



High-temperature corrosion of Ti6Al4V and in-situ reinforced composites fabricated by laser additive manufacturing

Matshela Tshepho Hosia Kgomo¹ · Bathusile Masina¹ · Ipfi Mathoho^{1,3} · Vusimuzi Mulaudzi²

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Abstract

This study investigates the high-temperature corrosion behaviour of directed energy deposited (DED) Ti6Al4V (Ti64) and its in-situ composites (TiC/Ti64 and TiBw/Ti64) in oxygen-rich NaCl- Na₂SO₄ environments at 300 °C, 600 °C, and 900 °C. DED produces refined microstructures with reinforcement phases distributed along grain boundaries, fundamentally altering corrosion mechanisms. Thermogravimetric analysis revealed that TiBw/Ti64 exhibited superior resistance (activation energy: 282 kJ/mol) due to the formation of stable boron oxides (B₂O₃) that maintained protective layer integrity through self-healing mechanisms. TiC/Ti64 showed intermediate performance (276 kJ/mol), with TiC particles acting as oxygen diffusion barriers but undergoing oxidation at >800 °C to form TiO₂ and carbon residues. Unreinforced Ti64 suffered severe material loss (198 kJ/mol) via volatile TiCl₄ formation that disrupted the oxide scale. Microstructural analysis demonstrated that AM-induced grain refinement enhanced oxide nucleation site density, while reinforcement distribution influenced galvanic interactions. These findings establish that in-situ TiBw/Ti64 fabricated by DED offers optimal performance for aerospace and marine applications below 600 °C, with degradation mechanisms transitioning from surface oxidation to bulk volatilization above this threshold.

Keywords Additive manufacturing · High temperature corrosion · Titanium-based matrix composites

1 Introduction

Ti6Al4V (commonly referred to as Ti64) is the most commercially significant titanium alloy, often regarded as the “workhorse” of titanium alloys [1]. Comprising 6% aluminium (an α -phase stabilizer) and 4% vanadium (a β -phase stabilizer), Ti64 exhibits a dual-phase microstructure of α

and β phases. Its exceptional strength-to-weight ratio, corrosion resistance in harsh environments such as seawater and acidic media, and outstanding biocompatibility have made it indispensable in aerospace, biomedical, and marine applications [2]. Specifically, its use in medical implants (e.g., hip and knee replacements, dental implants, and surgical instruments) and fatigue-critical aerospace components underscores its versatility. Despite these advantages, Ti64 is limited in high-temperature applications to approximately 315 °C. Above this temperature, rapid oxidation and the formation of a non-protective oxide scale significantly reduce its durability, often leading to premature failure [3, 4].

To overcome these limitations, titanium matrix composites (TMCs) incorporating ceramic reinforcements such as TiC and TiB have been developed [5–8]. These reinforcements modify oxidation kinetics by acting as diffusion barriers and promoting protective oxide formation [9].

Recent studies have provided valuable insights into TMC corrosion behaviour. Kang et al. [10] investigated TiBw/TA15 composites at 800 °C in NaCl environments, demonstrating that TiB whiskers promote dense TiO₂-Al₂O₃ scale formation through grain refinement. Li et al. [11] reported

Bathusile Masina, Ipfi Mathoho and Vusimuzi Mulaudzi contributed equally.

✉ Matshela Tshepho Hosia Kgomo
hosiakgomo1@gmail.com

Vusimuzi Mulaudzi
Vusimuzi.mulaudzi@ul.ac.za

¹ Photonic Center, Manufacturing Cluster, CSIR, Pretoria, South Africa

² Department of Chemistry, University of Limpopo, Polokwane, South Africa

³ Department of Mechanical Engineering Science, Faculty of Engineering and the Built Environment, University of Johannesburg, Johannesburg 2006, South Africa

that TiC+TiB reinforced TB8 composites exhibited 57.5% lower mass gain than unreinforced alloys, attributed to TiB acting as nucleation sites for protective oxides. Chen et al.

[12] and Lv et al. [13] similarly showed that TiC reinforcement in nickel-based coatings and composites refined microstructures and enhanced Cr₂O₃ layer integrity. Liu et al. [14] emphasized that while mechanical properties of TMCs are well-characterized, corrosion studies remain limited.

Despite these promising findings, three critical gaps persist. First, existing studies predominantly utilize conventionally processed materials (sintering, powder metallurgy), leaving the influence of additive manufacturing (AM) on corrosion behaviour unexplored. AM processes such as directed energy deposition (DED) produce unique microstructural features refined grains, non-equilibrium phases, and reinforcement distributions that fundamentally alter corrosion mechanisms. Second, systematic comparisons of TiC versus TiB reinforcements under identical conditions are lacking, preventing rational material selection. Third, the interaction between AM-induced microstructures and molten salt corrosion mechanisms remains poorly understood, particularly regarding how reinforcement distribution affects oxide scale stability and volatile species formation.

This study addresses these gaps by systematically investigating the high-temperature corrosion behaviour of DED-fabricated Ti64, TiC/Ti64, and in-situ TiBw/Ti64 composites in 50% NaCl- 50% Na₂SO₄ environments. This study specifically examines how addition of TiC, TiB and AM- induced microstructural features reinforcement distribution, grain boundary pinning, and phase refinement influence corrosion kinetics, oxide scale development, and degradation mechanisms across 300–900 °C. By comparing TiC and TiB reinforcements under identical conditions and provide actionable guidance for TMC design in high-temperature applications.

2 Experimental procedures

2.1 Material

TiC, TiB₂, and Ti64 grade 5 powders were utilized in the fabrication of TMCs. Ti6Al4V was supplied by TLS Technik GmbH & Co company, while TiC and TiB₂ were supplied by Nanografi company. Ti6Al4V showed smooth spherical particles with particles size ranging between 45 and 100 µm and this is good for flowability. TiB₂ showed fine and irregular particles with particle size distribution of 20–100 µm as shown in Fig. 1 (b). TiC showed irregular shaped particles with particle size ranging from 45 to 100 µm Fig. 1 (c).

2.2 Sample manufacturing

The Ti64 grade 5, TiC/Ti64, and in-situ TiBw/Ti64 samples were fabricated using the DED process. The sandblasting of Ti64 base plates (50×50 mm L × B) was carried out using a Storm Machinery model SM5005. Sand was used as the blasting medium, at a pressure of 6 MPa for a duration of 3 min. The DED system used in this study consist of a high-precision KUKA robotic arm model KR80L30 supplied by KUKA company from Germany as shown in Fig. 2, which provided multi-axis movement of the deposition head consisting of two optics (Reflection mirror and lens) and also cover slide for protection.

The system was equipped with a dual-hopper powder feeder, which played a critical role in delivering different powders simultaneously into the melt pool. For the fabrication of the composite samples, Ti64 powder was fed from one hopper, while the second hopper was used to deliver either TiC or TiB₂ powder, depending on the desired composite. This configuration enabled the in-situ formation of TiC/Ti64 and in-situ TiBw/Ti64 composites during the deposition process.

