

STUDY AND EFFECT OF PROCESS PARAMETERS OF ELECTRODEPOSITED TiO₂-HAP COMPOSITE COATED Ti-6Al-4V SUBSTRATE

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Abstract— Higher micro hardness, wear resistance and adhesion of composite coatings on surface biomaterials is required to achieve a longer service life of implant. In this paper, TiO₂-HAP composite coatings were prepared on Ti-6Al-4V substrate with electrodeposition process to improve hardness, adhesion strength and wear resistance of coated substrate. The effect of process parameters Voltage, pH of electrolyte and Titania (TiO₂) concentration on micro hardness of TiO₂-HAP composite coated Ti-6Al-4V substrate was investigated. The microstructure and elemental compositions of coating were analyzed by using scanning electron microscope and energy dispersive spectroscopy. The incorporation of TiO₂ results in refined structure and increased hardness, adhesion and wear resistance.

Keywords—composite coating, electrodeposition, hydroxyapatite, hardness, adhesion

I. INTRODUCTION

Titanium alloys are most extensively used category of biomaterials in orthopaedic and dental applications due to various properties linked with alloys such as low modulus, high corrosion resistance, excellent oxide film formation capability on surface, and better biocompatibility etc. [1]. However performance of the implant during its service period in the body is affected by various factors [2]. The bone-implant contact should be sufficient to bear service loads [3]. The implant should have high wear resistance so as to avoid formation of wear debris due to joint movements. The implant should not release harmful toxic ions within the body [4].

Various techniques have been used and developed to impart specific surface properties by incorporation of specific ions on to surface such as hardness and adhesion between coating and metal surface [5–7]. It is well known practice now days to substitute specific minerals and ions into the lattice structure of HAP to make its composition closer to bone and enhanced biodegradation properties. These ions include calcium, phosphorus, silicon, carbonate, magnesium, zinc and strontium. Ionic substituted apatite has been tailored to meet specific needs and extensive work has been done in this emerging field. Biocompatible composite coatings have been prepared to obtain better cell adhesion and cell growth on the surface. Calcium-phosphate based coatings have been extensively deposited on the substrate surface by various methods and techniques such as physical vapour deposition, plasma spray method, chemical vapour deposition, sol-gel technique, ion implantation, and electrochemical deposition [8–12].

Electrochemical deposition method is widely accepted by the researchers due to no thermal stresses produced during the process, lower cost, easy control of process parameters, and easy deposition procedure to obtain specific properties from the electrolyte solution itself. The potential, temperature of electrolyte, current density, electrolyte concentration and pH of electrolyte solution are the various process parameters which can be effectively controlled to obtain a deposit with better properties [13,14]. Hydroxyapatite, HAP (Ca₁₀(PO₄)₆(OH)₂) coating possesses superior bioactivity and high chemical binding capability to living tissue and bone. Complex and porous HAP coated structures can be developed by electrodeposition process economically [15-16]. Chemically stable, biocompatible and antimicrobial active HAP composite coatings containing materials such as alumina, silica, zirconia, diamond-like carbon, bio-glasses and polymers, have been developed on the alloy surface [17-20]. In this study, TiO₂-HAP composite coatings on Ti-6Al-4V substrates have been prepared by adding TiO₂ nano particles to HAP electrolyte solution to produce hard and adherent composite coatings.

II. EXPERIMENTAL DETAILS

The rectangular shaped specimens of 2.5mm × 20mm × 25mm size were cut from the titanium plate on Electric Discharge Wire Cut Machine. The samples were grinded with emery papers of 80, 200, 400, 800, 1000 no. respectively to obtain a better surface finish. The substrate was rinsed in acetone for 24 hours before deposition and then washed with distilled water followed by drying in air. The electrolyte solution of specific concentration in aqueous media was prepared

