Aseel M. Al-Khafaji [1]
Wasmaa S. Mahmood [1]
Ihab Nabeel Safi [1]
Ahmed A. Ali [2]

[1] *Department of Prosthodontics, College of Dentistry, University of Baghdad, Baghdad, IRAQ*
[2] *Applied Laser and Research Unit, Dijlah University College, Baghdad, IRAQ*

Surface Characteristics and Corrosion Behavior Assessment of RF-Sputtered PEKK on Titanium

In this study, radiofrequency magnetron sputtering technique (RFMS) was used to coat the titanium with polymer Polyetherketoneketone (PEKK). The corrosion behavior was tested by the electrochemical test in Hank's solution, the corrosion rate was studied by the polarization test. Furthermore, to investigate the phases of the tested samples XRD technique was performed. The titanium samples coated with polymer were compared to untreated titanium and titanium treated by fiber laser followed by PEKK coated samples.

Keywords: Titanium; Corrosion: RF magnetron sputtering; Polyetherketoneketone
Received: 25 January 2024; **Revised:** 19 February; **Accepted:** 26 February 2024

1. Introduction

Dental implants remain one of the most demanding options for tooth replacement in the last few decades. Thus, attention should be drawn toward maintaining the restoration in optimal shape and quality to minimize the risk of implant failure such as mobility, and inflammation [1]. Since, the oral environment and body fluids contain complex materials such as organic material, protein, amino acids, chlorine, and so on. Thus, corrosion and ion release are possible complications of implanting titanium into the human body. This could lead to biological complications such as inflammation, toxicity, and hypersensitivity [2-4].

Accelerating the rate of bone formation, and shortening the healing time, are significant factors for the success of dental implants. Thus, various attempts have been made to change the properties of implant surface morphology and composition [5-8]. In particular, the topography of the implant surface gained wide attention, as it plays a major role in implant success [9].

Coating with thin film is considered an effective method for metal protection. Various methods of film deposition were developed despite several restrictions that may accompany the process. Physical vapor deposition (PVD) is a widely used technique such as magnetron sputtering deposition with film deposition ranging from a few millimeters to several micrometers [10]. Introducing the magnetic field becomes an extensive method since it can be used with a vast range of substrates of different sizes. Ceramics, polymers, ionic and metallic materials can be deposited using the RFMS method [11,12]. RF sputtering is known as 'green technology' because of the absence of (gas and liquid precursors) compared with plasma chemical vapor deposition (CVD). It permits a uniform distribution and directional deposition of the nanoparticles (NPs,) in addition, pattern surface structure can be obtained, and the deposition of nanoparticles on any substrate is possible in conditions that it tolerate high vacuum conditions [13].

Polyetherketoneketone (PEKK) is a new polymer material with superior physical and mechanical properties. It has gained good attention in the biomedical field because of its' valuable features such as being highly resistant to thermo-oxidative degradation, light weight, anti-bacterial properties, resisting hydrolysis, highly biocompatible, and high mechanical strength [14]. The presence of an extra ketone ring gives better properties compared to the other polyaryletherketone polymers group [15]. Earlier research used different polymers for metal coating [16,17] but, the authors found no previous work on the use of PEKK as a polymeric coating material on titanium using RFMS technique.

Due to the unique features of laser, such as specific patterns that can be obtained even with sophisticated parts due to the directional pattern of the laser beam that can be highly controlled. It became an effective method to improve the properties of titanium [18].

This study aimed to assess the efficacy of RFMS in polymer coating (with or without laser surface treatment) to minimize the corrosion rate of titanium when immersed in Hank's solution.

2. Experimental Part

Disc shape samples were fabricated by cutting the titanium rod with a wire cut (Lathe machine) according to the manufacturer's instructions, measured 7 mm in diameter and a thickness of 2 mm.

A- For untreated substrates: titanium samples were polished with silicon carbide paper starting from 500 to 2400 grit to grind and bring the disks to a uniform smooth mirror surface using a rotated grinding and polishing machine.

B- For laser-treated substrates: roughening of titanium surface will be built up by CNC fiber laser machine (Jinan JinQiang 20W laser, China) by prompting dot structure. Dot laser structure design with 25 laser scan (D-L 25) [19]

Then, the substrate was cleaned using an ultrasonic bath immersed in absolute ethanol for 30 min and then dried in air. A custom stainless steel plate holder is designed to hold the circular substrates in the vacuum chamber during sputtering to ensure uniformity of the coating,

The target was made by mixing 16 g of PEEK powder with a few drops of polyvinyl alcohol (PVA) as a binder. Then the mixture was loaded and pressed in a cylindrical stainless-steel mold with the dimension of 50 mm in diameter and 3 mm in height, the pressing was done under 8 tons pressure for 2 min. The electrical press was used, to obtain a uniform target and to avoid target fracture. A copper cover to protect the target from cracks was used.

