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Study on the effect of crystal changes on acid resistance of erbium laser etched enamel surface

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To investigate the mechanism underlying high acid resistance of enamel after erbium laser etching. Forty-five premolars were collected and assigned to three groups. A 4×4×1 mm enamel sample was prepared, the left side was the control side, the right side was the treated side, which was treated with different surface treatments, including 35% phosphoric acid etching, Er:YAG laser etching, and Er,Cr:YSGG laser etching. The hydroxyapatite crystal size on the enamel surface of the samples was observed. The contents of Ca, P, O, F, Cl, C, Mg were detected. The crystallinity of the hydroxyapatite crystal was analyzed. After erbium laser etching, the enamel surface had high hydroxyapatite crystal size, beneficial content of chemical elements and crystallinity. The morphological and composition changes of crystals in the enamel surface after erbium laser etching may be one of the crucial mechanisms underlying the enhancement of acid resistance of enamel after erbium laser etching.

Keywords: Erbium laser etching, Crystal size, Chemical element, Crystallinity

INTRODUCTION

Enamel surface treatment is crucial before bracket and accessories bonding in fixed orthodontic treatment. 35%–37% phosphoric acid etching for treating enamel surfaces has been used as a traditional treatment method. The mechanism underlying this treatment involves creating a honeycomb appearance of the enamel surface to increase the bonding area of brackets. However, the demineralization of the enamel surface after acid etching reduces the acid resistance and hardness of the enamel surface, increasing the incidence of caries. In recent years, many attempts, including the modification of enamel binder and the use of antibacterial binder[1], or adding antibacterial sustained-release ingredients in brackets[1,2], as well as changing enamel surface treatment methods, such as laser etching to increase the acid resistance of enamel surface[3], have been made to reduce the incidence of caries around orthodontic brackets.

Erbium laser belongs to the mid-infrared band and has gradually become the most widely used laser in the oral clinic since it can effectively act on the hard tissues of teeth[4,5]. The enamel surface is mainly treated using Er:YAG laser at a wavelength of 2,940 nm and Er,Cr:YSGG laser with a wavelength of 2,780 nm[6]. Erbium laser is easily absorbed by water and hydroxyapatite in tooth hard tissue, causing the OH^- bond to break. Due to the rapid accumulation of energy, the pressure inside the tissue increases, leading to micro-explosion, disintegrating the hard tissue of the tooth[3]. In addition, the erbium laser has a shallow penetration depth, and the operation process is accompanied by water or air cooling, which can avoid pulp damage by the thermal effects of hard tissue. Therefore, erbium laser is theoretically suitable for the surface roughing of enamel.

Previous studies have demonstrated that erbium laser etching of enamel with appropriate parameters obtains shear bond strength (SBS) close to that of phosphoric acid etching in the initial bonding process[3,7,8]. When rebonding, there is a tendency for the SBS of Er:YAG laser etching group to be higher than that of the phosphoric acid etching group[9]. In addition, several studies have reported that erbium laser etching enhances the acid resistance of the enamel[9-14]. However, few studies have investigated the mechanism underlying the enhancement of the acid resistance of enamel. The mechanisms by which erbium laser enhances the acid resistance of enamel may include three aspects: changes in crystal size, chemical element contents, and crystallinity[10,15]. Melting of organic matter blocks the diffusion channel of enamel and delays demineralization[16,17]. And the micro-cracks on the enamel surface caused by laser etching capture the calcium, phosphorus, and fluoride ions which were released during demineralization, promoting enamel remineralization[10]. However, most of previous studies used erbium laser irradiation to remove decay or prevent caries. Enamel etching has different parameters and could have a different photothermal effect. Therefore, this study focused on the mechanism that enhances enamel acid resistance after erbium laser etching.

MATERIALS AND METHODS

According to the results of the pre-experiment, the sample size of each group was 15 premolars, so a total of 45 premolars free of caries, cracks, fillings or endodontic treatment were collected from 15 patients, three from each patient. The teeth of each patient were extracted from three different quadrants and assigned into three

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groups. The protocol for this study was approved by the human subjects ethics board of Xuanwu Hospital, Capital Medical University (Ethical Approval: LYWS [2019]008) and conducted in accordance with the Helsinki Declaration of 1975. After collection, the teeth were stored in a saline solution. All teeth were collected within six months, and the saline solution was replaced weekly to avoid bacterial growth.

