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Influence of plasma treatment on surface properties of zirconia

Yuki Ito, Takahisa Okawa, Takamasa Fujii and Masahiro Tanaka

Department of Fixed Prosthodontics and Occlusion, Osaka Dental University, 8-1 Kuzuhahanazono-cho, Hirakata-shi, Osaka 573-1121, Japan

We investigated the influence of atmospheric-pressure low-temperature plasma treatment on the surface properties of zirconia. After polishing zirconia sections up to #800 with a waterproof abrasive paper, ultrasonic cleaning was performed in acetone and distilled water. Surface treatment was conducted in three groups : non-treated (control), alumina sandblast-treated (Sb), and atmospheric-pressure low-temperature plasma-treated (Ps) groups. The surface properties were examined for surface roughness, scanning electron microscopy (SEM) properties, contact angle, and X-ray photoelectron spectroscopy (XPS) properties.

No changes in the surface roughness and SEM observations were noted for Ps. Wettability was enhanced by Sb and Ps with respect to the contact angle. Ps showed the lowest contact angle. XPS analysis revealed that Ps remarkably reduced the amount of carbon, allowing removal of contaminants. Atmospheric-pressure low-temperature plasma treatment enables the removal of carbon derived from organic contaminants and improves wettability without increasing the surface roughness of the sample. Therefore, it can be considered a new pre-adhesion treatment method in clinical dental practice. (J Osaka Dent Univ 2016 ; 50 : 79-84)

Key words : Plasma treatment ; Contact angle ; Surface roughness ; XPS

INTRODUCTION

Recently, zirconia has been extensively applied in the field of crown restoration.[1, 2] Usually, an alumina sandblast treatment is performed as a surface treatment before adhesion.[3, 4] However, zirconia is prone to alteration of its physical characteristics, and thus, is not considered suitable for reliable bonding techniques.[5] To date, much research has been conducted on the influence of atmospheric-pressure low-temperature plasma treatment on the shear bond strength between zirconia and resin cement. The results confirmed that atmospheric-pressure low-temperature plasma treatment is as effective in increasing bonding strength as alumina sandblast treatment. Furthermore, it has been reported that a change in the surface crystalline structure of zirconia induced by the alumina sandblast treatment does not occur with atmospheric-pressure low-temperature plasma treatment.[6]

However, modification of the surface characteristics of zirconia by atmospheric-pressure low-temperature plasma treatment has not yet been studied. Therefore, we examined the influence of this treatment on the surface properties of zirconia based on the null hypotheses for multiple comparisons : (1) there is no increase in surface roughness when performing atmospheric-pressure low-temperature plasma treatment on zirconia, and (2) wettability is not enhanced by atmospheric-pressure low-temperature plasma treatment of zirconia.

MATERIALS AND METHODS

Tested materials and devices

In this study, zirconia was sourced from KATANA (Kuraray Noritake Dental, Tokyo, Japan). The sandblast treating device used was a Jet Blast II (Morita, Tokyo, Japan), and the atmospheric-pres-

sure low-temperature plasma treatment device used was a Piezo Brush PZ1 (Reinhausen Plasma, Regensburg, Germany).

Method for producing samples

After polishing zirconia sections up to #800 with a waterproof abrasive paper, ultrasonic cleaning was performed in acetone and distilled water for 15 min each. The surface-treated material was used as the test sample. The surface treatment methods included (1) a non-treated group (control), (2) an alumina sandblast-treated group (Sb), and (3) an atmospheric-pressure low-temperature plasma treated group (Ps). For (1), no surface treatment was performed after the ultrasonic cleaning. For (2), alumina sandblasting was performed using alumina with a particle size of 50-70 μm under an injection pressure of 0.3 MPa from an injection distance of 30 mm and for an injection time of 10 s. For (3), helium gas was used as the active gas in atmospheric-pressure low-temperature plasma treatment under irradiation at 0.2 MPa, for 30 s at 10 mm. Scanning electron microscopic (SEM) observations were done, the surface roughness was evaluated, the contact angle was measured, and X-ray photoelectron spectroscopy (XPS) analysis was performed.

Measurement of surface roughness

Thirty samples were prepared, ten for each surface treatment condition, and then their surface was evaluated using a surface roughness measuring instrument (Surfcorder SE 300, Kosaka Laboratory, Tokyo, Japan). The measured sample area was 2 mm $\times$ 2 mm, the operating speed was 0.5 mm/s, and the cut-off value was 0.8 mm.

SEM observation

The samples were analyzed with the S-4000 (Hitachi, Tokyo, Japan) scanning electron microscope. Because zirconia is not conductive, a platinum coating was applied to impart conductivity, using an E-1030 ion sputterer (Hitachi). Argon ion etching was performed for 40 s, followed by application of a platinum film and SEM measurements.

