

Surface Analysis and Biocorrosion Properties of Nanostructured Surface Sol–Gel Coatings on Ti6Al4V Titanium Alloy Implants

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Abstract: Surfaces of biocompatible alloys used as implants play a significant role in their osseointegration. Surface sol–gel processing (SSP), a variant of the bulk sol–gel technique, is a relatively new process to prepare bioactive nanostructured titanium oxide for thin film coatings. The surface topography, roughness, and composition of sol–gel processed Ti6Al4V titanium alloy coatings was investigated by atomic force microscopy (AFM) and X-ray electron spectroscopy (XPS). This was correlated with corrosion properties, adhesive strength, and bioreactivity in simulated body fluids (SBF). Electroimpedance spectroscopy (EIS) and polarization studies indicated similar advantageous corrosion properties between sol–gel coated and uncoated Ti6Al4V, which was attributed to the stable TiO₂ composition, topography, and adhesive strength of the sol–gel coating. In addition, inductive coupled plasma (ICP) and scanning electron microscopy with energy dispersive spectrometry (SEM-EDS) analysis of substrates immersed in SBF revealed higher deposition of calcium and phosphate and low release rates of alloying elements from the sol–gel modified alloys. The equivalent corrosion behavior and the definite increase in nucleation of calcium apatite indicate the potential of the sol–gel coating for enhanced bioimplant applications. © 2006 Wiley Periodicals, Inc. *J Biomed Mater Res Part B: Appl Biomater* 80B: 107–120, 2007

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INTRODUCTION

The surface coatings of titanium alloys for biomedical applications are of great importance to their “osseointegration” or bone-bonding feature. They determine the biocompatibility of the device and also influence dynamic physiological processes that take place at the implant/host interface. It has been shown that the localized corrosion and dissolution of the surface zone can adversely affect the performance and bioactivity of metals and alloys, resulting in early implant failure. Titanium alloys are the most frequently used metallics for medical implants due in part to the spontaneous protective oxide coating that forms on its surface. It has been suggested that the physicochemical and dielectric properties of the oxide film play an important role in determining implant biocompatibility.¹ Although titanium alloys have exhibited excellent overall corrosion properties, metallic ions released

in the physiological environment is still a concern.^{2–5} Potential adverse effects of released titanium or alloying elements such as vanadium have been reported.^{6,7} Passivation protocols using nitric acid, heat treatment, aging in 100°C water, etc. are methods that have been adopted to reduce the release of ions from surgical implants. However, the significant increase in trace levels of Ti, Al, and V in passivated Ti alloys, for some of these procedures, have caused many researchers to re-evaluate these surface treatments to reduce metal ion release.⁸ The high concentration of ions and proteins in the body present an aggressive environment that can force the device to undergo compositional change over time, resulting in early failure. The dissolution process has been proposed to occur across a number of layers, including the metal oxide layer, the oxide/liquid interface, a boundary layer at the oxide/liquid interface composed of surface complexes, serum proteins, hydrated oxides, and the bulk liquid.⁹ Another important aspect of the surface coating is the ability to promote advantageous bone formation or “tissue engineering” of the implant. Bone formation and cell growth may be promoted by coatings modified with bioceramics such as hydroxyapatite, calcium phosphate, etc.^{10–12}

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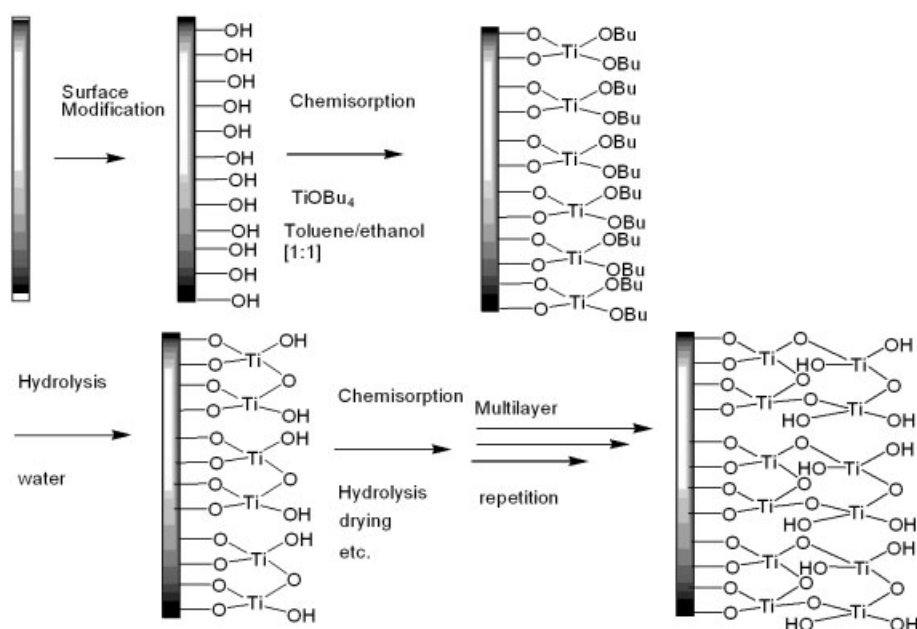


Figure 1. Schematic diagram of the layer-by-layer SSP deposition processes.

The sol-gel technique is a simple, low temperature coating method to form pure, stoichiometrically homogeneous films of up to micrometer thick dimensions.¹³ This is commonly used on other metals such as stainless steel (SS) or nickel-titanium, aside from titanium alloys, to improve their corrosion resistance.^{3,14–16} Considerably decreased release of titanium and vanadium ions from sol-gel coated titanium alloy has also been found.^{5,17} In addition, sol-gel oxide films provide nucleation sites for calcium phosphate deposition followed by bone regeneration because of abundant hydroxyl (OH) groups, Si—OH or Ti—OH remaining on sol-gel derived silica or titanium.^{12,18} The presence of mesopores (>2 and <50 nm) favor hydroxyapatite (HCA) nucleation or promoted early nucleation of apatite.^{19–21} However, since most thin sol-gel coatings are processed at high sintering temperatures (mostly above 400°C),¹⁵ they often have poor strength, lack adhesion, and have nonuniform coverage.^{13,22} Also, if biological molecules are incorporated, the relatively high temperature causes the organic dopants (peptides, drugs, etc) to lose their biological activity, discounting the possibility for drug delivery or tissue engineering.²³

Surface sol-gel processing or SSP, a variant of the bulk sol-gel dip-coating method, can be used to form ultrathin metallic oxides with nanometer precise control.²⁴ The layer-by-layer process begins with the chemisorption of a hydroxyl functionalized surface in a metal alkoxide solution followed by rinsing, hydrolysis, and drying of the film,²⁴ as shown in Figure 1. This sol-gel reaction occurs on the surface of the substrate each time the hydroxyl groups Ti—OH are regenerated to form a monolayer of TiO₂ and repetition of the entire process results in multilayers of the thin oxide film. A calcination or sintering process may be applied if a denser or more crystalline oxide is desired, but this is often unnecessary.²⁵ The process is readily applied to any hydroxylated

surface, using a metal alkoxide reactive to OH groups, and the sol-gel procedure is independent of each cycle, which allows individual layers to be nanostructured.²⁶ The nanoscale thickness of titanium oxide produced by SSP have also found utility in the fabrication of photonic devices, sensors, multicomponent organic films, nanocomposite coatings, molecular templates, sensor devices, etc., where the physicochemical, and electrooptical properties of the film depend on the ability to control nanostructure.^{27,28} However, the physicochemical, mechanical, and corrosion properties, as they relate to biocorrosion and bioreactivity of the film in implant applications, have not been systematically investigated. We have recently investigated the protein adsorption properties of self-assembled monolayer modified (SAM) sol-gel SSP coatings with a variety of surface sensitive spectroscopic and microscopic techniques.²⁹

This paper reports the evaluation of surface properties and biocorrosion of nanostructured titanium oxide coatings prepared by SSP on Ti6Al4V alloys. Specifically, the topography, roughness, corrosion behavior, and adhesive strength were investigated. Furthermore, to determine its bioreactivity, the *in vitro* deposition of calcium apatite in SBF and the simultaneous release of Ti, Al, and V were investigated. The aim of this study was to establish whether an uncalcined layer-by-layer SSP prepared film can perform well as a passive coating for the alloy substrate and whether biocorrosion properties may be enhanced.

