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Effect of TiC Reinforcement on the Microstructure, Hardness, and Electrochemical Corrosion Behavior of Laser-Clad Ti6Al4V Alloys

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ABSTRACT

Various coatings are commonly applied to titanium alloys to enhance their corrosion resistance for industrial applications. This study investigates the fabrication of TiC-reinforced coatings on Ti6Al4V substrates via laser cladding using TiC powder feedstocks. The research focuses on the influence of these coatings on phase constituents, microstructural evolution, and electrochemical corrosion resistance. Scanning electron microscopy (SEM) analysis revealed that the addition of TiC significantly refined the crystalline grains within the coating matrix. The electrochemical behavior of uncoated Ti6Al4V and TiC/Ti6Al4V coatings was evaluated at room temperature in a sodium chloride solution. Corrosion parameters, specifically the corrosion potential (E_{corr}) and corrosion current density (I_{corr}), were analyzed, and cathodic and anodic Tafel extrapolation was employed to determine the polarization resistance and corrosion rate. The results indicate that the TiC/Ti6Al4V coating exhibits superior corrosion resistance compared to the base alloy, confirming the enhanced protective performance of the composite. Additionally, the microhardness of the material increased significantly from 302 to 598 HV, demonstrating a simultaneous improvement in both mechanical and electrochemical properties.

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1. INTRODUCTION

Titanium alloys are extensively utilized in the aerospace industry owing to their high strength-to-weight ratio, excellent corrosion resistance, fatigue and crack growth resistance, and high-temperature creep resistance (Gomez-Gallegos, Mandal, Gonzalez, Zuelli, & Blackwell, 2018). Moreover, titanium's remarkable corrosion resistance has made it invaluable in the

chemical and petrochemical industries, particularly for manufacturing pipes, heat exchangers, and filters. Titanium also finds application in the pulp and paper industries, where it withstands corrosive environments involving sodium hypochlorite and wet chlorine gases. Its exceptional resistance to saltwater makes it a preferred material for ship propeller shafts. Furthermore, titanium alloys are employed in various

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sports industries for manufacturing tennis rackets ([Li, Pan, & Zou, 2021](#)), bicycle frames, and skis. The biocompatibility of titanium with the human body has significantly expanded its medical applications, including the production of body and dental implants and heart valves ([Jun Yang et al., 2022](#)).

Despite these advantageous properties, the widespread engineering applications of titanium alloys are often constrained by limitations such as low wear resistance, low hardness, a high friction coefficient, poor hardenability, and susceptibility to flaking. Consequently, implementing strategies to mitigate or eliminate these drawbacks is crucial. Enhancing and optimizing the surface properties of titanium and its alloys while preserving their bulk characteristics is essential. Since the surface characteristics significantly influence the fracture behavior of titanium and its alloys, surface modification techniques can effectively improve properties such as alloy hardness ([Kurup, Dhatrik, & Khasnis, 2021](#); [Xue et al., 2020](#)). Surface engineering techniques, including laser surface modification (such as laser surface alloying and laser coating), ion implantation, physical vapor deposition (PVD), chemical vapor deposition (CVD), carbonization, nitriding, thermal oxidation, and arc welding protection methods, can be utilized to enhance surface properties such as the hardness of titanium and its alloys ([Bloyce, Qi, Dong, & Bell, 1998](#); [Rautray, Narayanan, Kwon, & Kim, 2010](#); [Tian, Chen, Li, & Huo, 2005](#)). The use of lasers has become increasingly popular due to their unique characteristics, such as adjustable wavelength, output power, and the ability to concentrate high energy at a single point, enabling the precise optimization and modification of material surfaces for diverse applications. Laser coating, a form of laser-based surface alloying, has gained prominence in recent years for applications including metal coating, part repair, prototyping, and small-scale production. This process involves melting a layer of alloy onto the base material (substrate) with minimal melting of the substrate itself, thereby forming a metallurgical bond between the two materials ([Baker, 2010](#); [Ganjali, Ganjali, Sadrnezhad, & Pakzad, 2020](#)).