to deposit TiO₂-HAP on titanium substrate by electrodeposition process. The electrolyte solution was prepared by taking 0.042M Ca (NO₃)₂.4H₂O and 0.025 M NH₄H₂PO₄ concentration of constituent salts. To prepare TiO₂- HAP composite coatings, 3-5 g/L TiO₂ was added into the electrolyte. The pH of the electrolyte was maintained at 3.3 at 28 °C by adding nitric acid and ammonia as per need. The electrolyte solution was ultrasonically agitated for 30 minutes at 50 KHz frequency to break up the salts particles into nano particles to obtain a saturated solution. Electrolyte beaker was placed over the magnetic stirrer with temperature control to agitate the solution at 701 rpm along with heating up to 50⁰C. An Auto lab Potentiostat, PGSTAT302N, three electrode electrochemical workstation was used to deposit TiO₂-HAP electrochemically on Ti-6Al-4V alloy substrate. Metal substrate is connected to working electrode of system. Platinum rod and Ag/AgCl were used as counter electrode to complete the circuit and reference electrode to measure potentials between reference electrodes and working electrode respectively. The potentiostatic mode was used to produce composite coating at 1.5 V potential and 50°C temperature of electrolyte solution for 30 minutes duration of process. After deposition, deionised water was used to wash the coated samples. Samples were dried in air after deposition. Table I provides the composition of watt's solution along with deposition conditions and experimental setup used is depicted in Fig. 1.

TABLE I WATT'S SOLUTION FOR TiO₂-HAP COATINGS

Electrolyte (Watt's) Solution Composition	
Concentration of Ca (NO ₃) ₂ .4H ₂ O, g/L	9.91
Concentration of NH ₄ H ₂ PO ₄ , g/L	2.87
Concentration of TiO ₂ , g/L	3-5
pH of electrolyte	3.3-5.3
Temperature, ⁰ C	30-50
Substrate	Ti-6Al-4V alloy
Voltage, V	1.5
Agitation, rpm	701

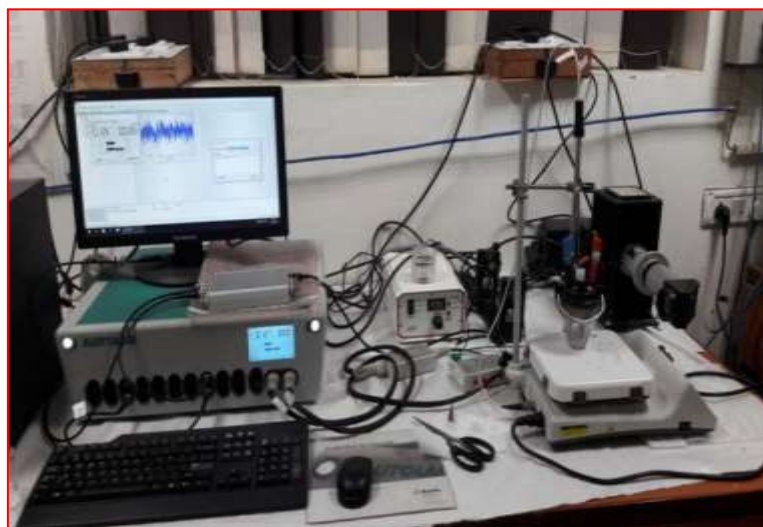


Fig. 1 Autolab Potentiostat, PGSTAT302N

The microstructure of the coated samples were examined directly by scanning electron microscope JEOL JSM-IT 100 at 20KV with EDS facility to determine the element composition. Micro hardness of TiO₂-HAP composite coatings were measured by Mitutoyo Vickers Micro Hardness Tester at a load of 0.2kgf for a time period of 15 seconds. Scratch test was performed at a ramp load of 1000 mN to 1600mN to evaluate adhesion of coatings onto the coated substrate using Scratch Tester (TR-102 model of Ducom Instruments Pvt. Ltd., India). An indenter is moved against the workpiece at a specified load and speed to peel off the coating from the substrate. The progressive load is applied to determine the critical load of failure of the coating. Pin-on-disc machine was used to conduct dry sliding wear tests for specimens. The substrate was annealed in a range of temperature of 280-300⁰C for 1 hour. The effect of annealing on micro hardness, scratch resistance and wear resistance were also evaluated.

