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Wear resistance of pulsed laser deposition of hydroxyapatite on Stainless Steel 316L

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ABSTRACT

Background: 316 l st.st. are frequently used as orthopedic implants because their mechanical properties and formability. **Objective:** This research aims to improve the surface of stainless steel by coating it by (HA). HA Used in this search pressed at pressure (150MPa) with partical size (2.745 µm) and used as a target in coating by (PLD) techniquesEffects of the number of pulses (3000,4500 and 6000) on the coating layer properties have been studied. Effects of the annealing temperature (450 0C) for one hour and Under an empty atmosphere on the coating layer properties have been studied, also. Surface characterization studies of the coatings. **Results:** results show The mechanical property of the coating was evaluated by Vickers micro hardness and wear test. XRD analysis of coated sample indicate the formation of the HA layer. SEM results shows evident improvement in microstructure and grow HA film with increasing in pulses number. In bioactivity test the percentage of (Ca) and (P) are increased Significantly after 14 days immersion in SBF which Confirms that the samples are bioactive. From above results conclude that PLD coating processes may be used to modify the surface of the 316 l st .st implant advices. They can provide a bioactive HAP top layer with good electrochemical and biochemical stability in the human body environment. The wear resistance of the 316 l samples increased after HA coatings and its increased also as number of pulsed increase. **Conclusion:** Success of the study in the deposition of Hydroxyapatite (Ca10 (PO4)6 (OH)2) powders using pulse laser deposition on st.st 316L.2. The films micro hardness increased with increasing of number of pulses.A significant decrease in wear rate for coating sample was observed, It was (0.000062 cm3) after one hour compared with (0.00047 cm3) for the uncoated stainless steel sample .andAnother interesting increase in biocompatibility was achieved during the work for the coated sample compare to the uncoated 316 L stainless steel sample.

KEYWORDS: Photovoltaic (PV)

INTRODUCTION

Metallic materials such as stainless steels, titanium and its alloys, and cobalt alloys are commonly used as bone implants due to their excellent strength, toughness and relatively low corrosion rate[1].Among the various implant materials, austenitic stainless steel AISI 316 L is one of the most popular and economical choices in spite of the potential risks associated with release of toxic nickel and chromium ions in physiological media [2]. It is known that the leached metal ions can cause sarcomas, fibrous encapsulation, osteolysis, genotoxicity, carcinogenicity, and metal sensitivity [3]. Moreover, these metallic implants are not bioactive and achieving satisfactory osseointegration is always a concern. Earlier research has shown that these problems can be overcome by depositing bioactive hydroxyapatite (HAP) (Ca10(PO4)6(OH)2) coatings on metallic implants. HAP coatings were first reported in the mid-1980s for improving the fixation between the bone and the implant [3]. bioactive HA coating in the metallic implant has many advantages, including improved corrosion resistance of implant surface and enhanced biointeraction with the surrounding tissues[4]. HAp is one of the naturally available biocompatible and bioactive materials that show the ability to interact with surrounding bone [5]. A variety of techniques have been developed since then for depositing HAP coatings on metallic substrates,

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including thermal spraying, sputter coating, sol–gel coating, dip coating, electrophoretic deposition, and electrochemical deposition [3]. Recently, the implant, deposition of hydroxyapatite by laser surface modification has also been used to improve the microstructure, tribological, wear, corrosion and biocompatibility properties of 316L stainless steel.

MATERIALS AND METHODS

2-1 Powder and target preparation:

A (20) g of HA powder was collected and processed beginning with manual grinding using mortar to get the semi-finished powder. The powder was sieved using sieve number of (200) meshes. The resulted powder was crushed and milled to obtain a nano-size powder by using of a planetary ball milling,. The milling was done for (24) hr at (350) rpm. The particle size of the powder obtained from milling process was measured using Particle Size Analyzer Bettersize 2000 laser particle size analyzer. The powder was (0.668-12.99)µm. Then, the powder was mixed with (3ml) of poly vinyl alcohol (PVA) as a binding material. Then, the mixture was mold in (Ø 20 mm), and pressed at different pressures (150 MPa), After that, the target was dried using the dry box at 150℃ for 4 hr for dehumidify and PVA releasing.

2-2 Preparation of St.St.316L Substrates:

St.St.316L plate with diameter of 12mm was cut in to 3mm thickness samples. The chemical composition of the St.St 316L plate was done in state Company for Inspection and Engineering Rehabilitation (SIER)/Ministry of Industry and Minerals, Table 1 shows the chemical analysis of St.St, the samples were wet ground using 120, 220, 320, 600, 1000, 1200 and 2000, grit silicon carbide papers Then these samples were then cleaned for 10 minutes in each of distilled water, acetone, and ethanol, respectively using ultra sound cleaning device.

Table 1: Chemical analysis of St.St 316L.

Element	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Co	Cu	V	Fe
Percentage %	0.023	0.322	1.00	0.038	0.00	17.91	2.06	9.85	0.001	0.153	0.286	0.112	Bal.

