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Effect of Dual Surface Activation on the Surface Roughness of Titanium Dental Implant

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Abstract
Titanium is the most prevalent material for use in dental implants because of its mechanical properties and intrinsic osteoconductivity. In dental implant, the surface treatment is used to modify surface topography resulting in an improved biocompatibility. In this research surface activation were used for commercial pure Ti alloys manufactured by two different methods; the first method involved the use of commercial pure titanium rod converted to form implant screw by using wire cut machine and lathe. The second method included the use of powder technology for producing the implant screws. Then dual surface treatments were used for samples in two treatment stages. A primary treatment used to prepare the surface for subsequent treatment which involves acid and alkali etching. The second surface activation treatment process were employed; ulrasonic surface treatment, Nd:YAG laser pulses . The characterization of samples before and after surface treatment procedure have been done to examine implant samples in terms of the best surface treatment method which produced the preferable surface properties .The characterization included ; microstructure observation, surface chemical composition analysis(EDS) , surface roughness (AFM) , ion release analysis. From microstructure observation The use of dual chemical treatment (HCl and NaOH etching) as primary treatment resulted in a change in the surface topography by the formation of sodium titanate hydro gel layer. The surface topography was displayed by Atomic-force microscopy (AFM). From the master group, the powder technology process produced samples with high surface roughness compared with machining process. While there was a large decrease in roughness of samples treated primarily by the acid and alkaline etching. After laser treatment, all samples had the same response to laser irradiation and slight differences in roughness were observed. From the results of ion release analysis, it was found that all samples in all groups had similar ion release behavior when the samples immersed in Hank's solution for seven days. It was observed that the release of Ti ion rose in first three days and after that it began to stabilize.
Keywords: Surface Activation, Surface Roughness Dental Implant

1. Introduction

Titanium is the chosen for dental implant due to its properties that meet the most important requirements such as excellent biocompatibility, corrosion resistance, and high strength, relatively low modulus of elasticity, good formability, and machinability [1]. The material surface plays an extremely important role in the response of the biological environment to the artificial medical devices. Surface modifications are used for implant surfaces, mainly to improve wettability, cell-implant adhesion and attachment, cell proliferation, and osseointegration, and thus faster healing and shorter treatment duration [2]. When a metallic material is implanted into a human body, immediate reaction occurs between its surface and the living tissues. With surface modification, biofunction of surface layer could be improved. For these purposes, many techniques for surface modification of metals are attempted [3].

Chemical treatment of titanium and its alloys are mainly based on chemical reactions occurring at the interface between titanium and a solution. The common ones are acid, alkali, H2O2, heat, and passivation treatments [4]. Acid treatment is often used to remove oxide and contamination to obtain clean and uniform surface finishes. A combination of acids is frequently used to pre-treat titanium. In acid etching, the use of acids on metal surfaces is not only to clean the surface but also to modify the roughness. In addition, the acid treatment was often used to combine other treatment methods to improve the properties of titanium and its alloys .Wen et al. reported that the bioactivity of Ti alloy could be improved by two-step chemical treatments employing (HCl + H2SO4) and alkaline solution [5]. And Wanye Tan et al. studied the use of ultrasonic irradiation (UI) along two different routes to obtain several modified surfaces on titanium plates; the first group was first treated by a NaOH solution, and then UI is used to wash them in double distilled water; while the second were modified by a NaOH solution in an ultrasonic cleaner with UI at 50 W. It was demonstrated that the UI energy can easily remove any weakly bound layers (WBL) on the titanium surface, leaving a strongly bounded layer (SBL) [6]. Modification of surfaces using ultrasonic treatment leads to significant changes in surface properties, and most of the effects of interest regarding ultrasonication are related to cavitation. Cavitation causes solute thermolysis along with the formation of highly reactive radicals and reagents, such as hydroxyl radicals and hydrogen peroxide, which induce drastic reactive conditions in the liquid media .In addition, if a solid is present in solution, the sample size of the particles is diminished by solid disruption, thereby increasing the total solid surface in contact with the solvent. In this way, ultrasonication remains unique, since no other method of sample treatment

can produce such effects [7, 8]. Also the laser treatments for surfaces already has numerous industrial applications, this was observed with M. Bereznai et al. who modified the titanium surface by excimer laser irradiation of titanium samples in order to improve their surface characteristics so as to facilitate biointegration, and to enlarge the effective interfacial area of bone–implant contact, holes were ablated by laser pulses of ns or sub-ps length. This process results in titanium surface microstructures with greatly increased hardness, corrosion resistance [8].