III. RESULTS AND DISCUSSION

A. SEM and EDS Analysis

Different microstructures of coatings can be obtained under different set of process parameters in electrodeposition process. Microstructure of TiO₂-HAP composite coatings has been studied under Scanning Electron Microscope. The microstructure image along with process parameters conditions is depicted in Fig. 2.

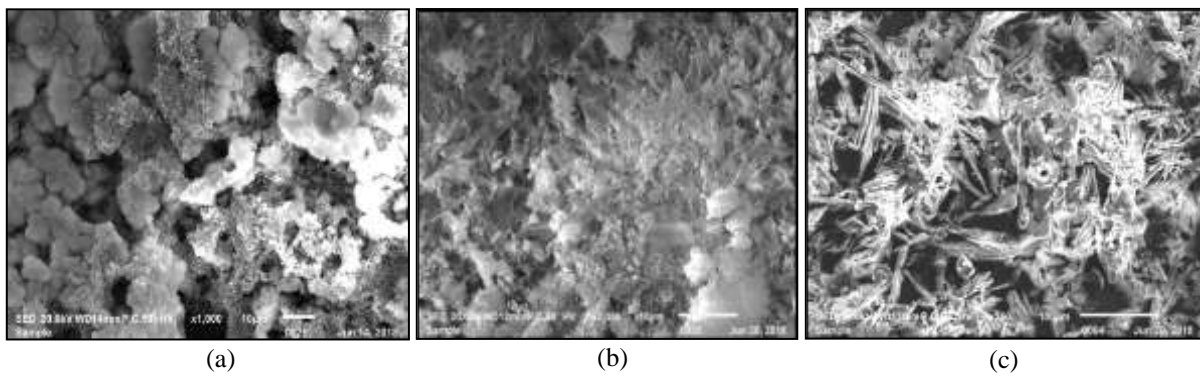


Fig. 2 SEM image of TiO₂-HAP coating at 1.5 Volt with (a) 4g/L TiO₂ & 3.3 pH (b) 5g/L TiO₂ & 4.3 pH, and (c) 3g/L TiO₂ & 5.3pH

When voltage is 1.5 Volt and 4g/L TiO₂ particle concentration at a pH value of 3.3, a dense coating of HAP with TiO₂ crystals entrapped in between has been obtained which is depicted in Fig. 2(a). When voltage is 1.5 V and 5g/L TiO₂ particle concentration at a pH value of 4.3, needle like crystals of HAP were formed along with flower like crystals of TiO₂ as depicted in Fig. 2(b). At pH value of 5.3 with 3g/L of TiO₂ particle concentration, TiO₂-HAP composite coating consists of flake like crystals of HAP with entrapped spherical TiO₂ particles which is shown in Fig. 2(c). It was observed that HAP crystals appeared to grow perpendicular to surface of coating. Uniform dispersion of TiO₂ particles between the HAP crystals were noticed, which resulted in dense composite coating due to low porosity. The spectrum confirmed the presence of Calcium (Ca), Phosphorus (P), Titanium (Ti) and Oxygen (O₂). Fig. 3 (a), (b) and (c) represents the EDS spectrum obtained in TiO₂-HAP coating at 1.5 Volt with 4g/L TiO₂ & 3.3 pH, at 5g/L TiO₂ & 4.3 pH, and 3g/L TiO₂ & 5.3pH respectively and elemental composition of coatings is shown in Table II.

