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SURFACE CHARACTERIZATION OF COMMERCIALLY PURE TITANIUM AND TITANIUM ALLOY AFTER MECHANICAL STRESSES AND FLUORIDE APPLICATION

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ABSTRACT

Objectives: To characterize topographically and chemically, the surface of commercially pure titanium (CpTi) and titanium aluminum vanadium (Ti-6Al-4V) alloy after mechanical stresses, fluoride application and their combined effect.

Methods: CpTi and Ti-6Al-4V alloy cylinders 6mm in diameter and 8 mm in length were used in this study. The specimens were grouped according to the treatment applied into 5 experimental groups; group I included the as-received cylinders; group II included specimens that were immersed in artificial saliva for 28 days; in group III, specimens were subjected to 50,000 cycles of 100N axial loading under compression while immersed in artificial saliva; group IV included specimens that were immersed in artificial saliva containing 1500 ppm sodium fluoride for 28 days and in group V, specimens were subjected to 50,000 cycles of 100N axial loading under compression while immersed in artificial saliva containing 1500 ppm sodium fluoride. Surface topography was evaluated using atomic force microscope (AFM), scanning electron microscope (SEM) and chemical changes were assessed using Energy-Dispersive X-ray Spectroscopy (EDX).

Results: AFM results showed increased mean roughness (Ra) of both CpTi and Ti-6Al-4V alloy after exposure to fluoride as well as combination of mechanical stresses and fluoride. SEM evaluation showed alteration in surface topography of both groups showing deposits, cracks and concavities. EDX analysis for both groups revealed the presence of Ca, P, Na and F together with Ti for CpTi or Ti, Al, V for titanium alloy suggesting the formation of sodium and fluoride complexes with titanium, in addition to Ca/P deposits.

Conclusions: Fluoride application as well as combination of mechanical stresses and fluoride application can induce surface chemical and topographical changes which may have an impact on corrosion behavior of CpTi and Ti-6Al-4V alloy.

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INTRODUCTION

Analysis of the implant surface is necessary to ensure a two-fold requirement. First, the implant materials cannot adversely affect body tissues and organs; second, the in-vivo environment cannot degrade the implant and compromise its long-term function. The interfacial zone between the implant and the surrounding tissue is therefore the most important entity for defining the biological response to the implant and the response of the implant to the body. Surface analysis in implantology therefore aids in material characterization, determining structural and composition changes occurring during processing, identifying biologically induced surface reactions, and analyzing environmental effects on the interfaces. [1]

Commercially pure titanium and titanium aluminum vanadium alloys are widely used in manufacturing dental implants [1-4] owing to their favorable mechanical properties, good corrosion resistance and acceptable biocompatibility.[2-4] The biological environment is highly aggressive for metallic implants.[5] Titanium in the oral cavity is not inert to corrosion when exposed to acids and fluoride.[5,6] Resistance to corrosion and biocompatibility are directly related to the passive oxide layer formed on titanium's surface and its alloys. [7,8] However, the mere presence of the oxide layer does not maintain the stability, since its surface may not be fully protected in the very complex chemistry of the oral cavity. This layer may be mechanically or chemically removed or destroyed. [7]

Corrosion products can directly influence adjacent tissues and the formation of a biofilm on supracrevicular or intracrevicular implant restoration surfaces. The metal ions released into the surrounding tissues may induce the release of potentially osteolytic cytokines involved in implant loosening [9] causing discoloration of the tissues and even more severe problems such as inflammatory reaction of the tissues.[10] As a result, many publications have dealt with the corrosion resistance of titanium implants under various conditions. [11-19]

Whilst titanium shows high resistance to corrosion in artificial saliva, [20,21] 0.9% NaCl [21] and physiological saline solution,[21] fluoride ions from toothpastes, dental gels and mouth rinses can cause deleterious effects on CpTi and Ti–6Al–4V.[3,20-28] Alteration in surface topography of titanium surface exposed to fluorides have been reported. [3,23,29] The fluoride content of commercially fluoridated acidic toothpastes, mouth rinses or cariostatic gels is between 0.1% (1000ppm) to 1% (10,000ppm) and is most often added as the sodium salt, NaF. [30]

During service, dental implants are subjected to cyclic loading[31] which results in microscopically small zones of stress concentration produced by notches or microstructural inhomogeneities. [32] The material starts to develop internal micro-cracks that may increase in number and size according to the number of cycles. [33] Fluoride-containing solutions, together with applied stresses may enhance corrosion in prosthetic devices. Since the corrosion of titanium is a complicated phenomenon, the susceptibility of titanium to degradation by any type of corrosion should always be considered in the application environment. [34]

Accordingly, this study has been conducted to investigate the individual effect of fluoride application, mechanical stresses and their combined effect on the surface characteristics and hence the corrosion behavior of CpTi and Ti–6Al–4V. The null hypothesis tested was that mechanical stresses, fluoride application and their combined effect would not affect the surface characteristics and hence the corrosion behavior of CpTi and Ti–6Al–4V.

