

Effect of Topical Fluoride on Surface of Cast Titanium and Nickel-Chromium: An In Vitro Study

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Abstract

Objectives: The aim of this in-vitro study was to evaluate the effect of topical fluoride on surface of cast titanium and nickel-chromium.

Materials and Methods: Thirty-nine rectangular specimens of titanium (grade 2) and 39 rectangular specimens of nickel-chromium were cast in equal dimensions and divided into three groups of 13 samples each. Group one specimens of titanium and nickel-chromium were placed in 2% neutral sodium fluoride (NaF) solution for 16 minutes. Group two specimens of titanium and nickel-chromium were immersed in 1.23% acidulated phosphate fluoride (APF) gel for eight minutes. Group three specimens of titanium and nickel-chromium were immersed in distilled water for 16 minutes. The surface roughness of the specimens was evaluated and the data were analyzed using two-way ANOVA and post-hoc comparison test with the level of significance set at 5% ($P < 0.05$). The surface of the specimens was further analyzed using a scanning electron microscope (SEM) and energy dispersive spectrometer (EDS).

Results: Group two titanium specimens showed a statistically significant increase in surface roughness ($P < 0.05$); but no statistically significant increase was noted in the surface roughness of nickel-chromium specimens in groups one, two and three ($P > 0.05$). Qualitative SEM and EDS analyses further revealed the surface corrosion of titanium (group two) and localized mild corrosive pitting of nickel-chromium specimens (group two).

Conclusion: Topical fluoride with acidic pH affects the surface roughness of titanium and to a certain extent, nickel-chromium. Neutral NaF solutions cause no significant change in corrosion resistance of titanium or nickel-chromium.

Key words: Titanium; Fluorides; Corrosion

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INTRODUCTION

The use of commercially pure titanium in dentistry particularly for implant and fixed and

removable partial dentures has increased dramatically in the past few years. The use of titanium and its alloys has increased because of

their favorable mechanical properties, excellent biocompatibility and corrosion resistance, low density, relatively low thermal conductivity and high strength-to-weight ratio [1]. Titanium is well known for its excellent stability in oral and body fluids and for this reason, it is the metal of choice for dental implants. The electrochemical oxidation potential of titanium is -1.63V; making titanium a very active metal. Because of its high chemical reactivity, it forms a thin stable oxide (TiO₂) layer within one minute of exposure to air, which prevents further oxidation. This phenomenon is called passivation and also occurs in aluminum; it is commercially utilized as a protective coating in a process called anodization. Access to the metal is possible only through the pores of the oxide layer. With this protective layer, titanium behaves like a noble metal. It is very resistant to the action of strong acids [2-4]. Travaglini et al. showed that this layer did not break down even in aggressive conditions i.e. exposure to concentrated solutions containing strong acids such as HCl or H₂SO₄, and thus the titanium corrosion remains extremely low [5].

Similarly, cast nickel-chromium has been used extensively in dentistry since 1960 for crowns, bridges and intracanal posts. It consists of 80% nickel and 15% chromium with traces of aluminum, molybdenum and manganese. Excellent corrosion resistance of these alloys has led to the usage of this alloy for dental crowns, bridge repair and cast partial denture frameworks. It is also known to be resistant to further decay and is famous for being durable, non-corrosive and minimally invasive. It also resists leaks and is inexpensive.

Hayes et al. showed that the corrosion resistance of nickel-chromium especially in acidic solutions including HCl, H₂SO₄, HNO₃, HF and H₃PO₄ was attributed to chromium, which is the primary element influencing the general corrosion resistance. The repassivation potential is strongly dependent on the content of molybdenum. This indicates that chromium

plays a strong role in maintaining the passivity of the alloy, while molybdenum acts to stabilize the passive film after a localized breakdown event [6]. On the other hand, a rapid development has been noticed in utilization of fluoridated prophylactic gels. During the past 40 years, prophylactic application of gels and solutions containing high concentrations of fluoride at regular time intervals has become more frequent and has a noticeable impact on dental caries [7].

