

Article

MOCVD Nano-Structured TiO₂ Coatings for Corrosion Protection of Stainless Steel in Accelerated Sulfuric Acid

Héctor Herrera Hernández ¹, Jorge A. Galaviz-Pérez ^{2,*}, María Guadalupe Hernández Cruz ² ,
Jorge Morales Hernández ³ , Héctor J. Dorantes Rosales ⁴, J. J. A. Flores Cuautle ^{5,*} , G. Lara Hernández ⁶ 
and Manuela Díaz Cruz ⁴

- ¹ Laboratorio de Investigación en Electroquímica y Corrosión de Materiales Industriales, Universidad Autónoma del Estado de México, C.U. UAEM Valle de México, Blvd. Universitario s/n, Predio San Javier, Atizapán de Zaragoza 54500, Estado de México, Mexico; hherrera@uaemex.mx
- ² División Académica Multidisciplinaria de Jalpa de Méndez, Universidad Juárez Autónoma de Tabasco (UJAT), Carretera Federal Villahermosa–Comalcalco Km. 27 s/n, Ribera Alta, Jalpa de Méndez 86205, Tabasco, Mexico; mguadalupe.hernandez@ujat.mx
- ³ Centro de Investigación y Desarrollo Tecnológico en Electroquímica (CIDETEQ), Parque Tecnológico Querétaro s/n, Sanfandila, Pedro Escobedo 76703, Querétaro, Mexico; jmorales@cideteq.mx
- ⁴ Departamento de Ingeniería Metalúrgica, ESIQIE, Instituto Politécnico Nacional, S/N, UPALM Edif. 7, Zacatenco, Ciudad de México 07308, Mexico; hdorantesr@ipn.mx (H.J.D.R.); mdiazc@ipn.mx (M.D.C.)
- ⁵ Secihti/Tecnológico Nacional de México/I.T., Orizaba 94300, Veracruz, Mexico
- ⁶ Tecnológico Nacional de México/I.T., Orizaba 94300, Veracruz, Mexico; larag_139@hotmail.com
- * Correspondence: jorge.galaviz@ujat.mx (J.A.G.-P.); jflores_cuautle@hotmail.com (J.J.A.F.C.)

Abstract

This study reports that titanium nanoparticles can be used as a surface coating to enhance the corrosion resistance of 316 stainless steel. It specifically examines the influence of the deposition temperature (T_{dep}) on the coating's structural and morphological properties, including corrosion behavior. TiO₂ nanoparticles were thoughtfully deposited on steel substrates at temperatures of 300, 400, and 500 °C using a horizontal hot-wall tubular reactor. This equipment was expertly engineered at the CIDETEQ laboratory through the metal–organic chemical vapor deposition (MOCVD) concept. Titanium isopropoxide [Ti(OC₃H₇)₄] was used as the precursor for the coating synthesis. Structural analysis was conducted using X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), and scanning electron microscopy (SEM). Corrosion performance was evaluated under accelerated conditions in 0.5 M H₂SO₄ using potentiodynamic anodic polarization (AP), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). The corrosion test indicates that increasing T_{dep} significantly differentiates the coating morphology and improves corrosion resistance. AP revealed that the pitting potential (E_{pit}) shifted to more positive values, ranging from +1.4 to +1.5 V. CV voltammograms indicated that coated samples had lower passive current densities ($I_p \approx 10^4$ to 10^5 A/cm²) than the bare substrate. EIS analysis demonstrated that the coating deposited at 500 °C processed the most favorable electrochemical performance, resisting corrosion for over 28 days. This coating achieved the highest electrical resistance (297 kΩ·cm²) and the lowest capacitance (2.7 μF/cm²), attributed to the formation of a crystalline anatase phase composed of pyramidal-like nanoparticle agglomerates (~40 nm). The dense packing structure effectively blocks charge-transfer pathways, restricting electron and ion transfer. Finally, MOCVD-based chemical surface modification with TiO₂ nanoparticles is considered an innovative method to improve the corrosion resistance of stainless steel, thereby prolonging its durability under accelerated sulfuric acid exposure.



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Keywords: nano-structured TiO₂ coatings; stainless steel protection; accelerated corrosion; sulfuric acid; MOCVD deposition method; corrosion resistance; morphology of TiO₂ coatings

1. Introduction

Stainless steel (SS) is a widely used metallic material, particularly in high-demand industrial applications. Its excellent properties and adaptability have made it the focus of extensive research interest. Among its wide range of SS alloys, 316 stainless steel (316SS) is considered an ideal material for chemical processing, petrochemicals, metal manufacturing, and the marine industry. Additionally, it is widely used in water treatment, food and beverage production, and, most notably, in biomedical and pharmaceutical applications. The rapid widespread implementation of this material in various industrial sectors, service industries, and broader community applications is primarily attributed to its outstanding corrosion resistance, high mechanical strength, favorable formability, and remarkable thermal and chemical stability [1–7].

The selection of this material is particularly promising for high-performance applications that demand resistance to corrosive chemicals and prolonged exposure to humid environments, where durability and structural integrity are essential [8–10]. Therefore, one of the reasons that stainless steel is considered extraordinary in resisting corrosion damage is that it contains about 16–18 wt.% of chromium (Cr) in the steel structure [11]. The crystal structure of stainless steel, with its face-centered cubic (fcc) lattice, facilitates the diffusion of chromium (Cr) atoms by altering the atomic arrangement, allowing Cr atoms to displace iron (Fe) atoms from the outer surface more efficiently. A high chromium content promotes this preferential displacement, enabling Cr atoms to react immediately with the oxygen (O₂) present in the outdoor environment. This reaction results in the spontaneous formation of a stable oxide layer on the surface, composed mainly of chromium oxide (Cr₂O₃) or oxyhydroxides [CrO_x(OH)_{3–2x}] as well as anhydrous products. The resulting film is so thin that it appears invisible to the naked eye. However, it serves as an effective barrier against ionic transport from chemical reactions, thus reducing active metal dissolution and maintaining surface integrity in many corrosive environments. Additionally, this protective layer possesses self-healing capabilities; that is, chromium oxide can spontaneously regenerate if it is locally disrupted or mechanically removed, thus still maintaining its protective function over time. Despite these properties, in highly aggressive environments, such as concentrated acid solutions (H₂SO₄ or HCl 1M) or physiological fluids containing NaCl and KCl, the passive layer may degrade or become locally disrupted, leading to a significant increase in corrosion susceptibility [12–20].

Based on the previous arguments, 316 stainless steel is susceptible to localized corrosion, particularly pitting, when exposed to highly acidic environments, which can severely compromise its structural integrity. This structural failure occurs when aggressive anions, such as chloride or sulfate, penetrate the passive chromium oxide film, locally disrupting it, initiating pit formation, and accelerating localized dissolution. Additionally, stainless steel undergoes sensitization when exposed to temperatures between 400 and 800 °C for prolonged periods [20]. During this heat treatment, chromium is depleted from the solid solution, forming chromium carbides at grain boundaries, thereby reducing the alloy's ability to sustain a protective passive layer. As a consequence, the material becomes vulnerable to intergranular corrosion, further compromising its durability in any acidic environments. In biomedical contexts, corrosion diminishes the biocompatibility functions of components manufactured from 316 stainless steel. The catastrophic failure of an implantable orthope-

dic 316SS screw may result from localized corrosion, which forms pits that compromise the component's structural integrity and functional performance. Surface degradation not only alters the mechanical stability of implants but can also release metallic ions (for example, Fe^+ , Ni^+ , Cr^+ , Mo^+) into the physiological environment. These ions have the potential to induce cytotoxic effects, inflammatory responses, or allergic reactions, thereby reducing tissue compatibility. Consequently, this type of degradation may result in adverse biological responses or provoke implant failure, thereby posing a serious risk to human health and patient safety [5,10,21,22].

To address this limitation, this research focuses on developing advanced protective surface coatings that have become a principal concern in materials engineering for biomedical applications exposed to corrosive environments, particularly for components manufactured from 316 stainless steel. Such coatings are intended to improve the electrochemical stability of stainless-steel substrates, thus increasing their corrosion resistance and prolonging their functional lifetime in physiological conditions. In the development of stainless steel coatings, Ni-Cr-Mo claddings are widely recognized for their thermodynamic stability in reducing corrosion conditions. Nonetheless, the use of Ni-Cr-Mo claddings presents a critical challenge due to the thermal stress generated by the Laser-based deposition method [23,24]. Additionally, tantalum thin films are also an effective solution, providing a ductile coating for stainless steel. However, it is important to note that this coating carries a high corrosion potential, which can lead to failures, particularly in the pores of scratches [25].

Among surface engineering approaches, nanostructured titanium dioxide (TiO_2) coatings have received considerable attention over the last two decades due to their chemical stability, photocatalytic activity, thermal durability, biocompatibility, and, most importantly, their corrosion resistance [26–28]. These attributes make TiO_2 a highly suitable material for protecting 316SS steel used in implantable medical components and demanding industrial conditions. In particular, nanostructured TiO_2 coatings form a compact, uniform barrier layer that effectively restricts the transport of aggressive ions and electrons, improving the corrosion resistance of 316SS [28]. TiO_2 coatings can be synthesized by several methods, including sol–gel, spray pyrolysis, thermal spraying, electrostatic spray, reactive magnetron sputtering, pulse laser deposition, and dip coating [29–36]. Among these approaches, Metal–Organic Chemical Vapor Deposition (MOCVD) offers significant advantages for producing high-purity, dense TiO_2 films by carefully controlling deposition variables, including temperature, precursor chemistry, pressure, and gas flow rates. MOCVD provides precise control of film morphology, crystallinity, and phase composition, making it ideal for stainless steel substrates [37–40]. This method enables the deposition of uniform films with strong adhesion and customizable functional properties, which are essential for biomedical and industrial applications.

Nevertheless, despite the benefits of MOCVD, few studies have examined [41,42] the influence of deposition temperature (T_{dep}) on the corrosion resistance of deposited coatings, particularly under prolonged immersion in acidic conditions. Furthermore, the relationship between microstructural characteristics and the corresponding electrochemical performance remains insufficiently explored in the current literature. In conclusion, this study aims to evaluate the influence of MOCVD deposition temperature (300, 400, and 500 °C) on the structural, morphological, and electrochemical properties of TiO_2 nanoparticles forming coatings on 316SS substrates. This research uses prolonged exposure to an acidic environment to accelerate corrosion, thereby facilitating a comprehensive assessment of the effects of deposition parameters.

2. Experimental Procedure

2.1. Preparation of TiO₂ Coatings

TiO₂ coatings were deposited onto stainless steel (316SS) substrates through the use of a horizontal hot-wall Metal–Organic Chemical Vapor Deposition (MOCVD) reactor (CIDETEQ, Queretaro, Mexico), similar to that one depicted in Figure 1, located at the CIDETEQ Laboratory, Queretaro Unit [43,44]. The organometallic precursor selected for this deposition process was titanium tetra-isopropoxide (TTIP) [Ti(OCH(CH₃)₂)₄], with about 98% purity and a molecular weight of 284.22 g/mol. TTIP, supplied by Aldrich Chemical (Milwaukee, WI, USA), was provided as a liquid at room temperature and has a melting point of 20 °C. During the deposition process, TTIP precursor was evaporated at controlled temperatures between 40 and 100 °C (T_{prec}) and then carried into the tubular reactor using argon gas at a flow rate of 30 sccm. The precursor delivery system was maintained at 250 °C, providing optimal coating conditions for promoting uniform vapor distribution [40,44].

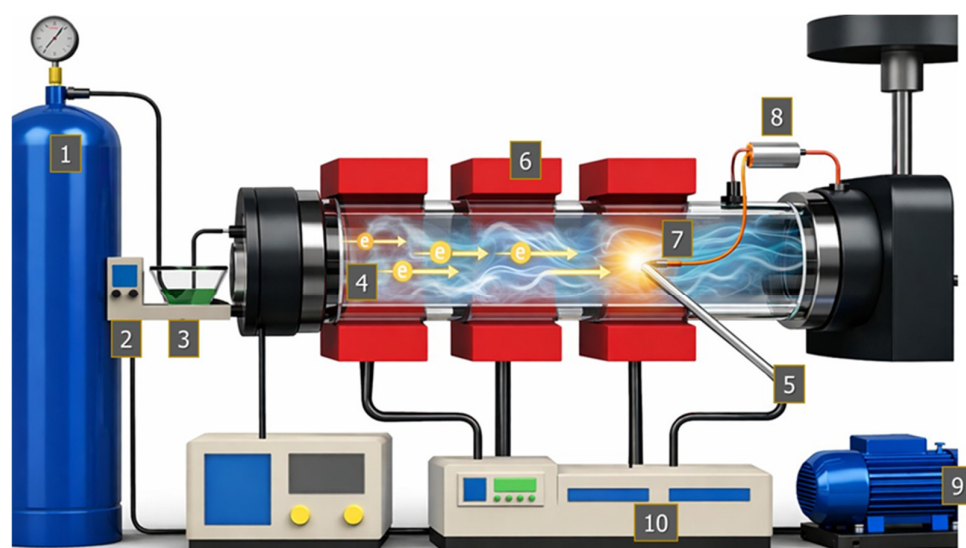


Figure 1. Schematic diagram of the MOCVD reactor used for TiO₂ thin film deposition on 316 stainless steel substrates. The apparatus consists of; (1) Argon gas container, (2) Thermal bath setup, (3) TTIP precursor bubbler reservoir, (4) Vapor intake to the reactor, (5) Thermocouple system, (6) Furnace heating zones, (7) Substrate holder, (8) Pressure valve, (9) Vacuum pump, (10) Temperature controller.

