

## Corrosion and Hardness Characteristics of Laser Surface-Modified Ti6Al4V/Zr+TiC and Ti6Al4V/Ti+TiC Composites

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The corrosion and hardness characteristics of laser clad Ti6Al4V alloy with and without coaxial nozzle with respect to variable laser power was investigated. The electrochemical behaviour of pure Ti-6Al-4V alloy coated with Zr-Ti and Ti-TiC ceramic powders were studied with respect to open circuit potentiodynamic polarization test. Passivation tendency of Ti-6Al-4V alloy as a result of different compositions of Zr and TiC reinforcement additions was examined at room temperature in .1 M H<sub>2</sub>SO<sub>4</sub> + 3.75% NaCl solution. It was observed that modified MMCs 70%Zr+30%TiC without coaxial nozzle at 750 W gave higher hardness value as compared with the same ratio in composition at 1.4 kW. Experimental results indicated that the corrosion rate of the developed composites decreased significantly with addition of ceramic powder admixture. The result obtained from the polarization behavior show a decrease in polarization resistance with decrease in zirconium content and increase in composition of TiC because of the carbide phase. While the open-circuit potential for the alloy was found to reduce with time due to oxide film thickening on the metal surface.

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**Keywords:** Laser metal deposition, Ti6Al4V, film thickening, polarization, interface.

### 1. INTRODUCTION

Titanium and its alloys exhibit attractive properties such as mechanical strength, biocompatibility and high temperature performance. These properties make them applicable in majority of industries such as aerospace, electronics, biomedical, energy and defense [1-5]. However, the performance requirements and expectation under some service conditions that necessitates high hardness, wear and aggressive corrosion environment are not met adequately. This is basically because of it exhibits low hardness in the as-received conditions. Ti6Al4V alloy may fail after some time in a corrosive environment. The combination of metals and ceramics to form refractory material has been

proved to be effective reinforcement. Refractory metal cermets have attractive mechanical properties good for high temperature applications, but display poor resistance to oxidation attack [6,7]. The increasing application of these types of alloys in the chemical and marine industry has led to its modification. There are quite a number of modification techniques employed in the surface modification of titanium alloy such as nitriding, carburizing and boriding, thermal spray and laser surface treatment. Among the surface modification techniques, laser surface alloying (LSA) have been reported to be promising due to the advantages derived therein [8]. In this study, the corrosion resistance and hardness characteristics of Ti6Al4V/Zr-TiC and Ti6Al4V/Ti-TiC composite produced by laser cladding process has been investigated using electrochemical technique.

## 2. EXPERIMENTAL PROCEDURES

### 2.1 Materials

Commercial titanium alloy (Ti-6Al-4V) was laser cladded with combination of ceramic powders consisting of Zr and TiC. The samples were sectioned into square like electrodes and mounted with a transparent epoxy resin. The exposed surface area of the investigated materials was about 1 cm<sup>2</sup>. The electrode was connected opposite the coated surface after polishing with successive grades of emery paper down to 1200 grit, polishing was done using 1 μm diamond paste after which it was rinsed with distilled water and ethanol.

### 2.2 Material preparation

Samples with different coating compositions were then obtained after mechanical cutting under flowing cooling solution. Samples for corrosion studies were prepared using standard metallographic preparation methods. Thicknesses of cladded samples were taken, grinded and polished mechanically to obtain smooth surface.