2. Experimental

Preparation of implant samples involved using two different methods in order to make comparison between them and to study the effect of manufacturing process on the surface roughness which may affect the biological behavior of the implant in the body by elimination of healing period (rapid osseointegration) .The first method involved the use of commercial pure titanium rod. The rod was converted to implant screw by machining. The second method included the use of powder technology in order to produce the implant screws with some porosity. The surface state of an implant alters the bone response and fixation .In present stage surface treatments have been done in order to change the surface characteristics such as surface composition and topography. The surface activation stage was devided into two steps primary and secondary, The primary surface activation treatment involved chemical surface treatments (acid and alkali etching) in order to precipitate some elemnts to make more effective surface. Acid etching in HCl was done because HCl is an excellent decontamination agent, it could easily dissolve titanium salts and not weaken Ti surfaces before alkali treatment .While the purpose of using NaOH was to improve the bioactivity of titanium surface. At first and before the treatment all implant samples were ultrasonicIly cleaned using ultrasonic cleaner type in ultrapure water for 10 mintues then dried in an oven at 40o C for 15 minute. after the samples were cleaned they were immersed in HCl acid with concentration 0.5mM for 90 mintues at 40oC after that the samples were washed with ultrapure water and dried in an oven for 15 minutes. Then the samples were immersed again in NaOH with concentration 10 M for 24 hours at 60oC then washed in ultrapure water and dried in an oven for 15 minutes . In order to obtain the etching temperature and maintain the samples at this temperature. After this step the acid and alkaline treatment process were complete and the samples was ready for the secondary treatments. The purpose of using this type of treatmens as a final surface activation process is to improve topographical characteristics of the surface and to get a final strong active surface layer that can make the implant more active and safe inside the bone. The ultrasonic surface treatment involved the utilization of the energy resulting from the ultrasonic wave. This energy is considered to be the main source of chemical and mechanical effects on the implant surface by creating Transient bubble collapsing on the implant surface which is act to change the surface topograghy . The source of the ultrasonic wave used was the ultrasonic cleaner path type (KQ3200E) , samples was immersed in ethanol and then placed inside a path of water as a physical medium in which the ultrasonic wave was transmitted . The samples remain in the ultrasonic cleaner for five hours then they were removed and washed in ultrapure water and dried in an oven at 40oC for 15 minutes . The laser employed is Nd:YAG system produced by Quanta System Srl.-Solbiate. the irradiation wavelength was 1064 nm ,and the pulse duration (6ns) with maximum power (1J). The samples then divided in to four groups each group contain two samples one produced from titanium powder and other from titanium rod, as shown in table (1).

Table (1): Samples Group

Group number		Surface treatment procedure
Group A	A1: prepared by powder technology	none
	A2: prepared by machining	
Group B	B1: prepared by powder technology	Acid and alkaline treatment followed by ultrasonic treatment
	B2: prepared by machining	
Group C	C1: prepared by powder technology	Acid and alkaline treatment followed by laser pulses.
	C2: prepared by machining	

Various analytical techniques were used for characterization of the titanium implant samples Surface morphology was monitored by optical microscopy ,scanning electron microscopy (SEM; AIS2300C) as well as by atomic force microscopy (AFM;PHYWE,nano,compact AFM). The SEM was connected to an energy dispersive analyzer for determining surface compositions of the targets. The metal ion release from the implant material occurs as a direct consequence of the corrosion process. Release of metal ions can cause local and systemic health problems, due to the ions diffusion through the whole body. Ion release was conducted in static conditions by immersion in which the sample is exposed to a corrosive solution with minimum relative motion between sample and solution. Hank's solution was employed with composition and the type and concentration of ions released from the metallic implant materials was determined using Inductively Coupled Plasma optical emission spectrometry ICP-OES type Agilent Technologies 700 series ICP-OES made in U.S.A.

3. Results and discussions:

3.1 Microstructure Characterization:

The microstructure observation was done using the scanning electron microscope device to see the effect of surface treatments on surface texture. Figures (1) and (2) show the surface morphologies of master samples (group A). These two samples differ in manufacturing process but both of them are without any surface treatment. There are some inconsiderable morphological differences between samples (A1) and (A2) as a result of the manufacturing process .For sample (A1) produced by powder technology it obvious to have a degree of porosity which result in roughen surface than sample (A2) which was produced by machining .The tool marks created by the turning process made the surface anisotropic with clear directional surface irregularities. Bioactivity of titanium implant surfaces were improved by the utilization of two-step chemical treatment (acid and alkaline etching), which resulted in the formation of sodium titanate hydrogel on the titanium substrate. As found in Jonšov L.[8]. The acid etched of implant surface presents a superficial morphology. From The acid etching of samples with HCl, a uniform initial titanium surface with the formation of TiO2 oxide layer was observed. During the alkali treatment, the TiO2 layer partially dissolves in the alkaline solution because of the attack by hydroxyl groups.

