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Investigation of the Effect of Bioactive Glass Coating on the Corrosion Behavior of Pre-treated Ti6Al4V Alloy

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Abstract: Titanium alloys, especially Ti6Al4V, are widely used in in-body implants due to their superior mechanical properties, corrosion resistance and biocompatibility. However, due to their higher modulus of elasticity than bone, they do not bond well with the bone structure, leading to loosening. In addition, they contain the elements Al and V, both of which are dangerous when released into the body. Therefore, these alloys are subjected to a number of surface treatments to improve their surface properties. In this study, Ti6Al4V alloys were produced by selective laser melting in dimensions of 10x10x2 mm^3 and then surface treated. The alloy surfaces were first anodized and then coated with 45S5 bioglass powder. After all surface processes, structural analyzes were performed and the effectiveness of the coating was examined. The untreated and coated samples were subjected to corrosion tests by cyclic polarization method and their corrosion behaviors were investigated.

Biyoaktif Cam Kaplamanın Ön İşlem Görmüş Ti6Al4V Alaşımının Korozyon Davranışı Üzerindeki Etkisinin Araştırılması

Anahtar Kelimeler
Elektrokimyasal empedans spektoskopisi,
45S5 Biyocam,
Oksitleme,
CoCr Alaşımı

Öz: Titanyum alaşımları, özellikle Ti6Al4V alaşımı üstün mekanik özellikleri, korozyon direnci ve biyouyumlulukları nedeniyle vücut içi implantlarda yaygın olarak kullanılmaktadır. Bununla birlikte, bu alaşımlar sahip oldukları kemikten daha yüksek elastisite modülleri ile kemik yapısıyla iyi bağlanamazlar ve gevşemeye neden olurlar. Ayrıca, her ikisi de vücuda salındığında tehlikeli olan Al ve V elementlerini içerirler. Bu nedenle, bu alaşımlar yüzey özelliklerini iyileştirmek için bir dizi yüzey işlemine tabi tutulur. Bu çalışmada, Ti6Al4V alaşımları 10x10x2 mm^3 boyutlarında seçici lazer eritme yöntemiyle üretilmiş ve ardından yüzey işlemine tabi tutulmuştur. Alaşım yüzeyleri önce anodize edilmiş ve daha sonra 45S5 biyocam tozu ile kaplanmıştır. Tüm yüzey işlemlerinden sonra yapısal analizler yapılarak kaplamanın etkinliği incelenmiştir. İşlem görmemiş ve kaplanmış numuneler döngüsel polarizasyon yöntemi ile korozyon testlerine tabi tutulmuş ve korozyon davranışları incelenmiştir.

1. INTRODUCTION

Titanium and its alloys are among the most preferred biomaterials in implant and prosthetic applications due to their properties such as complete inertness in terms of biocompatibility in the body environment, low density, high strength, low modulus of elasticity compared to other biometals, and high corrosion and wear resistance [1,2]. Among Ti and its alloys, Ti6Al4V alloy is widely used in dental and hip prosthesis where high strength and biocompatibility are required due to many structural and biological factors. However, these alloys generally exhibit poor bioactivity and the combination of surface and tissue in contact with living tissue results in the formation of fibrous tissue [3,4]. Furthermore, due to their higher modulus of elasticity than bone, they do not adhere well

to the bone structure and lead to loosening, and they contain the elements Al and V, both of which are dangerous when released into the body [5]. Therefore, there are still many unresolved problems such as structural, chemical and biological incompatibilities that may lead to rejection and failure of implants and prostheses by the body. A study by Mei et al. reported that implants made of titanium alloys often fail due to bacterial invasion [6]. To overcome this situation, surface treatments such as sandblasting, acid etching, anodization or a combination of these can be applied to the surfaces of Ti and its alloys [7-9]. Among these surface treatments, anodization is an electrochemical oxidation process in which nanostructured TiO_2 nanotubes are formed on the surface [9,10]. The anodization process, like any other electrochemical process, can be easily controlled once conditions such as solution, voltage or time are optimized [11]. The type of solution (electrolyte), which is one of the control parameters, allows to impart different properties to the TiO_2 structure grown as a result of anodization [12]. In the industry and literature, the most common electrolytes known and preferred for anodizing Ti and its alloys are phosphoric acid (H_3PO_4) and sulfuric acid (H_2SO_4) [13]. However, sulfuric acid has a larger dissociation constant in water than phosphoric acid, making it easier to oxidize than phosphoric acid to form TiO_2 coatings [14]. Therefore, since the oxidation power of H_2SO_4 facilitates anodic oxidation more easily, it is possible to obtain anodized coatings with a thicker and crystalline structure. In addition, sulfate ions (SO_4^{2-}) are also known to promote the growth of bone cells [15,16].

