Modifications of Hydroxyapatite by Gallium Ion as a Coating on Dental Ti6Al4V for Corrosion Protection

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Abstract

Gallium ion (Ga) was substituted for bioactive ions in the hydroxyapatite "HA" coating formed on the "Ti-6Al-4V ELI" dental alloy (Gr.23) utilizing electrochemical deposition in this study. Scanning electron microscopy was used to examine the deposited layers (SEM). Electrochemical methods potentiodynamic polarization curves were used to study and characterize the corrosion behavior of Gr.23 alloy in an artificial saliva environment at temperatures ranging from 298 to 328K. After modification coating of HA with Ga at 298K, corrosion protection increased from (50.49) percent (coated Gr.23 by HA without Ga) to (76.0) percent. The coating thickness was estimated using a cross-sectional SEM micrograph; the thickness of the coatings for HA and Ga-HA coatings were (3.51 and 3.62 m, respectively).

Introduction

Titanium alloys are among the ideal bio-materials for dental applications due to their low toxicity, outstanding corrosion resistance, good mechanical quality, and bio-compatibility with bone (Rautray et. al. 2010; Wang et. al. 2014). Due to its predisposition towards self-passivation, the greatest biotolerance is estimated among all currently used dental biomaterials. (Simka *et al.* 2014).

Because live tissue readily accepts apatite, it can be deposited on the surface of dental implants. Apatite can also promote a strong attachment between cells and the surfaces of a dental implant (Sobieszczyk and Klotzke, 2011). By its similarity to the inorganic portion of human bones, hydroxyapatite (HA) is a desirable bone repair and regeneration material. (Al Mashhadani 2019).

The flow of "Ca_2+ and PO_{43}" ions into the adjacent oral environment contributes to the creation of good interfacial adhesion between the implants and the bones, and HA has been widely employed as a coating material for titanium dental implants in a variety of applications. (Raja et. al 2008).

The structure of synthetic HA was selectively integrated into an extensive range of various ions, such as "Ga, Zn, Fe, Ag, CO3-1", F and SR, replacing "Ca/PO43−", Ion replacement in HA alters the crystalline and crystal size and material properties, notably, temperature and phase stability, solubility, surface responsiveness and absorption capacity (Aryal et. al; 2015).

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Gallium ions are much less hazardous than other ions and are based primarily on substituting iron ions for protein metabolism, leading to cell functional impairment. Gallium ions are particularly beneficial for bone tissue induction by osteoporosis (Chitambar, 2010) and protection from enhanced resorption by blocking osteoclastic activities and altering crystal resolvability. The addition of Ga with HA reduces crystallinity and enhances cell adhesion. Electrochemical deposition approach Ga-HA distributed at a specified pH in an appropriate solvent. These coatings require improved coating effects (Yajing et. al. 2014).

In this research, Ga-HA dental alloy coating on Ti-6Al-4V ELI was examined with electrochemical deposition, and the scanning microscopy for the electrons was characterized (SEM).

Experimental Part

1. Titanium Preparation

"Ti-6Al-4V ELI" dental alloys "Green 23" circular form samples were cut in sizes with a diameter of "1 cm and a thickness of 4-5 mm". These samples were polishes made using emery papers of various grades, "600, 800, 1200, and 2000 grit", and were rinsed with tap water, distilled water, and ethanol. (Al Mashhadani and Saleh 2020a).

2. Artificial Saliva Preparation

A method described in this paper was utilized to modify the electrolyte reference Fusayama artificial saliva(19) which is very similar to real saliva, the composition shown in Table (1), and the pH of that electrolyte was 6.2.

Table 1. The composition of artificial saliva (AlMashhadani and Saleh 2020b) ".

	"K Cl"	"Na Cl"	"CaCl$_2$. H$_2$O"	"NaH$_2$PO$_4$ .2H$_2$O"	"Na$_2$S. 9H$_2$O"	"ur ea"
"g /l"	"0. 4"	"0. 4"	"0.906 "	"0.69"	"0.005 "	"1"

3. Electrochemical Deposition of Ga-HA

HA replaced with 10% Ga covered have been manufactured immediately on a Gr.23 alloy surface by electrochemical deposition. The (Ca+Ga)/P experimental ratio was kept to 1.7 (molar ratio).

