Tantalum carbide coating on Ti-6Al-4V by electron beam physical vapor deposition method: Study of corrosion and biocompatibility behavior

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Abstract
This study aimed to improve the corrosion resistance and biocompatibility of titanium alloy (Ti-6Al-4V) by tantalum carbide (TaC) deposition through electron beam physical vapor deposition (EB-PVD) method. The physical and chemical characteristics of the coated surface are comprehensively evaluated. The corrosion resistance and ion release are assessed. Cytocompatibility assay and cell morphology observation are performed to assess toxicity and cell interaction, respectively. The TaC-coated Ti-6Al-4V exhibits more resistance to corrosion and ion release. It provides a surface, which is appropriate for cell adhesion, an expansion as well as better biocompatible performance. So, it could improve osseointegration Ti-alloy implants in clinical applications.

KEYWORDS
biocompatibility, coating, corrosion resistance, electron beam PVD, tantalum carbide, titanium alloy

1 | INTRODUCTION

Nowadays, composite-based biomaterials have been attracted much more attention in implant designing due to their tunable combinatorial properties, such as physicochemical, mechanical, and biological properties. Among the metallic implants, titanium (Ti)-based alloys serve as an excellent candidate for orthopedic applications due to their unique properties, such as high strength to weight ratio, high fatigue resistance, passivity, excellent corrosion resistance, and Young’s modulus similar to the bone.1 Moreover, the excellent biological properties such as high osseointegration potential could guarantee its excellent biocompatibility.2 However, the inherent poor wear resistance of the Ti-based biomaterials restricts their application in high shear stress conditions and increases the possibility of in vivo implant loosening. The other challenging issue is a subsequent undesired ions release (eg Vanadium) from Ti-based alloy, such as Ti-6Al-4V which in the long term could result in chronic diseases like Alzheimer’s and neuropathy.1

The investigation of Ti-based biomaterial’s surface modifications aiming to increase the surface hardness, wear resistance, and osseointegration is one of the most active research areas in orthopedic implantology.3 Ceramic coatings on the Ti-based alloys could greatly improve their surface properties, particularly the wear resistance. Recently, Ti-6Al-4V coatings with carbide-based ceramics, such as vanadium carbide (VC), silicon carbide (SiC), tungsten carbide (WC), and titanium carbide (TiC) have been progressively developed. Previous studies have demonstrated that the carbide coatings, in addition to increasing corrosion resistance, enhance the material’s hardness.4

Recently, tantalum (Ta)-based materials have been interestingly investigated for biomedical applications, particularly implants that are designing due to their good biocompatibility.5,6 Ta-based biomaterials also show high resistance to corrosion in physiological environments,5 good feasibility, and high fracture toughness.7,8 Unfortunately, despite its excellent clinical results, Tantalum is rarely used as a bulk material for manufacturing implants due to its extremely high density, low volume porosity, high elastic modulus, and most importantly, its relatively high cost. The Ta-based coatings have been utilized to improve the surface properties of the Ti-based implants or scaffolds.9-11
Sun et al. investigated the Ti surface coating using an amorphous Ta2O5 layer with a porous micro/nanoscale topography through a hydrolysis-condensation process. The results proved the presence of an amorphous Ta2O5 layer on the Ti surface that increased the corrosion resistance and cell attachment ability of Ti surface.12

In the other study, the Ti substrate is coated with a micron-sized Ta layer using radio frequency (RF) magnetron sputtering and further increased the surface hardness by oxygen diffusion hardening (ODH) method.13

Compared to the pure Ta or Ta oxide, Ta carbide (TaC) has been recently attracted much more attention as Ti coatings. However, the method of TaC coating seems to be a challenging issue to immobilize a thin and uniformed layer on the implant surface. Chang et al. compared the Ta and TaC coating on the Ti surface using twin-gun unbalanced magnetron sputtering. The results showed more biocompatibility, cell adhesion, and proliferation of TaC coating rather than Ta coating.14

The electron beam method provides unique characteristics in the coating structure, leading to a dense, uniform, and continuous coating with excellent substrate adhesion.15 Further, this technique allows very good control of the coating morphology during deposition, the use of high melting point materials, such as TaC which has a melting point of 4780°C, and most importantly, the deposition at different coating rates ranging from 1 nm/min to several µm/min.15

Although the different surface treatment methods have been utilized to coat the Ta-based layers onto the pure Ti, the electron beam physical vapor deposition (EB-PVD) method has not been investigated for the TaC on the Ti-Al6-4V substrate had a thickness value around 240 nm.