A 4×4×1 mm enamel block was prepared from the buccal surface of each tooth (1 mm was the thickest part of the sample) (Fig. 1). The samples were marked left and right along the long axis of the clinical crowns. The left side was the control side that received no treatment. Transpore TM medical tape (Minnesota Mining and Manufacturing, St. Paul, MN, USA) was pasted on the left side along the labeled line. The right side was the treated side.

The following treatments were performed on the experimental sides of the samples (n=45): 35% phosphoric acid group (n=15), where the enamel surface was treated with 35% phosphoric acid gel etching for 30 s; Er:YAG laser etching group (n=15), in which the enamel surface was treated with Er:YAG laser (LiteTouch, Syneron, Yokneam, Israel) etching for 15 s. A 1.3×1.9 mm tip accompanied by water cooling was used for laser emission, with the laser positioned 2 mm from the tooth surface at 60° angle. The parameters of Er:YAG laser came from our initial study[8,18] and are detailed in Table 1; Er,Cr:YSGG laser etching group (n=15), where the enamel surface was treated with Er,Cr:YSGG laser (Waterlase, Biolaser, CA, USA) etching for 15 s. An MZ 6-6 tip accompanied by water and air cooling was used for laser emission, with the laser positioned 2 mm from the tooth surface at 60° angle. The Er,Cr:YSGG laser parameters were obtained from previous studies[19,20] and are detailed in Table 1.

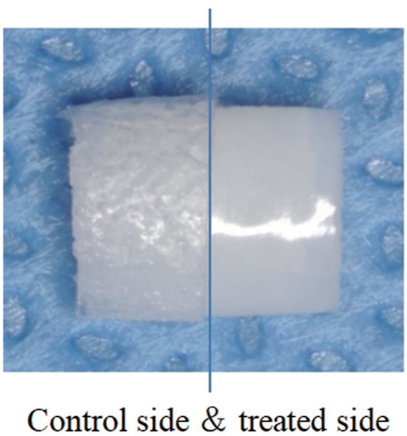

Fig. 1 A 4×4×1 mm enamel block prepared from the buccal surface of each tooth.
The sample was marked left and right along the long axis of the crowns. The left side was the control side, and the medical tape was pasted for protection.

Field emission scanning electron microscope (FESEM) observation of the crystal size on the enamel surface

The crystal size changes on the enamel surface of the samples were observed using FESEM (HITACHI Su8010, Tokyo, Japan).

X-ray photoelectron spectroscopy (XPS) test for the content of chemical elements on the enamel surface

The contents of Ca, P, F, Cl, O, C, Mg, CO_3^{2-}, PO_4^{3-}, and Ca/P on the enamel surface of the samples were quantified using XPS (Thermo escalab 250Xi, Cymofield, MA, USA) and AVantage software. Each side of the samples was tested three times to ensure the repeatability of the results.

X-ray diffraction (XRD) assessment of the crystallinity of the samples

Each sample from the control and treated side was sliced 500 um from the enamel surface and ground into powder. The crystallinity of the enamel crystals was analyzed using XRD (Smarlab, Japan).

Statistical analysis

Statistical analyses were performed using SPSS13.0 software. $p<0.05$ was considered statistically significant. Normally distributed XPS data for the three groups was analyzed using the Kolmogorov–Smirnov test.

Table 1 Treatment group parameters

Group	Parameters	Etching time (s)	Rinse and dry time (s)
35% phosphoric group	—	30	15
Er:YAG group	E 250 mJ F 30 Hz W 6/8	15	15
Er,Cr:YSGG group	E 83 mJ F 20 Hz W 45% A 55%	15	15

E: energy; Er:YAG: erbium-doped yttrium aluminum garnet; Er,Cr:YSGG: Erbium,chromium:yttrium-scandium-gallium-garnet; F: frequency; W: water; A: air

Differences in the changes of Ca, P, F, Cl, O, C, Mg, CO_3^{2-}, PO_4^{3-} and Ca/P on the enamel surface before and after treatment between groups were analyzed using the paired-sample *t*-test. Differences in the Ca, P, F, Cl, O, C, Mg, CO_3^{2-}, PO_4^{3-}, and Ca/P among the three groups were analyzed using independent-sample *t*-test.