MATERIALS AND METHODS

Surface Activation and Sol-Gel Coating

Ti6Al4V titanium alloy disks with diameter of 0.71 cm² were mechanically polished using silicon (Si) carbide papers of

decreasing particle size (240, 320, 400, 600 grits) to produce a grooved finish. This starting surface was found to have a root mean square (rms) roughness of approximately $0.06\ \mu\text{m}$. The samples were sonicated sequentially in acetone, ethanol, and water for 10 min each to degrease and clean the surface followed by immersion in 30/70% (v/v) solution of H_2O_2 and H_2SO_4 (Fisher Scientific) for 10 min. This solution, also known as *Piranha* acid, removes the native oxide and forms a fresh OH-rich oxide on the surface.³⁰ The substrates were sonicated three times in deionized (DI) water (resistivity = $18.2\ \text{M}\Omega$, pH = 6.82; Millipore) and three times in methanol (Aldrich, Milwaukee, WI) before drying with N_2 gas. This substrate was hereby denoted as “hydroxylated.” The samples were immediately coated with titanium sol-gel and hereby denoted as “sol-gel coated substrate.” Titanium samples were also cleaned and passivated with 30% HNO_3 for 1 h per ASTM F86 protocol and denoted as “passivated substrate,” which served as a control.

Nanostructured titanium oxide was deposited on the surface using the layer-by-layer surface sol-gel process.²⁴ Briefly, the wafers were immersed in 100 mM solution of titanium butoxide (Aldrich) in 1:1 toluene (Sigma, St. Louis, MO) and ethanol (Sigma) for 5 min in a sealed screw cap jar after being purged with N_2 gas. The titanium alkoxide was kept in a desiccator until use since it is highly moisture sensitive and easily hydrolyzed. The titanium butoxide reacted with the negatively charged hydroxy-functionalized surface of titanium during this chemisorption process. This is consistent with the schematic diagram shown in Figure 1. After rinsing with copious solvent to remove unbound alkoxides, the samples were immersed in DI water for 1 min to regenerate the hydroxyl groups and then dried by airflow. The chemisorption, rinsing, hydrolysis, and drying steps were repeated for 5 cycles and the specimens were stored in a desiccator prior to analysis. Several groups including our group have reported the nanometer thickness dimensions of each layer (cycle) of deposited sol-gel material analyzed using surface sensitive techniques such as ellipsometry and surface plasmon resonance spectroscopy.³¹

Surface Characterization

Composition Analysis. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Kratos Axis 165 electron spectrometer with a 165 mm mean radius concentric hemispherical analyzer operated in fixed analyzer transmission mode and a pass energy of 160 eV. Typical sampling depth of the analysis is about 3 nm from the surface. The analyzed area is approximately $0.8\ \text{mm} \times 0.2\ \text{mm}$. The analysis chamber pressure during XPS is 1×10^{-9} torr. Sample charging during XPS was compensated by low energy electrons from an integral charge neutralizer system in Axis 165. The binding energy scale was referenced to the adventitious carbon C 1s at 285.0 eV. A depth profile analysis of the oxide was done with an etch rate of 5 nm/min previously determined for the instrument using a silicon oxide control.

Morphology and Roughness. A Philips XL30 SEM equipped with an Energy Dispersive Spectrometer (EDS) was used to obtain the elemental composition before and after immersion in SBF. Primary beam energies of 10–15 kV were used. Typical sampling depth is a few microns. Atomic force microscopy (AFM) images of the sol-gel coated disks were obtained using a PicoScan system (Molecular Imaging (Agilent), Phoenix, AZ) equipped with a $7\ \mu\text{m} \times 7\ \mu\text{m}$ scanner. All images were collected using the magnetic alternating current (MAC[®]) mode in air. The AFM tip consisted of a MAC lever[®] silicon-nitride-based cantilever coated with magnetic film. The force constant of the tip was around 0.5 N/m and the resonance frequency was around 100 kHz. The average roughness represented by the root mean square (rms) roughness of the surface (which is the standard deviation of the heights or Z values) was calculated based on a standard formula integrated in the software.

Adhesive Strength. The adhesive strength of the substrates was measured by a tension test. An aluminum stud pin (0.106 inch diameter attached to the head by epoxy resin adhesive) was fixed onto the substrates by metal clips. After the specimens were heated for 1 h in an oven at 150°C (to cure the epoxy), the disk was cooled to room temperature and the adhesive strength was measured using a tensile test machine (Sebastian V, Quad group, Washington, D.C.). Four replications were carried out for each group.

Electrochemical Impedance Spectroscopy. Electrochemical impedance analysis (EIS) measurements were carried out to determine the electrochemical properties of the coating. EIS was done in a N_2 gas deaerated Hank's balanced salt solution (HBSS) at 37°C , pH 7.4. The test was conducted using a potentiostat/galvanostat system (Model 273A, EG&G Parc.) coupled to a lock-in amplifier (Model 5210, EG & G Instrument). A conventional three-electrode electrochemical cell was used. The counter electrodes consisted of two graphite rods and a saturated calomel electrode (SCE) served as reference electrode. Four samples per group were tested. The EIS spectra were obtained at the open-circuit potential of the specimen in HBSS with an amplitude of 10 mV. The frequency span was from 100 kHz down to 1 mHz. Data registration and analysis were performed on an interfaced computer. The impedance spectra were fitted by an electrical equivalent circuit (EEC) model using a Perkin-Elmer ZSimpWin software and the nonlinear least-squares fitting procedure developed by Boukamp.³² The quality of fitting to the equivalent circuit was judged first by the χ^2 value and secondly by the error distribution versus frequency, comparing experimental with simulated data that came with the software.

Potentiodynamic Polarization Test. After an hour of equilibration, polarization data were generated by conducting a forward scan from 100 mV more active than the corrosion potential (E_{corr}) to a threshold anodic current density of $10\ \text{mA cm}^{-2}$. The scan direction was reversed until the protec-

tion potential was achieved, or the potential was 0 mV with reference to the E_{corr} . The Tafel extrapolation and Stern-Geary currents were used to calculate the corrosion current density (I_{corr}) in nA cm^{-2} at the ParCalc® Routine, Technical notes/software manual (EC&G, Princeton applied Research).

In Vitro Apatite Nucleation in SBF. Immersion in simulated body fluid (SBF) is a well established method to investigate the *in vitro* bioreactivity or bioactivity of an implant surface.¹² Detailed preparation and composition of the SBF used in this experiment can be found elsewhere.²¹ Each sample (three samples per group) was immersed in 10 mL of the SBF at pH 7.4 at 37°C in a sealable polyethylene culture tube. The samples were placed to a snug fit at the bottom of the tubes. The surface area to solution volume ratio (SA/V) was 0.07 cm^{-1} . An immersion protocol with some modifications was followed.⁸ The test solution was exchanged periodically at 1-, 3-, 7- and 14-day time periods for a total of 25 days. SBF solutions without the specimens were also incubated as controls. After the immersion experiment, the disks were carefully rinsed with DI water, air-dried, and then stored in a desiccator prior to analysis. Concentrations were expressed in parts per billion (ppb) or ng/mL.

Ion Concentration Analysis. The SBF samples were diluted 1:10 with blank solutions and analyzed for C, P, Ti, Al, V ion contents by ICP-AES (Perkin-Elmer Optima 3300 DV, Norwalk, CT). Data was analyzed by WinLab 32 software (Perkin-Elmer). Calcium and phosphate precipitate on the substrates were also determined by SEM-EDS.

Statistical Analysis

Statistical analysis was performed using SSPS software®. Data sets were tested for normality using Shapiro-Wilk test for normality. Subsets within the normal distribution were tested using one way ANOVA and independent *t*-test and Mann-Whitney for those samples that did not pass normality test. The mean difference was found significant at $p \leq 0.05$.