Anodization of titanium and its alloys produces TiO_2 nanotubes on their surfaces, which provide an interface for the formation of bioactive species that promote osseointegration between bone tissue and the implant [17-19]. However, a study found that macrophage cells, which support the antibacterial effect, reduce the adhesion of anodized titanium foils to the surface [20]. Therefore, bioactive coatings with 45S5 bioglass can be applied on TiO_2 nanotubes to increase the osseointegration between the implant-bone cell tissue without disrupting the natural cell formation of the living tissue [21,22]. Bioactive glasses form bone-like hydroxyapatite layers between the implant and living tissue, allowing the formation of highly durable bonds with hard and soft tissues. In addition, many studies have reported that SiO_2, CaO, Na_2O, P_2O_5 and their derivatives in the ionic solutions of bioactive glasses increase enzyme activity and exhibit antibacterial properties [23].

Bioactive glass coatings can be made by thermochemical as flame spraying, chemical as sol-gel or electrochemical deposition as electrophoretic deposition methods. Electrophoretic deposition (EPD) offers the possibility of depositing films of desired thicknesses on a wide variety of base materials with complex forms as long as they are controlled. The basic working principle of the EPD method is known as the movement and deposition of electrostatically charged powder particles in water or an organic solvent on the surface of the base material under opposite voltage by the effect of an electric field [24]. The method is remarkable for bioactive coatings due to its simplicity, low equipment cost, ability to deposit at room temperature, and high purity and microstructural homogeneity of the films obtained. In the literature, hydroxyapatite coatings on biometals such as 316L stainless steel, titanium and its alloys have been generally reported. In the general results of these studies, it was reported that the HA films obtained by EPD method bonded to the surface of the base material with strong adhesion. In a few of these studies, it was also reported that the HA films obtained increased corrosion resistance in simulated body fluid (SBF) compared to untreated samples [25].

Only a few studies have been conducted for coating other types of bioactive coatings by EPD technique. In this study, 10x10x2 mm^3 Ti6Al4V alloys produced by selective laser melting (SLM) were coated with commercial 45S5 bioactive glass powder by EPD method. In the study, the electrochemical behavior of 45S5 bioglass coating on anodized Ti6Al4V alloy was investigated by corrosion tests. In this context, untreated, 45S5 bioglass coated, 45S5 bioglass coated on anodized Ti6Al4V samples were subjected to open circuit potential and cyclic polarization in stimulated body fluid (SBF) environment for corrosion tests. Before the tests, all samples were subjected to structural and morphological examinations by XRD and SEM analyses to see the effectiveness of the coating. After the tests, the current-voltage graphs obtained from cyclic polarization were interpreted and the study was completed.

2. MATERIAL AND METHOD

2.1. Materials and Surface Treatments

Selective laser melting (SLM) is an additive manufacturing method that uses a direct laser beam focused through computer-aided design (CAD) data to fuse metal powders layer by layer to form a metallic structure by melting metal powders and then laying down metal powders again and repeating these processes. Ti6Al4V samples with dimensions of 10x10x2 mm^3 were produced with alloy powders according to ASTM B348 using the CONCEPT LASER MLab Cusing device. The fabrication parameters were 75 W laser power, 1000 mm/s plane and contour scanning speed and 25 μm layer thickness. Furthermore, the fabrication was performed using simple straightline scans to melt each layer. Ti6Al4V alloy generally contains balance % Ti, max. 6.7% Al, max. 4.5% Fe, trace amounts of O, C, H. After production, the substrates were grinded using SiC papers with 80, 220, 400, 800, 1200, 2000 mesh grid respectively, and after polished by alumina powder (grain size of 1 μm), cleaned with ethanol, and dried.

