Electrochemical studies on the corrosion behavior of orthodontic wire made of thermo active super elastic (TASE) alloy in artificial saliva in the presence of a mouthwash

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Abstract

All metals may have the tendency to undergo tarnish or corrosion. The percentage of corrosion varies from metal to metal. Metal/alloys are used in dentistry in various forms such as metallic curative materials in the mouth, which undergo chemical or electrochemical reaction with the oral environment. The objective of the present investigation is to study the corrosion resistance of thermos active super elastic alloy (TASE) immersed in artificial saliva in the absence and presence of Colgate Max Fresh mouthwash. This has been investigated by polarization study and AC impedance spectra. The corrosion parameters such as corrosion potential (E_{corr}), linear polarization resistance (LPR) and corrosion current density (i_{corr}) values have been derived from polarization study. The corrosion parameters such as charge transfer resistance (R_t) impedance and double layer capacitance (C_{dl}) have been derived from AC impedance spectra. The influence of Colgate Max Fresh mouthwash on the corrosion resistance of TASE in artificial saliva has been investigated and the corrosion parameter values have been compared. SEM and AFM have been used to analyze the surface morphology.

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Keywords: *corrosion resistance, TASE alloy, artificial saliva, Colgate Max Fresh mouthwash, polarization study, AC impedance spectroscopy, SEM, AFM.*

Introduction

Orthodontic wires are used to prevent and correct the misalignment of the teeth and jaws. They are made of SS 18/8, Ni–Cr, Ni–Ti, SS316, Gold 18 K *etc.* They are used to regulate the growth of teeth. Many alloys are used for the orthodontic treatment. They undergo chemical or electrochemical reaction with the oral environment. Corrosion resistance of several alloys in artificial saliva has been studied by several researchers [1–10].

Eduok [1] has investigated the release of certain metallic constituents within some dental implants could contribute to peri-implantitis and mucositis. While the release rate into surrounding bones and tissues may be dependent on the biocompatibility of dental materials and their designs, the patient's oral hygiene and even the prevalence of certain resident oral bacteria may also affect the service lives of these dental implants by altering their gross corrosion rates. Anees *et al.* [2] have evaluated the study of Chitosan (Ch) which is a naturally occurring biocompatible and bio-degradable material with high corrosion protective capacities for metals in various corrosive media and Hydroxyapatite (HA) used as a significant biodegradable and bioactive material. In the present work, chitosan–hydroxyapatite (Ch–HA) composite coatings with various concentrations of chitosan were made on 316L stainless steel (316L SS) using sol–gel dip coating technique. Dinu *et al.* [3] have studied the failures of metal-ceramic dental restorations happen due to the initiation of a corrosive process that leads to the deterioration of restorations from a mechanical and aesthetic point of view, by releasing ions and corrosion products, causing patient hypersensitivity, as well as by detaching the ceramic from the metal support. The purpose of this study was to improve the metal-ceramic adhesion of dental prosthetic frameworks by covering their metallic components with biocompatible inorganic coatings, resistant to corrosion in the oral cavity environment. The corrosion behavior of WE43 alloy in artificial saliva containing different fluoride ion concentrations was investigated by Zheng *et al.* [4]. The WE43 alloy with an average grain size of 10–30 μm was mainly composed of α-Mg matrix and some RE-containing precipitates. The results of electrochemical corrosion and immersion corrosion tests indicated that the corrosion behavior of WE43 alloy was continuously deteriorated with increasing F- concentration. Liaquat *et al.* [5] have analysed the electrochemical behaviour of alloys (Au50–Ag25–Pd25 and Ni88.6–Cr11.4) was studied in Fusayama’s artificial saliva at pH 6.5 and 37°C by using open circuit potential, electrochemical impedance spectroscopy, and potentiodynamic polarization measurements. All obtained results revealed that Au50–Ag25–Pd25 alloy is much more resistive than Ni88.6–Cr11.4 and can be recommended for the effective treatment of patients with dental prosthetics that have metal frameworks. The corrosion response of heat-treated Beta C titanium alloy in three distinct electrolytes at different temperatures was examined by Nichul *et al.* [6]. All the recrystallized specimens with the random orientation of the grains showed similar corrosion behavior in fluoride-free electrolytes, whereas, in the case of fluoridated saliva a state transition occurred. Larger grain-sized specimens with lower in-grain misorientation ensured higher corrosion resistance. Losiewicz *et al.* [7] have worked on the Carbon nanotubes which are a promising material for use in innovative biomedical solutions due to their unique chemical, mechanical, electrical, and magnetic properties. This work provides a method for the development of ultrasonically assisted electrophoretic deposition of multi-walled carbon nanotubes on a CoCrMo dental alloy. Functionalization of multi-walled carbon nanotubes was carried out by chemical oxidation in a mixture of nitric and sulfuric acids. Kaewnisai *et al*. [8] have reported that the plasma nitriding process of Ti–6Al–4V alloy, commonly used as implant material in biomedical applications. The nitriding process was carried out using an N_2–H_2 plasma (1000:500 sccm) at an operating pressure of about 866 Pa. The results showed that all the nitrided samples had a surface hardness approximately three times that of the unnitrided sample. BajtLeban *et al*. [9] have observed the corrosion behaviour of the microstructural properties of a dental Ti_6Al_4V alloy in oral environments. With the introduction of new, emerging technologies, such as selective laser melting and post heat treatments, the effect of the microstructure on an alloy's corrosion properties has become increasingly interesting from a scientific perspective. The corrosion behavior and *in vitro* biocompatibility of Ti–Nb–Sn alloy in various dental applications were explored by Xie *et al*. [10]. By using the mechanical alloying and mold sintering process, the corrosion resistance and *in vitro* biocompatibility of Nb on the microstructure were investigated.

Orthodontic wires undergo corrosion in the saliva environment. Corrosion of orthodontic wires can lead to roughening of the surface and weakening of the appliances. It can severely affect the ultimate strength of the material, leading to mechanical failure or even fracture of the orthodontic materials. Apart from this, they undergo corrosion by the juices, food items, candies, tablets taken in. Mouthwashes are used to clean the teeth.

The present work is undertaken to investigate the influence of Colgate Max Fresh mouthwash on the corrosion resistance of TASE alloy in artificial saliva by electrochemical studies such as polarization study and AC impedance spectra.

Experimental Methods

Orthodontic wire

Orthodontic wire made of TASE alloy was used as test material for this work. TASE consists of 54.52% of nickel and of 45.48% titanium. It is mainly composed of nickel and titanium. It has ultimate tensile strength and elasticity. It is used in catheters, stents, orthodontics for brackets and super elastic needles.

The TASE alloy was encapsulated in Teflon rod. It was polished to mirror finish and used for electrochemical studies. The metal specimens encapsulated in a Teflon rod were immersed in artificial saliva, whose composition was: 0.4 g/l of KCl, 0.4 g/l of NaCl, 0.906 g/l of $CaCl_2 \cdot 2H_2O$, 0.690 g/l of $NaH_2PO_4 \cdot 2H_2O$, 0.005 g/l of $Na_2S \cdot 9H_2O$ and 1 g/l of urea with the pH of the artificial saliva is approximately 6.9.

Benefits of Colgate Max Fresh mouthwash

Colgate Max Fresh mouthwash kills 99% of bad breath causing germs in your mouth. It can protect the mouth from cavities and keep the gums healthy. It has antibacterial properties. It keeps the mouth fresh and cool while ensuring healthy gums.

Ingredients of Colgate Max Fresh mouthwash

Colgate Max Fresh mouthwash contains glycerin, propylene glycol, sodium benzoate, sodium fluoride, sodium saccharin, flavour, sorbitol, polysorbate and menthol. The active ingredient sodium benzoate present in Colgate Max Fresh mouthwash plays a significant role in decreasing the presence of bacteria and fungi in the mouth. Anti-corrosive and preservative properties of sodium benzoate present in Colgate Max Fresh mouthwash, lead to inhibit the growth of microbes in the mouth.