The deposition temperatures investigated were 300, 400, and 500 °C, with a fixed deposition time of 30 min, as reported in the literature [44,45]. The total reactor pressure (P_{tot}) was maintained at 1 Torr. The coating thickness was carefully controlled through the deposition time, with preliminary thickness estimates derived from the interference color observed on the coated surface. Selected samples were thoroughly analyzed using Scanning Electron Microscopy (SEM). Stainless steel 316 plates measuring 25 × 25 mm² and 1 mm thick were used as substrates. These plates were specifically chosen to minimize the risk of surface defects typically associated with mechanical damage. Before deposition, the substrates were ground successively using SiC abrasive papers, progressing through grit sizes of 180, 220, 360, 400, and 600. An effective degreasing procedure in ethanol using an ultrasonic bath, followed by rinsing with distilled water, is performed before the surface modification treatment. Table 1 provides a detailed summary of the experimental conditions used during deposition.

Table 1. Summary of the experimental parameters for TiO₂ coating deposition using the MOCVD reactor located at CIDETEQ Queretaro.

Parameter	Value/Description
Precursor	Titanium tetra-isopropoxide (TTIP), Ti(OC ₃ H ₇) ₄ , purity ≥ 98%
Vaporization temperature (T _V)	40 °C (bubbler heated to ensure precursor vaporization)
Carrier gas	Argon, high purity (99.999%)
Total reactor pressure	1 torr
Carrier gas flow rate	30 cm ³ /min
Substrate	316 of Stainless-Steel plates (25 × 25 mm ² , 1 mm thickness)
Substrate temperatures (T _{dep})	300–500 °C

2.2. Microstructural Characterization

The surface morphology, microstructure, and thickness of the TiO₂ coatings were analyzed using a JEOL JXA-8200 SEM equipped with WDS/EDS microanalysis detectors. Before analysis, the coated samples were mounted on conductive holders and sputter-coated with a thin gold layer to minimize surface charging during imaging. SEM provided high-resolution images of the coating surface and cross-sectional morphologies. At the same time, EDS allowed for semi-quantitative elemental analysis to confirm the presence and distribution of titanium. The phase composition and crystallographic structure of the deposited TiO₂ coatings were identified by X-ray diffraction (XRD) using a Siemens D-5000 diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 30 mA. Diffraction patterns were collected over a 2θ range of 10° to 80° at a scan rate of 1° per minute.

2.3. Electrochemical Measurements

The corrosion behavior of coated and bare 316 stainless steel samples was systematically evaluated using electrochemical impedance spectroscopy (EIS), potentiodynamic anodic polarization (AP), and cyclic voltammetry (CV) techniques. In corrosion testing, the most commonly used acids include nitric (HNO₃), hydrochloric (HCl), oxalic (H₂C₂O₄), citric (C₆H₈O₇), and sulfuric (H₂SO₄). Among these, sulfuric acid is often preferred due to its strong oxidizing properties, which facilitate the rapid dissolution of the metal matrix, particularly when chromium-rich carbides have precipitated at grain boundaries. It is effective for determining general corrosion rates. Additionally, sulfuric acid accelerates the breakdown of passive films by attacking the protective oxide layer on the metal surface. This characteristic allows for a clear differentiation in coating performance at varying deposition temperatures. For these reasons, a 0.5 M H₂SO₄ was chosen as the electrolyte for accelerated corrosion testing. Its aggressive nature makes it exceptionally suitable for evaluating the durability of protective TiO₂ coatings under corrosive conditions. This approach is consistent with previous studies on stainless steel corrosion and provides a reliable target for assessing protective efficiency [46,47].

All electrochemical measurements were conducted in an aqueous 0.5 M H₂SO₄ solution as the electrolyte at room temperature (25 °C), using a three-electrode electrochemical cell designed in the laboratory, as described by Herrera, H.H. et al. [48–52]. The cell configuration, shown in Figure 2, included a working electrode (WE) made of stainless steel, either coated or uncoated. The WE was positioned horizontally at the bottom of the cell, exposing a 1 cm² surface area directly to the electrolyte. A cylindrical 316 stainless steel rod served as the counter electrode (CE), and a saturated Ag/AgCl electrode served as the reference electrode (RE). Both the CE and RE electrodes were vertically suspended from the top of the cell and aligned parallel to the WE surface. To minimize phase-shift effects at high

frequencies during EIS measurements, a platinum wire was connected to a 36 μF capacitor and then placed in parallel with the RE tip. Before each electrochemical test, the open-circuit potential (E_{oc}) was monitored for at least 15 min until a stable value was reached. This experimental configuration provides reproducible and reliable electrochemical conditions for evaluating the corrosion resistance of coated and uncoated stainless-steel surfaces.

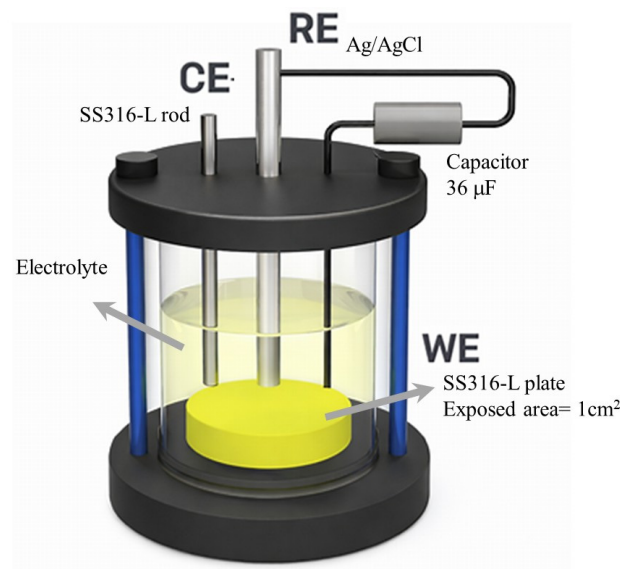


Figure 2. Schematic diagram illustrating the configuration of the custom-built three-electrode electrochemical cell designed by Herrera H.H. [48,49].

Electrochemical experiments utilized the following instrumentation: (a) BAS-Zahner IM6 electrochemical workstation for impedance measurements, (b) Gamry CMS105 potentiostat for open-circuit potential (OCP) monitoring and potentiodynamic anodic polarization (AP) experiments, and (c) Metrohm-Autolab PGSTAT100 potentiostat/galvanostat for cyclic voltammetry (CV) measurements.

EIS data were collected at the stabilized corrosion potential (E_{corr}) over a wide frequency range from 10^6 to 10^{-3} Hz, using a sinusoidal perturbation signal of ± 10 mV. Data acquisition was performed at five points per decade. The resulting Bode plots were fitted to appropriate equivalent electrical circuit (EEC) models using Z_{simp} Win software (Version 3.0) to extract quantitative electrochemical parameters, including solution resistance (R_s), charge transfer resistance (R_{ct}), coating resistance (R_c), double-layer capacitance (C_{dl}), and coating capacitance (C_c). For the anodic polarization experiments, the potential was swept from -250 mV below E_{corr} to $+1600$ mV (vs. Ag/AgCl) at a scan rate of 2 mV/s. These measurements were initiated strategically after the OCP reached a steady-state value, typically after about 15 min of immersion in the electrolyte. Additionally, cyclic voltammetry was recorded at a scan rate of 100 mV/s, covering a potential range from -500 mV to $+1600$ mV (vs. Ag/AgCl). These electrochemical techniques provided valuable information on the redox behavior, passive film stability, and susceptibility to pitting corrosion of the evaluated surfaces, contributing to a deeper understanding of their corrosion performance.

3. Results and Discussion

3.1. Microstructure and Morphology Analysis

Figures 3–5 show SEM images of TiO_2 nanoparticles deposited on 316SS plates at three deposition temperatures. For the 300°C coating, nanoparticles exhibit significant agglomeration into disordered clusters, resulting in a relatively smooth, fine-grained, cauliflower-like surface. This morphology is commonly observed in MOCVD coatings

at lower temperatures, as small quasi-spherical nanoparticles randomly form irregular clusters on the surface, lacking a preferred orientation pattern. This randomness deposition leads to amorphous nucleation, as clearly illustrated in the inset of Figure 3(b*). These closely packed clusters create a porous layer with a notable density of grain boundaries and vacancies, characteristic of low crystallinity. Cross-sectional SEM images in the insets of Figure 3(a*,b*) confirm the formation of a continuous coating with an estimated thickness of about 5 μm .

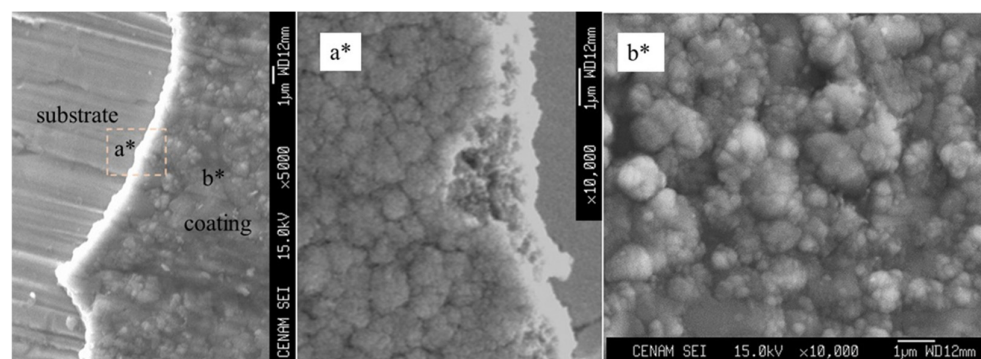


Figure 3. Surface and cross-sectional SEM images of coating deposited at 300 °C by MOCVD, exhibiting a porous structure with irregularly shaped clusters that form a disordered agglomerate. (a*) surface SEM image showing the porous agglomerated clusters, and (b*) cross-sectional SEM image highlighting the coating thickness and interface with the substrate.

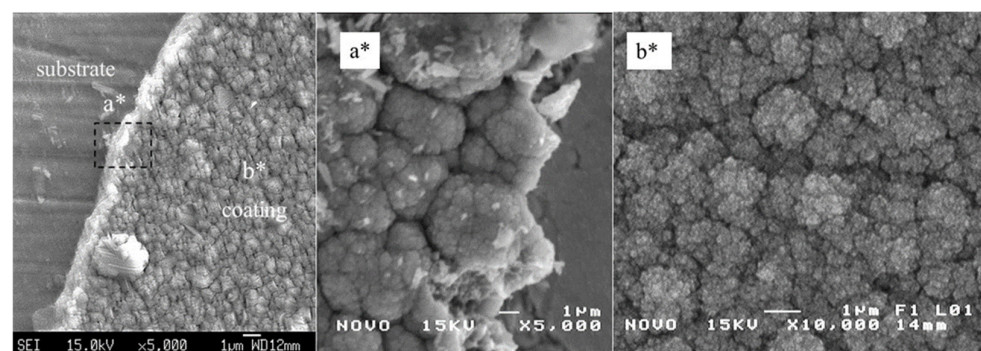


Figure 4. Surface and cross-sectional SEM images of coating deposited at 400 °C by MOCVD, exhibiting increased grain coarsening, a columnar structure, a roughened surface, and agglomerated morphology. (a*) Magnified SEM view showing coarse grains and columnar structure, and (b*) magnified SEM view of the surface region highlighting roughened and agglomerated morphology.

Additionally, it is noteworthy that moderate surface roughness and irregularities are evident in the inset of Figure 3(b*). These observations can be explained by the limited surface diffusion and incomplete crystallization at 300 °C. The thermal energy at this temperature is insufficient for adequate atomic mobility, resulting in incomplete structural arrangement during the coating growth.

However, when the deposition temperature approaches 400 °C, the coating morphology changes into a tightly packed, columnar structure, as shown in Figure 4. Insets of Figure 4(a*,b*) reveal a more textured surface, consistent with an intensification of diffusion mobility of precursor atoms through the metal surface, due to increased thermal energy activation. Consequently, this morphological transition of TiO₂ nanoparticles results in a more defined crystalline structure. In this sense, atoms nucleate at energetically favorable sites on the substrate, forming fine crystallites that subsequently grow into vertically aligned columnar structures, thereby enhancing coating density and thickness to approximately 10 μm . The cross-sections in insets Figure 4(a*,b*) show that the coating remains

well-adhered to the substrate, exhibiting a distinct granular microstructure and a relatively uniform nanoparticle network. These morphological features suggest that atoms diffuse with sufficient energy during the early stages of structural rearrangement at 400 °C, thereby facilitating the formation of a crystalline structure.