Several sputtering trials were conducted in a pilot study to determine the suitable sputtering parameters for optimal coating deposition. A magnetron sputtering device (Torr International Inc., USA) was used with different variables, for the magnetron power, working pressure, substrate temperature, and the time of the sputtering. Whereas only target-to-substrate distance was fixed, three sputtering intervals (runs) were performed. The working conditions are summarized in table (1).

Table (1) Different parameters for coating metal by radiofrequency magnetron sputtering technique

Sample	Power (W)	Pressure (Torr)	Substrate Temperature (°C)	Time of Deposition (min)
A	50	$3x10^{-2}$	60	180
	50	$3x10^{-2}$	60	120
C	50	$3x10^{-2}$	60	60

The results of the pilot showed that A and B samples the PEKK target became black after the RF sputtering which indicated the damage of polymer during the sputtering process while no damage was seen in group C. Thus, one hour exposure was considered as a suitable time for confirming the sputtering process. A thin film of PEKK was obtained after fixing the substrate temperature at 60°C and the working PF with 50W power for one hour.

The sputtering target of the PEKK disk was 50mm in diameter and 4mm in thickness and was attached to the anode (positive charge) of the system. The substrate (titanium) was attached to the cathode (negative charge) with a rotating disk, and a magnetron power of 50W was applied to the target. The substrates were heated gradually; the temperature was fixed at 60°C for one hour according to the pilot study. During the sputtering process, water passes through the system, and the procedure was performed under a vacuum of 3×10^{-2} torr. To achieve this vacuum pressure first, the mechanical pressure worked until the pressure reached the operating pressure (rotary pressure) of the turbomolecular pump (5×10^{-1} torr) the chamber was then evacuated to a high vacuum at $\sim10^{-4}$ torr. Then the substrates were moved in a rotary direction at 2 rpm during the deposition; with a steady rotary speed. The operation frequency of the RF-generator and the distance between the substrate and magnetron target were fixed to 10cm. The sputtering chamber was evacuated and the argon was introduced as a sputter gas.

The specimens were grouped according to the type of surface treatment.

1. CG represents the Control group.
2. L-ArG represents laser-treated group coated with PEKK using Argon gas by RFMS technique.
3. ArG represents a group coated with PEKK using Argon gas by RFMS technique without laser treatment.

Then all the groups were measured using XRD and Electrochemical test.

An automated x-ray diffractometer was employed for phase characterization using Cu-Kα radiation (λ=1.5406Å). The operation was done at 40 mA and 40 kV. Ambient laboratory temperature using 10s/angular step (1 angular step = 0.02°) was used for taking diffraction patterns.

Metal corrosion resistance is usually characterized by the corrosion rate that can be achieved using the polarization technique. Polarization test is one of the measurements of corrosion rate. The polarization means no (equilibrium potential) is obtained but can be obtained through open circuit potential (OCP). Three electrodes were connected to the corrosion cell which are (reference electrode, auxiliary electrode, and working electrode). The difference potential between (working and reference) electrodes represents the corrosion behavior of titanium. A freshly prepared Hank's solution at 37±2°C was prepared for each measurement to simulate normal biological conditions.

3. Results and Discussion

The high demand for dental implants brings challenges to researchers to provide restorations with optimum outcomes by minimizing the rate of failure. To achieve this, modification and coating the metal surfaces is an interesting choice for improving the properties of the materials such as corrosion resistance, biocompatibility, and scratch resistance [20-23].

Various polymers were introduced as effective coating materials, but the selection of PEKK as a protective barrier depends on its wide satisfying features which render it a good candidate for the present work. The coating technique is another challenge because of the wide range of methods available, but RFMS being a 'green technology' in addition to the ability to deposit a wide range of materials with various particle sizes [24] proved to be an effective method of coating.

The XRD patterns for all measured groups are seen in Fig. (1). The peak indexing of the titanium was carried out based on the Joint Committee on Powder Diffraction Standards (JCPDS) (JCPDS-ICDD file 55-0898) [25].