RESULTS

Surface Characterization

Previous investigations have been made on the layer-by-layer nature of the sol-gel deposition, surface morphology, wetting (surface energy), dielectric properties, and nanometer thickness of these films on ideal flat surfaces.^{31,33} More data on the nature of this coating process can be obtained from these publications and from other groups.²⁴⁻²⁷ The focus of this work is to characterize surface properties for biocorrosion and bioreactivity directly on titanium alloy substrates. The use of these mechanically polished disk substrates of titanium alloys is significant because of the goal to approximate conditions and properties of actual devices.

TABLE I. Normalized Atomic Percentage Composition of Passivated and Sol-Gel Coated Ti6Al4V Substrates

	Passivated	Sol-Gel Coated
O 1s	49.14	44.07
Ti 2p	17.77	6.48
C 1s	33.08	49.44

Composition. The composition of the sol-gel coating is summarized in Table I. High resolution scans of Ti, O, and C show that the oxide is predominantly in the form of TiO_2 with Ti 2p at binding energy of 458.5 eV and O at 529.5 eV (Figure 2). In addition, a high intensity peak was observed at 533 eV, corresponded to hydroxyl groups in the form of Ti—OH. Depth profile analysis indicated the presence of nonstoichiometric oxide (Ti_xO_y) aside from TiO_2 on the hydroxylated and sol-gel coated substrates, as shown in Figure 3. The combined TiO_2 and Ti_xO_y thickness on the passivated substrate was estimated to be $<10 \text{ nm}$, 140 nm on the hydroxylated substrate, and on the sol-gel substrate was 220 nm, indicating that the TiO_2 is roughly 80 nm. However, real thickness of the oxidized layers maybe about 10% larger than that measured by the depth profile since bombardment by Ar^+ ions causes the reduction of Ti^{4+} , Ti^{3+} , or Ti^{2+} ions to lower oxidation states. In addition, the TiO_2 concentration and the Ti_xO_y concentration are progressively underestimated as the ion sputtering progresses.³³ Small concentrations of N, Na, S, and Cl were detected, which may have come from surface preparation. The C scan can be resolved to different C—O—, CH groups. These moieties therefore indicate that the film is amorphous.

Morphology and Roughness. The microtopography of the sol-gel coated and passivated Ti6Al4V substrates are shown in Figure 4. The images of clean (polished) and hydroxylated substrates were also included as controls. All substrates showed uniform amorphous morphologies at the scan area of $7 \mu\text{m} \times 7 \mu\text{m}$ scan (representative of four different areas scanned on the substrate). The surface of the starting material showed the presence of particle debris, which were simply removed upon passivation. The clean and passivated substrates were thin and flat when compared with the clustered appearance of oxide domains on the hydroxylated and sol-gel coated substrates. In addition, concavity produced by acid etching was observed on the hydroxylated substrate. The decrease in the depth of pits after coating as represented by the horizontal scan indicates some filling of the voids on the surface. The rms roughness values and maximum peak to valley distance are given in nanometers ($0.001 \mu\text{m}$) and are shown in Table II. The roughness of clean and passivated surface did not vary significantly. The data further shows that the surface roughness was increased after hydroxylation, and after sol-gel deposition ($p < 0.05$). The roughness of the passivated surface was significantly different from the sol-gel coated surface ($p = 0.027$). The hydroxylated and passivated surfaces have similar roughness ($p = 0.287$).

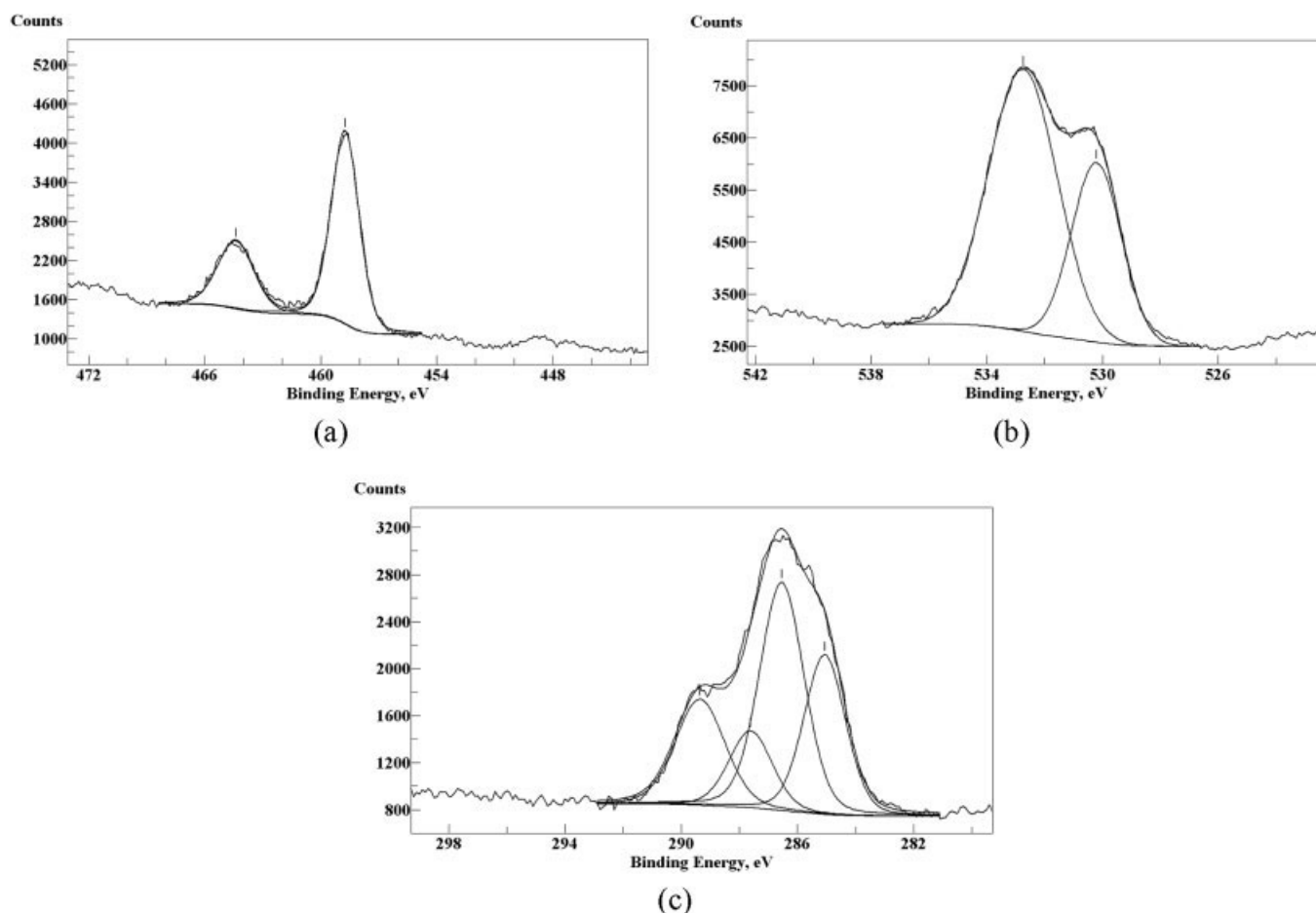


Figure 2. High-resolution scan and depth profile analysis of sol-gel coated substrate. High-resolution scan shows the deconvoluted peaks of (a) Ti, (b) O, and (c) C found on the sol-gel Coating.

Adhesive Strength of the Coating. There was no significant difference in the adhesive strength between different substrates. Both substrates had bond strengths of approximately 76 MPa, which was almost as high as the adhesive. XPS scan of the Al pull stud did not show the presence of debonded Ti (Figure 5). However, optical microscopy of the alloy substrates (Figure 6) indicate a mixture of debonded and bonded zones along the fracture surfaces for both. This indicates that a mixed failure mode has occurred with cohesive failure along the surface sol-gel coating and adhesive failure at the coating-substrate interface. In the absence of further studies and correlation with the coating thickness, viscoelastic properties, and surface energy comparison between substrates, it is not easy to interpret these observations. However, the main result does indicate a similarity of adhesion properties between the two substrates.