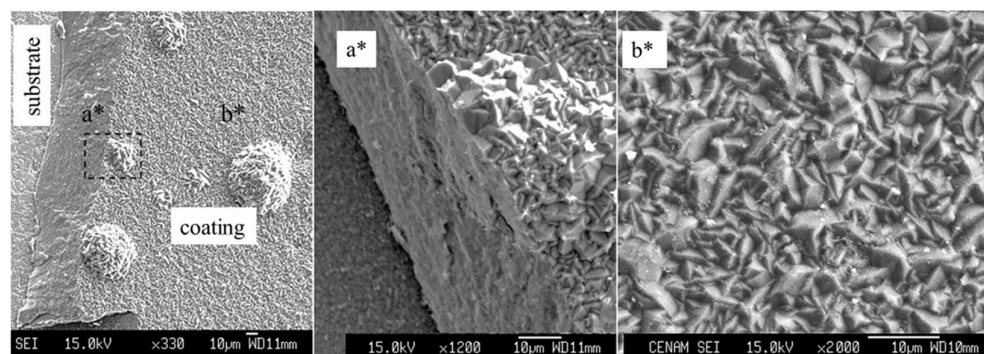


Figure 5. Surface and cross-sectional SEM images of coating deposited at 500 °C by MOCVD, exhibiting a highly crystalline structure with a distinct network of prismatic faceted crystals and a pronounced rough surface texture. The dotted frame indicates the region selected for magnification: (a*) Cross-sectional SEM image showing a rough prismatic crystalline structure, and (b*) surface SEM image highlighting densely packed faceted crystals with pronounced roughness.

At 500 °C, the coating undergoes distinct morphological changes, as noted in Figure 5. It shows a well-defined structural transformation due to increased thermal energy used in MOCVD deposition. At this temperature, diffusion promotes grain boundary migration, allowing atoms to rearrange into a more stable crystal facet configuration. Crystals grow in both lateral and vertical directions, leading to faceted shapes, typically pyramidal. The coating exhibits a highly crystalline structure, with a dense surface and a distinct network of faceted, platelet-like crystals consolidated into a prismatic appearance, as seen in Figure 5(b*). At this elevated temperature, atoms organize into anisotropic crystalline domains, and the structure transitions from amorphous to crystalline. Cross-sectional data Figure 5(a*) reveal a continuous, fully dense coating about 20 µm thick, demonstrating excellent coverage, substrate integration, and atomic packing. Notably, these results indicate that 500 °C is identified as the optimal temperature for producing a well-organized, high-coverage barrier layer on 316SS substrates.

The results show that the structure and morphology of the nanoparticles are significantly influenced by the substrate temperature (T_{dep}) during MOCVD deposition. Similar findings have been reported in other studies [53–57]. As the substrate temperature increases from 300 to 500 °C, notable changes in surface morphology occur. This is attributed to the thermal energy, which enhances precursor decomposition, increases surface diffusion rates, and improves crystallinity, ultimately altering the surface topography and internal structure of the coatings. In addition, the surface appearance of the coatings varies with film thickness. Coatings deposited at 300 °C appear dark, those deposited at 400 °C exhibit a gray tone, and coatings deposited at 500 °C develop a light-gray coloration. This color variation is consistent with optical interference effects resulting from the increasing thickness of the deposited coatings. Based on these observations, Figure 6 compares the surface structures of coatings deposited at 300 °C, 400 °C, and 500 °C. The SEM micrographs were taken at magnifications between 5000× and 10,000× to ensure comparability. The top schematic illustrations of Figure 6 represent the morphological evolution observed by scanning electron microscopy, showing the transition from a disordered cauliflower-like morphology at 300 °C to columnar grains at 400 °C, and finally to dense pyramidal faceting at 500 °C. The bottom row of the same figure shows the corresponding SEM

images, confirming a progressive increase in crystallinity and surface order with increasing deposition temperature.

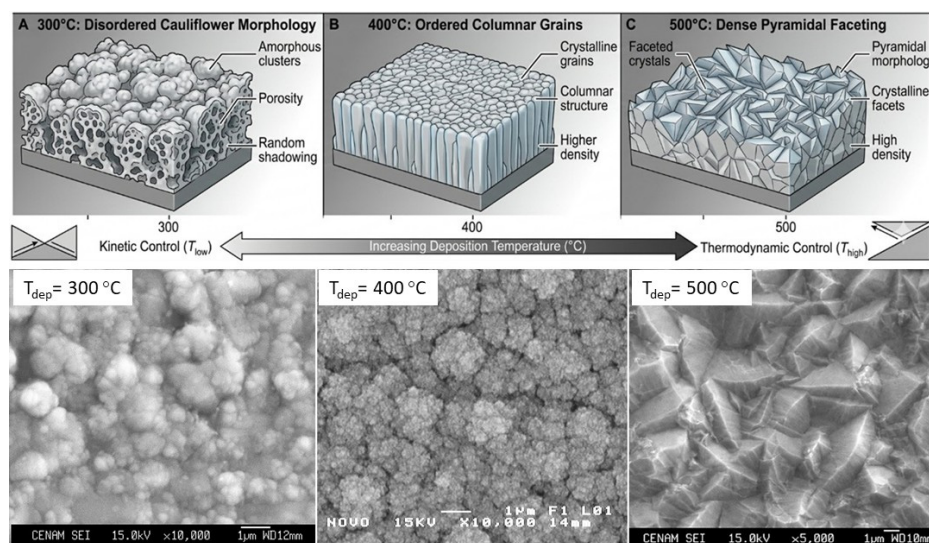


Figure 6. Schematic illustrations and corresponding SEM images of coatings deposited at different temperatures by MOCVD, showing the evolution of thin film morphology with increasing deposition temperature. (A) At 300 °C, disordered cauliflower-like morphology with amorphous clusters, random shadowing, and high porosity under kinetic control (T_{low}). (B) At 400 °C, ordered columnar grains with higher density, representing an intermediate morphology. (C) At 500 °C, dense pyramidal faceting with crystalline facets and high density under thermodynamic control (T_{high}).

Consequently, the coatings were analyzed by energy-dispersive X-ray spectroscopy (SEM-EDS) to determine their elemental composition. EDS spectra of the cross-sectional SEM image of the coating deposited at 400 °C, illustrated in the Figure 7(a*), clearly confirm the presence of titanium (Ti) as the only detectable constituent on the surface coating, related to the TiO_2 component. In contrast, the EDS spectra corresponding to Figure 7(b*), strategically located within the substrate (no coating), show characteristic signals for Fe, Cr, and Ni, which represent the principal alloying elements of the stainless-steel base alloy that was used as the substrate for coating deposition. These EDS spectra unequivocally highlight the distinct compositional differences between the coating and the underlying substrate, demonstrating the successful deposition of TiO_2 nanoparticles on 316SS at the specific processing temperature investigated.

3.2. X-Ray Diffraction Analysis

Figure 8 shows X-ray diffraction patterns for TiO_2 nanoparticles deposited at 300, 400, and 500 °C. The pattern signals indicate that under all MOCVD deposition conditions, the coatings consist exclusively of the anatase crystalline phase. Notably, the diffraction patterns are dominated by reflections associated with the metal SS substrate, as indicated by open circles (○). These reflections correspond to the characteristic diffraction planes of austenitic stainless-steel (Fe- γ) with a face-centered cubic (fcc) structure at the (111), (200), and (220), pattern (d*). At 300 °C, the anatase reflections (e*), marked with black triangles (▲), appear relatively weak and broad. This suggests partial crystallization in the TiO_2 coating with small crystallite size and a significant fraction of amorphous structure characterized by poorly ordered atoms. The broadening of these peaks indicates reduced coherence of diffraction domains and possible microstrain within the coating. In contrast, at 400 °C (pattern b*), there is a notable improvement in crystallinity, as evidenced by a substantial increase in the intensity and sharpening of the (101) reflection, which exceeds

that observed at the 300 °C sample. Such results demonstrate that phase progress, resulting from atomic rearrangement into a more ordered crystalline structure, occurs during high-temperature treatment. The principal anatase reflections appear on the (004), (200), and (211) planes. At 500 °C, the diffractogram exhibits the most intense and well-defined reflections, corresponding to the anatase phase, particularly the dominant (101) reflection located at $2\theta \approx 25.3^\circ$. This signal is characteristic of the anatase structure, as reported in the literature [37,41,53–57], and is associated with the highest degree of crystallinity in a preferential orientation.

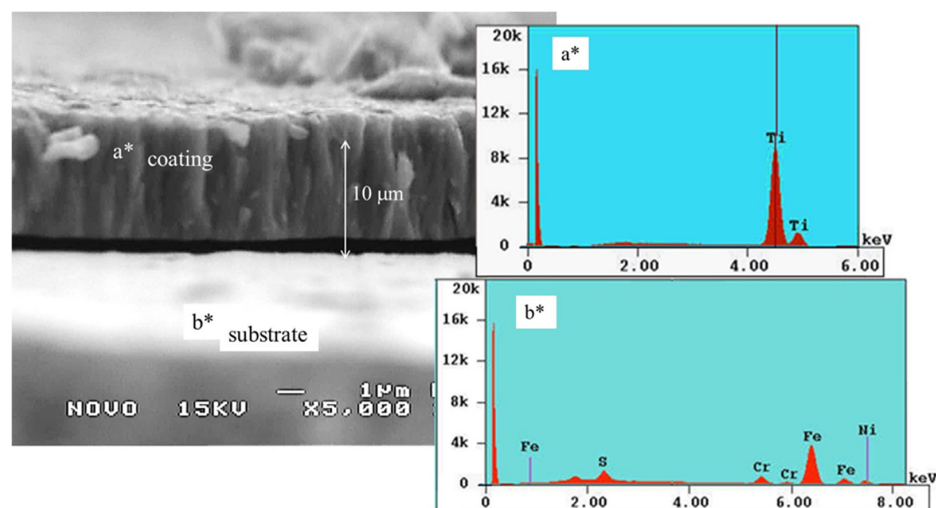


Figure 7. Cross-sectional SEM micrograph and EDS spectra of the TiO₂ coating deposited on 316SS at 400 °C. The EDS spectrum acquired from region; (a*) coating region showing a strong Ti peak, and (b*) substrate region showing Fe, Cr, Ni, and S peaks.

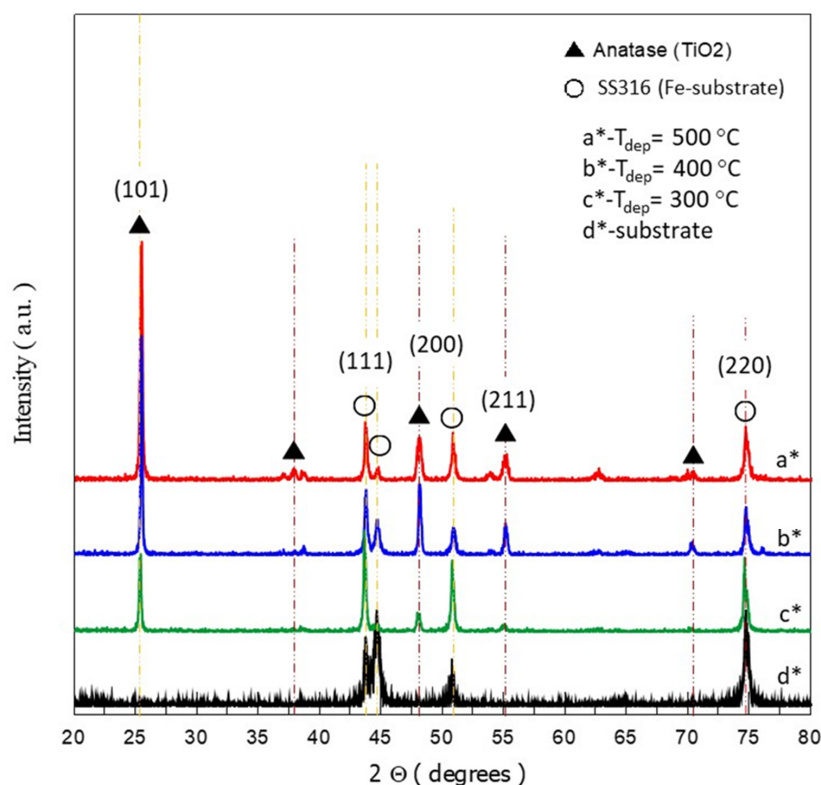


Figure 8. XRD patterns of TiO₂ coatings deposited on 316SS substrates by the MOCVD method at 300, 400, and 500 °C, showing the exclusive formation of the anatase phase. Peaks marked with ▲ correspond to anatase, while ○ indicate reflections from the stainless-steel substrate.

