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CORROSION AND TRIBOLOGICAL STUDY OF Ti-6Al-4V ALLOY IN RINGER SOLUTION

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Ti-6Al-4V is an alloy used for biomedical implant. Thus, it is necessary to study its wear characteristics and corrosion behaviour as a function of immersion time in presence of biofluid. In present work, corrosion study is performed with the help of potentiostat and alloy is also tested for wear behaviour on pin on disk apparatus for dry and wet condition. The samples for electrochemical study were kept in ringer solution for an immersion time of 0Hr, 6Hr, 12Hr, 24Hr, 48Hr, 72Hr, 120Hr and 240Hr. The surface was observed under optical microscope and results were correlated to obtain the conclusion.

Keywords: Ti-6Al-4V, Wear, Optical microscopy, Corrosion

1. Introduction

In the competitive era of advance technology there is a need of material with less weight but equal or more strength [1]. One of the main requirements of bioimplant is that it should not react easily with body fluids and tissue. Also, it should have corrosion rate below 0.01 mils per year [2]. Ti-6Al-4V act as a ultimate choice for bioimplants because of strong and stable passive layer formed on surface as compared to SS 316L where stability of oxide layer is not very strong and it releases ions to corrode rapidly. According to FDA (Food and Drug administration, USA) corrosion studies on orthopaedic biomaterials are carriedout either in Hank's solution or Ringer's solution [2]. Ringer solution is asterile solution that is used to replace fluid lost by the body. It is commonly used for fluid resuscitation, meaning that the patient needs aggressive fluid replacement for their injury or illness. Thus, it is important to study corrosion and Tribological behaviour ofTi-6Al-4Vin this biofluid. Previously Ti-6Al-4V is studied by J.F. Floreset al.by taking hank solution as ane nvironment [3], in this study they have obtained XRD results which had shown the presence of TiO_2 layer on alloy surface. Again study had been performed by Marcin Basiaga et al. in Ringer solution as a function of different cycles of deposition of TiO_2layers [4][5]in which they had shown that application of TiO_2 layers is useful in improving properties of Ti-6Al-4V.Present research work mainly focuses on examining behaviour of Ti-6Al-4V in Ringer solution as a function of time of immersion, investigating wear behaviour and comparing wear behaviour in dry and wet condition (i.e. Ringer solution).

2.1. Methods and Material

2.1.1 Composition of Ti-6Al-4V and Electrolyte

Table1.shows the composition of Ti-6Al-4V used for the present study. The metal under study was purchased from Bharat aerospace materials Ltd. Separate sample were used for each new experiment with fresh solution of Ringer solution. Disk used for carrying out wear test is of En31 which is hardened to 60 HRc and ground to 1.6 Ra with diameter 165 mm and thickness 8 mm.

Table1.

Composition of Ti-6Al-4V alloy under study

Element	Al	V	C	Fe	Ti
Weight %	5.92	3.62	0.041	0.27	Balanced

(Manufactured by Bharat Aerospace Metals Pvt Ltd)

2.1.2 Sample preparation and parameters for Wear study

Ti-6Al-4V samples of height 35 mm were prepared from cylindrical rod of 8 mm diameter by referring standard ASTM G-99[6]. The surface in contact with the disk is made flat. For each experiment of dry and wet condition 3 samples were tested. The disk is made clean and smooth by polishing it with 800, 1200 grit size paper. The Ti-6Al-4V pin with 8mm diameter remains stationary for entire span of experiment while disk keeps rotating till the completion of experiment. The pin is applied with 3 Kg load and it is set in such a way that, it will make a track diameter of 100 mm on the disk. While the disk is given with speed of 300 RPM to rotate for completing wear path of 3 Km.