2-3 Pulsed laser deposition PLD process:

In this step, targets were placed onto a rotating holder(Figure 1) and ablated using excimer lasers with pulses of ArF (λ = 1064 nm), and applied energy of (600) m J .The ablated area was approximately 20 mm2 and the number of pulses was in the (1500-6000) range. Thin layers were deposited onto St.St.316l substrate heated at t temperature (300)˚C,). Target–substrate distance was set to 3 cm and the pressure in the PLD chamber was 1.5×10−5 Torr. The samples coding shown in table(2)

Fig. 1: (a): Deposition chamber (b): Base of the deposition chamber

Table 2: samples coding

Sample code	A	B1	B2	B3
Number of pulses	Uncoated	3000	4500	6000

2-4 Annealing process

The deposited films were post-annealed at temperature (450)˚C for one hour in vacuum furnace at heating rate 5˚C/min.

Categorization:

1- X-Ray Deflection (XRD):

The material and phases of powders and composite material were identified with XRD- system type (DX-2700, X- Ray Diffractometer, using Cu Kα radiation (λ = 1.5405 Å), and a scanning speed of 5θ˚/min from (10º to 90º) of 2θ (Bragg angle).

2- Light Optical Microscope (LOM):

Involved identification and measurement of the phases, shape and grain size are some characteristics of grain boundaries. Each of these has distinct characteristics. The microstructure evaluated with (100x and 400x) magnification

3- SEM Analysis:

The microstructure and topography of the films were examined using Scanning electron microscopy (SEM),

4- AFM Analysis:

The depth morphology, roughness of surface thin film was investigated with a type AA3000 Angstrom advanced Inc atomic force microscope (AFM).

5- Energy Dispersive Spectroscopic (EDX):

Energy Dispersive X-ray (EDX-7000) was used to analyze the chemical composition of sample surface before and after immersion in SBFfor duration 3, 7 and 14 days, respectively.

6- Bioactivity Estimation (in vitro):

The prepared samples were immersed for (3,7,14) days, in simulated body fluid (SBF) that has inorganic ions concentration similar to those of human extracellular fluid. The ions concentration of SBF is given in Table (3.6) nearly equal to those of human blood plasma.

6-1 Preparation of Stimulated Body Fluid (SBF):

SBF is a metastable solution containing calcium and phosphate ions already supersaturated with respect to the apatite. Therefore SBF is prepared as follows:

• Reagents (Table 3.7) were sequentially added to 700 ml of H2O, with the restriction that a new precursor (as per table 4-5) was added only after the previous addition had completely dissolved.

• A total of 40 ml of 1M HCl solution was used for pH adjustments during the preparation of 1L of SBF solution. 15 ml of this acid solution was added just before the addition of 6th reagent (CaCl2.2H2 O) in order to avoid turbity.

• After addition of the 8th reagent ((CH2 OH) 3 CNH2), the solution temperature was raised from ambient to 37ºC. It was then titrated with 1M HCl to a pH of 7.4 at 37°C.

• During titration process, it was required to dilute the solution with consecutive additions of de-ionized water in order to make the final volume to 1L.

The prepared sample of SBF solutions is to be capable of being stored at 5°C for a month without degradation. The simulated body fluid, solution was changed every 4 days to provide constant chemical composition of solution [6].

Table 3: alchemical combination of stimulated body fluid solution .

Demand	1	2	3	4	5	6	7	8
Substance	NaCl	NaHCO3	KCl	Na2HPO4.2H2O	MgCl2.6H2O	CaCl2 .2H2O	Na2SO4	(CH2OH)3CNH2
Quantity	6.547	2.268	0.373	0.178	0.305	0.368	0.071	6.057

7- Hardness Test:

Vickers Hardness (TH-717 Digital Micro Vickers Hardness Tester) was used to measure the hardness of HA thin film, at load (1.96N) and holding time 15 seconds.

8- Wear Test:

Before wear test the samples were drying in (50 C0) for (2 h) and cooling in the furnace, this process had been done by using vacuum drying furnace ,then the samples saved in well- knit boxes with silica gel material to keep them completely dry.

The dry sliding wear studied by using pin on disk concept using (150 rpm)and constant radios (8mm) with different sliding distance and the loads were (2N) .the ball of the pin was 4mm in radius made from carbide steel. The sample is weighted before teat using (0.0001) accuracy electric balance .after a period of time (10,

20 ,30,40,50 and 60 min) the sample test is weighted and the dry sliding wear rate had determined according to equation (3-3).The test method had been covered according to ASTM G 99 [7].

Wear rate =(weight loss(g))/(ρ(g/cm3)) (1-1)

Where:

Weight loss (g)= quantity loss after(10 ,20 ,30,40,50 and 60)min.

ρ (g/cm³) = theoretical density of the element formed for the specimen (g/cm³). Calculated from equation (3-3).

RESULTS AND DISCUSSION

1- X-ray Diffraction:

Fig.(2) and Fig.(3) show the hydroxyapatite and the XRD results of the HA thin films after annealing in the range of 10º to 50º diffracted angle. The pattern refers to the existence peaks of HA phase Ca10 (PO4)6(OH)2 . The observed positions of the diffraction lines (2θ and corresponding d for the patterns shown in Figure (2) and(3) are in full agreement with the corresponding values reported for hexagonal hydroxyapatite (JCPDS, C and No.09-0432) shown in fig. 4