In addition, reflections from the stainless-steel substrate remain; their relative intensities decrease with increasing coating thickness. This reduction is due to atomic diffusion and improved surface coverage. A systematic increase in the anatase reflection intensity is observed with increasing deposition temperature (T_{dep}), confirming that the substrate temperature strongly affects the crystallinity of the deposited TiO_2 coatings. So, higher deposition temperatures promote more efficient precursor decomposition, enhanced surface diffusion, and accelerated crystal growth, all of which contribute to improved structural ordering of the coatings. Important note: no diffraction reflections associated with rutile, brookite, or amorphous phases were detected in any of the samples.

3.3. X-Crystallographic Analysis

Anatase is a tetragonal polymorph of titanium dioxide (TiO_2) known for its impressive properties. Its non-close-packed crystal structure facilitates abundant sites for molecular adsorption, diffusion, and charge transport, thereby enhancing the functional performance of anatase-based coatings. When TiO_2 is deposited on stainless steel, anatase can provide several benefits. The dense, crystalline arrangement acts as an effective physical barrier within the metal matrix, providing exceptional corrosion protection. The pyramidal surface morphology seen in highly crystalline anatase (Figures 5(b*) and 6), particularly at deposition temperatures near 500°C , also contributes to the long-term durability of SS steel.

The XRD analysis of Figure 8 confirmed that all coatings deposited at 300 , 400 , and 500°C crystallize exclusively in the pure anatase (TiO_2) phase. The progressive increase in reflection intensity and sharpness with increasing substrate temperature clearly demonstrates that 500°C is the optimal condition under the studied parameters. At 500°C , the coating exhibits: (i) a strong and dominant anatase (101) reflection, (ii) high stability of the anatase phase at deposition temperatures between 400 – 500°C , avoiding early transformation into rutile, (iii) multiple well-defined secondary anatase reflections indicative of excellent crystallinity, and (iv) reduced interference from substrate signal, attributed to the increased coating thickness.

The average crystallite size of anatase TiO_2 nanoparticles deposited at three different temperatures can be estimated according to Scherrer's equation [58–60] for the (101) reflection plane. This equation is expressed as follows:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

D represents the crystallite size (nm), K is the shape factor for a spherical particles (dimensionless, typically 0.89), λ denotes the X-ray wavelength ($\text{Cu-K}\alpha = 0.15406 \text{ nm}$), β is the full width at half maximum (FWHM) of the diffraction reflection (in radians), and θ is the diffraction angle (2θ , in radians). Crystallite size was determined from the anatase (101) diffraction signal, as shown in Figure 8, for deposition temperatures of 300 , 400 , and 500°C . At these temperatures, TiO_2 crystals tend to grow preferentially along the (101) crystallographic plane, which has the highest atomic packing density in the tetragonal structure and lowest energy, making it thermodynamically favored. With increasing T_{dep} , the FWHM of the anatase (101) reflection narrows, indicating that the crystallites are growing, as predicted by Scherrer's Equation (1). This result shows that higher substrate temperatures during the MOCVD process improve crystallinity by increasing atomic mobility, facilitating atom movement across the surface, and promoting grain coarsening. These effects result in the formation of larger, more coherent crystallite domains, accompanied by a more defined lattice structure within the TiO_2 coatings. The simultaneous increase in peak intensity further indicates a crystalline configuration and preferential atomic orientation along the (101) plane, resulting from elevated thermal energy during MOCVD deposition. In this

sense, it is expected that the sample deposited at 500 °C exhibited the largest crystallites, which correlates well with the enhanced peak intensity and sharpness observed in the XRD pattern shown in Figure 8. The lattice parameter a of anatase-phase TiO_2 was calculated from the (101) plane diffraction peak in the XRD patterns using Bragg's law and the tetragonal structure equation. Equation (2) describes the relationship between the reciprocal of the squared interplanar spacing d of a crystal plane (Miller indices, h, k, l) and the lattice parameter constants a and c , assuming a tetragonal symmetry in the crystal structure. The unit-cell parameters of anatase differ along different axes. Equation (3) represents Bragg's law, which determines the spacing between crystal planes based on the angle θ at which X-rays are diffracted. λ corresponds to the wavelength of the incident X-ray; its value is about 0.15406 nm for Cu-K α radiation, and the value of C is about 2.51 a .

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (2)$$

$$d = \frac{\lambda}{2 \sin \theta} \quad (3)$$

Assuming a constant c/a ratio of 2.51, as reported for anatase TiO_2 [58], the lattice parameter a was calculated for each coating deposited at different substrate temperatures. These calculations were based on the principal anatase (101) diffraction signal, typically located at $2\theta \approx 25.3^\circ$. Small peak shifts toward higher deposition temperatures due to improved crystallinity were also accounted for in the calculations. Table 2 summarizes the crystallographic parameters derived from the XRD patterns obtained at various deposition temperatures. The extracted crystallographic parameters reveal a clear dependence of the TiO_2 film structure on the deposition temperature. In all cases, the coatings crystallize exclusively in the anatase phase, with the dominant (101) diffraction peak confirming phase purity. The systematic narrowing of the diffraction peaks, along with a slight increase in lattice parameter values at higher temperatures, suggests enhanced crystallinity and grain growth.

Table 2. Crystallographic parameters of anatase TiO_2 coatings deposited by the MOCVD method at different substrate temperatures, calculated from the (101) reflection plane using Scherrer's equation and Bragg's law.

Deposition Temperature °C	FWHM (°)	Crystallite Size (nm)	Interplanar Spacing d_{101} (nm)	Lattice Parameter a (nm)
300	0.35	23.26	0.3511	0.3261
400	0.28	29.08	0.3517	0.3268
500	0.20	40.71	0.3524	0.3274

As the deposition temperature increases from 300 to 500 °C, a noticeable shift of the anatase (101) diffraction peak toward lower angles is observed, decreasing from 0.35° to 0.20° which corresponds to a gradual increase in the interplanar spacing d_{101} and lattice parameter a . This narrowing of the diffraction peak indicates crystal lattice relaxation and grain coarsening, associated with improved crystallinity and reduced lattice strain at higher temperatures. These results are consistent with the increased peak sharpness and intensity observed in the XRD patterns, confirming the enhanced crystallinity of the TiO_2 coatings deposited at elevated temperatures.

In general speaking, at a deposition temperature of 500 °C, the presence of multiple well-defined anatase diffraction peaks indicates the formation of a highly ordered crystalline structure. This observation is consistent with the well-defined crystalline tetrahedrons

observed in the surface morphology and with the calculated data summarized in Table 2. At this temperature, the crystallite size of the TiO_2 coating reaches approximately 40.71 nm. At the same time, FWHM (Full Width at Half Maximum) is the narrowest broadening of the peak (101) reflection decreases to 0.20° ; this behavior reflects a significant improvement in crystallinity of the structure, which is characteristic of the anatase TiO_2 phase when sufficient energy allows for long-range atomic arrangement and crystallized in a surface-energy minimization during growth. Additionally, the interplanar spacing $d_{(101)}$ shows a slight increase from 0.3511 nm to 0.3524 nm, and lattice parameter a slightly increase from 0.3261 to 0.3274 with increasing deposition temperature. This behavior suggests minor lattice relaxation and reduced microstrain within the TiO_2 crystal lattice as crystallinity improves, remaining in good agreement with reported values for anatase TiO_2 [57–59]. Importantly, these discrete changes indicate that the atoms are ordering at higher deposition temperatures without inducing any phase transformation or significant lattice distortion.

According to the calculated crystallographic parameters of the TiO_2 coating deposited at 500°C , the unit cell of the tetragonal crystal structure characteristic of the anatase phase is adopted, as designed in Figure 9. In this structure, Ti^{4+} ions occupy the centers of slightly distorted TiO_6 octahedra, which are connected through shared corners and edges in a zigzag packing arrangement. Each Ti^{4+} ion is six-coordinated by O^{2-} ions, while each O^{2-} ion bridges three neighboring Ti^{4+} ions, resulting in a robust three-dimensional network of corner-sharing octahedra. This periodic three-dimensional arrangement yields a regular, stable crystalline framework in which each octahedron is connected to eight nearest neighbors. Overall, these results demonstrate that increasing the substrate temperature during the MOCVD method significantly increases crystallite size, structural ordering, and lattice coherence in anatase TiO_2 coatings. Among the investigated conditions, the coating deposited at 500°C exhibits the most favorable crystallographic characteristics, consistent with its improved crystallinity and well-developed anatase structure.

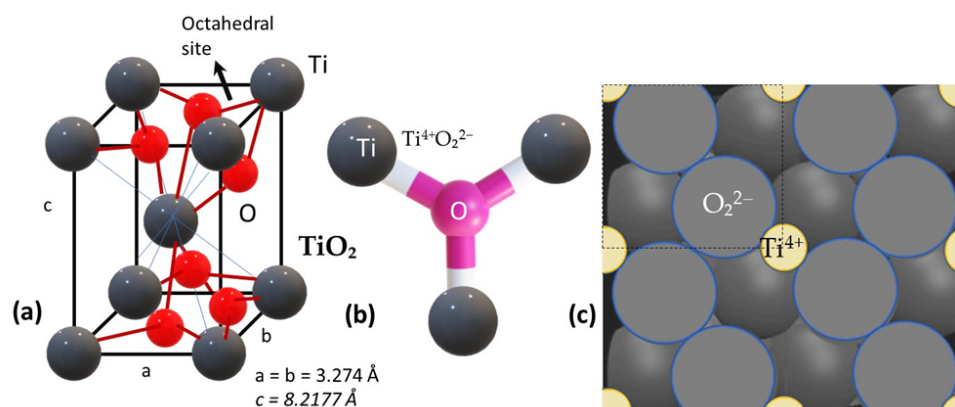


Figure 9. Schematic illustration of the crystallographic structure and atomic arrangement of the anatase TiO_2 coating deposited at 500°C ; (a) Tetragonal unit cell, (b) Ti–O octahedral bonding configuration, and (c) atomic arrangement in the (101) crystallographic plane.

Figure 9a shows the tetragonal unit cell of anatase TiO_2 , where red spheres represent oxygen atoms (O^{2-}) and dark gray spheres represent titanium atoms (Ti^{4+}). The lattice parameters are $a = b = 3.274 \text{ \AA}$ and $c = 8.2177 \text{ \AA}$, satisfying the tetragonal condition ($a = b \neq c$) and assuming a c/a ratio of approximately 2.51. These values correspond to a structure that is about 86.5% close to the ideal anatase configuration reported in the literature [60,61]. Within the unit cell, titanium atoms occupy specific crystallographic positions, while oxygen atoms are arranged to form slightly distorted TiO_6 octahedra. This confirms a high degree of crystallinity, with atoms arranged in a well-ordered tetragonal anatase phase and minimal lattice distortion achieved through thermal treatment at 500°C . This

deposition temperature provides the necessary energy to promote atomic rearrangement, crystallization, and lattice relaxation, thereby enhancing the coating's functional properties. This slight deviation from the ideal anatase structure is likely associated with residual lattice strain, point defects, or interfacial interactions between the TiO₂ film and the stainless-steel substrate during growth. The distortion of the TiO₆ octahedra is further reflected in the Ti–O bond lengths, measured to be approximately 1.94 Å, which is close to the sum of the ionic radii of Ti⁴⁺ (≈0.605 Å) and O^{2−} (≈1.38 Å). This structural configuration indicates the presence of mixed ionic–covalent bonding, which contributes to the anatase TiO₂ coating's structural stability and functional performance. Figure 9b illustrates the local coordination of titanium in anatase TiO₂, showing a Ti⁴⁺ ion located at the center of a slightly distorted TiO₆ octahedron. In this coordination geometry, each Ti⁴⁺ ion is surrounded by six O^{2−} ions, forming a distorted octahedral structure. These Ti–O bonds exhibit predominantly ionic character with partial covalent contribution, which enhances the structural stability of the TiO₂ lattice. This octahedral arrangement is critical for controlling the material's electronic, dielectric, photocatalytic, and corrosion-resistant properties. Figure 9c presents a schematic projection of the atomic packing, highlighting the spatial distribution of Ti⁴⁺ and O^{2−} ions within the crystal lattice. Oxygen anions form a dense, closely packed sublattice, while titanium cations fill interstitial positions in a uniform pattern (octahedral interstitial sites). This atomic arrangement produces a dense anatase structure and is consistent with the formation of a well-crystallized coating at 500 °C, characterized by an interconnected network of corner- and edge-sharing TiO₆ octahedra. A summary of the crystallographic parameters associated with this tetragonal structure is provided in Table 3.

Table 3. Crystallographic parameters and Physical Properties of Anatase TiO₂ structure.

