University of Manitoba
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The Photocatalytic Effect: Nanoscale Surface Composition of Ultraviolet Exposed Orthodontic Miniscrews

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Introduction

Successful orthodontic treatment requires excellent anchorage control for the movement of teeth [1-3]. Anchorage can be defined as the "resistance to unwanted tooth movement" [4]. This anchorage has been obtained traditionally through the use of headgears, transpalatal arches, lip bumpers, and other extraoral appliances, many of which rely heavily on patient compliance [5].

Since the 1980's, temporary anchorage devices such as orthodontic miniscrews have become increasingly favored due to their small size, convenient insertion and removal, low cost, and their ability to be immediately loaded directly after implantation into bone [5]. Orthodontic miniscrews can be used for many orthodontic movements such as molar protraction, canine retraction, dental midline correction, space closure, maxillary incisor retraction, molar distalization, correction of occlusal plane, extrusion and uprighting of maxillary molars, the correction of vertical skeletal discrepancies in lieu of orthognathic surgery, along with other more complicated movements [1, 4, 6]. One major limitation to the use of orthodontic miniscrews is the relatively low success rate. Survival rates of orthodontic miniscrews are found in the literature ranging from 93.8% to as low as 70% with many studies finding failure rates of around 85% [1-3, 5, 7]. A major reason for failure of orthodontic miniscrews is peri-implantitis and loss of the screw following implantation [2, 4, 8-13]. Research has shown that the initial time after implantation is critical as that is when biofilm is introduced to the implant surface. This biofilm formation is a major contributor to post-insertion peri-implantitis and may lead to loss of the miniscrew [8]. A second area of concern for orthodontic miniscrews is that of osseointegration. The failure to osseointegrate will result in loss of the screw and a further negative impact on orthodontic treatment. Aging titanium alloy implants have been shown to accumulate carbon on their surface, increase in hydrophobicity, and exhibit a positive to negative change in electrostatic charge. These factors continue to change unfavorably from the time the implants are machined. These surface changes of the implant have negative effects on the biocompatibility of the miniscrews [14].

Orthodontic miniscrews are primarily composed of a titanium-aluminum-vanadium (Ti_6Al_4V) alloy. This alloy allows osseointegration which is the mark of success of any dental implant [15]. Titanium-aluminum-vanadium alloy allows for the benefits of titanium metal while gaining the stabilizing properties and improved microstructure over pure titanium. The titanium metal naturally undergoes a process called air induced passivation. Oxygen from the air reacts with the titanium metal to form an outer shell of titanium dioxide (TiO_2) on the surface of orthodontic miniscrews. This protective shell minimizes harmful metal ion release from implant to tissue, limiting the inflammatory reaction from the body, allowing successful osseointegration [8].

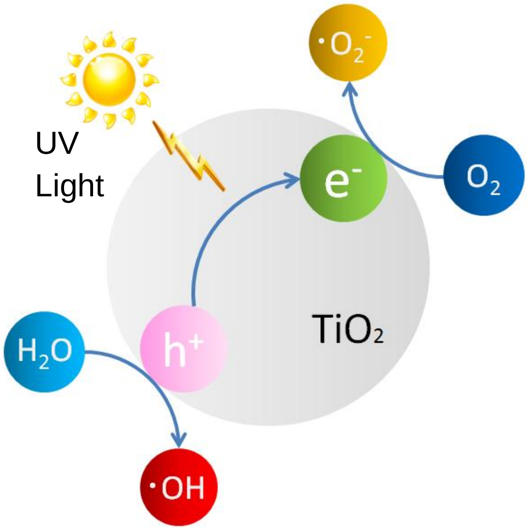


Figure 1: The Photocatalytic Effect
© 2014 Kentaro Sato [20].