Ti6Al4V alloys were subjected to anodization process before EPD process. For the anodization process, the samples were electrochemically treated in 1 M H_2SO_4 solution by applying 10 V DC voltage for 10 minutes. Afterwards, the untreated and anodized samples were coated with 45S5 bioglass with EPD. For the EPD process, firstly suspension was prepared. The suspension was prepared with 99 ml of distilled water, 1 ml of acetic

acid, 0.2 ml of phosphate ester and 2 g/L 45S5 Bioglass® (containing 45% SiO_2, 24.5% CaO, 24.5% Na_2O and 6.0% P2O5 by weight) commercial powder. They were stirred with a magnetic stirrer for 3 min before each deposition to avoid precipitation of particles. All EPD experiments were performed at ambient temperature, graphite was used as the counter electrode and the electrodes were placed with a distance of approximately 2 cm between them. The electrodes were washed with acetone before processing. Electrophoretic Deposition proses for all samples was performed using GW GPR-30H10D Laboratory DC Power Supply with untreated and pre-treated Ti6Al4V samples as the cathode electrode and graphite as the anode electrode, applying a constant voltage of 20 V for 20 minutes. The phases on the surface of the all samples were determined X-Ray Diffraction analysis using the XRD-GNR Explorer instrument operated at 40 kV and 30 mA Cu Kα (λ = 1.789 Å) source diffractometer.

2.2. 2.2. Corrosion Tests

Untreated, untreated-45S5 coated, pretreated and pretreated-45S5 coated Ti6Al4V samples were subjected to corrosion tests in stimulated body fluid (SBF) for electrochemical investigation. The chemical composition of the stimulated body fluid is given in Table 1. The corrosion tests were completed using Gamry G750 Potentiostat/Galvanostat system, first with Open Circuit Potential (OCP) and then with Cyclic Polarization. The test setup was constructed using a triple electrode system with untreated and coated samples as working electrode, graphite rod as counter electrode and Ag/AgCl as reference electrode. During the test, the corrosion surface area was set to 1 cm2 and the time required for the Open Circuit Potential reading was set to 7200 seconds. Cyclic Polarization measurements were performed with a scan rate of 1 mV/s beyond 0.5 V beyond the Open Circuit Potential values. The polarization curves obtained from the electrochemical analysis were examined in detail.

3. RESULTS

The XRD graph of untreated Ti6Al4V, anodization, 45S5 bioglass and anodization+45S5 bioglass coated samples are given in Figure 1. Ti6Al4V alloy consists of α and β phases. In the XRD graph given in Figure 1, it is seen that a hexagonal hexagonal tightly packed (α phase) crystalline phase is dominant in the structure as seen from the peaks of the Ti6Al4V alloy sample. During SLM production, the α phases in the structure transform into α′ martensite phase due to rapid cooling. The β-Ti (volume-centered cubic) phase in the structure is too small to be detected by XRD [26,27]. When the XRD peaks of the 45S5 Bioglass sample coated on Ti6Al4V alloy with EPD were examined, the presence of $CaCO_3$ (calcite), $Na_6Ca_3Si_6O_{18}$ (sodium calcium silicate) and $CaSiO_3$ (Wollastonite) phases were detected in the structure.

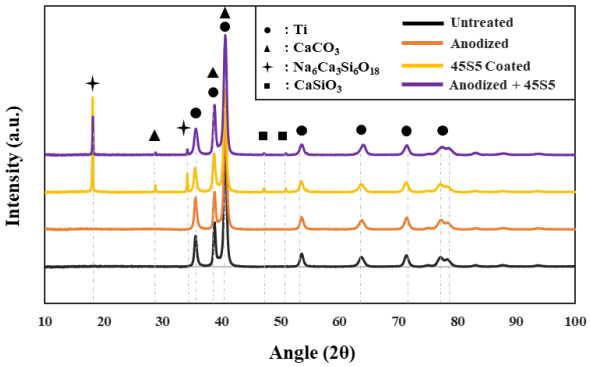

Figure 1. XRD graphs of all Ti6Al4V alloys.