Topical fluoride for prevention of tooth decay has become the most widely used prophylactic measure at home and in dental offices. Topical fluoride may be applied by the dental health personnel in dental offices and clinics or may be self-applied. Although some exceptions exist, generally high fluoride-concentration products are applied professionally while low-fluoride concentration products are used by individuals at home. In conditions such as xerostomia and dentinal hypersensitivity in adults, repeated application of topical fluoride is required. Topical fluoride is available in various forms such as solutions, gels, prophylactic pastes and varnishes. Fluoride gels were developed because they were much easier to use due to their consistency and could be easily applied to trays, and thus the entire dentition could be treated simultaneously. Sodium fluoride (NaF) and acidulated phosphate fluoride (APF) gels have the same concentrations of fluoride and pH as their respective aqueous solutions. In addition, the gels contain cellulose for viscosity. Some gels are formulated to be thixotropic, that is, they tend to flow under pressure but remain viscous otherwise. Thixotropic gels are considered to do better in interproximal penetration and do not drip from the tray as readily as non-thixotropic gels. Fluoride gels are considered to be as effective as their solution counterparts with desirable working characteristics and hence fluoride gel products have dominated the market for several years. Owing to the large

number of favorable results, concentrated fluoridated gels have obtained the approval of the US Food and Drug Administration. These approved dental gels have a pH range of 3.2 to 7.7; although acidic formulations are believed to result in fast formation of hydrofluoric acid. Moreover, the efficacy of topical fluoride can be enhanced by further decreasing its pH and accelerating the formation of calcium fluoride on the tooth surface [7]. In this context, many manufacturers have commercialized highly fluoridated gels with the fluoride ion content reaching 10,000 ppm and a pH of 5.5. However, such concentration may have some adverse effects on the corrosion resistance of metals like titanium and nickel-chromium due to the high fluoride ion content and low pH level [7].

There are a few studies comparing the potential risks and effects of concentrated and diluted topical fluorides on cast titanium and nickel-chromium. This study aimed at evaluating the effect of topical fluoride on the surface roughness of cast titanium and nickel-chromium. The surface defects caused by these fluoride gels and solutions may lead to increased plaque accumulation, calculus and microbial retention and may also affect esthetics.

MATERIALS AND METHODS

This study was conducted on 39 titanium (Orotig, Titec, Verona, Italy) and 39 nickel-chromium (MeAlloy, Dentsply, Rome, Italy) test specimens.

Seventy-eight wax patterns were fabricated by flowing molten casting inlay wax (Schuler-Dental GmbH & Co., Ulm, Germany) into the rectangular shaped mold space of 15mm × 10mm and a depth of 2mm with the help of a thermostat (Thermo mat, Dentaurem GmbH & Co., Ulm, Germany). Thirty-nine wax patterns were used for preparing cast titanium samples and 39 wax patterns were used for preparing cast nickel-chromium samples. All the 78 samples were inspected for internal porosity by

X-ray (Green, Platino International Co., Shanghai, China).

Samples with internal porosities were discarded and equal number of samples was fabricated. To ensure complete removal of the alpha-case layer in the titanium samples, surface finishing of the specimens was done using titanium finishing bur (Dentaurem, Ispringen, Germany) with a hand piece (KaVo Dental GmbH, Bismarckring, Germany) operating at 15,000 to 20,000 rpm. For the nickel-chromium samples, tungsten carbide burs (Dentsply, Rome, Italy) were used for removing surface irregularities and sequential rubber points (Dentaurem, Ispringen, Germany) were used for finishing and polishing. The samples were standardized by holding them to a fixed horizontal grinding unit (Aixin Medical, Tianjin, China). The movement of the bur was unidirectional with light strokes. For the purpose of standardization, the finishing was done by a single operator (to prevent inter-operator error), for a fixed period of time and used light pressure (to minimize intra-operator error) and only three samples were finished and polished per day (to minimize variation due to fatigue). All the samples were then inspected for their uniformly polished surfaces under a 189 × 152mm magnifying lens (BEST-8609E, Jiada Tools Co., Suzhom, China). The samples were cleaned in an ultrasonic bath for 10 minutes in distilled water and then air-dried [8].

Grouping of samples and surface treatment of the specimens in each group:

The titanium and nickel-chromium specimens were divided into three groups of 13 samples each. They were placed in the respective topical fluoride solutions based on their usage in one year.

Group one: 2% NaF was prepared by dissolving 20g of NaF powder (SigmaUltra, Missouri, USA) in one liter of distilled water in a plastic container [9].

Thirteen titanium and 13 nickel-chromium samples of group one were treated with 2%

NaF solution using cotton applicators for 16 minutes based on its usage in one year [10]. All the samples were then thoroughly rinsed with distilled water.