2.1.3 Sample preparation and Parameters for electrochemical study

The plate of Ti-6Al-4V alloy was first cut into specimens and then polished on silicon carbide paper of successive grit size of 200, 400, 800 and 1200. Buffing operation is performed on the surface until mirror finish is obtained. For preparation of metallographic specimen ASTM E3 standard was followed. The sample thus obtained is soldered to copper wire. The entire surface was coated with the epoxy resin with only polished surface remaining open and the copper wire is also coated with the epoxy up till the depth of immersion of the sample. Samples thus prepared are immersed in the Ringer Solution for a immersion time of 6Hr, 12Hr, 24Hr, 48 Hr, 72Hr, 120Hr, 240Hr. Each sample after completing the immersion time is loaded to potentiostat for further study. The etchant used for obtaining microstructure is Kroll’s Reagent with 3 ml HF and 6 ml HNO_3 in 100 ml distilled water

Electrochemical study is done by using potentiostat (Make-Gamry Instruments model Reference number 600). The three-electrode system consists of Saturated Calomel electrode (SCE) used as a reference electrode, Graphite as a counter electrode and sample under test as a working electrode. The OCP is carried out for 30 min so as to stabilize the potential. Then the EIS study [7, 8, 9, 10] is carried out for the frequency ranging between 100 Hz to 0.01 Hz. Tafel study is done for the voltage ranging in between -350 mV to +350 mV with respect to E_{OCP}. The potential was scanned at the rate of 1mV/sec. The whole experimental setup was controlled by computer with dedicated software. The results obtained were fitted using Gamry Echem Analyst Version 6.33. Separate batch of specimens, each batch containing 3 samples were polished according to ASTM E3 [11] standard and procedure explained as above. These samples were first loaded to potentiostat for Open circuit potential test for obtaining stabilized potential so as to carry out the further potentiodynamic tests at stabilized potential.

2.2 Results and Discussion

2.2.1 Optical microscopy, Chemical and Morphological analysis

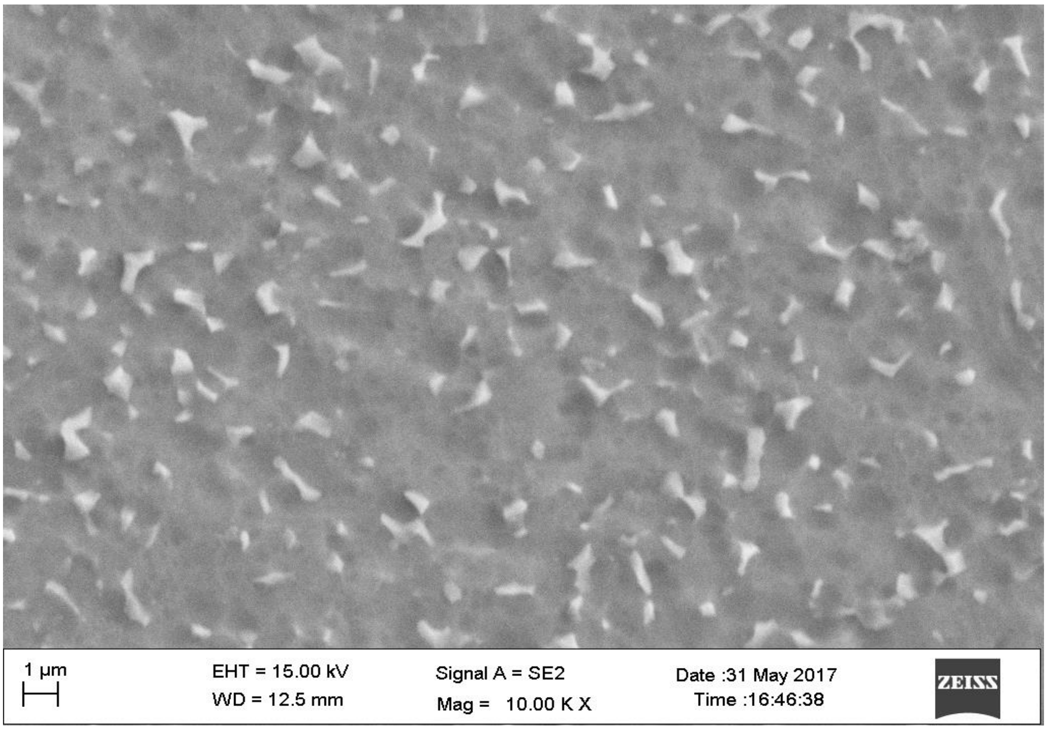


Fig1. As received Ti-6Al-4V sample.

