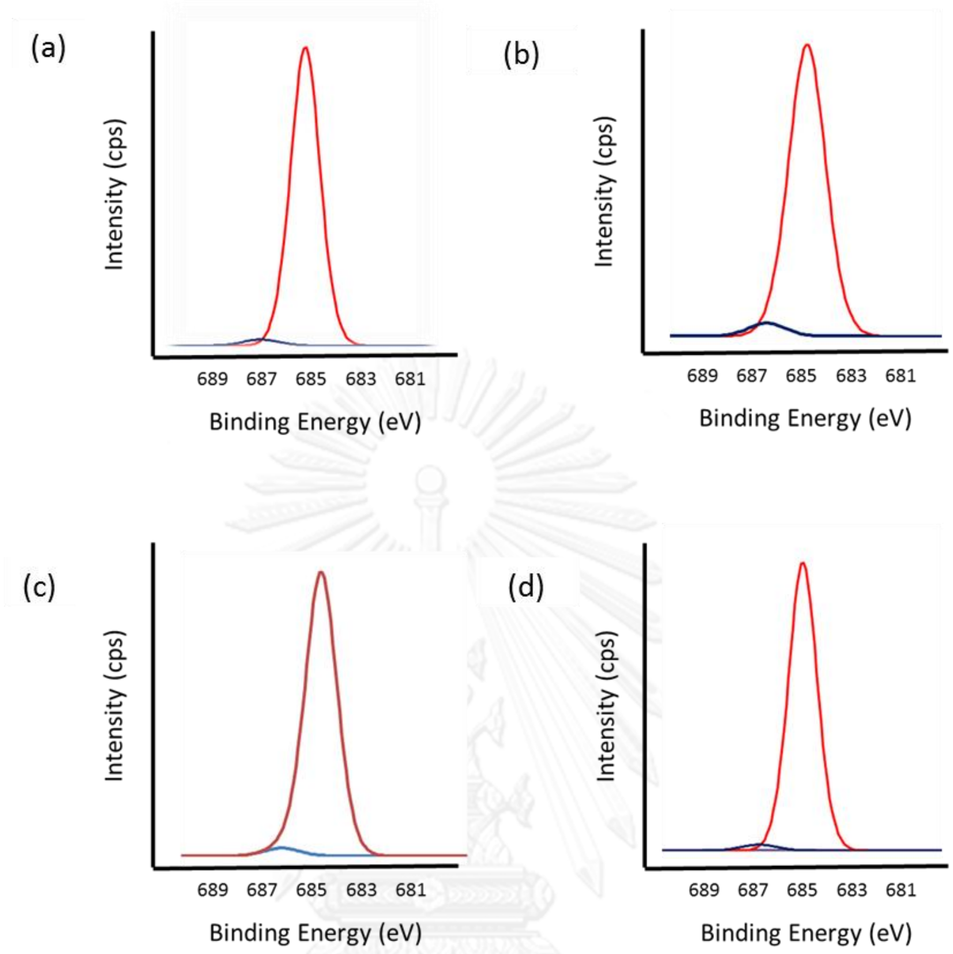


Figure 56 Narrow scan peak of F1 s spectra from all-HF treated zirconia surface of sample 2-5(a-d)

Table 13 XPS fitting parameters for Zr $3d_{5/2}$ Zr $3d_{3/2}$ and F1s

Zirconia phases	Binding energy (eV)		
	Zr $3d_{5/2}$	Zr $3d_{3/2}$	F 1s
ZrO_2	182.2±0.1	184.5±0.2	-
Zr-O-F	183.1±0.1	186.1±0.1	685
*Zr-F	184.8±0.2	187.2±0.4	686

*Phases have binding energy overlap.

Summary of XPS evaluation

The results from XPS analysis displayed that hydrofluoric acid could create zirconia-oxyfluoride and zirconia-fluoride compounds on treated zirconia surface.

CHAPTER V

DISCUSSION

Discussion: Part I

The results from hypothesis testing in part I revealed that hydrofluoric acid treatment was able to etch the zirconia ceramic, causing variations in surface topography. In addition, after zirconia immersion in hydrofluoric acid, the results showed the depositing fluoride element on zirconia surface and the dislodging zirconium element in acid solution occurred in all the tested groups. Based on these results all hypotheses were rejected.

Hydrofluoric acid or HF is the hydrogen fluoride compound acid. HF is a colorless. The concentration of HF ranges from less than 1% to as much as 70%. Industrially, HF is used to dissolve silica-based materials, clean metal surfaces, and etch silicon wafers[116-120]. In the dental application, the HF concentrations of 4%–10% are typically used. These concentration ranges are considered safe for dental clinic and dental laboratoy[121]. Even though dental silica-based materials can be etched by HF acid, creating the surface roughness , many studies have reported that silica-free materials including alumina-and zirconia-based ceramics cannot be etched with HF[15, 17, 20, 23, 24, 26, 31, 36-46].

However, the results in this study found that immersing three band zirconia specimens in HF solution at moderate conditions (9.5% HF at 80°C for 1 minute or at 25°C for 1 hour) can change surface topography (Figs 23 a.1-a.3 and Figs 22a.1-a.3, respectively). Furthermore, treated zirconia with the high HF concentration of 48% at 25°C for 30-60 minutes (Figs 24a.1-a.3 and Fig 24b.1-b.3, respectively) resulted in a highly uneven surface compared with treatment under moderate conditions or untreated specimens.

The results also showed that immersion times, levels of concentration, and temperature of the HF acid affected the rate of reaction leading to surface morphological changes. It also noted that the irregularities on the zirconia surface increased as immersion times were increased and at higher etching acid solution temperatures.

These results are in contrast to the works of Qeblawi et al.[25], Menezes et al[36], Derand and Derand[37], and Komine et al.[122]. They studied on the HF etching of zirconia with different concentrations ranging from 4.5–38% and etching times ranging from 1-12 minutes at room temperature[25, 36, 37, 122]. They reported that HF had no effect on the zirconia surface. As a consequence, they concluded that HF could not react with the dental zirconia ceramic surface due to its glass-free material.

It is known that dental zirconia is a single phase polycrystalline material; therefore, the chemical reactivity depends on the crystallographic orientation. The morphology changes of zirconia surface after HF etching may be explained that atoms around the crystal boundaries are more chemically reactive and dissolve faster than those inside the crystal, leading to the formation of irregular grooves around the crystals and grain size was reduced[123].

Figure 58 demonstrated the formation of irregularity grain after HF treatment. It can suggest that the zirconia surface was etched by corroding phenomenon. The image of the etched specimen surfaces revealed a decrease in grain size and an increase in the inter-grain space, creating dislodged zirconia grains. This probably results in producing porosities on the surface.

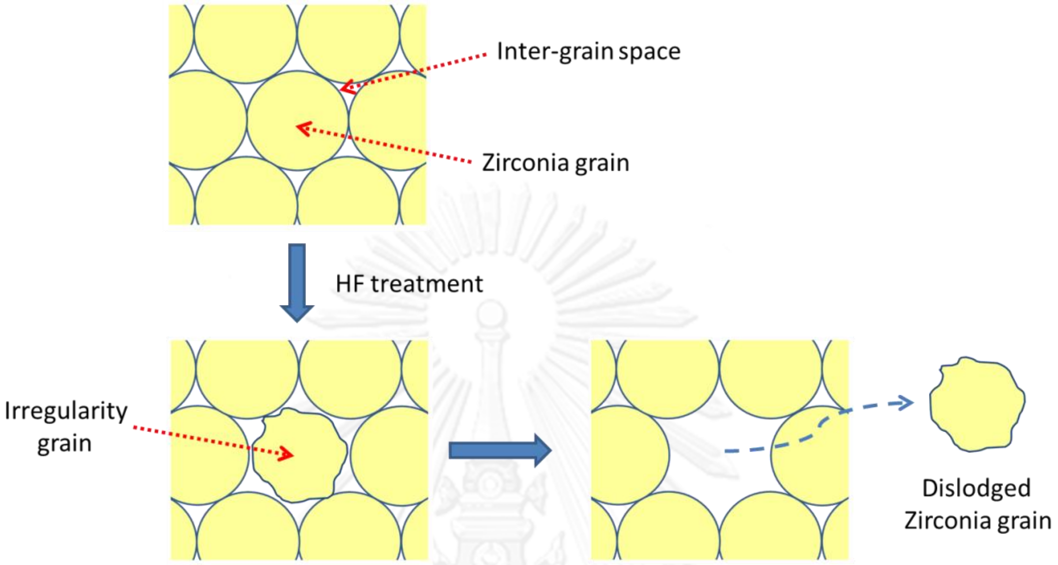


Figure 57 shows the formation of irregularity zirconia grain and dislodged zirconia grain after HF treatment.

The present of fluorine element as shown in Figures 30-32 may result from hydrofluoric acid etched zirconia. It can suggest that HF may react with zirconium oxide. This would be proved in part II.