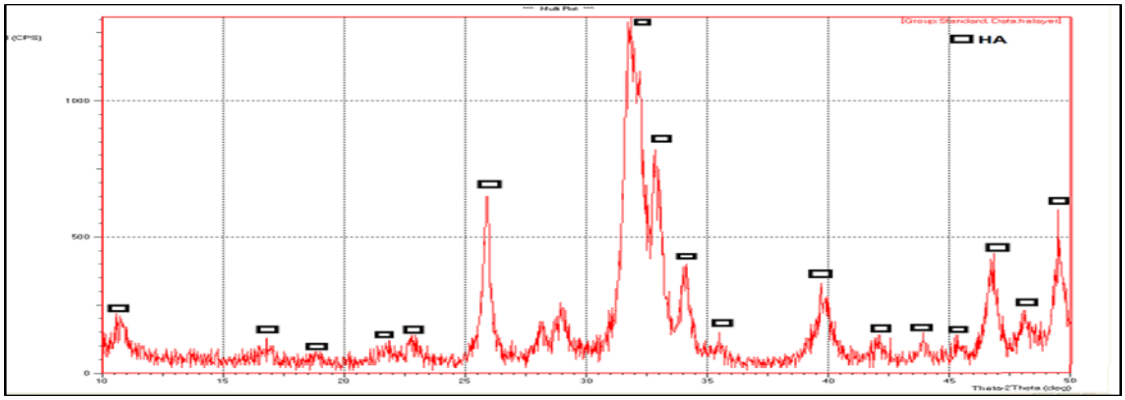

Fig. 2: XRD Pattern of HA Powder

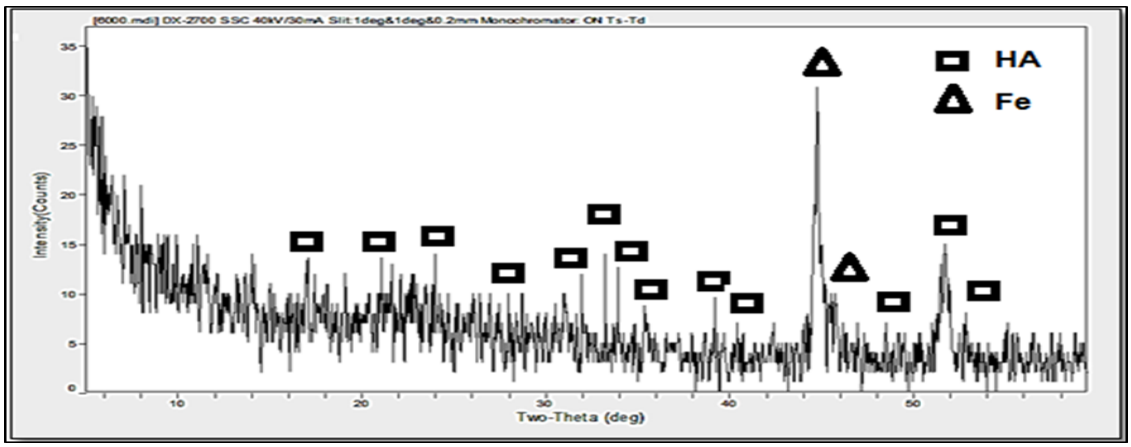

Fig. 3: XRD analysis of HA film

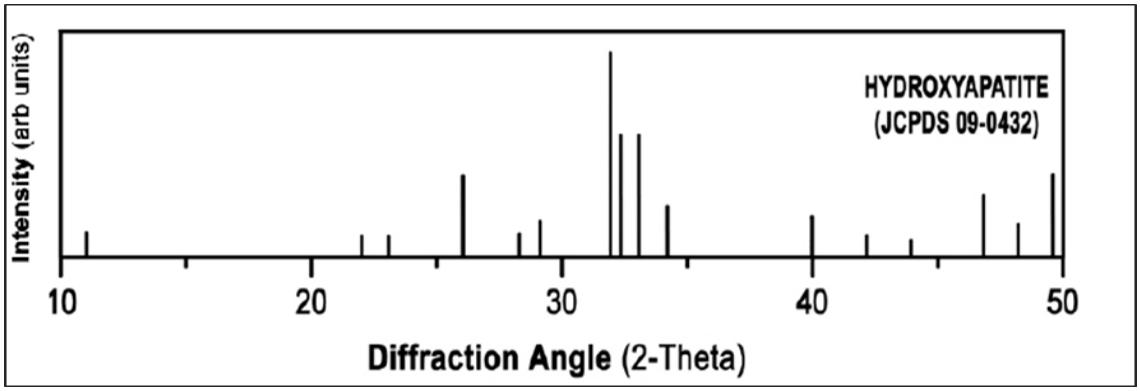

Fig. 4: XRD Standard Card for HA

2- SEM Results:

Fig.5shows SEM micrographs of 150MPa HA samples deposited at different pulses and at 300˚C substrate temprature and 550˚C annealing temp. It is clear the effect of pulses increasing the improvement of the microstrucrture of the HA Films. The HA particles deposited are grown to form clusters and seems to form a dense aggregated structure on the substrate Furthermore , More pulses will be beneficial in improving the film growing , density and microstructure .

