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Corrosion Protection of Pure Titanium Implant by Electrochemical Deposition of Hydroxyapatite Post-Anodizing.

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Abstract. In this study, a Hydroxyapatite (HA) coating was prepared on a titanium implant by an electrochemical deposition process. The titanium pre-treatment by anodizing in 1.65 mol/L sulfuric acid with (10V) at room temperature. The deposition was all conducted at a constant voltage of 6.0 V, for 1 h at room temperature. The coatings thus prepared were characterized with Fourier transform infrared spectroscopy (FTIR) and thickness of the coated layer.

The electrochemical deposition of HA occurred on the titanium as a cathode. Coated titanium by HA after anodizing revealed a good corrosion protection efficiency even at a temperature ranged (293- 323) K in artificial saliva. Activation energy and pre-exponential factor (kinetic parameters) were calculated and discussed. Also, thermodynamic values ΔG and ΔH were calculated and it shows that corrosion reaction was non-spontaneous and exothermic in nature before treatment but after anodizing the corrosion reaction become endothermic.

Keyword: Hydroxyapatite, Anodizing, Titanium, Electrochemical deposition, artificial saliva.

1. Introduction

Metallic bio-materials are largely used today in the dental field around the world. Metals and alloys introduce novel physical properties, such as excellent electrical conductivity and thermal conductivity and mechanical features. Some metals can be used as passive substitutes of hard tissues (dental implants). Others play more active roles, such as brackets using in orthodontic and orthodontic wires [1]. The most extensively used metallic bio-materials are commercially pure titanium and its alloys, stainless steel, and chromium-cobalt alloys.[2]

Titanium and its alloys are widely used for the development of orthopedic and dental implants because of good mechanical strength and low density. Titanium and its alloys have been used in medicine and dentistry for many years. Different specialties within the dental vocation take advantages of these materials. Titanium alloys with elements such as nickel, molybdenum and/or copper have wide-spread use in orthodontics [3]; the combinations of this metal with others, such as aluminum and/or vanadium, are used in the oral repair, implantology [1, 4, 5], and maxillofacial surgery [6-8].

Titanium and its alloys belong to the wide group of oxide passive metals that includes in particular the stainless steels, as well as nickel, cobalt and aluminum-based alloys. Pure titanium is a base-metal with a low standard potential (-1.63 V vs. NHE couple to Ti/Ti^{2+}). This shows a high reactivity of a bare Ti surface in aqueous environments. In most natural environments, however, titanium shows an excellent corrosion resistance due to the spontaneous formation of a thin but highly protective TiO_2 passive layer on the surface. Thermodynamically, TiO_2 is stable in a large pH range, as clarified by the potential_pH diagram of the $\text{Ti}/\text{H}_2\text{O}$ system (Figure.1).



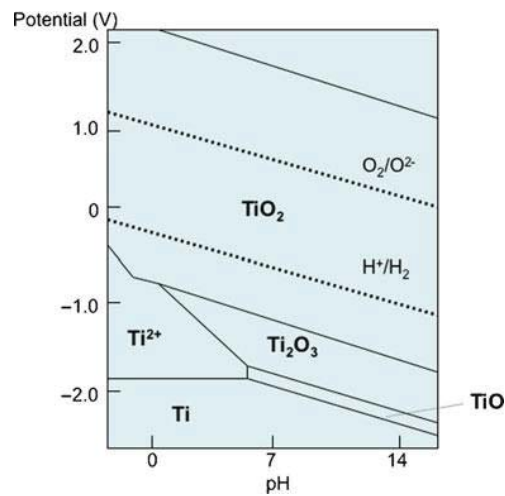


Figure.1 Potential–pH (Pourbaix) diagram for the system Ti/H₂O.[9]

However, titanium can still suffer from some corrosion problems such as galvanic corrosion when it is coupled to dissimilar materials in chloride ion containing electrolytes. Titanium differs from most materials in that, if it is coupled to a more noble metal in an aggressive electrolyte, the electrode potential of the titanium tends to decrease and the corrosion rate predicts to increase [10].

Thus, surface treatments of titanium were introduced in order to prevent corrosion, and one of the most important techniques which has been developed successfully is anodizing treatments to create a thick anodic oxide film on the metal substrate [11-15]. A study of the corrosion resistance of titanium is basically a study of the properties of the oxide film. The oxide film on titanium is very stable and is attacked only by a few substances including hot concentration reducing acids, most notably hydrofluoric acid.[16]

Other attempts to improve the corrosion resistance of titanium involves coating titanium-based implants with hydroxyapatite (HA) or other calcium phosphates, which is commonly accomplished by electrochemical deposition. Therefore, this study is aimed at discussing the corrosion protection of pure titanium (grade 1) by electrochemically deposited HA coatings on anodized titanium.