MATERIALS AND METHODS

Commercially pure titanium grade II and titanium-aluminum-vanadium alloy (Modern Techniques center, Cairo-Egypt) were used in this study. The composition of the materials used in the study is shown in table 1. In an attempt to mimic the dimensions of one of the available dental implants, cylindrical specimens 6mm in diameter and 8 mm in length [35] were machined and their lateral sides were flattened (Star VNC-20 automatic Swiss lathe, Automatics & Machinery Co. Colorado, USA). The flattened lateral sides of the specimens were wet polished with 600 to 4000 grit silicon carbide papers, washed sequentially with distilled water, alcohol and acetone and ultrasonically cleaned in deionized water.

TABLE (1) The composition of the CpTi and Ti-6Al-4V.

Material	Composition (wt %)
CpTi grade II	Ti: base, O: 0.25, N: 0.03, C: 0.1, H: 0.015, Fe: 0.03
Ti-6Al-4V	Ti: base, O: 0.2, N: 0.05, C: 0.1, H: 0.01, Fe: 0.4, Al: 5.5-6.75, V: 3.5- 4.5

Polished specimens of CpTi and Ti-6Al-4V were randomized into 5 groups according to the applied treatment (n=5); group I included the as-received specimens that was not subjected to any treatment. Group II included specimens that were immersed in artificial saliva for 28 days; in group III, specimens were subjected to 50,000 cycles [36,37] of 100N axial loading under compression while immersed in artificial saliva; group IV included specimens that were immersed in artificial saliva containing 1500 ppm sodium fluoride for 28 days and group V included specimens that were subjected to 50,000 cycles of 100N axial loading under compression while immersed in artificial saliva containing 1500 ppm sodium fluoride.

Preparation of the solutions

Fusayama-Meyer's artificial saliva was prepared and used in this study. [38, 39] The composition of this solution, which closely resembles human natural saliva, is shown in table 2. The pH was adjusted at 5.8. [40]

The fluoride medium was prepared by dissolving 0.15gm sodium fluoride in 100 gm of artificial saliva to obtain a solution containing 1500 ppm NaF. Specimens of group II (artificial saliva group) and group IV (fluoride group) were individually immersed under static conditions in the intended solutions at 37°C up to 28 days where the solution was refreshed every 24h during the incubation period. After immersion, specimens were removed and rinsed with distilled water, followed by drying at room temperature for 24 h to be ready for surface characterization.

Application of mechanical stresses

Specimens of groups III (mechanical stresses) and V (mechanical stresses and fluoride) were individually mounted onto the lower fixed compartment of a computer controlled materials testing machine (Model 3345; Instron Instruments Ltd., USA) with a load cell of 5 kN and data were recorded using computer software (Bluehill Lite; Instron Instruments). Each specimen was subjected to 50,000 cycles axial loading under compression by means of a metallic rod with flat end of 6 mm diameter which was attached to the upper movable compartment of the machine. The metallic rod used for load application was made from the same material of the specimen tested. Each specimen was immersed in the test solution in a Teflon cup during stress application.

TABLE (2) The composition of the artificial saliva

Compounds	**NaCl**	**KCl**	**$Cacl_2.2H_2O$**	**$NaH_2PO_4.2H_2O$**	**$Na_2S.9H_2O$**	**Urea**
Concentration (g/l)	0.4 g	0.4 g	0.906 g	0.69 g	0.005 g	1 g

Load profile in the form of a sine wave at a rate of 1 Hz was applied. The rate was used as equivalent to the average masticatory cycle of 0.8–1.0 seconds.[41-43] The load was cycled at first between a specified maximum (100N) and small but non-zero minimum (20N) load to avoid lateral dislocation of the loading tip and help in stabilizing the specimen during testing.

AFM evaluation

Specimens of each group were collected and rinsed three times in deionized water. The AFM (Autoprobe, CP Research-Thermo-Microscopes; Sunnyvale, CA, USA) was used in the contact mode using nonconductive silicon nitride probe (MLCT-MT-A, Bruker AFM probes, Bruker Co., USA) and a scan rate of 1Hz. Surface examination of the flattened lateral surfaces of the specimens was performed and imaged for an area of 20μm X 20μm. Roughness average (Ra) measurement was determined by taking the mean value of three individual measures on each of the investigated specimens. The collected 3D data were analyzed using proscan 1.8 software for controlling the scan parameters and IP 2.1 software for image analysis.

SEM evaluation and EDX analysis

The flattened lateral surfaces of the treated specimens were examined using SEM at 10000X magnification and the chemical analysis of the examined surfaces was further analyzed by EDX spectroscopy. This was performed using Scanning Electron Microscope model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 K.V (FEI company, Netherlands).