Contact angle measurement

Thirty samples were prepared, ten for each surface treatment condition, and their surface energies were probed via contact angle measurements using an LSE-ME 2 instrument (Nick, Saitama, Japan). For this purpose, a 1 μL droplet of distilled water was applied to the sample surface. Immediately after application, image analysis was performed using a digital camera mounted on the main body of the instrument. The software used for image analysis was i 2 win (Nick).

XPS

XPS measurements were carried out with a PHI X-tool (ULVAC-PHI, Kanagawa, Japan) under the following conditions: 15 kV, 48 W, an acquisition area of 204 μm, and a take-off angle of 45°; the neutralization conditions were 1.2 eV and 20.0 μA. The target elements for evaluation were C1s, O1s, Y3d and Zr3d for the control and Ps groups, and C1s, O1s, Y3d, Zr3d and Al2p for the Sb group. The measurement was performed 20 times for each case, and six samples were analyzed in each group.

Statistical analysis

Statistical analysis was performed by determining the mean value and standard deviation of the surface roughness and contact angle data, followed by a one-way analysis of variance with the surface treatment method as a factor. Multiple comparisons were performed by the Bonferroni method as a post-correction when statistically significant differences were observed. SPSS ver.19 (IBM, Armonk, NY, USA) was used for the statistical analysis. The significance level was set to 1%. Power analysis was performed to support the sample size. The statistical power (1-β) was calculated from the sample size, significance level, and effect size. The effect size ω^2_p was used for computations.[7, 8] G Power software (Ver. 3.1, Heinrich Heine University, Düsseldorf, Germany) was used for power analysis.[9]

RESULTS

Surface roughness measurement

The results of the variance analysis and effect size are shown in Table 1. The statistical power (1-β) was 0.97. Statistically significant differences were observed depending on the surface treatment method used. The results concerning surface roughness are shown in Fig. 1. According to the results of multiple comparisons, Sb (0.42 ± 0.04 μm) gave significantly higher values than the control (0.14 ± 0.01 μm) and Ps (0.15 ± 0.01 μm). No statistically significant differences were found between the control and Ps. Atmospheric-pressure low-temperature plasma treatment caused no increase in surface roughness.

SEM observation

The SEM images are shown in Fig. 2. For control and Ps, only defects caused by zirconia polishing could be observed, and there was no change in the Ps sample surface. The morphology of the sample surface changed remarkably in the case of Sb.

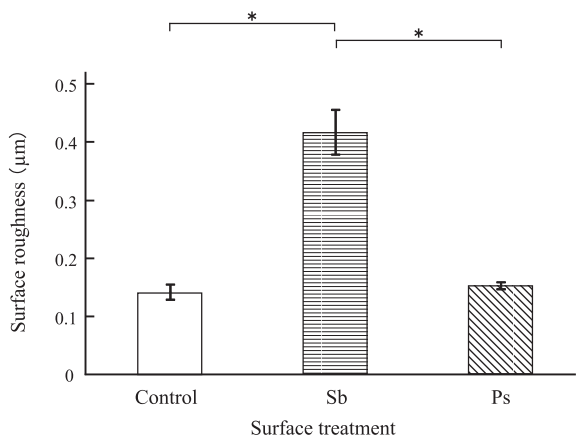
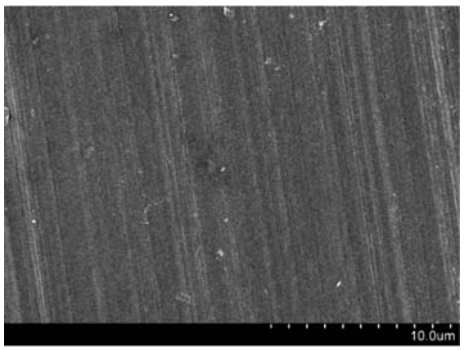
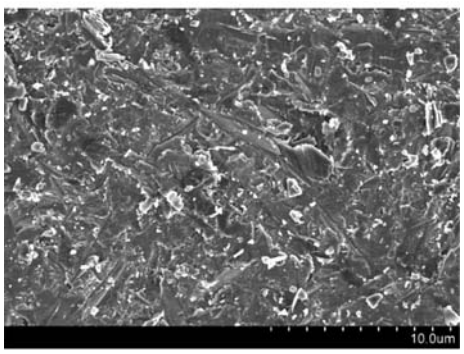


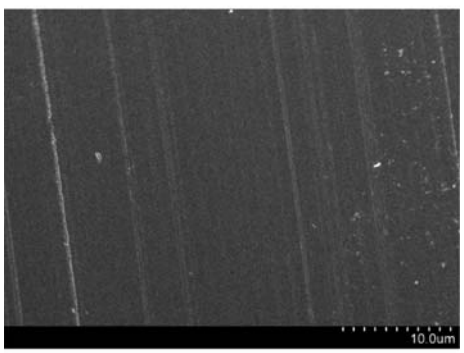
Fig. 1 Surface roughness (*p < 0.01, Mean ± SD).



