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Surface modification of silica-coated zirconia by chemical treatments

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Abstract:

Zirconia surface modification by various chemical treatments after silica coating by sandblasting was investigated in this study. The surface of silica-coated dental zirconia was hydroxylated by treatment with different acids at room temperature for 4 hr, rinsed with deionized water and air-dried. The modified surfaces were characterized by x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Shifts in binding energies for Zr $3d_{5/2}$ and Si 2p peaks were observed after treatment with acids, thereby showing a change in the chemical states of zirconium and silicon on the surface layer of silica-coated zirconia. The XPS analysis revealed that the silica-coated zirconia ($\text{SiO}_2\text{-ZrO}_2$) surfaces had changed to hydrous silica-coated zirconia ($\text{SiO}_2\text{-ZrO}_2\cdot n\text{H}_2\text{O}$). One-way ANOVA analysis revealed there was significant difference in both surface roughness parameters of silica-coated zirconia after chemical treatments and the surface topography varied depending on the acid treatment.

Keywords: surface treatment; hydroxylation; binding energy; surface roughness

1. Introduction

In dentistry, it is desirable that strong bonding is achieved between materials and dental tissues to ensure that the material, for example, as a dental restoration, survives in the oral environment. Zirconia has found wide applications in dental restorations such as crowns, bridges and implant abutments because of its high fracture toughness, semi-translucency, radiopacity and, most importantly, biocompatibility [1]. However, the bonding between resin cement and zirconia is relatively weak. The shear bond strength between yttria-stabilized zirconia and resin composite is reported to be only about 1.5 MPa, without any pretreatment or use of primer [2].

Many investigations have reported that the bond strength of resin cement to zirconia ceramic is greatly affected by surface modifications of zirconia. Methods such as acid etching by hydrofluoric acid (HF), air-particle abrasion using alumina of various particle sizes, sand-blasting with 3M ESPE Rocatec Pre (110 μm alumina), Plus (110 μm silica-coated alumina) or Soft (30 μm silica-coated alumina) and, more recently, laser irradiation are reported to improve adhesive strength [3-11]. Apart from HF acid etching, these methods mainly bring about physical changes of the surface topography of zirconia by different mechanisms to increase the surface roughness. Increased surface roughness in turn results in increased surface energy and better wetting for bonding. In principle, an alternative zirconia surface treatment is the chemical treatment by reaction with concentrated strong acids and bases [12].

At ambient temperature and humidity, a certain quantity of hydroxyl groups is formed on the surface of yttria-stabilized zirconia. The density of hydroxyl groups increases after treatment with concentrated acid [13]. Conceptual diagrams can illustrate this process for simplified 2D (Fig. 1) and a more realistic 3D surface mesh (Fig. 2). The zirconia surface must be silica-coated, because zirconia is inert and bond strength between resin composite and silanized zirconia is relatively weak [2]. When a silane solution after hydrolysis converts to the silanol ($\equiv\text{Si}-\text{OR}\rightarrow\equiv\text{Si}-\text{OH}$) and is then applied onto the silica-coated zirconia surface, the silanol reacts with surface hydroxyl groups by condensation to form siloxane bonds ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$). Therefore, the more hydroxyl groups there are on the surface of silica-coated zirconia, the higher the degree of bonding there will be between the silane primer and the silica-coated zirconia surface. More energy is required to break through the interfacial layer. The result is thus a strengthening of the adhesion between the resin cement and the silicatized and silanized zirconia.

In the present *in vitro* investigation, we studied surface treatments of yttria-stabilized zirconia with different mineral acids at room temperature. All surfaces were polished and sandblasted before acid treatment. These mineral acids are commonly used for etching on most metal surfaces in various industries. The quantitative atomic composition, the change of chemical states of Si and Zr and surface topography after various surface treatments were examined by x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The study provides valuable information on the future study of the shear bond strength between resin cement and silica-coated and silanized zirconia in dentistry [14, 15]. The hypotheses of this study were that acid

treatment leads to (1) a surface chemical reaction, *i.e.* hydroxylation, on the surface of silica-coated zirconia, and (2) changes of surface topography and surface roughness.

2. Experimental

2.1. Sample preparation

The materials used in this study are shown in Table 1. Ten samples of yttria-stabilized dental zirconia (Nobel Biocare, Göteborg, Sweden) were used for this investigation. The surfaces of all samples were polished with 400-grit silicon carbide paper. After polishing, the samples were placed in a beaker filled with 70% ethanol, cleaned in an ultrasonic bath (Decon Ultrasonics Ltd, Hove Sussex, England) for 10 min, rinsed with 70% ethanol and then air-dried at room temperature. One sample was left untreated as a control. The surfaces of eight zirconia samples were silica-coated by sandblasting using Rocatec Soft (3M ESPE, Seefeld, Germany) at a pressure of 280 kPa for 30 s/cm² at a perpendicular distance of 10 mm. The eight sandblasted samples were placed in a beaker of 70% ethanol, cleaned in the ultrasonic bath for 10 mins and air-dried at room temperature. Surfaces of two samples were etched by 5% HF gel (Ivoclar Vivadent AG, Liechtenstein) for 20 s according to the instruction manual and rinsed with deionized water and air dried at room temperature. When dry, one sample was further treated for 4 h in 69%-71% nitric acid (BDH, Poole, United Kingdom), whereas the other was treated for 4 h with Piranha solution (4:1 v/v of 98% sulphuric acid and 30% hydrogen peroxide (Merck, Darmstadt, Germany)). The surfaces of the other five