2. Experimental part

2.1. Titanium Preparation

Titanium specimens of $2 \times 2 \text{ cm}^2$ area were obtained from grade 2 commercially pure titanium sheet of 0.5 mm thickness. Polished titanium sheet by emery papers 600, 1200 and 2000 mesh grit, then the specimens were cleaned with distilled water, then ethanol and finally with acetone then dried by using a hair drier.

Before anodizing, the specimens were deoxidizing by NaOH 10% then de-smutting by nitric acid 50% after each step double rinsed with distilled water, finally with acetone.

2.2. Artificial Saliva Preparation

The electrolyte reference used was modified Fusayama artificial saliva according to a method that has been described in detail in a previous report, which closely resembles natural saliva, the composition show in table 1, and pH of this electrolyte was 6.2. [17]

Table 1. The composition of artificial saliva.

	KCl	NaCl	CaCl ₂ .H ₂ O	NaH ₂ PO ₄ .2H ₂ O	Na ₂ S.9H ₂ O	urea
g/l	0.4	0.4	0.906	0.69	0.005	1

2.3. Anodizing process of Titanium

The anodizing treatments employed two-electrode cell, with a large titanium sheet as the counter electrode. 1.65 mol/L H₂SO₄ solution was used as the electrolyte, the distance between the two electrodes was 3.0 cm. anodizing by applying (10 Volt) with duration time (5 min.) at room temperature. After the anodizing process, the titanium was rinsed with distilled water and dried by a hair dryer. Figure.2 shows anodizing cell.

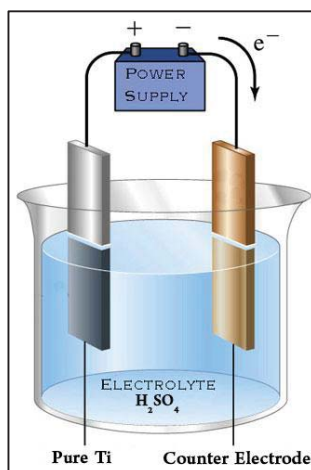


Figure.2: anodizing titanium cell

2.4. Electrochemical deposition of HA

Electrolyte for electrochemical deposition of HA in this study contained 0.042 mol/L calcium nitrate and 0.025 mol/L di-ammonium hydrogen phosphate and its pH value was adjusted to 4.4 by dilute HNO₃. The working electrode (pure titanium) and large sheet from titanium as a counter electrode was placed in an electrolyte, electrochemical deposition of HA on the titanium was conducted at room temperature and stirrer with direct current power (DC) (6 V) and the time was kept for 1 h. After deposition, the specimens were rinsed in distilled water and dried by a hair drier, then soaked in 1 mol/L NaOH solution at 80 °C for 2 h. The following reaction will take place in the synthesis of HA can be given by:[23]



2.5. Characterization and test

Spectroscopic analysis of the deposited powder was carried out with Fourier transform infrared spectroscopy using KBr pellet technique.

The galvanostatic polarization was measured using WENKING M Lab.(Germany). Polarization curves were obtained, for pure titanium before and after treatment. The polarization curve obtained involved the cathodic and anodic regions. Extensive data could be derived from the detailed analysis of each polarization region using the extrapolated method to determine both the corrosion current density (i_{corr}) and corrosion potential (E_{corr}).

3. Results and Discussion

3.1. Corrosion Behavior

The polarization curves for the corrosion of pure titanium immersed in artificial saliva before and after treatment by anodizing and electrochemical deposition of HA at different temperatures were recorded and plotted in figure 3. The polarization curves of blank pure titanium show corrosion potential ranged between (-146.7 to -165.7 mV) and this potential shifted to (-768.3 mV) after anodizing, these indicated to form an oxide film on the surface of titanium. But when coated the titanium with HA, the corrosion potential show slightly shifted to less active (-96.2 to -116.2 mV). This shifted in corrosion potential can be discussed as change in nature of titanium surface and shift to passive region.