Electrochemical study

In the present work corrosion resistance of TASE alloy immersed in various test solutions were measured by polarization study and AC impedance spectra. In the present exploration, polarization studies were carried out in a CHI Electrochemical work station/analyzer, model 660 A.

Polarization study

Polarization studies were carried out in a three electrode cell assembly. A SCE was the reference electrode. Platinum was the counter electrode. TASE alloy was the working electrode. From polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes anodic=b_a, and cathodic=b_c and LPR (linear polarization resistance) values were measured.

AC impedance spectra

In the present investigation the same instrument and set-up used for polarization study was used to record AC impedance spectra also. A time interval of 5 to 10 min was given for the system to attain a steady state open circuit potential. The real part (Z') and imaginary part ($-Z''$) of the cell impedance were measured in ohms at various frequencies. AC impedance spectra were recorded with initial E(v)=0, high frequency (Hz=$1\cdot10^5$), low frequency (Hz=1), amplitude (V) = 0.005 and quiet time (s) = 2. From Nyquist plot the values of charge transfer resistance (R_t) and double layer capacitance (C_{dl}) were calculated. From Bode plots impedance values and phase angle values were calculated.

Results and Discussion

The present investigation is undertaken to study the corrosion resistance of orthodontic wire made of TASE alloy in artificial saliva in the absence and presence of Colgate Max Fresh mouthwash, by electrochemical studies such as polarization study and AC impedance spectra [11].

Polarization study

The influence of Colgate Max Fresh mouthwash, on the corrosion resistance of TASE alloy in artificial saliva (AS), has been investigated by polarization study.

The polarization curves of TASE alloy in AS in the absence and in the presence of Colgate Max Fresh mouthwash are shown in Figure 1. The corrosion parameters are given in Table 1. The corrosion parameters are compared in Figures 2–4.

Table 1. Corrosion parameters of thermoactive superelastic shape memory alloy in artificial saliva in the presence of mouthwash obtained from polarization study.

System	E_{corr}, **mV *vs* SCE**	b_c, **mV/decade**	b_a, **mV/decade**	**LPR, Ohm·cm^2**	i_{corr}, **A/cm^2**
Alloy in artificial saliva (AS)	–827	155	230	$2.39 \cdot 10^5$	$168.6 \cdot 10^{-7}$
Alloy in AS + 2% v/v mouthwash	–492	140	305	$84.43 \cdot 10^5$	$4.928 \cdot 10^{-9}$
Inference	Anodic shift. Anodic reaction controlled predominantly			Increases. Corrosion resistance increases.	Decreases. Corrosion resistance increases.
	Implication		People clipped with orthodontic wire made of thermoactive superelastic shape memory alloy may use mouthwash without any hesitation		

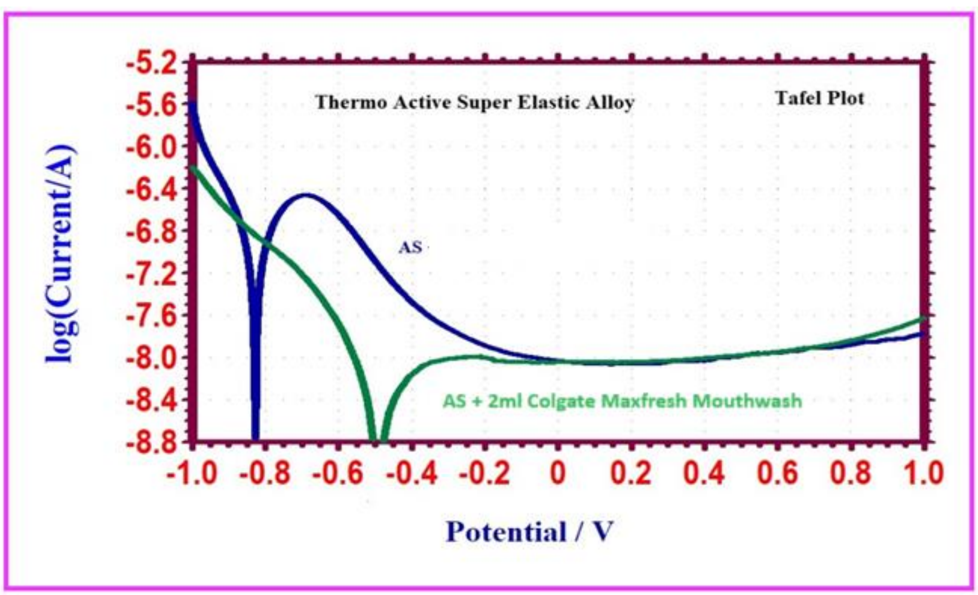

Figure 1. Polarization curves of TASE alloy immersed in Artificial Saliva/AS+2 ml Colgate Max Fresh mouthwash.

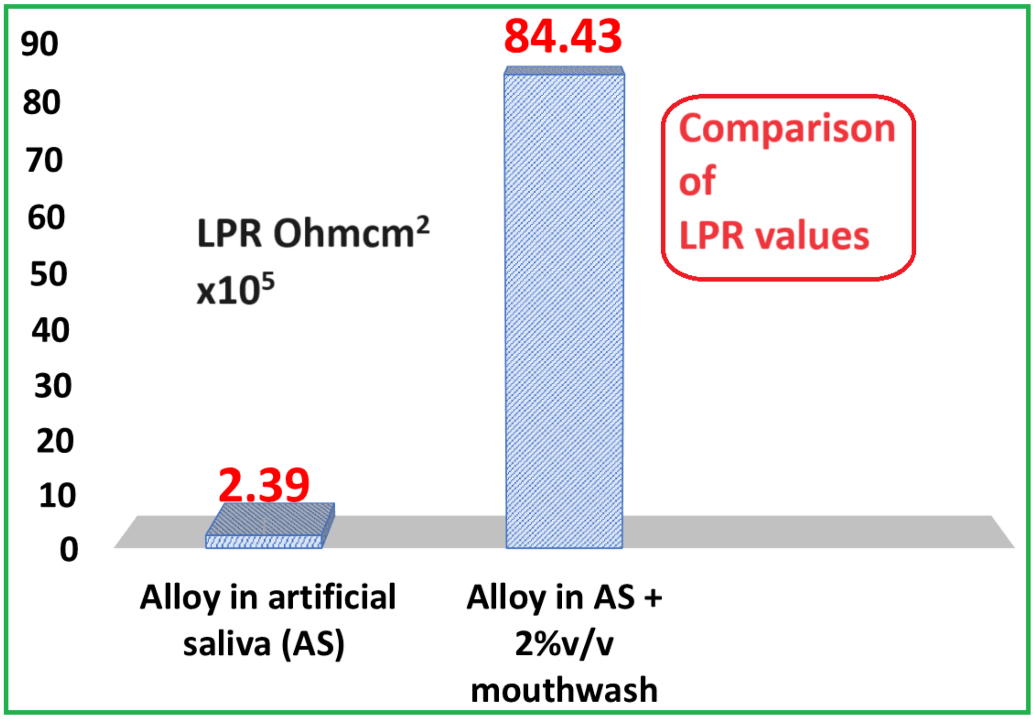

Figure 2. Comparison of LPR values of TASE alloy immersed in various test solutions.