Electroimpedance Spectroscopy. EIS is a useful and nondestructive method to determine the evolution of the protective coating and general corrosion properties with time (aging). Reproducible and consistent spectra were obtained for all groups. Typical bode plots presented as the measured (msd) impedance spectra and calculated (calc) spectra are

presented in Figure 7. The protective film of the sol-gel coated substrate is also hereby referred to as sol-gel coating. To separate the contribution of the clean and hydroxylated substrates on the system response, electrochemical measurement was also performed on these substrates. The impedance response of all samples was nearly similar. The resistance and capacitance values were not significantly different among groups. The passivated surfaces had similar impedance behavior to sol-gel ($p = 0.970$ and $p = 0.989$, respectively). The passivated sample exhibited a phase angle maximum, which gradually decreased to -57° . The linear variation between the electrode impedance ($\log Z$) and frequency ($\log f$), in a broad range of frequency, has a slope close to -1 . Similarly, the EIS spectra of sol-gel in the frequency range 10^3 – 0.1 Hz also contain only one response denoted by a phase angle, which closely approached -63° and a linear variation (impedance vs frequency) with slope close to -1 . No significant differences between the sol-gel and hydroxylated surfaces were observed. This indicates that the general passivation function of oxides irrespective of their derivation (native or sol-gel prepared) is consistent.

For fitting the spectra and data interpretation, an “equivalent circuit,” shown in Figure 7e was used to describe the

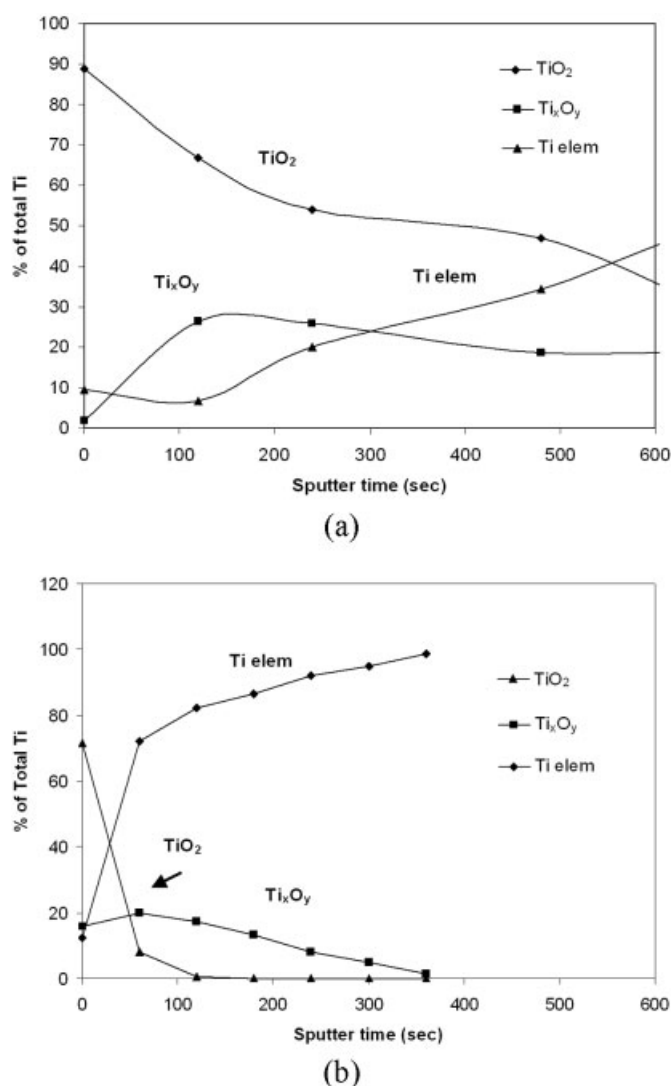


Figure 3. XPS Depth profile analysis of the (a) sol-gel coated Ti6Al4V and (b) Passivated-native oxide coating on Ti6Al4V. Ti_xO_y refers to nonstoichiometric titanium oxides

impedance response of the sol-gel coating. Taking into account the nature of the sol-gel coating, the impedance response cannot be simply represented by the Randles circuit. The film capacitance was described by a constant phase element (CPE), which gives more detailed information about the non-ideal dielectric properties of the coating. Using the CPE, errors can be minimized because it takes into consideration that experimentally, the barrier film never exhibits the theoretically expected phase shift of -90° and a slope of -1 for an ideal dielectric. The impedance representation is given as

$$Z(\text{CPE}) = [Q(j\omega)^n]^{-1}$$

Where j is the current density, ω , the rotation rate, and n , the dimensionless model parameter. Also, $j = \sqrt{-1}$, $\omega = 2\pi f$, and the exponent of the n is related to a nonequilibrium

current distribution due to surface roughness or fractal geometry (surface inhomogeneity) and Q is a constant representing pure (true) capacitance of the barrier film for $n = 1$.³ The chi square values (χ^2) at 10^{-4} indicated excellent agreement between the experimental and simulated values, using the CPE. The results of the modeling are shown in Table III. These values are consistent with the known long-term performance and aging properties of these alloys.

Potentiodynamic Polarization Test. Representative potentiodynamic polarization plots are presented in overlaid format in Figure 8. The calculated E_{corr} and I_{corr} values are shown in Table IV. The potential, E_{corr} ($p = 0.123$) and I_{corr} ($p = 0.508$) values again did not differ significantly among groups. The E_{corr} values were active and the I_{corr} values were very consistent even at the nA cm^{-2} range. The calculated E_{corr} , I_{corr} , and E_{bd} values are shown in Table IV.

In Vitro Apatite Nucleation in SBF. To determine the effect of SBF on biocorrosion properties of the sol-gel coating, the substrates were immersed up to 25 days in SBF. The concentration of both ions in relation to the immersion period is shown in Figure 9. Both substrates have Ca and P concentrations lower than that of the original SBF, which indicate the deposition of these ions on the first day. However, Ca was deposited on the sol-gel coated samples at levels higher than the passivated samples on day 1 ($p = 0.001$) and day 14 ($p = 0.000$) while the P concentration was significantly higher at day 4 ($p = 0.000$), as indicated by the lower concentrations of these ions in the test solutions (Figure 9). The concentrations of Ca and P also decreased in the control SBF solutions but these remained higher than those obtained in the test solutions for each time point. The data in Table V shows the rate of release of Ti, Al, and V in SBF. The dissolution rate was calculated by dividing the concentration of the ion measured per exposed surface area of the sample by the elapsed immersion time. The levels of Ti released from the passivated substrates at days 1, 4, and 25 ($p < 0.05$) were significantly lower when compared with that from sol-gel coated substrates but the Al and V concentrations were not significantly different in both test solutions throughout the time period. Initially, the dissolution process occurs fast and then reaches a steady state or a slower release rate by day 25. The elemental composition by EDS shown in Table VI indicates the deposition of calcium and phosphate on both substrates. Both contained nonstoichiometric apatite, in accordance with other studies.¹⁸ These calcium phosphate deposits were also confirmed by SEM (not shown).

DISCUSSION

The surface properties of coating materials have important implications on both short- and long-term performance and bioactivity of an implant device. Properties of the oxide film such as stoichiometry, defect density, surface topography, and crystal structures determine long-term corrosion and bi-