Group two: 1.23% APF gel (Professional Gel, Pascal, USA) was dispensed from the bottle onto a plastic spatula. A uniform layer of the APF gel was applied to 13 titanium and 13 nickel-chromium samples in group two for eight minutes based on its usage in one year [10]. All the samples were then thoroughly rinsed with distilled water.

Group three (control): Distilled water was poured into a plastic container and 13 titanium and 13 nickel-chromium samples in group three were immersed in it for 16 minutes.

All the samples in each group were subjected to analysis by an optical profilometer (WYKO NT 1100, Tucson, AZ, USA) to estimate their roughness after their respective surface treatments.

The results obtained were statistically analyzed using two-way ANOVA and post-hoc comparison test.

The level of significance was set at 5% ($P < 0.05$).

One sample of titanium and one sample of nickel-chromium from each group were gold-sputtered by a 150-Å thin gold layer under vacuum (10⁻³ mbr) and then their surface topography was evaluated under scanning electron microscope SEM at ×500 magnification with a resolution of 10 μm and the accelerating voltage of 20 kV. The elemental compositions of these surfaces were further evaluated by energy dispersive spectrometer (EDS).

RESULTS

The titanium specimens in group two showed higher increase in the mean surface roughness from 4.8777±0.5200 μm to 6.7185±0.4067 μm with a difference of -1.8408±0.4732 (Table 1). The nickel-chromium specimens in group two showed higher increase in the mean surface roughness from 3.6492±0.6954 μm to 3.7000±0.6832 μm with a difference of 0.0508±0.1295 (Table 1).

Table 1. The mean and standard deviation (SD) of surface roughness of titanium and nickel-chromium specimens in groups one, two and three before and after surface treatment.

	Treatment	Summary	Group 1	Group 2	Group 3
Titanium	Before	Mean	4.7569	4.8777	5.0308
		SD	(0.5227)	(0.5200)	(0.3638)
	After	Mean	4.8346	6.7185	5.0323
		SD	(0.5259)	(0.4067)	(0.3635)
	Difference	Mean	0.0777	1.8408	0.0015
		SD	(0.0319)	(0.4732)	(0.0408)
Nickel-Chromium	Before	Mean	4.4985	3.6492	4.5685
		SD	(0.4454)	(0.6954)	(0.5238)
	After	Mean	4.5054	3.7000	4.5692
		SD	(0.4399)	(0.6832)	(0.5300)
	Difference	Mean	0.0069	0.0508	0.0008
		SD	(0.0350)	(0.1295)	(0.0345)

Two-way ANOVA revealed a significant difference in the mean surface roughness of the three groups of titanium and nickel-chromium ($P < 0.05$). Comparison among the three solutions used in the respective groups of titanium and nickel-chromium also showed a significant difference ($P < 0.05$). Similarly, comparison by two-way ANOVA between groups one, two and three of titanium and nickel-chromium, respectively also showed significant differences ($P < 0.05$) (Table 2).

Post-hoc test comparison showed that group two titanium specimens differed significantly from groups one and three titanium specimens (Table 3) and also from group two nickel-chromium specimens ($P < 0.05$) (Table 4).

However, there was no significant difference among the three groups of nickel-chromium ($P > 0.05$) (Table 3).

The nickel-chromium specimens in group two showed higher increase in the mean surface roughness from $3.6492 \pm 0.6954 \mu\text{m}$ to $3.7000 \pm 0.6832 \mu\text{m}$ with a difference of 0.0508 ± 0.1295 (Table 1). Two-way ANOVA revealed a significant difference in the mean surface roughness of the three groups of titanium and nickel-chromium ($P < 0.05$).

DISCUSSION

Topically applied fluorides are likely to be effective in preventing caries in susceptible patients of any age. Professional fluoride treatments are especially recommended for adults with dentinal hypersensitivity and with known risk factors, such as xerostomia that may be caused by medications, metabolic disturbances like Sjogren's syndrome or radiation therapy [11].