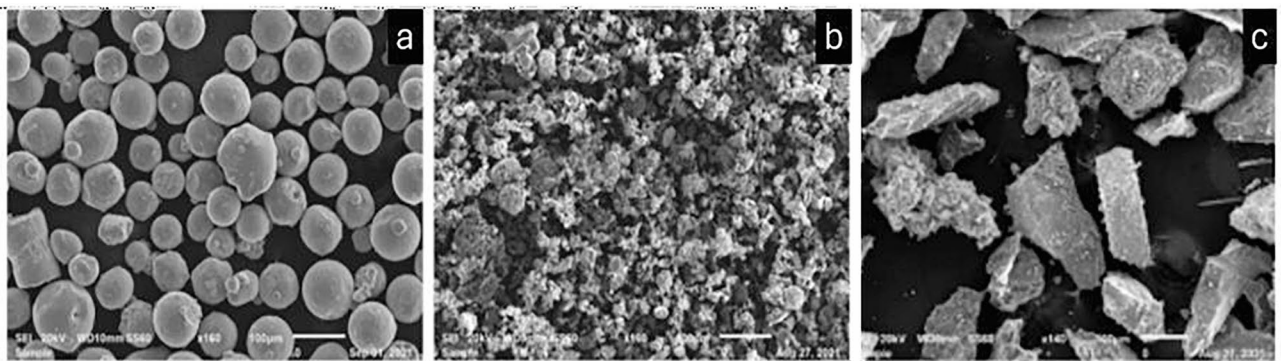


Fig. 1 SEM images of the starting powders: (a) Ti64 grade 5 showing smooth spherical particles; (b) TiB₂ showing fine irregular particles; (c) TiC showing irregular shaped particles

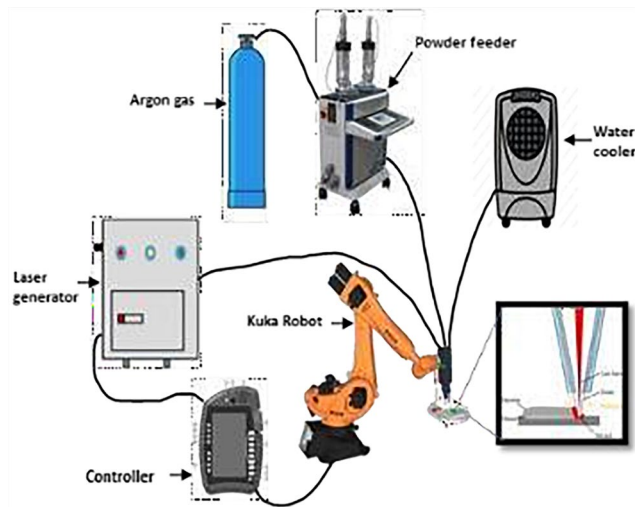


Fig. 2 Directed Energy Deposition (DED) system showing the KUKA robotic arm (model KR80L30) with dual-hopper powder feeder and IPG Photonics YLR-3000 fiber laser

The energy required to melt the powders and maintain a stable melt pool was provided by IPG Photonics YLR-3000 fiber laser (Ytterbium-based, continuous wave, 1073 nm, manufactured in United State of America). A constant laser energy density of 90 J/mm was applied throughout the manufacturing process to ensure consistent melting and bonding of the powders. Argon gas was employed both as the carrier gas, at a controlled flow rate of 1.5 L/min, and as the shielding gas, at a higher flow rate of 15 L/min. The carrier gas helped transport the powders from the hoppers to the melt pool, while the shielding gas protected the molten material from oxidation and atmospheric contamination. For both the TiC/Ti64 and in-situ TiBw/Ti64 composites, the mass ratio was set at 95% Ti64 and 5% of either TiC or TiB₂. The selection of 5 wt% reinforcement was based on preliminary optimization studies (not shown) and literature indicating that this concentration balances mechanical enhancement with processability in DED [15, 16]. This ratio was maintained through precise control of the powder feed rates from the individual hoppers and rectangular prism of 60 × 35 × 10 mm (L × W × H) were manufactured. The Ti64 sample, which served as the baseline for comparison, was fabricated using 100% Ti64 powder and a cube of 60 × 35 × 10 mm (L × W × H) was manufactured.

2.3 Sample preparation

The samples were cut using a Struers Labotom-5 abrasive cutting machine equipped with a Struers titanium cut-off wheel (20S25). Water cooling was applied throughout the process to prevent thermal and mechanical damage. A total of 9 samples were cut from each manufactured cubes of 60 × 35 × 10 mm (L × W × H) of Ti64, TiC/Ti64, and in-situ

TiBw/Ti64 resulting in 27 samples overall. These were divided between electrochemical corrosion testing and high-temperature corrosion testing, with three samples used per condition to ensure repeatability and reliable results. Each sample was cut to a size of 5 mm × 5 mm, suitable for the testing setups and to allow uniform exposure during experiments. The samples were mounted using an AMP 50 automatic mounting press machine in order to be grinded and polished. To mount each sample, an

Aka Resin Phenolic SEM black conductive resin was utilized. Mounted samples were grinded with Struers Tegrapol-25 grinding and polishing machine in order to be able to analyse them at micro level. For grinding samples, silicon carbide (SiC) grinding papers with grain sizes ranging from 80 to 320 and 1200 to 4000 were utilized. The samples underwent polishing using a Daipros MD- Mol 3 µm diamond suspension for a duration of 3 min, followed by a colloidal silica 0.04 µm OP- S suspension for the same length of time as the final polishing stage [2].

2.4 Characterization of materials before and after the test

Scanning Electron 50 Microscope (SEM) available at CSIR Laser Enabled Manufacturing Joel JSM-6010PLUS/LA was used to analyse the samples' microstructure of Ti64, TiC/Ti64 and in-situ TiBw/Ti64 characteristics for before and after to check the effect of corrosion. Microstructural pictures were captured at various positions to give an overview of the entire samples. The crystallographic structure of the samples was analysed using PANalytical X'Pert PRO X-ray diffraction available at CSIR Nano Center. X-ray diffraction was used to determine the phase composition of the materials before and after the test in order to confirm any phase transformation during the tests. The scan range of 2θ from 0° to 100° was used, which allows for the detection of a wide range of crystalline phases. X-rays are directed at the sample, and the diffracted rays are measured as a function of the angle (2θ).