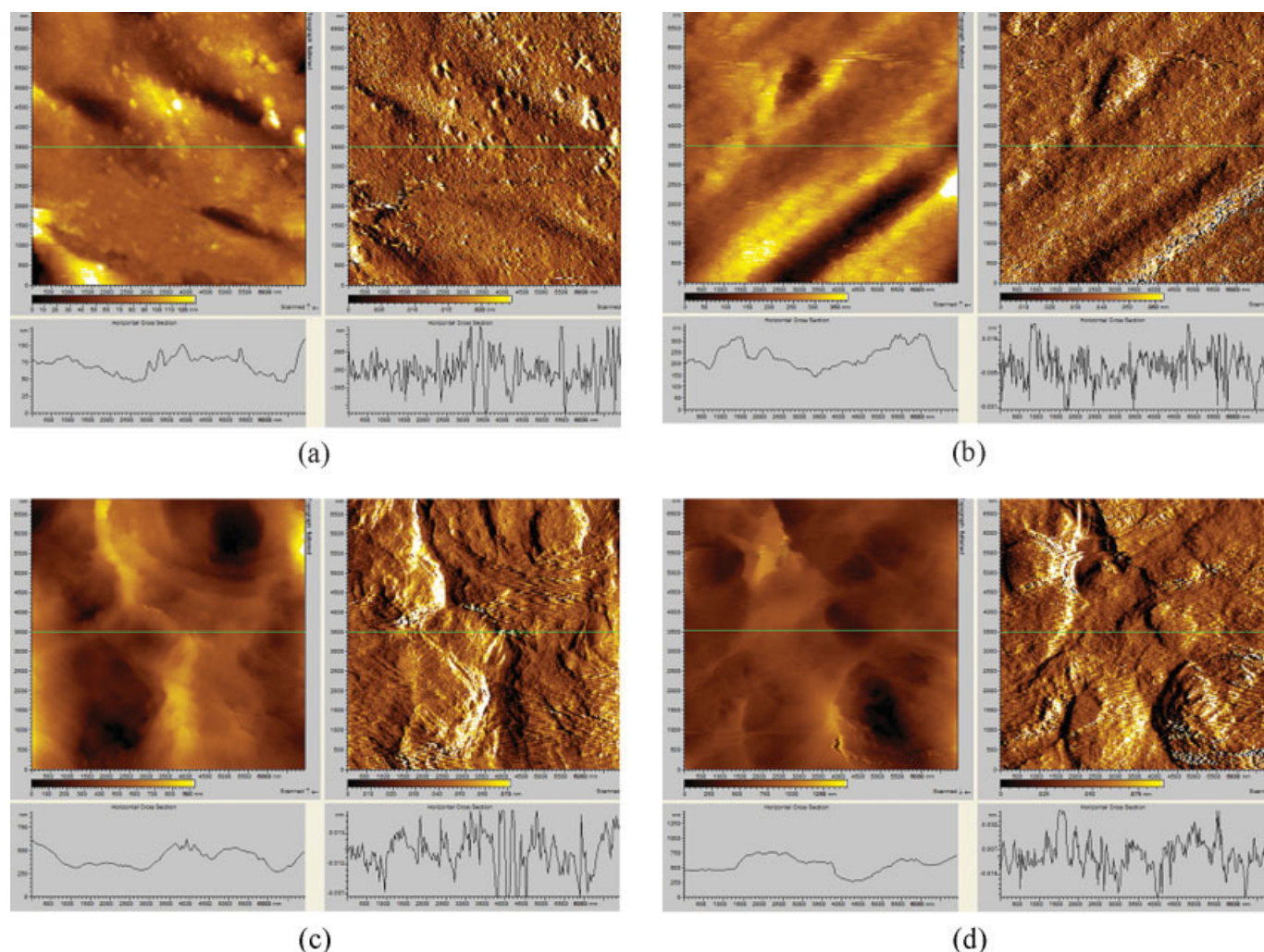


Figure 4. AFM microtopography showing height and phase images (MAC mode) of (a) clean (as polished), (b) passivated, (c) hydroxylated, and (d) sol-gel coated Ti6Al4V (7 μm × 7 μm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ological interactions with alloy implants.³ Although most macroscopic and bulk properties measured show that the passivated and sol-gel derivatized alloys have nearly similar properties, several indicators show that long-term properties will eventually be different.

XPS and Morphology Studies

Firstly, the composition data show that the sol-gel coatings have predominantly stoichiometric TiO₂ with abundant OH

TABLE II. Average Rms Roughness and Maximum Peak to Valley Distance of substrates at 7 μm × 7 μm

Sample	RMS Roughness (nm)	Max Peak-valley Distance (nm)
Clean	61	385
Passivated	66	381
Hydroxylated	149	787
Sol-gel coated	385	2269

groups. On the other hand, the OH content of the native titanium oxide comprises only 16% of the surface oxygen.³⁴ During rinsing and hydrolysis, water replaces the alkoxide groups to form Ti—OH. The iterative hydrolysis and chemisorption process leads to more hydrated Ti and forms a Ti—O—Ti network by surface-initiated nucleation and particle addition.²⁴ Considering the amorphous, hydrated nature of the gel, water or small molecules from the organic solvent can remain within the open structure unless drying is optimized. This, in part, accounts for the high carbon content observed on sol-gel coated substrates. The presence of organic moieties (—OH, C—O, —CH₃, etc) in such noncalcined sol-gel derived oxides increases roughness^{14,35} and as will be explained later, contributes to its biocorrosion property.

Piranha acid regenerates a fresh oxide surface on most oxidizable metal surfaces, e.g. oxides of Si-wafers. As a pretreatment in the study, it also increases the hydroxyl content of the native titanium oxide.³⁰ As expected, this treatment also altered the morphology of the alloys based on microtopography measurements by AFM. The strong oxidiz-

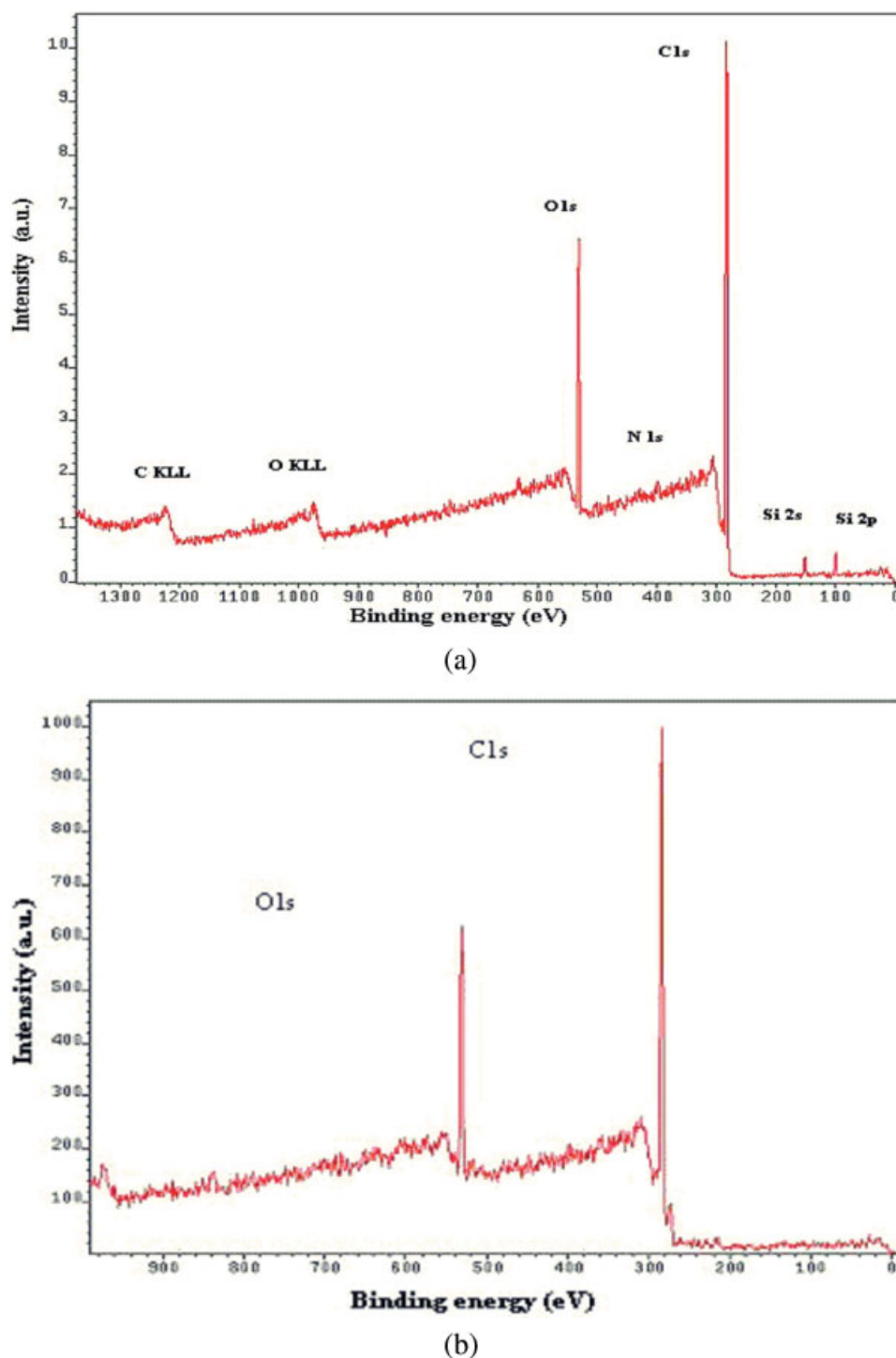


Figure 5. XPS analysis of studs after tension pull test of pull bonded to (a) passivated (b) sol-gel Coated substrates. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ing reagent not only removes the native oxide layer and embedded contaminants, it also roughens the surface.³⁶ This roughness was further increased after sol-gel processing. We have recently shown that this was due to the formation of micro- and mesopores along the surface.^{31,33} The influence of microtopography and roughness from sol-gel processes on cell behavior and adsorption of pro-adhesive proteins medi-

ating cell attachment or apatite formation have been reported by our group and others.^{19,23,33,37,38} The observed variation in roughness values for polished and passivated surfaces compared to those reported by others is due to differences in the scan area, scanning mode, hydrophobicity, and frictional forces which can affect sample-tip interaction, etc. in AFM.^{39,40} An advantage of the Magnetic-AC (MAC) mode