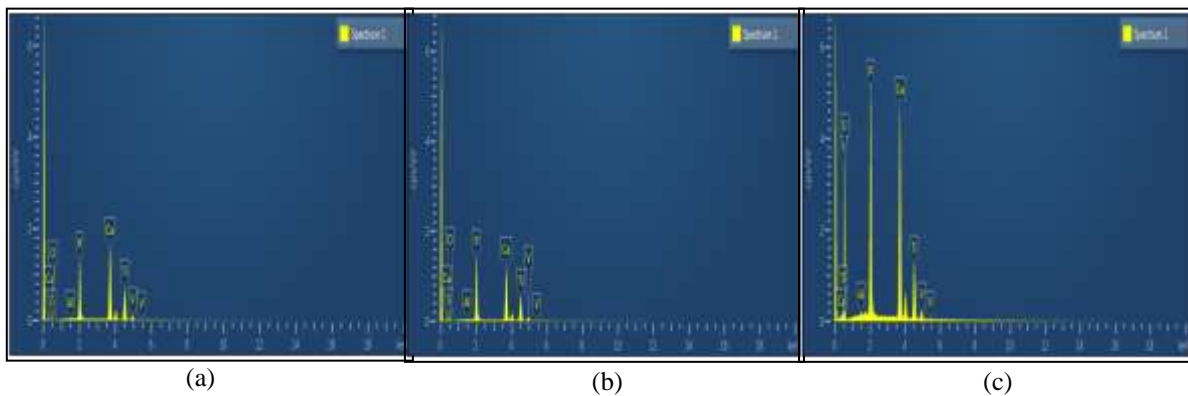


Fig. 3 EDS image of TiO₂-HAP coating at 1.5 Volt with (a) 4g/L TiO₂ & 3.3 pH (b) 5g/L TiO₂ & 4.3 pH, and (c) 3g/L TiO₂ & 5.3pH

TABLE II ELEMENTAL COMPOSITIONS OF TiO₂-HAP COMPOSITE COATINGS

Exp. No.	Element	Line Type	Weight %	Weight % Sigma	Atomic %
1	O	K series	58.45	0.43	76.78
	P		13.75	0.19	9.33
	Ca		18.93	0.24	9.93
	Ti		8.32	0.17	3.65
	Al		0.24	0.05	0.19
	V		0.30	0.10	0.13
	Total		100.00		100.00
2	P	K series	15.93	0.48	11.54
	Ca		26.98	0.70	15.11
	O		49.82	1.16	69.90
	Ti		6.80	0.36	3.19
	V		0.34	0.21	0.15
	Al		0.13	0.11	0.11
	Total		100.00		100.00
3	O	K series	49.40	1.06	70.54
	P		12.18	0.35	8.99
	Ca		22.52	0.54	12.84
	Ti		15.52	0.47	7.40
	Al		0.15	0.09	0.13
	V		0.23	0.21	0.10
	Total		100.00		100.00

Exp. No.	Element	Line Type	Weight %	Weight % Sigma	Atomic %
	Total		100.00		100.00

B. Ca/P Ratio

Another important aspect is to calculate Ca/P ratio of coatings. Coatings with Ca/P ratio closer to bone (1.68) exhibit better biocompatibility characteristics in biological testing. Table III show the Ca/P ratio of the composite coatings.

TABLE III Ca/P RATIO

Sample No.	Ca %	P %	Ca/P Ratio
S1	18.93	13.75	1.38
S2	26.98	15.93	1.69
S3	22.52	12.18	1.85

C. Micro Hardness Test Analysis

Vickers micro hardness test were performed to evaluate micro hardness of composite coating. Micro hardness Test was conducted on Vickers hardness tester by applying a load 0.2kgf load for duration of 15 seconds. Three readings were taken and average of readings was considered. Results for micro hardness of composite coating of TiO₂-HAP on Ti-6Al-4V obtained after the experiment are shown in the Table IV.

TABLE IV MICRO HARDNESS TEST RESULTS FOR TiO₂-HAP COATED Ti-6Al-4V

Sample No.	Input Parameters			Micro Hardness(HV)
	Voltage(V)	pH of Electrolyte	TiO ₂ Concentration (g/L)	
S1	1.5	3.3	4	564.07
S2	1.5	4.3	5	824.15
S3	1.5	5.3	3	987.00

It is found that for TiO₂-HAP coated Ti-6Al-4V, maximum micro hardness obtained at input voltage of 1.5 V, pH of 5.3 and TiO₂ concentration of 3g/L. The incorporation of TiO₂ particles in HAP matrix increases the hardness drastically.