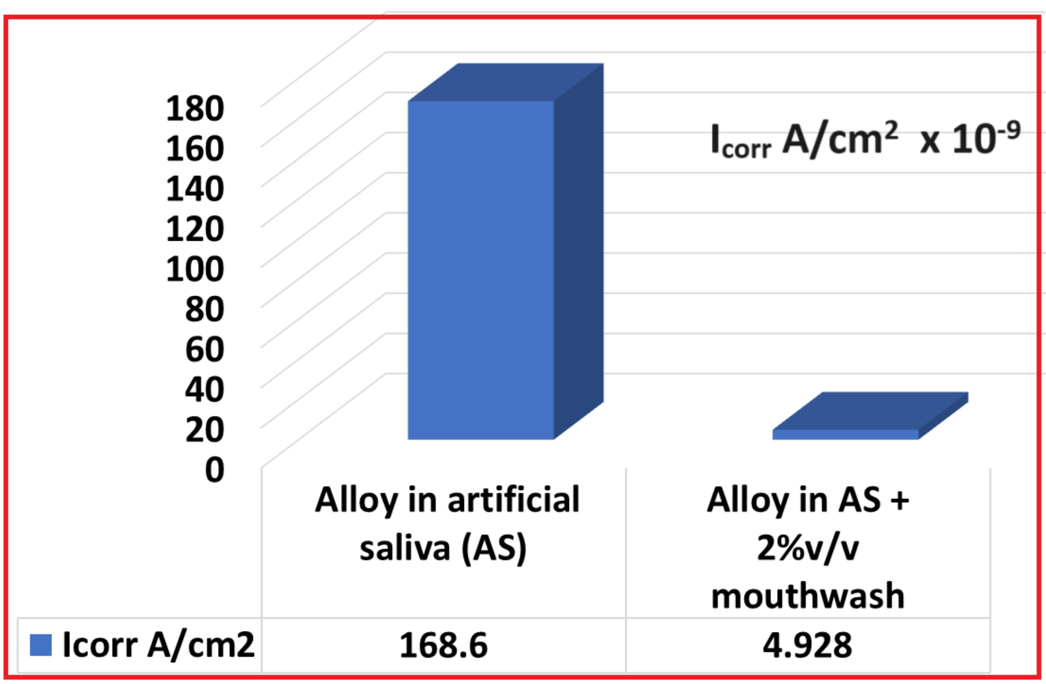

Figure 3. Comparison of i_{corr} values of TASE alloy immersed in various test solutions.

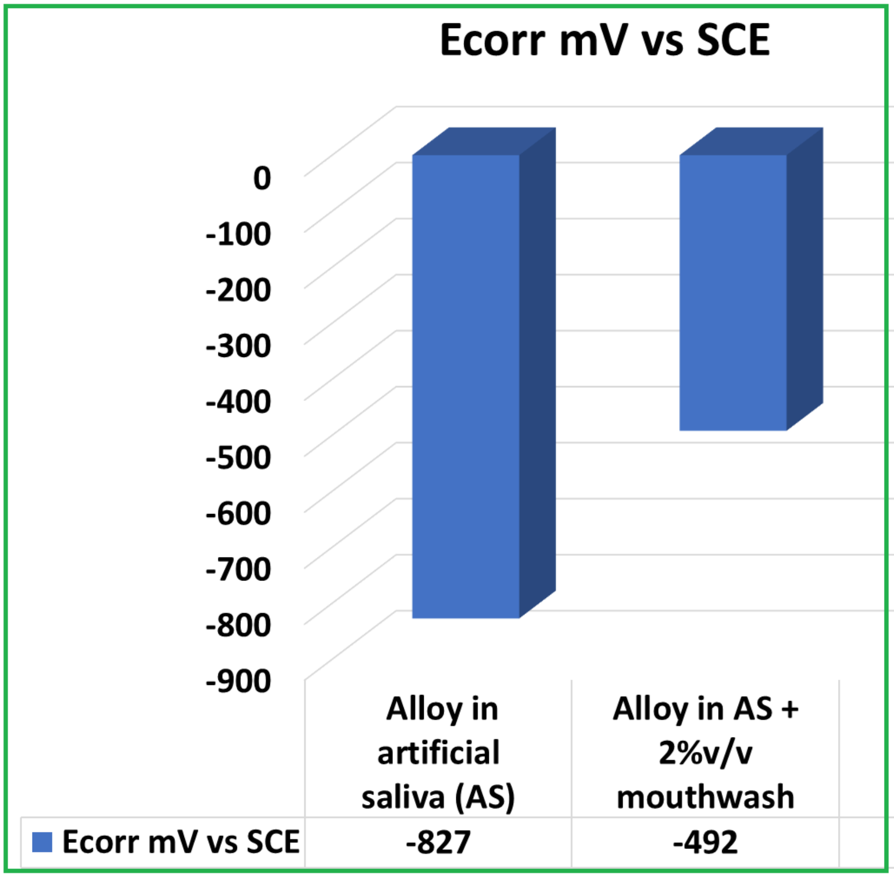

Figure 4. Comparison of E_{corr} values of TASE alloy immersed in various test solutions.

Correlation of corrosion parameters obtained by polarization study is shown in Figure 5.

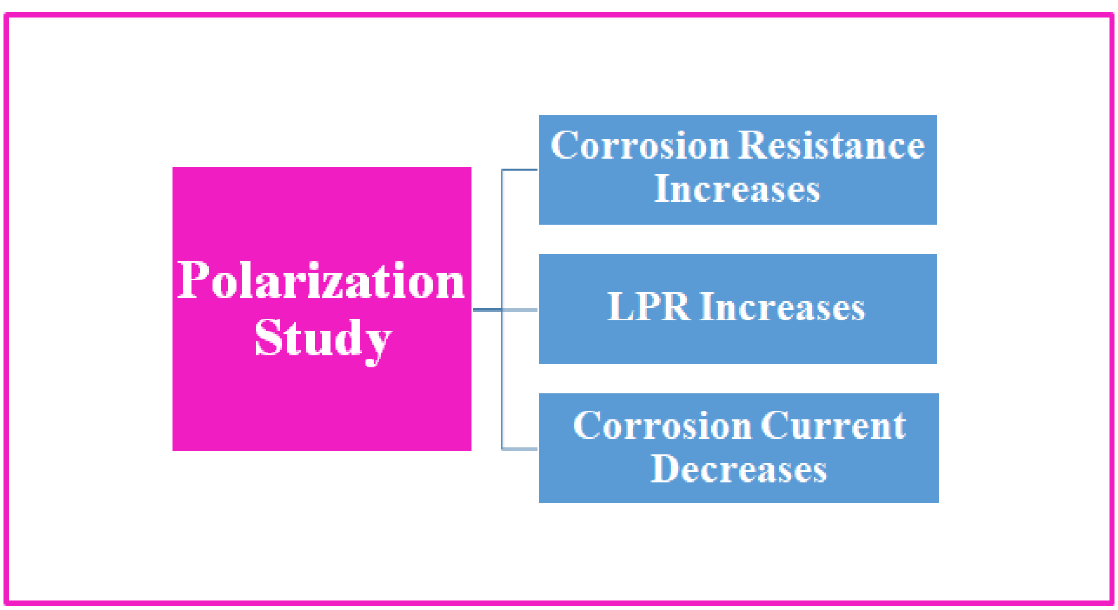

Figure 5. Correlation among corrosion parameters obtained by polarization study.

Based on these concepts, it is observed from Table 1, that in the presence of Colgate Max Fresh Mouthwash, the corrosion resistance of TASE in AS increases. This is revealed by the fact that, in the presence of Colgate Max Fresh mouthwash, LPR value of TASE increases and corrosion current decreases.

It is also inferred that in the presence of Colgate Max Fresh Mouthwash the corrosion potential shifts from –827 to –492 mV *vs.* SCE. It is inferred that in presence of Colgate max fresh mouthwash, the anodic reaction is controlled predominantly.

Implication

Corrosion resistance of TASE alloy in artificial saliva increases in the presence of Colgate Max Fresh mouthwash. Hence it is concluded that, people clipped with orthodontic wire made of TASE alloy in artificial saliva need not worry about using Colgate Max Fresh mouthwash for mouth washing.

AC Impedance spectra

The AC impedance spectra of TASE alloy in AS in the absence and presence of Colgate Max Fresh Mouthwash are shown in Figures 6–8. The Nyquist plots are shown in Figure 6. The Bode plots are shown in Figures 7 and 8. The 3D drawings are shown in Figures 9 and 10. The corrosion parameters are compared in Figures 11–14.

The corrosion parameters such as charge transfer resistance (R_t), impedance value and double layer capacitance (C_{dl}) values, impedance values and phase angle values are given in Table 2.