The curves obtained after cyclic potentiodynamic polarization tests of all sample groups in SBF solution are shown in Figure 2. Cyclic polarization tests were carried out to determine the corrosion susceptibility of Ti6Al4V alloy produced by SLM method and samples subjected to different surface treatments. When we look at the cyclic polarization curves given in Figure 5, the hysteresis curve area formed by the untreated sample is larger than the area formed by the coated surfaces. This indicates that the untreated sample exhibits lower pitting corrosion resistance. It is seen that 45S5 bioglass coated with EPD method and 45S5 bioglass coated surfaces after anodization exhibit high pitting corrosion resistance.

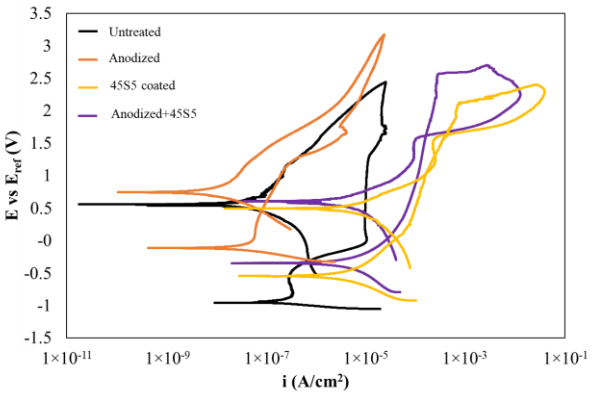

Figure 2. Cyclic polarization curves of all Ti6Al4V samples.

Anodic tafel slope (βa), cathodic tafel slope (βc), current density (icorr) and corrosion potential (Ecorr) values for all sample groups obtained from the lower arm of cyclic potentiodynamic polarization curves are given in Table 1. It is seen that the corrosion potentials (Ecorr) of the anodized, 45S5 and anodized+45S5 coated samples are even more inert when compared to the untreated sample (Table 1). The positive change in Ecorr indicates an increase in corrosion resistance [28]. The icorr values were measured as 213×10-9 A/cm2, 41.70×10-9 A/cm2, 295×10-9 A/cm2 and 88.70×10-9 A/cm2 for untreated, Anodized, 45S5 Coated and Anodized+45S5 coated samples, respectively. It is known that corrosion resistance increases with decreasing current density [29]. Thus, there is a decrease in icorr values compared to the untreated sample. According to Icorr values, the highest corrosion resistance is seen in the Anodized sample. In addition, since the surface ceramic-based coatings are applied to the samples, they act as a barrier in the

corrosive environment and cause an increase in corrosion resistance.

Table 1. The results of corrosion tests of all samples.

Samples	βa (V/decade)	βc (V/decade)	Ecorr [mV]	icorr [A/cm^2]	Corrosion Rate [mm/year]
Untreated	1.663	61.90×10^{-3}	- 958	213×10^{-9}	71.92×10^{-3}
Anodized	496.60×10^{-3}	138×10^{-3}	- 113	41.7×10^{-9}	14.70×10^{-3}
45S5 Coated	35.30×10^{-3}	43.10×10^{-3}	- 545	295×10^{-9}	99.50×10^{-3}
Anodized +45S5	7.60×10^{-3}	7.50×10^{-3}	- 345	88.7×10^{-9}	29.93×10^{-3}

The high porosity of the samples produced with SLM causes the materials to exhibit low corrosion resistance. The surroundings of the pores become suitable areas for corrosion to start. Thus, it progresses between other pores and accelerates the corrosion phenomenon. For this reason, the corrosion resistance of 45S5 bioglass has been increased by oxidation and EPD method.

4. DISCUSSION AND CONCLUSION

Anodization, 45S5 Bioglass and anodization + 45S5 Bioglass coatings were applied to Ti6Al4V alloy produced by SLM technique. The corrosion behaviors of the untreated and coated surfaces were investigated. The results obtained are given below:

- ✓ According to XRD results, α-Ti and β-Ti phases were obtained. In addition, peaks belonging to CaCO3 (calcite), $Na_6Ca_3Si_6O_{18}$ (sodium calcium silicate) and $CaSiO_3$ (Wollastonite) phases were obtained for 45S5 Bioglass.
- ✓ Corrosion tests were carried out in SBF solution and cyclic potentiodynamic polarization curves were obtained. It was determined that 45S5 Bioglass coated surface and anodization + 45S5 Bioglass coated surface exhibited high pitting corrosion resistance.
- ✓ The highest corrosion resistance was observed in the anodization treated sample with a value of -113 mV for Ecorr and 41.70×10^{-9} A/cm^2 for icorr.