2.5 High-temperature corrosion test

Nine samples of Ti64, TiC/Ti64, and in-situ TiB/Ti64 were prepared for high-temperature corrosion tests with constant duration and changing temperature. The conventional mass-change method (weighing samples before exposure; applying salt mixture; exposing at target temperature; cooling; cleaning; and re-weighing) was employed [11, 16]. The ultra-furnace was utilized for conducting high-temperature corrosion tests experiments. For each test, three samples of each material were tested per temperature to ensure repeatability [11]. Before testing, the samples were polished,

cleaned, and their initial weight and dimensions were recorded. The first test was performed at 300 °C for 6 h, followed by a second test at 600 °C for 6 h, and finally a third test at 900 °C for 6 h. A solution containing a combination of 5 g of NaCl and 5 g of NaSO₄ was prepared in a beaker for the purpose of studying corrosion at high temperatures. The solution was moistened with small amounts of distilled water. The mixture of the salts was applied onto the refined surface.

of the material using a brush and immediately they were put in the furnace. The high temperature corrosion test was conducted on three materials: Ti64, TiC/Ti64, and in-situ TiB/Ti64. The first test was performed at 300 °C for 6 h, followed by a second test at 600 °C for 6 h, and a third test at 900 °C for 6 h and all samples were air cooled, cleaned with ultrasonic bath and post-test weight measurements and surface characterization were performed. Test temperatures were selected to represent three distinct corrosion regimes: 300 °C (below the threshold for significant oxide formation, representing start-up/shutdown conditions), 600 °C (intermediate temperature where protective oxides form but molten salt interactions begin), and 900 °C (severe conditions simulating gas turbine or engine hot sections) [17–19].

3 Results and discussion

3.1 High temperature corrosion results

3.1.1 High temperature corrosion kinetics

Figure 3 illustrates the temperature-dependent corrosion kinetics, revealing three distinct regimes. At 300 °C, minimal mass gain across all materials indicates negligible corrosion, consistent with limited molecular collision kinetics below 400 °C [17]. This regime represents solid-state oxidation where the native TiO₂ layer provides temporary protection. Similar observations were made by Kumar et al. [17], who reported that Ti64 exhibits minimal oxidation below 400 °C due to the protective nature of the native oxide layer.

At 600 °C, all materials exhibited slightly increase in mass gain, with Ti64 showing the highest, followed by TiC/Ti64 and TiBw/Ti64 the lowest. This divergence reflects the onset of reinforcement-specific protection mechanisms. The increased mass corresponds to formation of a thermally grown oxide scale (primarily TiO₂) that, in reinforced composites, benefits from grain refinement-induced nucleation site density [11]. Li et al. [11] similarly reported that TiC+TiB reinforced TB8 composites exhibited significantly lower mass gain than unreinforced alloys, which they attributed to reinforcements acting as nucleation sites for protective oxides. TiBw/Ti64's superior performance stems

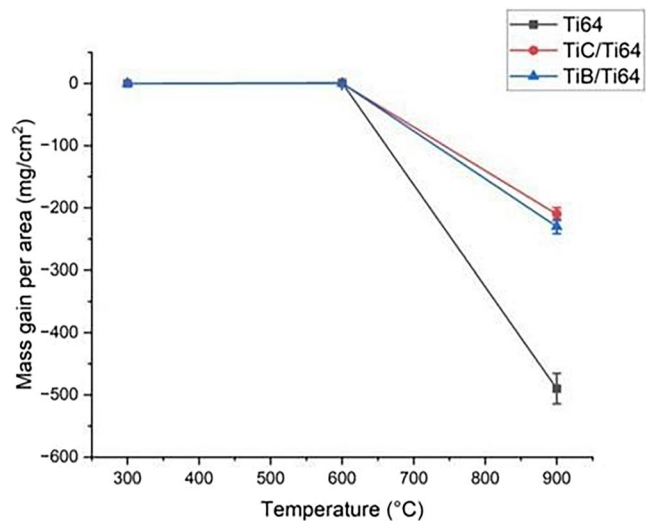


Fig. 3 Oxidation kinetics of high-temperature corrosion showing average mass gain per area versus temperature for Ti64, TiC/Ti64, and in-situ TiBw/Ti64 after 6 h exposure to 50% NaCl- 50% Na₂SO₄ at 300 °C, 600 °C, and 900 °C. Error bars represent standard deviation from three samples per condition

from boron oxide (B₂O₃) formation, which exhibits lower oxygen diffusivity and can flow to seal microcracks and a self-healing mechanism that is unavailable in unreinforced Ti64. This self-healing behaviour has been documented by Kang et al. [10], who observed that TiB whiskers promote dense oxide scale formation in TA15 composites.

At 900 °C, a sharp decline in mass gain particularly for Ti64 signals the transition from oxidation-dominated to volatilization-dominated corrosion. This inflection point occurs when the molten NaCl-Na₂SO₄ eutectic (melting point ~620 °C) fully penetrates the oxide scale, triggering fluxing reactions that convert protective TiO₂ to volatile TiCl₄ (Eqs. 2–4) and soluble sodium titanates (Eq. 3). The more gradual decline for TiC/Ti64 and TiBw/Ti64 indicates that reinforcements delay this transition by: (1) acting as physical barriers to salt penetration, (2) forming secondary oxides (B₂O₃, TiO₂ from TiC oxidation) that maintain scale integrity, and (3) stabilizing grain boundaries against rapid oxygen diffusion [11, 13]. Lv et al. [13] reported similar findings for TiC/GTD222 composites, where TiC reinforcement enhanced oxide layer integrity at elevated temperatures.

Critically, the DED fabrication process influences these kinetics through microstructural refinement. The rapid solidification inherent to DED produces finer prior-β grains and more uniform reinforcement distribution than conventional processing [19]. This refinement increases grain boundary density, providing more nucleation sites for protective oxides while simultaneously creating more potential diffusion paths a trade-off that favours corrosion resistance when.

reinforcements effectively pin boundaries. Similarly, Lekoadi et al. [27] reported that TiB whiskers in laser metal deposited in-situ TiBw/Ti64 composites reduce β -grain size, contributing to increased strength and potentially enhanced corrosion resistance through grain boundary pinning.

3.1.2 Activation energies for high temperature corrosion

The Arrhenius relationship (Fig. 4) provides quantitative insight into corrosion barriers. The activation energy for Ti64 (198 kJ/mol) aligns with reported values for TiO₂-dominated oxidation [19], suggesting that oxygen diffusion through the oxide scale is rate-limiting. Anuwar et al. [19] reported similar activation energies for Ti64 oxidation, confirming that oxygen diffusion through TiO₂ is the controlling mechanism. However, the higher activation energies for TiC/Ti64 (276 kJ/mol) and TiBw/Ti64 (282 kJ/mol) indicate that fundamentally different rate-controlling mechanisms operate in the composites.

For TiC/Ti64, the 39% increase in activation energy corresponds to the energy barrier for oxygen diffusion through TiC-containing boundaries. TiC particles (melting point ~3160 °C) remain stable at test temperatures, forcing oxygen to follow tortuous paths around reinforcements effectively increasing diffusion path length by 2–3× compared to unreinforced Ti64 [19]. Liu et al.