sandblasted zirconia samples were treated for 4 hr with 69%-71% nitric acid; Piranha (4:1 v/v 98% sulphuric acid and 30% hydrogen peroxide); 35.4% hydrochloric acid (BDH, Poole, United Kingdom); 85% phosphoric acid (Peking Chemical Works, Peking, China); and 5% HF gel. All specimens were rinsed with deionized water and air dried after treatment. Finally, one sample was sandblasted for 60 s/cm² only as a control. The surface treatments are summarized in Table 2.

2.2. Surface analysis

2.2.1.) XPS

The chemical composition of the surfaces of the samples was examined by XPS using a Perkin-Elmer PHI 5400 spectrometer that had a mean radius of 140 mm and was equipped with a resistive anode detector. The ionization source was Mg K α radiation ($h\nu=1253.6$ eV) from a twin-anode x-ray tube. Broad-range survey scans were performed to determine atomic concentration, at a pass energy of 89.45 eV and an entrance slit width of 4 mm. High-resolution narrow-range scans were also performed at a pass energy of 37.75 eV for selected specific photolines (Zr 3d, Si 2p, C 1s) to determine the chemical shifts. The base pressure in the chamber was maintained at about 6×10^{-10} Torr and the x-ray tube was operated at 200 W. The C 1s photopeaks were used to calibrate the binding energy scale of the high-resolution spectra for chemical shift measurements. The peak composition and energy positions were then determined using the least-squares curve-fitting technique in Igor Pro analysis environment with SPANCF macro package [16].

2.2.2.) AFM

The surface topography of the zirconia samples was examined by AFM using the Autoprobe CP (Park Scientific Instruments, CA, USA). All measurements were carried out at room temperature in the non-contact mode by means of the Autoprobe CP's Nano World NCSTR tip. Surface topography images were scanned over three different areas of 50x50 μm for each sample. Numerical parameters of surface roughness were determined from each scan.

3. Results and Discussion

3.1. XPS analysis

Zirconia surface modification by chemical reaction with various acids after sandblasting was investigated in this study. The change of state of zirconium and silicon on the surface of silica-coated zirconia after acid treatment reflects chemical reactions involving silica and zirconia, *i.e.* hydroxylation. According to the XPS analysis of the clean zirconia surface without any surface treatment consisted only of elemental C, O, Zr, Y, Al (Table 3). Wide scan x ray spectra and XPS analysis showed variations in atomic composition for zirconia samples under various treatments (Figs. 3a-3c and Table 4). Trace amounts of Al, F, N and P were also detected. Al comes from sandblasting. The Si content comes from the polishing with SiC paper and sandblasting with silica-coated

alumina, whereas other elements may come from polishing, sandblasting, rinsing and cleaning or acid treatment steps.

On the silica-coated zirconia surface, there are Zr-O- and Si-O- (dangling O), -Zr-O-Zr- and -Si-O-Si- (bridging O), Zr-OH (hydroxyl) and Si-OH groups, but oxide groups are mainly present. After chemical treatment with acids, a proportion of the surface oxide groups are converted to Zr-OH and Si-OH. The XPS spectra of binding energies of Zr 3d_{3/2}, 3d_{5/2} and Si 2p peaks after various surface treatments are shown in Figs. 4a-4b and the values are tabulated in Table 5.

The reported values for binding energies 3d_{5/2} of hydrous zirconia and 10% yttria-stabilized zirconia are 181.8 and 182.7 eV, respectively [17, 18]. The ratio of Y to Zr in the sample used in this study was determined by XPS analysis of the Zr clean surface under an ultra-high vacuum (2x10⁻⁸ mbar). From Table 3, the atomic concentration of Y is 2.4 % and Zr is 23.9%. So, the ratio of Y to Zr is 2.4/23.9 = 0.1. Hence, it can be concluded that the sample used consisted of 10% yttria-stabilized zirconia.

The binding energies of Zr 3d_{5/2} of the 10 zirconia samples lay within the range of 181.7 to 182.2 eV (Table 5). This peak contained two components: hydroxylated zirconia (Zr-OH) and yttria-stabilized zirconia (Y₂O₃-ZrO₂). The 3d photoelectron peaks were resolved into two components: the oxide (Y₂O₃-ZrO₂) and the hydroxide (Zr-OH), in the region of 178 to 186 eV according to curve fitting (Table 6). An example of curve fitting is shown in Fig. 5a for sample 6. The first peak component of Zr 3d_{5/2} for 10 samples lay between 181.7 and 182.2 eV, which is close to the reported value of 181.8 eV for hydrous

zirconia. The second peak component of Zr 3d_{5/2} for 10 samples lay between 182.3 and 183.0 eV, which is close to 182.7 eV for 10% yttria-stabilized zirconia. As a result, the chemical state of zirconium changed from zirconia to hydrous zirconia.