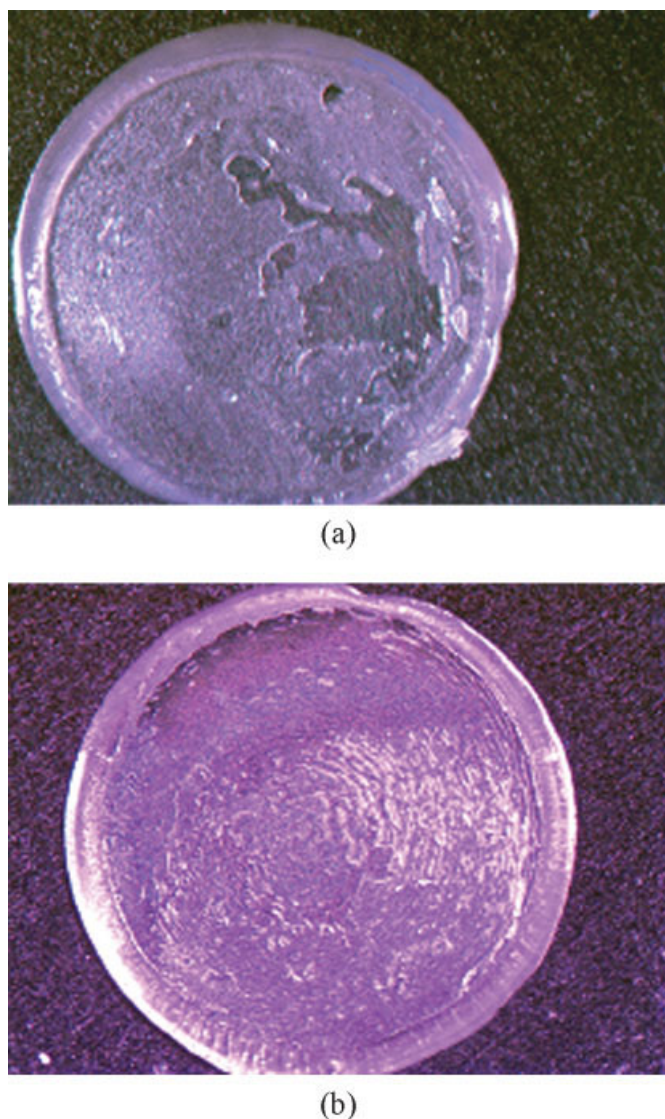


Figure 6. Optical micrographs of substrates after adhesion pull testing procedure of (a) passivated and (b) sol-gel coated substrates. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

used for imaging these surfaces is the sensitivity towards “soft-materials” and a noncontact procedure. Thus, the MAC mode AFM provided invaluable evidence that sol-gel deposition, in combination with hydroxylation of Ti alloy surfaces, produced a surface roughness and topography significantly different from either simple hydroxylation or passivation of these surfaces.

Impedance Spectroscopy

The coatings were evaluated by EIS to detect the evolution of the protective film and determine possible mechanisms of corrosion.¹⁴ This is a very useful and nondestructive method for evaluating electrochemical phenomena at the solid/electrolyte interface. As shown by the shapes of the curves, the impedance spectra consists of three frequency regions refer-

ring to the high, intermediate, and low frequency values. The high frequency plateau of the Z at $> 10^4$ Hz, with the phase angle approaching 0, yields the value of the electrode ohmic resistance, $I\Omega$, which includes the parameters: electrolyte resistance, apparatus geometry, impedance of the conductors and the reference electrode. The intermediate frequency region (10^3 – 10 Hz) has the maximum phase angle and the log Z vs log f slope approaching -1 . These impedance responses correspond to the capacitive behavior of the electrode and describe the dielectric properties of any electronically conducting surface film. The low frequency region (> 10 Hz) detects the electron charge transfer process, the mass transfer (diffusion or migration) processes, or other relaxation processes taking place at the film–electrolyte interface or within the pores of the surface film.³ The capacitive behavior, which decreased with low frequencies, and the high values of Z ($> 10^6 \Omega \text{ cm}^2$) at the lowest frequencies of sol-gel coating indicate good dielectric and protecting properties of the oxide. The slightly higher phase angle value of the sol-gel coating at lower frequency may indicate in addition, the presence of pores and relaxation or diffusion effects inside these pores. This was further verified by the roughness and microtopography of the substrates, as determined by AFM. However, the similarity of the curves with the passivated and the controls indicate that the impedance response was dominated by the titanium dioxide (TiO_2) properties. The similarity of the barrier film is further supported by the comparable adhesive strength with the passivated substrate. The tensile bond strength of heated resin adhesive to alumina (stud pin) was reported to be $\sim 77 \text{ MPa}$.¹⁷

Adhesion Properties

The specimens failed at the aluminum–epoxy and film–epoxy interfaces as shown by microscopy. This indicate a mixture of adhesive and cohesive failure modes that may arise from various causes, including difference in surface energy, stretching of bonds, morphology, and structure of the oxide. The strong binding of the film to the alloy substrate, which was also comparable to the adhesive strength of the passivated substrate, is mainly attributed to the strong Ti–O–Ti bonds of these alloys. The sol-gel process induced the surface condensation and structural relaxation of the bonds, which further strengthened the film’s network and adherence to the substrate. A film is considered to bond strongly to titanium metals if the adhesion strength is higher than pure titanium casting surfaces (tensile strength, $> 55 \text{ MPa}$). Also, the value reported here was higher than reported values for thin sol-gel derived silica on pure titanium dental casting.¹⁷ The difference in values can be attributed to composition, film thickness, and presence of density gradient, which can be further optimized. Since the surface sol-gel processed film is thinner than the oxide produced by a bulk coating technique,¹⁷ film condensation and substrate adherence is ex-