Table 2. Corrosion parameters of thermoactive superelastic shape memory alloy immersed in artificial saliva in the presence of mouthwash obtained from AC impedance spectra

System	R_t, Ohm·cm^2	Impedance (log$Z$/Ohm)	Phase angle, °	C_{dl}, F/cm^2
Alloy in artificial saliva (AS)	$7.83 \cdot 10^5$	6.383	79	$6.52 \cdot 10^{-12}$
Alloy in AS+2% v/v mouthwash	$10.09 \cdot 10^5$	6.632	81.68	$5.05 \cdot 10^{-12}$
Inference	Increases. Corrosion resistance increases	Increases. Corrosion protection increases	Increases. Corrosion protection increases	Decreases. Corrosion protection increases
Implication		People clipped with orthodontic wire made of thermoactive superelastic shape memory alloy may use mouthwash without any hesitation		

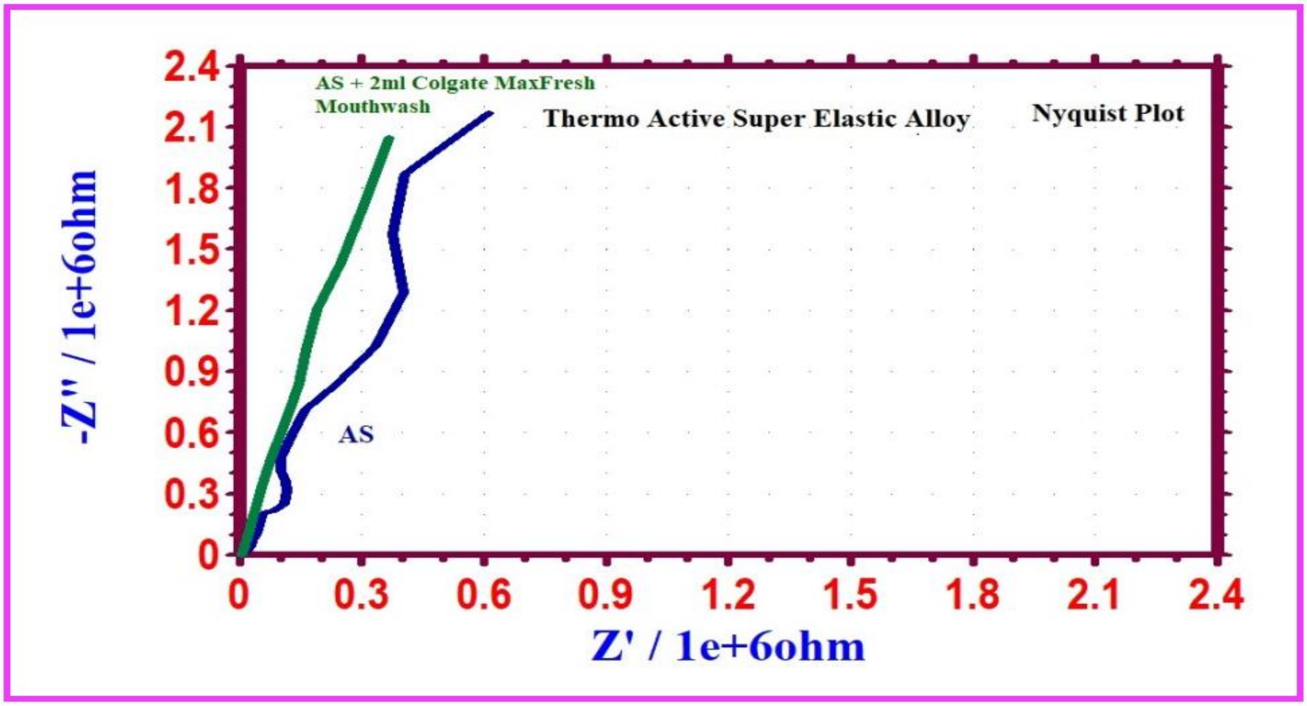

Figure 6. Nyquist plots of TASE alloy immersed in artificial saliva/AS + 2 ml Colgate Max Fresh mouthwash.

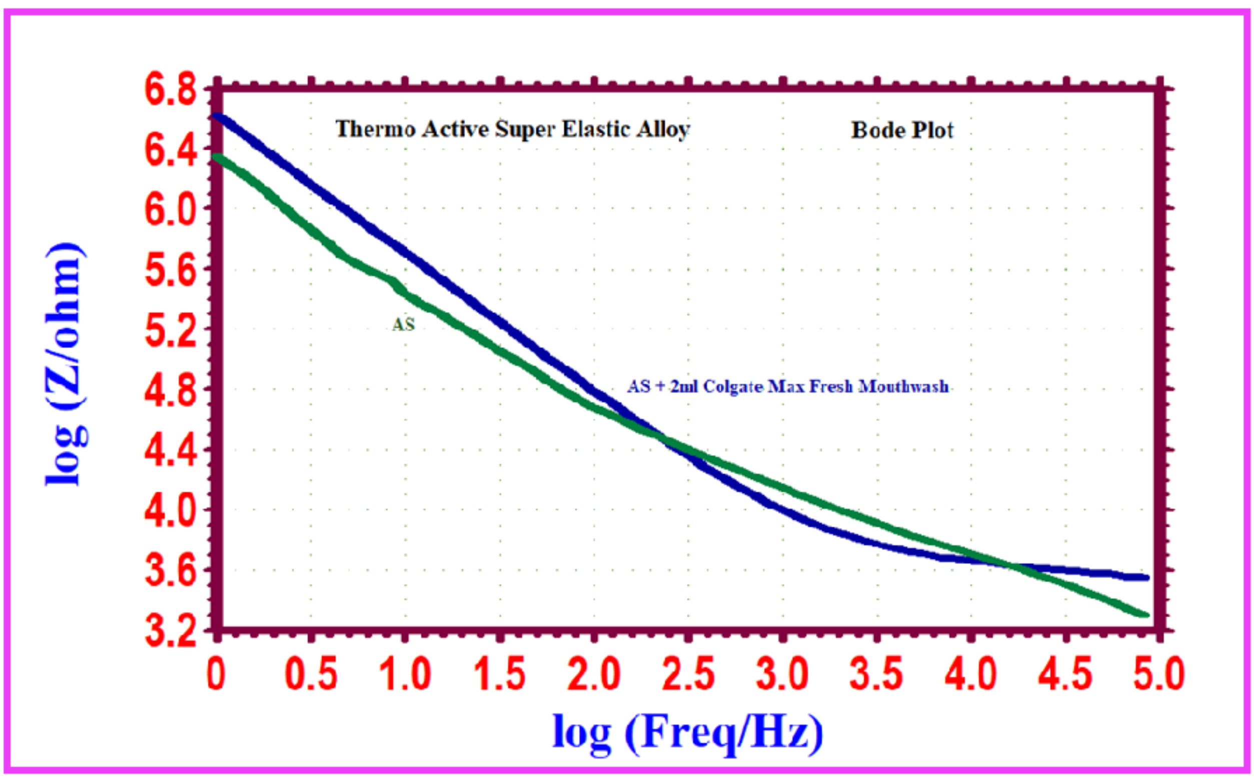

Figure 7. log(Z/Ohm) *vs* log(Freq/Hz) Bode plots of TASE alloy immersed in artificial saliva/AS + 2 ml Colgate Max Fresh mouthwash.