Results from ICP techniques (Tables 6-8 and Figure 35) discovered the dislodged zirconium element in the acid solution. These results associated with SEM images can be concluded that the morphology changes of treated zirconia surface depend on 3 factors: immersion times, levels of concentration and temperature of acid solution.

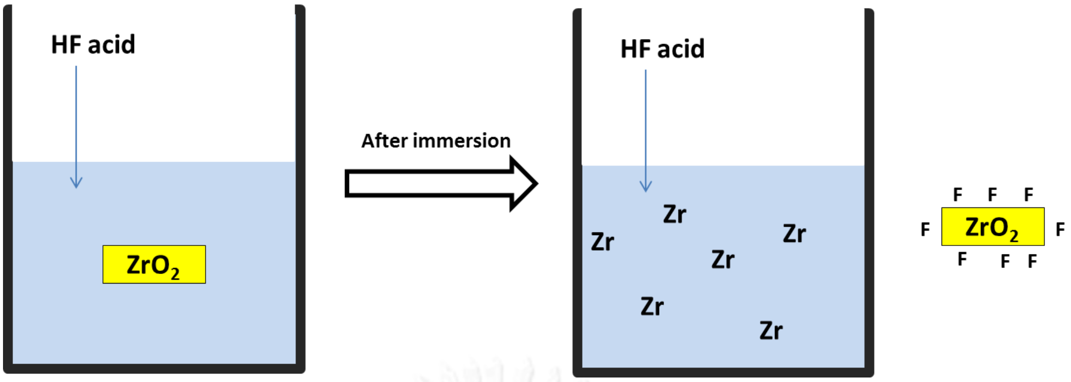


Figure 58 The diagram shows that hydrofluoric acid treatment is able to dislodge the zirconium element in the acid solution and to create the fluorine element on the zirconia surface.

Discussion: Part II

From SEM images at 200, 500 and 2,000X magnifications, HF etched porcelain surfaces showed the most morphological changes. They displayed dominant crystal structure with deep irregularity grooves that produced morphological honeycomb-like surfaces (Figs 40b.1-b.3 and Figs 45b.1-b.3). In contrast, the blasted zirconia and porcelain surfaces demonstrated the irregular rough surface. The morphology looks like shadow wave in the sea. (Figs 36c.1-c.3, 40c.1-c.3, 41c.1-c.3 and 45c.1-c.3). However, a rather smooth surface with very small porosities was presented in all of the HF treated zirconia (Fig 37-39 and Figs 42-44).

The etching pattern of HF treated porcelain surface can be explained based on chemical knowledge. From equation 1, the interaction between silica-based materials or glass-ceramic and HF can be occurred (Ref).

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O \text{ .... } (1)$$

It is known that, the dental porcelain is a silica-based material, consisting of glassy and crystal phase (Figure 60). The crystal phase is a closed- packed of repeating structure. According to the atomic randomly pattern structure, in the process of etching the glassy phase is simply etched by acid in comparison with the crystalline phase [32-34]. Consequently, the major remains on the surface are in the crystal phase. These remains then develop the rough-surface. Therefore, the roughness degree of etched- porcelain depends on the size of remaining crystalline structures (Figure 61).

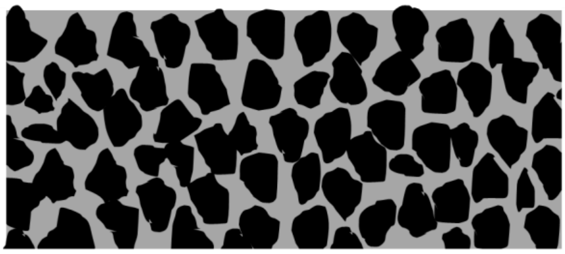


Figure 59 Drawing picture demonstrates lateral view of dental porcelain surface, composing glassy matrix (gray color) and crystal grains (dark color) with the average particle size in micrometer scale.

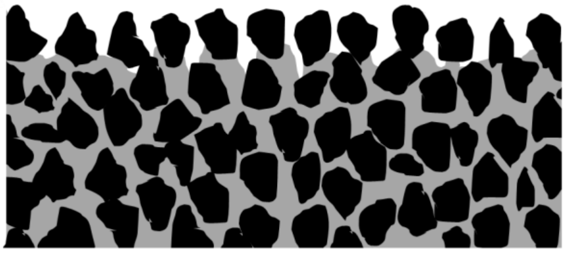


Figure 60 Drawing picture demonstrates lateral view of HF etched porcelain surface, the glassy matrix (gray color) was dissolved by Hydrofluoric acid and the crystal grains (dark color) remained at the top of surface and created roughness on the surface.

Mackert and William (1996) found that the commercial dental porcelain contained the leucite crystals sized which had their average size about 5-10 μm[124]. Giordano and McLaren (2010) also noted that the new generations of dental feldspathic porcelains have been developed with very fine leucite crystals sized about 10-20 μm[125]. Therefore, it can indicate that the roughness of porcelain surface created by hydrofluoric acid would be in a range of micro-scale. From the present study, the SEM images (Figures 40b.1-b.3 and Figures 45b.1-b.3) showed the surface roughness of etched-porcelain in micro-scale level. Therefore, this finding confirmed that the degree of roughness of etched-porcelain depended on its crystal size.

In contrast, HF etched zirconia showed a very small porosities spreading on the surface. This may be explained as follows. Generally, zirconium oxide is a monophasic polycrystalline ceramic material (Figure 62). Its chemical reactions could occur only on crystallographic structure. However, the weak points that would be corroded are the boundaries around the crystal. After etching, it led to the formation of irregular grooves around the crystals, reduction of grain size and grain dislodgment, respectively (Figure 63). Giordano and McLaren (2010) reported that the grain size of commercial sintered zirconia ranged from 0.1 to 0.5 µm (100-500 nm)[125]. In this study, the grain size measured was in agreement with that of Giordano and McLaren that was in the range of 0.1- 0.25 µm. However, the roughness in micro-scale of etched zirconia surface is much lower than that of etched porcelain. Therefore, in this study the roughness scale of HF treated zirconia could be namely as nano-scale.

It appeared that the group of severe conditions such as zirconia immersion in 9.5%HF 25°C 3 hours and 80°C 30 minutes (Figure 37c.1-c.3 and 38d.1-d.3) created large holes as a result of a bulk grain dislodgment (Figure 64). However, the level of surface roughness of the severe condition group was still lower than those of HF etched porcelain and alumina blasting groups.

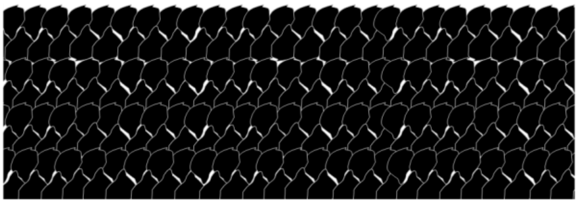


Figure 61 Drawing picture demonstrates lateral view of dental zironia composing only one crystal phase with the average grain size in nanometer scale

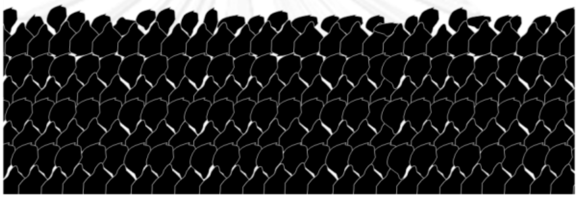


Figure 62 Drawing picture demonstrates lateral view of dental zironia, grain boundaries were etched by hydrofluoric acid and the grain sizes were reduced leading to the creation of surface roughness.

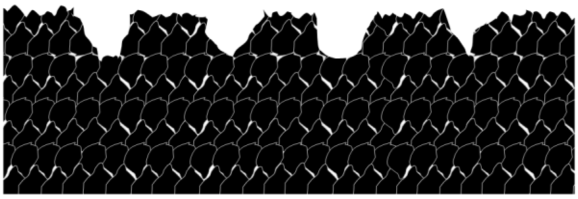


Figure 63 Drawing picture demonstrates lateral view of dental zironia, grain boundaries were etched and the bulbs of etched-grains were dislodged leading to the creation of surface roughness as well as the hole on the surface.

The SEM images from Figures 36c.1-c.3 and Figures 40c.1-c.3 displayed a micro-roughness on the alumina blasting zirconia and porcelain surface, respectively.

The image results demonstrated that the alumina blasted zirconia created the shallow irregularities as same as alumina blasted porcelain. The most commonly used particle size of alumina in the blasting application of dentistry was ranged from 50 to 250 μm[17, 31, 37, 43, 85, 126, 127]. Therefore, the roughness scale in blasted zirconia and porcelain in this study appeared in micro-scale. Tsuo et al. (2006) reported that increasing alumina particle size gave rise to an increase of surface roughness[128]. According to the Moh's scale of hardness, the hardness values of porcelain, zirconia and alumina are approximately 5, 8 and 9, respectively. These values indicate that alumina has the highest surface hardness among the three different materials. As a result, it can damage supra-structure of specimens. Furthermore, alumina particles can abrade zirconia grains as well as both glassy phase and crystalline phase of porcelain (Figure 65). Because the air abrasion with 110-μm alumina particles was applied, it suggested that alumina blasting could induce the surface roughness of both porcelain and zirconia specimens in micro-scale.