XPS analysis of Si 2p peaks showed that elemental silicon was also present. The Si 2p photoelectron peaks were resolved into three components: the element, oxide and hydroxylated silica in the region of 96 to 104 eV. An example of Si curve fitting is shown in Fig. 5b for sample 6. The binding energies of Si peak structures resolved by curve fitting are tabulated in Table 7. The first peak binding energies of samples 1-9 lay between 99.1 and 99.7 eV, which corresponds to elemental Si. However, the presence of elemental silicon detected from polishing with SiC is negligibly small. For specimen 10, the atomic concentration of elemental Si was beyond the detection limit of the XPS spectrometer. The second peak binding energies for the 10 samples lay between 101.0 and 101.6 eV owing to SiO_x where x ranges from 1 to 2. The third peak binding energies for 10 samples lay between 102.1 and 102.5 eV, which corresponds to hydrous silica. The reported binding energy is 102.6 eV for SiO, and 103.0 eV for SiO₂ whereas for hydrous SiO₂·nH₂O it is 103.5 eV [19]. The shift in binding energies for the SiO₂ and hydrous silica Si 2p peaks to lower values is due to the bonding of silica to zirconia (-SiO₂-ZrO₂-) on the surface layer after the sandblasting process.

For samples 1, 2 and 10, which were not treated with acids, surface hydroxylation also occurred. Probably, the silicized zirconia surface was hydroxylated during rinsing with 70% ethanol in the ultra-sonic bath. The application of ultrasound would speed up

the rate of hydroxylation which varies with the vibration frequency applied. However, we did not study the hydroxylation of the zirconia surface in acid solution by the ultrasonic method using an ultrasonicator. This would be a topic for future study.

Huang *et al.* [20] pointed out the difference between zirconium hydroxide ($\text{Zr}(\text{OH})_4 \cdot n\text{H}_2\text{O}$) and hydrous zirconia ($\text{ZrO}_2 \cdot n\text{H}_2\text{O}$), in that the binding energies of Zr $3d_{5/2}$ in zirconium hydroxide and hydrous zirconia are 183.6 eV and 181.8 eV, respectively. In contrast, the reported value for Zr $3d_{5/2}$ for zirconia is 182.2 eV [20]. Structures of zirconium hydroxide and hydrous zirconia were proposed by Huang *et al.* [20] to underlie the difference between the two compounds. Both structures contain hydroxyl groups on the first layer of the structure. The difference lies in the inner bulk structure because the Zr ions are linked by a pair of OH bridges in zirconium hydroxide but by O bridges in hydrous zirconia. Basically, the inner bulk structure of hydrous zirconia resembles that of zirconia. This resemblance may explain why the binding energy of Zr $3d_{5/2}$ in hydrous zirconia is close to that of zirconia, but is higher in zirconium hydroxide. Given these facts and the results, we may conclude that the silica-coated zirconia surface after various acid treatment, is changed from silica-coated zirconia ($\text{SiO}_2\text{-ZrO}_2$) to hydrous silica-coated zirconia ($\text{SiO}_2\text{-ZrO}_2 \cdot n\text{H}_2\text{O}$).

On the surface of zirconia, the dangling bonds of surface oxygen atoms are the reactive site for surface chemical reactions. Tamura *et al.* [21] reported that the surface hydroxyl site density (mol/m^2) of various metal oxides were similar. They suggested a common mechanism of surface hydroxylation for different oxides, — namely, closely

packed lattice oxide ions instead of lattice metal ions are exposed to the surface because of their large anionic size and low polarizability. These ions are not fully coordinated to the lattice metal ions and act as strong Lewis bases which react with water and acid when the zirconia surface is treated with acid. Hydroxyl groups are formed on the surface oxide layer. A suggested mechanism for hydroxylation of silica-coated zirconia surface by acid treatment is shown in Fig. 6. The extent of hydroxylation depends on the type of acid and the duration and temperature of treatment. In this study, the duration and temperature for the surface treatments were kept at constant for 4 hr and at room temperature, respectively, for each acid. In general, use of a stronger and more concentrated acid, higher temperature and longer treatment time would yield a greater extent of hydroxylation. A high temperature ($\geq 200^{\circ}\text{C}$) for surface treatment is not recommended because this would cause dehydroxylation [22].

3.2. AFM analysis

The AFM images showing the detail of surface topography for each sample are shown in Fig. 7. The root mean square (R_{rms}) and average surface roughness (R_a) coefficients (Table 8) were calculated using the following equations, with z coordinate as the scanned area:

$$R_{\text{rms}} = \sqrt{\frac{\sum_{n=1}^N (z_n - \bar{z})^2}{N-1}} \quad (1)$$

$$R_a = \sum_{n=1}^N \frac{|z_n - \bar{z}|}{N} \quad (2)$$

The mean surface roughness for both surface parameters was analyzed by one-way analysis of variance (ANOVA) at a significant level of $p < 0.05$.