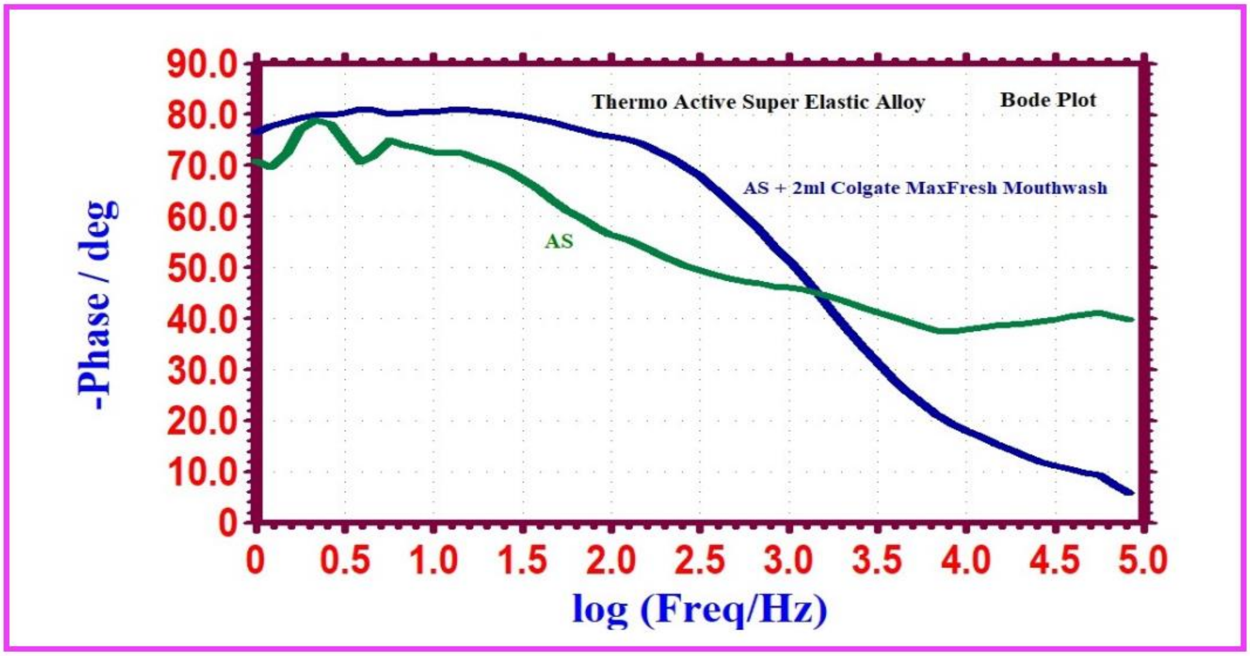

Figure 8. Phase/deg *vs.* log(Freq/Hz) Bode plots of TASE alloy immersed in artificial saliva/AS+2 ml Colgate Max Fresh mouthwash.

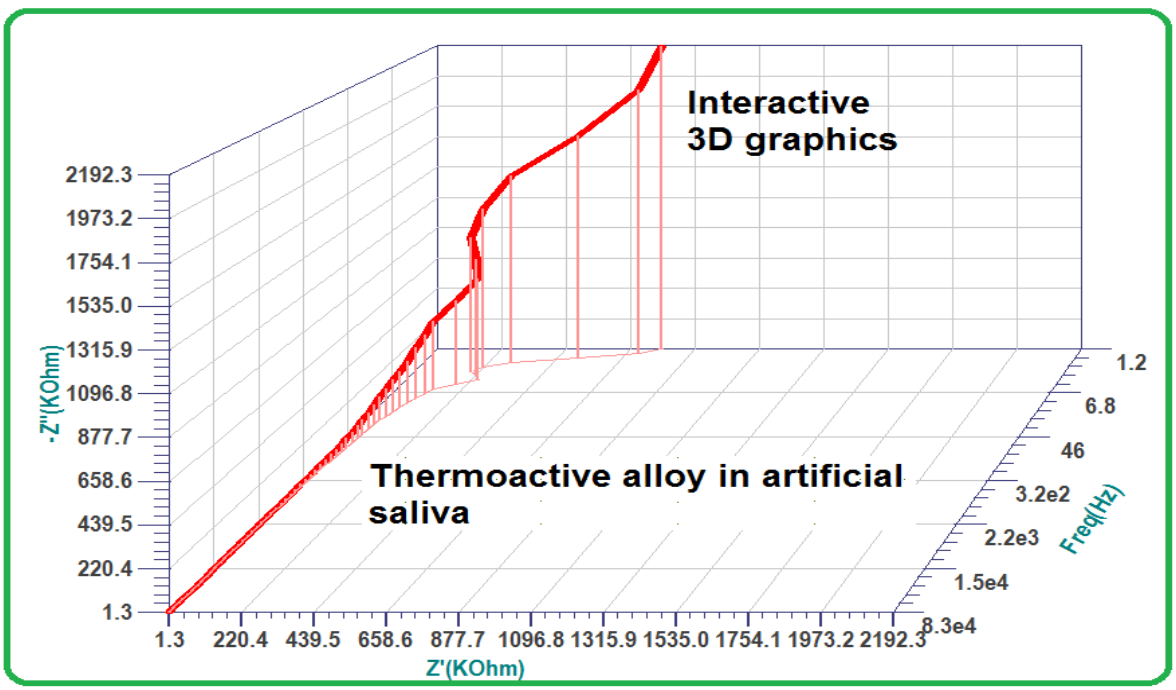

Figure 9. Interactive 3D graphics of TASE alloy immersed in AS.

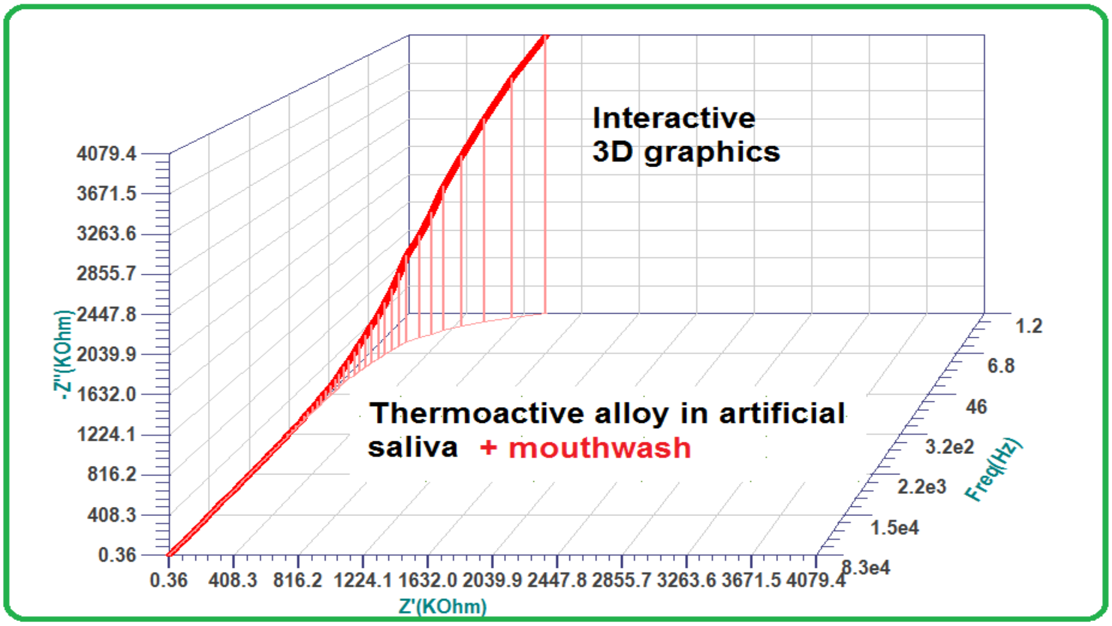

Figure 10. Interactive 3D graphics of TASE alloy immersed in AS+mouthwash.