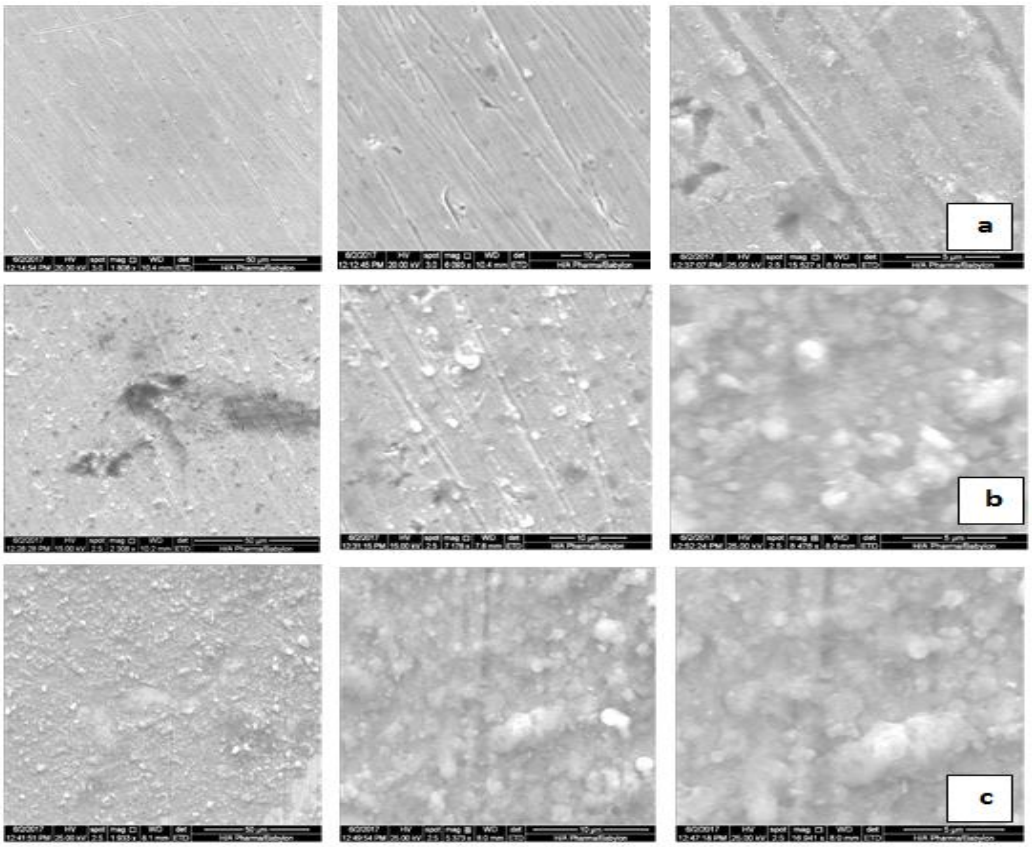

Fig 5: SEM Micrographs of Samples (a) B1, (b) B2, and (c) B3

3- AFM Results:

Fig.6 and .7 show results from AFM of HA coating deposited at different pulses laser before and after annealing annealing . It can be noticed that deposition rate of HA particles is affected by increasing the pulses laser to (6000). It can be seen that the roughness decreased with the pulses increasing to (6000), and the roughness decreased before annealing to (5.26 nm) and then increased to (30.3 nm) with increasing temperatures after annealing ,and this result in agreement with Samausz et al, [8]. Fig. 6 and 7 shows the effect of number of pulses on surface roughness of HA coating before and after annealing .

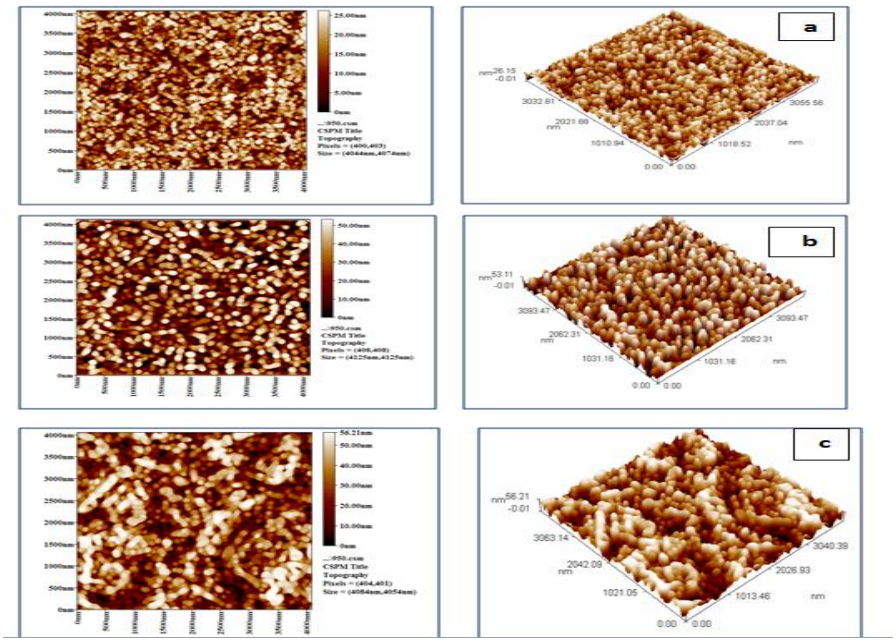

Fig. 6: AFM Pattern of 150 MPa Samples at (a) B1, (b) B2 and (c) B3 before the Annealing