Statistical analysis

SPSS version 20.0 was used for statistical analysis of the data. Two-way ANOVA was used to compare the effect of material and treatment and their interaction on surface roughness. One-way ANOVA was applied followed by Tukey Kramer post hoc test for pairwise multiple comparisons. The significance level was set at $P< 0.05$.

RESULTS

The results of this study are shown in tables 3&4 and figures 1-5. Statistical analysis of surface roughness measurements for the different experimental groups using two-way ANOVA (table 3) revealed significant effect for the material, treatment and their interaction on surface roughness.

Regarding the effect of treatment for CpTi, statistical analysis showed insignificant difference for the as-received, saliva and mechanical stresses groups. There was also insignificant difference between fluoride group and combined mechanical stresses and fluoride group, where both groups were statistically higher than all other experimental

TABLE (3) Two way ANOVA for the effect of material, treatment and their interaction on surface roughness

Source	Type III Sum of Squares	Df	Mean Square	F	Sig.
Material	243.278	1	243.278	42.410	.000
Treatment	7001.796	4	1750.449	305.148	.000
Material*Treatment	85.219	4	21.305	3.714	.012
Error	229.456	40	5.736		
Total	77013.139	50			
Corrected Total	7559.748	49			

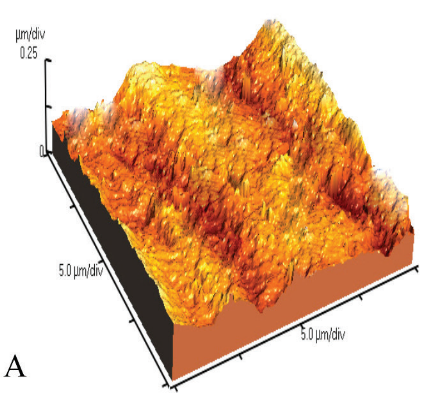
groups. For Ti-6Al-4V, combined mechanical stresses and fluoride group revealed the highest significant mean roughness followed by fluoride group with significant difference between the two groups. Both groups were significantly higher than the other experimental groups. There were insignificant difference in mean surface roughness values of the as-received, saliva and mechanical stresses groups. Statistical analysis for the effect of material showed insignificant difference in surface roughness between CpTi and Ti-6Al-4V for the as-received, saliva and mechanical stresses groups. On the other hand, Ti-6Al-4V showed significantly higher surface roughness for the fluoride group and the combined mechanical stresses and fluoride group (table 4).

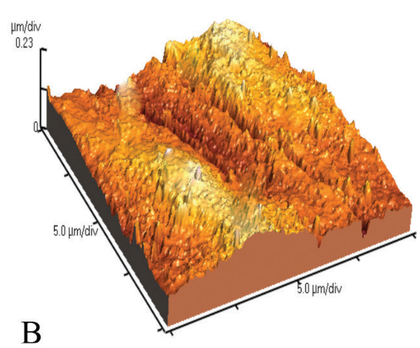
TABLE (4) Means, standard deviation values (SD) and significance of surface roughness (nm) of the different groups for CpTi and Ti-6Al-4V alloy

	AS received Group	Saliva group	Mechanical stresses group	Fluoride group	Mechanical stresses and fluoride group	Significance
CpTi	23.98 (2.85) Ba	25.35 (3.21) Ba	30.58 (3.78) Ba	45.62 (4.46) Ab	50.16 (4.3) Ab	P<0.0001
Ti-6Al-4V	26.75 (1.61) Ca	29.89 (3.96) Ca	31.23 (2.34) Ca	51.79 (3.59) Ba	58.46 (4.12) Aa	P<0.0001
Significance	P=0.095	P=0.0816	P=0.752	P=0.0425	P=0.0143	

Groups with different upper case letters indicates significance between different groups within the same materials (among rows).

Groups with different lower case letters indicates significance between different materials within the same treatment modalitiy (among columns).

<table>
<tr><th></th><th>CPTi</th><th>Ti-6Al-4V</th></tr>
<tr><td>AS received</td><td>