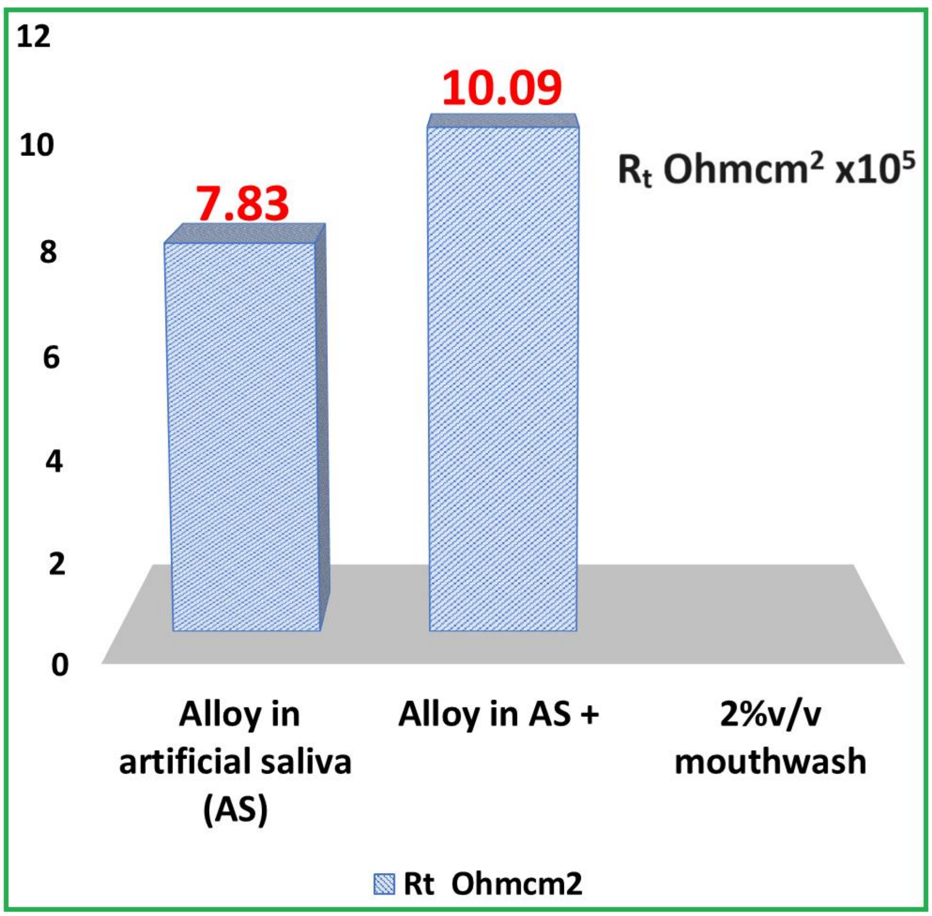

Figure 11. R_t values of TASE alloy immersed in various test solutions.

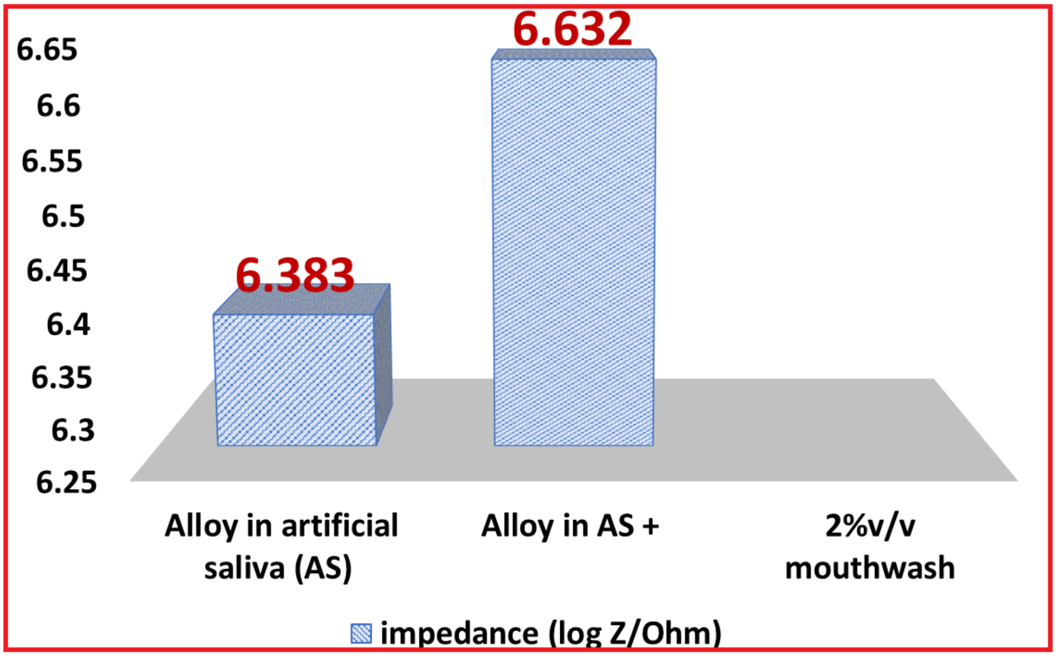

Figure 12. Impedance values of TASE alloy immersed in various test solutions.

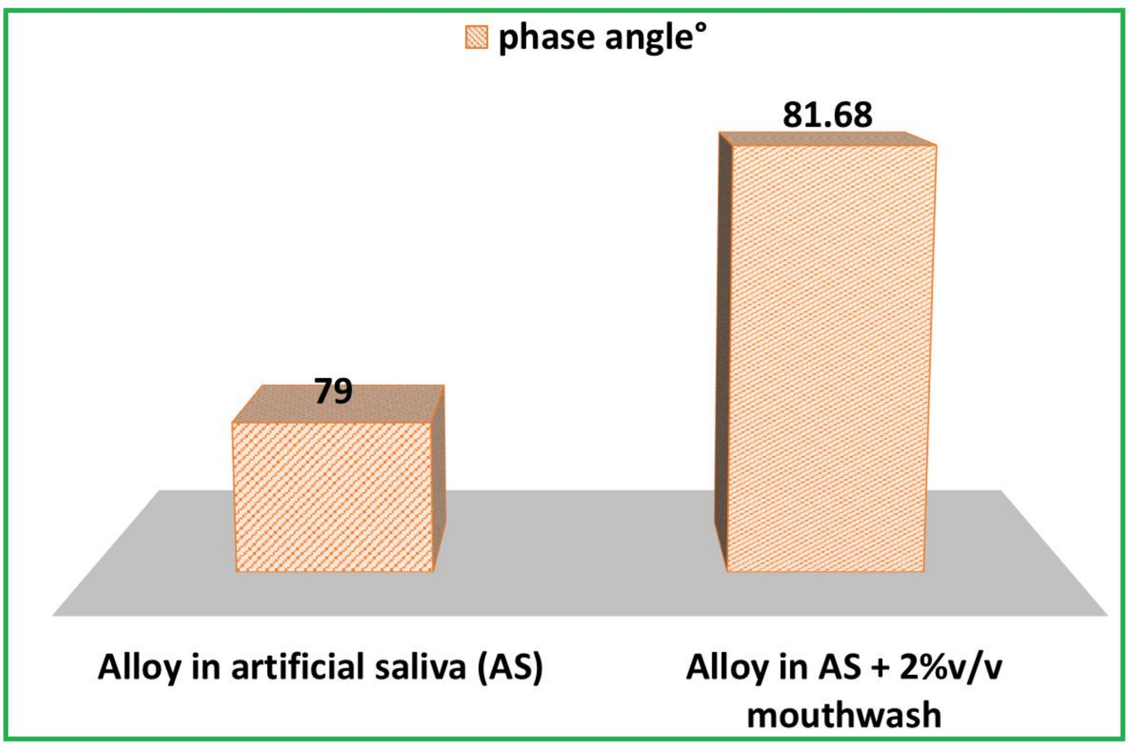

Figure 13. Phase angle values of TASE alloy immersed in various test solutions.