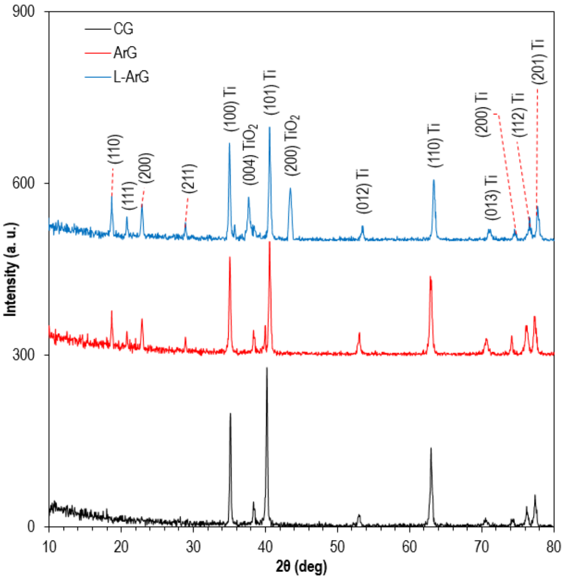

Fig. (1) XRD analysis for the experimental groups

The XRD result showed that the titanium phase remained constant after surface laser treatment. Signifying no change in the titanium phase was observed, which is important when dealing with the titanium. The new peaks of TiO_2 observed beside the Ti after laser structuring are due to the titanium air interaction during the surface structuring. Whereas the XRD pattern of the control group showed only titanium peaks as no other peaks were observed. New titanium oxide peaks were seen at 37.65° and 43.45° according to the diffraction plane of (002) and (200) which revealed an increase in oxygen percentage in L-ArG.

The new coat of PEKK on L-ArG and ArG showed diffraction peaks at 18.70°, 20.80°, 22.90° and 28.90°, which correspond to the diffraction planes of (110), (111), (200) and (211) based on Leiner [26].

The process of corrosion is known as an electrochemical behavior of metals, so the electrical method is an acceptable tool of measurement. The titanium behavior of the experimental groups is seen in the open circuit potential (OCP) curve (Fig. 2), where the PEKK-coated groups showed a shift toward positive values with time, whereas CG moved toward negative values. Table (2) presents the (I_{corr}, E_{corr}, and corrosion rate), where a slight decrease in (I_{corr}) value in ArG group followed by a gradual decrease in L-ArG. The improvement of corrosion resistance in L-ArG can be ascribed to the strong boundaries among the metal grains and the increase in the homogeneity which is due to the refinement of the grain size that improved the titanium oxide layer formation [27]. A study conducted by Tian et al explained the increase in corrosion resistance after laser treatment due to the formation of a new titanium oxide layer [28].

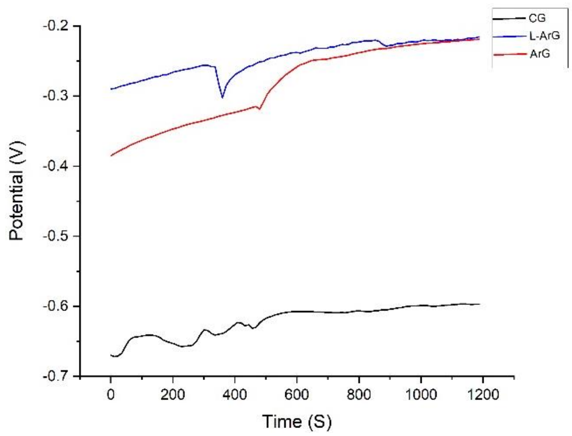

Fig. (2) Open-circuit potential for the experimental groups

Table (2) Different parameters of corrosion behavior for all the experimental groups

Group	$E_{(i=0)}$ (V)	$I_{corrosion}$ (A/cm^2)	Corr. Rate (mm/y)
CG	-0.485	$2.032x10^{-6}$	0.1651
ArG	-0.332	$3.677x10^{-6}$	0.1480
L-ArG	-0.305	$9.424x10^{-7}$	0.0398

From our previous work, an increase in surface roughness after the modification of the titanium surface by laser was found [19]. At the same time, other studies related the decrease in corrosion rate after laser treatment was due to the increase in surface roughness and the formation of titanium oxide layer [25,27,29]. Conradi explained the decrease in corrosion after laser treatment was ascribed to the increase in surface roughness which slightly turned the surface properties from hydrophilic to a more hydrophobic nature. This feature will repel liquids from adhering to metal and improve the titanium's properties [30].

The presence of a PEKK layer on the titanium surface clearly showed the shifting of anodic and cathodic curves to more positive E_{corr} values as presented in Fig. (3) of the Tafel plot. This behavior explains the decrease in corrosion rate, because the PEKK coat may retard the process of anodic dissolution. The presence of a PEKK coat acts as a barrier permitting minimum electrolyte to pass through and inhibits the ionic conduct which will impede the passage of solutions that inhibit corrosion [31].