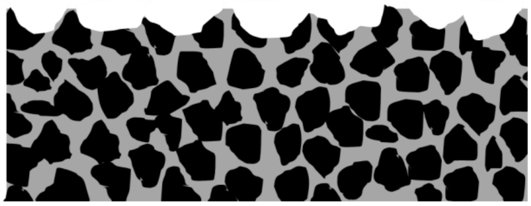


Figure 64 Drawing picture demonstrates lateral view of air-abrading dental porcelain, both of glassy matrixes (gray color) and crystal particles (dark color) were abraded by alumina particles created micro-pits on the surface.

In general, the surface roughness values are important in the etched ceramics because it could describe the etching rate of ceramic and the texture of etched surface[129]. The conventional profilometer is a device used to measure the surface roughness between the low and high points of cut-off surface. The use of micro-profilometer is popular to measure the roughness surface in dentistry because it is easy to perform and require minimal equipment. However, for the conventional profilometer, the roughness evaluation limit in a range of approximately 0.1 µm height (micro-scale). For measurement in nano-scale, Atomic Force Microscopy (AFM) has become an increasing important tool because the surface topography can be evaluated at a level of extremely high vertical and lateral resolution[130, 131].

For the surface roughness measurement in this study, the researcher only evaluated the zirconia specimens according to the hypothesis. The testing was divided into two different measurement methods; 1) using the profilometer to evaluate the micro roughness scale and 2) using the AFM techniques to evaluate the nano-scale roughness value.

By using profilometer (Table 9), the airborne particle produced the highest roughness value on zirconia surface. HF treatment at different conditions was statistically negligible of roughness. In addition, the roughness of control group was insignificantly different from that of mind treated group. However, the results from profilometer contradicted the data provided by SEM. From Table 10, the AFM results showed the roughness of both control and HF treated zirconia in nano-scale. In addition, the roughness values increased after increasing immersion times. The results confirmed that HF is able to etch zirconia at a level of nano-scale. These AFM results were in consistent with the results from SEM analysis. It is probably that AFM accurately detect the roughness of HF-treated zirconia better than the profilometer. The results of nano-surface roughness, increased surface roughness values probably cause by dislodged of zirconia grain. The first reaction probably reacts between HF acid and inter-grain space and then zirconia grains dislodged. The results from SEM, EDS and ICP studies in Part I can be support this explanation.

Recently, published research has focused on functional groups of dental zirconia surface because hydroxyl functional groups (-OH) can chemically react with the phosphoric derivative monomers. (Kern et al., (1998)[64] and Wolfart et al., (2007)[132]). While Lohbauer et al. reported that native surface of dental zirconia had very little of –OH group which was approximate 5.4%. Even though –OH group is still an important functional group[133]. It was interested to know what happened on the HF-etched zirconia surface. Therefore, FTIR was carried out to evaluate the –OH group because this technique is simple and most useful for identifying chemicals that are either organic or inorganic substrates. In addition, it can be used to identify chemical bond, functional group and quantitate some components of the unknown mixture.

The results from FTIR analysis of the unetched zirconia and HF-treated zirconia powder, the main peaks and functional group of ZrO_2 system displaying in the FTIR spectra could be related to 1) –OH stretching and bending vibration, 2) Zr-OH stretching and bending vibration, 3) Zr-O stretching vibration, and 4)Zr-F vibration, when the chemical reaction between ZrO_2 and HF can occur.

In the present study , the FTIR spectra of untreated zirconia group showed 4 importance points of -OH functional groups, the band at 3000-3600 cm^{-1} and peak at 1630 cm^{-1} corresponded to hydroxyl group (-OH) while peaks at 1353 cm^{-1} and 1565 cm^{-1} corresponded to Zr-OH group. The observation of the last 2 peaks was the similar findings by Simmons, Le Toullec et al.[134], Liu et al. and Sarkar et al.[135]. They reported that adsorbent's peak at 1353 cm^{-1} was assigned to the bending vibration of Zr–OH groups. Simmons and Le Toullec et al[134]. evaluated the peak at 1565 cm^{-1} was due to Zr–OH vibration.

In this study, the white powder of the HF-treated zirconia was obtained from the top of specimen surface by scratching with a clean blade No.11 for FTIR analysis. Besides the 4 importance points of peaks that showed in unetched zirconia group, there were the two new main peaks could be observed at approximately 250-500 cm^{-1}. These two peaks were assigned to bending vibration of F-Zr-F group (240–350 cm^{-1}) and stretching of Zr-F and group (375–475 cm^{-1}). This finding corresponded to Jare and Santhamma studies and the results suggested that the chemical reaction between HF and zirconia probably occurs[136].

Y-TZP is a main compound of Zirconium (Zr) and Oxygen (O). However, it also consists of other materials such as yttria oxide and hafnium oxide. The results from FTIR analysis of both of unetched and etched zirconia showed that the peak corresponded to Zr-O did not observe. Sarkar et al. reported that the absorption bands of FTIR evaluation at 514-523 cm^{-1} probably correspond to Zr-O vibrations[135]. In contrast, the present study displayed that the main peak of both diagrams of FTIR disappearance Zr-O vibration at approximately 514-523 cm^{-1}. This finding was related to Dou et al. (2012) [137]and Borilo and Spivakava (2012) who analyzed hydrous ZrO_2 by using FTIR technique, their studies did not show IR peak of Zr-O at about 500 cm^{-1}[138]. The disappearance of peak probably corresponding to the substrate had many main compositions, leading to interruption of the peak of Zr-O. Therefore, the additional special techniques should be required to analyze the functional groups of HF-treated zirconia because the IR peaks of pure single material are generally so unique that they are like a “finger print”. While compound materials have a rich peak, and that makes identification become difficult. Thus, the present study combined FTIR technique with other special techniques, including XRD and XPS analysis, for accurate identification of etched zirconia which was a mixed substrate.

It could be observed that the thin layer of the white powder was deposited on the HF treated zirconia surface (Figure 25). This layer can be removed and scratched off by blade no.11. The SEM evaluation of this layer demonstrated various cracks and grooves morphology at the low magnification (Figure 27a and 27b). It also displayed a new structure of pine leaf-like appearance at 10,000x magnification (27c). As described previously, after ultrasonic cleaning, the white layer can be subsequently removed as well. As a result, the presence of irregularity zirconia grain was shown on the surface (Figure 26).

From XRD analysis of HF-etched zirconia showed that the monoclinic phase was present in all of the etched specimens (Figure 48, 49 and 51). The result also displayed that the white layer consists of monoclinic phase of zirconium oxide and zirconium fluoride compound (ZrF_4).

It is probably explained that the HF-treated zirconia specimen surface may consist of 3 zones (Figure 66). 1) Dislodged white powder zone: It is the outer zone and looks like white loose powder. It can be removed by immersion in water or ultrasonic vibration at room temperature or gently scratched off by blade no11. This zone consists of the new compounds (ZrF_4), and monoclinic zirconia phase. 2) Irregularity zirconia grain zone: This intermediate zone consists of both monoclinic and tetragonal phase zirconia. It cannot be removed by immersion in water and scratched off. 3) Non-reacted zirconia zone: It is beneath the intermediate zone. Only a tetragonal phase zirconia was presented in this zone.

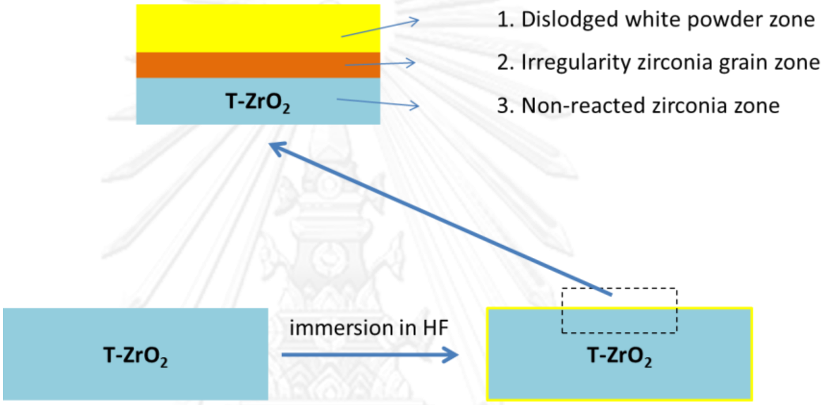


Figure 65 The three zones on the surface of HF-treated zirconia specimen

The transformation of tetragonal to monoclinic phase and the formation of zirconium fluoride compound could be explained with two hypotheses corresponding to the theories of etching mechanism 1) Low temperature degradation (LTD) phenomena 2) The chemical reaction between hydrofluoric acid and zirconium oxide, respectively.

