

Investigation of the corrosion behaviour of TiC/Ti6Al4V manufactured through laser additive manufacturing

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Abstract. This research study focuses on investigating of the corrosion response of TiC/Ti6Al4V composite manufactured by laser additive manufacturing. Corrosion tests for TiC/Ti6Al4V were carried out with 3.5% of NaCl solution at room temperature 25°C (remaining constant) and varying the time. Corrosion test results were used to obtain the Tafel plot graph, which determined the corrosion potential and current density of TiC/Ti6Al4V. Scanning electron microscopy (SEM) was used to analyse the microstructure of the material and X-ray diffraction (XRD) was used for phase analysis of the material. Comparison studies were done on the corrosion behaviour of TiC/Ti6Al4V and Ti6Al4V. TiC/Ti6Al4V showed better corrosion resistance than Ti6Al4V

1 Introduction

Titanium alloys, such as Ti6Al4V (Ti64), have gained significant attention in various industries due to their exceptional combination of high strength-to-weight ratio, corrosion resistance, and biocompatibility [1-2]. However, at high temperatures, Ti64 is susceptible to oxidation and corrosion, leading to the degradation of its mechanical properties and limiting its use in demanding applications [3].

Hee et al. (2016) coated Ti64 with Ta in order to improve the corrosion resistance of Ti64. In the study it was reported that the corrosion current of coated Ti64 was $2.4 \times 10^{-9} \text{ A} \cdot \text{cm}^{-2}$ at a slow scan rate while coated Ti64 showed similar low current density of $2.85 \times 10^{-9} \text{ A} \cdot \text{cm}^{-2}$. It was concluded that Ta coating is a promising option to improve the corrosion resistance of Ti64 and further studies need to be done to confirm how do Ta coating improves the corrosion resistance of Ti64.

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From the study of Hee et al. (2016) it can be confirmed that there is no clear view of how Ta coating improves the corrosion resistance of Ti64, therefore Asgar et al. (2019) used graphene oxide to coat Ti64 in order to improve its corrosion resistance. From the results obtained, coated Ti64 showed improvement in electrochemical properties with a low corrosion rate while uncoated Ti64 had a higher corrosion rate and mentioned that further investigation is still required. Jin et al. (2020) used alternative way (heat treatment) of improving the corrosion resistance of the Ti64. It was found that hot isotactic pressing attributed to the microstructure of Ti64, where the formation of more beta phase and less alpha prime was observed. The formation of the beta phase resulted in an increase in the corrosion resistance of Ti64. From above mentioned studies/many researchers focus on improving the corrosion of the material by post-processing and surface coating which require more time [4]. An alternative way of improving the corrosion resistance of Ti64 is to add ceramics such as TiC or TiB₂ due to their high hardness and strength. The addition of ceramic TiC or TiB₂ to Ti64 forms a titanium-based matrix composite. Pan et al. (2022) used a titanium-based matrix composite to improve the mechanical properties (strength and ductility) of Ti64. It was reported that titanium-based matrix composite had unique network microstructure which had an exceptional impact on mechanical properties. Ti64-based matrix composites are promising materials as they have shown great potential in improving the mechanical properties of Ti64, therefore in this study the corrosion behaviour of Ti64-based matrix composites manufactured through laser additive manufactured DED will be investigated.

Liu et al. (2023) investigated electrochemical corrosion of titanium-based matrix composite. It was found out that the addition of TiC refines the beta grains in the microstructure which resulted in improvement of corrosion resistance of Ti64 and said that “research on corrosion resistance of Ti64-based matrix composites fabricated by DED is still lacking”. Understanding the corrosion behaviour of Ti64-based matrix composites manufactured via additive manufacturing (AM) is critical to their safe and effective use in various applications.

The response to corrosion of Ti64-based matrix composites produced through AM is essential to determine their suitability for specific applications and to develop strategies to mitigate any potential corrosion-related issues as it is envisaged that the product will have a significant improvement as compared to the conventional process of Ti64-based matrix manufacturing. Ti64-based matrix composites are promising material for high-temperature applications due to their high strength and good corrosion resistance [9]. This research can lead to the development of improved corrosion-resistant Ti64-based matrix composites, ultimately improving the performance, durability, and safety of the end products.

2 Methodology

Fig. 1 shows the DED system and components. The TiC/Ti64 and Ti64 were fabricated using a laser additive manufacturing technique (DED). One of the major components of the DED system is the KUKA robotic arm for easy movement, the powder feeder system for delivering the powders (Ti64 and TiC) into the melt pool created by a focused energy source of the 1073 nm, IPG fiber laser, which enables the layer-by-layer fabrication of the TiC/Ti64 composite and Ti64 samples. The laser energy density used to manufacture all the samples was 90 J/mm. Argon gas was used as the carrier, 1.5 l/min and shielding gas, 15 L/min. Since TiC/Ti64 is fabricated by in-situ process, the mass percentage of Ti64 was 95% while for TiC was 5% and for as-built Ti64 the mass percentage was 100%.