A</td><td>

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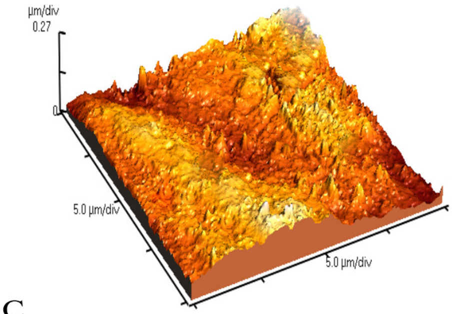
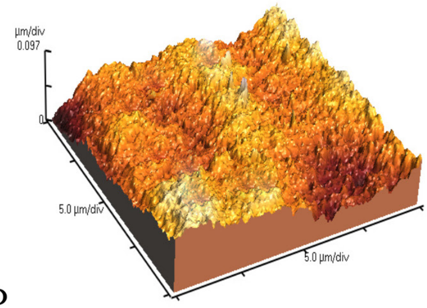
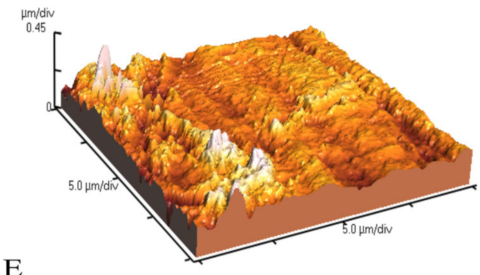
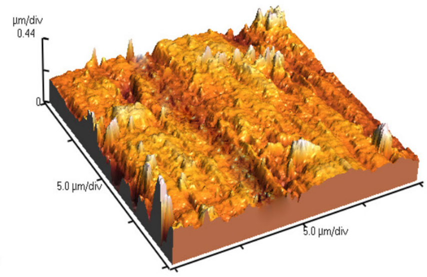
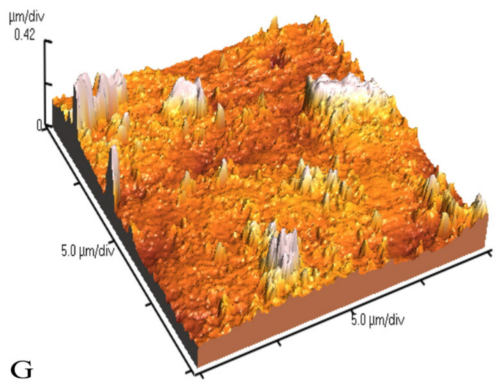
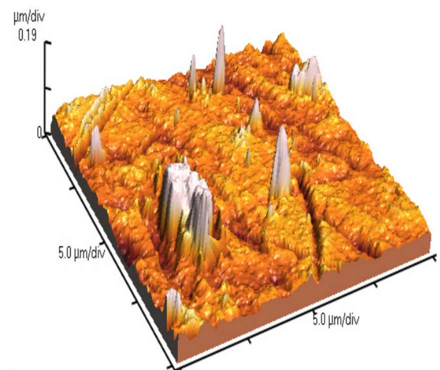
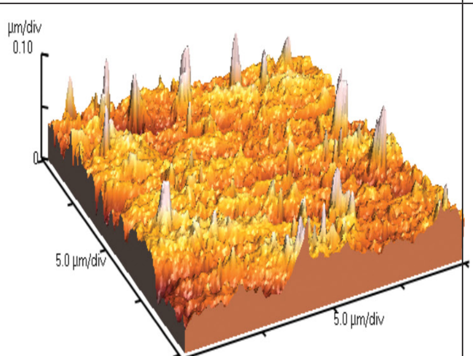
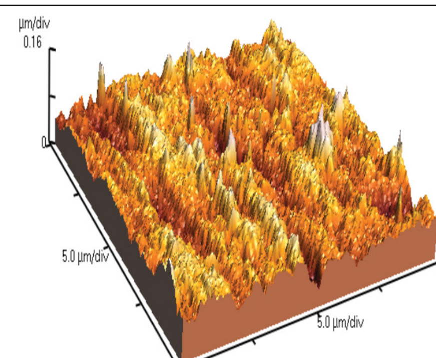
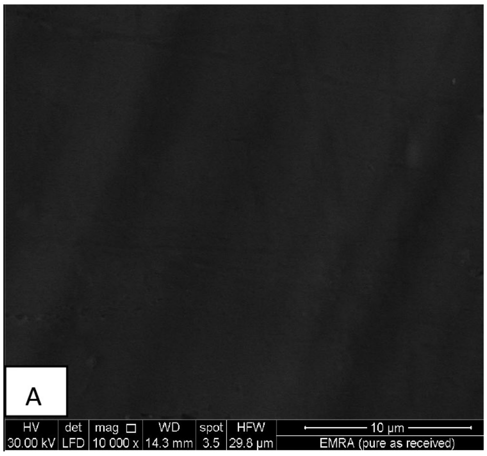