RESULTS

FESEM observation of the crystal size on the enamel surface

FESEM images (Figs. 2 and 3) showed that the crystal size of the enamel surface on the control sides of the three groups was about 40–50 nm. After 35% phosphoric acid etching, the crystal gap increased, but no change was observed in the crystal size. However, after Er:YAG and Er,Cr:YSGG laser etching, the crystal size increased 2–3 times up to 100–150 nm. At the same time, the crystal gap increased slightly.

XPS test for the content of chemical elements on the enamel surface

The XPS results showed no significant difference in the contents of Ca, P, F, Cl, O, C, Mg, CO_3^{2-}, PO_4^{3-}, and Ca/P (p>0.05) among the three groups. The contents of the chemical elements on the enamel surface before treatments were close, so the baseline was consistent. After 35% phosphoric acid etching, the contents of Ca (p<0.001), P, O, PO_4^{3-}, and Ca/P (p<0.05) decreased. At the same time, the contents of C, CO_3^{2-} (p<0.001) and Mg (p<0.01) increased. The enamel surface resistance to acid was lower in the 35% phosphoric acid group due to the changes in the chemical elements on the enamel surface. While after Er:YAG laser etching, the contents of Ca, P, O, F, Cl, PO_4^{3-} (p<0.001), and Ca/P (p<0.01) increased. At the same time, the contents of C, Mg, and CO_3^{2-} (p<0.001) decreased significantly. After Er,Cr:YSGG laser etching, the contents of Ca, P, O (p<0.001), F (p<0.01), Cl, PO_4^{3-}, and Ca/P (p<0.05) were high. At the same time, the contents of C, CO_3^{2-} (p<0.001) and Mg (p<0.01) decreased significantly (Table 2). The number of elements that contribute to the enhancement of acid resistance of enamel increased, whereas the contents of elements against the enhancement of acid resistance of enamel decreased. The changes of the chemical elements in Er:YAG and Er,Cr:YSGG laser group enhanced the resistance of enamel to acid.

The comparison of changes of chemical element content on enamel surface showed that Ca, P, O, F, Cl, PO_4^{3-}, and Ca/P were significantly higher in the Er:YAG laser group than in the 35% phosphoric acid group, while C, Mg, and CO_3^{2-} were significantly lower in the Er:YAG laser group than in the 35% phosphoric acid group (p<0.001). The Ca, P, O, F (p<0.001), PO_4^{3-}, Ca/P (p<0.01) and Cl (p<0.05) were significantly higher in the Er,Cr:YSGG laser group than in the 35% phosphoric acid group, whereas C, Mg, and CO_3^{2-} (p<0.001) were significantly lower in the Er,Cr:YSGG laser group than in the 35% phosphoric acid group. F was significantly higher in Er:YAG laser group than in Er,Cr:YSGG laser group (p<0.05), whereas O was significantly higher in the Er,Cr:YSGG laser group than in the Er:YAG laser group (p<0.05). No significant difference was observed in the changes of Ca, P, Cl, PO_4^{3-}, C, Mg, CO_3^{2-} and Ca/P (p>0.05) between the two erbium laser etching groups (Table 3).

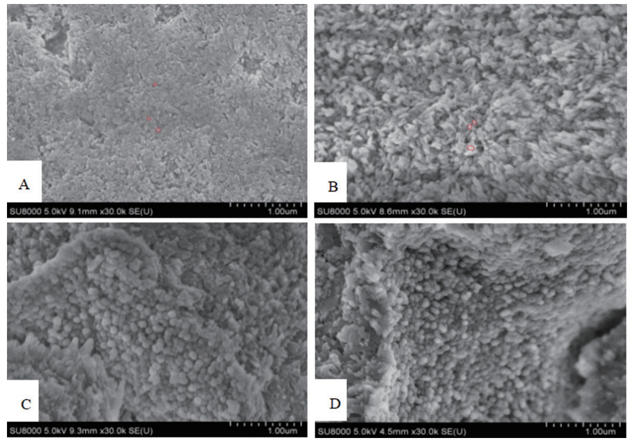

Fig. 2 FESEM images of crystal on enamel surface (×30,000).
Control group(A): the crystal size of the enamel surface was about 40-50nm. The 35% phosphoric group (B): the crystal gap increased, and the crystal size did not change. Er:YAG group (C) and Er,Cr:YSGG group (D): the crystal size increased 2–3 times up to 100–150 nm, and the crystal gap increased slightly.