[15] demonstrated that TiC particles in DED-fabricated Ti64 composites act as effective barriers to oxygen diffusion, contributing to enhanced corrosion resistance. Additionally, TiC partially oxidizes at >800 °C to form TiO₂, consuming oxygen that would otherwise reach the matrix. Kim et al. [16] observed similar TiC oxidation behaviour

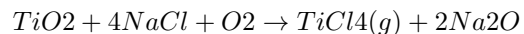
in TMCs, noting that TiC reinforcement modifies oxidation kinetics through sacrificial oxidation mechanisms.

For TiBw/Ti64, the 42% increase reflects the combined effects of: (1) B₂O₃ formation (melting point ~450 °C) producing a glassy phase that seals pores, (2) TiB whiskers acting as “grain boundary pins” that limit coarsening of the oxide scale, and (3) reduced Ti ion activity in TiB-containing regions [11]. The slightly higher activation energy for TiBw/Ti64 versus TiC/Ti64 (282 vs. 276 kJ/mol) suggests that boron oxide’s self-healing capability provides marginal benefit over TiC’s barrier mechanism under these conditions. Kang et al. [28] reported that network structured TiBw/TA15 composites exhibit enhanced hot corrosion resistance due to the formation of protective oxide scales, consistent with our findings for TiBw/Ti64.

3.1.3 Microstructure analysis for high-temperature corrosion test

The as-built Ti64 microstructure (Fig. 5a) exhibits martensites characteristic of rapid solidification during DED [19]. The fine, interlocking of α phase with intermittent β phase at lath boundaries result from the high cooling rates inherent to AM. This refined microstructure is significantly finer than the conventionally processed Ti64 provides increased grain boundary area that influences subsequent oxidation behaviour by providing more nucleation sites for oxide formation [19]. Simonelli et al. [19] documented similar martensitic structures in additively manufactured Ti64, confirming that rapid solidification produces characteristic α morphologies.

At 300 °C (Fig. 5b), the martensitic structure is not clearly visible, and the surface exhibits scattered dark corrosion pits. These pits are absent in as-built samples, and they represent sites where localized chloride-induced corrosion initiated via:



The minimal microstructural alteration despite visible pitting explains the negligible mass gain at this temperature (Fig. 3) corrosion products were volatile TiCl₄ that evaporated without accumulating. Some of retained martensitic features confirm that 300 °C is below the threshold for bulk oxidation, consistent with literature reporting minimal Ti64 oxidation below 400 °C [17]. Kumar et al. [17] similarly observed that Ti64 maintains its microstructure at temperatures below 400 °C, with only localized attack occurring at surface defects.

At 600 °C (Fig. 5c), the martensitic structure is completely obscured by a thick, granular corrosion layer. This transformation signals the transition from localized to uniform corrosion,

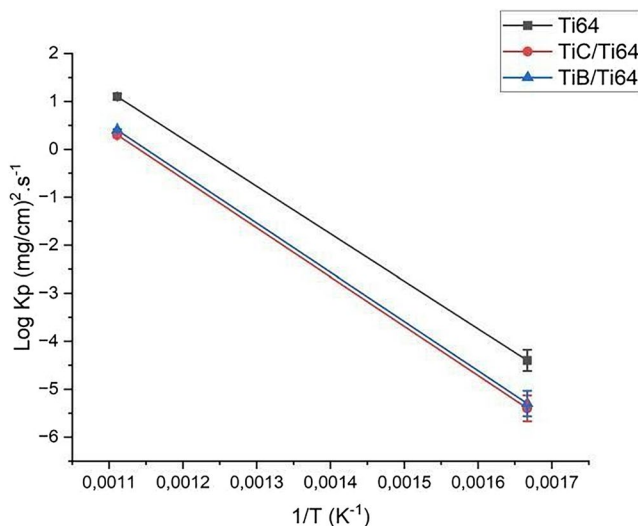
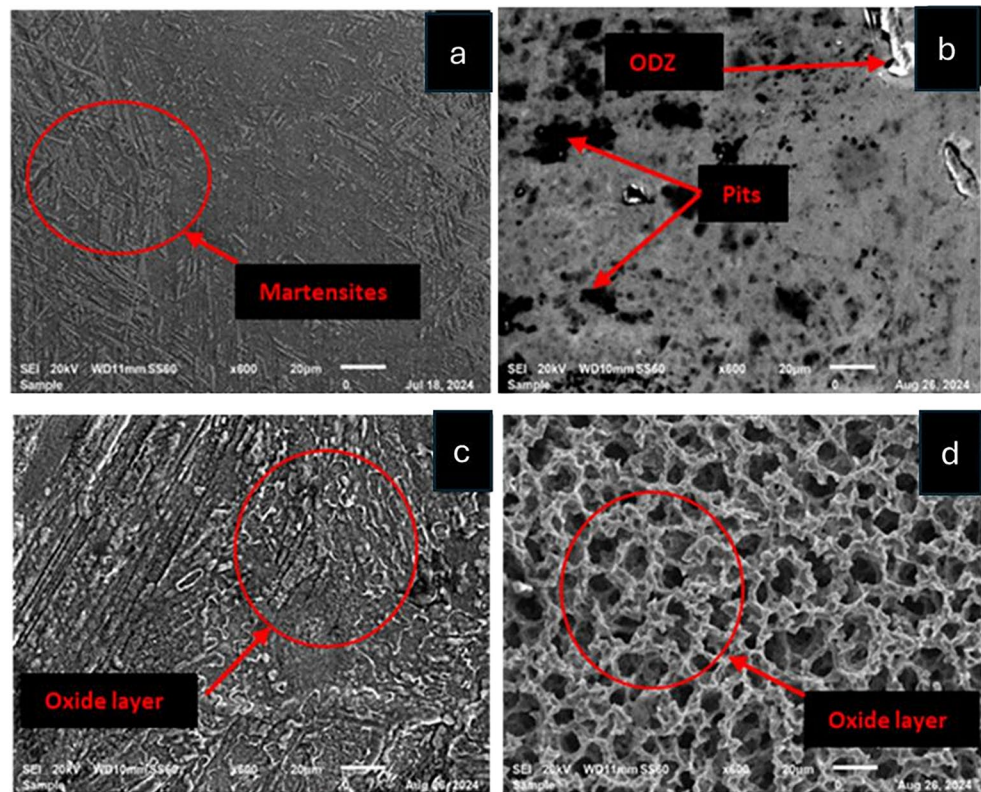


Fig. 4 Arrhenius plot showing logarithm of parabolic rate constant (log Kp) versus inverse temperature (1/T) for Ti64, TiC/Ti64, and in-situ TiBw/Ti64. Activation energies calculated from slopes: Ti64 (198 kJ/mol), TiC/Ti64 (276 kJ/mol), and TiBw/Ti64 (282 kJ/mol)

Fig. 5 Microstructural evolution of DED-fabricated Ti64 before and after corrosion in 50% NaCl-50% Na₂SO₄: (a) as-built α martensite with β phase; (b) after 300 °C showing corrosion pits; (c) after 600 °C showing granular corrosion layer obscuring structure; (d) after 900 °C showing porous sponge-like structure from volatile evaporation.



driven by molten salt penetration (NaCl-Na₂SO₄). The granular morphology is composed of TiO₂, Na₂TiO₃, and residual salts which indicate non-protective scale growth where continuous dissolution and reprecipitation (fluxing) prevents formation of a dense barrier. The complete coverage explains the peak mass gain observed in Fig. 3, as corrosion products accumulate before volatilization becomes dominant. Anuwar et al. [18] reported similar oxide scale formation on Ti64 at 600 °C, confirming that this temperature marks the onset of significant oxidation in saline environments.