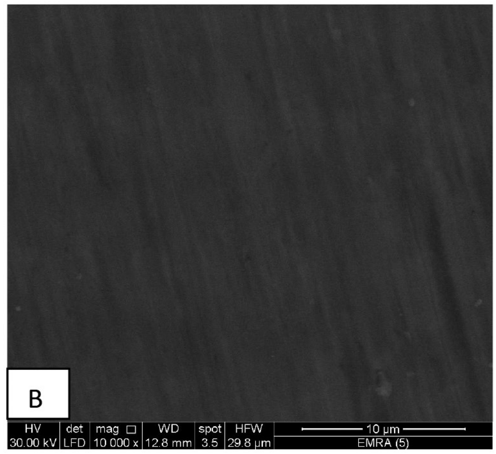
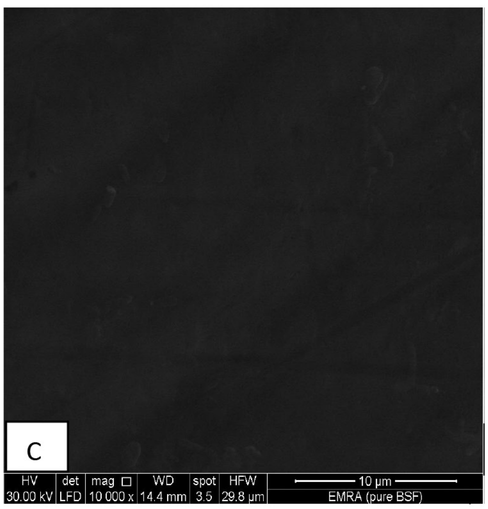
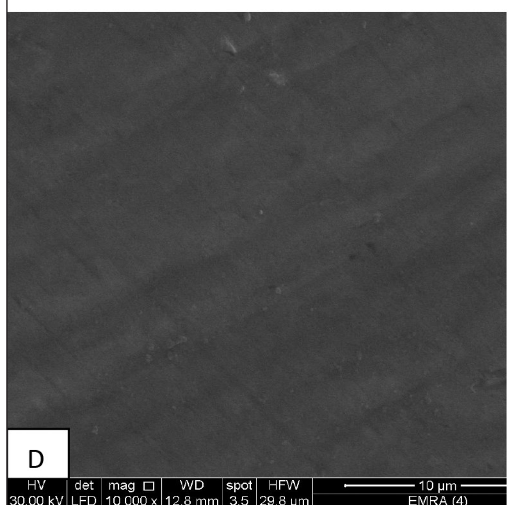
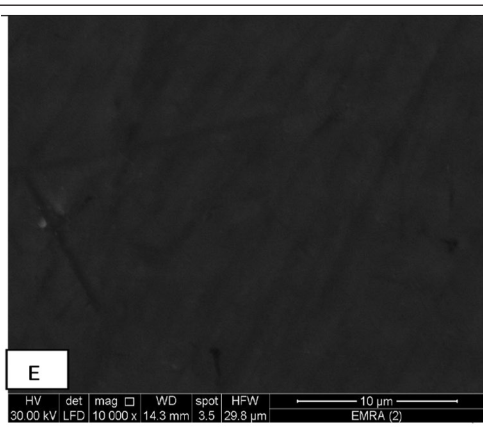
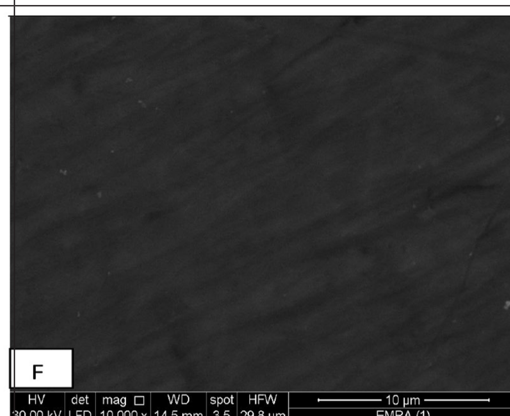
Group immersed in artificial saliva	 C	 D
Group subjected to mechanical stresses while immersed in artificial saliva	 E	 F
Group immersed in sodium fluoride solution	 G	 H
Group subjected to mechanical stresses and fluoride	 I	 J