2.2 Coating process

A TaC layer was coated on the Ti-6Al-4V substrate through an electron beam PVD with a target-to-substrate distance of 120 mm. An electron gun (EDS160) with a power of 3000 W was used to evaporate TaC. The coating was performed in vacuum conditions with 5×10⁻⁵ mbar pressure and a deposition rate of 2 Å/s, at 500°C. After 20 minutes of depositing process, the TaC layer on the Ti-6Al-4V substrate had a thickness value around 240 nm.

2.3 Evaluation of surface morphology

Scanning electron microscopy (SEM) (VEGA II TESCAN-LMU, Brno, Czech Republic, Korea) was used to examine the surface morphology of the control samples (Ti-6Al-4V) and the Ti-6Al-4V/TaC. The elemental composition of samples from different points was assessed by X-ray distribution spectroscopy (EDS).

2.4 X-ray diffraction analysis

A surface chemical characterization was performed using X-ray diffraction (XRD) analysis (Philips, X’Pert Pro, Eindhoven, The Netherlands) to identify the phases and assess the crystallinity of Ti-6Al-4V/TaC and control samples. Using a PANalytical Software, (X’Pert High Score Plus) and PDF-2 files, the different phases in the samples were also determined.

2.5 Surface roughness

The surface roughness of uncoated Ti-Al6-4V and Ti-6Al-4V/TaC samples was assessed by a portable micro roughness instrument (MARSURF M300C- Mahr-Germany) according to DIN EN ISO 4287 (1998). During the measurements, the temperature and humidity of the environment were adjusted at 25°C and 40%, respectively.

2.6 Microhardness measurements

The microhardness analysis was carried out using a Future-Tech Crop FM700 microindenter (Kawasaki, Kanagawa, Louis, MO) with 98% purity were prepared as disc pieces with 18-mm diameter to deposit on the substrate surface. As substrate, a circular disk shape (2-mm thick, 18 mm diameter) was die-cut from a commercial Ti-6Al-4V (ASTM F136, Sigma). In order to achieve a uniform coating, the Ti-6Al-4V disk was polished with 400-1200 mesh cloths. To remove any grease or contamination, the polished sample was washed by acetone and double distilled water followed by drying overnight at room temperature.

2 MATERIALS AND METHODS

2.1 Substrate preparation

The electron beam PVD technique was selected for coating process due to the high melting temperature of the TaC. The TaC powder nanoparticles (3-06-12070, Sigma, St.
Japan) with a diamond Vickers point. The measurements were performed using a 50 g force for 5 seconds duration. The maximum load used was 2 mN and the loading-unloading rate was kept constant at 50 μN/s. The hardness measurements were performed at three different points on each sample surface.

2.7 Corrosion resistance analysis

The corrosion resistance of Ti-6Al-4V/TaC and the control sample was evaluated using a Potentiostat/Galvanostat (Autolab with PGSTAT12 and FRA module, Eco Chemie, the Netherlands). The potentiodynamic polarization value was measured in Hanks’ solution (code H9269-SIGMA). The Hanks’ solution was degassed using Argon for 1 hour before starting corrosion test and its pH and temperature were maintained at 7.4 and 37±2°C, respectively. Platinum was used as the counter electrode and saturated Calomel as the reference surface electrode; samples with a 25 mm² area were used as the working electrode. The potentiodynamic polarization curves were obtained at a scan rate of 1 mV/s from an initial potential of 250 mV below the open circuit potential (OCP) up to 1000 mV above the OCP. Eventually, corrosion parameters were calculated for the samples according to anodic-cathodic polarization plots and the Tafel extrapolation method. The polarization resistance is obtained from the potentiodynamic polarization curve using Equation (1).

\[
R_P = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c) i_{corr}}
\]

where \(\beta_a\) and \(\beta_c\) are, respectively, the anodic and cathodic Tafel slopes, and \(i_{corr}\) is the corrosion current density (A/cm²).