The white loose powder appearing on the top of etched zirconia may cause from HF damaged grain structure. This damage process leads to destroy the adhesion between grains which is easily removed by instrument. Generally, the partially stabilized zirconia can be transformed from tetragonal to monoclinic structure. This phenomenal can be caused by pressure or dry conditions known as “transformation toughening”, and moist conditions known as “Low Temperature Degradation (LTD)”. In this work etching with hydrofluoric acid under moist conditions was carried out. In addition all samples exhibited a monoclinic zirconia peak in the XRD spectrum. This would indicate that HF etching can induce the phase transformation of zirconia due to LTD. This likely occurred because the HF etching was applied with prolonged exposure to humidity at low temperature (room temperature–400°C).

At present, there is no acceptable mechanism to explain the LTD phenomenon but the hypotheses are still speculated and many authors try to explain their opinions as follows.

Sato and Shimada (1985) reported that the breakage of Zr-O-Zr bonds could be induced by chemisorbed water on zirconia surface, resulting in stress corrosion[139]. While Lange et al. (1986) suggested that H_2O would react with the stabilizer (Y_2O_3) to create the new compound in the formation of $Y(OH)_3$ as observed by using TEM evaluation. A decreased in this stabilizer at around zirconia grains caused tetragonal-to-monoclinic transformation[140]. In 1987 Yoshimura et al. proposed that the breaking Zr-O bond was attacked by water vapor due to movement of –OH group leading to a stress accumulation. The phenomenon led to turn generates lattice defects and then transform tetragonal to monoclinic[141]. According to Chevalier et al. (2009) who described the sequence of LTD. First, H_2O was chemically adsorbed on the zirconia surface and then the reaction between H_2O and O_2 on the zirconia surface was occurred. This led to the formation of hydroxyl ions. These ions penetrated into the inner part by grain boundary diffusion and then bonded with oxygen vacancies leading to the formation of proton defects. Thus, oxygen vacancy concentration was reduced and then came the occurrence of a tetragonal to monoclinic transformation[49].

Although the LTD mechanism was explained in several different ways but the results had an agreement that the tetragonal transformed to monoclinic phase at fairly low temperature. Furthermore, the phase transformation processes continuously proceeded to cause a surface uplift, dislodged grain and micro-cracks. These occurrences enhanced opened-grain and penetrated-water along micro-crack. Consequently, a further transformation led to an increased in surface roughness[47].

The results from XRD technique analysis of HF- etched zirconia surface found that HF can be reacted zirconia surface, crated Zr-F compounds. There would be further explanations and descriptions in the XPS study. In addition, tetragonal-to-monoclinic was induced on the treated zirconia surface.

XPS is the sensitive equipment and widely used to analyze the surface composition of material. Normally, a composition of ~95% ZrO_2 and 2-5% Y_2O_3 displays the ideal commercially available of dental zirconia so Zr, O and Y should be shown in scanning XPS analysis.

The results in scanning peak of XPS evaluation showed that fluorine element occurred on the zirconia specimen after HF treatment (Figure 53) as same as showed in EDS analysis (Figure 30-32). These confirmed that fluorine element occurred on the etched zirconia surface. The non-ultrasonic of HF-etched zirconia group showed the F atomic concentration at approximately 37.34- 53.46%. While after ultrasonic cleaning, the HF-treated zirconia specimen group demonstrated the decreasing of F atomic concentration at approximately 2.19% (Table 12). This indicated that the fluorine compound on the etched zirconia surface can be removed by ultrasonic cleaning method. In the present study, EDS and XRD results did not present the F element on the HF treated specimen after ultrasonic cleaning these may be explained that XPS technique is a high surface sensitivity analysis. The sensitivity to atomic% resolution is in order of 0.1[142]. For example, one atom is different from 1,000 atoms on the surface this difference can be detected by XPS but EDS and XRD technique do not. Therefore, XPS is more sensitive to analyze a very small percentage of foreign atoms.

From the XPS spectra, both of untreated zirconia and HF treated zirconia showed the peaks of $Zr3d_{5/2}$ and $Zr3d_{3/2}$ (Figure 54 and Figure 55). But HF treated zirconia also displayed the others new peaks which indicate of zirconium oxyfluoride (Zr-O-F, 184.8 $Zr3d_{5/2}$, 685 eV for F1s) and zirconium fluoride (ZrF, 187.2 $Zr3d_{5/2}$, 686 eV for F1s).The other new peaks confirm that HF could react with zirconia surface (Figure 55 and Figure 56). The characteristic peaks of Zr-O-F and Zr-F compound were similar to those in previous studies by Pantano and Brow (1988), [143]who evaluated the hydrolysis reactions of fluorozirconate glass, and Wolter et al., (2011)[144] who studied on the plasma fluorinated zirconia.

According to Pantano and Brow and Vilakazi et al., they reported that the structure characteristic formulas of zirconium-fluoride and zirconium oxy-fluoride have many species such as ZrF_4, ZrF_6, $Zr_3O_2F_8$, $ZrO_{0.33}F_{1.33}$, $ZrO_{1.3}F_{1.4}$, $ZrO_{8.79}F_{9.71}$, ZrO_2F_5 or ZrO_3F_4[143, 145].

In 1988 Patano and Brown[143] suggested that the XPS peak position of zirconium-fluoride and zirconium oxy-fluoride relative to oxide or fluoride bonding states enabled identification of its stoichiometric form based on the associated Pauling charge on the Zr species. In 2011and 2012, there were two studies about the relationship between Zr_{3d} binding energy and the Pauling charge on Zr-species[58]. Therefore, the data can be plotted and shown in the Figure 67.

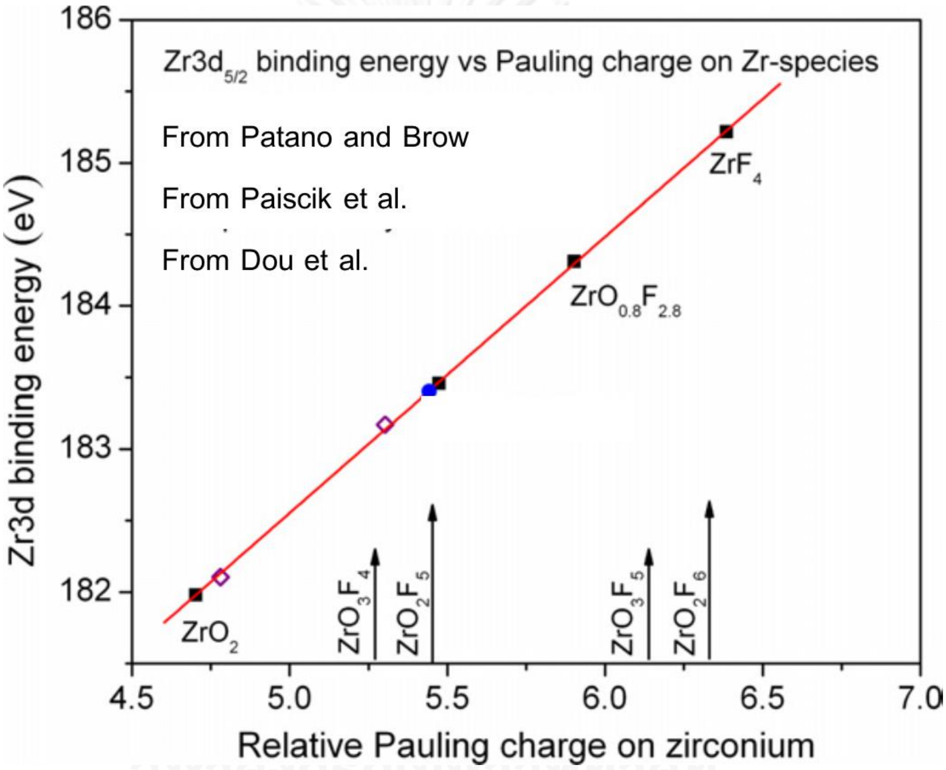


Figure 66 Relationship between Zr3d biding energy and the Pauling charge on Zr-species from Patano and Brow (1988)[54], from Paiscik et al. (2011)[57], and from Dou et al (2012)[46].

With this correlation, they reported that a peak at ~183.5eV of $Zr3d_{5/2}$ to the coordinate surface species of ZrO_2F_5 or ZrO_3F_4 and a peak at ~184.8eV of $Zr3d_{5/2}$ to the coordinate surface species of ZrF_4.