The decrease of I_{corr} value for ArG and L-ArG explains the efficiency of the PEKK coat by RFMS method since this technique permits a longer distance for the generated electrons to move for every half cycle. This will generate plasma of high density which enhances the sputtering process efficiency

[24]. In other words, permitting an even dense coat formation that resists cracks which prohibits seepage of fluids thus increasing corrosion resistance.

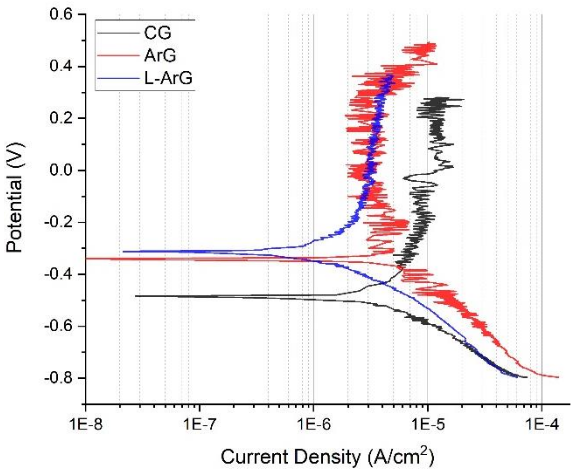

Fig. (3) Tafel plot for the experimental groups

Several authors demonstrated the importance of surface treatment before bonding to create a good mechanical interlock [32]. Good adhesion promotes corrosion resistance by enhancing the coat integrity. Thus, the formation of small metal projections after laser treatment will provide a better bond between the metal and polymer, consequently minimizing the risk of external forces and corrosion attacks [33]. This explains the lowest value of corrosion rate in L-ArG compared to the other experimental groups. The result agrees with an earlier study that found an improvement in the metal/polymer interface after surface laser treatment, increasing resistance against degradation and humidity [34].

4. Conclusion

RF magnetron sputtering proved to be an effective method to coat the titanium with polymer (PEKK), a decrease in corrosion rate showed the efficacy of the polymer coat. XRD analysis verifies the results by the formation of new peaks of PEKK. The laser surface treatment of the titanium before PEKK coating enhances the polymer adhesion to the metal, therefore it prevents the electrolytes from reaching the metal.

References

[1] X. Shen et al., "Mesenchymal stem cell growth behavior on micro/nano hierarchical surfaces of titanium substrates", *Colloids Surf. B: Biointerfac.*, 172 (2015) 221-232.
[2] D.F. Williams, "Tissue-biomaterial interactions", *J. Mater. Sci*., 22 (1987) 3421-3445.
[3] M. Idrees and A.Z. Jebakumar, "A review on corrosion scenario of bio implants in human body", *Am. j. Biol. Chem. Pharm. Sci.*, 1 (2014) 100-104.
[4] N.S. Manam et al., "Study of corrosion in biocompatible metals for implants: A review", *J. Alloys Comp*., 701 (2017) 698-715.
[5] H. Kim et al., "The biocompatibility of SLA-treated titanium implants", *Biomed. Mater.*, 3 (2008) 025011.
[6] G. Wang et al., "Magnesium ion implantation on a micro/nanostructured titanium surface promotes its bioactivity and osteogenic differentiation function", *Int. J. Nanomed.*, 9 (2014) 2387-2398.
[7] A. Fukuda et al., "Bone bonding bioactivity of Ti metal and Ti-Zr-Nb-Ta alloys with Ca ions incorporated on their surfaces by simple chemical and heat treatments", *Acta Biomater*., 7 (2011) 1379-1386.
[8] J. Park et al., "Nanosize and vitality: TiO_2 nanotube diameter directs cell fate", *Nano Lett.*, 7 (2007) 1686-1691.
[9] R.G. Flemming et al., "Effects of synthetic micro-and nano-structured surfaces on cell behavior", *Biomater*., 20 (1999) 573-588.
[10] A. Fragiel et al., "Influence of the N2 partial pressure on the mechanical properties and tribological behavior of zirconium nitride deposited by reactive magnetron sputtering", *Surf. Coat. Technol.*, 202 (2008) 3653–3660.
[11] J.W. Lee et al., "The mechanical properties evaluation of the CrN coatings deposited by the pulsed DC reactive magnetron sputtering", *Surf. Coat. Technol.*, 200 (2006) 3330–3335.
[12] T. Elangovan et al., "Nanostructured CrN thin films prepared by reactive pulsed DC magnetron sputtering", *Mater. Sci. Eng. B*, 167 (2010) 17–25.
[13] S. Swann, "Magnetron sputtering", *Phys. Technol*., 19(2) (1988) 67.
[14] S. Najeeb et al., "Applications of polyetheretherketone (PEEK) in oral implantology and prosthodontics", *J Prosthodontic Res.*, 60 (2016) 12–19.
[15] Z. Horák et al., "Polyetheretherketone (PEEK). Part I: prospects for use in orthopaedics and traumatology", *Acta Chir. Orthop. Traumatol. Cech.*, 77 (2010) 463-469.
[16] N.N. Kumar et al., "Effect of Argon Plasma Treatment on Tribological Properties of UHMWPE/MWCNT Nanocomposites", *Polym.*, 8 (2016) 295.
[17] T. Moskalewicz et al., "The Effect of the Polymer Structure in Composite Alumina/Polyetheretherketone Coatings on Corrosion Resistance, Micro-mechanical and Tribological Properties of the Ti-6Al-4V Alloy" *J. Mater. Eng. Perform.*, 29 (2020) 1426-1438.
[18] Y.S. Tian et al., "Laser surface modification of titanium alloys - a review", *Surf. Rev. Lett.*, 12 (2005) 123–130.
[19] A.M. Al-Khafaji and T.I. Hamad, "Assessment of Surface Roughness and Surface Wettability of