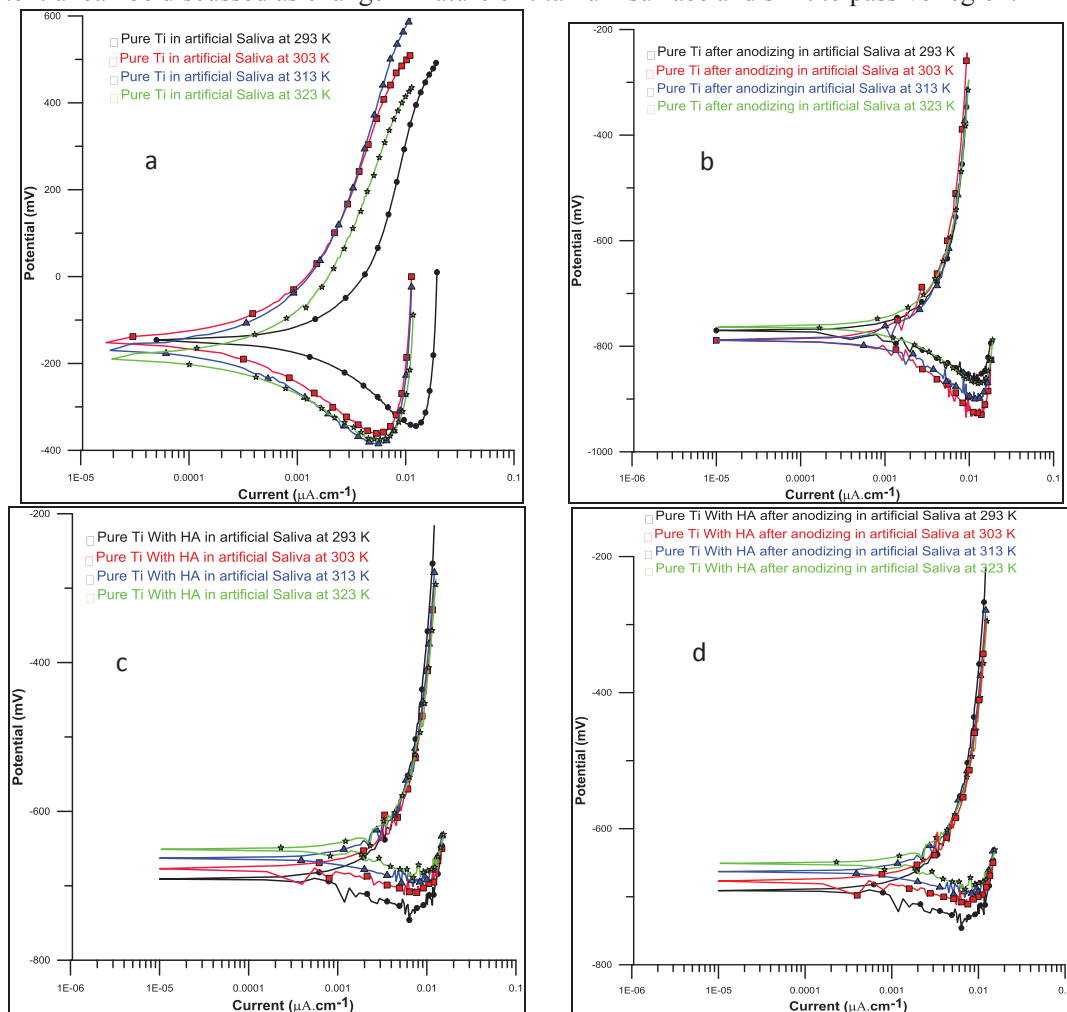


Figure.3. Polarization curves for a) Pure Ti (Blank), b) Ti after anodizing, c) Ti with HA, and d) Ti with HA after anodizing.

The data of the Table (2) shows that the corrosion current density, slightly increased with temperature increasing. The value of i_{corr} of pure titanium after treatment in artificial saliva smaller than the value of i_{corr} pure titanium pre-treatment.

Table 2. Corrosion kinetic parameters for pure titanium in artificial saliva at different temperature in the range (288-318)K.