2.8 Ion release assay

The concentration of released ions was determined and compared to evaluate the role of the TaC coating on preventing the release of toxic elements from the titanium alloy. Following the corrosion tests, the control sample and Ti-6Al-4V/TaC were removed from the Hanks’ solution and the remaining solution was used for quantitative analysis in order to quantification of released ion concentrations using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Varian, Melbourne, Australia).

2.9 Cell proliferation and viability analysis

In vitro experiments were performed with osteosarcoma-derived human cell lines (MG63) purchased from Iranian National Cell Bank of Pasteur Institute. The MG63 were grown in Dulbeco’s-modified Eagle’s medium (DMEM, Invitrogen, Karslruhe, Germany) with 10% fetal bovine serum (FBS, Invitrogen) and antibiotics (penicillin/streptomycin/mL; Invitrogen) in a humidified 5% CO₂ atmosphere at 37°C.

The MG63 cell viability and proliferation were examined by the Methyl thiazol tetrazolium (MTT) assay. Briefly, the disk-shaped samples were cleaned with alcohol, and sterilized on both surfaces under UV-C radiation (30 minutes) before the MG-63 cell culturing experiments. Cells were seeded onto the samples in 24-well plates at a density of 10⁵ cells/well and grown on the disks in culture medium for 48 hours. An aliquot of 20 μL of MTT solution (Invitrogen) at a concentration of 5 mg/mL was added to the wells. After incubation for 4 hours under standard culturing conditions, the medium was removed and 200 μL of dimethyl sulfoxide (DMSO, Invitrogen) was added to solubilize the formed crystallized formazan dye. The optical density of the solution was determined using an Elisa Reader device (BioTek, Elx808, Winooski, VT, USA) at a wavelength of 570 nm. The relative cell viability in contact with the samples was calculated compared to the negative control (tissue culture palate) based on Equation (2):

Relative Cell Viability \(\% = A_t/A_c \times 100\)

where \(A_t\) and \(A_c\) are sample and negative control optical density, respectively.

2.10 Cell morphology assessment

The SEM was utilized to study MG67 cell attachment and morphology cultured on the TaC-coated and control sample. Cells were placed on the sterilized disks at a density of 3×10⁴ cells in 1 mL culture media. The attachment was observed after 72 hours. In order to perform SEM, the samples were immersed into a 2.5% glutaraldehyde solution (Merck, Hohenbrunn, Germany) for 90 minutes and subsequently dehydrated in graded ethanol (60%, 70%, 80%, 90%, and 100%). The dried samples were gold-coated, and viewed under the SEM.

2.11 Statistical analysis

Statistical analysis was carried out using SPSS software (v 17.0; IBM New York, NY), when statistical differences were detected, a student’s comparison t test was performed. Data are reported as mean±SD at a significant level of P<.05.

3 RESULTS AND DISCUSSION

Despite pure tantalum’s excellent corrosion resistance and biocompatibility, its use in medicine is, unfortunately, limited due to its high density and cost. Previous studies have
shown that the surface modification of biomaterials by carbide coatings can improve the material properties for medical implants. Therefore, in this study, a TaC layer was coated onto Ti-6Al-4V via EB-PVD method in order to enhance the surface properties and corrosion resistance of the substrate.

3.1 Coating characterizations

The microstructure and surface morphology of the Ti-6Al-4V/TaC and the control sample were assessed by SEM (Figure 1). Comparing the images before and after coating process, it was evident that the TaC coating is smooth, uniform, and continuous, covering all surface of Ti-6Al-4V and appropriately filling any substrate cracks. Due to the heating of the substrate in the coating chamber at 500°C, no thermal stresses were created at the coating-substrate interface, which may have prevented scabbing and cracking. Moreover, it should be noted that, following the completion of deposition, the samples were allowed to cool in the chamber over a prolonged time to prevent possible thermal stresses.