All the consumables are upto the required chemical and morphological conditions. Table1. Indicates the compositional analysis of alloy satisfying the α+ β morphology. Fig1.shows the surface microstructure of as received Ti-6Al-4V alloy. It shows α precipitates in the form of small dots in the β matrix [12]. Table 2 indicates the composition of Ringer solution saline used in medical treatments [2].

Table2.

Composition of Ringer Solution (per 100 ml composition) used for present corrosion study.

Element	Sodium Lactate	Sodium chloride	Potassium Chloride	Calcium Chloride
Weight (gram per 100ml)	0.32	0.6	0.04	0.027

(Manufactured by Baxter india Pvt Ltd.)

2.2.2 Wear and Tribological Study

$$Volume\ loss(cc) = \frac{mass\ loss\ (gram)}{Density(\frac{g}{cc})} \qquad \text{................................ (Eq.1)}$$

Here,

mass loss, M_{dry} =8.1495-7.9725=0.177 g

M_{ringer}=8.3845-8.3072=0.0773 g

Density=4.3842 g/cc

Wear loss for dry condition in terms of volume=0.04037cc

Wear loss for taking ringer solution as a environment in terms of volume=0.0176cc

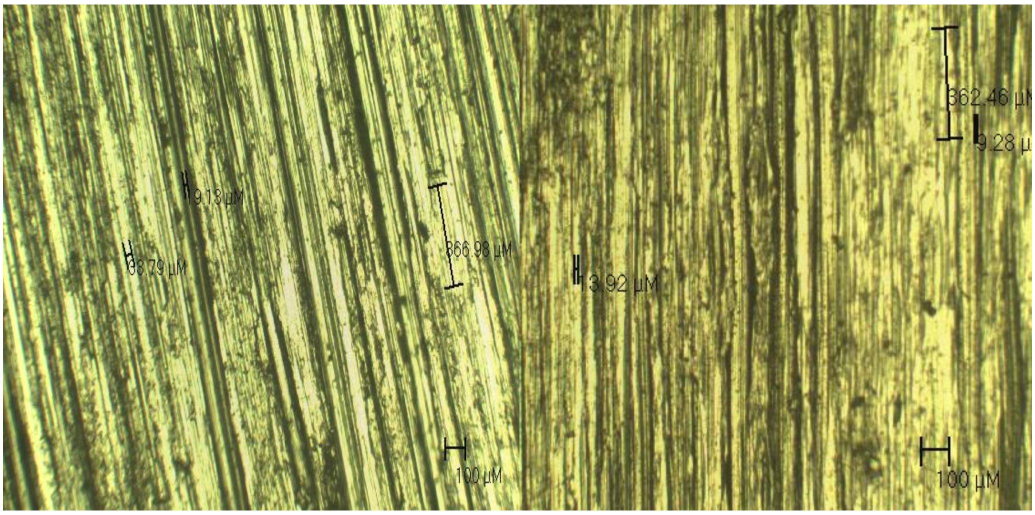
Table.3.

Results of wear experiment

Environment	Frictional force(N)	C.O.F(μ)	Volume loss cm^3
Dry	10.3005	0.35	0.04037
Ringer Solution	10.0062	0.34	0.0176

Here, Wear path=3 Km, Load=3 Kg and pin speed = 300 RPM.

Table.3 shows the results obtained after wear test. It shows lower values of Frictional force, wear loss, coefficients of friction are obtained for ringer solution as compared to dry condition. This indicates ringer solution act as a lubricant.