D. Scratch Test Analysis

The scratch test was performed at a ramp load of 1000mN to 1600mN, and at a scratch speed of 0.2 m/sec for a scratch length of 3 mm. When ramp load is applied on the coated substrate, the length at which the coating just starts peels off is known as Initial critical length (L1) and corresponding load is called initial critical load (LC1). When load is further increased after that point, the length at which coating delaminates completely is called as final critical length (L2) and load is noted as final critical load (LC2). Also there is drastic change in acoustic emission and coefficient friction at these critical loads. The normal loads at which there is sudden change in acoustic emissions is measured at two successive points of change are noted from the graph. Fig. 4 represents the scratch track and critical length (L1 and L2) on the surface of coating during of the test and results of scratch test performed on each sample are given in Table V.

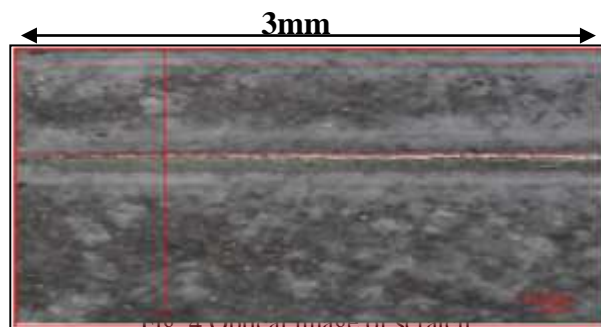


TABLE V RESULTS OF SCRATCH TEST

Sample No.	Critical Load L _{C1} (mN)	Critical Load L _{C2} (mN)
S1	1028	1042
S2	1052	1076
S3	1070	1081

It can be found that maximum initial critical load of 1070 mN can be sustained by sample S3 and maximum final critical load of 1081 mN can be sustained by sample S3. The addition of TiO₂ in electrolyte resulted in increase in adhesion strength at when deposition was carried out at 1.5V, 5.3pH and 3g/L of TiO₂ particles concentration.

E. Wear Test Analysis

Cylindrical specimens of 3mm diameter and 40mm length of Ti-6Al-4V substrate were prepared and composite coating of TiO₂-HAP were electrodeposited on Ti-6Al-4V at 1.5V, 3g/L TiO₂ and 5.3 pH of electrolyte solution. Wear resistance was calculated for uncoated Ti-6Al-4V substrate (S0), TiO₂-HAP coated Ti-6Al-4V (S3) by volume loss method at test

load of 2kgf at 500 rpm for 180 seconds. Coefficient of friction was also evaluated during the process. Table VI represents the results of wear test conducted on uncoated, coated and coated-annealed Ti-6Al-4V substrate.

TABLE VI RESULTS OF WEAR TEST

S.NO.	Parameters	Units	Uncoated Ti-6Al-4V (S0)	Coated Ti-6Al-4V (S4)
1	Wear Rate	mm ³ /m	0.864	0.621
2	Wear Resistance	m/mm ³	1.160	1.610
3	Mean Coefficient of Friction	-	0.302	0.289

It has been observed that wear rate of coated substrate decreases due to composite coating wear resistance of coated alloy increases due to incorporation of TiO₂ particles in HAP matrix.

F. Comparative Analysis Of Coatings

A drastic change has been observed on micro hardness, adhesion strength and wears resistance Ti-6Al-4V after electrodeposition. Annealing operation was performed on sample number S3. Micro hardness and scratch resistance was measured to observe the effect of annealing operation on properties of electrodeposits. The cylindrical specimen was electrodeposited at 1.5 V, 5.3 pH and 3 g/L TiO₂. Annealing operation was also performed on cylindrical specimen o observe its effect on wear rate and wear resistance of coated- annealed sample. The performance of Ti-6Al-4V alloy was compared on the basis of micro hardness, scratch resistance and wear resistance in uncoated, coated and coated-annealed condition of Ti-6Al-4V alloy. Nomenclature S0, S3 and S4 has been assigned to uncoated substrate, TiO₂-HAP coated substrate at optimized parameters and TiO₂-HAP coated-annealed substrate at optimized parameters respectively as shown in Table VII.