$$TiO2 + NaOH \rightarrow HTiO3 - + Na +$$

This reaction is assumed to proceed simultaneously with hydration of titanium, as follows:

$$Ti + 3OH - \rightarrow Ti(OH)3+ + 4e -$$

$$Ti(OH)3+ + e - \rightarrow TiO2 .H2O + \tfrac{1}{2} H2 \uparrow$$

$$Ti(OH)3+ + OH- \leftrightarrow Ti(OH)4$$

A further hydroxyl attack on the hydrated TiO2 produces negatively charged hydrates on the surfaces of the substrates as follows:

$$TiO2 . H2O + OH- \leftrightarrow HTiO3 - + nH2O$$

These negatively charged species combine with the alkali ions in the aqueous solution to produce an alkalinic titanate hydrogel layer. During heat treatment, the hydrogel layer is dehydrated and densifies to form a stable amorphous or crystalline alkali titanate layer.It was found that the thickness of the precipitated apatite layer increased continuously with time and the treatment of titanium by a two-step HCl and subsequent NaOH process appears to be a suitable method to enhance the surface bone bonding ability. The using of ultrasound treatment after initial chemical etching caused heterogeneous surface morphologies. From the SEM image of samples B1 in figure (3) and B2 in figure (4), it can be seen more clearly that there are significant changes in the surface irregularity after ultra-sonic irradiation which refers to change in surface morphology. This is due to the mechanical effect of ultra-sonic on the samples surface, in ultrasonic treatment the force is applied by formation of cavitation bubbles which considered being the main source of the chemical and mechanical effects of ultrasonic energy.

In the case of samples (C1, and C2) at figure (5), and (6) where the samples are chemically treated by acid and alkaline etching before the laser pulses, it was found that the laser pulses result in damage the sodium titanate hydrogel layer that was formed after etching treatment and make the surface relatively smooth so that the surface irregularity and roughness was increased after the laser treatment for these samples.

Finally From the microstructure observation of laser group it was found that the technique is a method of choice for complex surface geometries. The technique generates short pulses of light of single wavelength, providing energy focused on one spot especially in the inside of implant thread. It is rapid, extremely clean, and suitable for the selective modification of surfaces and allows the generation of complex microstructures/ features with high resolution.