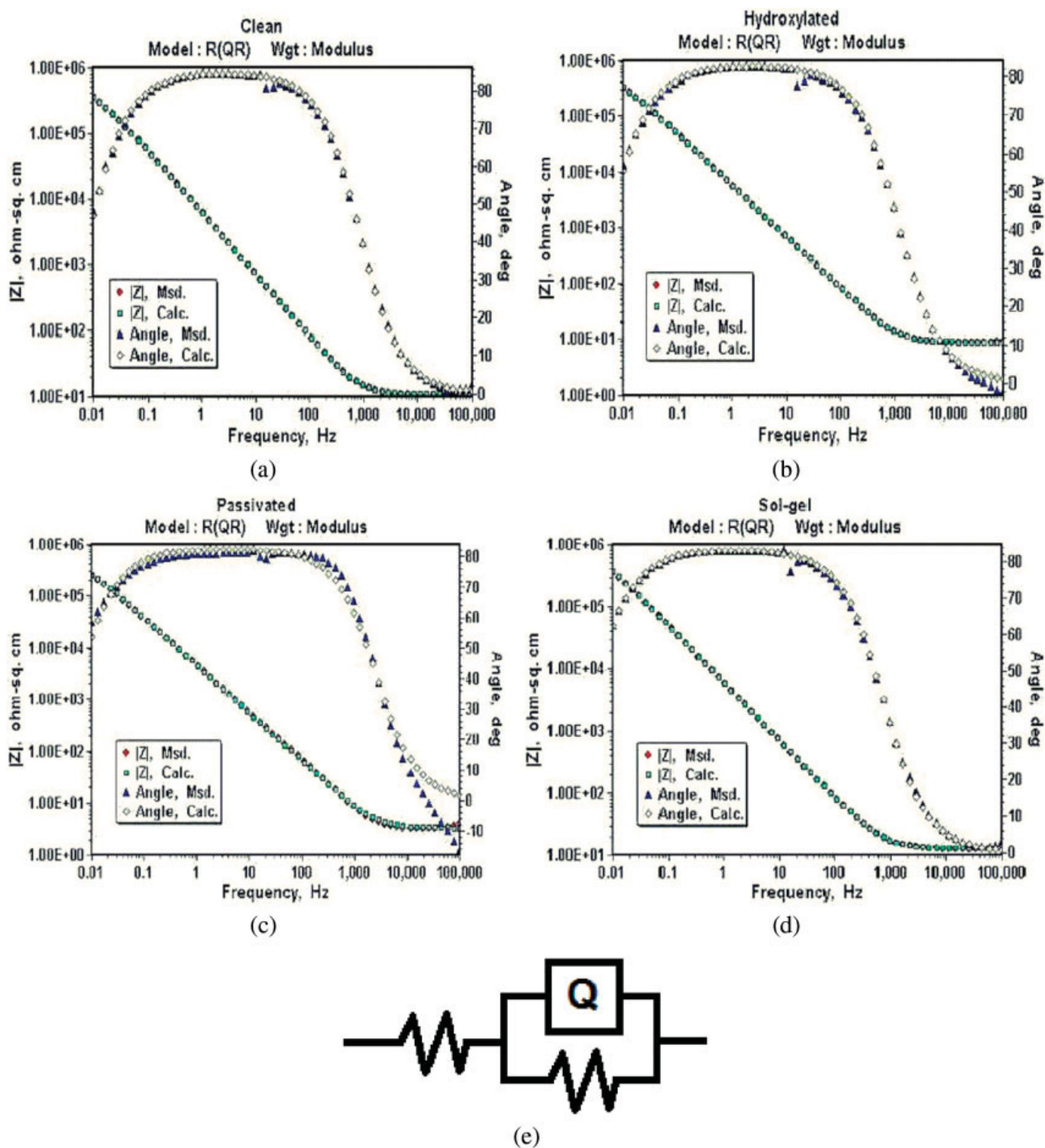


Figure 7. EIS curves of (a) clean, (b) hydroxylated, (c) passivated, (d) sol-gel coated Ti6Al4V, and (e) Equivalent electric circuit model. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

pected to be more uniform. Essentially, the main result that can be concluded is that the adhesion properties of the passivated and sol-gel coated substrates are again nearly the same.

Potentiodynamic Polarization Tests

The polarization curves for all samples show potential independent current densities characteristic of “valve-metal” behavior of titanium. This suggests a high-field mechanism for

TABLE III. Values of the Electrical Equivalent Circuit Elements Corresponding to the Fitted Function for the Ti6Al4V Spectra (sample size, $n = 3$)*

Sample	$R1$ (Ω)	$Q2$ (μF)	n	$R2$ (M Ω)	χ^2 (10^{-4})
Clean	12 (5)	28 (3)	0.93	0.52 (0.07)	3.95
Hydroxylated	11 (1)	29 (6)	0.92	0.76 (0.22)	5.99
Passivated	9 (3)	32 (9)	0.92	0.78 (0.24)	3.96
Sol-gel	12 (4)	31 (3)	0.93	0.86 (0.17)	4.36

* Values in parenthesis represent standard deviation with $n = 3$ sampling.

ionic conduction across the oxide film.² Both passivated and sol-gel coated substrates showed similar corrosion behavior in physiological Hank's balanced salt solution, that is, very low corrosion rates. The open circuit potential was fairly noble and the material translated directly into a stable passive behavior.⁴¹ Since the E_{corr} is an indicator of the stability of surface conditions, less variability in E_{corr} values from different samples is indicative of a more consistent surface processing. Since I_{corr} is a relative measure of corrosion and relates to how much material will be lost during the corrosion process, the higher the I_{corr} the more material is lost.⁴ Although the polarization curve of the sol-gel coated substrate is similar to the passivated substrate, the interpretation might be different because of the nature of the coating. The corrosion behavior exhibited by the sol-gel coating indicates that the surface topography and roughness, for a 5-layer sol-gel oxide, did not significantly affect the ability of the film to provide passivation in physiologic solution. One concern is that because of the pores and low thickness of the film, corrosion processes may be induced through these defects along the film.

However, since a passive underlayer is present due to the acid etching process, the corrosion resistance was not significantly affected. The oxide thickness reported here is in agreement with another study wherein the corrosion resis-

tance of sol-gel coated CpTi and Ti6Al4V were increased with oxide thickness of approximately 100 nm.⁴² It was thought that corrosion products can accumulate in the pores of sol-gel coated SS, causing the resistance of the film to increase with time.¹⁷

As noted by other studies, a low sintering temperature is usually preferred for sol-gel coatings to preserve their hybrid character.^{17,23} From impedance studies, Gallardo et al. found that Z increased with the $-\text{CH}_3$ content of a low temperature sintered sol-gel coating. The higher Z can be related to a strong barrier effect and decreased probability of microcracking due to higher secondary compound content and plasticity.¹⁴ In this study, it was found that the sol-gel coating in its amorphous noncalcined form exhibits good impedance and corrosion behavior, similar to the oxide film of titanium passivated by conventional methods. It is not known though, whether the $-\text{CH}_3$ content contributes to the bioreactivity or the ability of the sol-gel coated substrate to nucleate calcium phosphate. The effect of heat and drying on the nature of the sol-gel coating will be the subject of future studies. The ability of sol-gel derived oxides, in general, to promote calcium phosphate nucleation has been attributed to the presence of higher Si-OH or Ti-OH content.¹⁰

In Vitro Apatite Nucleation in SBF Studies

In previous studies, it was hypothesized that Ti hydrolysis was hastened by promoting exchange of calcium and phosphate. A high volume and distribution of mesopores (2–50 nm) was also shown to favor hydroxyapatite nucleation on sol-gel derived silica gels immersed in SBF.²⁰ A negatively charged surface producing an electric double layer with an increased number of cations have a direct influence on apatite nucleation.³⁹ It has been shown that titania gel with rougher but equal porosity to a titania-silica gel promoted greater nucleation of apatite.³⁹ The decrease in Ca and P concentra-

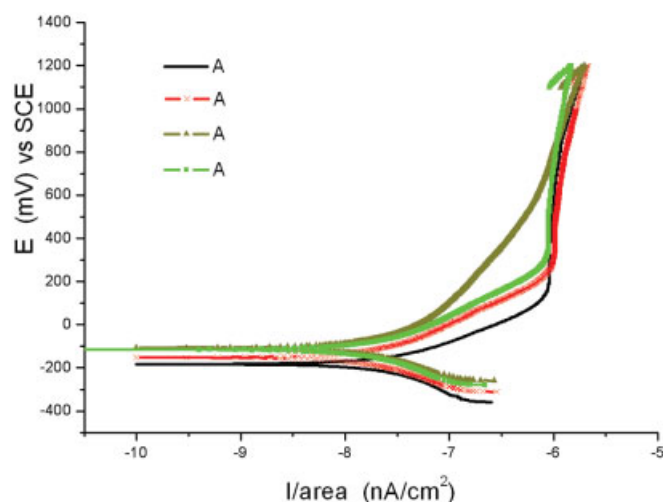


Figure 8. Polarization curves in overlaid format. Polarization analysis was also done on clean and hydroxylated substrates to determine their contribution to the system response. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV. Potentiodynamic Polarization Test Results (sample size, $n = 3$)*

Sample name	E_{corr} (mV) vs SCE	I_{corr} (nA cm $^{-2}$)
Clean	−168 (19)	61 (36)
Hydroxylated	−129 (11)	26 (5)
Passivated	−87 (17)	46 (40)
Sol-gel	−105 (45)	39 (9)

* Values in parenthesis represent standard deviation with $n = 3$ sampling.