Titanium dioxide has a major role in the industrial sector by taking advantage of the photocatalytic effect, which is the activation of reactive oxygen species by the exposure of titanium dioxide to ultraviolet [UV] radiation [13, 16-19]. UV light strikes titanium dioxide, exciting an electron which reacts with oxygen in the air to create a superoxide which is responsible for the antimicrobial effect, while adsorbed water reacts with the resultant electron hole to create a hydroxide anion, responsible for the superhydrophilic properties all shown in Figure 1 [20]. The photocatalytic effect and its antimicrobial properties have been well documented and taken advantage of for decades and are applicable in many different areas such as air condition filters, sanitization of food preparation surfaces, and purification of drinking water [8]. Titanium dioxide exposed to UV radiation, utilizing the photocatalytic effect, has been shown in multiple studies to be useful in killing bacteria [8, 12, 16, 18, 21], bacterial endotoxin [22], and viruses [19]. Though the photocatalytic effect has been shown to break down microorganisms, the effect has been shown to not be harmful to human fibroblasts [16], is used to create antibacterial biomedical materials, and can even propagate hydroxyapatite formation on implant surfaces [15]. Titanium-aluminum-vanadium alloys have been shown to exhibit the same antimicrobial activity after exposure to UV light without affecting its biocompatibility [8]. Titanium dioxide has been shown to become superhydrophilic following exposure to UV light and this effect was shown to last for days [20]. The superhydrophilic property of photocatalyzed titanium dioxide has been credited for the enhancement of osseointegration and has been shown to cause increases in recruitment, attachment, retention, and proliferation of osteogenic cells critical in the integration of titanium implants into bone [23]. In addition, the titanium dioxide photocatalyst has been shown to have reduced or nearly eliminate carbon contamination and exhibit electropositivity. These three characteristics have been shown in the literature to positively affect osseointegration [14]

The passivation layer formed by the reaction of oxygen from air and titanium in the orthodontic miniscrew alloy is protective in nature and increases biocompatibility. When this titanium dioxide layer is exposed to UV light, the antimicrobial and superhydrophilic properties may be realized. The purpose of this study is to quantify the chemical change both qualitatively and quantitatively at the surface of photocatalyzed titanium-aluminum-vanadium orthodontic miniscrews. The null hypothesis being tested is that there will be no difference in the nanoscale surface composition of UV light exposed miniscrews when compared to as received miniscrews when comparing UV light exposed screws.

Materials and Methods

The orthodontic miniscrews (n=3) used in this study were IMTEC Ortho [IMT] (3M Unitek, IMTEC, Ardmore, Okla). The miniscrews are a Ti_6Al_4V alloy and are individually packaged by the manufacturer. In a previous study, the surface composition of an IMTEC miniscrew, which was not exposed to any UV lighting, was determined without etch, and at depths of 10, 20, 30 and 80 nm. The IMTEC miniscrew was chosen over the others tested in the study as it was found to have the least amount of titanium dioxide as it was etched and therefore our study would be able to find the most profound impact of photocatalysis [24]**.** This untreated miniscrew was used as the control to compare with the UV light exposed miniscrews.

UV Light Exposure

The light source used to induce the photocatalytic effect on the orthodontic miniscrew was a Sunlite 20 watt compact fluorescent blacklight blue bulb with a 365 nm peak emission (320-398 nm). This bulb was mounted in resealable black light box with mirrors mounted on the floor and all sides to maximize the contact of UV radiation with the screw. The UV light box was constructed from wood and is 11×5.5×5.5 inches in size (Figure 2).

Figure 2: Ultraviolet light box used in this study

The distance between the light source and miniscrew was chosen to be 10cm, as light emitted at that distance was shown to activate the titanium dioxide photocatalyst [8, 12]**.** The photocatalytic effect has been shown to be initiated at wavelengths below 385 nm [8, 15-17]. Before placement of the miniscrews into the UV light box, the mirror surfaces were sterilized with OPTIM 33TB Wipes. Packages of IMTEC orthodontic miniscrews were opened only immediately prior to placement in the UV light box. They were handled with nitrile gloves to prevent contamination of the implant surface. Three IMTEC Orthodontic miniscrews were exposed to UV light for three different times: five minutes, 20 minutes and 24 hours. Immediately following UV light exposure, all three miniscrews were placed into the X-ray Photoelectron Spectrometer (XPS) and were subjected to surface analysis.

XPS Analysis

The chemical compositions of the UV light exposed miniscrews at the different depths were determined through XPS analysis. The spectrometer emits x-rays which interact with the miniscrews and provides the resultant energy distribution of electrons that are released from the material. These energy distributions provide information on the elements present (qualitative aspect) as well as the amount of each element present (quantitative aspect) in each slice of the biomaterial. It also outputs information on the bonds in which the elements are involved.