Feature	Value/Description
Unit cell	Tetragonal, $a = b \approx 3.274 \text{ Å}$, $c \approx 8.2177 \text{ Å}$
Ti coordination	Octahedral (6 O neighbors)
O coordination	Trigonal planar (3 Ti neighbors)
Ti–O bond length	~1.91–2.01 Å
Ionic radii	Ti ⁴⁺ ≈ 0.605 Å; O ^{2−} ≈ 1.38 Å
(101) Plane	Most stable and defining facet in morphology

Table 3 summarizes the crystallographic parameters of anatase (TiO₂) that are relevant to understanding its functional performance. At 500 °C, TiO₂ coating crystallizes in the anatase phase with a tetragonal structure, determining lattice parameters of approximately $a = b \approx 3.274 \text{ Å}$ and $c \approx 8.2177 \text{ Å}$. This represents a significant contraction of about 13.5% compared to the ideal bulk anatase value ($a = b = 3.7845 \text{ Å}$) [61,62]. This deviation suggests noticeable lattice distortion, associated with several factors: (i) non-equilibrium growth during MOCVD synthesis, (ii) variations in crystallite size, (iii) residual stress induced from thermal expansion, (iv) defects caused by the mobility of oxygen vacancies or Ti³⁺ ions. In this structure, Ti⁴⁺ ions adopt octahedral coordination with six O^{2−} atoms arranged along the (101) crystallographic plane. Each oxygen atom has trigonal-planar coordination with three titanium ions, yielding Ti–O bond lengths of 1.91 to 2.01 Å, indicating slight distortion of the TiO₆ octahedra.

Furthermore, Table 4 summarizes the evolution of morphology, the average crystallite size, and coating thickness of TiO₂ films as a function of deposition temperature. A clear and systematic trend is observed as the temperature increases from 300 to 500 °C. At 300 °C, the TiO₂ coating exhibits a cluster with the smallest average crystallite size (23.26 nm) and the thinnest film thickness (~5 µm). When the deposition temperature is increased to 400 °C, the average crystallite size increases to 29.08 nm, accompanied by a significant

increase in coating thickness ($\sim 10\ \mu\text{m}$) and vertical elongated grains. At $500\ ^\circ\text{C}$, the TiO_2 coating reaches the largest crystallite size ($40.71\ \text{nm}$), with a pyramidal geometric shape and a maximum thickness ($\sim 20\ \mu\text{m}$). These results clearly confirm that higher deposition temperatures strongly promote grain coarsening, crystallite growth, and film densification. The increased coating thickness also reduces the substrate signal in XRD patterns, and improves structural continuity, both of which are beneficial for functional properties such as corrosion resistance, mechanical integrity, and long-term durability.

Table 4. Average size of crystallites and thickness of TiO_2 coatings deposited by the MOCVD method at different substrate temperatures.

Deposition Temperature ($^\circ\text{C}$)	Average Size of the Crystallites (nm)	Coating Thickness (μm)	Morphology
300	23.26	5	rounded spheres or clusters
400	29.08	10	vertical, elongated grains
500	40.71	20	pyramidal facet

3.4. Potentiodynamic Anodic Polarization (AP) Test for Corrosion Behavior

The electrochemical response in Figure 10 illustrates the AP behavior of coatings on 316SS steel deposited at the investigated temperatures. For comparison, untreated samples were also tested. Corrosion tests in $0.5\ \text{M}\ \text{H}_2\text{SO}_4$ involved (a) untreated 316SS as polished, (b) untreated 316SS as received, and 316SS coated with TiO_2 at $300\ ^\circ\text{C}$ (c), $400\ ^\circ\text{C}$ (d), and $500\ ^\circ\text{C}$ (e). The electrochemical parameters, corrosion potential (E_{corr}), pitting potential (E_{pit}), and corrosion current density (i_{corr}), were determined from $\log I\ (\text{A})$ vs. $E\ (\text{mV}/\text{Ag}/\text{AgCl})$ curves, as those plotted in Figure 10.

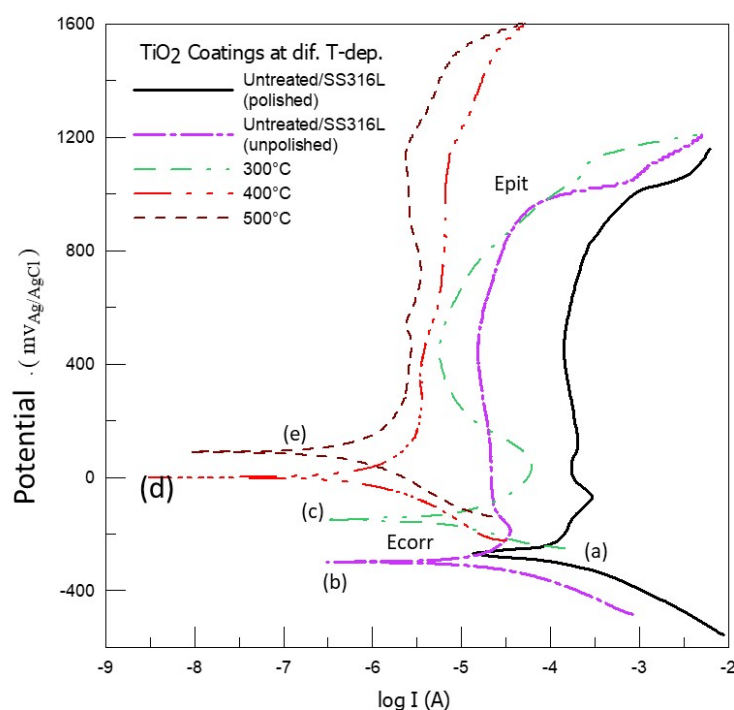


Figure 10. The electrochemical behavior of 316SS stainless steel was studied under various surface conditions using potentiodynamic anodic polarization (AP) in an accelerated $0.5\ \text{M}\ \text{H}_2\text{SO}_4$ solution.

An important property of stainless steel (316SS) is its ability to spontaneously form a thin, stable chromium oxide (Cr_2O_3) layer when exposed to water, air, or a humid

environment. Chromium atoms dispersed in the steel react immediately with oxygen to promptly form an adherent oxide layer, according to the reaction $4\text{Cr} + 3\text{O}_2 \rightarrow 2\text{Cr}_2\text{O}_3$. This self-passivation mechanism fundamentally maintains stainless steel's passivity in acidic environments. However, if an area of the film is damaged, scratched, disrupted, or removed, exposed chromium at the new surface reacts with oxygen again to regenerate the oxide through a self-healing process, thus limiting corrosion attack. An experimental demonstration of this mechanism is evident in AP curves measured in 0.5 M H_2SO_4 , as shown in Figure 10 (curves a and b). The curves show a typical passive region followed by the breakdown potential, E_{pit} .

The experiment compared two surface conditions of 316SS steel: (a) mechanically polished, where the pre-existing oxide film was removed by abrasion, and (b) unpolished, where the native oxide film was left unaltered as received. The AP curves show clear differences in passivation trend. The polished sample (curve a) displays the corrosion potential (E_{corr}) of about -270 mV with a higher corrosion current density (i_{corr}) of 10^{-3} A/cm². This transient indicates early corrosion activity due to a continuous increase in current density by the direct contact between the bare metal surface and the acidic solution. As polarization proceeds, a passive oxide layer reforms gradually after reaching -100 mV, but this film breaks down at a potential near of $+800$ mV (E_{pit}), marking the initiation of active Fe dissolution by localized corrosion.

In contrast, the unpolished sample (curve b) exhibits a slightly more negative corrosion potential ($E_{\text{corr}} -300$ mV) and lower corrosion current density ($i_{\text{corr}} \approx 10^{-4}$ A/cm²), indicating good corrosion resistance from the naturally remaining oxide (Cr_2O_3) layer. The AP (curve b) displays a stable passive region. This region is characterized by no current transfer allowed, reflecting that the native oxide film works as an effective barrier. The passive region persists unchanged until the oxide layer breaks down at a potential near $+950$ mV (E_{pit}). In summary, as potential increases during the anodic scan, the polished sample rapidly forms a new passive layer, as seen by the sudden control in current in the passivation region. This behavior demonstrates that SS steel can spontaneously regenerate its passive oxide (Cr_2O_3) layer under optimal oxidizing conditions, even after sudden mechanical damage or local scratching. As documented in the literature [63,64], this inherent self-passivating ability confers exceptional corrosion resistance even in aggressive acid environments.

The AP (curve c) for the TiO_2 coating deposited at 300°C is very similar to that of the untreated 316SS samples, suggesting poor corrosion protection. The coating formed at this temperature is relatively thin and porous, resulting in incomplete coverage of the underlying metal. The limited protection can be attributed to the presence of structural defects induced during the MOCVD thermal treatment, including interconnected porosity, atomic disorder, vacancies, microdefects, and fissures. These defects serve as pathways for electrolyte access and ion transmission, eventually promoting coating delamination, as evidenced in Figure 11. These imperfections expose the substrate to the corrosive ions, thus promoting corrosion initiation. This behavior is evident in the AP response (curve c), where the corrosion current density (i_{corr}) increases significantly after the pitting potential ($E_{\text{pit}} \sim +500$ mV).

Additionally, the passive region becomes unstable, indicating that the coating's performance deteriorates during the electrochemical test. In contrast, the TiO_2 coatings deposited at 400 and 500°C (curves d and e) exhibit significantly superior corrosion resistance relative to the 300°C coating. This enhancement is attributed to higher deposition temperatures, which promote microstructural transitions, resulting in a thicker, more compact structure and a less porous structure that effectively blocks electrolyte ingress. Their polarization curves shift toward more positive potentials at $+100$ mV, with significantly lower current

densities ($i_{\text{corr}} \approx 10^{-6} \text{ A/cm}^2$) and maintain a stable passive region from +100 to +1500 mV. This behavior indicates enhanced corrosion resistance and effective suppression of metal dissolution. In particular, the TiO_2 coating at 500 °C achieves the best passivation performance for 316SS in H_2SO_4 . Notably, the pyramidal morphology promotes the formation of a highly uniform, compact, and dense structure than that obtained at 400 °C, acting as an effective physical and chemical barrier against metal dissolution. Table 5 summarizes the influence of deposition temperature (T_{dep}) on corrosion protection, as determined by anodic polarization. Therefore, under inadequate thermal conditions, such as 300 °C, the coatings become more susceptible to corrosion. Low atomic diffusion promotes a poorly crystalline structure with disordered domains, which, in combination with thermal stress, leads to cracks and a porous network in the coating. This amorphous microstructure compromises the coating's integrity, leaving the steel substrate vulnerable to corrosion.

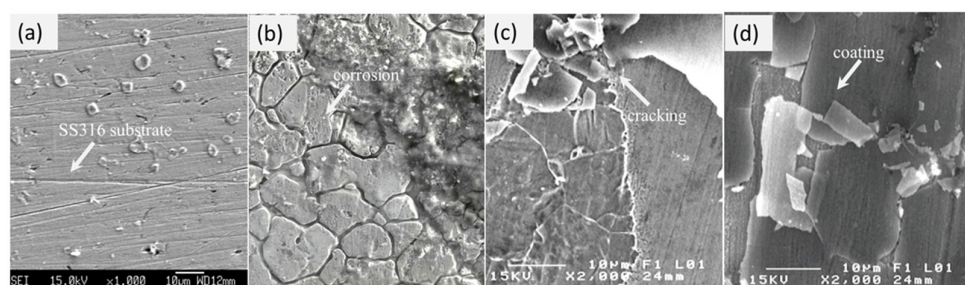


Figure 11. SEM micrographs; surface appearance of 316SS after corrosion testing in an accelerated 0.5 M H_2SO_4 : (a) un corroded substrate, (b) severe corrosion on uncoated steel, (c) cracked and delaminated TiO_2 coating (300 °C), and (d) protective TiO_2 coating (500 °C).

Table 5. Electrochemical parameters derived from anodic polarization, showing the effect of deposition temperature on the corrosion performance of TiO_2 -coated 316SS in an accelerated 0.5 M H_2SO_4 .

Sample	E_{corr} [mV]	E_{pit} [mV]	I_{corr} [A/cm ²]	Dominant Mechanism/ Coating Morphology
Polished	−270	+800	0.6×10^{-4}	No oxide film; partial passivation, high susceptibility to corrosion
Unpolished	−300	+950	8.5×10^{-4}	Native chromium oxide (Cr_2O_3) film; temporal passive stage
TiO_2 -300 °C	−150	+500	3.0×10^{-5}	Cluster-like growth; disordered structure, structural defects; partial protection
TiO_2 -400 °C	0	+1400	1.9×10^{-6}	Columnar growth; stable passivation
TiO_2 -500 °C	+100	+1500	8.0×10^{-6}	Pyramidal crystals assembly; fully dense, highly adherent barrier; excellent corrosion performance

Figure 11 illustrates the corrosion behavior of uncoated and TiO_2 -coated 316SS in 0.5 M H_2SO_4 . The uncoated surface prior to testing (Figure 11a) shows characteristic abrasion marks. After AP measurements (Figure 11b), the uncoated steel exhibits severe corrosion with extensive pitting and grain-boundary attack, confirming active dissolution in the acidic environment. TiO_2 coatings improve corrosion resistance, though performance varies with deposition temperature. The 300 °C coating (Figure 11c) shows partial delamination and microcracks after testing; defects act as preferential pathways for aggressive ions, significantly reducing the protective barrier.