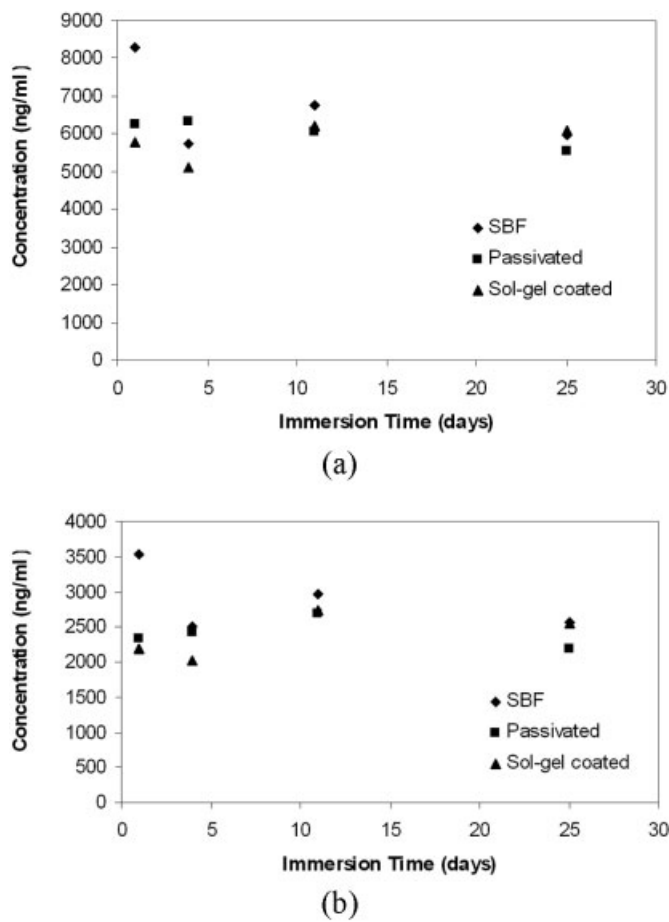


Figure 9. Concentration of Ca, P ions in SBF. (a) Ca and (b) P concentration in SBF. The level of Ca and P deposited on the sol-gel coated substrate was significantly higher ($p < 0.05$).

tions in SBF and the deposition of these ions on the sol-gel coated substrates early in the immersion period show that the sol-gel coated substrate induces formation of nonstoichiometric apatite on the surface.¹² This is especially significant when one considers that the success of osseointegration is defined by tissue-material interaction during the first few days of implantation. Because of the nature of a hydrated Ti—OH network in the sol-gel derived film, the electrostatic attraction of Ca and hydrogen bonding or chelation of phosphate group results in the accumulation of Ca and P ions within the hydrated titania.¹² Thus, the precipitation and dissolution of Ca and P ions on the implant surface is a dynamic process, as explained by other studies.^{18,21,38} We also found that the

TABLE V. Rate of Release of Ti, Al and V in SBF (ng/mL cm²)

Days\Ions	Passivated			Sol-Gel coated		
	TI	AL	V	TI	AL	V
1	32	7	4	49	9	6
4	65	14	8	89	20	10
11	66	41	8	90	52	11
25	97	49	14	111	58	14

TABLE VI. Elemental Compositional Analysis by EDS after Immersion in SBF

Sample	O	Al	P	Ca	Ti	V	*Ca/P
Passivated	17.34	8.95	0.22	0.46	69.41	3.64	2.09
Sol-gel	58.29	4.44	0.86	1.15	34.41	0.85	1.34

* Ca/P is the ratio of calcium to phosphate.

deposition of Ca and P on passivated substrates could be due to the reactivity of O with Ti and the electrostatic attraction for Ca. (The isoelectric point of Ti is $pI = 6.0-6.3$). In this study, it appears that the decrease in concentrations of Ca and P in control solutions of SBF after 25 days is due to deposition of these ions at the bottom or sides of the tube. SBF is a metastable solution that has been known to form critical nuclei and precipitate apatite only in the presence of a chemical stimulus.¹⁸ Since the culture tubes were not expected to react with the SBF, we speculate that the decrease in concentration of ions is due to the lack of physical stimulus (e.g. agitation, exchange, etc.) that promotes precipitation of particles when compared with the influence of more reactive surfaces sites. This highlights the importance of using experimental systems that approximate the dynamic processes occurring *in vivo*. An extended incubation time may give a more conclusive precipitation/dissolution kinetics of the ions. It may also allow elucidation of long-term compositional differences between the passivated and sol-gel coated substrates.

The presence of alloying elements on the metal oxide film may have either a beneficial or deleterious effects depending on the following factors: (1) affinity of the component metals for each other and for nonmetal species, particularly oxygen; (2) diffusion rate of atoms in the alloy and ions in the oxide; (3) the mutual solubility in the oxidation layers; and finally (4) the relative volumes of the various phases.³ The presence of Al on the surface oxide of Ti6Al4V or the associated residual stresses transferred to the oxide during surface treatment can result in increased reactivity of the surface and decreased resistance to dissolution.⁹ Furthermore, it has been shown that Ti, Al, V ions released can inhibit apatite formation *in vitro*.⁴³ The dissolution process has been proposed to occur across a number of layers including the metal oxide layer, the oxide/liquid interface, the boundary layer at the oxide/liquid interface composed of surface complexes, serum proteins, hydrated oxides, and the bulk liquid.⁹ Biological fluids consist of various ions that may aggressively react with the surface of titanium. As a dielectric film, the passive oxide supposedly maintains the integrity of the surface. But because of the dynamic processes occurring *in vivo*, particularly where an implant is involved, some corrosion and dissolution of ions can occur. In general, the concentration of Ti, Al, V ions released in SBF in our study were lower when compared with what others have found in other physiologic solutions.^{8,9} In another study, It has been found that the Ti ion concentration released in cell culture medium by passivated substrates was found to be 2× lower than the values reported.⁴⁴

As for Ti ion released from the sol-gel coating, our results show that the dissolution behavior of Ti6Al4V vary with composition of the corroding medium. Nevertheless, these values are in the range of concentration observed by other studies on sol-gel derived TiO₂.^{17,45,46} The long term effects of the higher release rate of Ti from sol-gel coated substrates, compared with passivated substrates, are not known but the increased hydration of titania early in the dissolution process may enhance attraction for Ca in SBF and the formation of a "boundary" like layer that mediate the ion exchange process as mentioned.^{12,46,47} In summary, high OH content, different degrees of ordering within the oxide, anisotropic behavior from preferred dissolution sites (due to higher sub-stoichiometric oxides), and oxide thickness on the sol-gel coated substrate, all influences this enhanced bioreactivity.⁸

CONCLUSIONS

We have investigated the differences between biocorrosion and bioreactivity properties of simple passivated and sol-gel, SSP coated titanium alloy substrates relevant for implants. The sol-gel derived film does not significantly alter the adhesion, corrosion, dielectric properties or release of metal ions from the surface. However, a significant difference was observed in the ability to promote calcium phosphate deposition and release of Ti ion in SBF. This dissolution behavior of the alloy was significantly influenced by the properties of the surface. In agreement with other studies, we attributed our results to the presence of a stable TiO₂ layer, which minimized the release of other elements from the alloy, and to surface hydroxyls (OH), which promoted nucleation sites for calcium phosphate deposition. The stable layer, which is common to all the substrates used, is characteristic of titanium alloys. On the other hand, the presence of greater OH groups and pores on the sol-gel coated substrates increased the hydrolysis of surface Ti and attraction for Ca and P. Given that the sol-gel derived oxide performed well even with only 5 layers, we can expect further optimized properties with other thicknesses or composition. Thus, this thin film coating may be clinically useful in enhancing the bioactivity of implants. By incorporating drugs, growth factors, enzymes, etc. in the layer-by-layer process, it is possible to find applications in drug delivery and tissue engineering. Investigation of other nanostructured composites of this sol-gel derived film is currently being undertaken by our group.

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