The XPS analyses were performed using a Kratos Axis Ultra X-ray Photoelectron Spectrometer (Wharfside, Manchester, UK). The spectrometer was calibrated to the Au 4f and Cu 2p lines and the detection limit was 0.1 at%. Certain parameters included a base pressure of $2x10^{-9}$ torr, an x-ray gun emission set to 15 mA, and an x-ray anode set to 15 kV, which equates to a power setting of 225W. The type of anode used was aluminum monochromatic x-rays. The elements were observed using both survey and high resolution spectra. Additional factors included a detector normal to the surface for the take-off angle geometry (15 degrees), a hybrid lens (magnetic and electrostatic), the use of a charged neutralizer during data acquisition set to 2A and 4V, and aperture set to 700X300 µm. The greater aperture dimension was oriented along the length of the screw. A pass energy of 20eV was used during the high resolution scan. The estimated sampling depth of XPS analysis was 10nm. Composition of the surface layer of the three miniscrews was measured prior to argon etching and after etching at depths of 10, 20, 30, 90, and 170 nm. The area of analysis of each miniscrew was identical and was in the threads of the screw. The results of the X-ray Photoelectron Spectroscopy were analyzed and interpreted using Casa Software Ltd. The XPS binding energy values were charge corrected and calibrated to that of uncharged carbon (CH-CH) at 285.0 eV.

Results

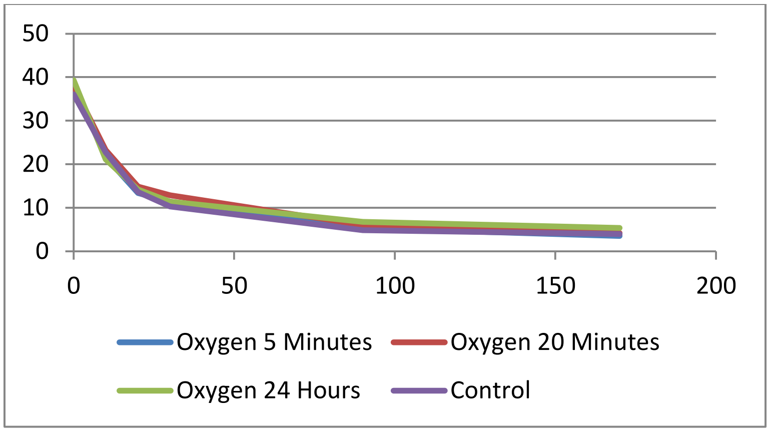
The purpose of this study was to qualitatively and quantitatively determine the effect of photocatalysis on the surface of titanium-aluminum-vanadium orthodontic miniscrews. Analysis of XPS allowed for the quantification of various elements found within the different layers of the titanium-aluminum-vanadium miniscrews at different UV exposure times, the results are displayed in Table 1.

Table 1: XPS survey results of the atomic concentration (%) of principal elements according to treatments and different levels (in nm).

	5 minutes			**20 minutes**			**24 hours**		
	0	10	90	0	10	90	0	10	90
Titanium	6.69	46.65	54	6.76	57	65.77	7.16	49.03	65.18
Oxygen	38.19	21.64	13.38	37.89	23.28	6.04	39.28	21.1	6.74
Aluminum	2.4	5.01	8.34	3.42	5.14	8.3	2.36	4.18	5.21
Vanadium	0	0	0.47	0	0	0	0	0	0.64
Carbon	33.2	9.38	8.01	32.58	9.05	4.51	36.14	9.93	5.04
Sodium	0.54	7.39	7.94	0.56	7.08	9.31	0.84	7.57	9.88
Nitrogen	0.64	2.18	2.38	0.48	1.62	3.29	0.68	2.07	4.14
Silicone	15.55	4.58	2.47	15.69	3.27	0	13.09	2.27	0
Argon	0	2.42	2.37	0	2.83	2.42	0	3.05	2.76
Ruthenium	2.66	0.75	0.64	2.61	0.72	0.36	0	0.79	0.4

XPS is a powerful quantitative technique; it can be able to detect trace concentration as low as 0.1% in the survey mode. The numbers in Table 1 show the mean of atomic concentration that was probed in the miniscrews. As the amount of each element that has been probed was higher than thousands of millions, the standard deviation was less than 0.001%, and it was not included.

Figure 3 shows the atomic percentage of oxygen and titanium. As displayed in this figure the concentrations of these elements are different according to the depth analyzed. Oxygen concentration drops from 40% at 0 nm to less than 10% at 170 nm, and titanium increase from ~ 10% at 0 nm to more than 60% at 170 nm.