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REFERENCES

[1] Molina J, Valero-Gómez A, Belda, J, Bosch F, Bernabé-Quispe P, Tormo-Mas MA. Long-term antibacterial Ag+-release biomaterials based on anodized Ti6Al4V and silver nanoparticles. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2023; 676(B): 1-15.

[2] Atik, B., Bozkurt, Y. B., Kavasoğlu, Y. S., Kovacı, H., & Çelik, A. (2024). Pitting corrosion performance of plasma oxidized Cp-Ti and effects of fabrication methods. Surface and Coatings Technology, 130384.

[3] Zhang LC, Chen, LY. A review on biomedical titanium alloys: recent progress and prospect. Adv. Eng. Mater. 2019; 21: 1801215.

[4] Magesh S, Vasanth G, Revathi A, Geeth M. Use of nanostructured materials in implants, in: R. Narayan (Ed.). Nanobiomaterials, Nanostructured Materials for Biomedical Applications, Woodhead Publishing. 2018; 481-501.

[5] Leban MB, Kosec T, Finšgar M. Corrosion characterization and ion release in SLM-manufactured and wrought Ti6Al4V alloy in an oral environment. Corrosion Science. 2022; 209: 1-15.

[6] Mei S, Wang H, Wang W, Tong L, Pan H, Ruan C, Ma Q, Liu M, Yang H, Zhang L, Cheng Y, Zhang Y, Zhao L, Chu PK. Antibacterial effects and biocompatibility of titanium surfaces with graded silver incorporation in titania nanotubes. Biomaterials. 2014; 35: 4255-4265.

[7] He W, Yin X, Xie L, Liu Z, Li J, Zou S, Chen J. Enhancing osseointegration of titanium implants through large-grit sandblasting combined with micro-arc oxidation surface modification. J. Mater. Sci: Mater. Med. 2019; 30: 73.

[8] Herrero-Climent M, Lázaro P, Vicente Rios J, Lluch S, Marqués M, Guillem-Martí J, Gil FJ. Influence of acid-etching after grit-blasted on osseointegration of titanium dental implants: in vitro and in vivo studies. J. Mater. Sci.: Mater. Med. 2013; 24: 2047-2055.

[9] Jarosz M, Grudzień J, Kapusta-Kołodziej J, Chudecka A, Sołtys M, Sulka GD. Anodizing of titanium alloys for biomedical applications, in: G.D. Sulka (Ed.), Nanostructured Anodic Metal Oxides Synthesis and Applications. Elsevier. 2020; 211-275.

[10] Cheung KH, Pabbruwe MB, Chen W, Koshy P, Sorrell CC. Effects of substrate preparation on TiO2 morphology and topography during anodization of biomedical Ti6Al4V. Materials Chemistry and Physics. 2020; 252: 1-13.

[11] Acharya S, Suwas S, Chatterjee K. Review of recent developments in surface nanocrystallization of metallic biomaterials. Nanoscale. 2021; 13: 2286-2301.

[12] Cai Q, Paulose M, Varghese OK, Grimes CA. The effect of electrolyte composition on the fabrication of self-organized titanium oxide nanotube arrays by anodic oxidation. J. Mater. Res. 2005; 20: 230-236.

[13] Cheung KH, Pabbruwe MB, Chen W, Koshy P, Sorrell CC. Thermodynamic and microstructural analyses of photocatalytic TiO2 from the anodization of biomedical-grade Ti6Al4V in phosphoric acid or sulfuric acid. Ceramics International. 2020; 47(2): 1609-1624.

[14] Rumble JR. Electro Thermo, Solution chemistry. CRC Handbook of Chemistry and Physics, 98th Edition, CRC Press/Taylor&Francis, Boca Raton, FL. 2018; 86.