TABLE VII SAMPLE NOMENCLATURE

Sample Name	Nomenclature
S0	Uncoated Ti-6Al-4V
S3	Coated Ti-6Al-4V
S4	Coated & Annealed Ti-6Al-4V

1) Comparative Analysis of Micro Hardness of Composite Coatings

Micro hardness of the coated samples is one of the important mechanical properties, which directly relates to the wear resistant of the coatings. Increase in micro hardness of the coatings can lead to better implant life. TiO₂-HAP coating increases the micro hardness of on Ti-6Al-4V. Annealing of composite coated substrate decreases micro hardness. Table VIII represents comparison of micro hardness and graphical representation is shown in Fig. 5

TABLE VIII MICRO HARDNESS OF DIFFERENT CONDITIONED SUBSTRATES

Micro Hardness(HV)	Different Substrate Conditions		
	Uncoated Ti-6Al-4V (S0)	Coated Ti-6Al-4V (S3)	Coated & Annealed Ti-6Al-4V (S4)
	350	987	631

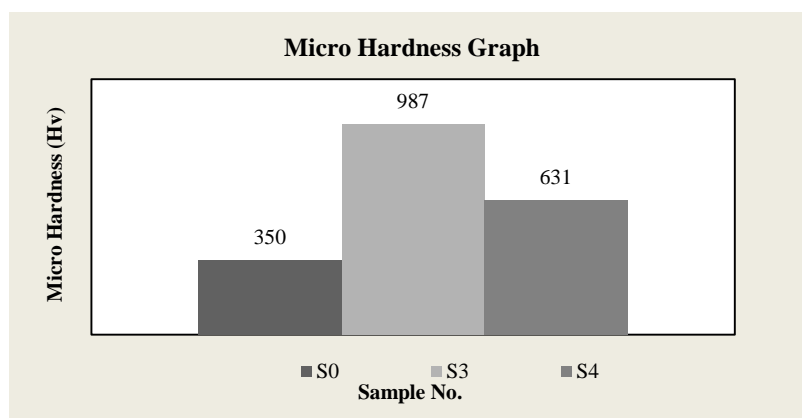


Fig. 5 Comparison of micro hardness

Comparison was made to calculate percentage increase and decrease of microhardness of substrate after deposition and after annealing process. Table IX shows comparison of percentage increase and decrease of micro hardness value for uncoated, coated, coated-annealed Ti-6Al-4V substrate.

TABLE IX COMPARISON OF MICRO HARDNESS OF UNCOATED (S0), COATED (S3), COATED-ANNEALED (S4) SUBSTRATE

Type S0	Type S3	Type S4	
	184.85 %	80.28%	Type S0
		-39.07%	Type S3
			Type S4

It was observed that micro hardness of Ti-6Al-4V (Type S0) was 350 HV, whereas of TiO₂-HAP coated Ti-6Al-4V (Type S3) was 987 on HV scale. It was observed that there was a considerable increase of 184.85 % in the micro hardness of the coated substrate after electro deposition, due to presence of TiO₂ particles. There is 80.28% increase in coated and annealed (S0-S4) condition than the without coating substrate (S0). Decrease of 39.07% in micro hardness was observed after annealing operation on coated sample (S3-S4).

2) *Comparative Analysis of Adhesion Strength of Composite Coatings*

Comparison was made for adhesion strength of various conditions of Ti-6Al-4V. The adhesion strength of coatings on substrates was measured in following conditions:-

- (i) TiO₂-HAP coated Ti-6Al-4V substrate (S3)
- (ii) TiO₂-HAP coated and annealed Ti-6Al-4V substrate (S4)

It can be observed that adhesion strength increased drastically after annealing of coated substrates. Table X shows the comparison of adhesion strength for coated (S3) and coated-annealed (S4) Ti-6Al-4V and Fig. 6 depicts the results the graphically.