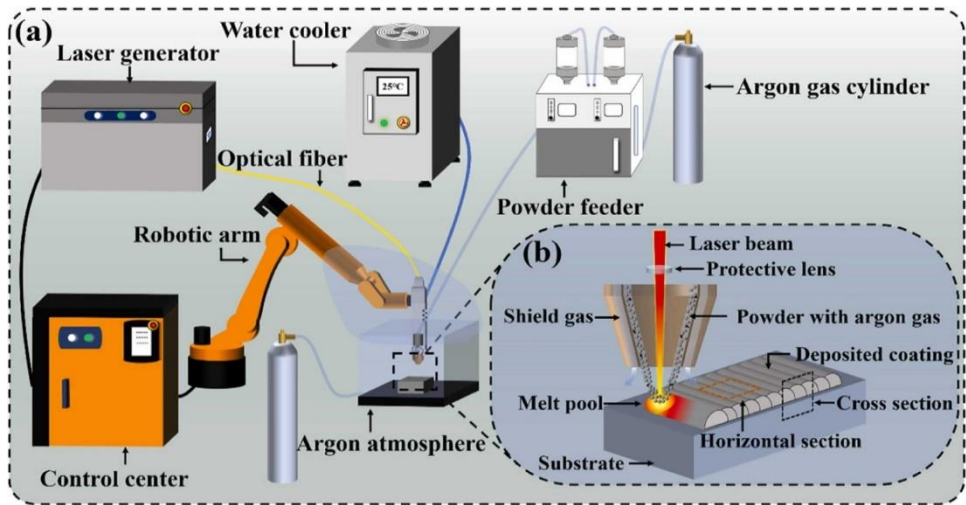


Fig. 1. Direct Energy Deposition system [9].

2.1 Sample preparation and material characterization

The samples were cut into square shapes (1x1 cm) using cutting machine and mounted on resin and polished to a mirror-like finish. The microstructure of the sample was analysed using scanning electron microscopy (SEM) and X-ray diffraction (XRD) was used for phase analysis of the material to obtain initial the microstructure and phase analysis of TiC/Ti64 and Ti64 before running the corrosion test.

2.2 Electrochemical experiment

Fig. 2 shows the electrochemical system (potentiostat) used to conduct the corrosion test. 3.5% of NaCl was prepared in 500ml of distilled water with a mass of 17.62 g. Silver-Silver chloride (SSC or Ag/AgCl) was used as the reference electrode and the Pt sheet was used as the auxiliary electrode. The corrosion test of TiC/Ti64 and Ti64 was carried out with 3.5% of NaCl solution at room temperature 25° (remaining constant) with varying time and electrochemical tests such as open circuit potential (OCP) and potentiodynamic polarization were done. The microstructures of the samples were analysed again using SEM after corrosion testing.

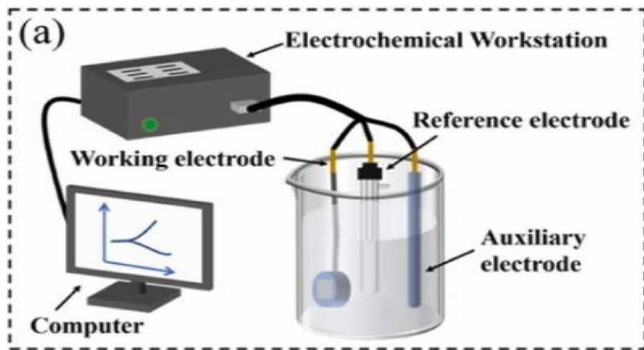


Fig. 2. Electrochemical system setup [10]