Nevertheless, the coating deposited at 500 °C (Figure 11d) displays superior performance. Their thicker, denser, and more adherent morphology provides an effective barrier, suppressing corrosion almost entirely in sulfuric acid. These results demonstrate that TiO₂ coatings significantly improve the corrosion resistance of 316SS in acid. Protective efficiency depends critically on coating integrity and microstructure, with higher deposition temperatures promoting denser, more adherent coatings that are essential for long-term protection.

3.5. Cyclic Voltammetry Test for Corrosion Behavior

Cyclic voltammetry (CV) was employed as an essential diagnostic to evaluate the electrochemical performance of TiO₂ coatings deposited on 316SS substrates at various temperatures. CV measures oxidation-reduction behavior, charge-transfer kinetics, surface passivation, and coating persistence under the pressure of cyclic polarization in 0.5 M H₂SO₄. By analyzing changes in current as a function of applied potential (Figure 12), the resulting voltammograms (plots of *I* vs. *V*) reveal reversible and irreversible electrochemical reactions, which serve as indicators of coating durability over 25 consecutive cycles.

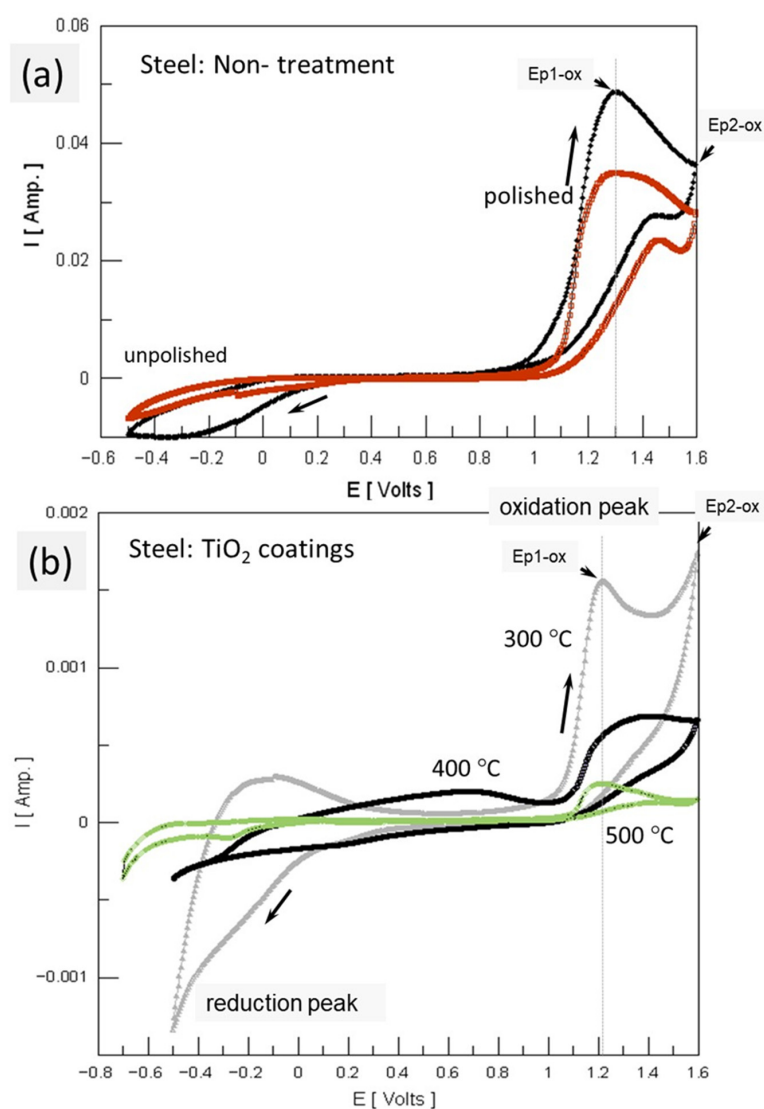
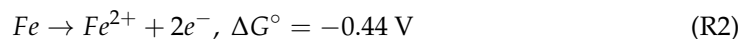
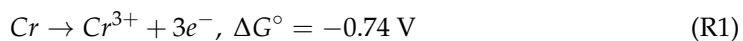


Figure 12. Cyclic voltammetry behavior of 316SS steel under various surface conditions, evaluated in an accelerated 0.5 M H₂SO₄; (a) Uncoated substrate, (b) TiO₂ coating deposited at 300 °C, 400 °C, and 500 °C. All curves represent the last 25th cycle.

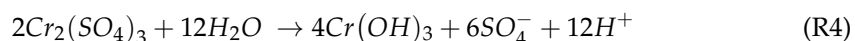
The CVs were recorded by cyclically sweeping the working electrode potential from -1.00 to $+1.60$ V (vs. Ag/AgCl RE) at a scan rate of 0.01 V/s for over 25 consecutive cycles. Figure 12a compares the cyclic voltammetry response of polished and unpolished steel surfaces in 0.5 M H_2SO_4 . The polished specimen corresponds to a condition where the native oxide products were removed to expose a fresh metallic surface. The unpolished specimen retains its original, air-formed oxide film. Accordingly, the voltammogram response of the polished specimen exhibits a distinct anodic peak (E_{p1-ox}) at approximately $+1.32$ V, with a current density of 0.04870 A/cm² (i_p). This is followed by a broad passive domain extending from about $+1.2$ to $+1.6$ V. This anodic peak is attributed to the immediate formation of a protective oxide (Cr_2O_3). This film nucleates and grows under thermodynamically favorable conditions, resulting in a homogeneous oxide film. However, the relatively slow kinetics of film formation appear to compromise the repassivation process's efficiency.

In contrast, the unpolished steel surface shows a sharper oxidation profile. Two distinct anodic peaks appear at $+1.28$ V (E_{p1-ox}) and $+1.60$ V (E_{p2-ox}), with a lower current density of 0.0349 A/cm² (I_{p1-ox}) compared to the polished condition. This response is consistent with slower reaction kinetics, attributed to a pre-existing native oxide film that progressively thickened over time due to prolonged exposure to the environment. The thicker oxide offers better initial protection than the freshly formed film on the polished surface. Furthermore, in the passive region, the current drops to near zero (0.0 V) for both samples, confirming the formation of a compact passive film that serves as an effective physical barrier, preventing further metal dissolution.

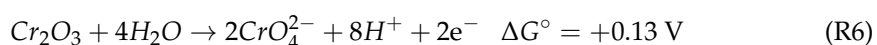
In general, the electrochemical behavior can be described by the voltammograms as follows: Active dissolution occurs at potentials above $+1.0$ V. At this value, the corresponding protective oxide layer becomes unstable, allowing Cr and Fe in the steel to oxidize during acid exposure. This leads to Cr^{3+} and Fe^{2+} cations dissolving into the sulfuric acid, as described in reactions (R1) and (R2);



During cyclic polarization, chromium undergoes partial dissolution as Cr^{3+} . This promotes the transition process involving the growth of a thin oxide film between $+0.2$ and $+1.3$ V, as described in reactions (R3)–(R5). For polished steel, a well-defined, intense anodic signal appears near $+1.28$ V, which corresponds primarily to the oxidation of chromium Cr^{3+} . This characteristic response shows rapid regeneration of the passive layer on bare metal; such regeneration requires a relatively high current density due to the direct exposure of the fresh surface. After this peak, the chromium-rich film partially dissolves as Cr^{6+} ions. The current then decreases suddenly as the potential approaches $+1.6$ V. This drop indicates the exposure of a surface enriched in iron. A second peak at $+1.6$ V is associated with the oxygen evolution reaction. It also indicates further oxidation of Fe and the remaining Cr, showing partial dissolution of the passive film. The unpolished sample, in contrast, exhibits a less intense, broader, and flatter signal at $+1.28$ V. This suggests slower oxidation kinetics due to a pre-existing oxide layer that limits charge transfer. The current drops gradually, reaching $+1.6$ V. Because the passive film is irregular and defective, incomplete dissolution occurs, leaving some areas passive.



The oxide (Cr_2O_3) film, formed in reaction (R5), represents the transition from active metal dissolution to a stable passivated state. Although Fe also undergoes oxidation, Cr remains the primary alloying element that imparts long-term corrosion resistance by forming a dense Cr_2O_3 film. As a result, the passive region occurs at potentials from +0.2 V to +1.0 V/Ag/AgCl, where the current density stabilizes at low values, referred to as the passive current density (i_{pass}). This behavior shows the protective role of the chromium oxide film, which effectively suppresses further metal dissolution and limits charge transfer at the metal–electrolyte interface. When potentials exceeding +1.3 V/Ag/AgCl, the system enters the transpassive region. In this condition, a secondary anodic signal of lower intensity emerges, associated with transpassive chromium dissolution. Under these highly oxidizing conditions, the Cr_2O_3 passive film undergoes further oxidation, producing soluble hexavalent chromium species (Cr^{6+}) and causing a gradual loss of passivity.



Additionally, Fe^{2+} may oxidize to higher valence states (Fe^{3+}), forming soluble iron oxides and sulfates. In this electrochemical stage, the passive film partially breaks down, local dissolution occurs, and protective properties are gradually lost, resulting in corrosion. The anodic response observed in this study is consistent with earlier research of 316SS in sulfuric acid, which reports passivation near +1.3 V_{Ag/AgCl} and transpassive oxidation above +1.6 V [65,66]. These results show that surface preparation significantly influences passivation kinetics in acidic media.

The CV profiles of 31SS6 coated with TiO_2 at 300, 400, and 500 °C are shown in Figure 12b. These transient curves reveal distinct electrochemical responses that depend on the coating morphology. Voltammograms for coatings deposited at 300 °C exhibit two well-defined anodic oxidation peaks, Ep1-ox and Ep2-ox. The first peak, Ep1-ox, occurs at +1.2 V_{Ag/AgCl} and is accompanied by a corresponding cathodic peak during the reverse scan, which is attributed to hydrogen reduction. This behavior is attributed to the oxidation of alloying elements, particularly chromium ions, which form hydrated chromium oxide ($\text{Cr}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) products into the porous structure of the TiO_2 coating. This process represents the transition from active dissolution to a passivated state, during which Cr^{3+} species nucleate and precipitate on the coating. The TiO_2 coating notably reduces anodic current density at this potential compared to uncoated samples, indicating that the barrier limits charge transfer and potential metal dissolution. The second peak, Ep2-ox, is very sharp at approximately +1.6 V_{Ag/AgCl}, corresponding to the transpassive region. At this potential, the current increases and passive chromium oxide is further oxidized to soluble Cr^{6+} ions (e.g., chromate, CrO_4^{2-}), signifying partial degradation of the passive film. This process is associated with localized coating dissolution, Fe dissolution, and a progressive loss of protective efficiency.

The TiO_2 coating modifies the electrochemical response by delaying transpassivity and reducing anodic current intensity compared to the uncoated condition. At 400 °C, the anodic peaks become significantly less intense than those observed at 300 °C. The passivation onset shifts slightly toward lower current densities. This suggests the formation of a denser, more uniform coating, attributed to the increased thermal energy during MOCVD deposition; this increased energy promotes a columnar structure with improved barrier properties. This structure suppresses the ingress of aggressive ions from the acidic environment.

Nevertheless, chromium oxidation persists at the coating surface, and hydration reactions within pores and defects continue to generate anodic currents, as indicated by the remaining oxidation peaks. At 500 °C, the TiO_2 coating exhibits the lowest anodic and cathodic current densities, with a broad and weakly defined oxidation peak. This is attributed to the development of a dense, crystalline, and well-adhered TiO_2 coating with

enhanced barrier properties. The higher deposition temperature results in greater film thickness, improved crystallinity, and stronger interfacial adhesion. These factors help limit charge transfer and reduce redox activity. Table 6 summarizes the electrochemical parameters derived from cyclic voltammetry in 0.5 M H₂SO₄ at the last 25-cycle test.

Table 6. Summary of electrochemical parameters from the 25th CV cycle, showing the effect of TiO₂ deposition temperature on the corrosion resistance of 316SS in an accelerated 0.5 M H₂SO₄.

Sample	* Ep ₁ -Cr ³⁺ [V/Ag/AgCl]	Ip ₁ -Cr ³⁺ (A/cm ²)	** Ep ₂ -Cr ⁶⁺ [V/Ag/AgCl]	Ip ₂ -Cr ⁶⁺ (A/cm ²)	Stability Properties
Polished	1.32	4.87 × 10 ^{−2}	1.60	3.48 × 10 ^{−2}	Broad anodic peak; corrosion
Unpolished	1.28	3.49 × 10 ^{−2}	1.60	2.80 × 10 ^{−2}	Sharper anodic peak; pre-existing Cr ₂ O ₃ ; stable passivation.
TiO ₂ -300 °C	1.20	1.54 × 10 ^{−3}	1.60	1.71 × 10 ^{−3}	Pronounced Cr ³⁺ oxidation; porous and less compact coating; moderate passivation.
TiO ₂ -400 °C	1.41	6.87 × 10 ^{−4}	1.60	6.60 × 10 ^{−4}	Reduced anodic current; improved passivation
TiO ₂ -500 °C	1.22	1.20 × 10 ^{−5}	1.60	8.67 × 10 ^{−5}	Strongly suppressed redox activity; highest protective efficiency.