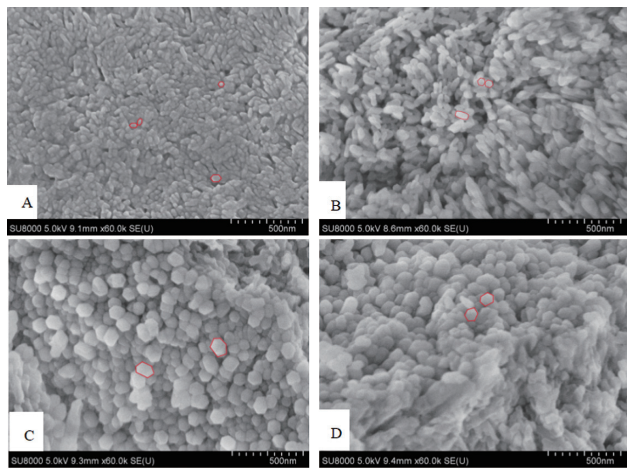

Fig. 3 FESEM images of crystal on enamel surface (×60,000).
Control group(A): the crystal size of the enamel surface was about 40-50nm. The 35% phosphoric group (B): the crystal gap increased, and the crystal size did not change. Er:YAG group (C) and Er,Cr:YSGG group (D): the crystal size increased 2–3 times up to 100–150 nm, and the crystal gap increased slightly.

Table 2 Chemical element content on enamel surface before and after different treatments (wt%)

Chemical elements	Acid (A group)			Er:YAG (B group)			Er,Cr:YSGG (C group)		
	A_0 ($\bar{x}$±s)	A_1 ($\bar{x}$±s)	P	B_0 ($\bar{x}$±s)	B_1 ($\bar{x}$±s)	p	C_0 ($\bar{x}$±s)	C_1 ($\bar{x}$±s)	p
P	9.28±0.74	7.76±1.12**	0.001	9.40±1.34	11.99±2.06***	<0.001	8.97±1.31	10.99±1.20***	<0.001
Ca	15.09±3.43	10.36±3.34***	<0.001	16.31±3.63	22.82±3.38***	<0.001	15.40±3.56	20.76±4.36***	<0.001
C	42.70±4.19	52.59±2.94***	<0.001	40.03±3.21	25.59±3.10***	<0.001	41.81±3.26	24.45±2.21***	<0.001
Cl	0.35±0.05	0.32±0.08	0.223	0.33±0.06	0.53±0.11***	<0.001	0.38±0.08	0.55±0.21*	0.034
O	31.39±4.27	27.54±2.93**	0.002	32.41±4.06	37.29±2.62***	<0.001	32.79±3.02	41.85±4.64***	<0.001
F	0.85±0.21	0.68±0.38	0.238	0.84±0.32	1.62±0.26***	<0.001	0.84±0.24	1.22±0.25**	0.001
Mg	0.34±0.13	0.75±0.37**	0.001	0.43±0.16	0.16±0.07***	<0.001	0.33±0.17	0.18±0.06**	0.005
CO_3^{2-}	3.84±0.96	5.40±1.20***	<0.001	4.03±0.87	1.70±0.24***	<0.001	3.69±1.12	2.00±0.63***	<0.001
PO_4^{3-}	8.27±1.83	6.51±1.86*	0.048	8.35±1.18	10.42±1.13***	<0.001	8.53±1.95	10.02±1.17*	0.039
Ca/P	1.61±0.40	1.34±0.41*	0.041	1.61±0.31	1.94±0.34*	0.012	1.64±0.46	1.88±0.32*	0.041

0: control side; 1: experimental side. *p<0.05, **p<0.01, ***p<0.001. wt%: percent by weight. Comparison between the baseline value of A_0, B_0, and C_0, p=0.154–0.983. There was no statistical difference in all tested elements.

Table 3 Comparison of changes in chemical element content on enamel surface before and after different treatments

Chemical elements	A_1–A_0 ($\bar{x}$±s)	B_1–B_0 ($\bar{x}$±s)	C_1–C_0 ($\bar{x}$±s)	P_{AB}	P_{AC}	P_{BC}
P	−1.67±1.12	2.98±1.65	1.85±1.63	<0.001***	<0.001***	0.33
Ca	−3.10±1.13	5.21±4.21	3.55±1.66	<0.001***	<0.001***	0.16
C	10.42±6.35	13.15±4.74	16.83±3.07	<0.001***	<0.001***	0.09
Cl	−0.01±0.11	0.21±0.13	0.07±0.13	<0.001***	0.016*	0.63
O	−5.94±5.79	4.31±7.55	11.13±3.58	<0.001***	<0.001***	0.02*
F	−0.12±0.63	0.71±0.35	0.37±0.31	<0.001***	<0.001***	0.02*
Mg	0.42±0.43	−0.28±0.19	−0.14±0.17	<0.001***	<0.001***	0.06
CO_3^{2-}	1.38±1.45	−2.27±1.09	−1.60±1.47	<0.001***	<0.001***	0.15
PO_4^{3-}	−0.34±3.37	2.12±2.30	0.87±2.07	<0.001***	0.004**	0.46
Ca/P	−0.02±0.30	0.22±0.51	0.15±0.35	<0.001***	0.004**	0.58