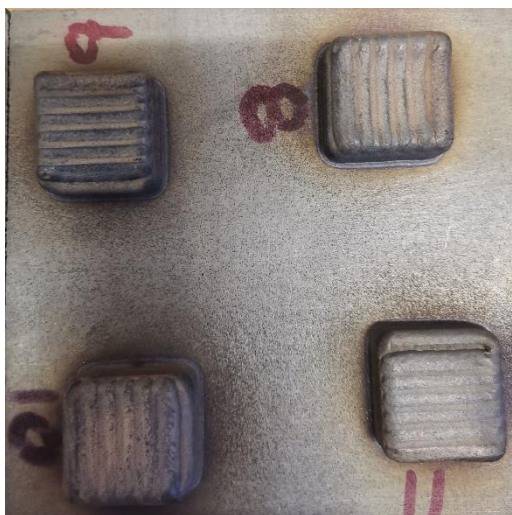


Fig. 3. As-built cube samples of TiC/Ti64

3 Results

3.1 Microstructure analysis

Fig. 4 (a) below shows an overview of the SEM microstructure of as-built TiC/Ti64 fabricated with laser additive manufacturing using the DED technique. The microstructure present in TiC/Ti64 is not homogeneous across the sample. It is observed that there is an existence of a novel/network microstructure in certain parts of the microstructure whereas a certain portion of the microstructure consists of randomly arranged TiC dendrites [10]. The microstructure also shows the presence of unmelted TiC and porosity. The cause of the microstructure not being homogeneous across the sample may be caused by several factors such as thermal gradient, composition segregation and process parameters [10]. Fig. 4 (b) shows the alpha and beta phases in the microstructure, due to the presence of Ti64 which is an alpha-beta alloy [12]. The existence of the alpha phase and beta phase in TiC/Ti64 was verified by the study conducted by Bai *et al.* (2019) which reported that the cellular morphology of the TiC phase is enclosed in TiC/Ti64 which contains a mixture of alpha and beta grains showing equiaxed microstructure with alpha grains being grey occurring inside the beta matrix and beta phase being lighter than the alpha phase. Fig. 4 (c) shows the microstructure of TiC/Ti64. From the image the novel/network microstructure can be observed which contains TiC at grain boundaries. The presence of TiC at grain boundaries was confirmed by the study conducted by Bai *et al.* (2019) using the Electron backscatter diffraction (EBSD) technique [13]. The presence of the TiC phase is also validated by XRD in Fig. 4. Fig. 4(d) shows TiC/Ti64 at high resolution with TiC/Ti64 at grain boundaries.

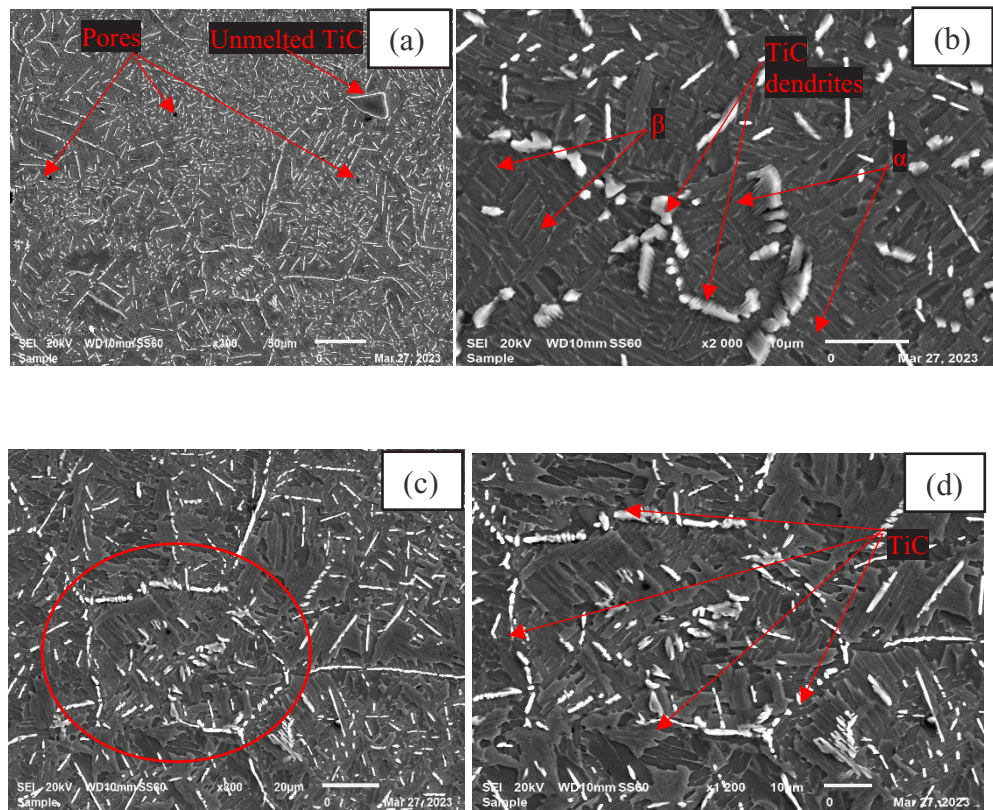


Fig. 4. SEM microstructure of as-built TiC/Ti64 (a) x300 magnification, (b) x200 magnification and (c) x800 magnification and (d) x1200 magnification.

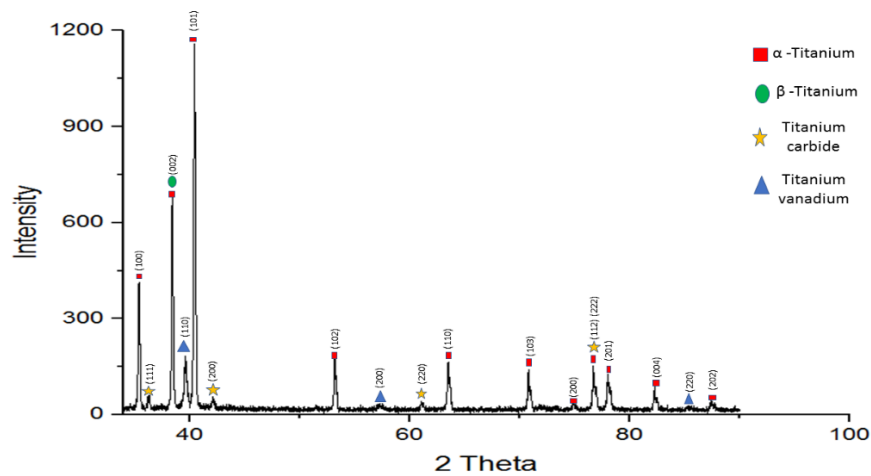


Fig. 5. XRD spectrum of as-built TiC/Ti64.