Titanium carbide (TiC) is a refractory ceramic material with a face-centered cubic crystal structure, offering excellent corrosion resistance, wear resistance, and high-temperature oxidation properties. It is commonly used as a reinforcement in metals for cutting tools and cermets, as well as in high-temperature applications such as heat exchangers and aerospace engines due to its oxidation and corrosion resistance ([Shanaghi, Chu, Rouhaghdam, Xu, & Hu, 2013](#)).

Titanium metal matrix composites (MMCs) have been fabricated on titanium alloy (Ti-6Al-4V) substrates using laser cladding to enhance hardness and wear properties ([Ochonogor, Meacock, Abdulwahab,](#)

[Pityana, & Popoola, 2012](#)). These materials exhibited a significant improvement in wear resistance, with a fifteen-fold reduction in wear rate attributed to the homogeneous distribution of ceramic particles and the formation of interstitial carbides, as confirmed by X-ray diffraction. In another study, the effect of laser scanning speed on the microstructure and wear characteristics of TiC coatings was investigated ([Xu, Cai, Li, Lu, & Zhu, 2022](#)). The study revealed that increasing the scanning speed led to decreased hardness and increased weight loss of the coatings. Consequently, wear resistance deteriorated despite the presence of TiC particles. A TiC/Ti composite layer was synthesized in situ on Ti6Al4V via laser cladding using Cr3C2 and Ti powders. Microstructures formed from various powder mixtures were analyzed, demonstrating that by adjusting the Cr3C2/Ti composition on the Ti6Al4V substrate, a β -Ti matrix could be achieved with a robust metallurgical bond between the clad layer and the substrate ([He, Song, & Kong, 2019](#)). In a related study, Liu et al. ([Liu et al., 2023](#)) fabricated nano/micron TiC coatings on Ti6Al4V alloy using directed energy deposition, which resulted in a significant enhancement of the corrosion resistance of the nano/micro TiC/Ti6Al4V composites. In the present work, TiC coatings were prepared on the Ti6Al4V alloy via laser cladding. The microstructure, phase composition, and corrosion resistance of both the substrate and the coating were investigated using multiple complementary characterization techniques. Subsequently, the relationship between microstructure and properties was studied to elucidate the modification mechanism.

2. MATERIALS AND METHODS

2.1. MATERIALS

The substrate material utilized in this study was Ti6Al4V plate specimens measuring 30 mm $\times$ 35 mm $\times$ 6 mm. The chemical composition of the Ti6Al4V substrate, in weight percent, was as follows: C (0.01%), N (0.01%), Fe (0.05%), V (4.06%), Al (6.37%), and Ti (89.5%). Prior to laser cladding, the substrate surfaces were ground using 600-grit abrasive paper to remove any existing oxide layers, followed by ultrasonic cleaning in acetone. The injected powder comprised TiC with a purity of at least 99.5% and a particle size of 257 nm (MERCK). Subsequently, the TiC powder, mixed with an organic binder, was applied to the substrate surfaces to a thickness of approximately 0.4 mm.

2.2. LASER CLADDING PROCESS

A pure TiC powder (50–100 μ m, 99% purity, Fluka) was used as the injected material. The coaxial laser cladding system incorporated a 0.7 kW pulsed Nd:YAG laser (PIM3475) operating at a wavelength of

1064 nm. A powder feeder divided the powder into four identical streams. Specimen movement in the X, Y, and Z directions was controlled by a CNC machine (Figure 1). The laser spot size was maintained at 1 mm, with a fixed pulse duration of 3 ms and a frequency of 30 Hz. Argon was employed as the shielding gas for both transporting the powder stream and protecting the laser beam, at a flow rate of 20 L/min. Detailed laser parameters are provided in Table 1.