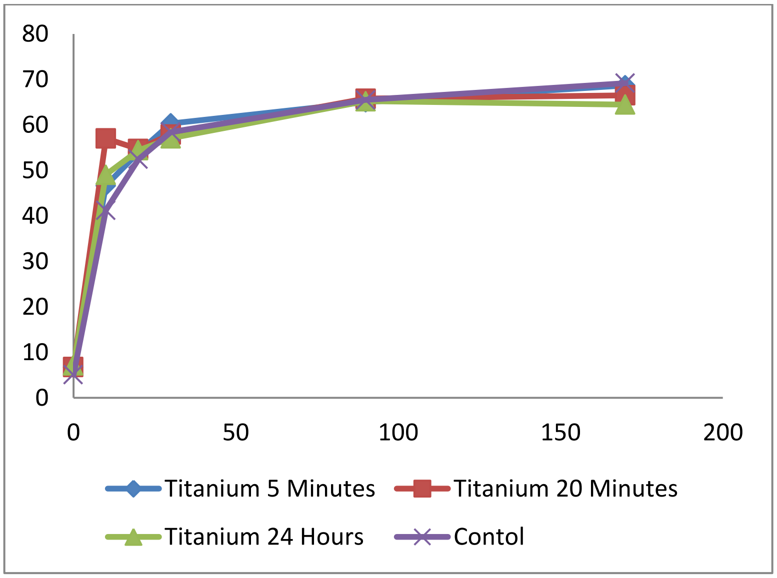


Figure 3: Atomic percentage of oxygen and titanium according to depth of analyses (in nm)

Also, XPS analyses allows for qualitative analyses of each element at the high resolution mode. Using a peak deconvolution it is possible to identify the interaction of the element with other atoms. In other words, it is possible to detect different compounds of the same atom. Using the titanium peak as an example, it is possible to distinguish presence of TiO_2, TiOH and /or Ti_2O_3 depending the position of the peak component.

Oxygen Analysis

Figure 4 (0 nm) shows a control of no UV exposure and miniscrews exposed to UV for five minutes, 20 minutes, and 24 hours. At the outer surface, no significant differences quantitatively or qualitatively are found in the different states of oxygen at the outer surface of the miniscrews regardless of UV light exposure.