Fig. 6(a) presents the SEM microstructure of the as-built Ti64 at x300 magnification manufactured through the DED process. The microstructure differs according to techniques used, and process parameters and, in this case the as-built Ti64 shows a lamellar microstructure [14]. It is observed that there is a long grain boundary, which is normally

caused by uneven growth when the material is crystallizing. The grain boundary is one of the preferred sites of corrosion including pores. Fig. 6(b) shows high magnification of the grain boundary. Fig. 6(c) shows the presence of lamellar β with white colour and lamellar α inside [16].

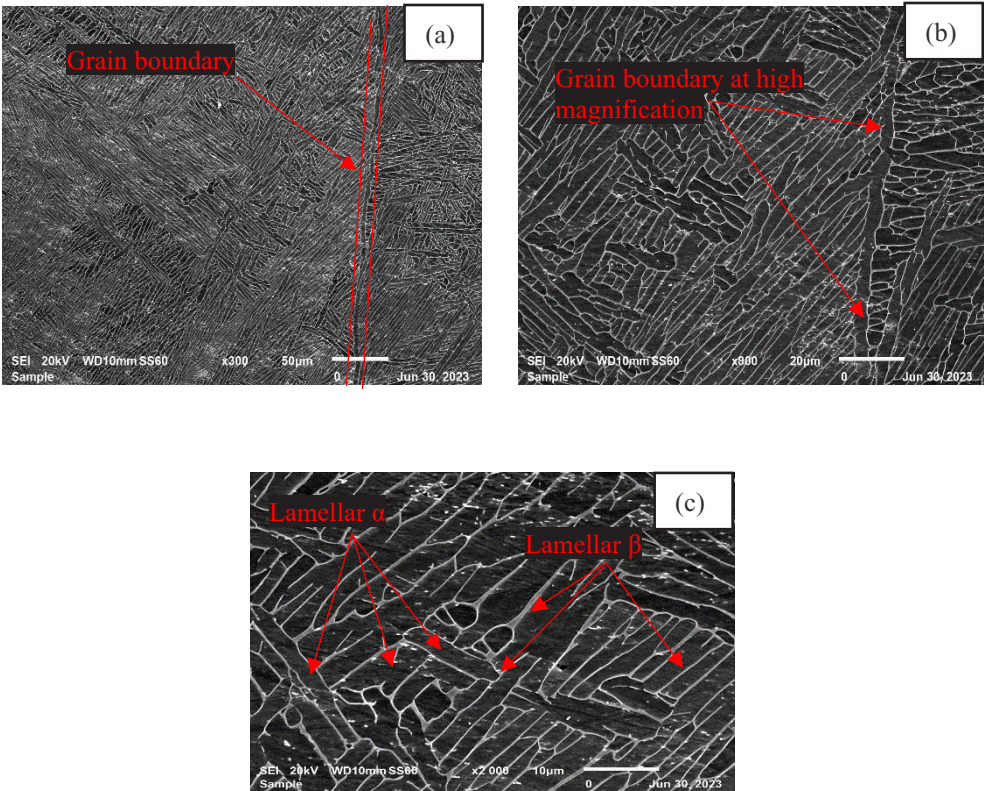


Fig. 6. SEM microstructure of as-built Ti64 (a) x300 magnification, (b) x900 magnification and (c) x2000 magnification.

Fig. 7(a) shows the SEM microstructure of as-built TiC/Ti64 which was discussed in Fig. 4 (a). Fig. 7(b) and Fig. 7(c) show the surface of TiC/Ti64 at 2 hours and 4 hours respectively after corrosion testing. In both TiC/Ti64 at 2 hours and 4 hours there is a presence of porosity that was caused by corrosion. Corrosion typically occurs at locations where pores exist within the material structure, leading to the enlargement of these pores, which, in turn, adversely impacts the material's properties. In light of the provided images, the presence of white-coloured sodium chloride (NaCl) inside these pores is indicative of corrosion activity targeted at these porous areas. [14]. The presence of NaCl inside the pores was confirmed by EDS in Fig. 9.