One-way ANOVA analysis revealed that there is significant difference of surface roughness among the 10 samples with different surface treatments ($p < 0.002$ for R_{rms} and $p < 0.002$ for R_a). There is also significant difference in surface roughness ($p < 0.0001$ for R_{rms} and $p < 0.0001$ for R_a) for different acid treatments (samples 3-9). However, there is no significant difference in surface roughness of zirconia between samples 2 and 10 for sandblasting 30 s and 60 s without acid treatment ($p > 0.3$ for R_{rms} and $p > 0.4$ for R_a), suggesting there is no marked effect in doubling the sandblasting time. The principle of sandblasting in dentistry is bombardment of high-energy particles (30 μm silica-coated alumina particles in this case) onto the zirconia ceramic surface to increase the surface roughness and thus surface area for better mechanical retention of the dental restoration.

There were changes in topographical features of the surface for the 10 samples after different surface treatments. The surfaces in all images were, in general, irregular with hillocks and deep pores (Fig. 7).

4. Conclusion

In this study, the effect of various acid treatments on silica-coated zirconia surface has been assessed by XPS and AFM analysis. Chemical reactions occurred between the

silica-coated zirconia surface and different acids. The chemical states of zirconium and silicon changed from silica-coated zirconia to hydrous silica-coated zirconia. Statistically significant difference was found for both surface roughness parameters of silica-coated zirconia by chemical treatments.

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Figure captions

Fig. 1. A conceptual schematic diagram of hydroxylation of silica-coated zirconia surface by reaction of different acids with some dangling oxygen bonds on the surface.

Fig. 2. Conceptual diagram of 3D zirconia surface mesh showing hydroxylation of silica-coated zirconia surface after acid treatment, O-bridges linking Zr and Si atoms and some O dangling bonds.

Fig. 3a). Wide scan of x-ray spectra of samples 1-3.

Fig. 3b). Wide scan of x-ray spectra of samples 4-6.

Fig. 3c). Wide scan of x-ray spectra of samples 7-10.

Fig. 4a). Variation of binding energy peaks of Zr 3d peaks under various surface treatments.

Fig. 4b). Variation of binding peaks of Si 2p peaks under various surface treatments.

Fig. 5a). Curve fitting of Zr 3d peaks structure for sample 6.

Fig. 5b). Curve fitting of Si 2p peaks structure for sample 6.

Fig. 6. Formation of hydroxyl groups on the surface of silica-coated zirconia using sulphuric acid as an example for illustration (modified from Tamura *et al.* [21]). Key: large white circles represent lattice oxide ions, small dark grey circles represent silicon ions and small dark circles represent lattice zirconium ions.

Fig. 7. AFM images of samples 1-10 after different surface treatments.

Table 1. Materials used in the study.

Materials	Chemical formula	Manufacturer	Composition	Lot. number
Procera zirconia	$Y_2O_3-ZrO_2$	Nobel Biocare, Göteborg, Sweden	Yttria stabilized zirconia	N.A.
Rocatec Soft	$SiO_2-Al_2O_3$	3M ESPE, Seefeld, Germany	30 μ m silica-coated alumina	353587
Hydrofluoric acid	HF	Ivoclar Vivadent AG, Liechtenstein	5% etching gel	671242
Sulphuric acid	H_2SO_4	BDH, Poole, United Kingdom	98%	5748880B
Hydrogen peroxide	H_2O_2	Merck, Darmstadt, Germany	30%	7247652
Nitric acid	HNO_3	BDH, Poole, United Kingdom	69-71%	10168
Hydrochloric acid	HCl	BDH, Poole, United Kingdom	35.4%	K31897252
Phosphoric acid	H_3PO_4	Peking Chemical Works, Peking, China	85%	798414

Table 2. Summary of various treatments on zirconia surfaces.

Sample	Surface treatment conditions
1	Polishing the surface of zirconia with a 400-grit silicon carbide paper
2	i) Polishing, ii) Sandblasting (30 s/cm ²) using Rocatec Soft sand (30- μ m silica-coated alumina) of the surface of zirconia
3	i) Polishing ii) Sandblasting, iii) 5% HF etching gel (20 s), iv) 69%-71% HNO ₃ (4 hr)
4	i) Polishing, ii) Sandblasting, iii) 5% HF etching gel (20 s), iv) 4:1 v/v 98% H ₂ SO ₄ and 30% H ₂ O ₂ (4 hr)
5	i) Polishing, ii) Sandblasting, iii) 69 - 71% HNO ₃ (4 hr)
6	i) Polishing, ii) Sandblasting, iii) 4:1 v/v 98% H ₂ SO ₄ and 30% H ₂ O ₂ (4 hr)
7	i) Polishing, ii) Sandblasting, iii) 35.4% HCl (4 hr)
8	i) Polishing, ii) Sandblasting, iii) 85% H ₃ PO ₄ (4 hr)
9	i) Polishing, ii) Sandblasting, iii) 5% HF etching gel (20 s)
10	i) Polishing, ii) Sandblasting (60 s/cm ²) using Rocatec Soft sand (30- μ m silica-coated alumina) of the surface of zirconia

Table 3. Atomic concentrations % of clean zirconia surface.