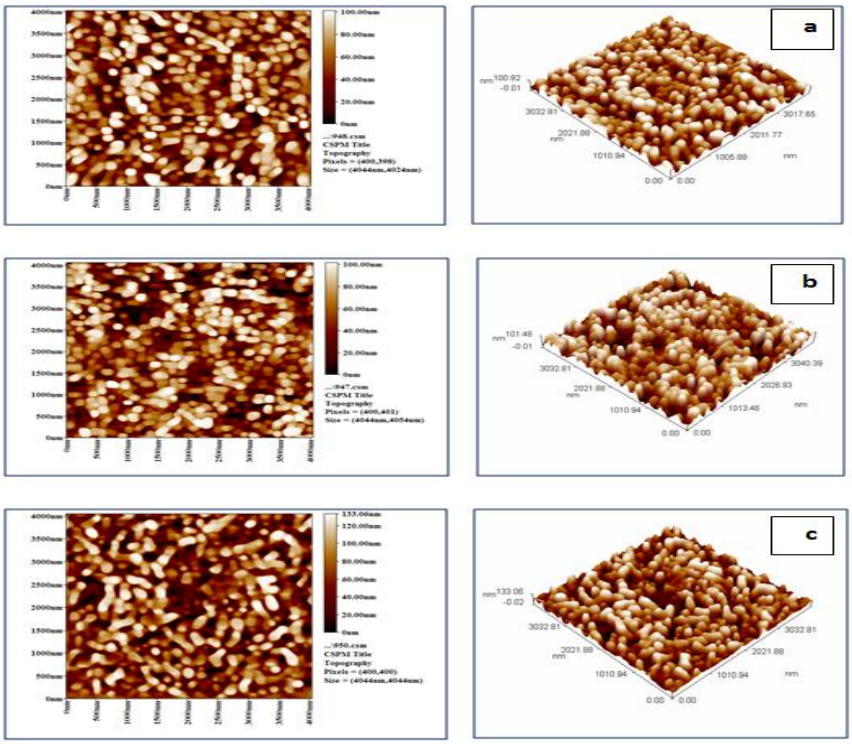

Fig. 7: AFM Pattern of 150 MPa Samples at (a) B1, (b) B2 ,and (c) B3 after the Annealing

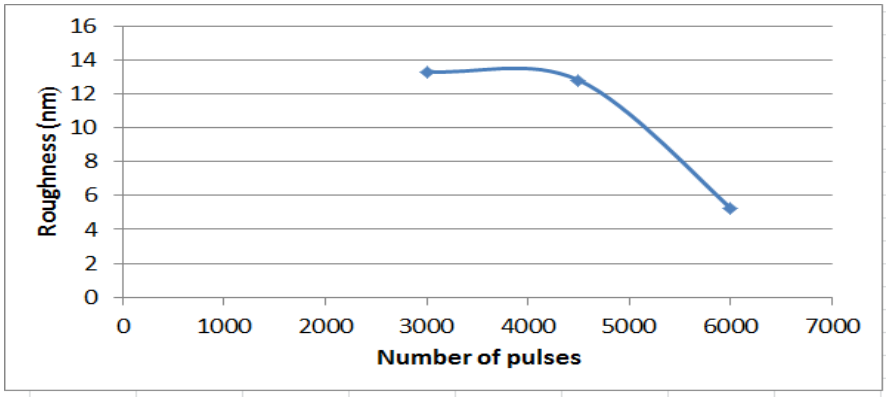

Fig. 8: The Effect of Number of Pulses on HA Coating surface roughness before annealing

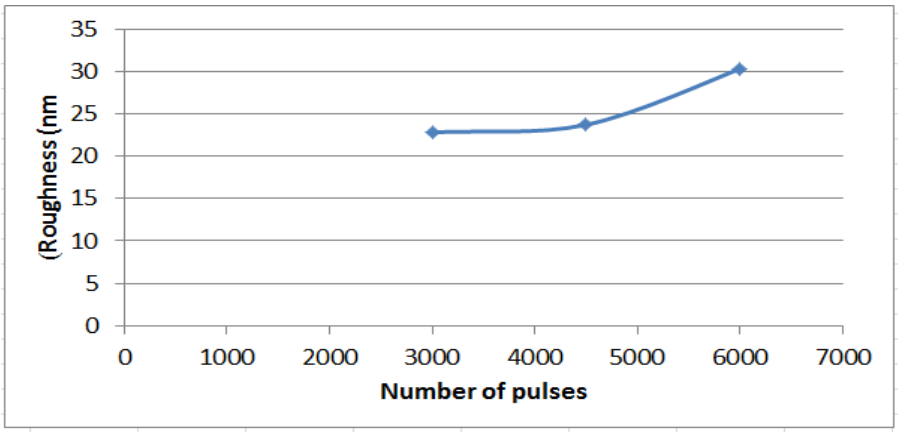

Fig. 9: The Effect of Number of Pulses on HA Coating surface roughness after annealing

4- EDX Results:

The percentages of (Ca) and (P) in HA films are increased with increase immersion time (3 day, 7 days, and 14 days) respectively as shown in Fig. 10 according to the results in tables4, 5 and 6 for the B3 sample. It will be interesting to know that the increasing of percentages is very slightly after (3) days in comparison with those after (7-14) days, This is due to intervals reduction resulted in reduce drown ions from SBF solution.This is agreement with the finding of reference [9].