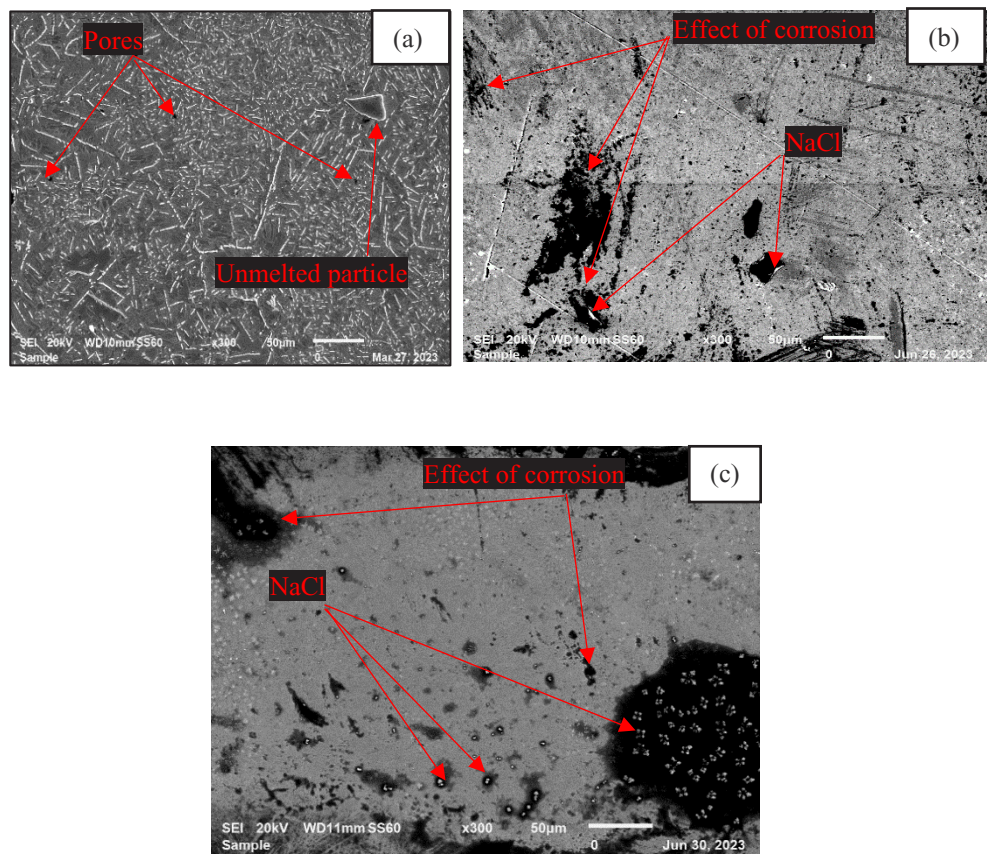


Fig. 7. SEM images (a) as-built TiC/Ti64, (b) Corrosion tested TiC/Ti64 at 2 hours and (c) Corrosion tested TiC/Ti64 at 4 hours all at x300 magnification.

Fig. 8 (a) presents the SEM microstructure of the as-built Ti64 which was discussed in Fig. 5(b). Fig. 8 (b) and (c) present the surface of Ti64 at 2 hours and 4 hours respectively after being subjected to corrosive environment of 3.5% of NaCl. There is an appearance of pores in Ti64 at 2 hours and 4 hours which were induced by corrosion reaction. NaCl is present inside pores caused by corrosion [16]. The presence of NaCl inside the pores was confirmed by EDS in Fig. 9.

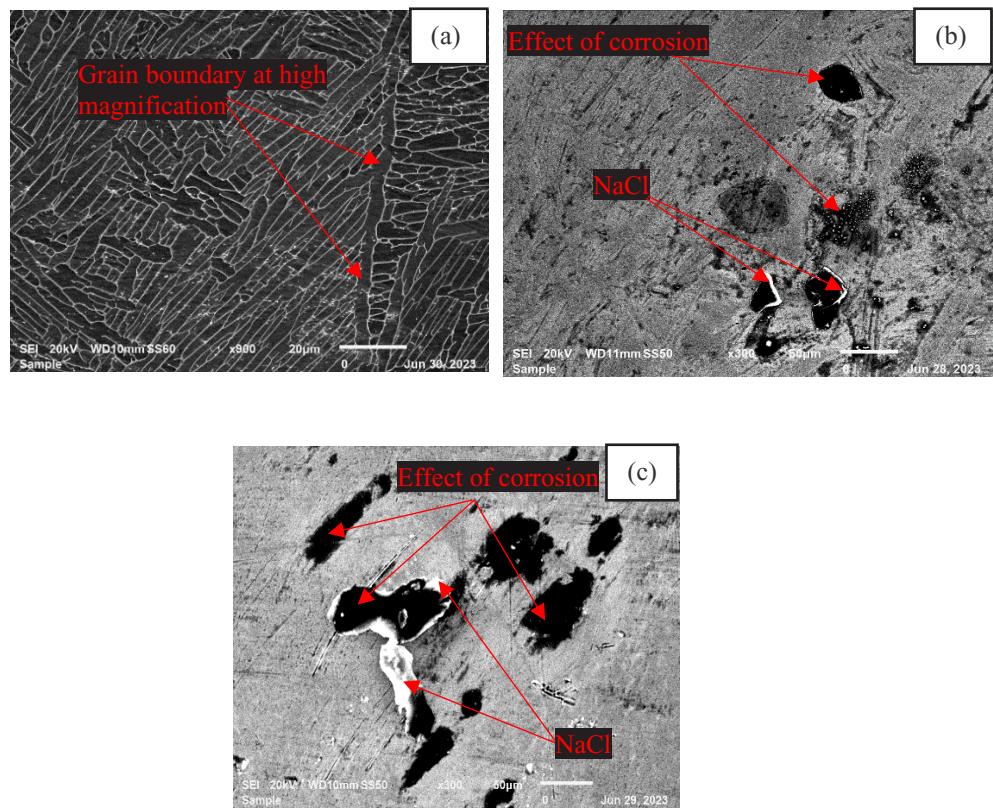


Fig. 8. SEM images (a) as-built Ti64, (b) Corrosion tested Ti64 at 2 hours and (c) Corrosion tested Ti64 at 4 hours all at x300 magnification