A



B



C

Fig. 2 SEM images of (A) a control sample, (B) a sandblast treated sample, and (C) a sample with atmospheric-pressure low-temperature plasma treatment.

Table 1 Surface roughness one-way ANOVA and effect size

Source	Sum of squares	Degree of freedom	Mean squares	f-value	p-value	Effect size (ω^2_p)
Surface treatment	0.487	2	0.243	384.435	< 0.01	0.96
Error	0.017	27	0.001			
Total	0.504	29				

Contact angle tests

Examples of contact angles acquired with the image analysis software are shown in Fig. 3. The results of variance analysis and effect size are summarized in Table 2. The statistical power (1-β) was 0.97. Statistically significant differences were observed depending on the method of surface treatment. The contact angle test results are shown in Fig. 4. According to the results of multiple comparisons, statistically significant differences were found among the control ($49.8 \pm 2.4^\circ$), Sb ($20.8 \pm 3.5^\circ$) and Ps ($5.17 \pm 1.1^\circ$). Ps gave the lowest contact angle.

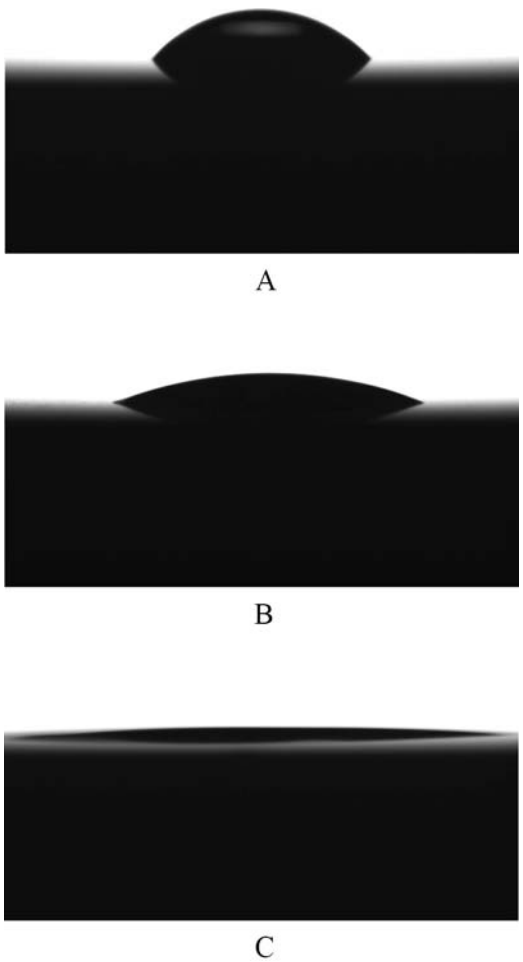


Fig. 3 Contact angle images of (A) a control sample, (B) a sandblast treated sample, and (C) a sample with atmospheric-pressure low-temperature plasma treatment.

XPS

The XPS results are shown in Table 3. Both Sb and Ps gave lower C values than the control; however, the decrease was more marked for Ps. Regarding O1s, Y3d and Zr3d, higher values were obtained for both Sb and Ps as compared with the control; however, the increase was more pronounced for Ps. The same trend could be observed for the other samples.

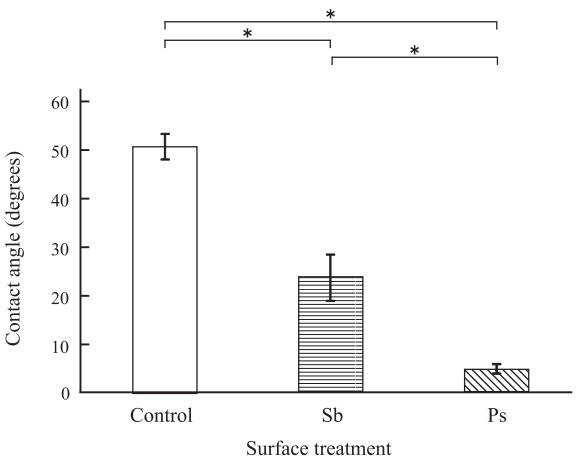


Fig. 4 Contact angle (*p＜0.01, Mean±SD).