Table 2. Comparison of the three groups of titanium and nickel-chromium by two-way ANOVA

Source of squares	Type III sum of squares	Difference	Mean	F-value	Significance
Among mean difference of the three groups of titanium and Ni-Cr	7.508	1	7.508	183.329	0.000
Among the three solutions used in groups 1, 2 and 3 of titanium and Ni-Cr, respectively	14.822	2	7.411	180.955	0.000
Among groups 1,2 and 3 of titanium and Ni-Cr, respectively	13.351	2	6.676	162.996	0.000
Error	2.949	72	0.041		
Total	38.63	77			

Table 3. Comparison among the three groups of titanium and the three groups of nickel-chromium by post-hoc test

Metal	(I) Solution	(J) Solution	Mean Difference (I-J)	Standard Error	P-value
Titanium	Group 1-NaF	Group 2-APF	-1.763	0.079	0.000
		Group 3-Control	0.076	0.079	0.341
	Group 2-APF	Group 3-Control	1.839	0.079	0.000
Ni-Cr	Group 1-NAF	Group 2-APF	-0.044	0.079	0.582
		Group 3-Control	0.006	0.079	0.938
	Group 2-APF	Group 3-Control	0.050	0.079	0.531

Table 4. Comparison among the three respective groups of titanium and nickel-chromium by post-hoc test

Solution	(I) Metal	(J) Metal	Mean Difference (I-J)	Standard Error	P-value
Group 1	Titanium	Ni-Cr	0.071	0.079	0.376
Group 2	Titanium	Ni-Cr	1.790	0.079	0.000
Group 3	Titanium	Ni-Cr	0.001	0.079	0.992

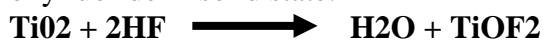
Similarly, patients undergoing orthodontic treatment exhibit a decrease in normal self-cleansing activity of the mouth. Such patients have higher risk of caries beneath and adjacent to orthodontic bands and are also susceptible to developing white opaque lesions on the enamel surface due to subsurface demineralization. Hence, topical fluoride is also recommended for such patients [12,13].

The aim of this study was to quantitatively and qualitatively analyze and compare the effect of topical fluorides on titanium and nickel-chromium. The comparison between the surface roughness values (Rz) of the groups showed a statistically significant increase after APF gel treatment in titanium specimens in group two as compared to 2% NaF solution treatment for specimens in group one and distilled water for specimens in group three. This can be justified by the fact that titanium is easily degraded by hydrofluoric acid (HF); and furthermore, it is rapidly dissolved by strong, and even weak acids such as acetic, formic, and phosphoric acids if the solution contains soluble fluoride [1-4,7].

This phenomenon is interpreted to be the result of incorporation of fluoride ions in the oxide layer, whose protective properties are considerably reduced. A low quantity of fluoride, in presence of acidic medium, induces the following chemical reaction:



The hydrofluoric acid molecules can react with titanium oxide to give rise to titanium oxyfluoride in solid state:



Many structural defects may be induced in the oxide coating due to the lattice parameters of these compounds, thereby loosening the protection from the oxide layer [7].

Boere [3] demonstrated that the corrosion of titanium was enhanced in an acidic environment, because F⁻ in the solution reacts with H⁺ to form HF, even if the NaF concentration is low.

The titanium specimens in group one did not show a statistically significant increase in surface roughness after treatment. This result can be attributed to the fact that corrosion resistance of titanium is maintained when the pH of the solution is neutral.

Nakagawa et al. reported that anodic polarization and immersion tests indicated that the passivation film on titanium was maintained in use of 2% NaF (9048.8 ppm F) solution at a pH higher than 6.2 [14].

The comparison between the Rz of the three groups of nickel-chromium specimens revealed that nickel-chromium displayed excellent corrosion resistance in fluoridated media. This can be justified by the fact that chromium in nickel-chromium alloys hinders active dissolution of the nickel matrix, by formation of an adherent passivating surface film [15]. Comparison between titanium and nickel-chromium specimens indicated that titanium was more susceptible to corrosion in acidic as well as neutral sodium fluoride preparations as compared to nickel-chromium.

SEM observations:

Group two titanium specimens (Fig. 2A) showed dark stains that were responsible for macroscopic color changes of the titanium surface, which might also be interpreted as imperfections in the oxide layer and areas where pitting corrosion started.

This corrosion is characterized by the formation of gaps, inside which there was no re-passivation of the oxide layer by oxygen inhibition [14].

The nickel-chromium specimens in group two (Fig. 2B) showed localized mild corrosive pitting with crystallized corrosion products on the surface.

This may be explained by the fact that chromium-passivized metals can be susceptible to pitting corrosion in fluoride solutions with low pH [16,17].

Group one titanium specimens (Fig. 3A) showed negligible corrosive pitting.