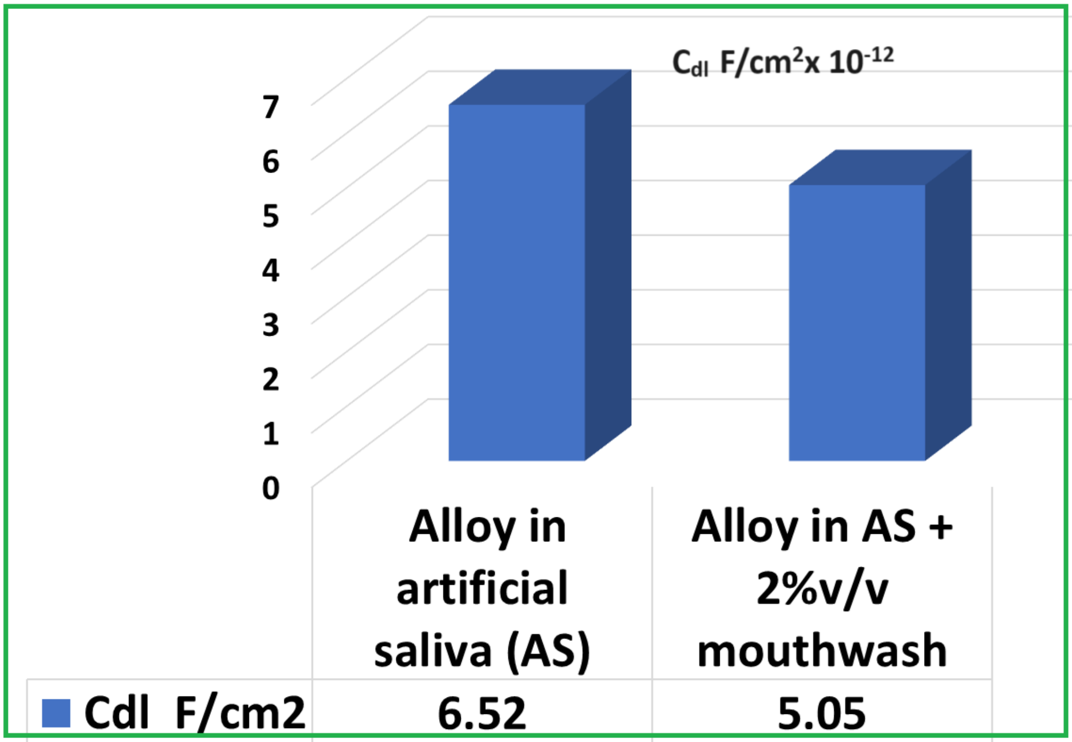

Figure 14. C_{dl} values of TASE alloy immersed in various test solutions.

Correlation of corrosion parameters obtained by AC impedance spectra is shown in Figure 15.

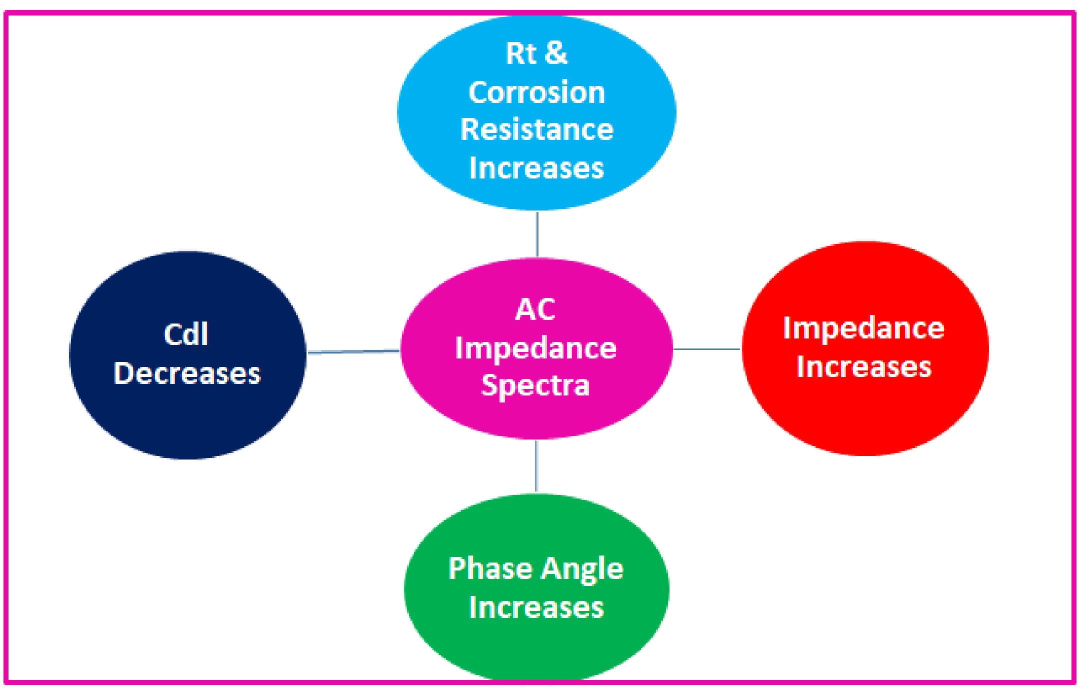

Figure 15. Correlation among corrosion parameters obtained by AC impedance spectra.

It is observed from Table 2, that in the presence of Colgate Max Fresh mouthwash the corrosion resistance of TASE in artificial saliva increases. This is revealed by the fact that in presence of Colgate Max Fresh mouthwash, R_t value increases, impedance value increases, phase angle value increases and C_{dl} value decreases.

When TASE alloy is immersed in artificial sweat in the presence of Colgate Max Fresh mouthwash, charge transfer resistance value increases from $7.83 \cdot 10^5$ Ohm·cm^2 to $10.09 \cdot 10^5$ Ohm·cm^2, the impedance value increases from 6.383 to 6.632, the double layer capacitance decreases from $6.52 \cdot 10^{-12}$ F/cm^2 to $5.05 \cdot 10^{-12}$ F/cm^2, and phase angle increases from 79° to 81.68°.

Implication

Corrosion resistance of TASE alloy in artificial saliva increases in the presence of Colgate Max Fresh mouthwash. Hence it is concluded that, people clipped with orthodontic wire made of TASE alloy in artificial saliva need not worry to use Colgate Max Fresh mouthwash for mouth washing.

Analysis of SEM images

SEM images have been used in corrosion inhibition studies [12]. The SEM images of various images are shown in Figure 16. When orthodontic wire is in contact with artificial saliva the surface is rough and pits are noticed. When orthodontic wire is in contact with artificial saliva + mouthwash the surface becomes smooth and corrosion resistance increases. This is in agreement with the conclusions derived from electrochemical studies.

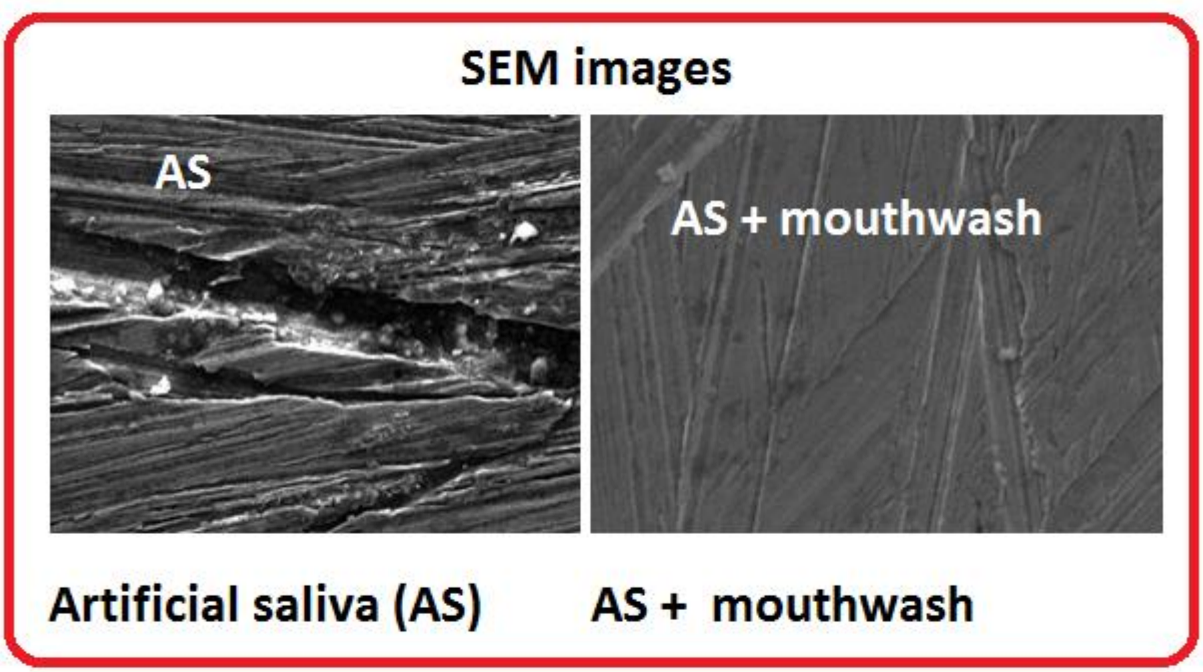

Figure 16. SEM images of various surfaces.