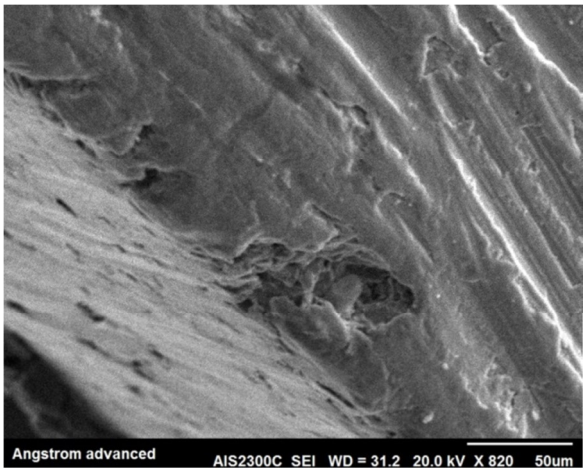

Figure (1): SEM image of sample A1

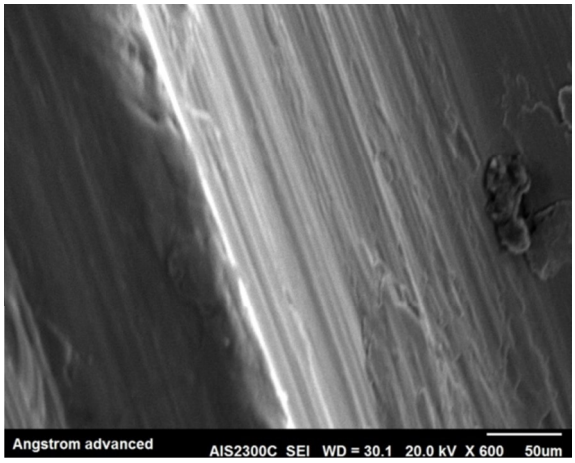

Figure (2): SEM image of sample A2

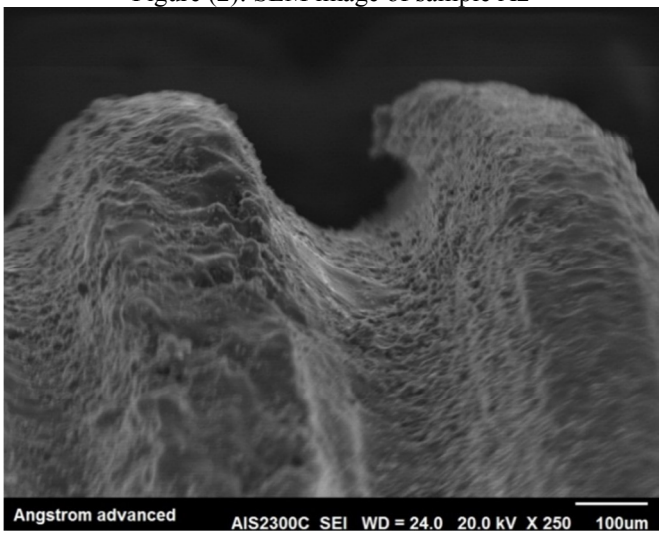

Figure (3): SEM image of sample B1

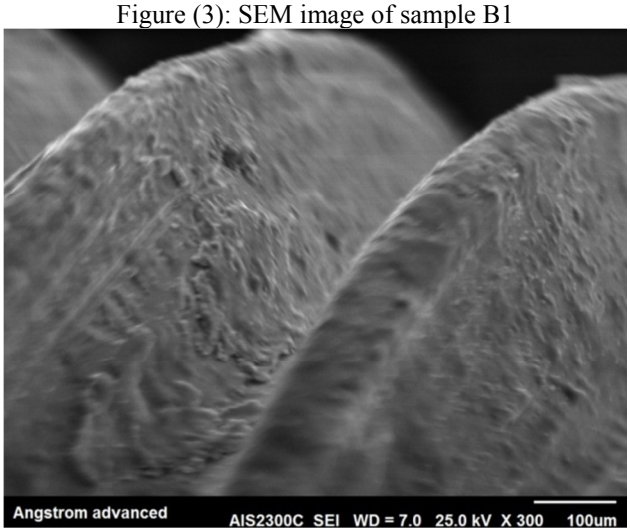

Figure (4): SEM image of sample B2

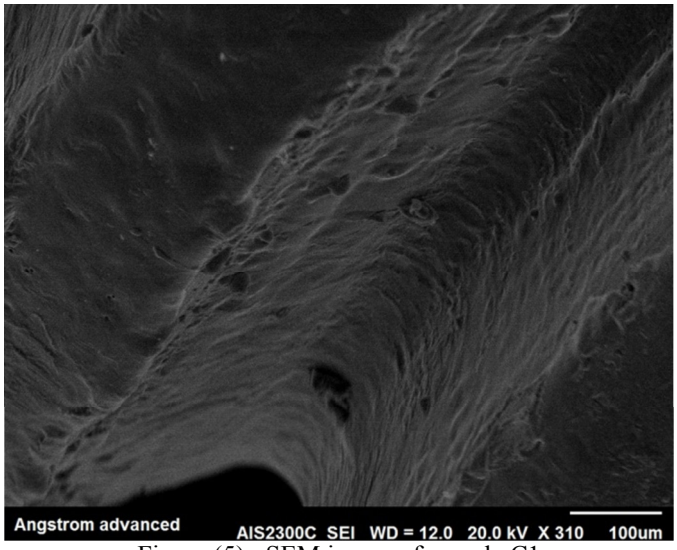

Figure (5) : SEM image of sample C1

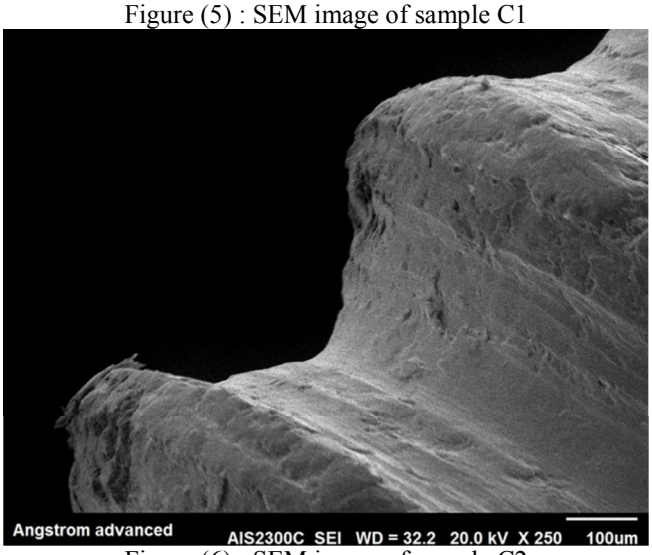

Figure (6) : SEM image of sample C2

3.2 Surface chemical composition analysis

The analytical technique that has been used for the elemental analysis or chemical characterization of implant surface before and after the surface treatment was done by using Energy-dispersive spectroscopy EDS.