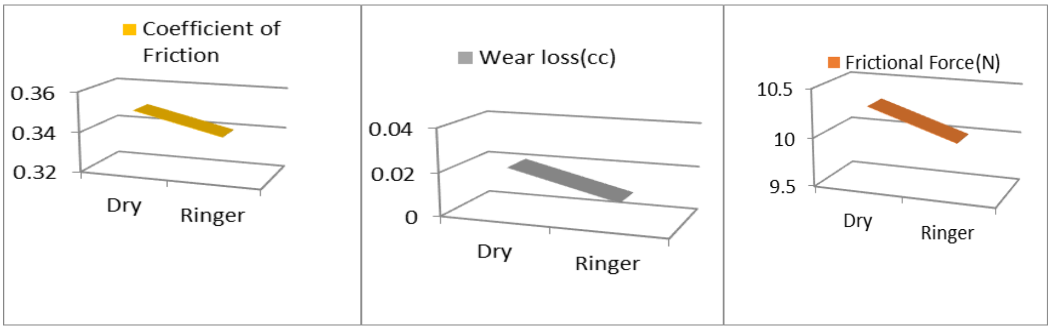


(a) (b)

Fig 2. (a) Image captured under optical microscope showing the surface condition after testing under dry condition and (b) in presence of Ringer solution.

Fig2(a, b) shows the width and length of wear track striations on Ti-6Al-4V pin surface after wear test in dry condition and in presence of Ringer solution as an environment. The striations marks are having greater width and length in dry condition (9.18 µm, 866.98 µm) as compare to those in wet condition (3.92 µm, 362.46 µm respectively). This greater width and length of striation is justified by the increased width and length of wear and friction graph with respect to time [13]. The more number of dark lines of striations obtained in the Ringer environment shows the filling of wear products within the troughs which is also helping in reducing the friction by maintaining even surface condition [13]. The heavy striations further increase the friction between the mating surface [13], [14] thus resulting in increased wear as compared to striation with narrow width [13], [15], [16]. The increasing friction trend is dominant in dry condition as compared to wet condition.

Wear loss obtained in wet condition is (0.0176 cc) less as compare to that obtained in dry condition (0.04037 cc). Thus Ti-6Al-4V shows improvement in property when used in ringer environment. The coefficient of friction in ringer environment is 0.34, which is smaller as compared to that of 0.35 in dry condition which is much less than previous study [13], [14]. Fig.3 gives the visual analysis of the data in Table.3 showing improved properties in ringer solution environment.



(a) (b) (c)

Fig.3.comparitive wear behaviour of Ti-6Al-4V alloy in dry condition and taking Ringer Solution as a environment as a function of (a)Frictional force (b) Wear loss (c)Coefficient of friction.