At 900 °C (Fig. 5d), the surface transforms into a highly porous, sponge-like structure with complete destruction of original microstructural features. The pore network results from extensive volatilization of titanium chlorides (TiCl₄) and aluminum chlorides (AlCl₃), which evaporate and leave voids. This morphology is coupled with the sharp mass decline in Fig. 3 which confirms that volatilization dominates over oxide formation above 800 °C. The interconnected pores provide channels for rapid salt penetration, creating a self-sustaining corrosion cycle. Lu et al. [20] observed similar porous structures in laser shock peened Ti64 after high-temperature corrosion, attributing the morphology to volatile species formation.

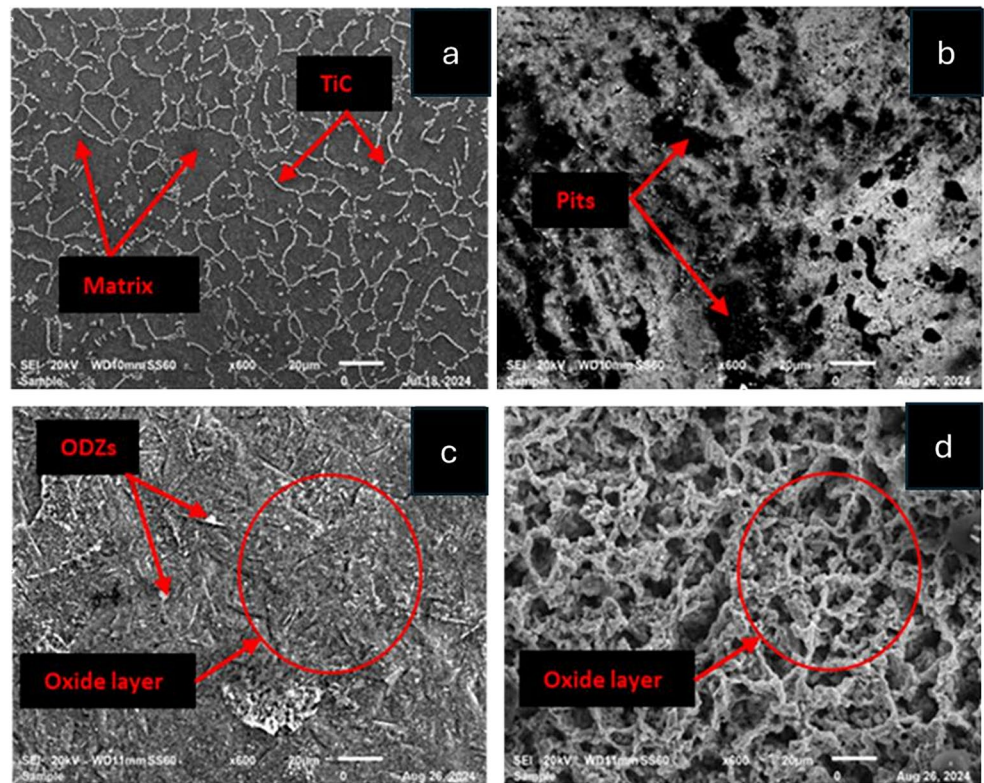
The as-built TiC/Ti64 microstructure (Fig. 6a) reveals TiC particles (bright, irregular morphology) preferentially located along β grain boundaries distribution characteristic of DED processing. During solidification, TiC

particles are pushed by the advancing solidification front and become trapped at grain boundaries. This distribution creates a continuous reinforcement network that fundamentally alters corrosion behavior by segmenting the surface into TiC-rich boundaries and TiC-depleted grain interiors. The Ti64 matrix exhibits the same α martensite as unreinforced material, confirming that TiC addition does not disrupt the DED solidification structure [21, 22]. Liu et al. [21] reported similar TiC distribution patterns in DED-fabricated Ti6Al4V composites, noting that reinforcement particles preferentially locate at grain boundaries. Bai et al. [22] also observed that TiC particles in spark plasma sintered composites form “necklace” structures along grain boundaries, consistent with our findings.

At 300 °C (Fig. 6b), the TiC particles are not visible, and the localized corrosion is evident as dark halos indicating galvanic coupling between conductive TiC and the Ti64 matrix. This microgalvanic corrosion occurs because TiC exhibits different electrochemical potential than the titanium matrix, creating localized cells where the matrix preferentially dissolves at particle interfaces. Despite this localized attack, the absence of mass gain (Fig. 3) confirms that corrosion products were volatile or minimal, consistent with TiCl₄ formation at particle interfaces. Liu et al.

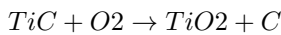
[15] documented similar galvanic effects in TiC-reinforced Ti64 composites, noting that the TiC-matrix interface becomes preferential sites for corrosion initiation.

Fig. 6 Microstructural evolution of DED-fabricated TiC/Ti64 before and after corrosion: (a) as-built showing TiC particles (bright) along grain boundaries in “necklace” pattern; (b) after 300 °C showing galvanic halos around TiC particles; (c) after 600 °C showing corrosion layer with TiC particles still visible; (d) after 900 °C showing porous structure with TiC replaced by TiO₂



At 900 °C (Fig. 6d), TiC particles are no longer distinguishable, indicating their oxidation.

via:



The resulting structure, while porous, retains more integrity than Ti64's sponge-like.

morphology (Fig. 5d) because TiC-derived TiO₂ partially fills pores. Carbon from TiC oxidation may also participate in carbothermal reduction ($\text{TiO}_2 + \text{C} \rightarrow \text{Ti} + \text{CO/CO}_2$), creating temporary local oxygen sinks. The complete disappearance of TiC marks the limit of its protective function beyond 800 °C, the reinforcement itself degrades, though its oxidation products provide some residual benefit. Yu et al. [23] reported similar TiC oxidation behaviour in laser-clad high entropy alloy coatings, noting that TiC decomposes above 800 °C to form TiO₂ and carbon species. Cao et al. [24] also observed that TiC reinforcements in TB8 matrix composites undergo oxidation at elevated temperatures, with the extent of degradation increasing with temperature.