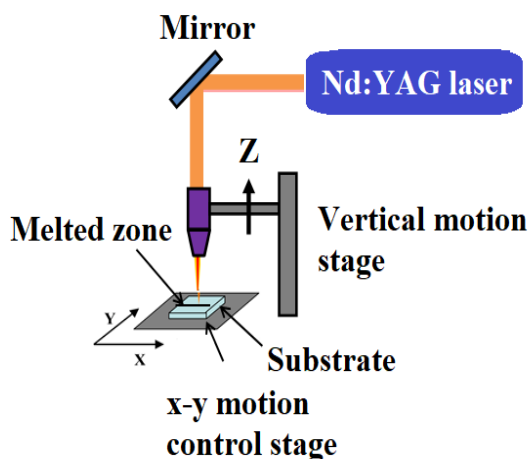


Figure 1. Schematic illustration of the laser-cladding system

2.3. MICROANALYSIS OF THE COATINGS

After a series of preparation and characterization steps, the cross-sectional morphologies and microstructures of the coatings were observed using a MIRA3 TESCAN scanning electron microscope (SEM; TESCAN Co., Brno, Czech Republic). First, the samples were sectioned by electrical discharge machining and then ground with SiC abrasive papers. Subsequently, they were polished using a 0.05 μm Al_2O_3 suspension and etched with Kroll's reagent (2% HF, 5% HNO_3 , balance H_2O) for 20 s. In addition, the phase compositions of the coatings were determined using a Rigaku D/max 2500 X-ray diffractometer (XRD; Bruker, Berne, Switzerland) with $\text{Cu K}\alpha$ radiation, operating at 60 kV and 40 mA, over a scanning range of $2\theta = 20^\circ$ to 80° .

TABLE 1. Laser parameters used in this research

Main process parameters	Main process parameters
Power (W)	200
Scan rate (mm/s)	3
Feed rate (mg/s)	15

2.4. CORROSION TEST

Corrosion testing was conducted using Tafel extrapolation with a Metrohm Autolab model PGSTAT302N potentiostat. The electrochemical cell comprised the working electrode (sample), a platinum counter electrode, a saturated calomel electrode (SCE)

as the reference electrode, and a 3.5% NaCl solution as the electrolyte. Corrosion samples were prepared by wire cutting into cuboids measuring 10 mm $\times$ 10 mm $\times$ 22 mm. The samples were ground with 80–2000 grit sandpaper, mirror-polished, and mounted in epoxy resin, exposing the 1 cm^2 laser-clad layer as the working surface for final polishing. The scan rate for both samples was maintained at 0.1 mV/s to evaluate the corrosion rates. The experiments were performed at room temperature.

2.5. MICROHARDNESS

Microhardness testing was performed on the coatings using an HVS-1000Z microhardness tester (KOOA PAZHOOHESH, Iran), applying a 0.5 kg load for a dwell time of 15 s.

3. RESULTS AND DISCUSSION

3.1. PHASES OF THE POWER AND COATING FABRICATED BY LASER CLADDING

The XRD patterns and field-emission scanning electron microscopy (FESEM) images of the as-received TiC powders are shown in Figure 2(a) and Figure 2(b), respectively. As revealed in Figure 2(a), no impurity phases were detected in the TiC powder. In addition, Figure 2(b) shows that the TiC powder exhibits a predominantly spherical morphology with a mean particle size of 257 nm.

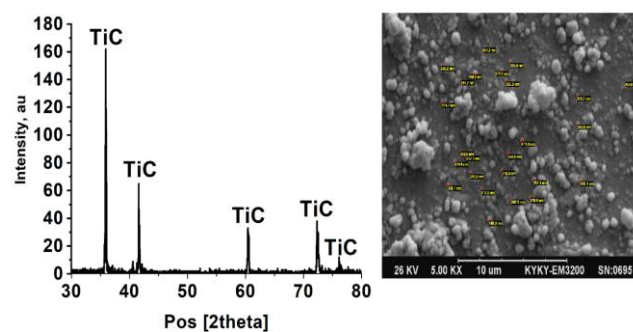


Figure 2. a) XRD spectrums and b) FESEM image of TiC powder

Figure 3 displays the SEM cross-sectional images of the laser cladding track. The images show that the coating is in good condition, exhibiting uniform coverage, good bonding to the substrate, and a consistent thickness of approximately 0.544 mm.