Fig. 1 (A-J): AFM images of CpTi and Ti-6Al-4V for the different treatment modalities.

	CPTi	**Ti-6Al-4V**
AS received		
Group immersed in artificial saliva		
Group subjected to mechanical stresses while immersed in artificial saliva		

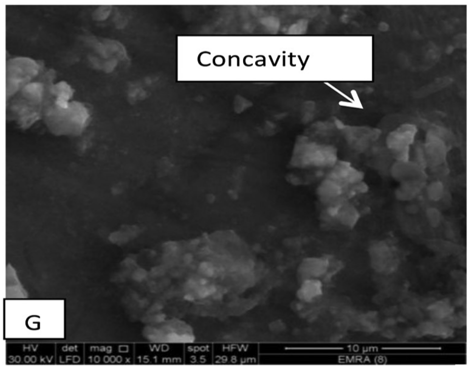
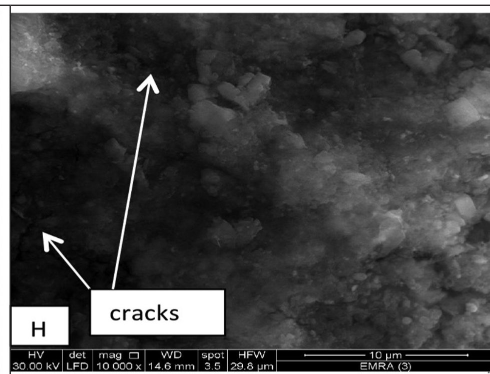
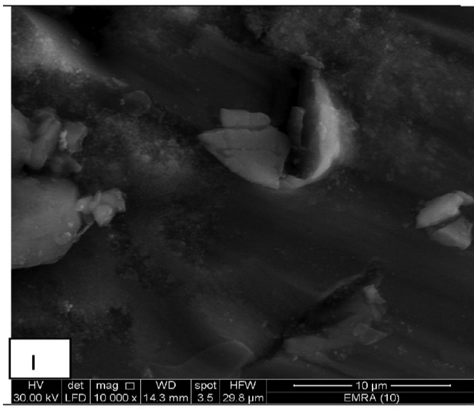
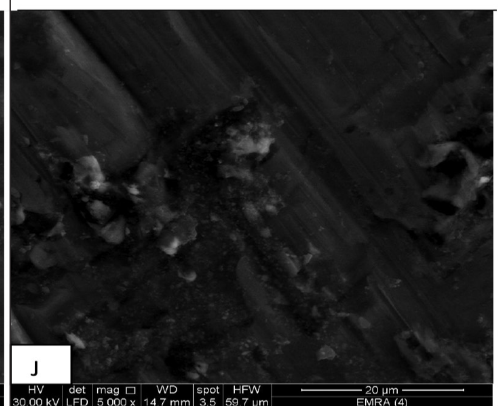
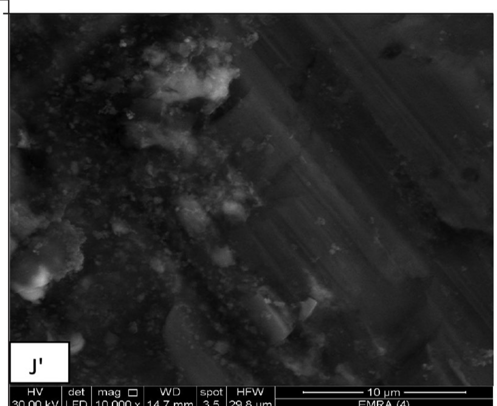
Group immersed in sodium fluoride solution		
Group subjected to mechanical stresses and fluoride		
		

Fig 2 (A-J’): SEM photomicrographs of CpTi and Ti-6Al-4V for the different treatment modalities.

AFM and SEM findings for surface topography of the as received, saliva and mechanically stressed groups of CpTi and Ti-6Al-4V revealed relatively smooth surfaces with homogenous surface texture except for finishing and grinding scratches (fig1A-F, 2A-F). AFM images showed highly irregular surfaces for the fluoride group and those subjected to combined mechanical stresses and fluoride compared to the as received, saliva, and mechanical stresses groups for both CpTi and Ti-6Al-4V (fig 1).

SEM images of Ti-6Al-4V immersed in artificial saliva and those subjected to mechanical stresses while immersed in saliva (fig 2D, F) revealed few deposits of Ca/P as identified by EDX (fig3 representative of alloy immersed in artificial saliva). SEM photomicrograph of specimens immersed in 0.1% NaF solution for 28 days showed precipitation of surface crystalline deposits on CpTi (fig 2G) and denser, less regular cloudy deposits together with the crystalline deposits on Ti-6Al-4V surface (fig 2H). They were identified by EDX analysis as Ca, P, Na and F together with Ti for CpTi or Ti, Al, V for titanium alloy. The ratio Na: Ti: F=24:11: 65 in atomic % suggested the formation of sodium and fluoride complexes with titanium together with Ca/P deposits (figs 4&5). In CpTi and Ti-6Al-4V, SEM images for specimens subjected to the combined action of mechanical stresses and fluoride revealed partial removal of the surface deposits leaving discrete isolated areas together with surface grooves, concavities and pits (fig 2I for CpTi and 2J, J' for Ti-6Al-4V).

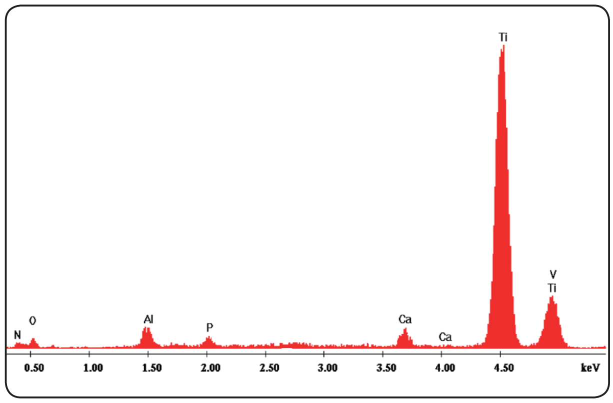


Fig. (3) EDX analysis of Ti-6Al-4V in artificial saliva.