Atomic concentration / %				
C 1s	O 1s	Al 2p	Zr 3d	Y 3d
17.3	54.6	1.7	23.9	2.4

Table 4. Atomic concentrations % of zirconia samples after various surface treatments.

Atomic concentration / %

Sample	C <i>1s</i>	N <i>1s</i>	O <i>1s</i>	F <i>1s</i>	Si <i>2p</i>	Zr <i>3d</i>	Al <i>2p</i>	S <i>2p</i>	P <i>2p</i>
1	39.4	1.3	37.7	1.4	6.0	10.6	2.9	4.2	0.7
2	52.0	2.0	31.1	0.9	1.8	9.4	2.1	3.7	0.7
3	55.9	3.0	28.3	0.5	1.6	8.7	0.7	3.5	1.1
4	55.5	2.4	27.6	1.0	2.6	9.3	0.9	4.0	0.6
5	59.9	2.3	24.6	0.9	2.5	8.0	1.0	3.3	0.8
6	50.1	1.5	31.0	0.5	1.8	12.9	1.3	5.7	0.7
7	68.2	3.1	18.6	1.5	2.4	5.0	0.7	2.0	0.6
8	57.4	2.0	25.0	0.4	2.2	9.8	1.6	4.3	1.5
9	63.0	1.8	26.0	1.3	1.7	5.4	0.5	2.4	0.3
10	58.4	1.3	24.5	0.3	5.4	4.5	5.4	2.0	0.2

Table 5. Binding energies of Zr 3d and Si 2p peaks.

Sample	Binding energy / eV		
	Zr 3d _{3/2}	Zr 3d _{5/2}	Si 2p
1	184.4	182.0	102.0
2	184.3	181.9	101.8
3	184.0	181.7	102.0
4	184.3	181.9	102.0
5	184.3	181.9	101.8
6	184.1	181.7	101.6
7	184.6	182.2	101.8
8	184.2	181.7	101.8
9	184.4	182.0	102.1
10	184.4	182.0	102.6

Table 6. Curve fitting of Zr 3d peaks of 10 samples.

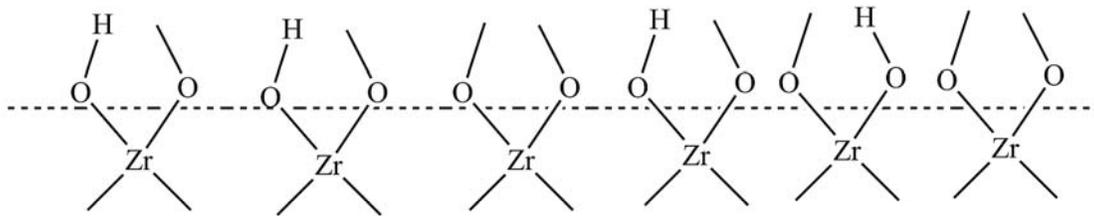
Sample	Profile 1		Profile 2	
	3d _{5/2}	3d _{3/2}	3d _{5/2}	3d _{3/2}
1	181.9	184.3	182.5	184.9
2	182.0	184.4	182.6	185.0
3	181.7	184.1	182.3	184.7
4	181.9	184.3	182.4	184.8
5	181.9	184.3	182.7	185.0
6	181.7	184.1	182.3	184.7
7	182.2	184.6	183.0	185.4
8	181.8	184.2	182.4	184.8
9	181.9	184.3	182.6	184.9
10	182.1	184.4	182.7	185.1

Table 7. Curve fitting of Si 2p peaks of 10 samples.

Sample	Profile 1	Profile 2	Profile 3
1	99.4	101.5	102.3
2	99.4	101.2	102.1
3	99.5	101.2	102.2
4	99.3	101.5	102.3
5	99.3	101.2	102.1
6	99.1	101.0	102.1
7	99.7	101.4	102.3
8	99.2	101.3	102.2
9	99.5	101.5	102.2
10	-	101.6	102.5

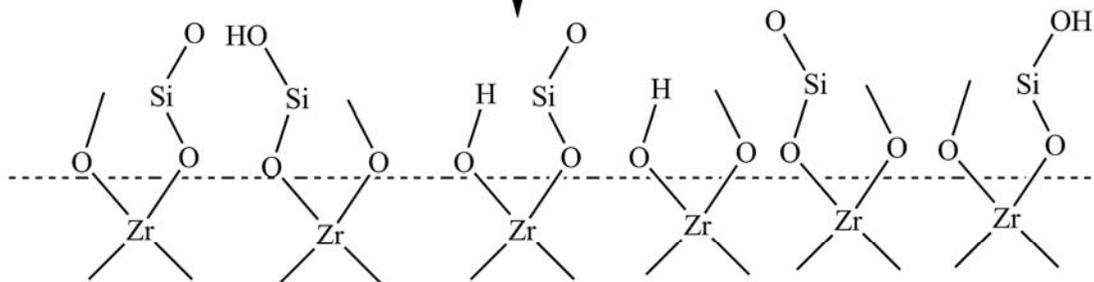
Table 8. Mean and standard deviation (SD) of root mean square (R_{rms}) and average surface roughness (R_a).