Temp./K	-E _{corr} /mV	I _{corr} /μA.cm ⁻²	-ba/ mV.dec ⁻¹	bc/ mV.dec ⁻¹	PE %	R _p /Ω.cm ²	
Blank	293	-146.7	1.41	226	336.4	-	41629.96
	303	-151.0	1.50	258.1	423.3	-	46413.99
	313	-165.7	1.60	282.8	455.5	-	47350.11
	323	-147.7	1.65	249	574.8	-	45721.07
Ti after Anodizing	293	-768.3	0.495	55.9	57.7	64.893	24906.35
	303	-769.0	0.691	55.0	82.8	53.933	20766.90
	313	-741.0	0.703	70.9	70.9	56.062	21896.11
	323	-725.0	0.757	51.9	84.7	54.121	18459.08
Ti With HA	293	-96.2	0.74	40.8	41.0	47.517	11999.55
	303	-100.0	0.746	36.6	42.0	50.266	11383.48
	313	-105.2	0.767	39.0	40.5	52.062	11247.68
	323	-116.2	0.873	43.1	45.8	47.090	11044.16
Ti with HA after Anodizing	293	-690.1	0.434	43.7	51.1	69.219	23567.32
	303	-677.6	0.580	28.5	53.5	61.333	13920.75
	313	-663.2	0.570	27.7	50.6	64.375	13636.39
	323	-650.4	0.649	29.8	39.2	60.666	11326.99

The Protection Efficiency PE (%) can be calculated by using the equation [17]:

$$PE\% = \frac{(i_{corr})_b - (i_{corr})_p}{(i_{corr})_p} \times 100 \dots \dots (2)$$

Where (i_{corr})_b and (i_{corr})_p are the corrosion current density (μA.cm⁻²) blank pure titanium and pure titanium after protection respectively.

The best PE% were obtained after coated titanium with HA post-anodizing which give PE reach to 69% at 293K, The data of the table (2) shows the PE% slightly decreased with temperature increasing, that indicate the protection coated of HA not effected by temperature.

The polarization resistance (R_p) can be determined by the following equation [18].

$$R_p = \frac{d(\Delta E)}{di} = \frac{b_a b_c}{2.303(b_a + b_c) i_{corr}} \dots \dots (3)$$

Where E and E_{corr} are in V, i_{corr} in A cm⁻² and R_p in Ω cm².

Discussion polarization resistance has such as requirements to the measurement of full polarization curves and it is particularly helpful in identifying corrosion trouble and initiates reconditioned action [19,20].

3.2. Kinetic parameters for the corrosion process

The influence of temperature on the kinetic process of titanium corrosion in artificial saliva leads to getting more information on the electrochemical behavior of metallic materials in aggressive media and for protection titanium.

Figure (4) shows log i_{corr} plotted against (1/T) for the corrosion of coated and uncoated titanium with and without anodizing titanium. The relationship between the corrosion current density (i_{corr}) of titanium in artificial saliva solution and temperature (T) is expressed by the modified Arrhenius equation [21,22]:

$$\log i_{corr} = \frac{-E_a}{2.303RT} + \log A \dots \dots \dots (4)$$

Where R is the gas constant ($R \approx 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), E_a represents the activation energy of the corrosion and A is the pre-exponential factor in the rate equation.

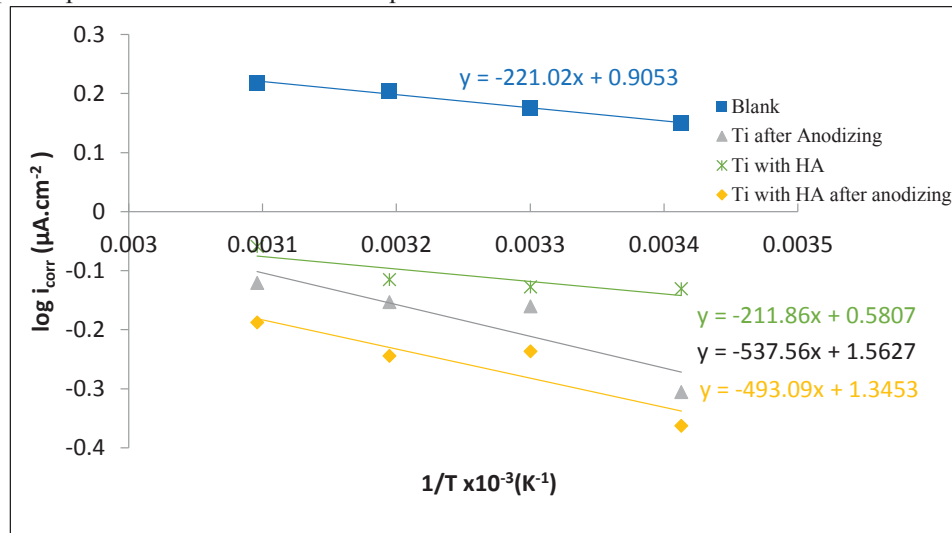


Figure.4. Arrhenius Plot of $\log i_{corr}$ Versus $1/T$ for the corrosion of titanium in artificial saliva solution.