Table 4: Results of EDX Analysis for B3 Sample

Measurement Condition

Instrumen t: EDX-7000 Atmosphere: Air Collimator: 10(mm)

Analyte	TG kV uA	FI Acq.(keV)	Anal.(keV)	Time(sec)	DT (%)
Na-Sc	Rh 15 65-Auto	0 - 2 0	0.00- 4.40	Live- 100	30
Al-U	Rh 50 9-Auto	0 - 4 0	0.00-40.00	Live- 100	29

Quantitative Result

Analyte	Result	[3-sigma]	Proc.-Calc	. Line	Int.(cps/uA)
Fe	67.721%	[0.111]	Quan-FP	FeKa	3751.5560
Cr	17.085o.	[0.049]	Quan-FP	CrKa	1206.7852
Ni	9.415%	[0.051]	Quan-FP	NiKa	344.2946
Si	1.351%	[0.189]	Quan-FP	SiKa	0.1547
Mo	1.241%	[0.008]	Quan-FP	MoKa	203.2511
Mn	1.120%	[0.007]	Quan-FP	MnKa	77.9553
P	0.850%	[0.089]	Quan-FP	P Ka	0.3019
Ca	0.621%	[0.009]	Quan-FP	CaKa	3.9280
Cu	0.396%	[0.007]	Quan-FP	CuKa	16.9738
K	0.097%	[0.013]	Quan-FP	K Ka	0.3715
V	0.051%	[0.006]	Quan-FP	V Ka	2.8483
Bi	0.051•6	[0.006]	Quan-FP	BiLa	2.0539

Table 5: Results of EDX Analysis for B3 Samplean Immersed for 3 Days in SBF Solution

Measurement Condition

Instrument : EDX-7000 Atmosphere: Air Collimator:10 (mm)

Analyte	TG kV	uA FI	Acq.(keV)	Anal.(keV)	Time (sec)	DT (%)
Al-U	Rh 50	8-Auto --- 0 - 4 0		0.00-40.00	Live- 100	31
Na-Sc	Rh 15	56-Auto --- 0 - 2 0		0.00- 4.40	Live- 100	30

Quantitative Result

Analyte	Result	[3-sigma]	Proc.-Calc .	Line	Int.(cps/uA)
Fe	65.744%	[0.104]	Quan-FP	FeKa	4477.9744
Cr	16.916%	[0.047]	Quan-FP	CrKa	1429.7657
Ni	9.359%	[0.048]	Quan-FP	NiKa	428.9210
P	2.922%	[0.085]	Quan-FP	P Ka	1.2986
Ca	1.405%	[0.015]	Quan-FP	CaKa	10.7604
Mo	1.232%	[0.008]	Quan-FP	MoKa	252.9362
Mn	1.046%	[0.006]	Quan-FP	MnKa	88.2150
Si	0.895%	[0.169]	Quan-FP	SiKa	0.1281
Cu	0.382%	[0.006]	Quan-FP	CuKa	20.5083
V	0.056%	[0.006]	Quan-FP	V Ka	3.7250
Bi	0.043%	[0.006]	Quan-FP	BiLa	2.2046

Table 6: Results of EDX Analysis for B3 Sample an Immersed for 7 Days in SBF Solution

Measurement Condition

Instrument: EDX-7000 Atmosphere: Air Collimator:10 (mm)

Analyte	TG kV	uA FI	Acq.(keV)	Anal.(keV)	Time (sec)	DT (%)
Al-U	Rh 50	8-Auto -- 0 - 4 0		0.00-40.00	Live- 100	30
Na-Sc	Rh 15	58-Auto -- 0 - 2 0		0.00- 4.40	Live- 100	31

Quantitative Result

Analyte	Result	[3-sigma]	Proc.-Calc.	Line	Int.(cps/uA)
Fe	64.858%>	[0.105]	Quan-FP	FeKa	4307.2926
Cr	17.011%	[0.049]	Quan-FP	CrKa	1387.5899
Ni	8.886%	[C.047]	Quan-FP	NiKa	401.8321
P	3.579%	[0.096]	Quan-FP	P Ka	1.5700
Ca	1.861%	[0.017]	Quan-FP	CaKa	13.8824
Mo	1.179%	[0.008]	Quan-FP	MoKa	240.2835
Mn	1.097%	[0.007]	Quan-FP	MnKa	89.8328
Si	1.030%	[0.169]	Quan-FP	SiKa	0.1459
Cu	0.346%	[0.006]	Quan-FP	CuKa	18.3426
K	0.088%	[0.011]	Quan-FP	K Ka	0.4000
V	0.063%	[0.006]	Quan-FP	V Ka	4.0326

Table 7: Results of EDX Analysis for B3 Sample an Immersed for 21 Days in SBF Solution

Measurement Condition

Instrument : EDX-7000 Atmosphere: Air Collimator:10 (mm)

Analyte	TG kV	uA FI	Acq.(keV)	Anal.(keV)	Time(sec)	DT (%)
Al-U	Rh 50	8-Auto --- 0 - 4 0		0.00-40.00	Live- 100	29
Na-Sc	Rh 15	59-Auto --- 0 - 2 0		0.00- 4.40	Live- 100	30

Quantitative Result

Analyte	Result	[3-sigma]	Proc.-Calc.	Line	Int.(cps/uA)
Fe	63.480%	[0.105]	Quan-FP	FeKa	4150.2036
Cr	16.728%	[0.049]	Quan-FP	CrKa	1315.1623
Ni	8.914%	[0.048]	Quan-FP	NiKa	401.5076
P	4.547%	[0.111]	Quan-FP	P Ka	1.9728
Ca	2.423%	[0.021]	Quan-FP	CaKa	17.5359
Mo	1.162%	[0.008]	Quan-FP	MoKa	235.5097
Si	1.131%	[0.180]	Quan-FP	SiKa	0.1590
Mn	1.035%	[0.007]	Quan-FP	MnKa	82.4261
Cu	0.381%	[0.006]	Quan-FP	CuKa	20.1177
K	0.143%	[0.014]	Quan-FP	K Ka	0.6298
V	0.056%	[0.006]	Quan-FP	V Ka	3.4339