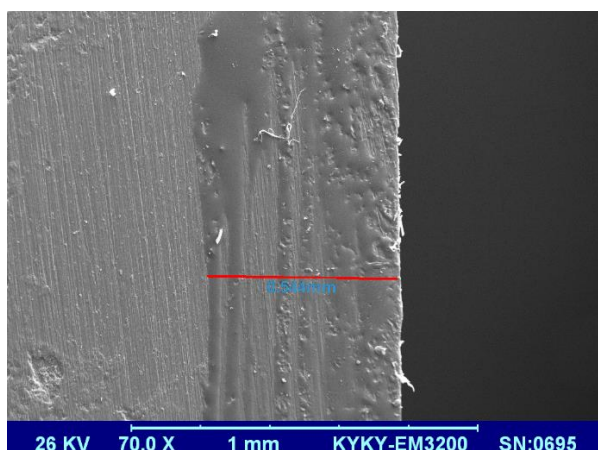
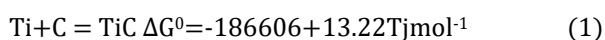


Figure 3. FESEM image of cross section of TiC coating

The XRD patterns, as depicted in Figure 4, confirm the presence of the TiC phase in the processed layer. Previous research suggests that the primary mechanism for TiC formation during laser processing involves the diffusion of carbon atoms into liquid Ti, followed by the nucleation and growth of TiC crystals. The chemical reaction and the change in Gibbs free energy for TiC formation can be expressed by Equation (1) (Coltters, 1985; Lu, Fuh, Chen, Leong, & Wong, 2000):



The Gibbs free energy remains negative across the temperature range of 298–3273 K, indicating that the aforementioned reaction is thermodynamically favorable, particularly in the liquid state of Ti (Courant, Hantzpergue, Benayoun, & L'Huillier, 2001). During laser surface processing, a plasma plume forms above the workpiece, interacting with the substrate, pre-coated material, and shielding gas. Due to the high surface temperatures (2500–3000°C, as determined by COMSOL™ analysis (Hamed, Torkamany, & Sabbaghzadeh, 2011)), Ti, with a melting point (T_m) of 1670°C and a boiling point (T_b) of 3287°C, can exist in either the liquid or vapor phase.

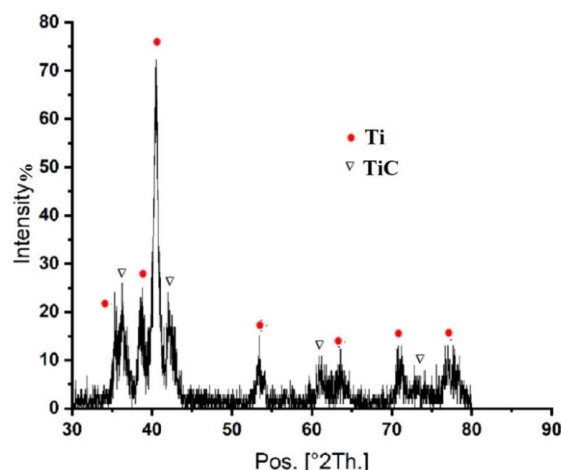


Figure 4. XRD spectrums of the coatings.

3.2. MICROSTRUCTURES OF THE COATINGS

The cross-sectional microstructure of the TiC coating is shown in Figure 5a, depicting a representative cladding layer. The interface between the coating and the substrate clearly reveals a metallurgical bond. To examine the microstructural evolution from the top surface to the interior of the coating, SEM analysis of the cross-sectional morphologies is crucial.