The suspension was generated with the addition of di-ammonion hydrogen phosphate ((NH4)$_2$HPO$_4$) in distilled water, and its "pH value" was adjusted to 4.4 by the diluting HNO3 by diluting calcium nitrate (Ca(NO$_3$)2), gallium nitrate trihydrate (Ga(NO$_3$)3.3 H$_2$O). At room temperature and at direct current "DC" "7.5 V", electrochemical Ga-HA deposition on G.23 was done and the time was kept for 30 min. The samples were rinsed in distilled water and dry with a hair-dryer after the exposure, and then dried in "1 mol/L of NaOH solution" at a temperature of 80°C for 2 h.

4. Characterization and Test

SEM was used to measure and characterize the surface morphology of the Ga-HA coating. WENKING M Lab. (Germany) was used to measure the static polarization of Galvano. For dental Titanium alloys before and after covering with HA and Ga-HA, polarization curves have been produced. Catholic and anode areas involved the polarization curves obtained. Extensive examination of each polarisation zone could be used to "determine the corrosion current (icorr) and corrosion potential using an extrapolated method" (Ecorr).

Result and Discussion

1. Potentiostate Polarization Measurement

In artificial salivary solution (298-328) K for HA without Ga ion, illustrated in the figure, the impact of the coating layer on the polarization curve of "Gr.23" was studied (1). Extrapolation Tafel lines determined the density of the corrosion current (icorr). Table shows the influence of replaced Ga on the HA layer on the corrosion parameter (2). Figure (1) shows that Ecorr Gr.23 Coated with HA and Ga-HA, compared to Ecorr values with the uncoated Gr.23, has shifted to a more active direction. Ecorr has been changed to a more active and uncoated direction with a temperature increase from (298 to 328) K for the HA and Ga-HA coated and Gr.23.
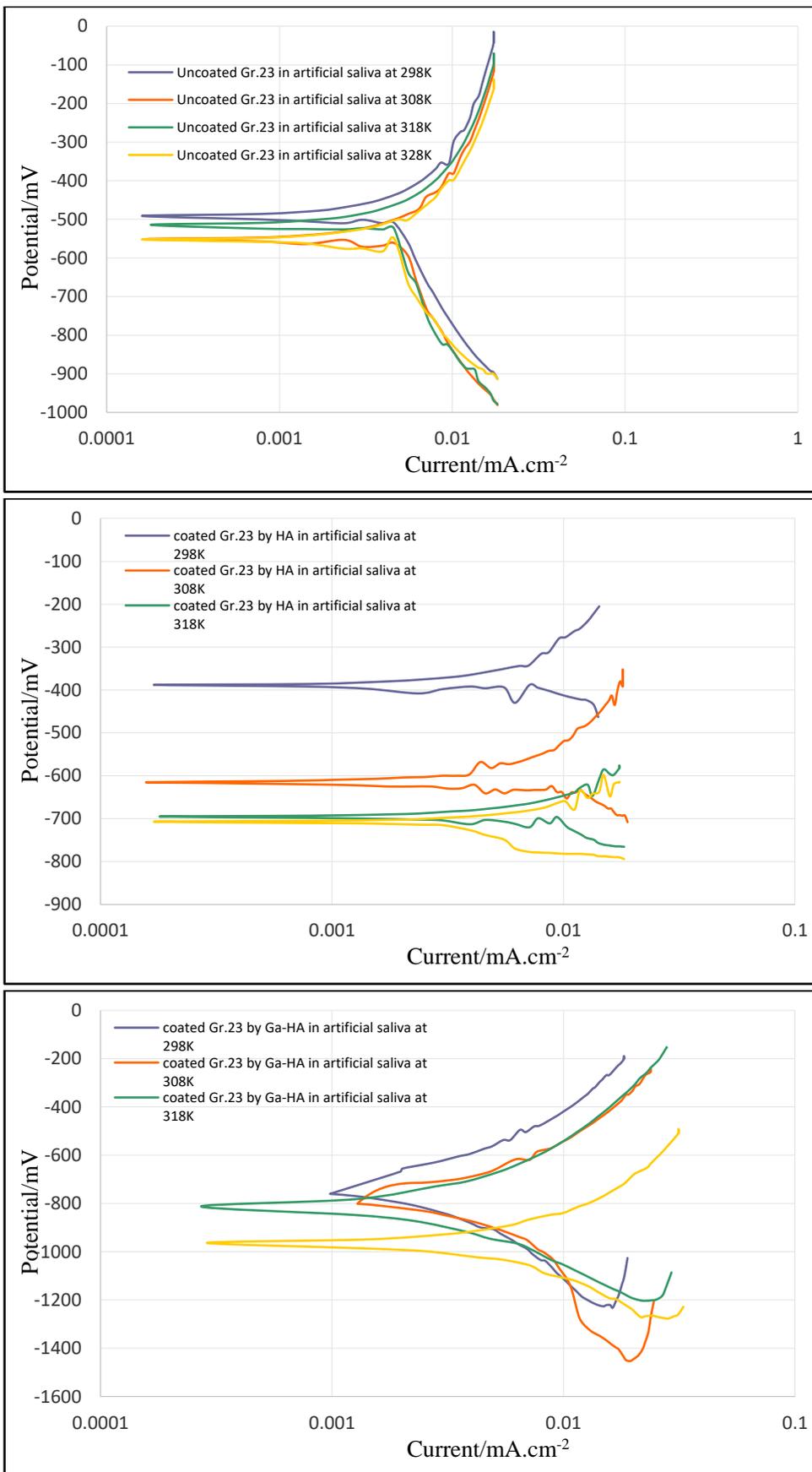
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Figure 1. Polarization curves for Gr.23 a) Uncoated, b) coated by HA only and c) coated by Ga-HA