Laser Structuring Commercial Pure Titanium", *J. Res. Med. Dent. Sci.*, 8 (2020) 81-85.

[20] F. Galliano and D. Landolt, "Evaluation of corrosion protection properties of additives for waterborne epoxy coatings on steel", *Prog. Org. Coat.*, 44 (2002) 217–225.

[21] A. Talo, O. Forsén and S. Yläsaari, "Corrosion protective polyaniline epoxy blend coatings on mild steel", *Synth. Met.*, 102 (1999) 1394–1395.

[22] H. Ali, S. Saleem and T.L. Al-Zubaydi, "Evaluation of corrosion behavior of bioceramics coated commercially pure titanium and Ti-6Al-4V alloy", *J. Baghdad College Dent.*, 26 (2014) 41- 48.

[23] M. Nasir and H,A. Rahman, "Mechanical Evaluation of Pure Titanium Dental Implants Coated with a Mixture of Nano Titanium Oxide and Nano Hydroxyapatite", *J Baghdad College Dent.*, 28 (2016) 38-43.

[24] L. Aissani et al., "Magnetron Sputtering of Transition Metal Nitride Thin Films for Environmental Remediation", *Coatings*, 12 (2022) 1746.

[25] I.N. Safi et al., "Implementation and characterization of coating pure titanium dental implant with sintered b-TCP by using Nd:YAG laser", *Saudi Dent. J.*, 31 (2019) 242–250.

[26] G.M. Leiner, D.P. Dennies and A. Yardimci, "High Performance Polymers in Additive Manufacturing Processes: Understanding Process, Structure and Property", *Microscop. Microanal.*, 21 (2015) 127-128.

[27] R. Kumari et al., "Laser surface textured titanium alloy (Ti-6Al-4V) Part II: Studies on bio-compatibility", *Appl. Surf. Sci.*, 357 (2015) 750–758.

[28] Y. Tian et al., "Research progress on laser surface modification of titanium alloys", *Appl. Surf. Sci.*, 242 (2005) 177–184.

[29] Y. Xu et al., "Electrochemical corrosion and anisotropic tribological properties of bioinspired hierarchical morphologies on Ti-6Al-4V fabricated by laser texturing", *Tribol. Int.*, 134 (2019) 352–364.

[30] M. Conardi et al., "Influence of Laser Texturing on Microstructure, Surface and Corrosion Properties of Ti-6Al-4V", *Metals*, 10(11) (2020) 1504.

[31] N. Madaoui et al., "Effect of Argon-Oxygen Mixing Gas during Magnetron Sputtering on TiO_2 Coatings", *Adv. Mater. Sci. Eng.*, 1 (2017) 1-6.

[32] V.M. Marinosci et al., "Effect of grit-blasting on the fracture toughness of hybrid titanium-thermoplastic composite joints", *Int. J. Adhes. Adhes.*, 109 (2021) 102893.

[33] S.G. Croll, "Surface roughness profile and its effect on coating adhesion and corrosion protection: A review", *Prog. Org. Coat.*, 148 (2020) 105847.

[34] J. Haubrich, K. Schulze and J. Hausmann, "Laser treatment of titanium surfaces in different atmospheres for improved adhesion properties", *Euro Hybr. Mater. Struct.*, (2014) 10-11.