EDS graph of the master samples (A1, and A2) in figure (7) and (8) show a large peak of titanium element without showing any other peaks of elements which refer to samples with high degree of purity and the manufacturing process will not affect or result in a change of the surface chemical composition. For samples (B1) and (B2) the EDS show wide variety elements peaks as illustrated in figures (9) and (10), which resulted from the dual surface treatment (acid and alkaline followed by ultrasonic treatment). The primary acid and alkaline treatment resulted in formation of sodium titanite hydrogel that caused the appearance of (Cl),(Na) and,(O) peaks and the ultra-sonic treatment caused appearance of carbon peak.From the results of the surface chemical composition analysis of the ultra-sonic treatment group it was found that using the ultrasonic as a second surface treatment do not change the surface chemical composition resulted from the primary treatments .The change will occur at the surface topography and roughness. In the EDS graph of sample (C1) and (C2) at figures (11) and (12) there are (Na) and (Cl) peaks appear result from the acid and alkali primary treatments. From the EDS graph of laser group it is found that the using increasing the oxygen content at the surface and therefore improving the effectiveness of the oxide layer that have been formed after laser pulses.

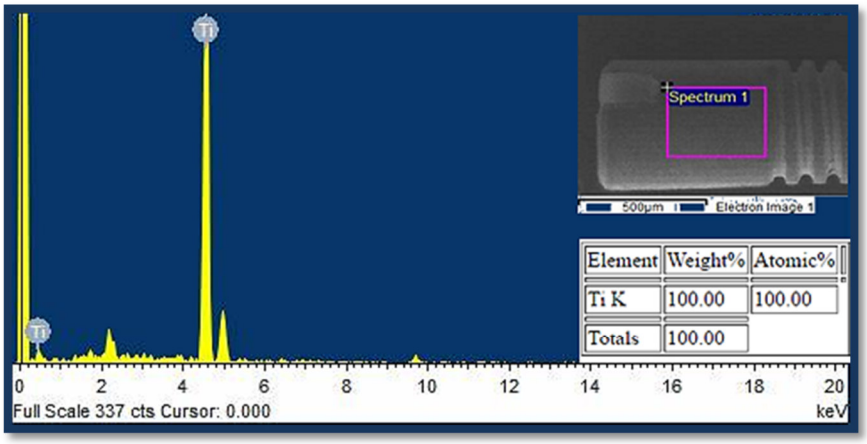

Figure (7): EDS graph of sample A1

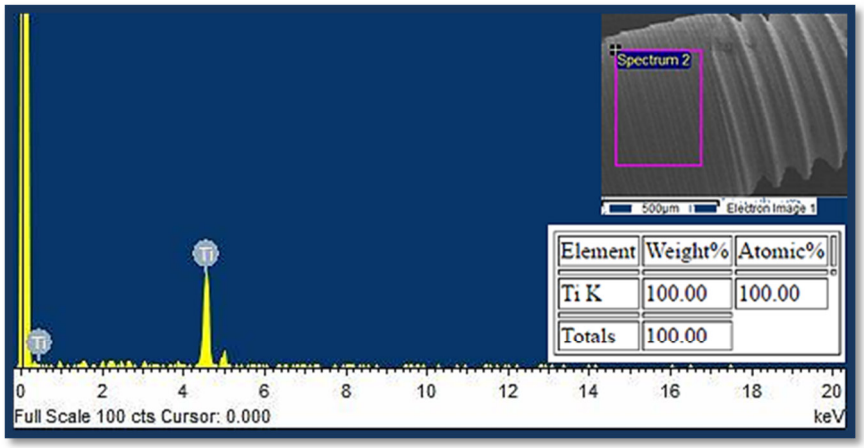

Figure (8): EDS graph of sample A2

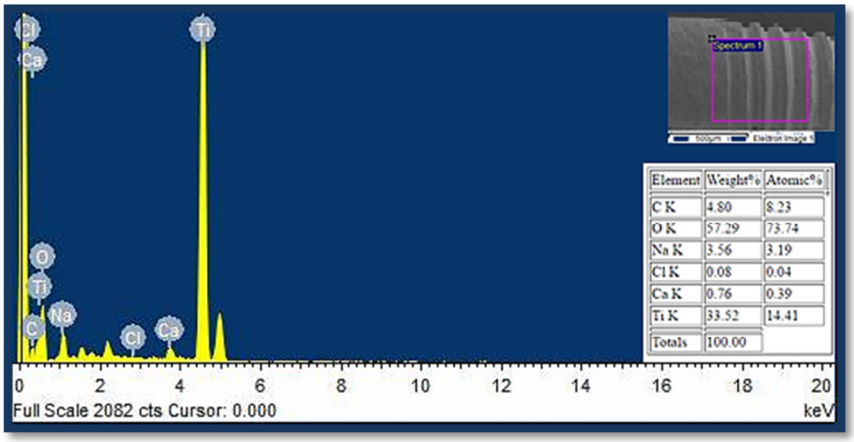

Figure (9): EDS graph of sample B1

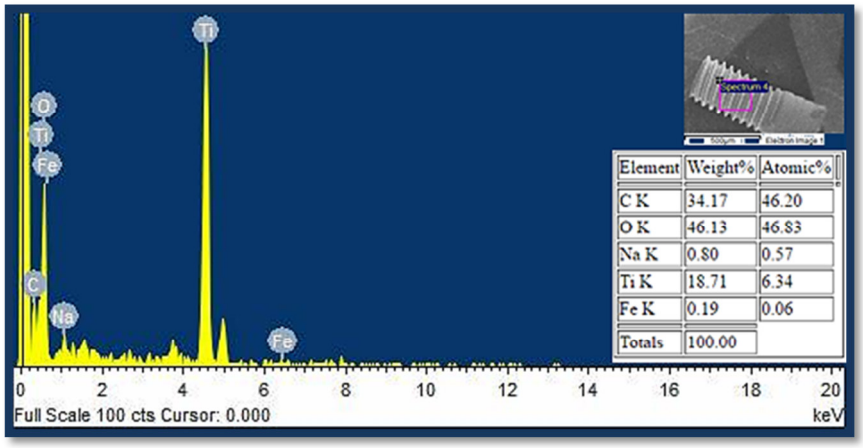

Figure (10): EDS graph of sample B2

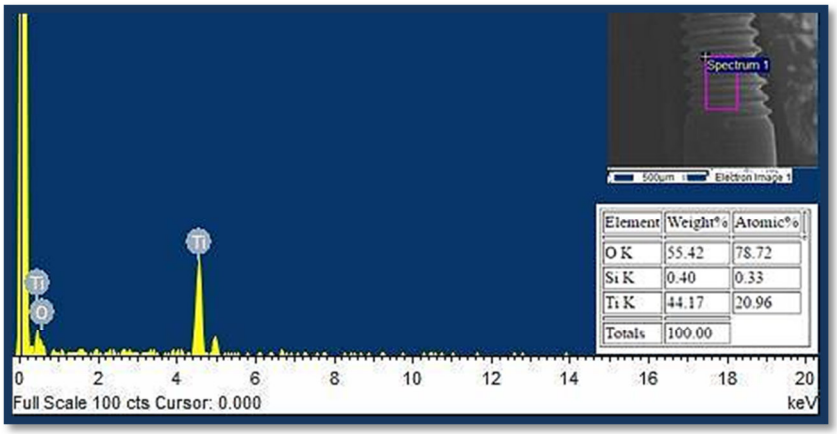

Figure (11) : EDS graph of sample C1

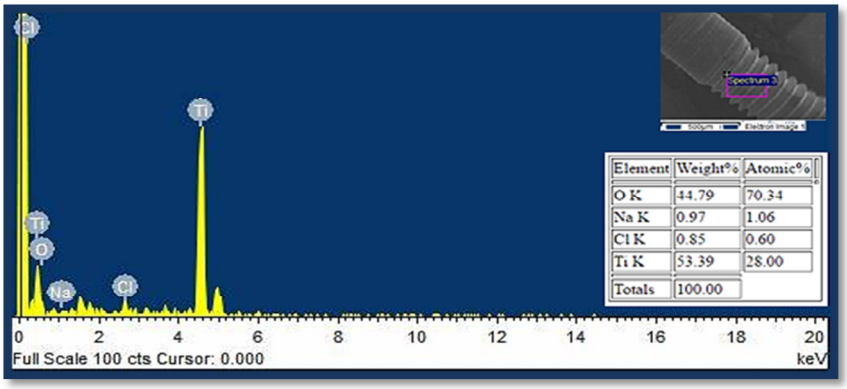

Figure (12): EDS graph of sample C2

3.3 Surface roughness investigation