Table 2. Corrosion parameter of coated Gr.23 in artificial saliva at different Temperatures

	Temp./K	E_{corr}/ mV	i_{corr}/µA.cm^{-2}	bc/mV.dec^{-1}	ba/mV.dec^{-1}	R_p / Ω.cm^2	PE%
Uncoated	298	-490.5	3.230	102.4	285.5	10800.64	-
	308	-551.2	3.690	106.1	391.9	10388.23	-
	318	-515.9	4.002	158.0	400.2	12943.94	-
	328	-550.6	4.020	135.3	495.8	12082.27	-
Coated with HA	298	-390.4	1.700	109.0	87.4	14041.42	50.49
	308	-635.3	1.770	36.5	78.8	6899.16	55.01
	318	-675.1	1.950	37.4	48.9	5258.21	53.94
	328	-712.1	2.090	28.3	48.2	4096.53	50.52
Coated with Ga-HA	298	-721.4	0.927	164.7	180.2	51395.71	76.00
	308	-768.4	0.960	146.5	159.6	43641.49	78.22
	318	-812.9	0.995	231.7	260.2	66941.49	79.07
	328	-958.1	1.102	170.2	161.2	39853.97	76.38

"The data in table (2) show that i_corr values for Gr.23 coated by HA are lower (1.7 to 2.09) µA.cm^{-2} than i_corr values for uncoated Gr.23 (3.23 to 4.02) µA.cm^{-2}. Protection efficiency (PE %) was calculated using the following equation (Shivakumar and Mohana 2013)):

$$\%PE = \frac{(i_{corr})b - (i_{corr})p}{(i_{corr})b} \times 100 \quad (1)$$

Where (i_corr)b and (i_corr)p are the corrosion current density (µA.cm^{-2}) for uncoated Gr.23 and for protected Gr.32 respectively.

This coating resulted in a corrosion-protection cap with a maximum of (PE percent) of 50,49% at 298K, which, as the temperature increases, increases to 53,94% at 318K and subsequently decreases to 50,52% at 328K. Whilst Ga-coating HA's Gr.23 led to a temperature protective layer where the PE percent did not have an impact by temperature (76.0-79.07) percent at 298-328K.

Polarization near corrosion potential. The polarization resistance is determined by Ecorr based on the following equation, namely Stern-Geary (Schorr 1972).

$$R_p = \frac{\Delta E}{\Delta i} = \frac{b_a b_c}{2.303(b_a+b_a)} \cdot \frac{1}{i_{corr}} \quad (2)$$

Where Rp is the system's polarization resistance, E is the difference between the potential E and the corrosion potential Ecorr, I is the difference between the measured current density I and the corrosion current density icorr, and ba and bc are the respective anodic and cathodic Tafel coefficients. The polarization resistance (Rp) values for Gr.23 coated with HA are lower than those for uncoated Gr.23, however coating with Ga-HA causes an increase in Rp values at temperatures between (298 and 328)K, as indicated in table (2).