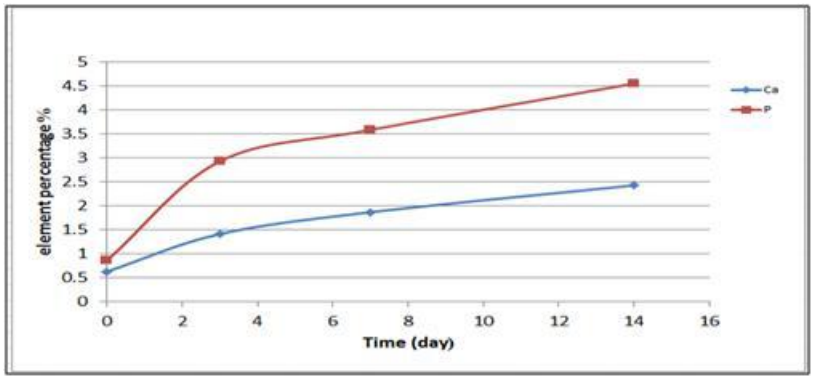

Fig.10: The percentages of calcium and phosphate of HA films with time after immersion in SBF after (3,7, and14) days.

5- Hardness Results:

The effect of laser pulses number on the HA coating hardness are shown in figure (3), the significant effect of pulses number on the resulted hardness. can be observed .Hardness of uncoated Samples are improved after coating it with HA , Furthermore increasing of pulses from 3000 to 6000 could improve the hardness from(310 HV) to (420 HV), this results are agreement with P. Rajesh et.al [10], Such improvement observed in SEM results as in Fig.11 . Most likely the pulse increasing could implant more HA particles on the substrate surfaces. Again.

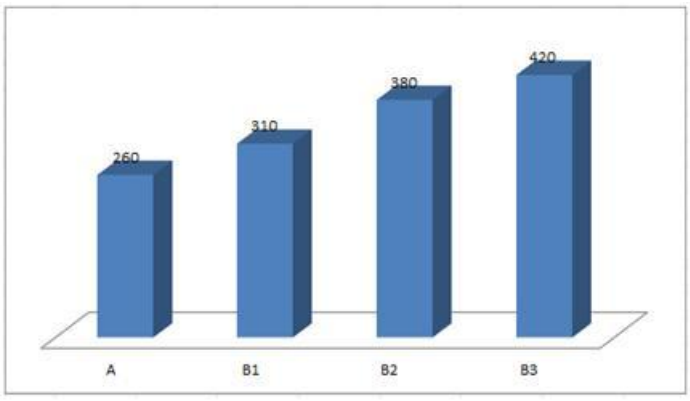

Fig. 11: The Effect of Laser Pulses on HA coating Hardness

6- Wear test:

A samples with (12) mm diameter subjected to wear test under (2)N load and for different times (10, 20,30,40,50 and 60)min in room temperature. The results have been presented and showed in fig 12.Fig.12 illustrated the wear rate vs time for all used samples under (2)N load . from the mentioned figures, it can be note that the wear rate of the (A) sample under 2N load is higher than that (B1 and B2) samples and (B1and B2) samples higher than that for(B3) sample. The reason behind this variation is very clear. This is due to increase in friction at the surface as the pulses decreases.

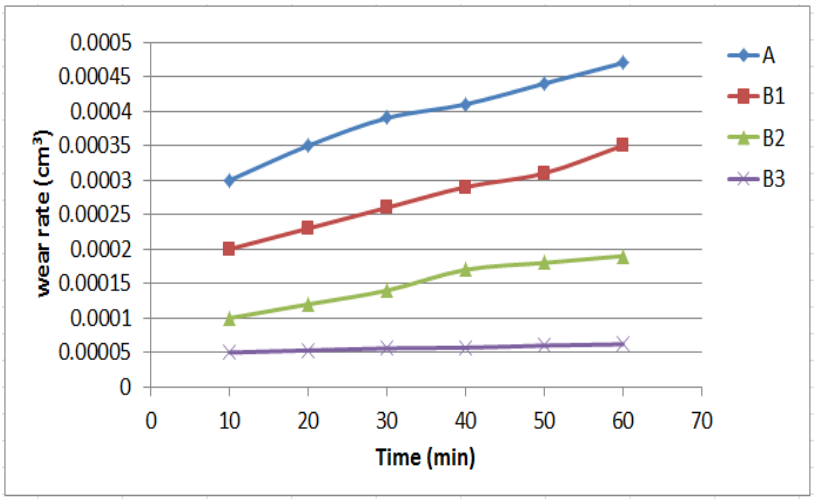

Fig. 12 :Wear Rate vs Time Under 2 N Load

In addition, the wear rate increase as the time increase for all tasted specimen, this is certainly because more time of friction tend to remove more material from the surface, this increases in wear rate that has been attributed to increase the plastic deformation for the material on the surface , particles of the material pull out [11].