Sample	$R_{rms} \pm SD / \mu\text{m}$	$R_a \pm SD / \mu\text{m}$
1	0.18 ± 0.02	0.123 ± 0.006
2	0.2 ± 0.2	0.17 ± 0.07
3	0.21 ± 0.01	0.16 ± 0.01
4	0.13 ± 0.02	0.09 ± 0.02
5	0.20 ± 0.03	0.13 ± 0.03
6	0.17 ± 0.05	0.13 ± 0.03
7	0.13 ± 0.04	0.09 ± 0.03
8	0.09 ± 0.03	0.06 ± 0.02
9	0.13 ± 0.02	0.10 ± 0.02
10	0.18 ± 0.02	0.14 ± 0.02



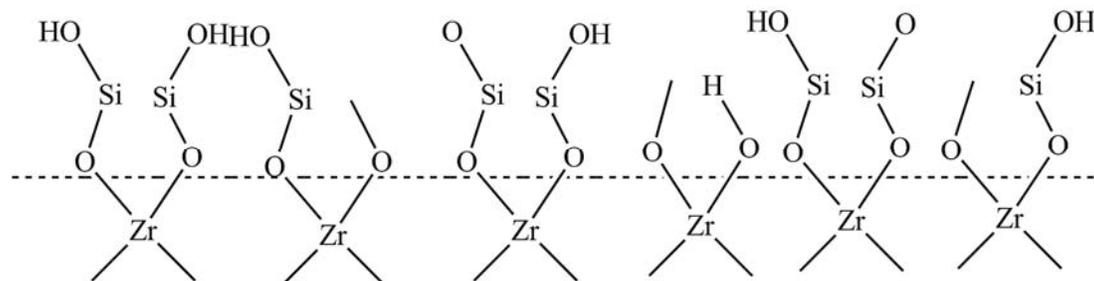
Partially hydroxylated zirconia surface at ambient temperature