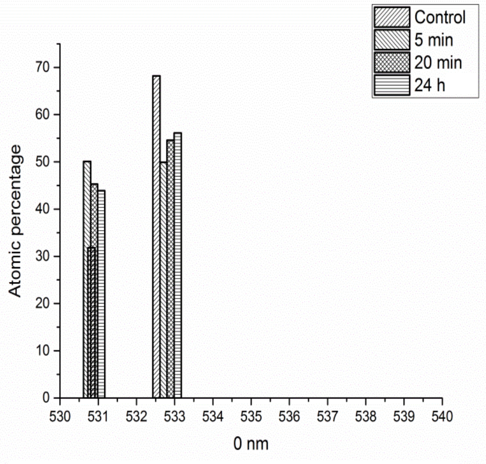


Figure 4: Binding Energies of Oxygen with No Etch

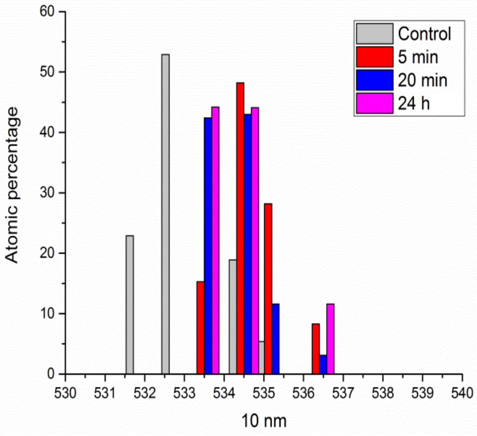


Figure 5: Binding Energies of Oxygen at 10 nm

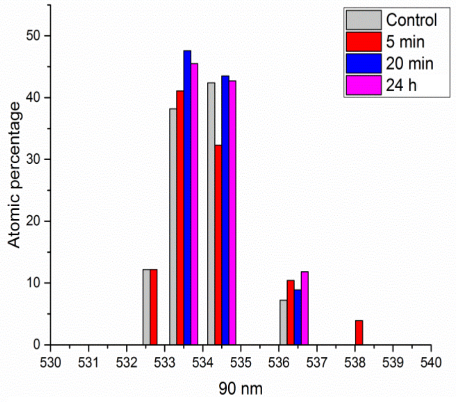


Figure 6: Binding Energies of Oxygen at 90 nm

Figure 5 (10 nm Etching Depth) shows the different oxygen states and the amount of each state at a depth of 10nm into the surface of the miniscrews. Figure 5 shows a control of no UV exposure and miniscrews exposed to UV for five minutes, 20 minutes, and 24 hours. When comparing to the control, the screw exposed to UV light for five minutes has a clear shift to the right when comparing the binding energies. The atomic percentage of the different oxygen states also vary greatly. The miniscrews exposed to UV for 20 minutes and 24 hours showed very similar qualitative and quantitative results at an etching depth of 10 nm to the miniscrew exposed for five minutes.

Figure 3 (90 nm) displays the different oxygen states and the amount of each state at a depth of 90 nm into the surface of the miniscrews. Figure 3 shows a control of no UV exposure and miniscrews exposed to UV light for five minutes, 20 minutes, and 24 hours. No significant difference was found in the amount and type of oxygen between the control miniscrew and any of the UV exposed miniscrews at this depth.

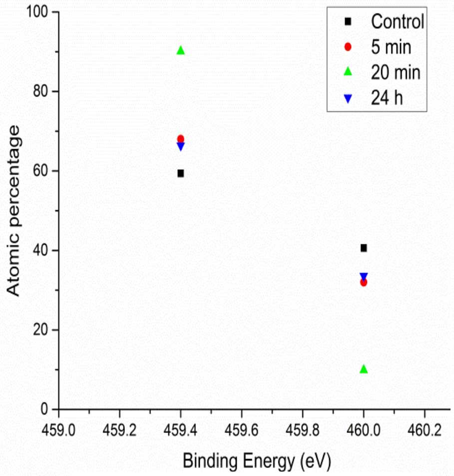


Figure 7: Binding Energies of Titanium with No Etch

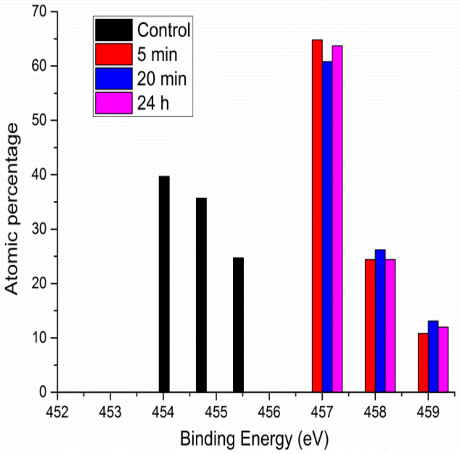


Figure 8: Binding Energies of Titanium at 10 nm

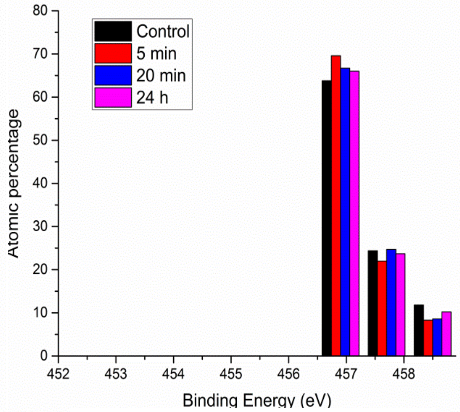


Figure 9: Binding Energies of Titanium at 90 nm

Titanium Analysis

Figures 7, 8, and 9 (No etch, 10 nm, 90 nm) show the atomic percentage and different states of titanium for various UV exposure times (0, 5 minutes, 20 minutes, and 24 hours) and at three different depths. At 0 nm, all different treatments have two peaks at the same position, indicating that they contain the same compounds. There appears to be a quantitative difference but it may be related to the concentration of adventitious carbon found at 0 nm. However, when comparing the control at the 10 nm depth (Figure 8) to the three UV light exposed screws, there is a definitive right shift in the type and quantity of different oxidation states of titanium. At 90 nm (Figure 9), the control and UV exposed miniscrews were found to have the very similar oxidation states of titanium as well as the same amounts of those states.