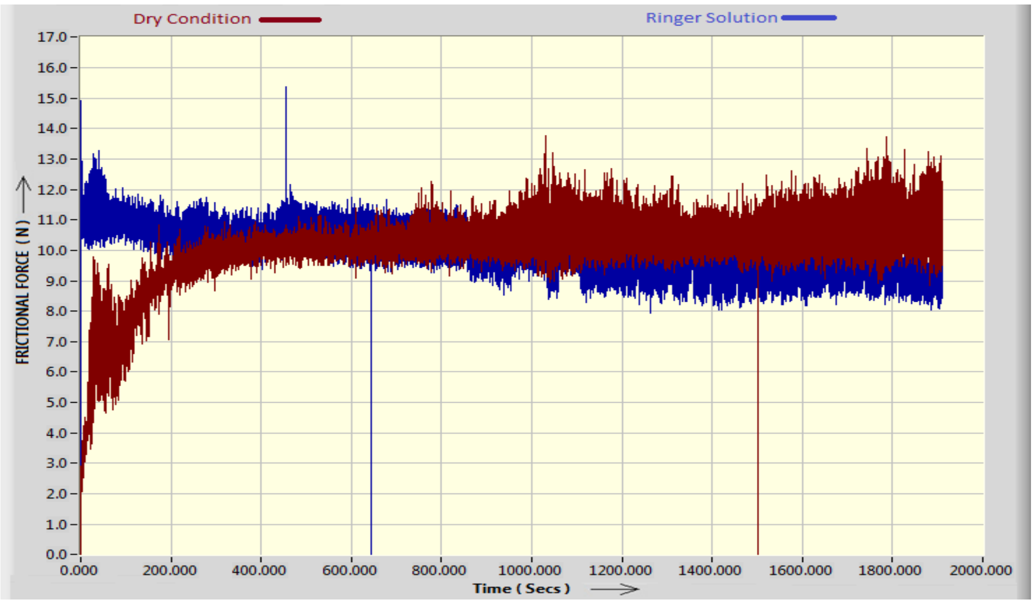


Fig.4.Variation of frictional force as a function of Time and Environment conditions.

Fig.4 shows the variation of frictional force as a function of time and environment conditions such as dry and ringer environment. Each and every point from start to the end of the graph shows the value of frictional force at that instant of time. Initially the frictional force was low for the dry condition (red coloured), but it had increased as soon as the wear of material progresses. But for the frictional force in ringer environment (blue coloured) had shown decrease in value of frictional force due to lubrication provided by the solution [15]. Fig.5 shows the variation of Coefficient of friction as a function of time and environment conditions such as dry and ringer environment. This graph shows the increase in coefficient of friction for dry condition (red coloured) as compared to coefficient of friction for ringer (wet condition) environment (blue coloured). This is due to the effect of ringer solution which provides smooth movement between disk and the Ti-6Al-4V pin. But when there is no liquid in between the pin and the disk, the material wear out and because of absence of lubrication or liquid medium there is increase in coefficient of friction. Another reason for increase in frictional force and coefficient of friction in dry condition is the wear out material which is present on disk as well as pin surface, as compare to the wet condition where it is removed by the flowing ringer solution resulting in decrease in values of both frictional force as well as coefficient of friction [14,16].

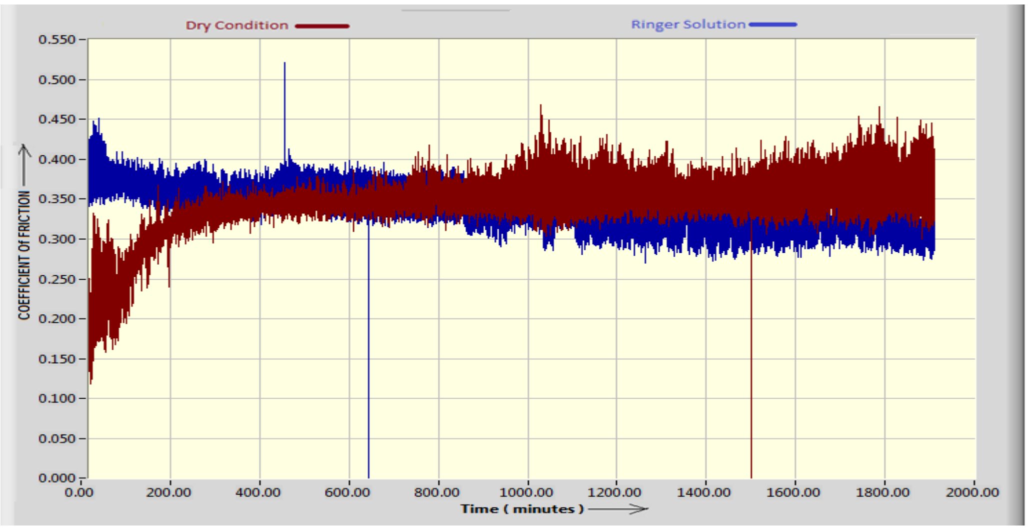


Fig.5.Variation of Coefficient of friction as a function of Time and Environment conditions.