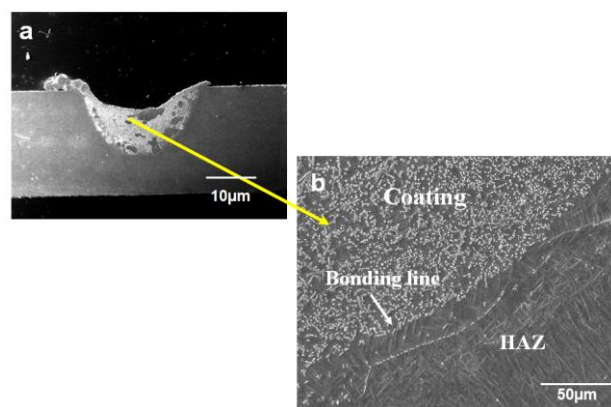


Figure 5. (a) The cross-sectional morphologies of laser-cladding coatings and (b) Top and heat affected zone (HAZ) of coating

Figure 6a further illustrates the cross-sectional morphology of the coating produced using injected TiC powders. As depicted in this figure, the microstructure reveals that the upper section is predominantly composed of dendritic structures, while the lower section is characterized by granular crystals. Previous research suggests that the solidification morphology observed in different regions during the cladding process is primarily governed by the stability of the solid/liquid interface, which is quantified by the ratio of the temperature gradient (G) to the solidification rate (R) (Lee, Nordin, Babu, & Farson, 2014). With constant processing parameters, R decreases

progressively from the surface toward the interior of the molten pool, while G follows an inverse trend. Therefore, the G/R ratio increases with depth, driving the observed microstructural transition from dendritic to granular morphology. This observation is further supported by the SEM micrographs in Figure 5, which illustrate detailed specimens processed at a laser power of 200 W and a scanning speed of 1 mm/s. Two distinct zones can be identified: (1) the coating layer, characterized by dendritic and fragmented morphologies, where dendrite density decreases and α' -martensite content increases with depth; and (2) the heat-affected zone (HAZ), which displays acicular α' -martensite resulting from the $\beta \rightarrow \alpha'$ phase transformation upon exceeding the β -transus temperature ($\sim 995^\circ\text{C}$). These findings are consistent with those of Simonelli et al. (Simonelli, Tse, & Tuck, 2014) who demonstrated that cooling rates exceeding 410 K/s induce martensitic transformation in the HAZ of Ti6Al4V. Similarly, the microstructural evolution observed in the present study agrees with previous findings for laser-melted Ti6Al4V (Jingjing Yang et al., 2016), and these observations can be extended to laser-clad TiC/Ti-6Al-4V composites because both processes involve similarly high solidification and cooling rates. Under these rapid cooling conditions, the β phase undergoes a diffusionless transformation into the supersaturated, non-equilibrium α' phase (Sun, Yang, Guo, & Dong, 2001).

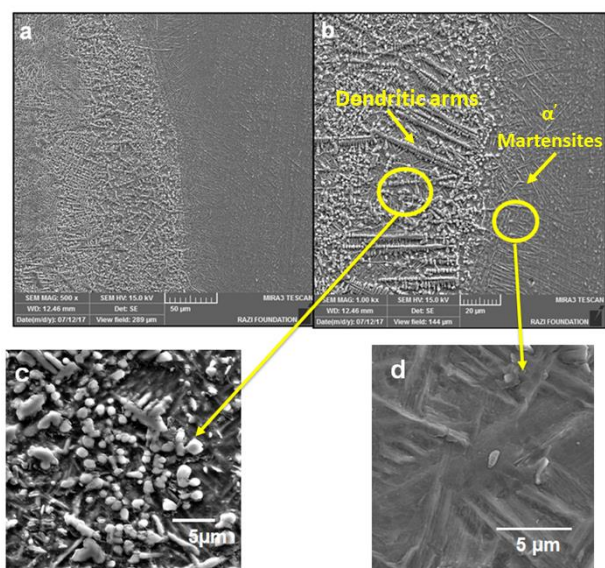


Figure 6. (a) Low and (b) high magnification of typical microstructure of the coating; high magnification of the (c) coating, and (d) HAZ

The absence of cracks and the defined grain boundaries observed at the coating/substrate interface indicate the formation of a strong metallurgical bond between the coating and the Ti6Al4V substrate. Such a

metallurgical bond is essential for ensuring the mechanical integrity and long-term functional performance of the coating.