EDS spectrum tests from different parts of surfaces and the weight percentage of chemical elements of Ti-6Al-4V/TaC and the control samples were presented in Figure 2 and Table 1. As it is obvious, Al, Ti, and V belong to Ti-6Al-4V substrate and Ta, O, and C to the TaC belong to the coating. In the surface of the Ti-6Al-4V/TaC sample, the weight percentage of Ta, C, and O were 27.54, 22.21, and 17.7 wt%, respectively. Besides, the significant reduction of the Ti, Al, and V weight percentage in the TaC-coated surface proves the successful TaC coating on the Ti-6Al-4V surface.

The XRD characterization of the Ti-6Al-4V/TaC and control samples was performed in the range of 2θ = 30°-90° (Figure 3). The peaks that are at 2θ = 87.5°, 82.5°, 78.1°, 76.8°, 74.9°, 70.9°, 63.5°, 53.2°, 40.4°, 38.5°, and 35.4° are correspond to the α-Ti phase (the crystalline planes are shown in Figure 3(A)). However, the peaks that are at 2θ = 85.8°, 72.2°, 57.5°, and 39.8° as well as crystalline planes of (220), (211), (200), and (110) are related to the β-Ti phase (Figure 3(A)), respectively; which are consistent with those in previous studies. The sharp peaks were observed at 2θ = 78.1°, 40.4°, and 35.4° attributed to the α-Ti phase, representing the degrees of crystallinity. Figure 3(B) shows the coating (TaO-TiC-TaC) phases and formation of TaC layer on the surface. The XRD spectrum test of the coating showed that peaks at 2θ = 71.8°, 38°,
36.4°, and 33.3° are corresponded to the tantalum carbide phase, as observed in previous studies. Further, the TiC phase was observed at 2θ=82.5°, 38.5°, and 33.3° and the TaO phase at 2θ=40.1° and 33° (The X’Pert XRD card No. is shown in Figure 3).

The surface morphology is one of the important factors affecting the abrasive wear resistance of implants in vivo. Surface morphology and roughness of the implant surface affect how cells and tissues respond to it. Table 2 shows the average roughness of the surface and hardness value of

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti</th>
<th>Al</th>
<th>V</th>
<th>Ta</th>
<th>C</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al-4V/TaC</td>
<td>29.42±1.21</td>
<td>2.58±0.06</td>
<td>1.37±0.01</td>
<td>27.54±2.04</td>
<td>22.21±3.1</td>
<td>17.7±1.2</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>86.33±4.31</td>
<td>7.70±0.07</td>
<td>5.96±0.04</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

**FIGURE 3** XRD patterns were obtained from the surface of the (A) Ti-6Al-4V and (B) Ti-6Al-4V/TaC samples. [Color figure can be viewed at wileyonlinelibrary.com]
the control samples and Ti-6Al-4V/TaC samples. As it is seen, the surface roughness of Ti-6Al-4V substrate was changed from 0.055±0.001 to 0.606±0.0008 µm after coating with TaC. This increased roughness can facilitate cell anchorage and enhance the cell-surface adhesion.

The surface hardness was assessed using Vickers microindenter. The average hardness value for Ti-6Al-4V/TaC was 640±3.00 HV, which is significantly greater than that for the control sample which is 346±4.72 HV (Figure 4); thus, the ceramic coating led to 1.8 times increase in surface microhardness. The presence of the TaC, TiC, and TaO phases on the substrate surface may be the reason of the observed increased hardness of the coated sample.27,28

### 3.2 Corrosion behavior analysis

Although Ti-based biomaterials have been widely utilized as an implant material due to their biocompatibility, corrosion still occurs when Ti is implanted.1 The corrosion characteristics of an alloy are affected by the formation of a passive layer on the surface. The formation of a VO layer on the surface and subsequent release of vanadium lead to corrosion in the implants.29