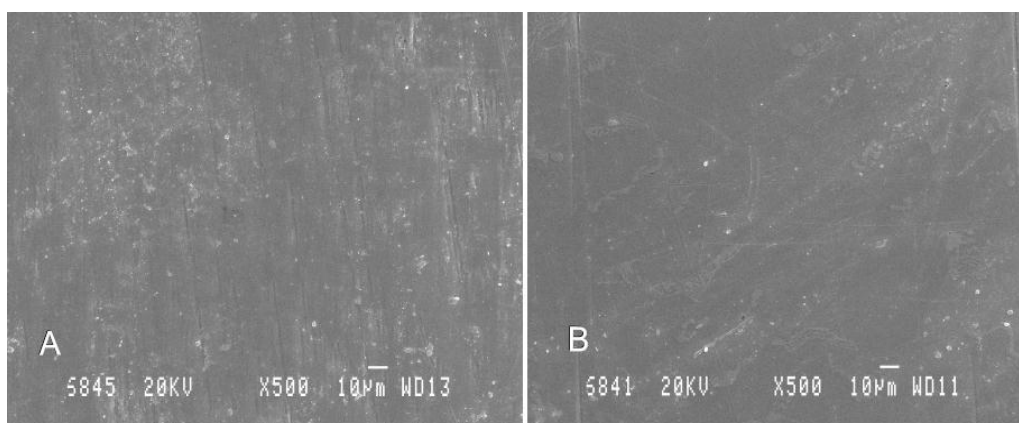


Fig. 1. SEM photomicrograph (A: titanium and B: nickel chromium at $\times 500$ magnification) of titanium and nickel-chromium specimens in group three

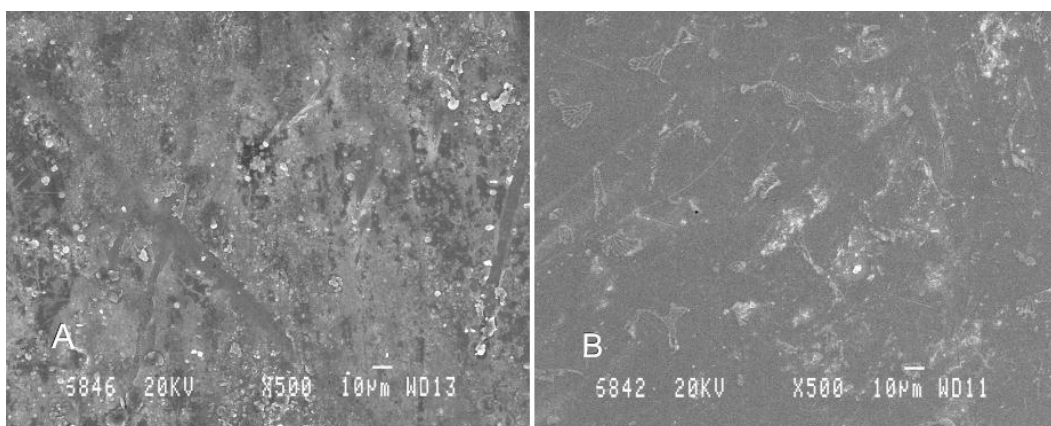


Fig. 2. SEM photomicrograph (A: titanium and B: nickel chromium at $\times 500$ magnification) of titanium and nickel-chromium specimens in group two

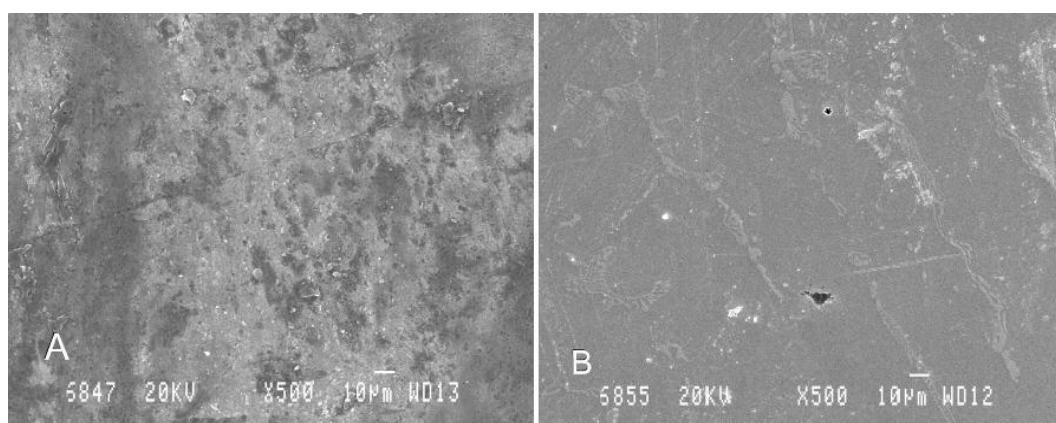


Fig. 3. SEM photomicrograph (A: titanium and B: nickel chromium at $\times 500$ magnification) of titanium and nickel-chromium specimens in group one