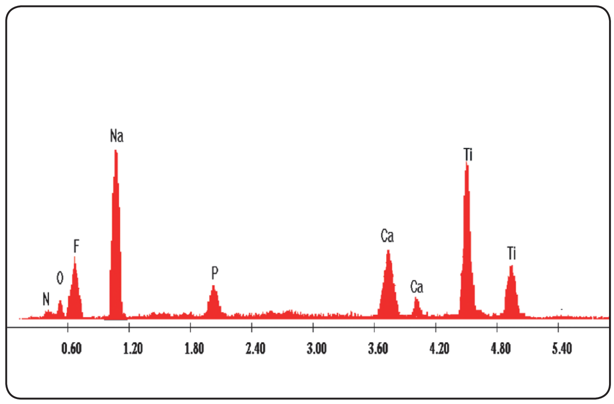


Fig. (4) EDX analysis of CpTi immersed in sodium fluoride.

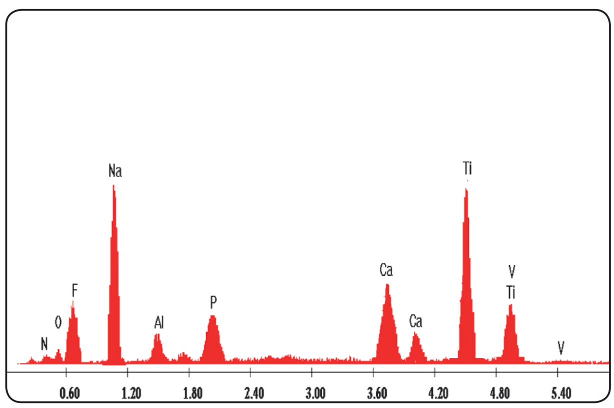


Fig (5) EDX analysis of Ti-6Al-4V immersed in sodium fluoride solution.

DISCUSSION

Degree of success of an implant is determined by the interaction between the implant and the surrounding environment at their interface.[44] Titanium is known to present a high degree of resistance against corrosion attacks by the majority of acids. The corrosion resistance of titanium and its alloys is a result of the material's ability to spontaneously form passive oxide films (TiO_2) when in contact with oxygen.[45] Titanium oxide is a stable and dense layer, which acts as a protective barrier to continued metallic oxidation. In the event of damage, TiO_2 has the ability to spontaneously reform under normal physiological conditions. However, events, such as loading conditions, implant micromotion, acidic environments and their conjoint effects, can result in permanent breakdown of the oxide film, which may consequently lead to exposure of the bulk metal to an electrolyte.[46]

Fluoride ions are considered to be one of the few means capable of attacking titanium surface with corrosive action. The use of fluoridated gels and mouth washes as a prophylactic measure in dentistry has been increasingly more widespread over the last 40 years, due to the great impact on caries prevention.[47] In this study, the concentration of fluoride used was within the range observed in tooth pastes reported in clinical studies [48] and used in dental implant research studies.[5,33] Similarly, Fusayama-Meyer solution was selected because it is common in dental implant [49,15] and orthodontic[50,51] corrosion studies. Electrolytes of the Fusayama-type have been regarded to closely resemble natural saliva when testing the electrochemical behavior of dental alloys and yield results that match clinical observations. [52,53] The pH was adjusted to 5.8 where the normal pH range for saliva is considered to be 5.6-7.9 [54] with children having an average pH of 7.5 while adults tend to be more acidic. Still, the characteristics of the oral environment are complex and difficult to replicate in any artificial saliva and in in-vitro studies in general.

The presence of mechanical stimulus and the synergistic effect of mechanical loading during fluoride immersion were also investigated in this study. During mechanical testing, the teeth were subjected to an axial loading of 100 N, which is considered to be within the normal functional range in-vivo (70 to 150 N) during chewing and swallowing. [55-57] For cyclic loading testing, axial load with constant amplitude was applied as a first step towards more complex testing conditions. The lateral sides of the specimens were examined to avoid possible damaging effects of the load applicator on the top surfaces.

The significant increase in roughness for the fluoride group compared to the as-received, saliva and mechanical stresses groups could be attributed to alteration in surface topography as a result of the formed surface deposits, concavities and cracks. When sodium fluoride agents come in contact with titanium, sodium and fluoride ions are released. Fluoride ions combine with hydrogen generating hydrofluoric acid (HF), which reacts with the oxide layer, dissolving titanium. The reaction with the oxide layer may contribute to the formation of titanium fluoride, titanium oxide fluoride or sodium titanium fluoride on the surface. [22,24,3,58,59] In addition, Ca/P deposits from solution have also been detected.[3]