2. Kinetic Parameters for the Corrosion Process

The corrosion kinetic parameter obtained are listed in "Table 3". "Gr.23" coated by HA without modification by Ga were caused slightly an increase in Ea values from (6.0205 to 6.290) kJ.mol^{-1}. While the Gr.23 coated by modification HA by Ga (Ga-HA) was caused decrease in activation energy with decrease in the number of corrosion active site from (2.4 x10^{25} to 0.52 x10^{25}). Figure (2) show logi_corr plotted against reciprocals temperature for the corrosion of uncoated and coated Gr.23 by HA and Ga-HA.

Table 3. Kinetic and thermodynamic parameters for Gr.23 in artificial saliva at different temperature in the range (298-328) K

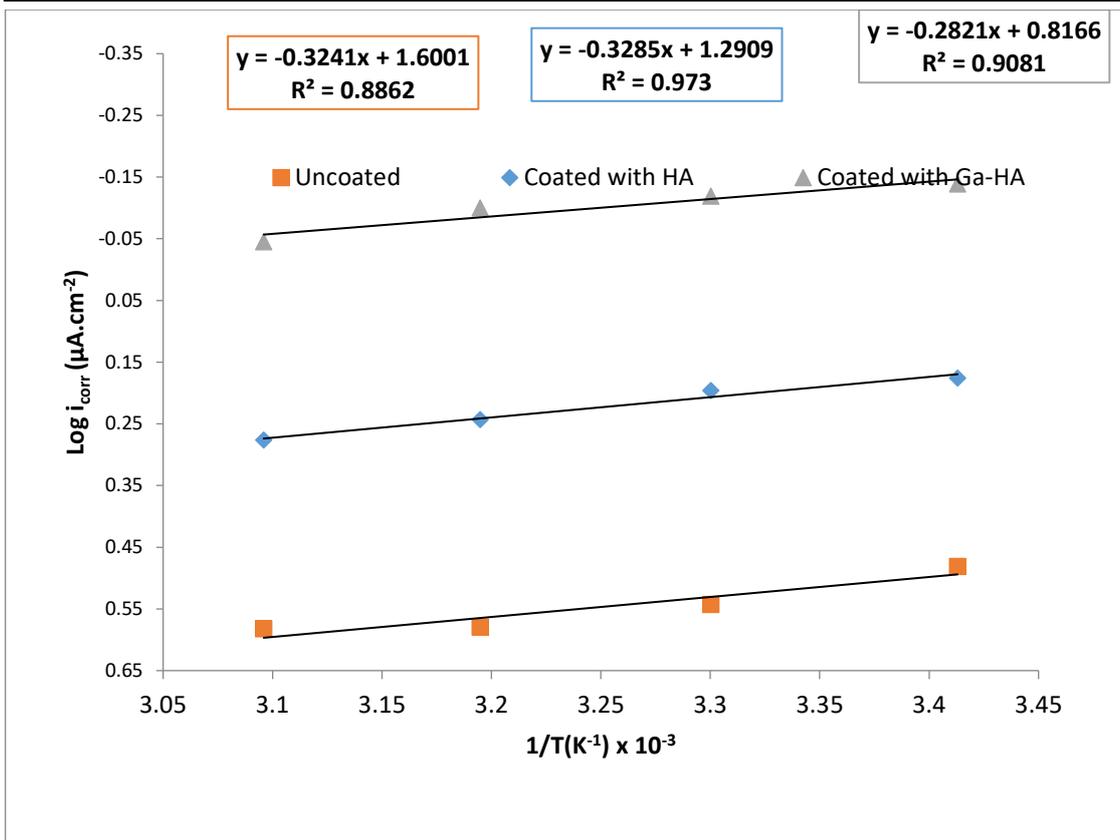|	"ΔG* /kJ.mol^{-1}"				"ΔH*/kJ.mol^{-1}"	"-ΔS*/ J.mol^{-1}·K^{-1}"	"Ea/kJ.mol^{-1}"	"A x10^{25} Molecules.cm^{-2}·S^{-1}"
	298	308	318	328				
"Uncoated"	"68.951"	"71.180"	"73.409"	75.638	3.649	222.88	6.205	2.4
coated by HA	70.771	73.059	75.347	77.635	3.734	228.8	6.290	0.118
coated by Ga-HA	71.36	73.716	76.072	78.428	2.333	235.59	4.890	0.520