0: control side; 1: expreimental side. *p<0.05, **p<0.01,***p<0.001

XRD assessment of the crystallinity of the samples

The results showed that compared with the control side, the crystallinity of crystals on the enamel surface increased slightly after 35% phosphoric acid etching. The crystallinity of enamel surface crystals increased significantly after Er:YAG and Er,Cr:YSGG laser etching, and the diffraction peaks were sharper and higher. In addition, the crystallinity of enamel surface crystals was significantly higher in the Er:YAG laser group than in the Er,Cr:YSGG laser group (Fig. 4).

DISCUSSION

Different views have been proposed on the mechanism by which erbium laser etching enhances the acid resistance of the tooth enamel, including crystal changes[10,15], organic matter melting[16,17], and the appearance of the micro-cracks on the enamel surface[10]. Among the three possible mechanisms summarized above, this study focused on the changes in enamel crystals. Studies have revealed that there may be three changes in enamel crystals after erbium laser etching. The thermal effect of laser leads to the melting and recrystallization of hydroxyapatite crystals in the enamel at high temperature, increasing the crystal size[10]. Due to the changes in crystal-chemical composition, carbonate is unstable in the crystal. Therefore, erbium laser breaks the synergistic effect of CO_3^{2-} and Mg^{2+} to weaken the acid resistance of the enamel and improve the crystal structure by removing the unstable carbonate[20]. The

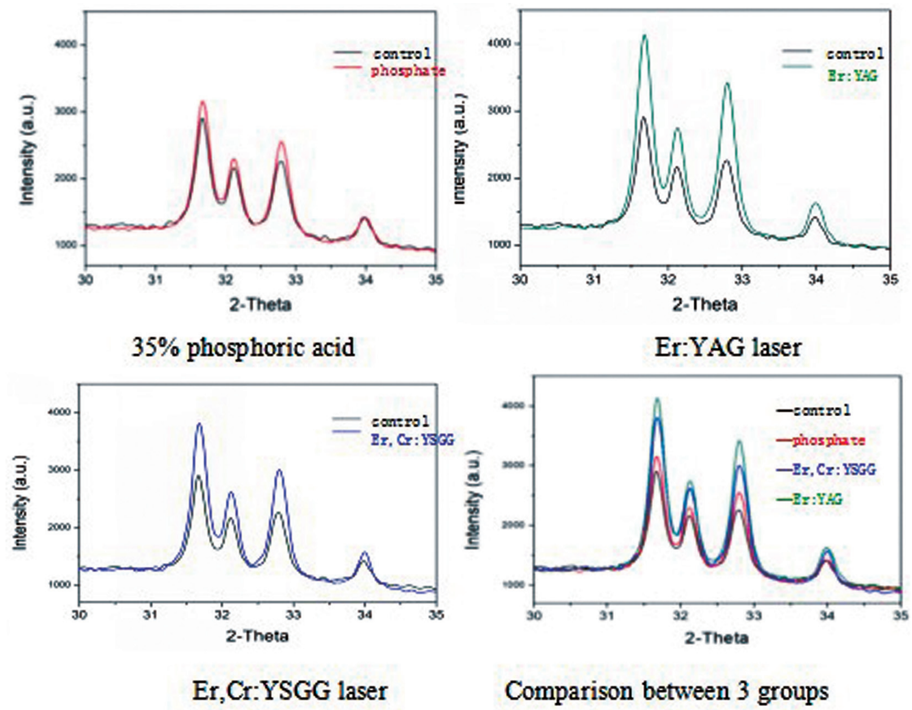

Fig. 4 The crystallinity of enamel surface crystals increased slightly after 35% phosphoric acid etching.
After Er:YAG and Er,Cr:YSGG laser etching, the crystallinity of enamel surface crystals increased significantly, and the crystallinity of enamel surface crystals increased more significantly in Er:YAG laser etching group.

crystal arrangement and internal structure are more stable, and the crystallinity increases[15].