Moreover, Piascik et al. (2011)[58] also noted that a seven-coordinate ZrO_3F_4 species based on a peak at 183.1eV of Zr3$d_{5/2}$. Wolter et al. (2011)[144] reported that the Zr3$d_{5/2}$ and Zr3$d_{3/2}$ at peak position at ~184.8 and ~187.2eV, respectively related to the zirconium-fluoride specie of ZrF_4

The zirconiumtetrafluorides (ZrF_4) is an inorganic of zirconium-fluoride compound and is a water insoluble material. It is prepared from the metal oxides using hydrogen fluoride. Zirconium tetrafluoride is widely used for the production of zirconium metal, glass fiber, precursor, oxygen-sensitive application [146-149]. The ZrF_4 is usually synthesized from pure-ZrO_2 or $ZrCl_4$ by interaction with HF or F_2. However, the production of ZrF_4 can be prepared by several methods, which is summarized by Blumental (1958)[147] as followed;

1. Synthesis from the elements (at temperature more than 300°C)

   $Zr + F_2 \rightarrow ZrF_4$

2. Displacement of oxygen (at temperature 525°C)

   $ZrO_2 + F_2 \rightarrow ZrF_4 + O_2$

3. Thermal decomposition of fluozirconate (at temperature 300°C)

   $(NH_4)2ZrF_6 \rightarrow ZrF_4 + 2NH_4F$

4. Metathesis from zirconium oxide (at temperature 550°C)

   $ZrO_2 + 4HF \rightarrow ZrF_4 + 2H_2O$

5. Metathesis from ZrO_2SiO_2 (at temperature 550°C)

   $ZrO_2SiO_2 + 8HF \rightarrow ZrF_4 + SiF_4 + H_2O$

6. Metathesis from the tetrachloride (at temperature 550°C)

   $ZrCl_4 + 4HF \rightarrow ZrF_4 + 4HCl$

7. Hydrofluorination of oxyfluozirconic acids (at temperature 550°C)

$$H_2ZrO_2F_2 + 2HF \rightarrow ZrF_4 + 2H_2O$$

It can be observed that all methods above were carried out at high temperature (more than 500°C). In contrast, the present study demonstrated that ZrF_4 could possibly be produced at lower temperature. Similarly to Robinson's work (1986), he reported that by using HF as a reactant, the conversion of pure ZrO_2 to ZrF_4 could occur at 227°C[150]. However, he stated that the reaction was not completed at this temperature. Withers (1991) noted that the zirconium oxide can converse to ZrF_4 at 300-600°C[151]. Haendler et al. also found that at 525°C the conversion of ZrO_2 to ZrF_4 was complete, but at 100°C the reaction did not occur[148]. Monnahela et al. (2012) supported that the formation of ZrF_4 can also occur at low temperature at approximately 300°C but it can create the intermediate product such as unidentified zirconium-oxyfluoride species[152]. They also reported at 525°C the reaction of zirconium oxide and fluoride gas are essentially completed, but peaks of oxyfluoride are still detectable. The study by Vilakazi et al. (2012) investigated the reaction of pure ZrO_2 with anhydrous hydrogen fluoride by using a thermo-gravimetric analyzer. This finding indicated that the reaction between ZrO_2 and hydrogen-fluoride probably can be explained according to the equation[145]:

$$ZrO_2 + 4HF \rightarrow Zr_xO_yF_z \rightarrow ZrF_4 + 2H_2O \ldots\ldots\ldots \quad (2)$$

From the reaction above, Vilakazi et al. implied that the $Zr_xO_yF_x$ would act as an intermediate prior to formation of ZrF_4. The presence of intermediated oxyfluorides was confirmed[145]. Therefore, the reaction between dental zirconia and hydrofluoric acid could be complied with the above equation.

However, this research is aimed to prove the effect of hydrofluoric on dental zirconia. In addition, the physical properties were used to evaluate this effect. Therefore, further investigations are needed to confirm the mechanical properties in terms of fractural strength and surface hardness. The biocompatibility also needs to be considered. Furthermore, the clinical application in terms of bond strength between resin cement and etch zirconia surface will be measured.

Conclusion

Based on these results the hypotheses number 1-4 are reject and a number of conclusions can be drawn.

Part I:

By using SEM, EDS and ICP techniques, three occurrences can be observed from this experiment. First, there was an increase in the level of nano-roughness on the zirconia surface. Second, there was a deposition of fluorine element on the specimen surface. Lastly, zirconium ions were also found in the HF solution. Therefore, it can be confirmed that hydrofluoric acid can etch dental zirconia.

Part II:

The SEM, profilometer, AFM, FTIR, XRD, and XPS were performed to investigate the physical properties of HF treated zirconia.

SEM evaluation at low magnification showed that all HF etched zirconia demonstrated a surface with small porosities at nano-scale level. In contrast, HF treated porcelain exhibited high irregularities and produced morphological honey comb-like surfaces. Furthermore, the blasted zirconia and porcelain surfaces displayed a very irregular rough surface at micro-scale level.

By using micro-profilometer, the surface roughness analysis of HF treated zirconia insignificantly increased compared with control group. In contrast, by using AFM the roughness of HF treated zirconia displayed in nano-scale which was in consistent with SEM results.

The etching phenomena of zirconia surface can be explained with two hypotheses

1) Low Temperature Degradation (LTD): It was revealed by using XRD analysis that tetragonal-to-monoclinic phase transformation was created. This led to a surface uplift, dislodged grain and roughness on surface.
2) Chemical reaction between HF and zirconium oxide: Using of FTIR, XRD, and XPS analyses, zirconium-fluoride compound was discovered. The surface was rough after this compound was removed.

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APPENDIX

APPENDIX

Pilot study

The previously observed pilot study consisted of three experiments.

The first pilot experiment was performed using the same protocol of Casucci et al. (2009, 2010)[21, 22]. The specimen used in this study was 10 x 20 x 2 mm sintering of Y-TZP ceramic (Katana). Firstly, the specimen was polished with SiC abrasive papers (grit #600, 1000, and 1200). Next, it was sonicated in 96 % ethanol and deionized water for 10 min in each solvent. An experimental hot etching solution: a hot acidic solution containing HCl and $FeCl_3$ (100°C) was applied to the specimen for 30 min. The zirconia specimen was subsequently sonicated in 96 % ethanol and deionized water for 10 min in each solvent and followed by air dry. Finally it was characterized with the scanning electron microscope (SEM). The resulting picture was compared with that from Casucci et al. (2009) at the same magnification of 10,000X.

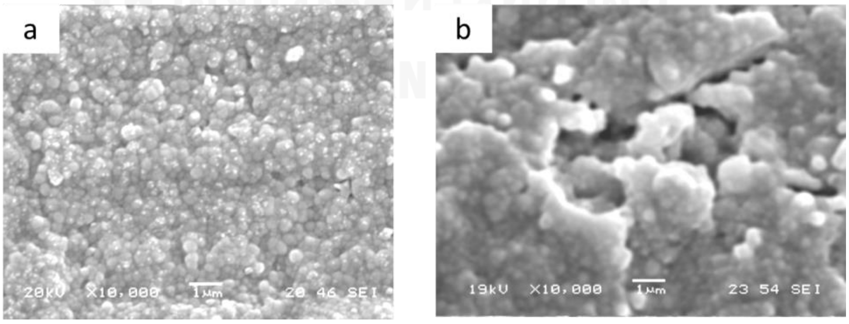


Figure 67 The surface topography of zirconia specimens from Casucci et al. (2009, 2010); (a) control, (b) experimental hot etching solution

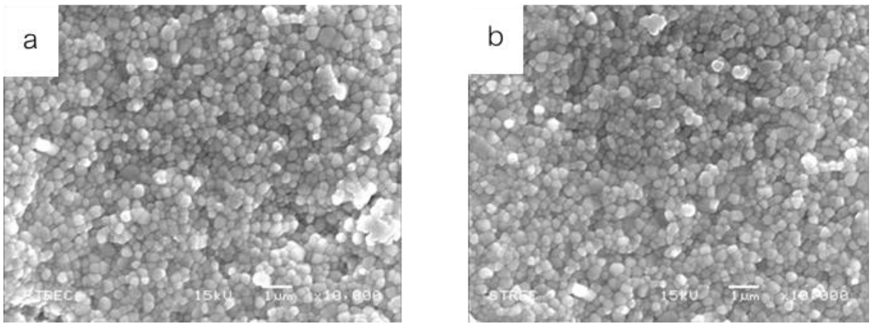
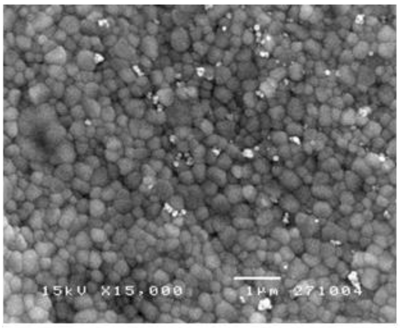


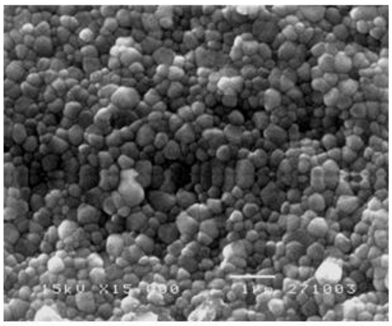
Figure 68 The surface topography of zirconia specimens from the first pilot study; (a) control, (b) experimental hot etching solution

From Figure 68a and 68b, it is clearly observed that the surface roughness after etching increases compared to control. In contrast, the surface topography from both Figure 69a and 69b is not different. It can be seen that the surface of zirconia cannot be etched using the first pilot study method.