* Ep₁-oxidation stage, Cr³⁺. ** Ep₂-transpassive stage, Cr⁶⁺.

The two anodic peaks observed correspond to the characteristic passivation and transpassivation behavior of stainless steels in sulfuric acid. TiO₂ coatings noticeably reduce anodic current density and modify peak intensity and sharpness, clearly demonstrating their function as an effective protective barrier. These coatings facilitate the formation of a more stable and homogeneous passive state and significantly delay passive film breakdown and transpassive dissolution at elevated anodic potentials. The effectiveness of this protection is influenced by the deposition temperature during MOCVD synthesis.

- At 300 °C, the protective performance of the coating is limited by the presence of microcracks and defects. The voltammogram shows a broad, poorly defined reduction peak and two pronounced anodic peaks, reflecting diffusion and kinetic limitations likely associated with a less-crystalline TiO₂ structure.
- At 400 °C, the anodic current drops by one order of magnitude, while oxidation and reduction peaks become sharper. This behavior suggests enhanced conductivity and improved electrochemical interactions, with barrier properties approaching reversibility.
- At 500 °C, anodic peaks are entirely suppressed, and the voltammetric response becomes narrow and stable. This is consistent with a dense, adherent TiO₂ coating observed by SEM, which has reached a more ordered anatase-phase crystalline structure, effectively blocks ionic transport, and provides better corrosion protection.

3.6. Electrochemical Impedance Spectroscopy Test for Corrosion Behavior

In addition to potentiodynamic polarization (AP) and cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) provides a complementary tool for assessing the corrosion protection of TiO₂ coatings on 316SS. AP focuses on corrosion kinetics by subjecting the metal surface to a swept potential, thereby causing electron pressure. E_{corr}, E_{pit}, and i_{corr} are measured and related to corrosion rate, passivation behavior, and film breakdown. CV reveals the active-to-passive transition and identifies oxidation-reduction reactions during repetitive potential cycles. EIS quantifies the resistance of the passive layer and its capacity for electron charge transfer, including the diffusion mechanism.

Unlike direct-current (DC) polarization methods, EIS employs a small-amplitude (alternating current, AC) signal over a wide frequency range, minimizing surface alteration from DC potential, allowing reliable monitoring of coating performance during extended immersion periods of 28 days. This aptitude preserves the surface's integrity, making EIS particularly relevant for TiO_2 -coated samples, where film stability depends on MOCVD deposition temperature.

In this regard, Figure 13 shows the Bode plots for the as-received steel exposed to 0.5 M H_2SO_4 during a 28-day immersion period. At the initial stage (after 3 h of exposure, 0 days, curve 1), a single time constant with a larger amplitude is observed in the entire tested frequency range. The corresponding phase angle approaches -80° , which is characteristic of a predominantly capacitive response. This behavior confirms charge separation at the interface between the oxide layer and the electrolyte, attributed to a pre-existing protective passive layer (naturally formed), probably composed of chromium oxide, that suppresses active metal dissolution. Consequently, the impedance modulus $|Z|$ reaches relatively high values, on the order of $10^5 \Omega \cdot \text{cm}^2$ at low frequencies. After one day of immersion, curve 2 shows a broader time constant, characterized by a sudden increase in $|Z|$ to values exceeding $10^5 \Omega \cdot \text{cm}^2$, and a phase angle shifting toward -85° . These changes are consistent with the continued Cr oxidation at the irregularities within the film, leading to layer thickening through defect repair. This self-repairing mechanism is clearly noticeable in curve 2 by the presence of a second protuberance located at the highest frequencies. However, at the intermediate stage of immersion, ranging from 7 to 14 days. A pronounced drop in $|Z|$ to values approaching $10^3 \Omega \cdot \text{cm}^2$ is denoted in curves 3 and 4, where two distinct time constants are seen. This indicates progressive degradation of the passive film under acidic conditions, accompanied by the initiation of localized corrosion processes on the metal substrate. Simultaneously, the phase angle shifts to -70° with lower magnitude, indicating increased charge-transfer activity and less ideal capacitive behavior. This evolution is consistent with increasing surface degradation and partial breakdown of the chromium oxide layer.

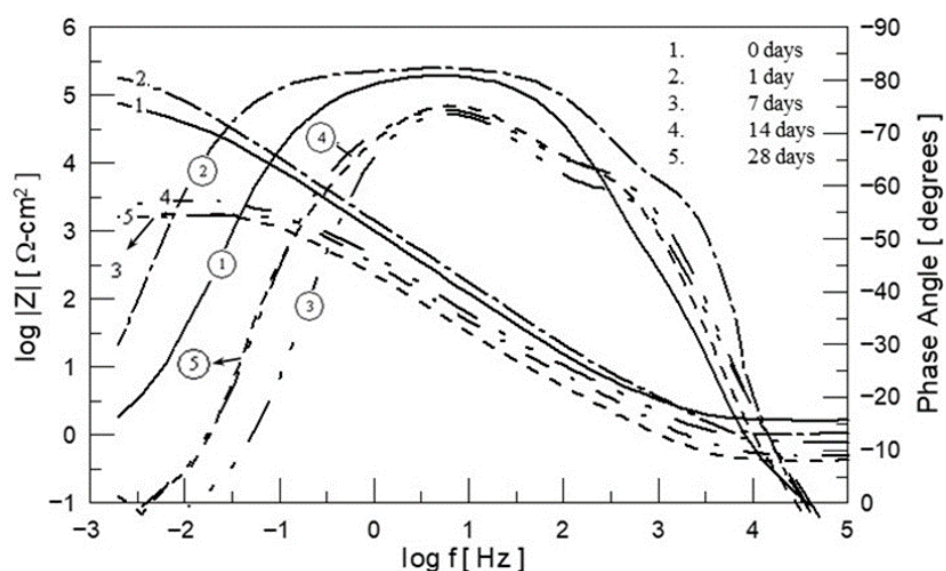


Figure 13. Electrochemical impedance spectroscopy (EIS) analysis of 316-stainless steel in the as-received condition tested in an accelerated 0.5 M H_2SO_4 . Bode plots recorded at different immersion times.

Behavior distinguished by noticeable changes in the Bode plots at intermediate frequencies in the phase angle, indicating the manifestation of a clearly defined alteration

in the time constant. At the final stage of the 28-day exposure, the impedance response is dominated by resistive behavior, with $|Z|$ dropping below $10^2 \Omega \cdot \text{cm}^2$. This behavior indicates severe deterioration of the passive film and the transition to an actively corroding state of the steel surface, where faradaic charge-transfer processes control the electrochemical response. The passive film is largely destroyed at boundary sites, leading to extensive Cr_2O_3 dissolution and the possible formation of soluble hexavalent chromium species (Cr^{6+}) under highly anodic conditions. These results confirm the limited long-term stability of the native Cr_2O_3 passive film on 316SS in 0.5 M H_2SO_4 . It should be noted that the impedance modulus $|Z|$ serves as an indicator of corrosion resistance. In this study, the evolution of $|Z|$ over time reflects changes in the protective performance of the oxide passive layer. Therefore, the observed drop in $|Z|$ to approximately $10^2 \Omega \cdot \text{cm}^2$ after 28 days confirms a significant loss of protectiveness.

On the other hand, Figure 14 shows the electrochemical impedance response of 316SS coated with TiO_2 at 300, 400, and 500 °C, after 28 days of immersion in 0.5 M H_2SO_4 . The Bode plots describe the electrochemical mechanisms and reactions occurring at the metal/coating interface, as well as the physical meaning of the charge-transfer resistance in terms of the impedance modulus $|Z|$.

All three coatings show a progressive evolution of the impedance response with immersion time, but the magnitude of $|Z|$ and stability differ markedly with deposition temperature. For the TiO_2 coating deposited at 500 °C (Figure 14a), the impedance modulus $|Z|$ remains on the order of 10^6 – $10^5 \Omega \cdot \text{cm}^2$ even after 28 days of exposure, indicating a highly resistive and stable coating. The impedance spectra exhibit two well-defined time constants, one at higher frequencies near -30° and a second loop with a broad maximum near -75° to -80° , characteristic of an ideal capacitive response. This response remains stable over 28 days of immersion due to the presence of a dense, adherent TiO_2 layer. The protective performance of this layer is improved by hydration-induced self-sealing, which fills surface imperfections, blocks ionic transport, and limits charge-transfer reactions at the metal/coating interface. The dominant electrochemical process is controlled by the capacitive response of the TiO_2 coating and the underlying Cr_2O_3 -rich passive film. The effective capacitance remains low, suggesting minimal surface roughening and negligible electrolyte penetration.

In contrast, Figure 14b presents the Bode plot of the TiO_2 coating deposited at 400 °C. The low-frequency impedance decreases gradually from approximately $10^5 \Omega \cdot \text{cm}^2$ to $10^4 \Omega \cdot \text{cm}^2$ at early immersion times. Two poorly defined time constants were observed in the Bode plot, indicating partial deviation from ideal capacitive behavior. These features imply the onset of localized electrolyte ingress through defects and porosity within the coating structure, leading to increased charge-transfer activity. This coating exhibits a columnar structure that facilitates hydration through its pores, thereby increasing effective capacitance. This behavior indicates moderate surface activation and partial degradation of the barrier properties, although passivation is still preserved even after 28 days of exposure. The TiO_2 coating deposited at 300 °C (Figure 14c) provides the weakest electrochemical protection, attributed to its disordered, non-crystalline structure. A single time constant dominates the entire frequency range, marking a clear behavior observed at higher deposition temperatures. The impedance modulus ($|Z|$) drops immediately from 10^5 to $10^3 \Omega \cdot \text{cm}^2$ over 28 days, while the phase angle declines to -60° , indicative of a Faradaic-controlled response. This behavior is associated with a high density of porous coating structure, which facilitates the penetration of sulfuric acid to the metal surface. Consequently, charge-transfer reactions become dominant, including Fe dissolution and partial destabilization of the chromium-based passive film. The inferred capacitance increases significantly, consistent with surface roughening, an increase in the electrochemically active

area, and progressive loss of coating integrity. So, the highly porous, low-crystallinity morphology and disordered structure of this coating facilitate rapid electrolyte ingress and early access to the metal surface, resulting in a weak barrier performance and active corrosion processes from the initial exposure.

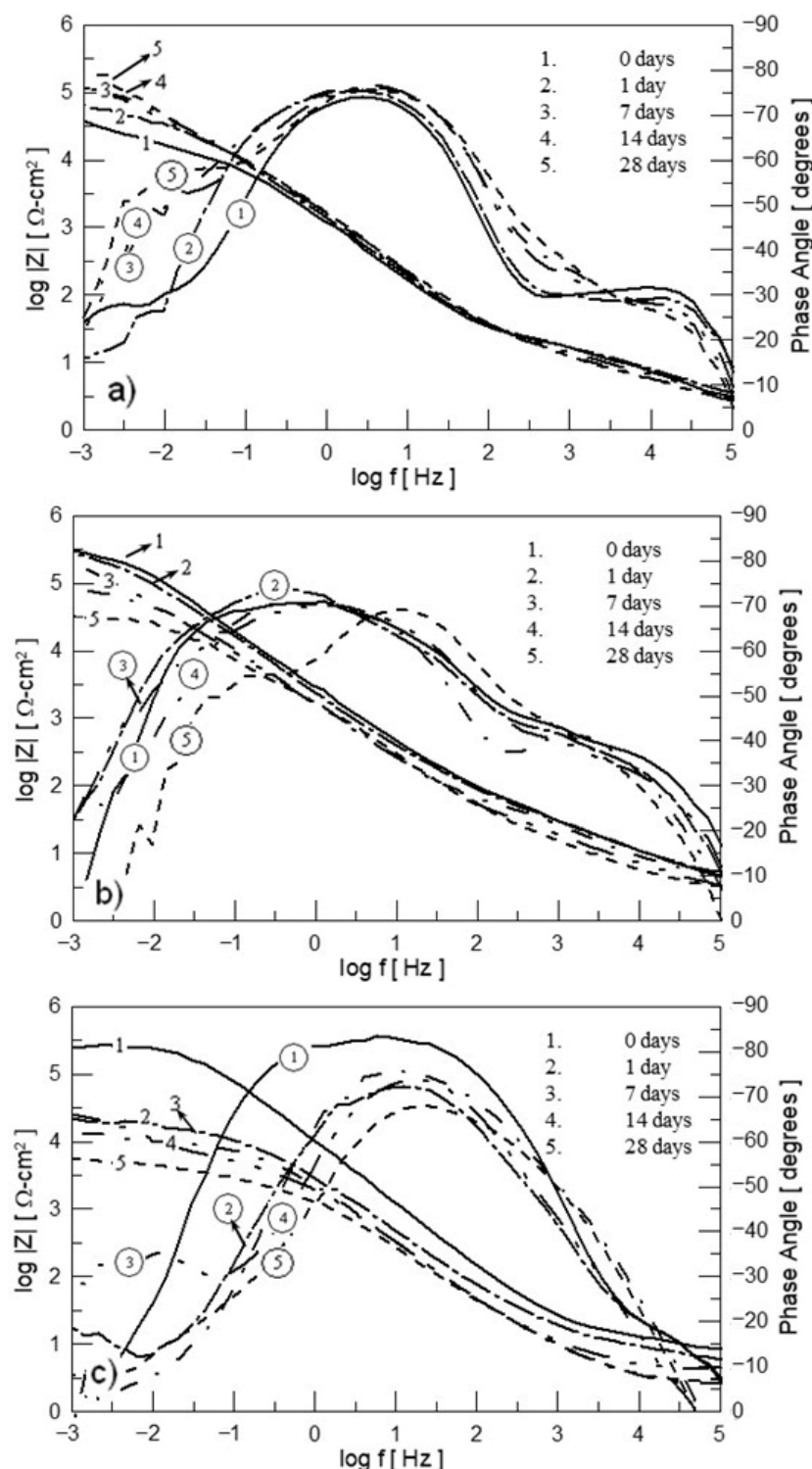


Figure 14. Evolution of electrochemical impedance response of 316 stainless steel coated with TiO_2 deposited at (a) 500, (b) 400, and (c) 300 °C, monitored continuously during 28 days of exposure to an accelerated 0.5 M H_2SO_4 .