The formation of the dendritic TiC structure in the titanium matrix within the composite layer can be described as follows: (i) first, the Ti powder pre-deposited on the substrate melts under laser irradiation because titanium has a significantly lower melting point (1668°C) than TiC (3250°C); and (ii) subsequently, according to the TiC phase diagram, the TiC particles partially dissolve in the molten titanium at temperatures well below their melting point (Courant et al., 2001; Saleh, Abboud, & Benyounis, 2010).

The molten pool undergoes progressive undercooling, and dendritic TiC precipitates from the liquid. Because both Ti and C are supplied from the molten liquid, TiC forms in situ, producing a uniformly distributed and well-bonded matrix–particle interface.

According to the TiC phase diagram, the carbon content of the TiC precipitated from the liquid phase, ranging from approximately 33 to 50%, differs from the ideal stoichiometric Ti ratio of 1:1. Following the initial precipitation of TiC, the remaining titanium-rich liquid infiltrates the spaces between the TiC dendrite arms, promoting interconnection of the dendritic network.

Fluid flow within the molten Ti disturbs the preferential alignment of the TiC dendrite arms, resulting in a more homogeneous microstructure while suppressing pore formation within the coating. In addition, rapid cooling transforms the titanium matrix into supersaturated hexagonal α' martensite through a diffusionless $\beta \rightarrow \alpha'$ transformation, with carbon remaining dissolved in the metastable matrix.

3.3. CORROSION CHARACTERIZATION

3.3.1. Open Circuit Potential (OCP) Analysis

Figure 7 shows the open circuit potential (OCP) curves of Ti6Al4V and TiC/Ti6Al4V samples immersed in a 3.5% NaCl solution. The OCP was monitored to evaluate the surface passivation behavior and corrosion resistance of the samples. Generally, materials exhibiting higher corrosion resistance possess more positive corrosion potentials (Akinlabi, Mathoho, & Mubiayi, 2019).

As shown in Figure 7, both samples exhibited a gradual increase in OCP with immersion time, indicating progressive surface stabilization and the formation of a protective passive oxide film. Compared with the Ti6Al4V substrate, the TiC/Ti6Al4V composite coating exhibited a more positive and stable OCP, suggesting enhanced passivation behavior and improved corrosion resistance in the chloride-containing environment.

The unreinforced Ti6Al4V sample (Figure 7a) exhibited a gradual increase in OCP, rising from approximately 0.071 V to 0.081 V during the 60 s immersion period. This smooth and monotonic trend indicates progressive surface stabilization through the formation of a uniform passive oxide film, reflecting the inherent passivation behavior of titanium alloys. In contrast, the TiC/Ti6Al4V composite (Figure 7b) exhibited a more positive initial OCP of approximately 0.0807 V, which further increased to about 0.0847 V over the same period. Although a slight transient fluctuation was observed at approximately 10 s, the overall trend remained stable and shifted toward more noble potentials.

Although a slight transient fluctuation was observed at approximately 10s, the OCP exhibited an overall positive and stable trend throughout the immersion period. The consistently more noble OCP values of the TiC-reinforced sample indicate enhanced surface passivation and improved corrosion resistance compared with the unreinforced Ti6Al4V alloy. This finding corroborates previous research indicating that TiC incorporation can significantly enhance the corrosion resistance of Ti6Al4V matrices by promoting the formation of a more stable and protective passive film (Liu et al., 2023). The positive shift in OCP observed for the TiC/Ti6Al4V composite indicates improved thermodynamic stability and enhanced surface passivation, which can be attributed to microstructural refinement and the formation of a denser, more protective passive film induced by TiC reinforcement. Although OCP measurements alone cannot quantitatively determine corrosion rates, the more noble and stable potential evolution strongly suggests that TiC incorporation enhances the electrochemical stability and corrosion resistance of the Ti6Al4V alloy under the investigated conditions.