Potentiodynamic polarization plots of Ti-6Al-4V/TaC and control samples in Hanks’ solution are shown in Figure 5. The corresponding electrochemical parameters derived from the polarization curve are summarized in Table 3. Figure 5 indicates that the corrosion potential of the Ti-6Al-4V/TaC was found to be nobler than control sample. Generally, the corrosion current density ($i_{corr}$) is an important parameter to evaluate the kinetic of corrosion reactions, and besides the corrosion rate is proportional to the corrosion current density measured via polarization. In other words, the lower $i_{corr}$ led to the lower corrosion rate. For the Ti-6Al-4V/TaC, the corrosion current density is low, and the value is about 1.5 µA/cm² which is lower than control sample with magnitude of 2 µA/cm². Therefore, it proves an increase in corrosion resistance ($R_p=10.49\times10^7$) that is due to the tantalum carbide coating and, a reduction in the release of harmful metal ions from the substrate. The cathodic Tafel slopes ($-\beta_c$) of the Ti-6Al-4V/TaC and control samples were 114 and 65 mV/decade, respectively. The larger anodic Tafel slopes value ($\beta_a=139.2$ mV/decade) in comparison with the $\beta_c$ value, indicates the existence of the protective ceramic film (TaC), which gives rise to a typical passive character of samples with a low corrosion current density.

For a better understanding of the disruptive behavior of the samples in the physiological environment, ICP was also performed using the Hanks’ solution, following the corrosion tests. The results showed a difference in the concentration of ions released from the Ti-6Al-4V/TaC and control sample (Figure 6). As shown, the TaC, TiC, and TaO layers present in the coated sample act as a barrier and decrease the release of toxic elements, such as vanadium, to less than half. Therefore, it can be concluded that Ti-6Al-4V/TaC has a higher chemical stability and could support biocompatibility compared to the control sample.

### 3.3 Biocompatibility performance and cell morphology observation

Improving biocompatibility and cells interaction were analyzed through the MTT assay and SEM observation. Figure 7 demonstrates the relative MG-63 cells viability after 48 hours incubation with the samples. The results
indicated an enhanced cell viability and proliferation on the surface of the sample coated with TaC. The relative viability of MG67 cells increased from 86% in the control sample to 92% in Ti-6Al-4V/TaC. It could be a result of decreasing ion releases from Ti-6Al-4V/TaC rather than Ti-6Al-4V.

SEM observations in Figure 8 demonstrate the morphology of MG-67 cells on the samples after 72 hours of culture. As can be observed, cells were well attached to both the surface. However, cell expansion and spreading on the surface were significantly enhanced in the Ti-6Al-4V/TaC surface, so that the surface was almost all covered by the cells. Regarding SEM analysis before cell culture (Figure 1) and Table 2, increasing the surface roughness could provide anchorages for the cells to spread and covering the surface.30 Much more cell spreading could support better osseointegration.31 The results indicate the improved biocompatibility of the coated substrate as well as enhancing cell spreading and osseointegration due to the TaC coating on Ti-6Al-4V. Consequently, TaC coatings can be used as a convenient coating for orthopedic implants.

### 4 | CONCLUSIONS

In this study, a TaC coating was deposited on a Ti-6Al-4V substrate through electron beam PVD method; this coating was continuous, uniform, and smooth. Ti-6Al-4V/TaC has a
higher corrosion resistance and hardness than the uncoated alloy, indicating a better chemical stability in the physiological environment and improved surface properties. Further, the TaC coating reduced the corrosion current density and the concentration of released ions during the corrosion assay to less than half. Potentiodynamic polarization showed that the TaC coating could be passivated in Hanks’ solution and showed a lower $i_{corr}$ than Ti-6Al-4V. Also, the resistance value ($R_p$) of the Ti-6Al-4V/TaC was larger than Ti-6Al-4V and the result showed that TaC coating has effective potential for the surface protection of biomaterial. In vitro experiments indicated that cells could spread on surface of the coated sample. Thus, the improved biocompatibility, adhesion, growth, and proliferation of bone cells on surface of the Ti-6Al-4V/TaC sample demonstrate that this material is an appropriate choice in orthopedic implant applications.

ACKNOWLEDGMENT

The authors wish to gratefully acknowledge the scientific help and assistance of Dr. Arman Zarebidaki.

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