This test was done in order to identify the topographic change after the surface treatments as well as the amount of roughness that have been produced after the treatments from micro to Nano scale in two or three dimensions of the surface texture. The test was carried out using Atomic Force Microscope (AFM). Figures (13) and (14) display the roughness values of the master group. It can be observed that sample (A1) which was produced by powder technology process without any surface treatment have higher roughness (700.26 nm) than sample (A2) produced by machining without any surface treatment (527.06 nm). Hence the powder technology process produced samples with higher surface roughness compared to the machining process. After dual surface activation the roughness was raised, first there was large decrease in surface roughness of the samples treated primarily by acid and alkaline etching due to the formation of smooth sodium titanate hydrogel layer on the surface. But the mechanical effect of the ultrasonic energy raised the surface roughness of samples (B1) with roughness (845.36 nm) and (B2) with roughness (531.7nm)in figures (15) and (16),because that there are two types of nanostructure layers formed on the titanium surface after NaOH treatment; the weakly bound layer

(WBL) and the strongly bound layer (SBL). The strongly attached to the titanium substrate. The pore diameter of the WBL is about two times larger than that of the SBL. Moreover, the WBL can be easily removed from the SBL by using UI, which may not promote the connection between host tissue and the titanium implant after implantation, and could in fact be detrimental to the surrounding cells due to the release of Na+ from the sodium titanate formed on the titanium surface. The use of laser pulses will also effect on the surface roughness of implant samples as illustrated in figures (17)and (18) which show that all samples of this group changed their roughness values either raised or reduced after the laser pulses this was due to the formation of a strong oxide layer, the slight differences in the roughness value was due to the change in the surface heating rate that result from the primary surface treatment that have been employed which cause a considerable change in chemical and structural surface properties.