[15] Lausmaa J, Kasemo B, Mattsson H, Odelius H. Multi-technique surface charaterization of oxide

films on electropolished and anodically oxidized titanium. Appl. Surf. Sci. 1990; 45: 189-200.
[16] Tay BK, Patel VV, Bradford DS. Calcium sulfate- and calcium phosphatebased bone substitutes. Orthop. Clin. 1999; 30: 615-623.
[17] Kunze J, Müller L, Macak JM, Greil P, Schmuki P, Müller FA. Time-dependent growth of biomimetic apatite on anodic TiO2 nanotubes. Electrochim. Acta. 2008; 53: 6995-7003.
[18] Roguska A, Pisarek M, Andrzejczuk M, Lewandowska M, Kurzydlowski KJ, Janik-Czachor M. Surface characterization of Ca-P/Ag/TiO2 nanotube composite layers on Ti intended for biomedical applications. J. Biomed. Mater. Res. Part A. 2012; 100A: 1954–1962.
[19] Pawlik A, Rehman MAU, Nawaz Q, Bastan FE, Sulka GD, Boccaccini AR. Fabrication and characterization of electrophoretically deposited chitosan-hydroxyapatite composite coatings on anodic titanium dioxide layers. Electrochim. Acta. 2009; 307: 465-473.
[20] Rajyalakshmi A, Ercan B, Balasubramanian K, Webster TJ. Reduced adhesion of macrophages on anodized titanium with select nanotube surface features. Int. J. Nanomedicine. 2011; 6: 1765-1771.
[21] Boccaccini AR, Peters C, Roether JA, Eifler D, Misra SK, Minay EJ. Electrophoretic deposition of polyetheretherketone (PEEK) and PEEK/Bioglass® coatings on NiTi shape memory alloy wires. J. Mater. Sci. 2006; 41: 8152-8159.
[22] Pishbin F, Simchi A, Ryan MP, Boccaccini AR. Electrophoretic deposition of chitosan/45S5 Bioglass® composite coatings for orthopaedic applications. Surf. Coatings Technol. 2011; 205: 5260-5268.
[23] Jugowiec D, Łukaszczyk A, Cieniek Ł, Kot M, Reczyńska K, Cholewa-kowalska K, Pamuła E, Moskalewicz T. Electrophoretic deposition and characterization of composite chitosan-based coatings incorporating bioglass and sol-gel glass particles on the Ti-13Nb-13Zr alloy. Surf. Coat. Technol. 2017; 319: 33-46.
[24] Azzouz I, Faure J, Khlifi K, Cheikh Larbi A, Benhayoune H. Electrophoretic Deposition of 45S5 Bioglass® Coatings on the Ti6Al4V Prosthetic Alloy with Improved Mechanical Properties. Coatings. 2020; 10.
[25] Khanmohammadi S, Ojaghi-Ilkhchi M, Farrokhi-Rad M. Evaluation of Bioactive glass and hydroxyapatite-based nanocomposite coatings obtained by electrophoretic deposition. Ceramics International. 2020; 46: 26069-26077.
[26] Azzouz I, Faure J, Khlifi K, Cheikh Larbi A, Benhayoune H. Electrophoretic Deposition of 45S5 Bioglass® Coatings on the Ti6Al4V Prosthetic Alloy with Improved Mechanical Properties. Coatings. 2020; 10(12):1192.
[27] Uzun Y., Biçer S., Tüzemen, Ş.M., Çelik, A. Investigation of Wear Resistance of Electrophoretic Deposition onto Ti6Al4V Alloy. 3rd International Natural Science, Engineering and Materials Technology Conference, NEM 2023.Gazimagusa, Cyprus (Kktc); 2023, p. 164-172.
[28] Uzun Y. Electrochemıcal Evaluatıon Of Ti45Nb Coated Wıth 63s Bıoglass By Electrophoretıc Deposıtıon. Surface Revıew And Letters. 2023; 30(11).
[29] Bozkurt YB, Seçer Kavasoğlu Y., Atik B., Kovacı H., Uzun Y., Çelik A. Comparison study of corrosion behavior for chitosan coated Ti6Al4V alloy produced by selective laser melting and forging. Progress in Organic Coatings. 2023; 182: 107655.