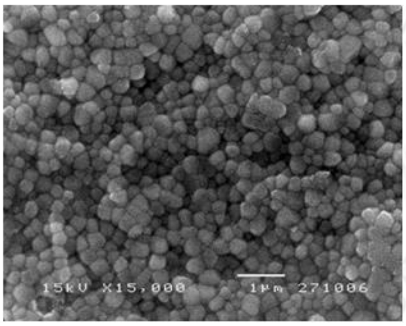
The second pilot experiment was prepared using the same zirconia ceramic materials as described in the first experiment. Firstly, the specimens were immersed in various acidic and alkaline solutions included 37% phosphoric acid (H_3PO_4), 70% hydrochloric acid (HCl), 20%vol potassium permanganate solution in deionized water, 10% sodium hypochlorite, 9.5% hydrofluoric acid (HF), 10% ferric chlorite solution, sulfuric acid, and acetic acid. Next, they were heated at 80 °C for 60 min. They were then sonicated in 96 % ethanol and deionized water for 10 min in each solution and followed by air dry. Finally, all specimens were investigated by scanning electron microscope at magnification of 15,000X. The results are shown in Figure 70.



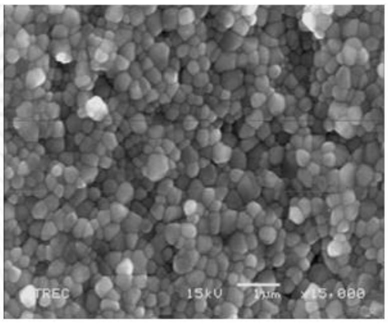
37% Phosphoric acid



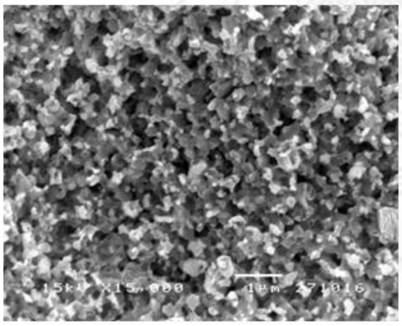
37% Hydrochloric acid (HCl)



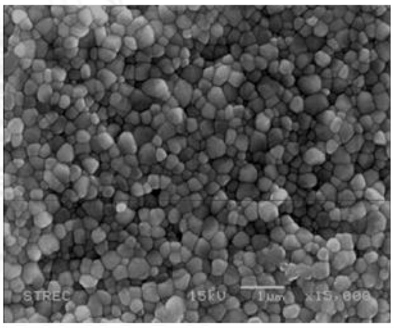
20%vol Potassium permanganate solution



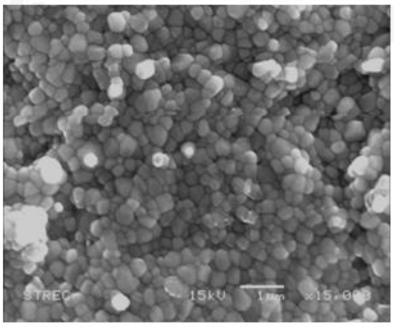
10% Sodium hypochlorite



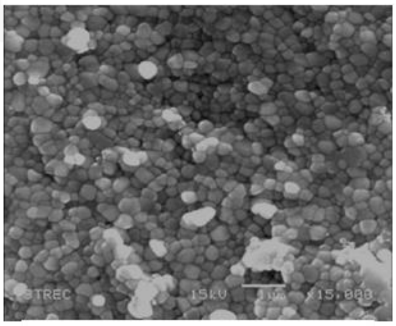
9.5 % Hydrofluoric acid



10% Ferric chlorite solution



Sulfuric acid

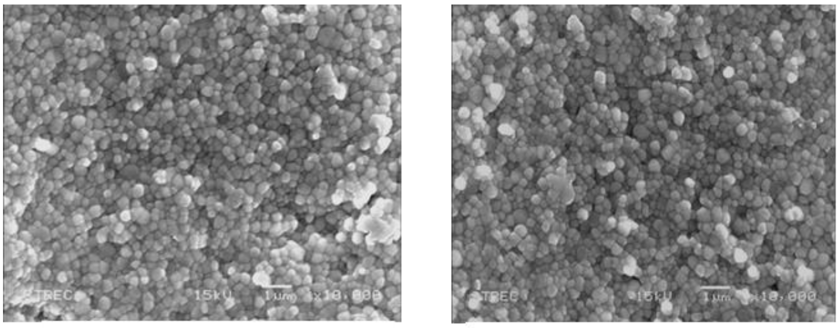


Acetic acid

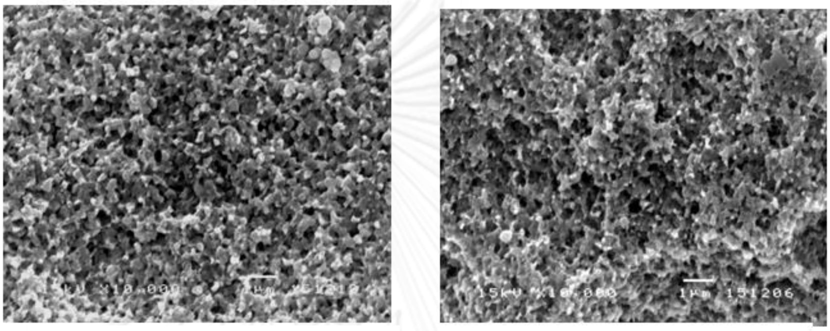
Figure 69 The surface topography of zirconia specimens after immersed in various acidic and alkaline solutions from the second pilot study

The results showed that hydrofluoric acid etching technique was effective on zirconia surface while the surface treated by using other solutions was not significantly changed compared to control.

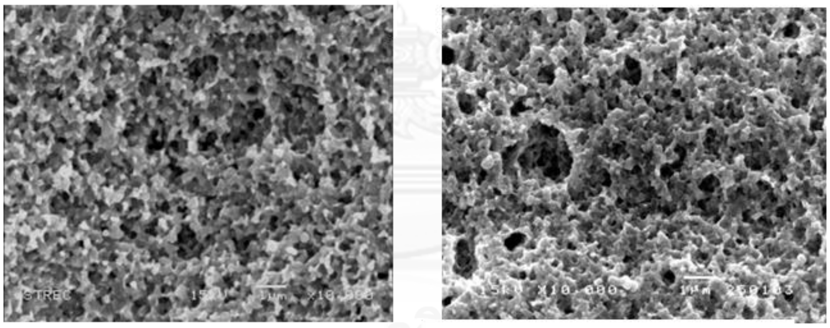
The third pilot experiment used two popular brands of sintering partially-stabilized zirconia ceramic (Katana, Cercon) with the same dimension as previously mentioned. The process of polishing and sonication was similar to the first experiment. The specimen was subsequently treated using two difference techniques; 1) immersed in 9.5% hydrofluoric acid followed by heating at 80 $^{\circ}$C for 1 hr, and 2) immersed in 9.5% hydrofluoric acid at room temperature for 1 day. Finally, all specimens were investigated by scanning electron microscope at magnification of 10,000X. The results are shown in Figure 71.



Katana zirconia (control) Cercon zirconia (control)



Katana zirconia (9.5% HF 80 °C for 1 hr) Cercon zirconia (9.5% HF 80 °C for 1 hr)



Katana zirconia (9.5% HF at room temperature for 1 day) Cercon zirconia (9.5% HF at room temperature for 1 day)

Figure 70 The surface topography of control zirconia specimens and etched zirconia specimens with hydrofluoric acid at different temperatures and times from the third pilot study

It can observe in Figure 71 that both treatments can improve surface roughness of both zirconia brands. From this result, it can be argued that silica-free zirconias can be etched by hydrofluoric acid. Though, they were treated at room temperature.

The conclusion of pilot experiment indicated that hydrofluoric acid can be change the surface morphology of sintered partially-stabilized zirconia ceramic. Because the figures show that surface roughness of dental zirconia specimens (Katana and Cercon) after heat and immersion in hydrofluoric acid.