Table 3 XPS analysis (%)

	C1s	O1s	Y3d	Zr3d	Al2p
Control	68.5	26.9	0.1	4.5	
Sb	46.6	36.5	9.5	7.1	9.5
Ps	20.6	60.6	0.9	17.9	

Table 2 Contact angle one-way ANOVA and effect size

Source	Sum of squares	Degree of freedom	Mean squares	f-value	p-value	Effect size (ω^2_p)
Surface treatment	10785.166	2	5392.583	384.435	＜0.01	0.97
Error	306.438	27	11.350			
Total	11091.604	29				

DISCUSSION

In this study, we examined the change in a superficial layer of zirconia subjected to atmospheric-pressure low-temperature plasma treatment. The function of the atmospheric-pressure low-temperature plasma device used for this purpose is based on the application of piezoelectricity. By utilizing mechanical piezoelectric resonance, the electric energy is amplified and high voltage created, whereby the active gas or the surrounding atmosphere becomes ionized and plasma is generated. Because there is no need for winding in this method, the equipment can be small and slim. Although plasma devices are also available, because of their need for a vacuum device, the degree of freedom for the treatment is small and the device is larger and more expensive. In comparison, the device we used was small and plasma was generated easily, making it suitable for chair-side usage in dental care, which is why this device was selected for this purpose.

Measurements showed no change in the surface roughness resulting from atmospheric-pressure low-temperature plasma treatment, despite the surface roughness of the samples being increased when sandblast treatment was used. Thus, the null hypothesis (1) was adopted. Assuming that minute changes cannot be tracked with a surface roughness measuring instrument, the occurrence of fine changes in the surface was probed via SEM. The SEM results revealed a marked unevenness in the surface because of the sandblast treatment, which caused the roughness. The image obtained after atmospheric-pressure low-temperature plasma treatment was conducted did not show significant differences compared with the control sample image. Surface roughness increases resulting from atmospheric-pressure low-temperature plasma treatment achieves etching via ionic impact.[10, 11] However, because the samples examined in this study were zirconia, a very hard substance, we believe there was no increase in surface roughness.

The contact angle test results demonstrated that both sandblast and atmospheric-pressure low-temperature plasma treatments caused an increase in wettability. This indicates rejection of the null hypothesis (2). Sandblast treatment of ceramic-type materials was reported to enhance wettability of the substance owing to the Kramer effect.[12] Nevertheless, better wettability could be attained by performing atmospheric-pressure low-temperature plasma treatment as compared to sandblast treatment. Atmospheric-pressure low-temperature plasma treatment introduces hydrophilic functional groups both into resin-type organic materials and inactive substances, such as zirconia and titanium.[13, 14] Better wettability enhances the compatibility of a primer with the sample surface and is believed to contribute to improved bonding strength.

The XPS results revealed that the carbon content derived from organic contaminants could be better removed by atmospheric-pressure low-temperature plasma treatment than by sandblasting. The impact of high-energy ions on the sample surface in an atmospheric-pressure low-temperature plasma treatment causes dissociation of the carbon bonds in the contaminants, which induces their evaporation.[15] The decrease in carbon content in this study was also likely caused by the same phenomenon. The increase in oxygen content is believed to be caused by greater exposure of metal oxide. Increased amounts of the elements Y and Zr also indicate exposure of a cut surface. The appearance of zirconia on the surface leads to an increase in the area of action with an adhesive monomer, which impacts the bonding strength. The reason for considering Al2p only for sandblast treatment was that the adhesion of alumina particles on the zirconia surface is unavoidable.

Given the limitations of this study, only helium gas could be employed in the equipment used for our investigations. However, gases like argon and nitrogen can also be used[16, 17] to generate atmospheric-pressure low-temperature plasma. Therefore, in the future it would be desirable to examine the effect of different gases by switching to the use of an atmospheric-pressure low-temperature plasma treatment apparatus suitable for multi-gas application. Furthermore, in this study, we performed the

experiments immediately after the surface treatment ; however, it may be productive to examine differences in the treatment effects over time.

CONCLUSION

We examined the influence of atmospheric-pressure low-temperature plasma treatment on the surface state of zirconia in terms of surface roughness, SEM data, contact angle measurements, and XPS analysis. We concluded that the surface roughness of zirconia does not increase even after atmospheric-pressure low-temperature plasma treatment. We found that both sandblast treatment and atmospheric-pressure low-temperature plasma treatment improved wettability, with better wettability being acquired with the latter. In addition, atmospheric -pressure low-temperature plasma treatment largely decreased the amount of Carbon originating from organic contaminants, resulting in exposure of zirconia on the surface. Accordingly, we conclude that atmospheric-pressure low-temperature plasma treatment is clinically useful as a pre-adhesion treatment.

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