TABLE X ADHESION STRENGTH OF DIFFERENT CONDITIONED SUBSTRATES

Adhesion Strength (mN)	Different Substrate Conditions	
	Coated Ti-6Al-4V (S3)	Coated & Annealed Ti-6Al-4V (S4)
	1078	2530

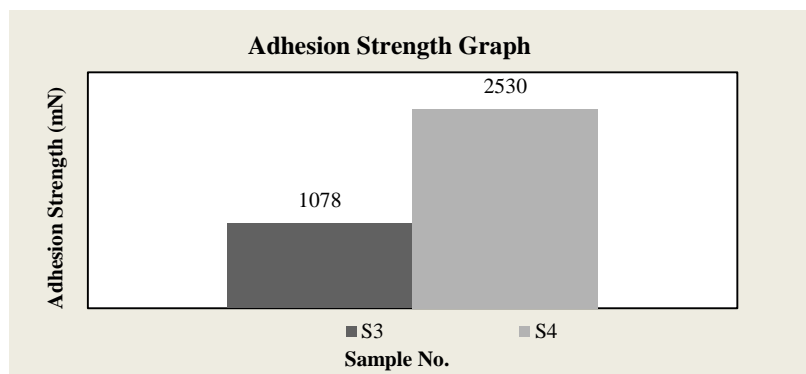


Fig. 6 Comparison of adhesion strength

Adhesion strength of TiO₂-HAP coated Ti-6Al-4V (Type S3) was 1078 mN, whereas of TiO₂-HAP coated-annealed Ti-6Al-4V (Type S4) was 2530 mN. It was observed that there was a significant 134.69% increase in adhesion strength of Ti-6Al-4V after annealing operation performed on composite coated substrate due to increase in bonding strength between coating and substrate.

3) *Comparative Analysis of Wear Rate and Wear Resistance of Composite Coatings*

The wear resistance and wear rate of coatings on substrates was measured in following conditions:-

- (i) Uncoated Ti-6Al-4V substrate (S0)
- (ii) TiO₂-HAP coated Ti-6Al-4V substrate (S3)
- (iii) TiO₂-HAP coated Ti-6Al-4V substrate and annealed substrate thereafter (S4)

The comparisons of result of wear rate of coatings in above conditions are given in Table XI and Fig. 7 represents comparison of wear rate in different conditions of substrate in the graphical form.

TABLE XI WEAR RATE OF DIFFERENT CONDITIONED SUBSTRATES

Wear Rate(mm ³ /m)	Different Substrate Conditions		
	Uncoated Ti-6Al-4V (S0)	Coated Ti-6Al-4V (S3)	Coated & Annealed Ti-6Al-4V (S4)
	0.864	0.621	0.495

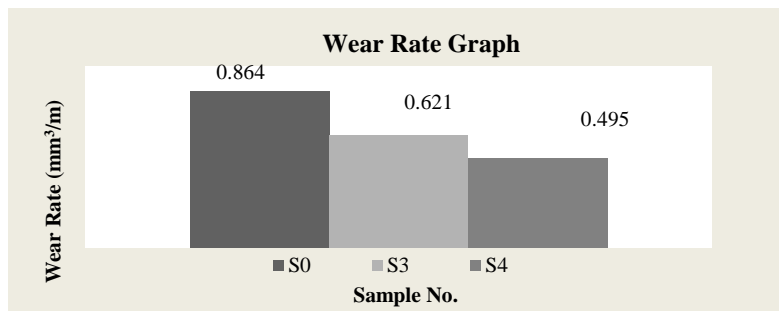


Fig. 7 Comparison of wear rate

Decrease in wear rate was observed due to composite coating on substrate in coated and annealed condition as well. Minimum wear observed on coated-annealed substrate and maximum wear was observed on uncoated substrate. Decrease in wear of coated substrate was due to increased hardness of composite coating. Table XII represents percentage decrease in wear rate in various conditions of substrate.

TABLE XII WEAR RATE OF OF UNCOATED (S0), COATED (S3), COATED-ANNEALED (S4) SUBSTRATE

Type S0	Type S3	Type S4	
	-28.13 %	-42.71%	Type S0
		-20.29 %	Type S3
			Type S4

It can be inferred that there is 28.13 % decrease in wear rate of Ti-6Al-4V after composite coating and 42.71% decrease in coated and annealed condition than the without coating substrate. A decrease of 20.29% in wear rate was observed after annealing operation on coated sample. The comparisons of result of wear resistance of coatings in different conditions are given in Table XIII and Fig. 8 represents the graphical representation of data.