Discussion

The importance of the photocatalytic effect on titanium dioxide has been demonstrated in multiple studies [8, 12-13, 16-19, 22]. Titanium alloy implant surfaces exhibit carbon accumulation, an increase in hydrophobicity, and exhibit an electrostatic charge changing from positive to negative over time. These factors negatively impact the miniscrew and conventional implant’s osseointegration potential. The titanium dioxide photocatalyst has been shown to prevent or even fully reverse these harmful properties [14].

Quantification of the Photocatalytic Effect

An attempt was made to quantify the photocatalytic effect on the surface of titanium-aluminum-vanadium orthodontic miniscrews. Previous studies have shown that UV light exposed titanium dioxide creates reactive oxygenated species responsible for the antimicrobial properties, as well as hydroxide anions, which cause the superhydrophilicity responsible for the improved osseointegration [20].

Many studies have focused on the photocatalytic effect on pure titanium dioxide and on titanium alloys which have undergone air-induced passivation. These studies have shown macro level effects including self-cleaning surfaces in industry [9], microorganism killing [8, 12, 16, 18-19, 22], breakdown of biofilm [25-26], and more recently, more effective and accelerated osseointegration of conventional titanium alloy implants in humans [23]. This is the first study of its kind to look at the atomic changes that occur as a result of photoactivation. Tables 5 and 8, at 10 nm of etching, all UV exposed miniscrews when compared to the non-UV exposed control display a well-defined shift in binding energies of the oxygen and titanium respectively. The shift represents a changing in oxidation states as UV light activates the titanium and oxygen bonds and causes a rearrangement. Furthermore, the photoactivation works on a very superficial level very near to the outer surface of the screw. Figures 5 and 8 (10 nm O and Ti) both show differences when comparing the UV light exposed screws to the control which was not exposed to UV light. Figures 6 and 9 (90 nm O and Ti), a deeper etch into the miniscrews, shows no difference between the experimental screws and the control. The effect is also virtually independent of time, with the maximal effect already occurring at five minutes of UV exposure. Figure 8 (10 nm Ti) shows a high atomic percentage grouping for all UV exposure times at 458 eV. This is of particular importance as this is the TiOH state of titanium. Hydroxyl anions build up on the surface of the titanium after UV exposure and impart the superhydrophilic properties [27]

Antimicrobial, Anti-biofilm, and Superhydrophilic Properties

The titanium dioxide photocatalyst has exhibited time and time again the ability to destroy microorganisms, break apart biofilms, and become superhydrophilic. All of these properties can potentially aid titanium-aluminum-vanadium miniscrews in avoiding peri-implantitis and aiding and accelerating osseointegration. This study has allowed us to have insight on the photocatalytic effect at an atomic level and we have gained a better understanding of the important elements involved, the different amounts of various states of the elements involved, and the depth to which the change is affected. Though titanium-aluminum-vanadium miniscrews gain seemingly volatile properties, the miniscrew was shown to not harm human fibroblast cells [16]. The benchmark 1997 paper by Wang, et al first demonstrated the superhydrophilic properties elicited by photoactivation. Their study demonstrated that water was able to have a much more intimate relationship with the normally hydrophobic titanium metal after UV exposure. They also showed that the surfaces with a titanium dioxide coating were cleaner than surfaces without. This was the first paper to propose a mechanism of action for this effect.

Further Studies

Recent literature has focused on UV exposure on conventional titanium implants that were placed in humans. Funato, et al found that UV exposed implants exhibited an increased rate of implant stability development and allowed for faster loading after implantation. A 2016 study by Kitajima, et al went one step further and placed photocatalyzed implants in very low primary stability areas in humans. It was found that the photocatalytic effect allowed these implants to have a very high success rate when compared to non-UV exposed implants. The literature still does not have studies specifically for orthodontic miniscrews exposed to UV placed in humans. This is needed to determine if there is a significant change in success rates between UV exposed orthodontic miniscrews and non-UV exposed screws.

Conclusions

The photocatalytic effect causes both qualitative and quantitative changes at the surface of titanium-aluminum-vanadium orthodontic miniscrews. The null hypothesis was rejected. UV exposed orthodontic miniscrews showed a different nanoscale composition than their non-UV exposed counterparts. This change in chemical oxidation states occurs very near to the surface of the miniscrew and only requires a short exposure to UV light. This may have a practical application in future use of orthodontic miniscrews in clinical practice. It may be helpful in preventing peri-implantitis and premature loss of the screws and recent studies have shown the positive effect on osseointegration due to the photocatalytic effect.

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