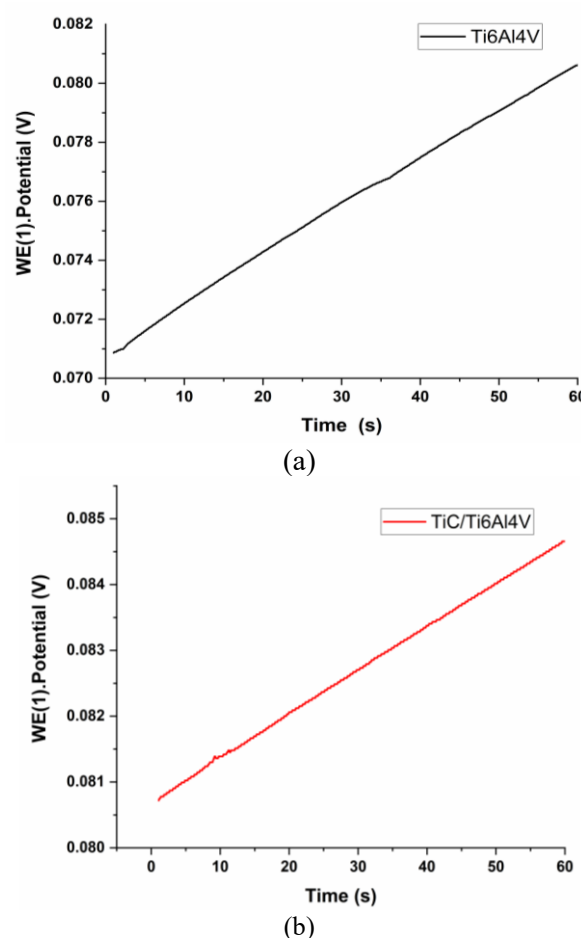


Figure 7. OCP graph of (a) Ti6Al4V and (b) TiC/ Ti6Al4V after 24 hours immersion

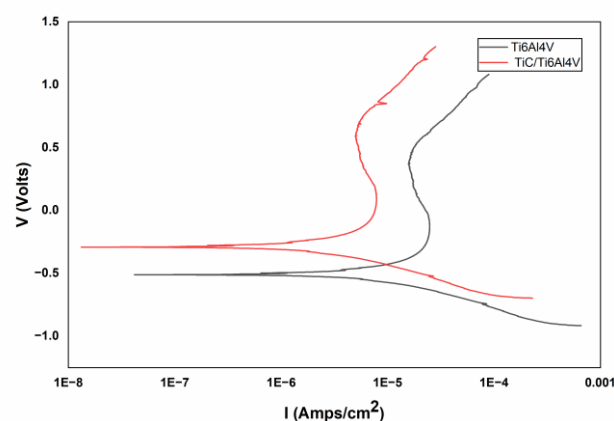


Figure 8. The polarization curves for Ti6Al4V TiC/ Ti6Al4V alloy

Figure 8 compares the Tafel polarization curves of Ti6Al4V and TiC/Ti6Al4V after 24 h of immersion in a 3.5 wt.% NaCl solution. As shown in Figure 8, both polarization curves exhibit a smooth V-shaped profile with minimal electrochemical noise, indicating stable

electrochemical behavior. This response is consistent with the formation of a protective passive oxide film on the sample surfaces during immersion. All polarization curves exhibit distinct cathodic and anodic branches, characteristic of passive metallic materials. Following the active anodic region, the Ti6Al4V alloy displays a stable passive region, indicating the formation of a protective oxide film on the surface. The TiC/Ti6Al4V composite exhibits more pronounced passive behavior, characterized by lower anodic current densities and a shift toward more noble potentials, suggesting the formation of a denser and more stable passive film ([Pan et al., 2022](#)). The corrosion current density (I_{corr}) is determined by extrapolating the cathodic and anodic Tafel slopes to the corrosion potential (E_{corr}), based on mixed potential theory. Furthermore, the polarization resistance (R_p) was calculated using the Stern–Geary Equation (2) ([Heitz & Schwenk, 1976](#)):