TABLE XIII WEAR RESISTANCE DIFFERENT CONDITIONED SUBSTRATES

Wear Resistance (m/mm ³)	Different Substrate Conditions		
	Uncoated Ti-6Al-4V (S0)	Coated Ti-6Al-4V (S3)	Coated & Annealed Ti-6Al-4V (S4)
	1.16	1.61	2.02

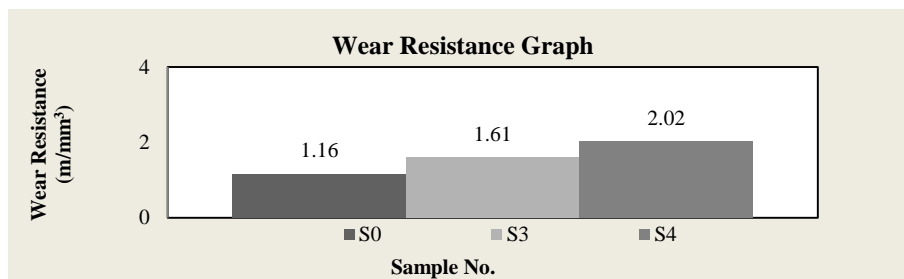


Fig. 8 Comparison of wear resistance

Table XIV represents the wear resistance behaviour of uncoated, coated, coated-annealed Ti-6Al-4V substrate.

TABLE XIV COMPARISON OF WEAR RESISTANCE OF UNCOATED (S0), COATED (S3), COATED-ANNEALED (S4) SUBSTRATE

Type S0	Type S3	Type S4	
	38.79%	74.14%	Type S0
		25.47%	Type S3

It can be noticed that there is 38.79% increase in wear resistance of Ti-6Al-4V after composite coating and 74.14% increase in coated and annealed condition than the without coating substrate. An increase of 25.47% in wear resistance was observed after annealing operation on coated sample.

IV. CONCLUSIONS

TiO₂-HAP composite coatings have been produced successfully on Ti-6Al-4V in potentiostatic mode. Different type of morphologies can be obtained at different levels of process parameters. Spherical/globular, flake type and needle type morphology can be obtained for HAP crystals while spherical and flower like crystals can be obtained for TiO₂ particles. Ca/P ratio of 1.38, 1.69 and 1.85 was obtained. Ca/P ratio of approx. 1.68 (closer to bone) is highly favorable for better biocompatibility. Using optimum parameters, micro hardness can be increased. At 3g/L TiO₂ concentration, dense and hard coatings have been produced. Micro hardness of uncoated Ti-6Al-4V which was 350 HV initially, found to be increased to a value of 987 HV in case of electrodeposited substrate. Maximum micro hardness of composite coatings

obtained at input voltage of 1.5 V, pH of 5.3 and TiO₂ concentration of 3g/L. Micro hardness increases with increase in pH of electrolyte. Significant increase in micro hardness of the Ti-6Al-4V was observed after electrodeposition, due to presence of TiO₂ particles. A dense and low porosity coating was obtained due to presence of TiO₂ particles in HAP matrix which resulted in hard adherent deposits. Maximum adhesion strength obtained at input voltage of 1.5 V, pH of 5.3 and TiO₂ concentration of 3g/L. Initial critical load of 1070 mN can be sustained over a length of 350 μm and maximum final critical load of 1078 mN can be sustained over a length of 390μm. The lower wear rate and higher wear resistance was observed in coated substrate. Due to composite coatings, micro hardness of substrate increases by 182% and wear resistance increases by 38.74%. Annealing operation on coated substrate decreases micro hardness by 39.07%, increases adhesion strength by 134.69% and wear resistance by 25.47%. Release of V ions from Ti-6Al-4V alloy into body was prevented due to TiO₂-HAP composite coating, which was a serious concern for application of the alloy requiring high service life.

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