Some controversy exists regarding whether exposure to fluoride is detrimental to titanium if the pH is closer to neutral. [60, 61] According to Nakagawa et al. [21,27,62] titanium changes induced by fluoride can be predicted by pH and fluoride concentration. Considering this predictive model, for a fluoride concentration of 1500 ppm, corrosion should only occur if pH is lower than 4.7 for CpTi and 5.1 for Ti–6Al–4V. Accordingly, at least 10,000 ppm F seem to be necessary in order to corrode titanium when toothpastes with pH equal to 6.3 are used. Reclaru and Meyer [63] found deposition of fluoride when titanium was immersed in a 1000 ppm F solution at a pH = 3.5. Sartori et al. [64] did not found fluoride ions or crystals on the surface of implants after immersion in NaF solution (1500 ppm F and pH ranging from 5.3 to 7.4). Though the pH of the artificial saliva in this study was 5.8 and only decreased to 5.6 with the addition of NaF, yet this was sufficient to affect the titanium surface particularly with the prolonged immersion period applied compared to the other studies, supporting Yokoyama et al [61] and Knutson and Berzins [40] where they showed that fluoride at more neutral pH (pH = 6.5) may also have an influencing effect on titanium. In addition, Schutz and Thomas [65] reported that solutions containing more than 20 ppm of fluoride ions may attack titanium surfaces when the pH falls below 6.0. Thus, it could be speculated that titanium changes induced by fluoride can be affected not only by pH and fluoride concentration but also by time of immersion.

Even though the application of mechanical stresses did not significantly alter surface roughness, the combined effect of mechanical stresses and fluoride application revealed a significant increase in surface roughness compared to the as-received, saliva and mechanical stresses groups for CpTi and showed the highest surface roughness values for Ti-6Al-4V groups. It has been reported [66] that the formation of oxide film in titanium provides corrosion resistance under static conditions, but the oxide film may not be sufficiently stable under different loading conditions. It has been shown that fluoride prophylactic agents attack the titanium surface creating surface pits, microcracks and grooves which can modify titanium performance under cyclic stresses.[28,60] As a consequence, mechanical stresses with even normal physiological load are concentrated in these surface defects [67] and act as crack nucleation sites.[68] In addition, in corrosive environment like fluoride solution, crack propagation is relatively rapid in stressed specimens.[68,69]

Thus, it can be assumed that the combined mechanical and chemical processes play a vital role in crack initiation and propagation. According to previous studies, the formation of titanium fluoride, titanium oxide fluoride or sodium titanium fluoride on titanium surface results in marked decrease in corrosion resistance.[3,22,24,58,59] However, accumulation of such deposits on the surface of CpTi and Ti-6Al-4V induced by the initial corrosion attack, together with the Ca/P deposited from the solution might provide a protective barrier for the so called active metal and decrease the susceptibility for further corrosion.[70-72] Unfortunately, the mechanical action would lead to partial removal of the layer of deposits formed on titanium surface (as revealed by SEM fig 2I,J,J'), eliminating the protective function of the layer, which leads to continuous exposure of the metal and hence promoting its degradation.

Ca/P deposits were detected in fluoride groups of CpTi and Ti-6Al-4V and sparse deposits were also seen on Ti-6Al-4V immersed in saliva and specimens subjected to mechanical stresses while immersed in saliva. This could be explained based on the bioactivation effect of fluoride in Ca and P containing solutions, where fluoridation increased the nucleation rate and accelerates the deposition of calcium phosphate.[73,74]

Regarding the effect of material, there was no significant difference in surface roughness between CpTi and Ti-6Al-4V for the as-received, saliva and mechanical stresses groups. On the other hand, Ti-6Al-4V showed significantly high surface roughness for the fluoride group and the combined mechanical stresses and fluoride group. This indicates that Ti-6Al-4V is more susceptible to corrosion in fluoride media compared to CpTi which could be attributed to the presence of Al and V causing the formation of a more defective surface oxide film. In fact, Al and V improve the alloy strength [65] but, on the other hand, they increase the anodic dissolution of the alloy.[75] Literature data have revealed the release of Al- and V-ions caused by passive film dissolution, though those alloying elements confer good mechanical properties to Ti-alloys.[76]

Based on the results obtained in this study, the null hypothesis was rejected as mechanical stresses, fluoride application and the synergistic effect of mechanical stresses and fluoride application affected surface roughness and topography of titanium based materials which may render them more prone to corrosion and surface degradation. Considering the fact that most implant patients use prophylactic fluoride-containing gels, dentifrices or supplementary fluoride, it is possible that fluoride ions may contribute to degradation of the accessible sites at implant surfaces. Finally, it is important to highlight that prolonged contact of titanium implants either CpTi or Ti-6Al-4V with even relatively low concentration of fluoride ions (1500 ppm) are considered harmful to the implant durability. Accordingly, even in cases where fluoride treatment is highly recommended, it should not be used on routine daily basis.

CONCLUSIONS

Within the limitations of this study, the following could be concluded:

1. Mechanical stresses, fluoride application and the combined effect of fluoride application and mechanical stresses altered the surface topography of titanium and titanium alloy.
2. The synergistic effect of mechanical stresses and fluoride application render titanium more prone to corrosion and surface degradation.
3. Ti-6Al-4V is more susceptible to corrosion attacks in fluoride media compared to CpTi.

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