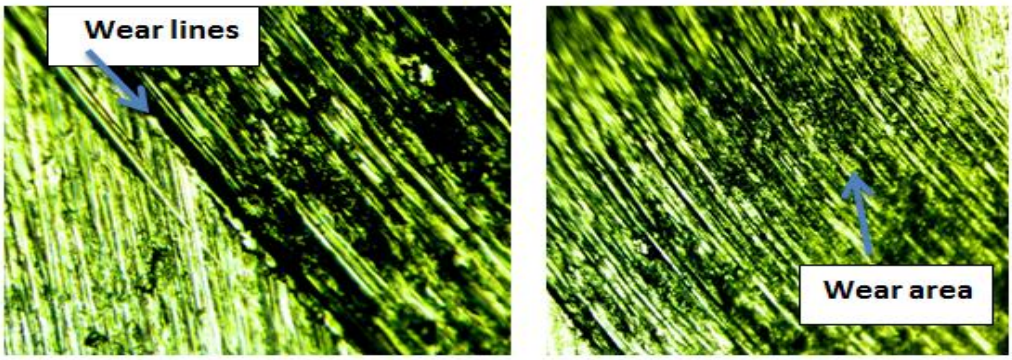

Fig.13: Microstructure for (A) Sample by Use Light Optical Microscope with Magnification 40X after Wear Test Under 2N Load and 60 min Time

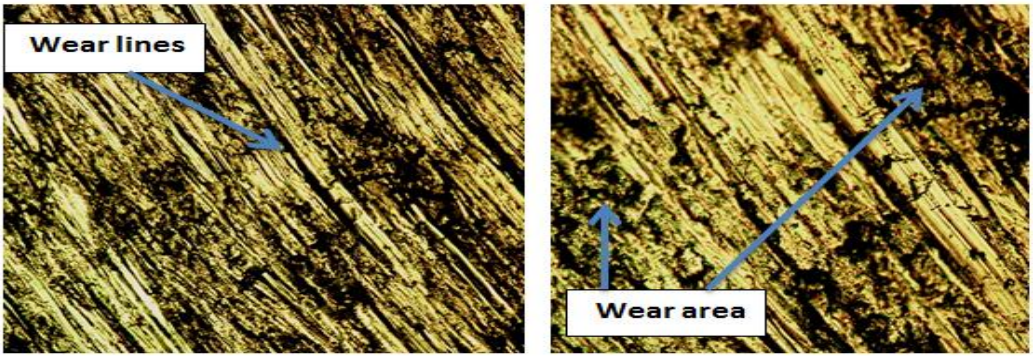

Fig. 14: Microstructure for B1 Sample by Use Light Optical Microscope with Magnification 40X after Wear Test Under 2N Load and 60 min Time

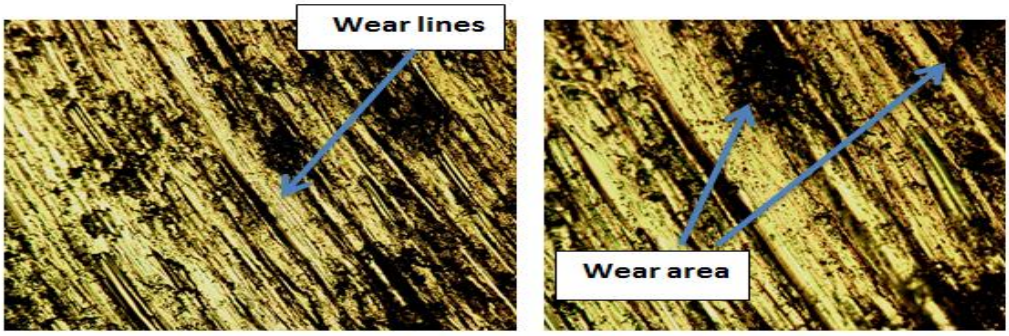

Fig. 15: Microstructure for B2 by Use Light Optical Microscope with Magnification 40X after Wear Test Under 2N Load and 60 min Time

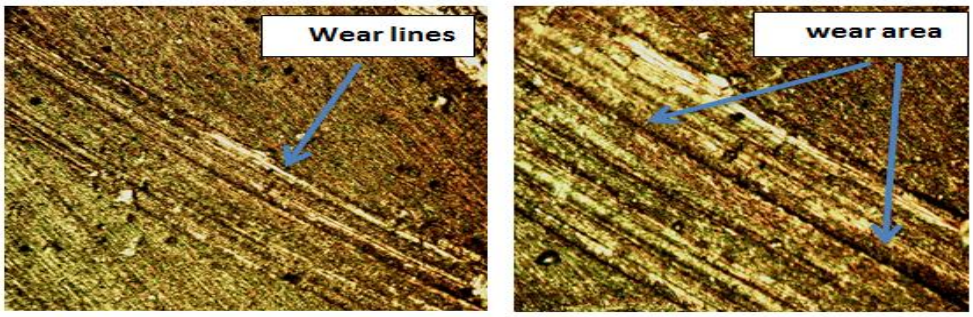

Fig. 16: Microstructure for B3 by Use Light Optical Microscope with Magnification 40X after Wear Test Under 2N Load and 60 min Time

Conclusion:

Based on the obtained result, the following conclusion are made:

A significant decrease in wear was observed, It was(0.0008 cm3) after one hour compared with (0.0004cm3) for the uncoated stainless steel sample.

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