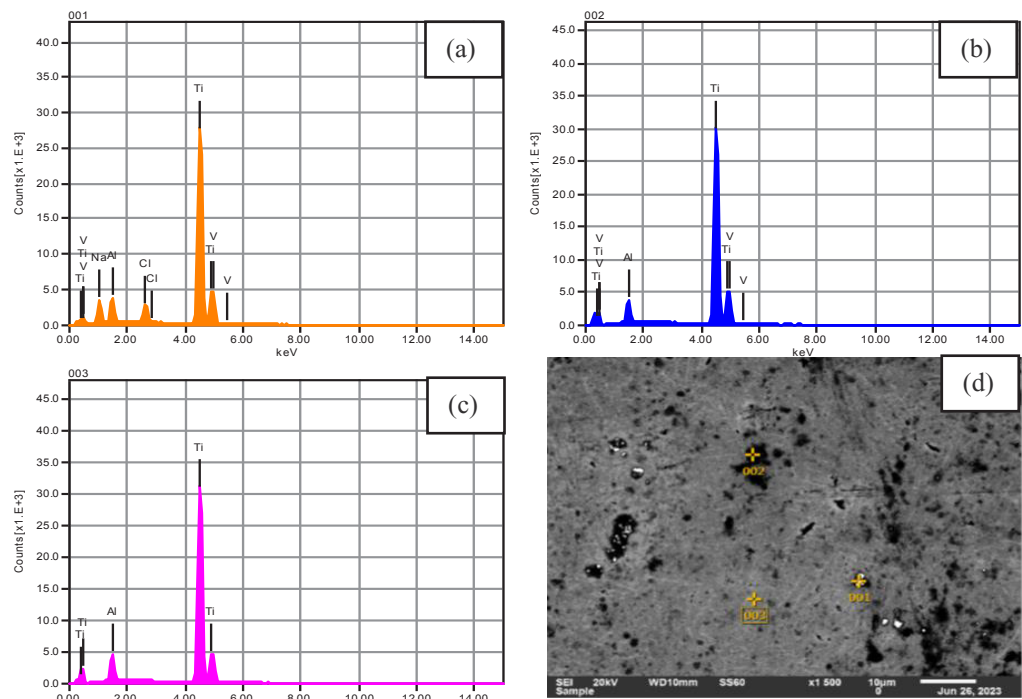


Fig. 9. (a), (b) and (c) shows the elements present in the sample and (d) shows the EDS analysed points

3.2 Electrochemical analysis

Fig. 10 shows the open circuit potential (OCP) of Ti64 and TiC/Ti64 which were exposed to a corrosive environment (3.5% of NaCl) for 2 hours at room temperature. In general, OCP gives an indication of the behaviour of the material in a corrosive medium and it is known that the material with higher corrosion resistance is characterized by higher values of corrosion potential [17]. From the OCP of TiC/Ti64 it was observed that initially the graph was constant and around the 1900s the graph slightly increased and this can be caused by the presence of pores in the sample [observed in Fig. 7 (a)]. Overall, it was observed that TiC/Ti64 is linear from the start to the point, and this is due to the presence of TiC at grain boundaries protecting the inner phases of the material against further corrosion. TiC/Ti64 showed no formation of a clear passive layer (confirmed in Fig. 12) but, in OCP graph confirms that TiC/Ti64 experienced a short-term corrosion reaction, and this is due to the presence of TiC in the material. The formation of the passive layers in Ti64 took longer to form than in TiC/Ti64 due to the lack of protection in the inner phases of Ti64, because of the prior beta grains presence.

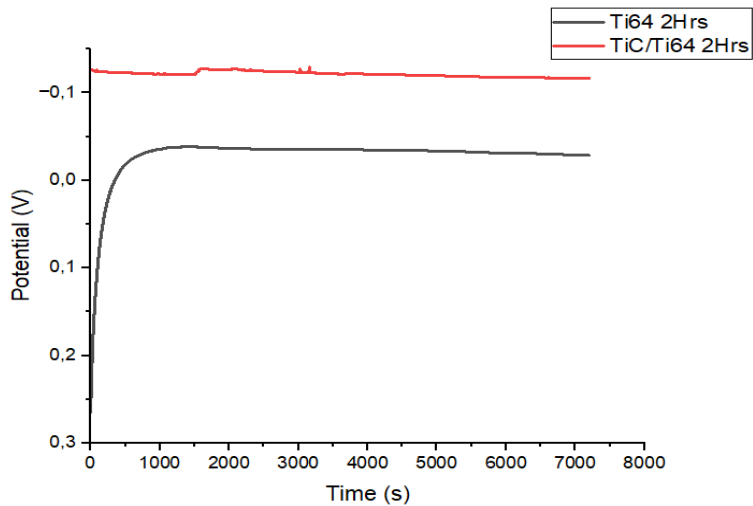


Fig. 10. OCP graph of Ti64 and TiC/Ti64 at 2 hours.