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Figure 2. Arrhenius Plot of logicorr Versus 1/T for the corrosion for Gr.23 in artificial saliva solution

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The activation enthalpy — kin* and the activation entropy – kin* — values were based on figure (3) and transition status eq.(3) and were calculated. Table S* values (3), reflecting the changes in the orientation corrosion order and transition state of Gr.23; the data shows somewhat effectuated * = Gr.23 HA coated, ** disorder increases by Ga-HA from (-222.88 to -235.59 (J.mol-1.K-1) after coated Gr.23.

$$log \frac{i_{corr}}{T} = log \frac{R}{Nh} + \frac{\Delta S^*}{2.303R} - \frac{\Delta H^*}{2.303RT} \qquad (3)$$

Where icorr "is the corrosion current density of titanium in artificial saliva calculated using the Tafel plot, h is the Plank's constant, N is the Avogadro number, S* is activation entropy, and H* is activation enthalpy". The values of H* and S* were computed from the plot of log "icorr/T" against reciprocals temperature, which yielded straight lines with a slope of "-H*/2.303 R" and an intercept of ((log(R/Nh)+(S*/2.303R)). The activation enthalpy H* is a component of activation energy; note that the values of H* are related to the values of (Ea). Gr.23, both uncoated and coated with HA and Ga-HA, possesses an endothermic corrosion process; however, covering Gr.23 with Ga-HA reduced the activation enthalpy value. The

values of G* became positive and changed only slightly as the temperature increased, showing "that the activated complex was not stable and that the chance of its creation dropped slightly as the temperature increased".
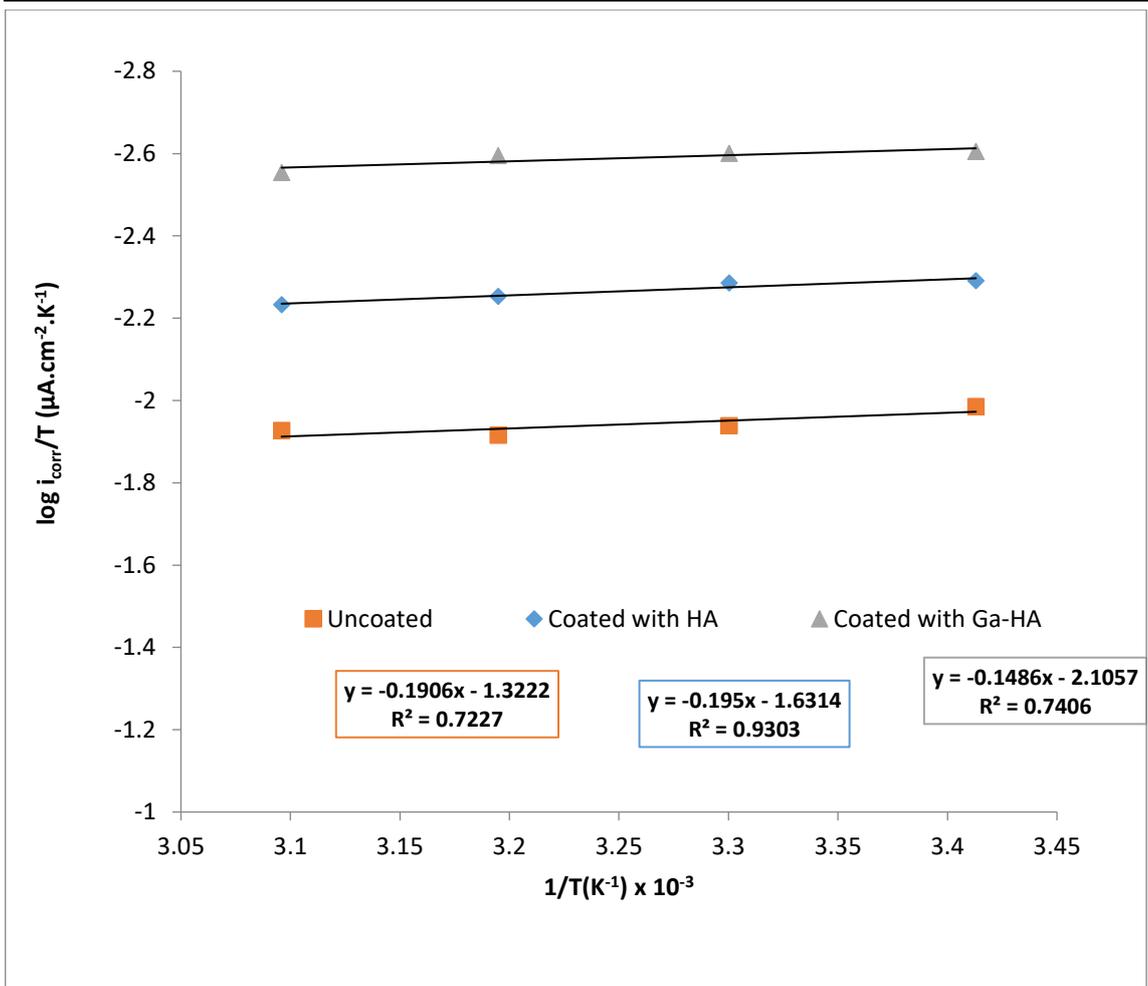
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Figure 3. A plot of $\log i_{corr}/T$ Vs $1/T$ for the corrosion of Gr.23 in artificial saliva