The as-built TiBw/Ti64 microstructure (Fig. 7a) reveals acicular TiB whiskers (bright, needle-like features) uniformly distributed throughout the Ti64 matrix. These whiskers form via in-situ reaction during DED:

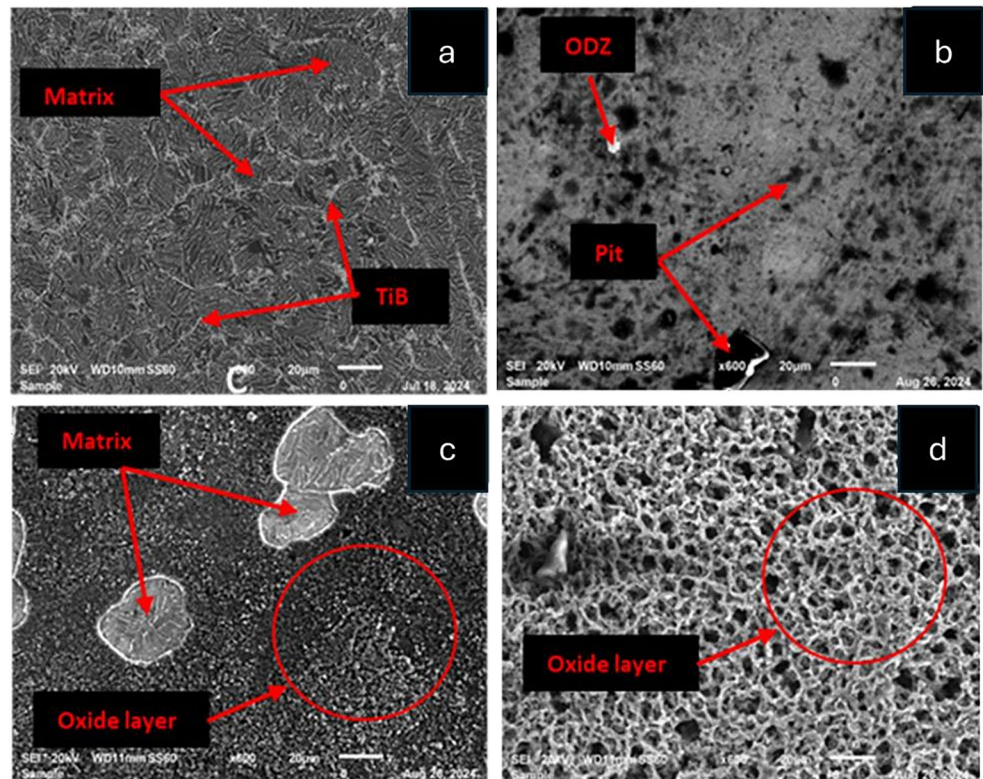


This reaction produces crystallographically aligned reinforcements with coherent interfaces and a key advantage of in-situ processing over ex-situ reinforcement addition. The TiB whiskers are preferentially located along grain boundaries and within grains, creating a three-dimensional network that pins grain boundaries and limits grain growth during solidification [25, 26]. The Ti64 matrix exhibits the same martensitic structure as unreinforced material, confirming that TiB formation does not disrupt the DED solidification microstructure. Ren et al.

[26] reported similar TiB whisker morphologies in in-situ TiB/Ti64 composites, noting that the acicular structure provides effective grain refinement. Lekoadi et al. [27] also observed that laser metal deposited TiB/Ti6Al4V-ELI composites exhibit network microstructures with TiB whiskers distributed along grain boundaries, contributing to enhanced mechanical properties.

At 300 °C (Fig. 7b), TiB whiskers are not clearly visible and minimal surface alteration and only faint dark spots which indicate limited corrosion at this temperature. The absence of mass gain (Fig. 3) confirms that 300 °C is below the threshold for significant TiB oxidation or matrix degradation. This stability exceeds that of TiC/Ti64, where galvanic halos were already evident at 300 °C. Kang et al. [10] similarly observed that TiB whiskers in TA15 composites remain stable at moderate temperatures, with degradation only occurring at elevated temperatures.

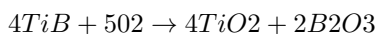
Fig. 7 Microstructural evolution of DED-fabricated in-situ TiBw/Ti64 before and after corrosion: (a) as-built showing acicular TiB whiskers (bright, needle-like); (b) after 300 °C showing intact TiB with minimal alteration; (c) after 600 °C showing granular products with TiB still identifiable; (d) after 900 °C showing porous structure with B₂O₃ glassy phase (smooth regions) filling pores



At 600 °C (Fig. 7c), TiB whiskers remain identifiable despite surface roughening and development of granular corrosion products. Crucially, whiskers are more persistent than TiC particles at the same temperature (Fig. 6c), reflecting TiB's higher thermal stability. The corrosion products preferentially form in TiB-depleted matrix regions, indicating that whiskers act as “corrosion barriers” that segment the surface into protected and unprotected zones. This

segmentation is more effective than TiC's because whiskers penetrate grain interiors rather than just boundaries and it explains TiBw/Ti64's superior kinetics in Fig. 3 and also, the matrix can still be observed. Li et al. [11] reported similar behaviour in TiC+TiB reinforced TB8 composites, noting that TiB whiskers provide more effective corrosion protection than TiC particles due to their acicular morphology and distribution.

At 900 °C (Fig. 7d), individual TiB whiskers are no longer distinguishable, indicating their oxidation via:



However, unlike TiC/Ti64 where oxidation led to complete structural degradation, TiBw/Ti64 exhibits regions of smooth glassy phase within pores identified as B₂O₃ (melting point 450 °C). This glassy boron oxide flows to fill cracks and pores, providing a self-healing mechanism unavailable in TiC-reinforced or unreinforced materials. The B₂O₃ phase exhibits oxygen diffusivity two orders of

magnitude lower than TiO₂, explaining why TiBw/Ti64 maintains the highest mass at 900 °C despite apparent microstructural degradation. Kang et al. [10] documented similar self-healing behaviour in TiBw/TA15 composites, where boron oxide formation contributed to enhanced corrosion resistance through pore sealing. Avila and Bandyopadhyay [25] also reported that in-situ formed reinforcements in titanium matrix composites can provide unique protection mechanisms through the formation of secondary phases.

4 Reactions of Ti64

4.1 Thermodynamic framework

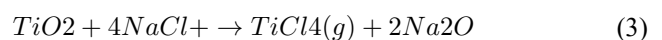
The corrosion mechanisms are governed by the relative stability of oxides, chlorides, and sulfates at each temperature.

4.1.1 Ti64 degradation sequence

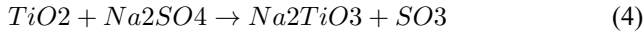
Stage 1 (T < 600 °C): Primary oxidation (Eq. 1) dominates, forming protective TiO₂.