Fig. 11 shows the OCP of Ti64 and TiC/Ti64 under the same conditions mentioned in the above discussion but, with different exposure times which in this case was 4 hours. In this experiment the behaviour of TiC/Ti64 is different from the one observed in Fig. 10. In this OCP graph TiC/Ti64 still showed no clear formation of a passive layer (confirmed in Fig 12), but it shows that TiC/Ti64 started to stabilize around -0.09 V which indicates that the material has reached a state of electrochemical equilibrium, where the corrosion rate remains relatively constant over time and it indicates that the material is relatively resistant to further corrosion in the given environment. The stabilization of the TiC/Ti64 layer started around 1500 s whereas in Ti64 the formation of the passive layer started around 3600 s. Although there is a slight difference in the stabilization of these two materials at a specific time, the stabilization of Ti64 occurs at more of a negative potential which indicates that it is more prone to corrosion. It can be confirmed from these OCP's that TiC/Ti64 and Ti64 stabilized at different times due to microstructure differences such as the presence of TiC at the grain boundaries of TiC/Ti64 [8].

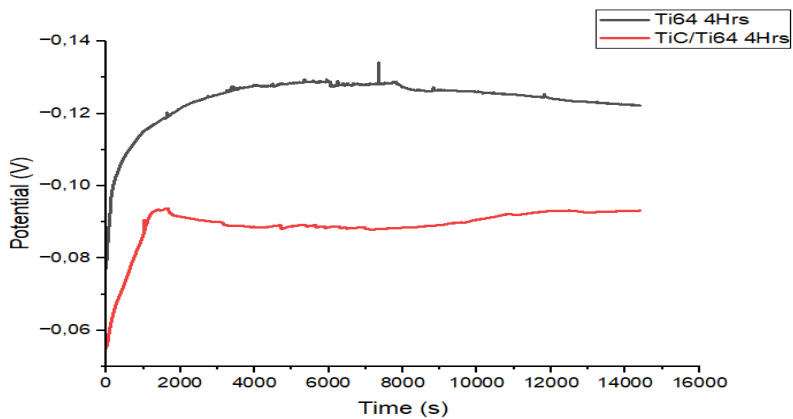


Fig. 11. OCP graph of Ti64 and TiC/Ti64 at 4 hours.

Fig 12 presents the Tafel plots of all tested material Ti64 and TiC/Ti64 immersed in corrosive environment(3.5% of NaCl solution) and all these polarization curves start around the same point with a slight absence of cathodic region which indicates that the formation of the passive layer occurs very fast and also TiC protection, which can also be confirmed OCP's presented in Fig 10 and 11. The polarization curves of Ti64 for 2 and 4 hours have a shorter cathodic region than TiC/Ti64 and this is due to the passive layer and TiC protection. The formation of a layer in Ti64 is clear due to its polarization curves becoming more linear after the anodic region and in TiC/Ti64 there is no clear formation of a passive layer as its polarization curves continue to the positive side of current and potential. As explained in Fig. 10 that due to the presence of TiC which enhances the formation of a solid protective layer in TiC/Ti64, hence TiC/Ti64 takes longer to reach the anodic region than Ti64 [8].

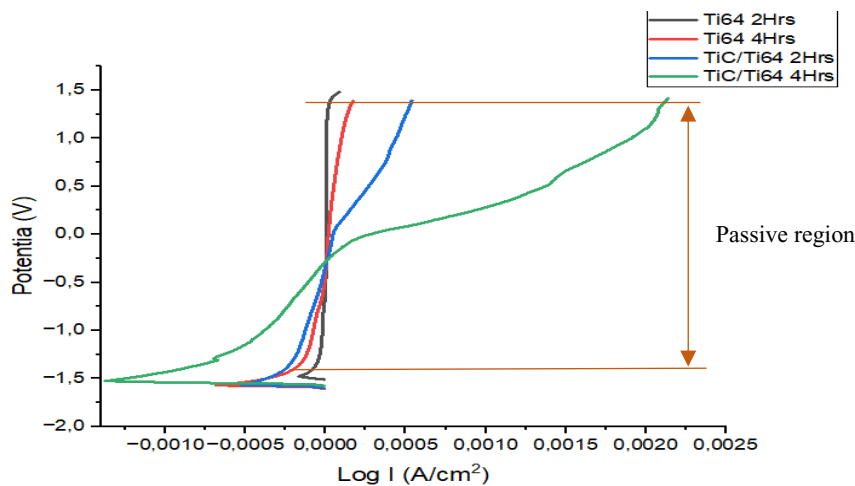


Fig. 12. Tafel data of Ti64 2 hours, TiC/Ti64 2 hours, Ti64 4 hours and TiC/Ti64 4 hours.

Fig. 13 presents the classic Tafel analysis where the corrosion current (I_{corr}) and corrosion potential (E_{corr}) in an electrochemical cell are estimated using the mathematical technique known as tafel extrapolation. The linear sections of the anodic and cathodic plots are extended back to their intersection to perform extrapolation. The corrosion current E_{corr} and I_{corr} are obtained at the point where these two lines intersect. The equations used to extrapolate/calculate E_{corr} , I_{corr} and J_{corr} are listed from equation (1) to (6) [18].