$$R_p = \beta_a \beta_c / 2.303 \times i_{corr} (\beta_a + \beta_c) \quad (2)$$

where I_{corr} is the corrosion current density ($A\ cm^{-2}$), and β_c and β_a are the cathodic and anodic Tafel slopes, respectively. The calculated polarization resistance (R_p) and corresponding electrochemical corrosion parameters for Ti6Al4V and TiC/Ti6Al4V are summarized in Table 2, indicating that TiC/Ti6Al4V exhibits higher polarization resistance than Ti6Al4V in NaCl solution. From the fundamentals of corrosion kinetics, it is known that current density is directly proportional to the corrosion rate. The corrosion rate determined by the polarization method, denoted as P_i (mm/year), was evaluated using Equation (3) ([Bahmani, Arthanari, & Shin, 2019, 2020](#); [Lotfpour et al., 2021](#)):

$$P_i = 22.85 \times i_{corr} \quad (3)$$

Based on the principles of corrosion kinetics, the corrosion current density is directly proportional to the corrosion rate. Consequently, any factor that increases the corrosion current density leads to a corresponding increase in the corrosion rate ([Goyal, Prasad, & Verma, 2025](#)).

TABLE 2. Corrosion results relate to the polarisation curves for Ti6Al4V & TiC/Ti6Al4V alloys after 24 hours immersion.

Material	E_{corr} (V _{SCE})	i_{corr} (Acm ⁻²)	β_a (mV/decade)	β_c (mV/decade)	R_p (Ω)	P_i (mm/year)
Ti6Al4V	-0.54494	6.16E-07	197.21	-120.6	52814.21	1.41E-05
TiC/ Ti6Al4V	-0.40287	1.45E-07	88.446	-74.072	121284.4	3.30E-06

3.4. Microhardness

The average microhardness of the as-received Ti6Al4V was measured to be 302 HV, whereas a maximum microhardness value of 598 HV was achieved after laser treatment. This significant increase in microhardness is consistent with the formation of a TiC-reinforced surface layer on the Ti6Al4V substrate. These results indicate that laser power is proportional to the induced heat input, which enhances dilution during the process. Furthermore, due to the higher laser absorption coefficient of TiC powder compared to carbon grains, an increase in laser power more significantly affects the TiC particles than the carbon released from the PVA. During cooling and solidification, the low solubility of carbon does not prevent the entrapment of carbon grains, leading to an increased carbon content in the coating ([Lin, Lin, & Chen, 2012](#); [Tjong & Chen, 2004](#)). Consequently, this process promotes the dissolution of carbon, which contributes to the enhanced hardness of the developed material, making it suitable for high-performance applications.

4. CONCLUSION

In this study, TiC-reinforced coatings were successfully deposited onto Ti6Al4V substrates using

laser cladding, resulting in uniform and defect-free layers. Microstructural analysis revealed a distinct transition from dendritic to granular crystalline structures from the coating surface toward the substrate interface. The incorporation of TiC significantly enhanced the mechanical and electrochemical performance of the alloy. Notably, the microhardness increased from 302 HV to 598 HV. Electrochemical evaluations in a NaCl solution demonstrated that the TiC/Ti6Al4V composite possesses superior corrosion resistance compared to the bare alloy, characterized by a higher polarization resistance (R_p) and a lower corrosion current density (I_{corr}). Quantitatively, the TiC coating improved the corrosion resistance by a factor of 2.3 and reduced the corrosion rate by a factor of 0.235. These findings confirm that laser cladding with TiC particles is an effective method for tailoring the kinetic parameters of Ti6Al4V to suit aggressive corrosive environments.

ACKNOWLEDGEMENT

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NOMENCLATURE

PVD	Physical vapor deposition
CVD	Chemical vapor deposition
TiC	Titanium carbide
MMCs	Titanium metal matrix composites
Ti-6Al-4V	Titanium alloy
SEM	Scanning electron microscope
XRD	X-ray diffractometer
SCE	Saturated calomel electrode
FESEM	Field-emission scanning electron microscopy
T _b	Boiling point
HAZ	Heat affected zone
G	Temperature gradient
R	Solidification rate
OCV	Open circuit potential
i _{corr}	Corrosion current density
E _{corr}	Corrosion potential
R _p	Polarization resistance
A/cm ²	Amperes per square centimeter
β _c β _a and β _a β _a	Cathodic and anodic Tafel slopes
HV	Vicker's hardness value
PVA	Poly vinyl alcohol

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