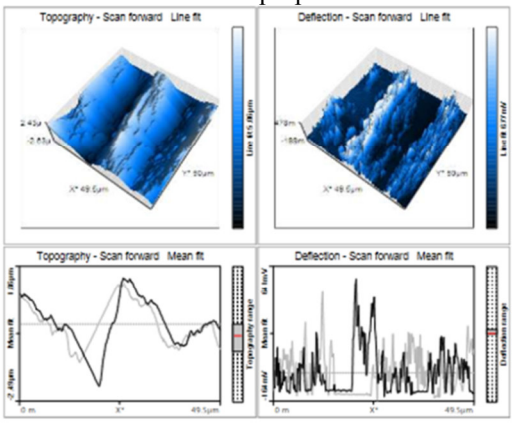

Figure (13) : AFM chart of sample A1

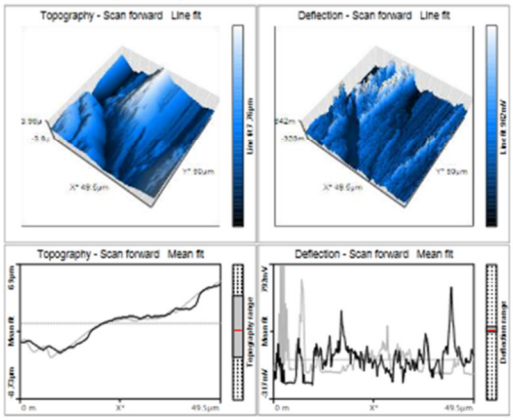

Figure (14) : AFM chart of sample A2

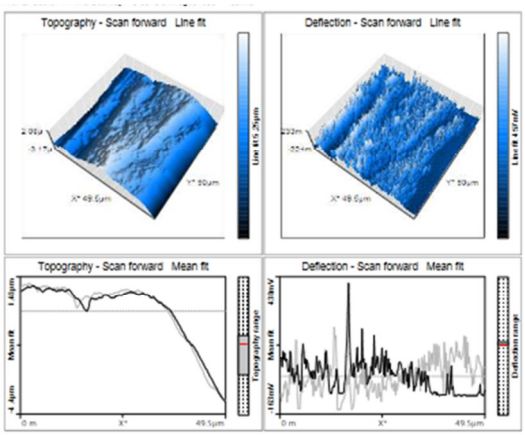

Figure (15) : AFM chart of sample B1

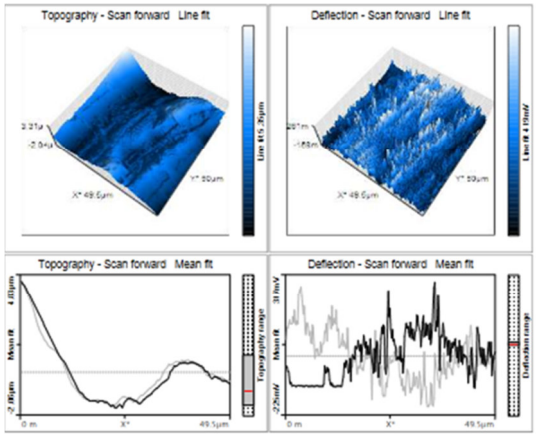

Figure (16) : AFM chart of sample B2

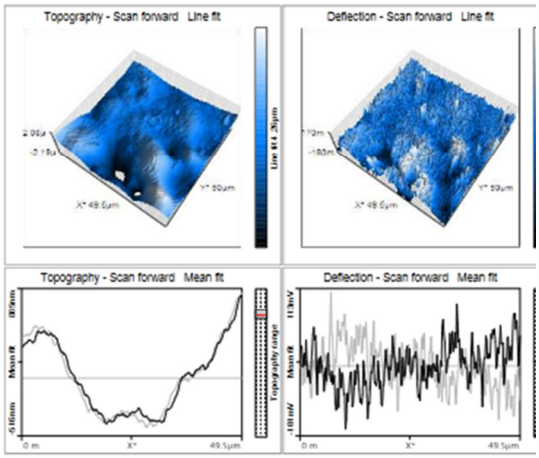

Figure (17) : AFM chart of sample C1

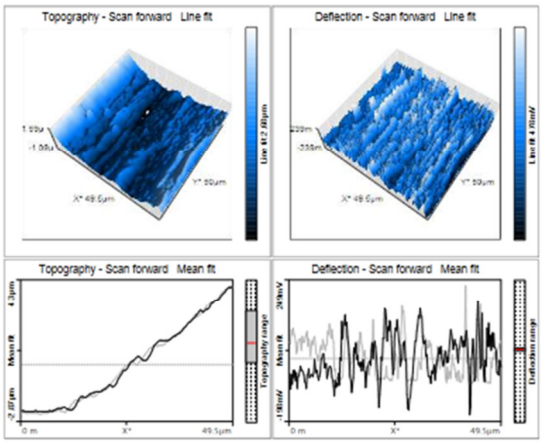

Figure (18) : AFM chart of sample C2

***3.4 Ion release analysis*:**

Release of metal ions can cause local and systemic health problems due to the ions diffusion through the whole body .The amount of Ti ions that have been released from all groups of implant samples in Hank's solution was measured.

It was found that the surface oxide films on titanium implant play an important role as an inhibitor of ion release also the regeneration time of the surface oxide film after disruption governs the amount of released ion. Low concentration of dissolved oxygen, inorganic ions, proteins, and cells may accelerate the metal ion release. It is obvious that the behavior of metal ion release into biofluid is governed by the electrochemical rule and the released metal ions do not always combine with biomolecules to show toxicity because the active ions immediately combine with a water molecule or an anion near the ion to form an oxide, hydroxide, or inorganic salt. Thus, there is only a small chance that the ion will combine with biomolecules to cause cytotoxicity, allergy, and other biological influences and this was not observed in the current titanium samples. From the results of ion release analysis it was found that all samples in all groups have similar ion release behavior when the samples are immersed in Hank's solution for seven days it is observed that the release of Ti ion rise in first three days and after that release of Ti ions begin to stabilized. This was due to the fact; when the metal is immersed inside the body