Analysis of AFM images

AFM images have been used in corrosion inhibition studies [12]. The AFM images are shown in Figures 17 and 18. The AFM parameters are given in Table 3. The RMS roughness of the orthodontic wire immersed in Artificial saliva is 553.2 nm. In the presence of mouthwash it decreases to 329.7 nm. This is due to the formation of a protective film formed on the orthodontic wire. Similar is the case with RMS (S_q) roughness and Maximum peak-to-valley height (S_y).

Table 3. AFM parameters (are a roughness) of orthodontic wire immersed in various systems.

Sample	RMS (S_q) roughness (nm)	Maximum peak to valley height (S_y) (nm)
Artificial saliva	553.2 nm	4.3 µm
Artificial saliva + mouthwash	329.7 nm	2735.4 nm
Inference	Roughness decreases. Surface becomes smooth	Decreases. Depth of valley decreases

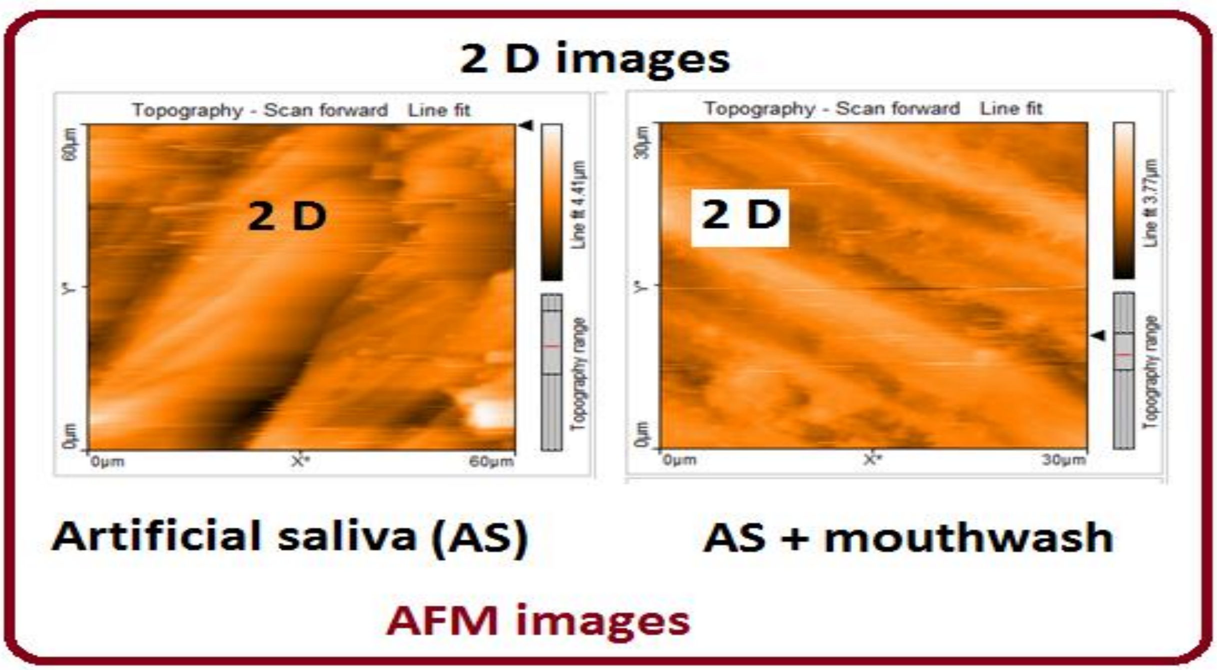

Figure 17. 2D AFM images of various surfaces.

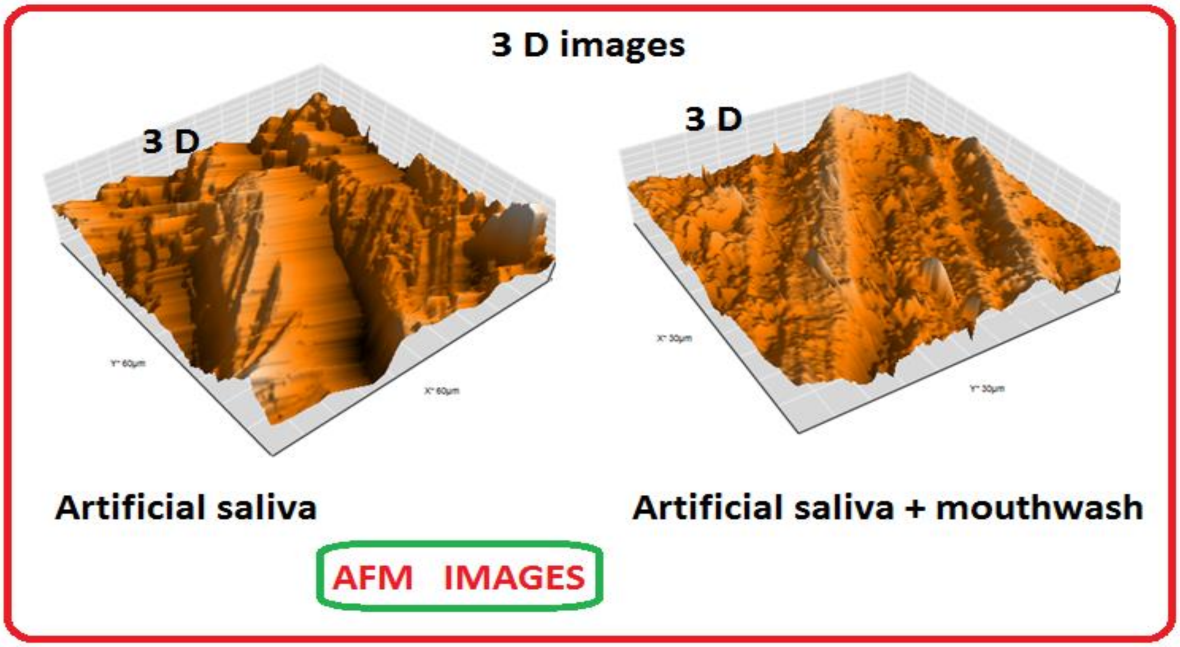

Figure 18. 3D AFM images of various surfaces.

Summary and Conclusions

Corrosion resistance of TASE alloy in artificial saliva (AS), in the absence and presence of Colgate Max Fresh mouthwash has been investigated by polarization study and AC impendence spectra. It is inferred that corrosion resistance of TASE alloy in artificial saliva increases in the presence of Colgate Max Fresh Mouthwash. This is revealed by increase in LPR value, increase in R_t value, increase in impedance value, decrease in corrosion current, increase in phase angle and decrease in double layer capacitance value. Hence it is concluded that, people clipped with orthodontic wire made of TASE alloy in artificial saliva need not worry to take Colgate Max Fresh mouthwash for mouth washing (Table 4). SEM and AFM have been used to analyze the surface morphology.

Table 4. Summary of the study.

Corrosion parameters	Artificial saliva (AS)	AS + Colgate Max Fresh mouthwash (increases/decreases)
LPR	$2.39 \cdot 10^5$	$84.43 \cdot 10^5$ (increases)
R_t	$7.83 \cdot 10^5$	$10.09 \cdot 10^5$ (increases)
Impedance	6.383	6.632 (increases)
Corrosion current density	$1.686 \cdot 10^{-7}$	$4.928 \cdot 10^{-9}$ (decreases)
Double layer capacitance	$6.52 \cdot 10^{-12}$	$5.05 \cdot 10^{-12}$ (decreases)
Phase angle	79°	81.68° (increases)

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