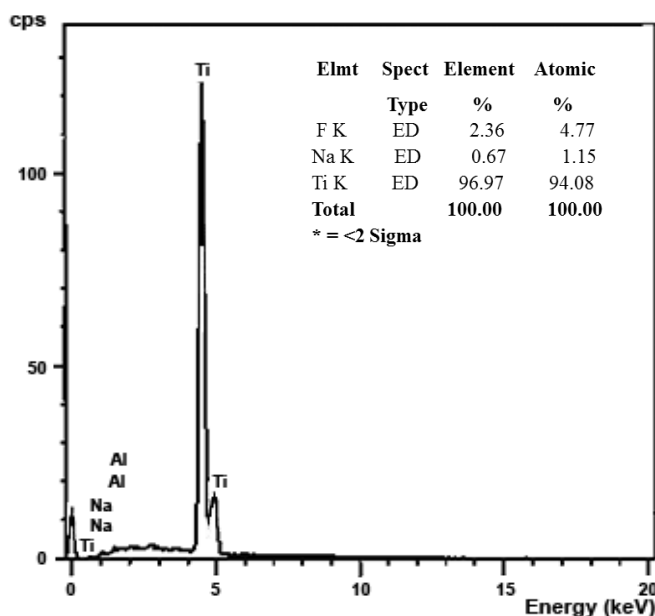


Fig. 4. Energy dispersive spectrometric analysis of titanium specimen in group two

Group three specimens of titanium and nickel-chromium (Fig. 1A and B) and group one specimens of nickel-chromium (Fig. 3B) showed surface irregularities and scratches produced during finishing and polishing.

Energy Dispersive Spectroscopy Observations: Energy Dispersive Spectroscopy is an analytical technique used for elemental analysis or chemical characterization of a sample. It is based on the principle that due to the unique atomic structure of each element, X rays that are characteristic of each element's atomic structure help in identification of these elements from each other. In our study, EDS analysis of titanium specimens (Fig. 4) in group two revealed the presence of fluoride, suggesting the presence of deposits on the surface of specimens after treatment with 1.23% APF gel.

Mabilleau et al. [18] identified these deposits by EDS to be composed of sodium fluorotitanate (Na_2TiF_6) that covered the whole surface of titanium disks immersed in saliva enriched with NaF at concentrations of 2.5% (i.e., 25 g/L or 25,000 ppm).

Energy Dispersive Spectroscopy analysis of nickel-chromium specimens in group two and titanium specimens in group one indicated the presence of negligible amounts of fluoride. It should be noted that in our study, during the preparation of test specimens, routine procedures like removal of alpha layer, sandblasting, finishing and polishing might have caused little variation in surface roughness. In clinical situations, the actual exposure time would be longer as the patients are instructed not to rinse for 30 minutes after topical fluoride application. Additional research may be carried out using different topical fluorides with variable concentrations and exposure times.

Further analysis with a color meter is recommended to study the macroscopic color changes occurring on the titanium surface following treatment with 1.23% APF gel.

The surface corrosion caused on these restorations may lead to increased adherence of microbial flora, which can be further evaluated. Based on the findings of this in vitro study, neutral NaF solutions cause no significant

alterations in the corrosion resistance of titanium or nickel-chromium; hence their usage is recommended. In patients with xerostomia wherein acidic fluoridated preparations are used, salivary substitutes like pilocarpine may be recommended. Similarly, in cases of dentinal hypersensitivity, desensitizing agents like potassium nitrate may be recommended.

CONCLUSION

Within the limitations of this study, it is concluded that topical fluorides with acidic pH have an effect on the surface roughness of titanium and also to a certain extent, on nickel-chromium. Therefore, careful consideration must be given to the usage of these acidic fluoridated preparations in patients with these restorations. The surface defects caused by these topical fluorides may lead to increased plaque and calculus retention and may compromise aesthetics. Precision attachments and fastening screws may be damaged due to surface corrosion.

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