### 2.3 Hardness and electrochemical measurement

The hardness measurement was done using Vickers microhardness tester with load of 100 g for 15 s dwell time. Concentrations of 0.1 M H<sub>2</sub>SO<sub>4</sub> with 3.75 % NaCl solution was used for the electrochemical corrosion test. Ten percent (10 %) of electrolyte used was 3.75% NaCl solution. Solutions for the study were prepared from analytical grade reagents and distilled water. Electrochemical corrosion test was conducted using the potentiodynamic polarization technique according to ASTM G 3-89 and ASTM 5-94 standards. The conventional three electrode electrochemical cell system was used. The electrochemical cell was made of 500 ml Pyrex glass conical flask suitable for the conventional three-electrode system. The cover of the cell had five holes for the reference electrode, working electrode, counter electrode, temperature measurement and aeration/de-aeration. The samples were used as the working electrode, graphite rods as the counter

electrodes and Ag/AgCl 3 M KCl electrode as the reference electrode (SCE). The electrochemical corrosion behaviour of the samples was investigated using cyclic potentiodynamic scan, open circuit corrosion potential measurements and employing the linear polarization technique. Electrochemical measurements were carried out with the General Purpose Electrochemical Software (NOVA 3.0) package. All the measurements were made at room temperature using 0.1 M H<sub>2</sub>SO<sub>4</sub> with 3.75 % NaCl solution.

### 3. RESULTS AND DISCUSSION

#### 3.1 Hardness variation in the developed MMCs

The result in Figure 1 showed that the hardness of the modified MMCs increases with increase in the ratio of blending. The addition of titanium with titanium carbide has a positive influence on the modified MMCs. It is noticed that the hardness of the substrate increased from 357.30 HV to 541.30 HV for 70%Ti+30%TiC MMC which have the highest hardness value in the Ti+TiC system. This is then followed by 80%Ti+20%TiC (484.09 HV) and 70%Zr+30%TiC (474.80 HV) gave the highest hardness value respectively using a coaxial nozzle at 1.4 kW laser power. The result indicated a decrease in hardness as the ceramic content (TiC) decreased. This trend generally shows that the MMCs developed are favored by higher addition of TiC ceramic powder [9]. Laser cladding with and without coaxial nozzle with respect to laser power does have a significant difference in terms of hardness variation. In Figures 1 and 2, samples without coaxial nozzle at 750 W was noticed for 60%Zr+40%TiC composition which gave a higher hardness value of 543.28 HV as compared with coaxial nozzle at 1.4 KW. This indicates that at lesser power (750 W), ceramic content tend to be harder as the power is not enough to melt some harder ceramic particles in the modified MMCs.

**Table 1.** Laser parameter for Ti6Al4V/Zr+TiC deposition with coaxial nozzle

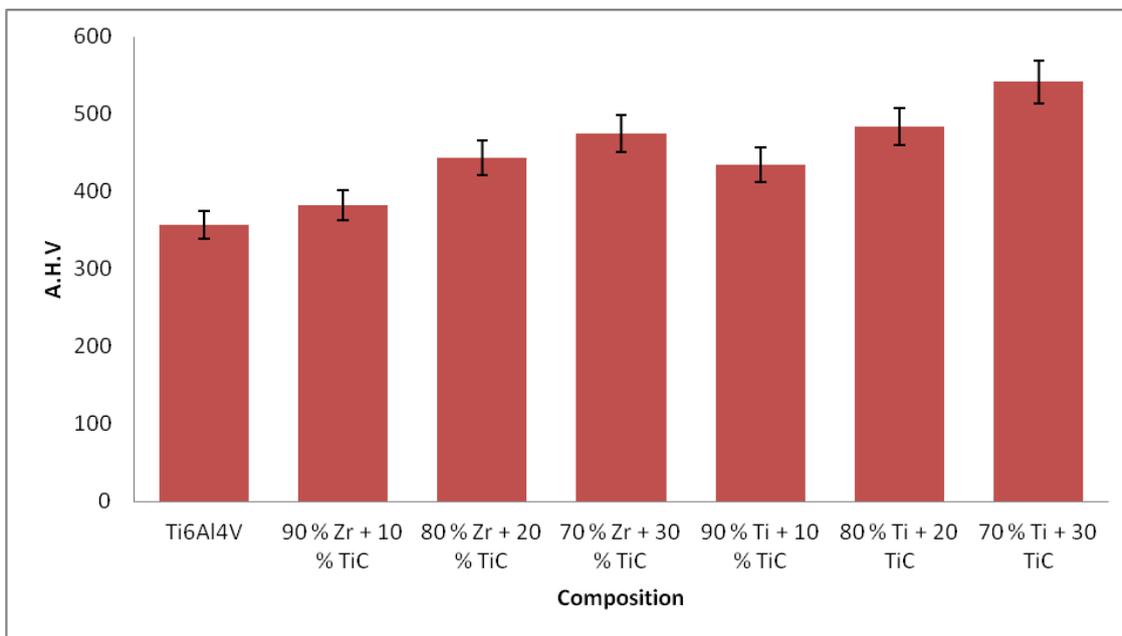
Sample Number	Laser Power (kW)	Scan Speed (mm/s)	Powder Feed Rate for Zr (g/min)	Powder Feed Rate for TiC (g/min)	Powder Composition
1	1.4	10	3.6	0.4	90%Zr+10%TiC
2	1.4	10	3.2	0.8	80%Zr+20%TiC
3	1.4	10	2.8	1.2	70%Zr+30%TiC