2.2.3 Electrochemical study

Table.4.

Results of corrosion experiments of Ti-6Al-4V as a function of immersion time.

Immersion Time (Hr)	R_P ($\times 10^{12}$ Ω)	Capicitance (10^{-9}F)	E_{corr} (V)	i_{corr} (pA/cm^2)	Corrosion Rate (×10-6 mpy)
0	1.134	0.338	1.72	7.310	28.07
6	0.149	3.507	1.86	6.017	23.12
12	1.334	0.596	2.44	4.17	16.03
24	1.654	0.063	1.44	4.68	18
48	1.066	0.084	2.39	3.77	14.51
72	1.576	0.076	3.31	3.35	12.88
120	1.284	0.070	2.79	8.61	33.07
240	0.011	0.569	4.18	6.38	24.52

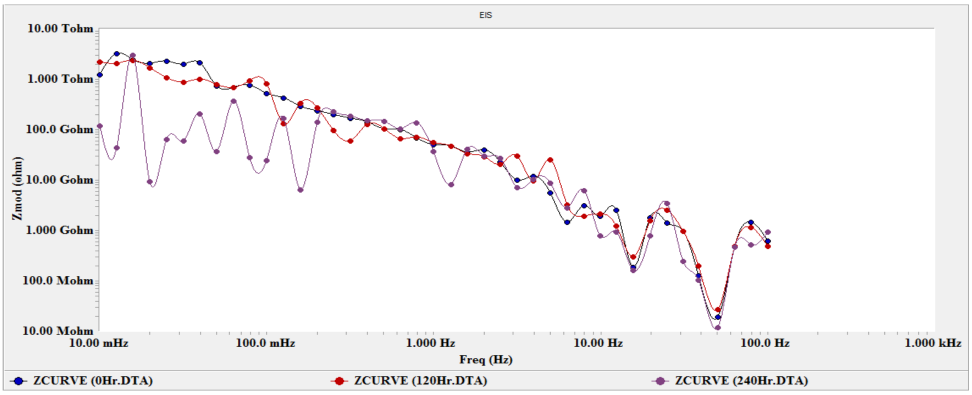


Fig.6 Z_{mod} Vs. Freq plot

Fig.6 shows the Z_{mod} Vs. Freq plot for unimmersed sample and the sample immersed for 240 Hr. The 'immersion time' everywhere in this paper indicates the time for which the sample is kept in the ringer solution before loading to corrosion test in the presence of ringer environment and the 0Hr immersed sample means the unimmersed sample which had come into contact with the ringer solution only during the time of corrosion test. According to previous research [19, 20] the titanium metal forms intermediate layers of passive layers. Thus, the nature of graph obtained is basically depends on the outer passive layer which directly comes in contact with the environment. From the fig9(a) it is clear that for unimmersed and 120Hr, 240Hr immersed sample has same nature above higher frequency range as they are coinciding but when we look for lower frequency range 240Hr immersed sample differ and also shows some fluctations whose peak extend upto the coinciding lines of other two. This is well indication of unstable passive layer[19, 20].