sandblasting using 30 μm silica-coated alumina

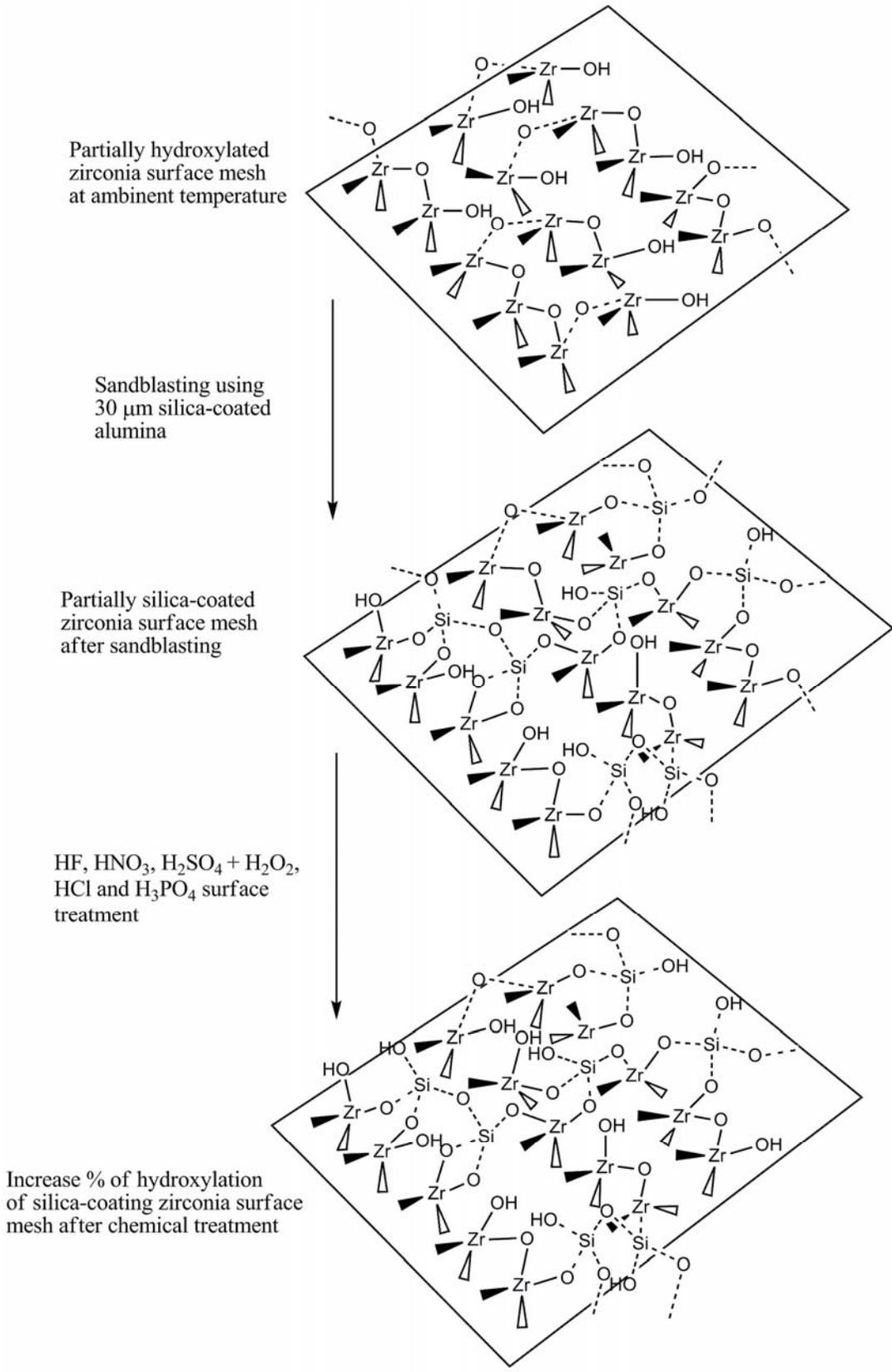


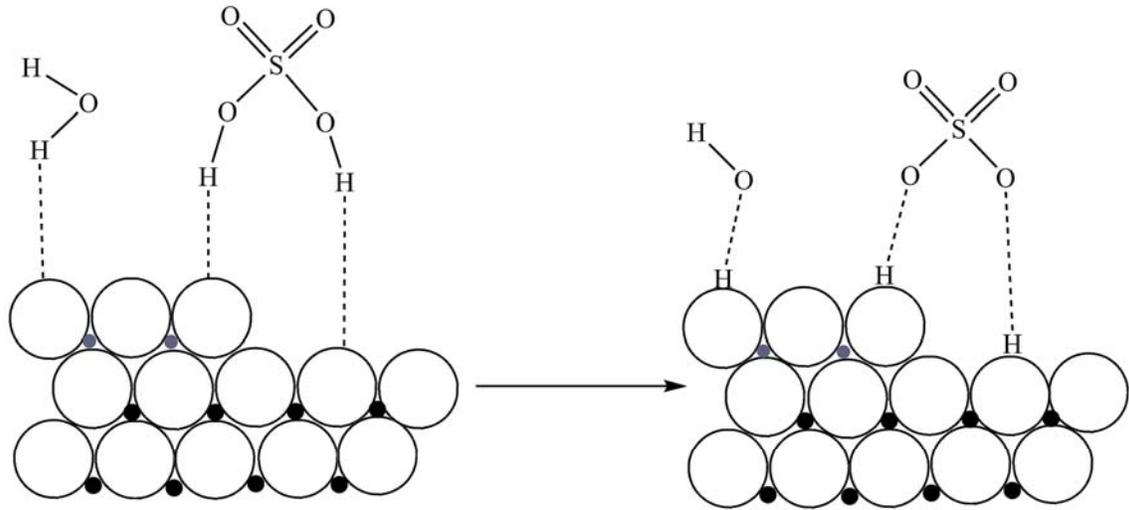
Partial silica-coated zirconia surface after sandblasting

HF, HNO₃, H₂SO₄ + H₂O₂, HCl
and H₃PO₄ surface treatment



Increase % of hydroxylation of silica-coating zirconia surface after chemical treatment

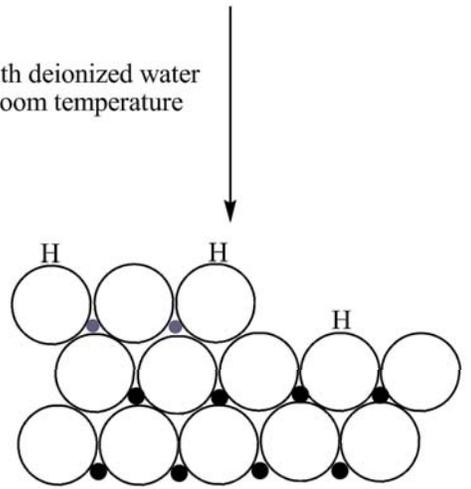




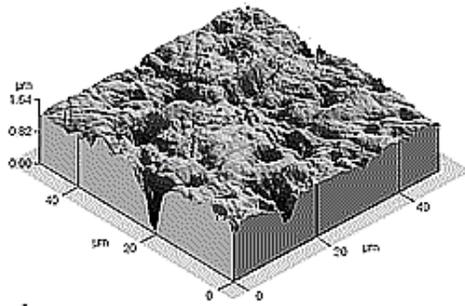
Partial silica-coated zirconia surface layer



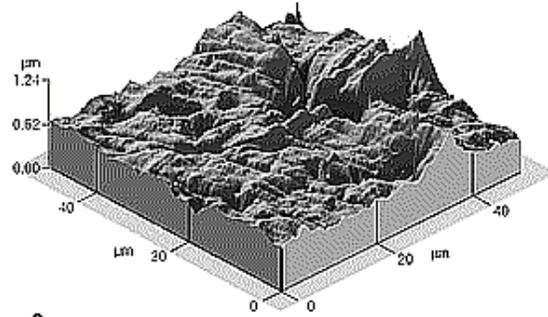
After rinsing with deionized water and air-dried at room temperature