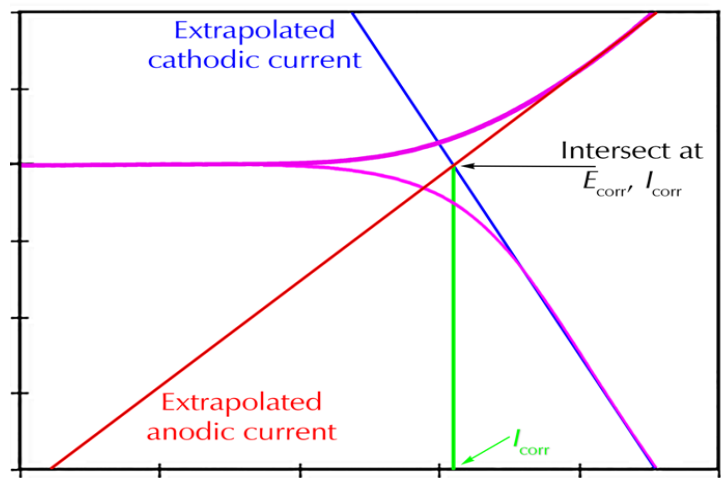


Fig. 13. shows classic Tafel analysis [19]

General equation of a tangent

- $Y_1 = mx + c$, for both anodic tangent
- $Y_2 = mx + c$, for cathodic tangent, where :
- $Y_1 = Y_2$, therefore:
- $y = E_{corr}$ (Corrosion potential at the intersection of anodic tangent and cathodic tangent)
- $x = I_{corr}$ (Corrosion current Corrosion potential at the intersection of anodic tangent and cathodic tangent)
- Current density (J_{corr})
- $J_{corr} = I_{corr}/A$ (A/cm²)

Table 1 presents the electrochemical corrosion parameters of Ti64 at 2 hours, TiC/Ti64 at 2 hours, Ti64 at 4 hours and TiC/Ti64 at 4 hours. From the fundamentals of corrosion kinetics, it is stated that the current density is directly proportional to the corrosion. From the table below TiC/Ti64 had a less negative current density of -3,61 X10⁻⁰⁵ A/cm² which indicates that TiC/Ti64 at 2 hours performed well or had higher corrosion resistance than all other samples, this can also be confirmed by the OCP in Fig. 10 where the graph was linear form the start to the end showing no corrosion reaction [17]. It is very rare for current density and corrosion rate to be negative but, it is possible due to the formation of the passive layers which act as a barrier against further corrosion. The negative current density and corrosion rate show that there is a gain of mass on the sample, and this is due to the formation of the passive layers. In a normal corrosion test it is expected to see material corroding but, in this case, the material is different due to the presence of TiC. For 4 hours samples TiC/Ti64 had a less negative current density of -9,65 X10⁻⁰⁵ which indicates that it has high corrosion resistance [9].

Table 1. Electrochemical corrosion parameters of Ti64 2 hours, TiC/Ti64 2 hours, Ti64 4 hours and TiC/Ti64 4 hours.

Materials	E_{corr} (V)	J_{corr} (A/cm ²)	I_{corr} (A)
TiC/Ti64 2 hours	-0,33042	-3,61 X10 ⁻⁰⁵	-3,61 X10 ⁻⁰⁵
Ti64 2 hours	-0,5837	-1,78 X10 ⁻⁰⁶	-1,78 X10 ⁻⁰⁶
TiC/Ti64 4 hours	-0,28525	-9,65 X10 ⁻⁰⁵	-9,65 X10 ⁻⁰⁵
Ti64 4 hours	-0,37548	-9,01 X10 ⁻⁰⁶	-9,01 X10 ⁻⁰⁶

4 Conclusion

The corrosion behaviour of TiC/Ti64 and Ti64 was successfully investigated. Overall, TiC/Ti64 exhibited a linear OCP behaviour, reflecting the protective role of TiC at grain boundaries, preventing further corrosion. While it showed no formation of a clear passive layer, the OCP graph showed minimal corrosion due to TiC presence. Furthermore, in the OCP graph analysis of 4-hour exposure time, TiC/Ti64Al4V exhibited a similar absence of a clear passive layer, but the graph stabilized around -0.09 V, where Ti64 took longer to form a passive layer, starting at around -0.13 V at a more negative potential. Additionally, the Tafel plots provided insight into the rapid formation of passive layers in Ti64. TiC/Ti64 and Ti64 exhibited shorter cathodic regions due to the presence of a passive layer in Ti64 and TiC in TiC/Ti64. In contrast, TiC/Ti64's polarization curves extended to the positive side of current and potential, as the absence of a clear passive layer allowed the material to resist anodic reactions. TiC/Ti64 showed superior corrosion resistance due to the ceramic (TiC) present and its unique microstructure. The addition of TiC to Ti64 can now be confirmed that it increases the corrosion resistance of Ti64.

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