Quantitative analysis of the impedance data was performed by fitting the experimental data to an appropriate equivalent electrical circuit (ECC) model to extract meaningful values of electrochemical parameters, which are summarized in Table 7. Typically, these ECC models are like that shown in Figure 15. Coatings deposited at 500 °C and 400 °C, showing two time constants, were fitted with a $(R_s(CPE_1(R_c(CPE_2-R_{ct}))))$, as shown in Figure 15a, consistent with an outer TiO_2 coating and the inner passive layer. The 300 °C coating, including the naturally formed oxide layer on the uncoated steel, exhibited a single time constant and was modeled using a simpler circuit $R_s(CPE_1-R_{ct})$, Figure 15b, thus confirming charge-transfer-controlled corrosion.

Table 7. Summary of the estimated resistance and capacitance parameters derived from EIS Bode plots for 316SS and TiO_2 -coated samples after 28 days of immersion in 0.5 M H_2SO_4 .

Sample	R _s [Ω-cm ²]	R _{ct} [KΩ-cm ²]	C _{dl} [μF/cm ²]	θ-PHASE _{max} [°]/[Hz]		Stability Property
TiO ₂ -500	2.97	296.9	2.7	−75	3.98	High protection, intact barrier; slow degradation kinetics
TiO ₂ -400	3.25	30.88	116.1	−72	8.46	Moderate protection; progressive electrolyte ingress
TiO ₂ -300	2.87	3.31	151.3	−68	26.20	Low protection; rapid barrier failure; charge-transfer dominated
316SS- substrate	2.5	0.2	590	−74	6.31	Significant film degradation; corrosion developing on metal, charge transfer dominated

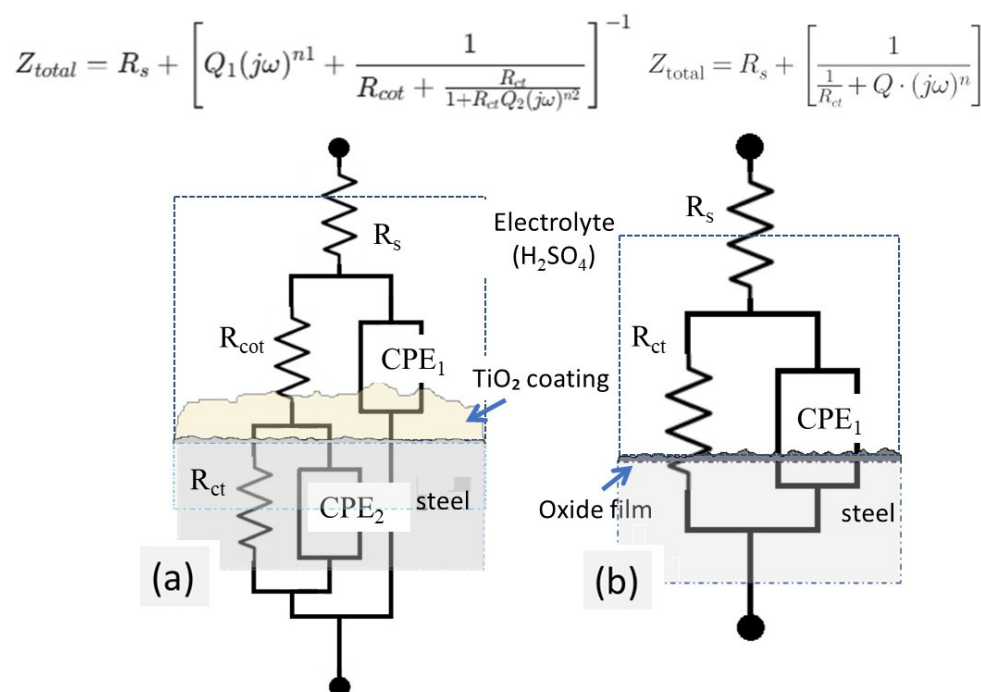


Figure 15. Equivalent circuit models used for fitting the impedance data: (a) two time constant model $(R_s(CPE_1(R_c(CPE_2-R_{ct}))))$ for TiO_2 coatings, and (b) single time constant model $R_s(CPE_1-R_{ct})$ for the native oxide interface. R_s -solution resistance, R_c -coating resistance, R_{ct} -passive film/charge transfer resistance, and CPE-constant phase element.

In summary, the impedance transients in Figure 14 establish a clear correlation between TiO_2 deposition temperature and the corrosion protection efficiency. Elevated deposition

temperatures promote atomic diffusion, crystallinity, densification, adhesion, and reduced defects, collectively enhancing charge-transfer resistance and stable capacitive behavior over prolonged immersion periods. Consequently, the dominant electrochemical response transitioned from a charge-transfer-controlled corrosion process at 300 °C to a capacitive passivation mechanism at 500 °C. This transition unequivocally demonstrates the decisive influence of coating microstructure in determining long-term corrosion resistance of 316SS in acidic environments, as shown in Figure 13.

Figure 16 shows three SEM micrographs obtained after the EIS corrosion test, comparing the surface appearance of the TiO₂-coated sample deposited at 500 °C with that of untreated 316 stainless steel after 28 days of immersion in 0.5 M H₂SO₄. In Figure 16a, the surface of the TiO₂ coating remains unaltered, exhibiting only some cracks, and maintains effective protection of the metal through prolonged exposure. This compact, adherent layer acts as a physical barrier, limiting electrolyte ingress, and correlates with the high charge-transfer resistance and low capacitance observed in the EIS analysis. In contrast, the untreated 316SS substrate (Figure 16b,c) displays severe degradation, with numerous pits distributed across the surface and preferential dissolution of Fe along grain boundaries. These features are characteristic of pitting corrosion and intergranular attack, mechanisms that dominate the corrosion process in the absence of a protective coating. The pits represent localized breakdown of the passive film, while the intergranular corrosion reflects microstructural vulnerability and accelerated dissolution along grain boundaries.

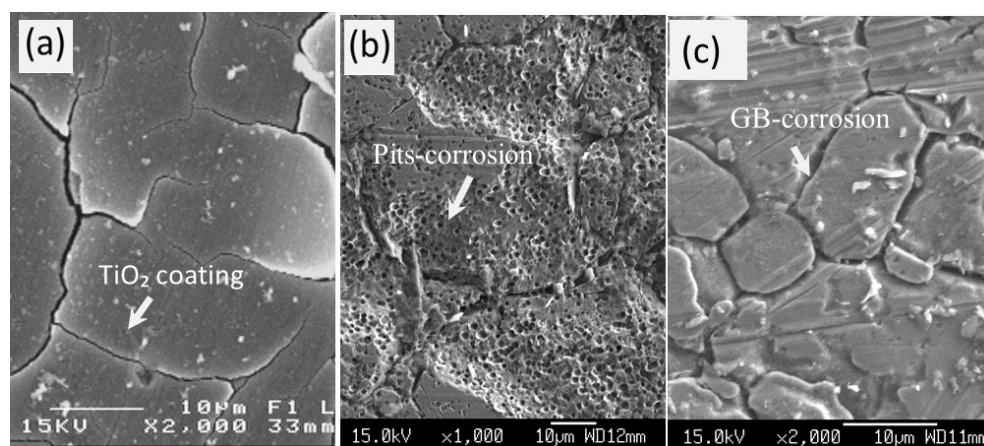


Figure 16. Scanning Electron Microscopy (SEM) Images of a substrate and a cracked TiO₂ Coating after corrosion test during 28 days of immersion in an accelerated 0.5 M H₂SO₄ solution. (a) TiO₂ coating surface showing cracks, (b) corroded surface with numerous pits (pitting corrosion), and (c) surface exhibiting grain boundary corrosion.

4. Conclusions

- TiO₂ coatings were successfully deposited on 316SS substrates using a laboratory-scale horizontal hot-wall tubular reactor based on the MOCVD method. The results of this research validate the feasibility and reproducibility of this in-laboratory engineered system for producing nanostructured coatings.
- A clear correlation between deposition temperature (T_{dep}) and crystallinity was found in this research. Coating deposited in the range of 400 to 500 °C exhibits a well-defined (101) diffraction peak, characteristic of the anatase phase and indicative of a highly crystalline structure. In contrast, coatings deposited at lower temperatures (300 °C) show a weaker anatase signal, suggesting poorer crystallinity.
- By X-ray analysis, this research demonstrates that anatase is the dominant phase, confirming that deposition temperature promotes the formation of a well-ordered anatase

lattice. The pronounced (101) diffraction peak observed at elevated temperatures indicates preferential orientation and high definition of this crystallographic plane, signaling the stabilization of the tetragonal anatase phase. In contrast, coatings deposited at lower temperatures, near 300 °C, predominantly exhibit an amorphous structure.

- The morphological evolution of TiO₂ coatings with increasing deposition temperature clearly demonstrates a transition in structure from a kinetically controlled, porous, cauliflower-like configuration at 300 °C to more ordered columnar grains at 400 °C, and ultimately to thermodynamically stabilized, dense pyramidal faceting at 500 °C. This progression emphasizes the essential role of thermal energy in determining crystallinity, density, and faceted growth, highlighting the shift from kinetic to thermodynamic control during the formation of thin films.
- The remarkable durability of stainless steel coated with TiO₂ at 500 °C, resisting acid exposure for over 28 days. Electrochemical testing revealed that this enhancement is directly attributed to the coating's microstructure: densely packed pyramidal-like anatase nanoparticles effectively impede charge-transfer pathways. While the untreated surface exhibits extensive pitting and intergranular corrosion, the coated surface preserves its integrity, even with minor coating defects.
- TiO₂ coatings markedly improve the corrosion resistance of stainless steel, as evidenced by the electrochemical test of Anodic Polarization (AP), which shows a significant reduction in corrosion current density. The film deposited at 400 °C achieves an I_{corr} (1.9×10^{-6} A/cm²), nearly two orders of magnitude lower than the as-received substrates (as polished 0.6×10^{-4} A/cm²), while the coating at 300 °C maintains consistently 3.0×10^{-5} A/cm². A lower value of I_{corr} (8.0×10^{-6} A/cm²) was measured for the coating deposited at 500 °C. This result confirms the excellent protective performance of TiO₂ coatings and highlights deposition temperature as a decisive factor in optimizing their effectiveness, as changes in coating morphology and structure occur.
- The cyclic voltammetry (CV) data support the protective findings by showing a significant suppression of anodic current peaks as the deposition temperature increases. Notably, at 500 °C, the anodic current density decreases by more than three orders of magnitude (1.2×10^{-5} A/cm²) relative to the bare substrate (as-polished, 4.87×10^{-2} A/cm²), indicating the highest protective efficiency and a marked reduction in redox activity.
- Electrochemical Impedance Spectroscopy (EIS) results corroborate the trend in deposition temperature over immersion time. The charge-transfer resistance (R_{ct}) increases from 0.2 KΩ·cm² for the bare substrate to nearly 297 KΩ·cm² for the coating deposited at 500 °C after prolonged immersion of 28 days in accelerated 0.5 M sulfuric acid. At the same time, double-layer capacitance (C_{dl}) decreases sharply from 590 to 2.7 μF/cm², confirming the formation of a highly effective protective TiO₂ barrier layer.
- In conclusion, the MOCVD deposition temperature (T_{dep}) emerged as a decisive factor in determining the structural and morphological properties of the TiO₂ coatings, consequently affecting their corrosion protection performance. The findings confirm that increasing T_{dep} from 300 to 500 °C not only promoted coating densification and improved adhesion but also favored phase evolution through diffusion kinetics.

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