The data in the table (3) shows the activation energy increased after anodizing titanium, change from ($4.231 \text{ kJ.mol}^{-1}$) to ($10.293 \text{ kJ.mol}^{-1}$), while after coated titanium by electrochemical deposition of HA, the activation energy not effected by coated with HA.

Table 3. Kinetic and thermodynamic parameters for pure titanium in artificial saliva at different temperature in the range (288-318)K.

	$\Delta G^* / \text{kJ.mol}^{-1}$				$\Delta H^* / \text{kJ.mol}^{-1}$	$\Delta S^* / \text{kJ.mol}^{-1} \cdot \text{K}^{-1}$	$E_a / \text{kJ.mol}^{-1}$	$A \times 10^{24} \text{ Molecules.c m}^{-2} \cdot \text{s}^{-1}$
	293	303	313	323				
Blank	70.876	73.238	75.599	77.962	1.676	-0.23618	4.232	4.84
Ti after Anodizing	73.249	75.485	77.721	79.957	7.736	-0.22359	10.293	22.00
Ti with HA	72.522	74.946	77.369	79.794	1.500	-0.2424	4.056	2.29
Ti with HA after anodizing	73.617	75.895	78.172	80.449	6.885	-0.22776	9.441	13.30

3.3. The Thermodynamic Studies

The change in Gibbs free energy (ΔG) for the corrosion of titanium at a different temperature can be determined from the following equation:

$$\Delta G = \Delta H - T\Delta S \dots \dots \dots (5)$$

Other kinetic date (enthalpy and entropy of activation) are accessible using the alternative formulation of Arrhenius equation [29].

$$\log \frac{i_{corr}}{T} = \log \frac{R}{Nh} + \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \dots \dots \dots (6)$$

Where CR (i_{corr}) is the corrosion rate, h is the Plank's constant ($6.626176 \times 10^{-34} \text{ Js}$), N is the Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$), ΔS_a is the entropy of activation and ΔH_a is the enthalpy of

activation. The plot of $\log i_{\text{corr}}/T$ vs. $1/T$ obtained straight lines were obtained with the slope of $(-\Delta H_a / 2.303 R)$ and an intercept of $[(\log (R/Nh) + (\Delta S_a/2.303 R))]$ from which the values of ΔH_a and ΔS_a , respectively were calculated.

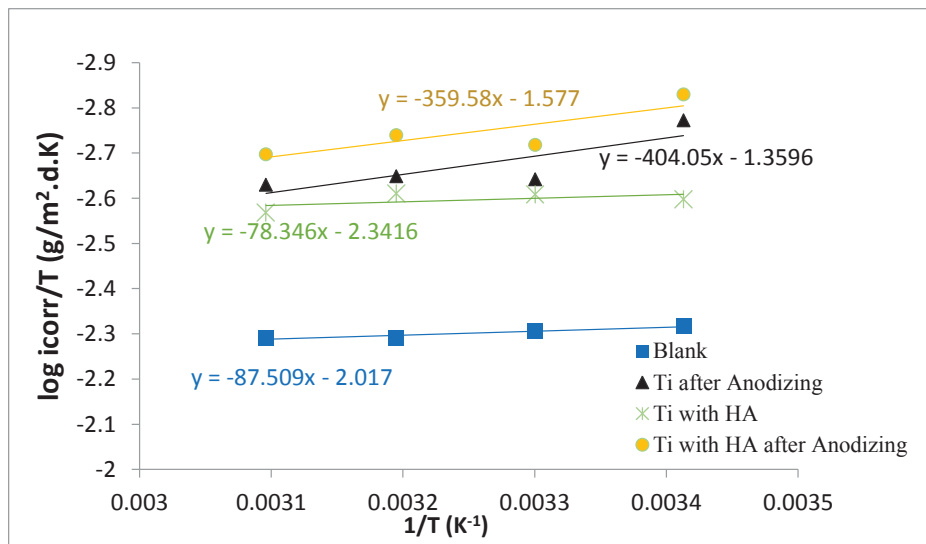


Figure.5. The plot of $\log i_{\text{corr}}/T$ Vs $1/T$ for titanium in artificial saliva.