Statistical analysis of the surface roughness data by using profilometer

One-Sample Kolmogorov-Smirnov Test

GROUP			SR
control	N		20
	Normal Parameters[a]	Mean	.1800
		Std. Deviation	.02884
	Most Extreme Differences	Absolute	.150
		Positive	.150
		Negative	-.109
	Kolmogorov-Smirnov Z		.671
	Asymp. Sig. (2-tailed)		.759
blasting	N		20
	Normal Parameters[a]	Mean	.5165
		Std. Deviation	.09005
	Most Extreme Differences	Absolute	.160
		Positive	.100
		Negative	-.160
	Kolmogorov-Smirnov Z		.714
	Asymp. Sig. (2-tailed)		.688
g3 9.5HF 25c 1hr	N		20
	Normal Parameters[a]	Mean	.1890
		Std. Deviation	.03523
	Most Extreme Differences	Absolute	.205
		Positive	.205
		Negative	-.128
	Kolmogorov-Smirnov Z		.918
	Asymp. Sig. (2-tailed)		.369

g3 9.5HF 25c 2hrs	N		20
	Normal Parameters[a]	Mean	.2245
		Std. Deviation	.03284
	Most Extreme Differences	Absolute	.169
		Positive	.169
		Negative	-.088
	Kolmogorov-Smirnov Z		.755
	Asymp. Sig. (2-tailed)		.619
g3 9.5HF 25c 3hrs	N		20
	Normal Parameters[a]	Mean	.2230
		Std. Deviation	.03342
	Most Extreme Differences	Absolute	.117
		Positive	.117
		Negative	-.099
	Kolmogorov-Smirnov Z		.523
	Asymp. Sig. (2-tailed)		.947
g4 9.5HF 80c 1min	N		20
	Normal Parameters[a]	Mean	.2115
		Std. Deviation	.06327
	Most Extreme Differences	Absolute	.247
		Positive	.247
		Negative	-.159
	Kolmogorov-Smirnov Z		1.103
	Asymp. Sig. (2-tailed)		.176
g4 9.5HF 80c 3mins	N		20
	Normal Parameters[a]	Mean	.2325
		Std. Deviation	.04089
	Most Extreme Differences	Absolute	.134
		Positive	.134

		Negative	-.084
	Kolmogorov-Smirnov Z		.601
	Asymp. Sig. (2-tailed)		.863
g4 9.5HF 80c 5mins	N		20
	Normal Parameters[a]	Mean	.2325
		Std. Deviation	.04102
	Most Extreme Differences	Absolute	.100
		Positive	.085
		Negative	-.100
	Kolmogorov-Smirnov Z		.448
	Asymp. Sig. (2-tailed)		.988
g5 9.5HF 80c 30mins	N		20
	Normal Parameters[a]	Mean	.2860
		Std. Deviation	.05205
	Most Extreme Differences	Absolute	.106
		Positive	.105
		Negative	-.106
	Kolmogorov-Smirnov Z		.474
	Asymp. Sig. (2-tailed)		.978
g5 48HF 30mins	N		20
	Normal Parameters[a]	Mean	.1915
		Std. Deviation	.03558
	Most Extreme Differences	Absolute	.227
		Positive	.227
		Negative	-.122
	Kolmogorov-Smirnov Z		1.014
	Asymp. Sig. (2-tailed)		.255
g4 48HF 60mins	N		20

	Normal Parameters[a]	Mean	.2205
		Std. Deviation	.06549
	Most Extreme Differences	Absolute	.183
		Positive	.183
		Negative	-.128
	Kolmogorov-Smirnov Z		.818
	Asymp. Sig. (2-tailed)		.515

a. Test distribution is Normal.

Descriptives

SR

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
control	20	.1800	.02884	.00645	.1665	.1935	.14	.24
blasting	20	.5165	.09005	.02013	.4744	.5586	.31	.64
g3 9.5HF 25c 1hr	20	.1890	.03523	.00788	.1725	.2055	.14	.25
g3 9.5HF 25c 2hrs	20	.2245	.03284	.00734	.2091	.2399	.18	.32
g3 9.5HF 25c 3hrs	20	.2230	.03342	.00747	.2074	.2386	.17	.30
g4 9.5HF 80c 1min	20	.2115	.06327	.01415	.1819	.2411	.14	.45
g4 9.5HF 80c 3mins	20	.2325	.04089	.00914	.2134	.2516	.17	.32
g4 9.5HF 80c 5mins	20	.2325	.04102	.00917	.2133	.2517	.14	.30
g5 9.5HF 80c 30mins	20	.2860	.05205	.01164	.2616	.3104	.18	.37
g5 48HF 30mins	20	.1915	.03558	.00796	.1748	.2082	.15	.27
g4 48HF 60mins	20	.2205	.06549	.01464	.1898	.2512	.14	.42
Total	220	.2461	.10254	.00691	.2325	.2598	.14	.64

Test of Homogeneity of Variances

SR

Levene Statistic	df1	df2	Sig.
4.967	10	209	.000

ANOVA

SR

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1.771	10	.177	69.570	.000
Within Groups	.532	209	.003		
Total	2.303	219			

Post Hoc Tests

Multiple Comparisons

Tukey

HSD

(I) GROUP	(J) GROUP	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
control	blasting	-.33650*	.01595	.000	-.3884	-.2846
	g3 9.5HF 25c 1hr	-.00900	.01595	1.000	-.0609	.0429

	g3 9.5HF 25c 2hrs	-.04450	.01595	.170	-.0964	.0074
	g3 9.5HF 25c 3hrs	-.04300	.01595	.209	-.0949	.0089
	g4 9.5HF 80c 1min	-.03150	.01595	.667	-.0834	.0204
	g4 9.5HF 80c 3mins	-.05250*	.01595	.045	-.1044	-.0006
	g4 9.5HF 80c 5mins	-.05250*	.01595	.045	-.1044	-.0006
	g5 9.5HF 80c 30mins	-.10600*	.01595	.000	-.1579	-.0541
	g5 48HF 30mins	-.01150	.01595	1.000	-.0634	.0404
	g4 48HF 60mins	-.04050	.01595	.289	-.0924	.0114
blasting	control	.33650*	.01595	.000	.2846	.3884
	g3 9.5HF 25c 1hr	.32750*	.01595	.000	.2756	.3794
	g3 9.5HF 25c 2hrs	.29200*	.01595	.000	.2401	.3439
	g3 9.5HF 25c 3hrs	.29350*	.01595	.000	.2416	.3454
	g4 9.5HF 80c 1min	.30500*	.01595	.000	.2531	.3569
	g4 9.5HF 80c 3mins	.28400*	.01595	.000	.2321	.3359
	g4 9.5HF 80c 5mins	.28400*	.01595	.000	.2321	.3359
	g5 9.5HF 80c 30mins	.23050*	.01595	.000	.1786	.2824
	g5 48HF 30mins	.32500*	.01595	.000	.2731	.3769
	g4 48HF 60mins	.29600*	.01595	.000	.2441	.3479
g3 9.5HF 25c 1hr	control	.00900	.01595	1.000	-.0429	.0609
	blasting	-.32750*	.01595	.000	-.3794	-.2756
	g3 9.5HF 25c 2hrs	-.03550	.01595	.490	-.0874	.0164
	g3 9.5HF 25c 3hrs	-.03400	.01595	.556	-.0859	.0179
	g4 9.5HF 80c 1min	-.02250	.01595	.945	-.0744	.0294
	g4 9.5HF 80c 3mins	-.04350	.01595	.195	-.0954	.0084
	g4 9.5HF 80c 5mins	-.04350	.01595	.195	-.0954	.0084

	g5 9.5HF 80c 30mins	-.09700*	.01595	.000	-.1489	-.0451
	g5 48HF 30mins	-.00250	.01595	1.000	-.0544	.0494
	g4 48HF 60mins	-.03150	.01595	.667	-.0834	.0204
g3 9.5HF 25c 2hrs	control	.04450	.01595	.170	-.0074	.0964
	blasting	-.29200*	.01595	.000	-.3439	-.2401
	g3 9.5HF 25c 1hr	.03550	.01595	.490	-.0164	.0874
	g3 9.5HF 25c 3hrs	.00150	.01595	1.000	-.0504	.0534
	g4 9.5HF 80c 1min	.01300	.01595	.999	-.0389	.0649
	g4 9.5HF 80c 3mins	-.00800	.01595	1.000	-.0599	.0439
	g4 9.5HF 80c 5mins	-.00800	.01595	1.000	-.0599	.0439
	g5 9.5HF 80c 30mins	-.06150*	.01595	.007	-.1134	-.0096
	g5 48HF 30mins	.03300	.01595	.601	-.0189	.0849
	g4 48HF 60mins	.00400	.01595	1.000	-.0479	.0559
g3 9.5HF 25c 3hrs	control	.04300	.01595	.209	-.0089	.0949
	blasting	-.29350*	.01595	.000	-.3454	-.2416
	g3 9.5HF 25c 1hr	.03400	.01595	.556	-.0179	.0859
	g3 9.5HF 25c 2hrs	-.00150	.01595	1.000	-.0534	.0504
	g4 9.5HF 80c 1min	.01150	.01595	1.000	-.0404	.0634
	g4 9.5HF 80c 3mins	-.00950	.01595	1.000	-.0614	.0424
	g4 9.5HF 80c 5mins	-.00950	.01595	1.000	-.0614	.0424
	g5 9.5HF 80c 30mins	-.06300*	.01595	.005	-.1149	-.0111
	g5 48HF 30mins	.03150	.01595	.667	-.0204	.0834
	g4 48HF 60mins	.00250	.01595	1.000	-.0494	.0544
g4 9.5HF 80c 1min	control	.03150	.01595	.667	-.0204	.0834
	blasting	-.30500*	.01595	.000	-.3569	-.2531