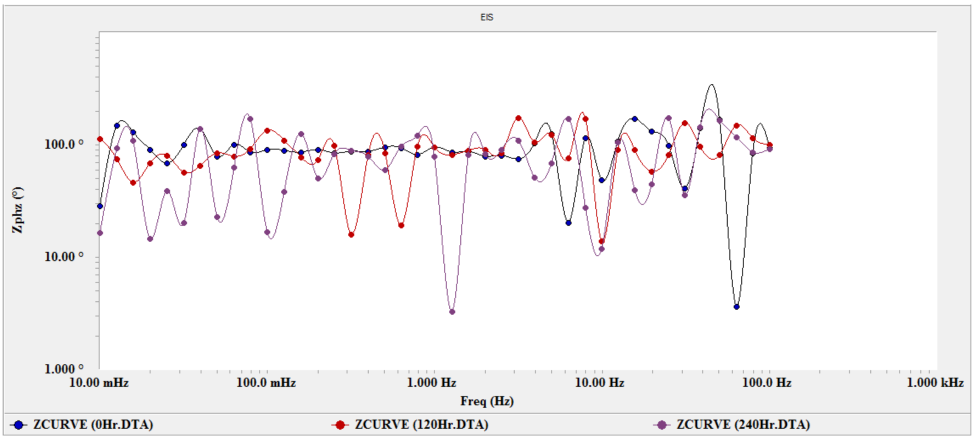


Fig.7 Phase angle Vs. Freq plot

Fig. 7 shows the Phase angle Vs. Freq plot for unimmersed and imersed sample with immersion time of 120Hr and 240Hr. Again the sample with 240 Hr immersion and sample with no immersion had shown fluctuations throught frequency range but they adhered to lie near the constant 100^0 phase angle. Sample with immersion time 120 Hr had shown stable nature throught the frequency range indicating stable passive layer formation[17, 20].

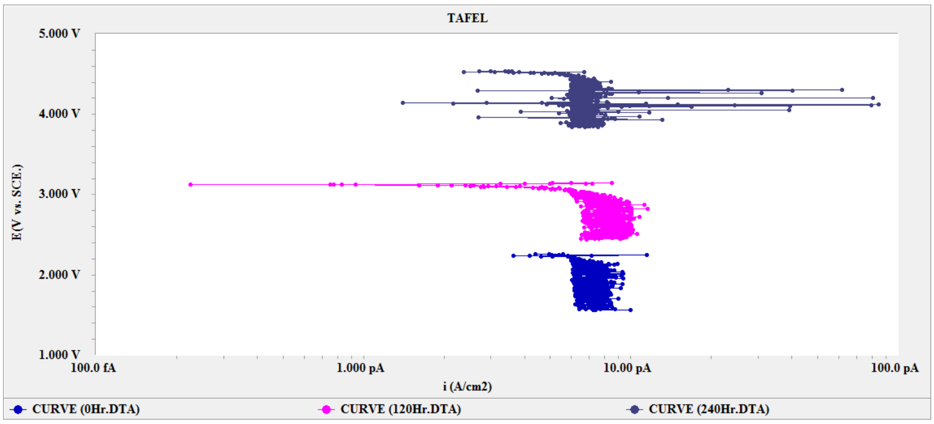


Fig.8 Tafel plot

Fig. 8 shows the Tafel plot for stabilised open circuit potential. As the immersion time was increased the potential values shifted to positive direction. The open circuit potential had shown high fluctuations although we got low and consistent value of corrosion density and also we got increase in corrosion potential value with increase in immersion time.The graphs were nearly straight vertical line on Tafel plot which is indication of negligible corrosion[9,17].

6. Conclusions

(1) Lower value of wear loss(0.0176cc), coefficient of friction (0.34) and frictional force (10.0062 KN) is obtained in presence of ringer solution as compare to dry condition, which indicates stability, suitability and inferiority of Ti-6Al-4V in presence of bio fluids.

(2) The thickness of striations (3.92 μm in Ringer solution Vs 9.18 μm in dry condition, Fig.2) due to friction between disk and Ti-6Al-4V pin after wear test have shown lower values in ringer solution as compare to dry condition.

(3) Very low value of corrosion current density (lowest for 72Hr immersion=3.35 pico Ampere/cm^2), Higher value of pore resistance (highest, 1.654 Tera ohm for 24 Hr Immersion), Very low value of capacitance (lowest, 0.063 pico Farad for 24 Hr immersion) indicate full proof corrosion resistance of Ti-6Al-4V alloy.

(4) Very low value of corrosion rate (lowest, 12.88×10^{-6} mpy for 72Hr Immersion) have been obtained for all the samples indicating dominance of Ti-

6Al-4V in material which are used in bio-implants as per as the corrosion behaviour is considered.

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