Chloride penetration causes localized pitting via:



Stage 2 (600–800 °C): Fluxing reactions dissolve the protective scale:



The molten salt (NaCl–Na₂SO₄ eutectic) penetrates grain boundaries, accelerating oxygen transport.

Stage 3 ($T > 800$ °C): Volatilization dominates:



V₂O₅ formation (Eq. 6) further destabilizes the scale by forming low-melting V-containing compounds.



4.1.2 TiC/Ti64 modified mechanisms

TiC introduces competing reactions that both help and hinder:

- Barrier effect: TiC particles block oxygen diffusion paths.
- Sacrificial oxidation:

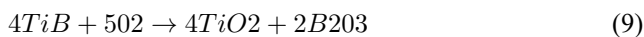


at > 800 °C.

Carbon from TiC oxidation can reduce adjacent TiO₂, creating local oxygen sinks that temporarily protect the matrix. However, CO/CO₂ evolution may generate pores that accelerate degradation at very high temperatures.

4.1.3 TiBw/Ti64 self-healing mechanism

TiB oxidation produces boron oxide:



B₂O₃ (melting point 450 °C) forms a glassy phase that:

- Flows to fill microcracks (self-healing).
- Reacts with NaCl to form NaBO₂, consuming chloride ions.

This self-healing capability explains TiBw/Ti64's superior performance despite galvanic challenges.

5 X-ray diffraction (XRD) analysis

5.1 Ti6Al4V

The XRD patterns in Fig. 8 reveal the progressive phase evolution of Ti64 with increasing temperature, providing crystallographic evidence for the corrosion mechanisms discussed in Sect. 3.2.1.

The as-built Ti64 exhibits strong α -Ti peaks (35.1°, 38.4°, 40.2°) with weak β -Ti peaks, confirming the martensitic α' structure characteristic of DED rapid solidification [19]. The absence of oxide peaks confirms that the native oxide layer is either amorphous or below detection threshold.

At 300 °C the XRD pattern remains essentially unchanged from as-built condition. No new phases appear, and peak positions are stable confirming that no bulk oxidation or phase transformation has occurred. This crystallographic stability correlates with the negligible mass gain in Fig. 3 and the retained martensitic structure in Fig. 5b. The absence of oxide peaks confirms that corrosion products (TiCl₄) were volatile and did not accumulate [19].

At 600 °C a significant phase evolution occurs. New peaks emerge corresponding to TiO₂- rutile (27.4°, 36.1°) and TiO₂-anatase (25.3°, 48.1°), confirming extensive oxidation. The appearance of weak Na₂TiO₃ peaks (32.8°, 47.5°) provides direct evidence for fluxing reactions (Eq. 3), where molten Na₂SO₄ reacts with TiO₂ to form sodium titanate. Concurrently, α -Ti peak intensities decrease as the oxide layer thickens and attenuates the matrix signal consistent with the granular corrosion layer observed in Fig. 5c.

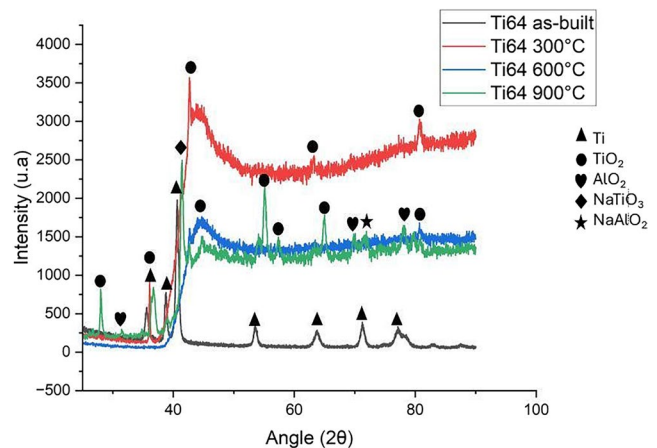


Fig. 8 XRD patterns of Ti64 in as-built condition and after 6 h exposure to 50% NaCl-50% Na₂SO₄ environment at 300 °C, 600 °C, and 900 °C

At 900 °C the pattern is dominated by TiO₂-rutile peaks, indicating complete surface oxidation. Na₂TiO₃ peaks intensify significantly, demonstrating accelerated molten salt attack at higher temperatures. Most importantly, α -Ti peaks are completely absent, and the matrix signal is entirely obscured by the thick oxide scale and/or the underlying metal has been consumed through volatilization (TiCl₄ formation). This complete disappearance correlates with the porous, sponge-like structure in Fig. 5d and the sharp mass decline in Fig. 3. Lu et al. [20] observed similar phase evolution in laser shock peened Ti64 after high-temperature corrosion, noting that complete surface oxidation occurs above 800 °C.

5.2 TiC/Ti64

The XRD patterns of TiC/Ti64 (Fig. 9) reveal how TiC reinforcement modifies phase evolution compared to unreinforced Ti64, providing insight into the improved corrosion kinetics observed in Fig. 3.

The as-built TiC/Ti64 exhibits α -Ti and β -Ti matrix peaks identical to unreinforced Ti64, with additional TiC peaks at 35.9°, 41.7°, and 60.5° corresponding to cubic TiC. No reaction products between TiC and matrix are detected, confirming TiC remains stable during DED processing without significant dissolution.

At 300 °C the XRD pattern remains essentially unchanged from as built. All matrix peaks and TiC peaks persist with similar relative intensities. This crystallographic stability is identical to unreinforced Ti64 at this temperature, and it confirms that 300 °C is below the threshold for both matrix oxidation and TiC degradation, consistent with minimal mass gain (Fig. 3) and the localized galvanic halos observed in Fig. 6b.

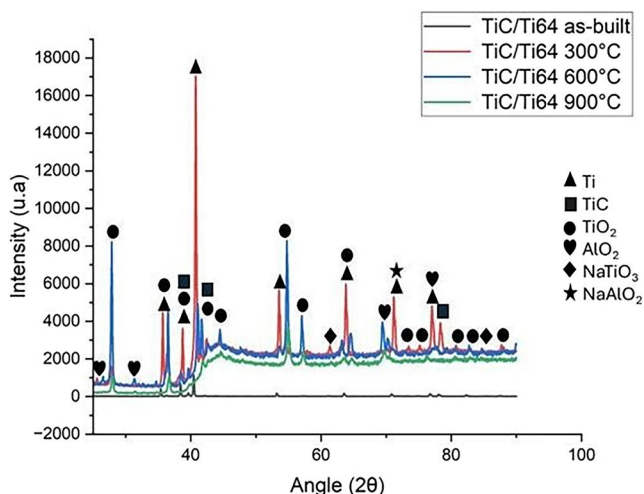


Fig. 9 XRD patterns of TiC/Ti64 in as-built condition and after 6 h exposure to 50% NaCl-50% Na₂SO₄ environment at 300 °C, 600 °C, and 900 °C

At 600 °C TiO₂ peaks (rutile at 27.4°, 36.1°; anatase at 25.3°, 48.1°) appear, confirming matrix oxidation. Critically, TiC peaks remain clearly visible unlike unreinforced Ti64 where matrix peaks attenuated significantly, TiC/Ti64 retains reinforcement-phase signals. This persistence indicates TiC acts as a stable framework within the oxidizing matrix. Weak NaTiO₂ peaks (32.5°, 47.2°) signal salt interaction, but their lower intensity compared to Na₂TiO₃ in unreinforced Ti64 suggests TiC partially inhibits fluxing reactions.