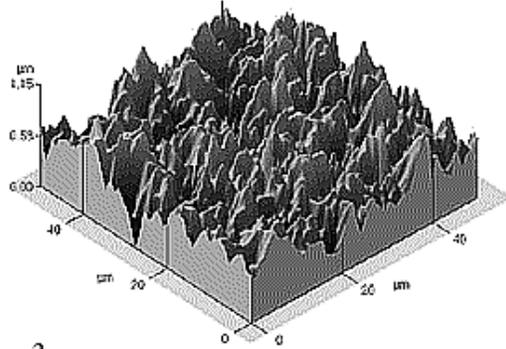
Formation of hydroxyl groups on the silica-coated zirconia surface after treatment with concentrated sulphuric acid



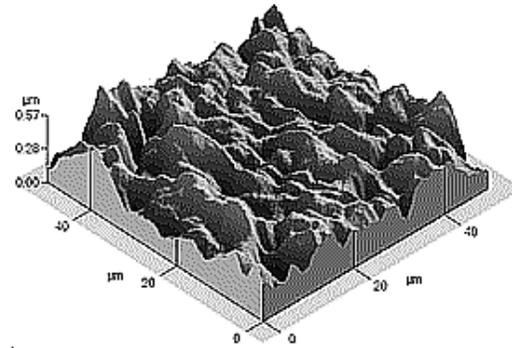
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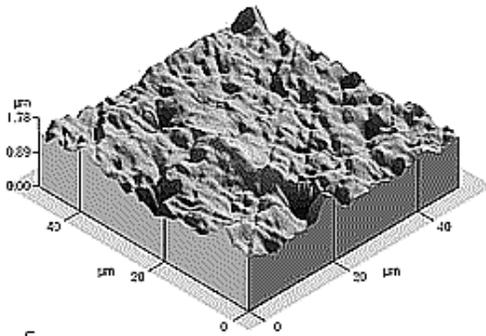
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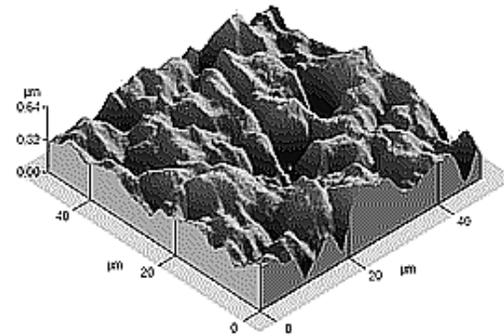
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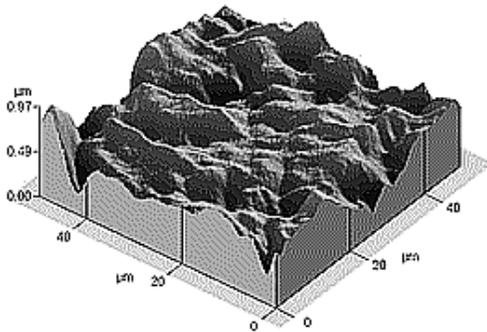
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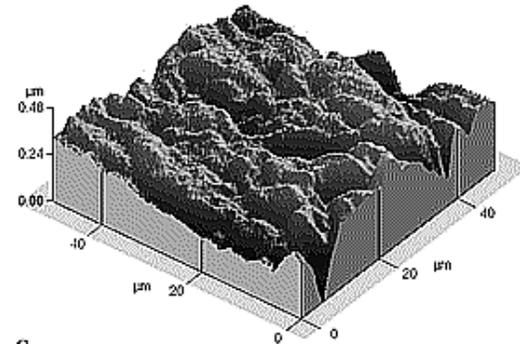
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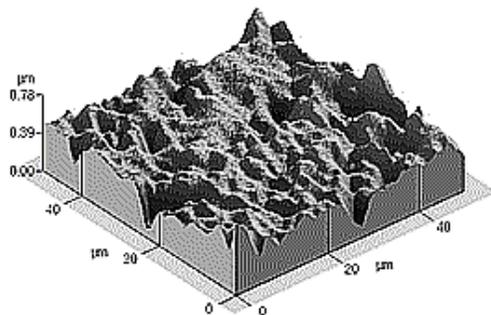
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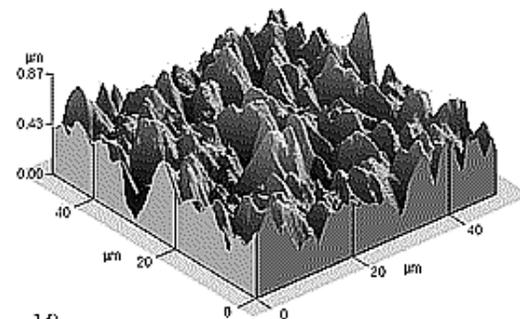
7.



8.



9.



10.