3. Chemical Structure and Morphology of Coating

"SEM Images" were taken for "coated Gr.23" by HA and "Ga-HA". Figure (4) depicts the surface morphologies scanned with SEM for Gr.23 coated with HA and Ga-HA. SEM micrographs of Gr.23 coated with HA alone are shown in "Figure 4a". It's obvious that the coating was mostly continuous, homogeneous, and like crystal needle.

"Figure 4b" explains an on going, homogeneous, and free-crack "Ga-HA coating" with globular hydroxyapatite coated on the surface and flake-shaped hydroxyapatite deposited on the Gr.23 with spot-like Ga nanoparticles sparsely scattered in the coating.

For Gr.23 coated with HA and Ga-HA, the average particle size of the coating was (54.16 and 49)nm, respectively. The particles of HA that had not been modified by Ga ions were larger than the particles of HA that had been modified by Ga ions on Gr.23, indicating that the growth conditions and nucleation on the surface were various in the presence of Ga ions. The coating thickness was (3.51 and 3.62 m) for the HA and Ga-HA coatings, respectively, as seen "in the cross-sectional SEM micrograph of the coating in figure (5)".
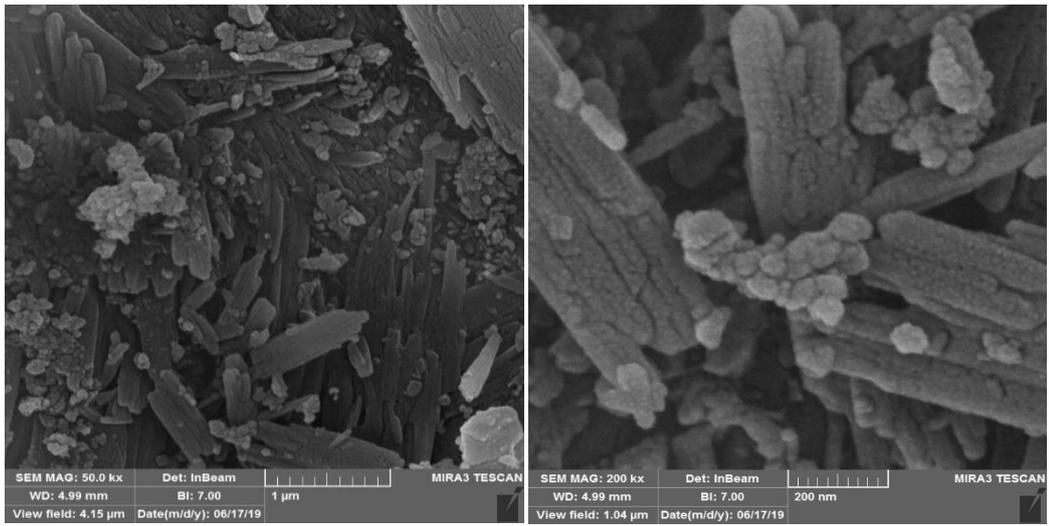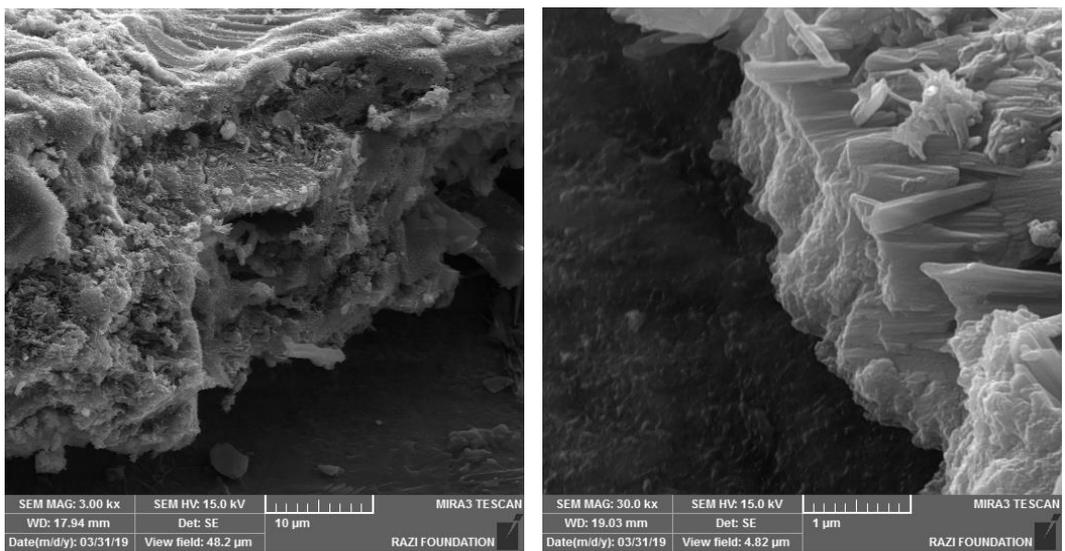
a)
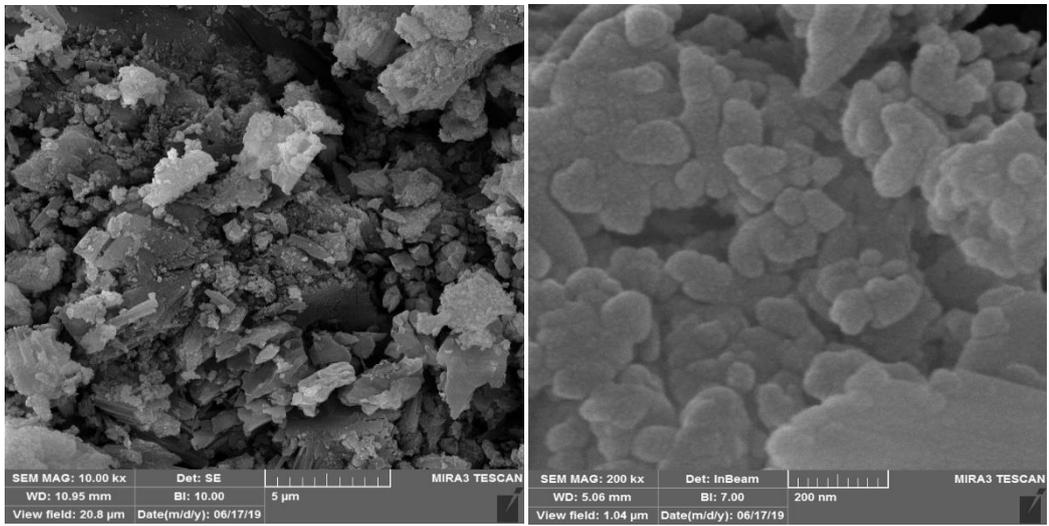
b)

Figure 4. Scanning electron micrographs of Gr.23 coated by (a) HA only and (b) Ga-HA

a)   b)

Figure 5. Cross Section scanning electron micrographs of Gr.23 coated by (a) HA only and (b) Ga-HA

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Conclusions

In comparison to Gr.23 coated with HA and coated with Ga-HA, electrochemical deposition of HA and Ga-HA coating on Ti-6Al-4V ELI dental alloy (Gr.23) increases corrosion efficiency from 50.49 to 76.00 percent at 298K. The size difference between the particles of HA coated on treated Gr.23 without Ga and the particles of Ga-HA coating on Gr.23 revealed that the nucleation and growth conditions on the surface were different in the presence of Ga ion. The coating thicknesses for the HA and Ga-HA coatings were (3.51 and 3.62 m, respectively).

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