At 900 °C, dramatic phase evolution occurs. TiC peaks are completely absent, indicating complete oxidation of the reinforcement via $\text{TiC} + \text{O}_2 \rightarrow \text{TiO}_2 + \text{C}$. TiO₂-rutile peaks dominate, while NaTiO₂ peaks strengthen significantly. Compared to unreinforced Ti64 at 900 °C, TiC/Ti64 shows: (1) no α -Ti peaks (matrix consumed in both), (2) stronger TiO₂ peaks (from both matrix and oxidized TiC), and (3) different titanate chemistry (NaTiO₂ vs. Na₂TiO₃) suggesting TiC oxidation products influence salt reactions. Yu et al. [23] and Cao et al. [24] documented similar TiC oxidation behaviour in various composite systems, noting that TiC decomposition above 800 °C produces TiO₂ and carbon species that modify subsequent corrosion mechanisms.

5.3 In-situ TiBw/Ti64

The XRD patterns of in-situ TiBw/Ti64 (Fig. 10) provide crystallographic evidence for the superior corrosion resistance observed kinetically (Fig. 3) and reveal the unique self-healing mechanism enabled by boron oxide formation.

The as-built TiBw/Ti64 exhibits α -Ti and β -Ti matrix peaks with additional peaks corresponding to orthorhombic TiB at 35.2°, 42.1°, and 61.3°. The TiB peaks confirm successful in-situ formation via $\text{Ti} + \text{TiB}_2 \rightarrow 2\text{TiB}$ during DED processing, correlating with the acicular TiB morphology observed in Fig. 7a.

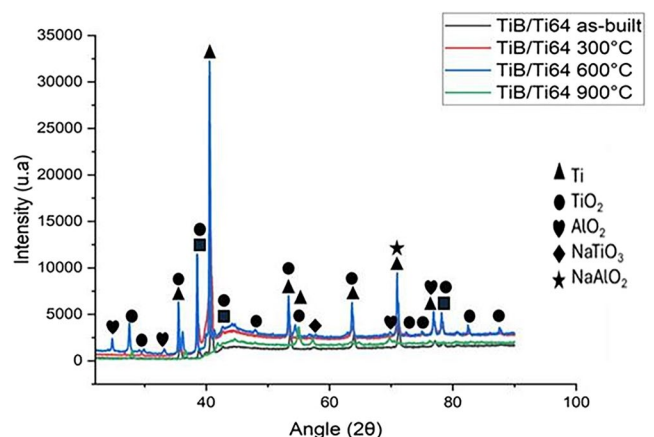


Fig. 10 XRD patterns of in-situ TiBw/Ti64 in as-built condition and after 6 h exposure to 50% NaCl-50% Na₂SO₄ environment at 300 °C, 600 °C, and 900 °C

At 300 °C the XRD pattern remains essentially unchanged from as built. All matrix and TiB peaks persist, and no oxide or borate peaks appear. This stability is comparable to TiC/Ti64 which confirms that 300 °C is below the oxidation threshold for both matrix and TiB reinforcement, consistent with minimal microstructural changes in Fig. 7b.

At 600 °C TiO₂ peaks appear, confirming matrix oxidation similar to the other materials. The TiB peaks remain clearly visible, demonstrating comparable thermal stability to TiC. Uniquely, weak broad peaks emerge at 14.5° and 27.8°, corresponding to B₂O₃ formation via $4\text{TiB} + 5\text{O}_2 \rightarrow 4\text{TiO}_2 + 2\text{B}_2\text{O}_3$. The broad nature of these B₂O₃ peaks indicates glassy/amorphous character. Notably, NaTiO₂ peaks are very weak or absent suggesting B₂O₃ formation may inhibit salt-matrix reactions by consuming oxygen or forming a physical barrier.

At 900 °C TiB peaks are completely absent (reinforcement oxidized). TiO₂-rutile dominates. Critically, B₂O₃ peaks persist and broaden further indicating the boron oxide remains as a glassy phase even after cooling. This glassy B₂O₃ can flow into cracks and pores at temperature (self-healing) and exhibits oxygen diffusivity two orders of magnitude lower than TiO₂. NaTiO₂ peaks appear but at moderate intensity, confirming some salt interaction but less severe than in unreinforced Ti64. Li et al. [11] observed similar persistence of boron-containing phases in TiC+TiB reinforced TB8 composites, attributing enhanced corrosion resistance to the formation of stable borate compounds. The self-healing capability of B₂O₃ has been documented by multiple researchers [10, 11, 28], confirming that this mechanism provides unique advantages for high-temperature applications.

6 Conclusions

- This study establishes the following key findings regarding DED-fabricated Ti64 and its composites in high-temperature saline environments:
- Corrosion mechanisms transition through three regimes: solid-state oxidation ($T < 400$ °C), protective scale formation with onset of salt interactions (400–700 °C), and volatilization dominated degradation ($T > 800$ °C). This transition temperature is delayed by 50–100 °C in composites versus unreinforced Ti64.
- DED processing critically influences corrosion behaviour through microstructural refinement.

and reinforcement distribution. The rapid solidification produces grain boundary-pinned reinforcement networks that segment corrosion damage and provide more nucleation sites for protective oxides.

- TiBw/Ti64 exhibits optimal performance (activation energy: 282 kJ/mol) due to B₂O₃ formation that provides self-healing crack sealing and a mechanism unique to boride reinforcements. However, galvanic coupling between TiB and the matrix creates localized attack zones requiring interface optimization.
- TiC/Ti64 shows intermediate performance (276 kJ/mol) through dual mechanisms: TiC particles act as oxygen diffusion barriers while their oxidation to TiO₂ at > 800 °C partially fills pores. The “necklace” grain boundary distribution from DED maximizes this barrier effect.
- Unreinforced Ti64 suffers catastrophic degradation above 600 °C via volatile TiCl₄ formation that disrupts oxide scale integrity, creating self-sustaining pore networks for rapid salt penetration.
- Engineering implications: For applications below 600 °C (e.g., compressor blades, marine components), TiBw/Ti64 offers the best combination of corrosion resistance and self-healing capability. Above 600 °C (e.g., turbine components), TiC/Ti64 provides adequate protection but requires oxidation-resistant coatings for extended service. The DED process enables tailored reinforcement placement that can be optimized for specific corrosion environments.

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Declarations

Competing Interests The authors have no relevant financial or non-financial interests to disclose.

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