consequently their ions begin to be released from the surface by adsorption process .At the same time these ions will combine with other molecules in the environment and desorb at other surface so that the amount of released ions is increased with increasing immersion time until the adsorption- desorption equilibrium is reached thus the amount of released ion will be fixed. As illustrated in figure (19) all samples were primarily treated with acid and alkaline etching in addition to the second treatment. It is obvious that there was increasing in the amount of Ti ions released at first three days. This was due to the formation of active sodium titanate hydrogel which have a large tendency to apatite formation when the sample immersed in the simulated body fluid . It was found that the surface of the sodium titanate was highly negatively charged in the SBF. The surface potential increased with increasing soaking time to a maximum positive value. Thereafter, it decreased with increasing soaking time, reached a negative value again, and finally converged to a constant negative value. The complex process of apatite formation described above can be interpreted in terms of the electrostatic interaction between the functional groups and ions in the fluid. The Ti-OH groups formed on the surface of sodium titanate after soaking in SBF are negatively charged and hence, combine selectively with the positively charged Ca2+ ions in the fluid to form calcium titanate as the calcium ions accumulate on the surface, the surface gradually gains an overall positive charge. As a result, the positively charged surface combines with negatively charged phosphate ions to form amorphous calcium phosphate. The calcium phosphate spontaneously transforms into apatite because apatite is the stable phase in the body environment.

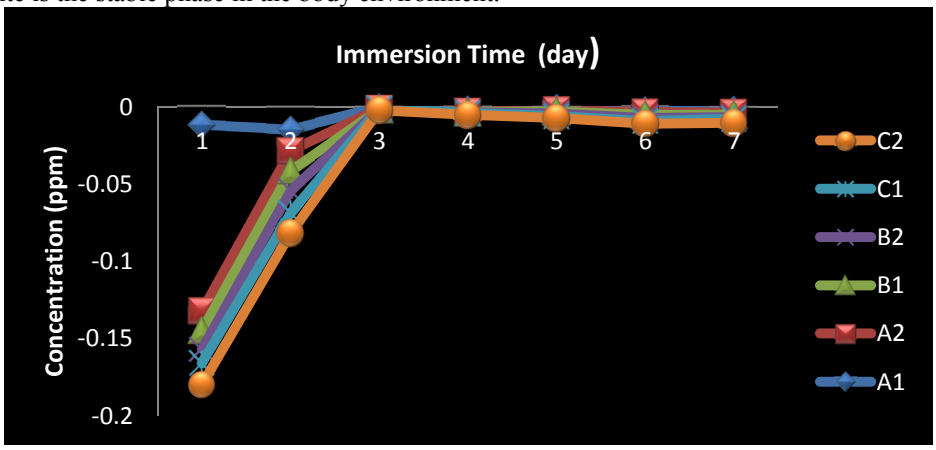

Figure (19) : Release amounts of Ti ions in Hank's solution.

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