Changes of crystal size after erbium laser irradiation
In 1989, Ferreira *et al.*[21] observed that after continuous irradiation using CO_2 laser with a wavelength of 10,600 nm under different energy densities, the ultrastructure of enamel crystals changed, and new recrystallized crystals appeared larger than the original enamel crystals. The size of enamel crystals in the high energy group could increase by 10 times that of the original crystals. In 1995, Tagomori and Iwase[22] irradiated the tooth enamel using Nd:YAG laser with a wavelength of 1,064 nm. The results also showed that the enamel had a larger crystal size, and some regions even formed polygonal crystals with a length larger than 2 um. In addition, the enamel surface had a higher microhardness, whereas the acid solubility of the enamel decreased. They concluded that the large crystal size might be the mechanism by which enamel became more acid-resistant. The study of Yilmaz *et al.*[23] in 2020 using Er,Cr:YSGG laser irradiation on enamel also found that recrystallization of crystals on the enamel surface was observed in all the laser-treated groups. Meanwhile, the acid resistance of enamel in laser-treated groups was significantly higher than that in non-laser treatment group. Although different laser wavelengths were used in the above studies, CO_2, Nd:YAG, and erbium laser were all in the infrared band. The photothermal effect of the infrared laser caused a temperature rise, and the crystals on the enamel surface melted and recrystallized. Scholars believed this was one of the mechanisms underlying the enhancement of acid resistance of enamel surface after laser etching. In this study, the crystals on the control side were mostly flat hexagons with a size of 40–50 nm, and there were a few gaps between the crystals. After erbium laser etching, the crystal size of the enamel surface generally increased to 2–3 times, which was perhaps related to the melting and recrystallization of crystals caused by the thermal effect of the laser. According to the study of Daculsi *et al.*[24], large crystal size increased enamel mineralization. Therefore, we speculated that the photothermal effect of erbium laser caused the melting and recrystallization of enamel crystals, resulting in large crystal size, which may be one of the mechanisms by which erbium laser etching enhances the acid resistance of enamel surface.

Changes in chemical composition and crystallinity of enamel crystal after erbium laser irradiation
The changes in crystallinity and solubility of apatite can be partly attributed to the changes in chemical elements in its crystal structure. For example, the crystallinity decreases when CO_3^{2-} replaces PO_4^{3-} or OH^- in the apatite structure. Whereas when Cl^- replaces OH^-, the crystallinity increases[25]. The substitution of F^- for OH^- to form F^- hydroxyapatite (FHA) or F^- apatite (FA) can

increase the stability of the structure and increase the crystal size and crystallinity. Therefore, the solubility of FHA or FA is lower than HA[26]. Combining Mg^{2+} and CO_3^{2-} can form small crystals, reduce the crystallinity of apatite, and increase the acid solubility of enamel[25,27,28].

It has been reported that laser irradiation decomposes the carbonate in unstable carbonate hydroxyapatite crystal, increasing the crystallinity of enamel, improving its structural stability, and reducing the solubility of enamel in acid[10,29,30]. Erbium laser irradiation increases Ca and PO_4^{3-} on the enamel surface and the chemical stability of hydroxyapatite[31]. In 2014, Diaz-Monroy *et al.*[31] irradiated human enamel with Er:YAG laser at a distance of 1 mm, and the parameters were 100 mJ (12.7 J/cm^2), 200 mJ (25.5 J/cm^2), and 300 mJ (38.2 J/cm^2), respectively. They found that the contents of Ca, P, and O on the enamel surface increased significantly after Er:YAG laser treatment, and the differences were more significant in the 200 mJ and 300 mJ groups. In 2019, Mansy *et al.*[33] reported that the average percentage decrease of Ca and P content on the human enamel surface after acid cycling was lower after Er,Cr:YSGG laser etching (0.75 W/20 Hz/10 s) than in the control group. They concluded that Er,Cr:YSGG laser enhances the acid resistance of the enamel by affecting the contents of the chemical elements on enamel surface. In our study, the contents of Ca, P, and PO_4^{3-} on the enamel surface increased after erbium laser etching, consistent with the above results. At the same time, the contents of Mg and CO_3^{2-} were significantly low, whereas the contents of O, F, and Cl were significantly high, which further confirmed that after erbium laser etching, carbonated hydroxyapatite was low. In addition, fluorochlorinated crystals increased, which may be related to the chemical basis for its enhanced acid resistance. So far, only a few studies have investigated the changes of these elements after erbium laser treatment.