	g3 9.5HF 25c 1hr	.02250	.01595	.945	-.0294	.0744
	g3 9.5HF 25c 2hrs	-.01300	.01595	.999	-.0649	.0389
	g3 9.5HF 25c 3hrs	-.01150	.01595	1.000	-.0634	.0404
	g4 9.5HF 80c 3mins	-.02100	.01595	.965	-.0729	.0309
	g4 9.5HF 80c 5mins	-.02100	.01595	.965	-.0729	.0309
	g5 9.5HF 80c 30mins	-.07450*	.01595	.000	-.1264	-.0226
	g5 48HF 30mins	.02000	.01595	.975	-.0319	.0719
	g4 48HF 60mins	-.00900	.01595	1.000	-.0609	.0429
g4 9.5HF 80c 3mins	control	.05250*	.01595	.045	.0006	.1044
	blasting	-.28400*	.01595	.000	-.3359	-.2321
	g3 9.5HF 25c 1hr	.04350	.01595	.195	-.0084	.0954
	g3 9.5HF 25c 2hrs	.00800	.01595	1.000	-.0439	.0599
	g3 9.5HF 25c 3hrs	.00950	.01595	1.000	-.0424	.0614
	g4 9.5HF 80c 1min	.02100	.01595	.965	-.0309	.0729
	g4 9.5HF 80c 5mins	.00000	.01595	1.000	-.0519	.0519
	g5 9.5HF 80c 30mins	-.05350*	.01595	.037	-.1054	-.0016
	g5 48HF 30mins	.04100	.01595	.272	-.0109	.0929
	g4 48HF 60mins	.01200	.01595	1.000	-.0399	.0639
g4 9.5HF 80c 5mins	control	.05250*	.01595	.045	.0006	.1044
	blasting	-.28400*	.01595	.000	-.3359	-.2321
	g3 9.5HF 25c 1hr	.04350	.01595	.195	-.0084	.0954
	g3 9.5HF 25c 2hrs	.00800	.01595	1.000	-.0439	.0599
	g3 9.5HF 25c 3hrs	.00950	.01595	1.000	-.0424	.0614
	g4 9.5HF 80c 1min	.02100	.01595	.965	-.0309	.0729
	g4 9.5HF 80c 3mins	.00000	.01595	1.000	-.0519	.0519

	g5 9.5HF 80c 30mins	-.05350*	.01595	.037	-.1054	-.0016
	g5 48HF 30mins	.04100	.01595	.272	-.0109	.0929
	g4 48HF 60mins	.01200	.01595	1.000	-.0399	.0639
g5 9.5HF 80c 30mins	control	.10600*	.01595	.000	.0541	.1579
	blasting	-.23050*	.01595	.000	-.2824	-.1786
	g3 9.5HF 25c 1hr	.09700*	.01595	.000	.0451	.1489
	g3 9.5HF 25c 2hrs	.06150*	.01595	.007	.0096	.1134
	g3 9.5HF 25c 3hrs	.06300*	.01595	.005	.0111	.1149
	g4 9.5HF 80c 1min	.07450*	.01595	.000	.0226	.1264
	g4 9.5HF 80c 3mins	.05350*	.01595	.037	.0016	.1054
	g4 9.5HF 80c 5mins	.05350*	.01595	.037	.0016	.1054
	g5 48HF 30mins	.09450*	.01595	.000	.0426	.1464
	g4 48HF 60mins	.06550*	.01595	.003	.0136	.1174
g5 48HF 30mins	control	.01150	.01595	1.000	-.0404	.0634
	blasting	-.32500*	.01595	.000	-.3769	-.2731
	g3 9.5HF 25c 1hr	.00250	.01595	1.000	-.0494	.0544
	g3 9.5HF 25c 2hrs	-.03300	.01595	.601	-.0849	.0189
	g3 9.5HF 25c 3hrs	-.03150	.01595	.667	-.0834	.0204
	g4 9.5HF 80c 1min	-.02000	.01595	.975	-.0719	.0319
	g4 9.5HF 80c 3mins	-.04100	.01595	.272	-.0929	.0109
	g4 9.5HF 80c 5mins	-.04100	.01595	.272	-.0929	.0109
	g5 9.5HF 80c 30mins	-.09450*	.01595	.000	-.1464	-.0426
	g4 48HF 60mins	-.02900	.01595	.768	-.0809	.0229
g4 48HF 60mins	control	.04050	.01595	.289	-.0114	.0924
	blasting	-.29600*	.01595	.000	-.3479	-.2441

	g3 9.5HF 25c 1hr	.03150	.01595	.667	-.0204	.0834
	g3 9.5HF 25c 2hrs	-.00400	.01595	1.000	-.0559	.0479
	g3 9.5HF 25c 3hrs	-.00250	.01595	1.000	-.0544	.0494
	g4 9.5HF 80c 1min	.00900	.01595	1.000	-.0429	.0609
	g4 9.5HF 80c 3mins	-.01200	.01595	1.000	-.0639	.0399
	g4 9.5HF 80c 5mins	-.01200	.01595	1.000	-.0639	.0399
	g5 9.5HF 80c 30mins	-.06550*	.01595	.003	-.1174	-.0136
	g5 48HF 30mins	.02900	.01595	.768	-.0229	.0809

*. The mean difference is significant at the

0.05 level.

Statistical analysis of the surface roughness data by using AFM

One-Sample Kolmogorov-Smirnov Test

Group			Ra
polishing	N		5
	Normal Parameters[a]	Mean	6.8420
		Std. Deviation	.91609
	Most Extreme Differences	Absolute	.270
		Positive	.270
		Negative	-.223
	Kolmogorov-Smirnov Z		.603
	Asymp. Sig. (2-tailed)		.860
1min	N		5
	Normal Parameters[a]	Mean	45.6080
		Std. Deviation	5.04093
	Most Extreme Differences	Absolute	.171
		Positive	.152
		Negative	-.171
	Kolmogorov-Smirnov Z		.382
	Asymp. Sig. (2-tailed)		.999
5mins	N		5
	Normal Parameters[a]	Mean	85.5360
		Std. Deviation	1.48370E1
	Most Extreme Differences	Absolute	.210
		Positive	.178

		Negative	-.210
	Kolmogorov-Smirnov Z		.470
	Asymp. Sig. (2-tailed)		.980
30mins	N		5
	Normal Parameters[a]	Mean	1.3207E2
		Std. Deviation	1.75295E1
	Most Extreme Differences	Absolute	.156
		Positive	.156
		Negative	-.142
	Kolmogorov-Smirnov Z		.348
	Asymp. Sig. (2-tailed)		1.000

a. Test distribution is Normal.

Descriptives

Ra

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
polishing	5	6.8420	.91609	.40969	5.7045	7.9795	6.02	7.96
1min	5	45.6080	5.04093	2.25437	39.3489	51.8671	38.04	50.80
5mins	5	85.5360	14.83699	6.63530	67.1134	103.9586	65.41	99.22
30mins	5	1.3207E2	17.52952	7.83944	110.3022	153.8338	113.26	158.28
Total	20	67.5135	48.92506	10.93998	44.6159	90.4111	6.02	158.28

Test of Homogeneity of Variances

Ra

Levene Statistic	df1	df2	Sig.
5.572	3	16	.008

ANOVA

Ra

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	43264.879	3	14421.626	104.189	.000
Within Groups	2214.683	16	138.418		
Total	45479.562	19			

Multiple Comparisons

Ra

Tukey HSD

(I) group	(J) group	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
polishing	1min	-38.76600*	7.44091	.000	-60.0546	-17.4774
	5mins	-78.69400*	7.44091	.000	-99.9826	-57.4054
	30mins	-125.22600*	7.44091	.000	-146.5146	-103.9374
1min	polishing	38.76600*	7.44091	.000	17.4774	60.0546
	5mins	-39.92800*	7.44091	.000	-61.2166	-18.6394
	30mins	-86.46000*	7.44091	.000	-107.7486	-65.1714
5mins	polishing	78.69400*	7.44091	.000	57.4054	99.9826

	1min	39.92800*	7.44091	.000	18.6394	61.2166
	30mins	-46.53200*	7.44091	.000	-67.8206	-25.2434
30mins	polishing	125.22600*	7.44091	.000	103.9374	146.5146
	1min	86.46000*	7.44091	.000	65.1714	107.7486
	5mins	46.53200*	7.44091	.000	25.2434	67.8206

*. The mean difference is significant at the 0.05 level.

Ra

Tukey HSD

group	N	Subset for alpha = 0.05			
		1	2	3	4
polishing	5	6.8420			
1min	5		45.6080		
5mins	5			85.5360	
30mins	5				1.3207E2
Sig.		1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

VITA

Mr.Tool Sriamporn was born in Phetchabun, Thailand on October 14, 1980. In 2006, he received the Degree of Doctor of Dental Surgery (D.D.S.) from the Faculty of Dentistry, Naresuan University. After graduation, he worked as a lecturer in Restorative Department, Faculty of Dentistry, Naresuan University. In 2008, he started his post-graduated study for the Master of Science in Prosthodontics Program (M.Sc.) at Faculty of Dentistry, Chulalongkorn University. After he finished his Master degree in 2010, he started his study for the Degree of Doctor of Philosophy Program in Prosthodontics at Faculty of Dentistry, Chulalongkorn University. At present, he works at private dental clinics.