Table (3) gives the values of the thermodynamic quantities ΔG , ΔS and ΔH for the corrosion of pre-treatment titanium and treatment titanium by anodizing and electrochemical deposition of HA. The data show positive values of ΔG refer to the non-spontaneous corrosion reaction. Value of ΔG for the corrosion of the titanium post-anodizing increased from (70.876 kJ) to (73.249 kJ) this indicated to change a surface of titanium to titanium oxide and become more stable, but the value of ΔG for titanium after coated by HA slightly increasing.

The positive values of ΔH for corrosion processes for pre-treatment titanium refer to exothermic nature of the titanium dissolution process, while after anodizing the value of ΔH become more positive refer to change the nature of titanium surface dissolution. And the value of entropy not effect by these treatment.

3.4. The thickness of HA coated

To measure the thickness of the coat layer of HA on Titanium surface, the basic following equation can be used [19]:

$$\rho = \frac{wt}{V} \dots\dots\dots (7)$$

Where: ρ = density of HA, Wt. = weight of coated and V= volume of coated.

$$V = L * W * d \dots\dots\dots (8)$$

Where: L = length of titanium piece, W= width of titanium piece and d = thickness of coating.

The thickness of HA coated on titanium surface calculated was (5 μm).

3.5. FTIR characterization of the coatings

FT-IR spectra for the coating as dried powders presented in Figure 5 have indicated the vibrational modes of PO_4 groups at 462, 568, 603 and 1039 cm^{-1} and OH group at 3454 cm^{-1} of apatite phase for the coated powder. The presence of adsorbed water could also be detected from FT-IR spectra in the region around 3319–3739 cm^{-1} . Other information can be indicate from the FT-IR spectra of the coated

powders is the presence of carbonates (CO_3) groups at 1654 and 1683 cm^{-1} . The presence of nitrates (NO_3) in the coated powders is clearly attended in the region around $1417\text{--}1458\text{ cm}^{-1}$.

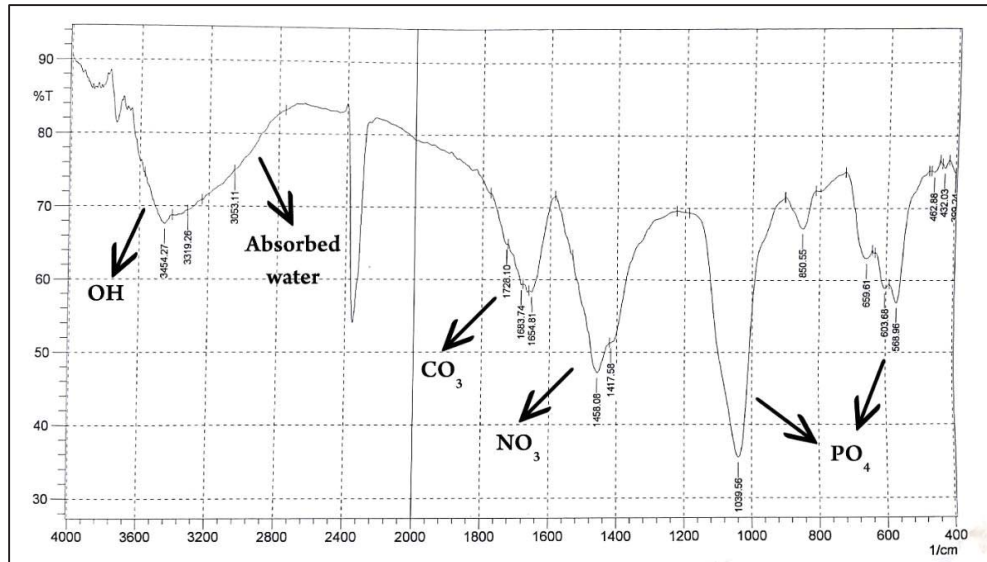


Figure.6 FT-IR spectra for coated powder of Hydroxyapatite.

4. Conclusion

Coated titanium with HA post-anodizing gives better results than HA without anodizing titanium. The protection efficiency of coated titanium by HA after anodizing unaffected by temperatures.

The activation energy of titanium corrosion increase after anodizing, refer to change in the nature of titanium surface (oxide layer form) become more stable. The corrosion reaction was non-spontaneous reaction (values of ΔG was positive) and this value increase after treatment titanium, with exothermic reaction (values of ΔH was negative) for blank titanium but the corrosion process change to endothermic after anodizing titanium.

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