The results of this study showed that the peak height of XRD patterns of enamel increased significantly after erbium laser etching. In addition, the peak shape was sharp and narrow, suggesting that the crystallinity of enamel crystals increased significantly, consistent with Kwon's results[15]. Furthermore, the crystal crystallinity of Er:YAG laser group was significantly higher than that of Er,Cr:YSGG laser group, consistent with the XPS results. At the same time, the Cl, PO_4^{3-} and Ca/P were significantly higher in the Er:YAG laser etching group than in the Er:Cr:YSGG laser group. Mg was significantly lower in the Er:YAG laser etching than in the Er,Cr:YSGG laser group. These results suggested that high crystallinity on the enamel surface after erbium laser etching may be related to low CO_3^{2-},Mg, and high Cl, F, and PO_4^{3-} contents, which may be one of the mechanisms of the enhanced acid resistance.

Changes of Ca/P of enamel crystal after erbium laser irradiation

Kwon *et al.*[15] believed that Ca/P reflected the changes in enamel components: Low Ca/P may be due to demineralization, and the redistribution of chemical elements may increase Ca/P through melting and recrystallization. Molten enamel may block ion channels in the enamel, delaying the infiltration of acid and mineral dissolution. Therefore, high Ca/P enhances the acid resistance of enamel. While the results on the changes of Ca/P on enamel surface after erbium laser irradiation were inconsistent. Andrade *et al.*[33] irradiated enamel for 3 s from a working distance of 13 mm using Er:YAG laser (100, 200, 300, and 400 mJ) and found that Ca/P on the enamel surface decreased slightly after irradiation. Díaz-Monroy *et al.*[31] found high Ca/P on the enamel surface after Er:YAG laser (100, 200, and 300 mJ) treatment from a working distance of 1 mm for 15 s. Sijing[34] reported high Ca/P on the enamel surface after Er,Cr:YSGG laser (2.5, 3.5 and 5 W) irradiation from a working distance of 1 mm for 6 s. These two authors suggested that high Ca/P may be due to the photothermal effect of the erbium laser, which increased the temperature of the irradiation area of the enamel surface, resulting in the formation of β-Tricalcium phosphate (β-TCP), which was more acid-resistant than the carbonated hydroxyapatite. In 2014, Kang *et al.*[4] suggested that the Ca/P of enamel would increase after two erbium laser irradiations, forming more stable and acid-resistant compounds. The reason for the inconsistency of the above studies is mainly due to the differences in working distance and irradiation time. The working distance in our study was 2 mm, and the irradiation time was 15 s. Therefore, the XPS results showed significantly high Ca/P on the enamel surface after the two erbium laser etching, consistent with Díaz -Monroy *et al.*[31] and Sijing[34].

Comparison between Er:YAG and Er,Cr:YSGG laser group

The results of this study showed that the contents of O and F in Er:YAG and Er,Cr:YSGG laser group were significantly different ($p<0.05$), the increase of F in Er:YAG laser group was higher than that in Er,Cr:YSGG laser group, and the increase of O in Er,Cr:YSGG laser group was higher than that in Er:YAG laser group. After Er:YAG laser etching, the diffraction curve showed a sharper and higher diffraction peak, and the crystallinities of the enamel surface increased more significantly, which was consistent with the fact that the increases of Cl, PO_4^{3-} and Ca/P and the decrease of Mg after Er:YAG laser etching were more significant than those in Er:Cr:YSGG laser group. The reason may be related to the different wavelengths of the two erbium lasers, the different penetration depth in enamel[5] (Er:YAG laser penetration depth is 5 um, Er,Cr:YSGG laser penetration depth is 15 um) and the different absorption efficiency of water and hydroxyapatite, and may need further investigations to prove.

CONCLUSION

Compared with 35% phosphoric acid etching, Er:YAG and Er,Cr:YSGG laser etching increased the crystal size of the enamel surface, changed the chemical composition, and increased the crystallinity of crystals so that the unstable carbonate decreased, and the stable apatite increased. The above changes in the enamel surface crystals are conducive to enhancing the acid resistance of enamel, which may be one of the mechanisms of enhancing the acid resistance of enamel after erbium laser etching.

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