**Table 2.** Laser parameter for Ti6Al4V/Ti+TiC deposition with coaxial nozzle

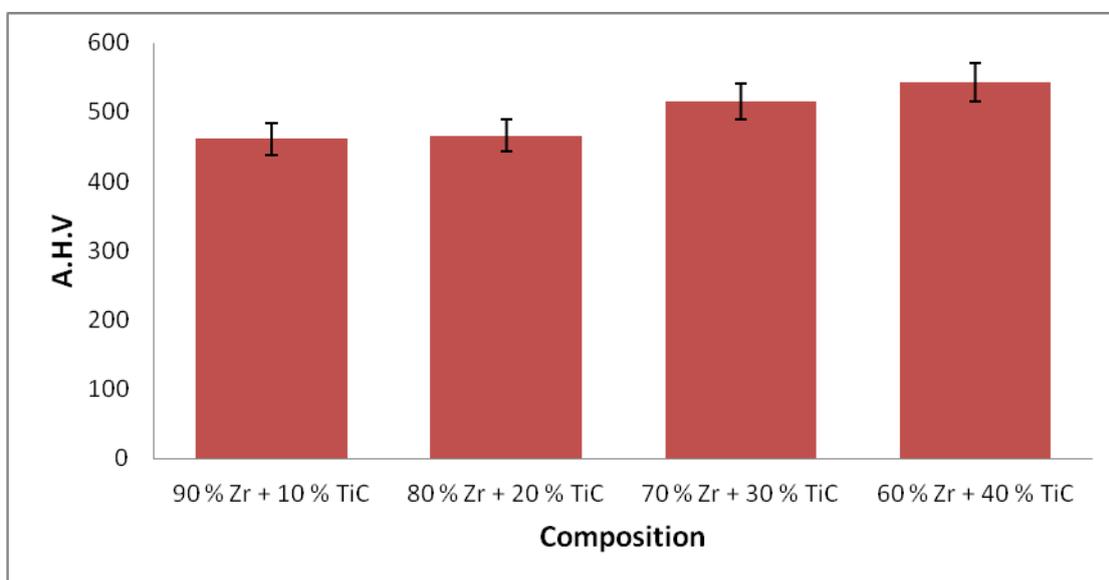
Sample Number	Laser Power (kW)	Scan Speed (mm/s)	Powder Feed Rate for Ti (g/min)	Powder Feed Rate for TiC (g/min)	Powder Composition
1	1.4	10	3.6	0.4	90%Ti+10%TiC
2	1.4	10	3.2	0.8	80%Ti+20%TiC
3	1.4	10	2.8	1.2	70%Ti+30%TiC

**Table 3.** Laser parameter for Ti6Al4V/Zr+TiC deposition without coaxial nozzle

Sample Number	Laser Power (W)	Scan Speed (mm/s)	Powder Feed Rate for Zr (g/min)	Powder Composition
1	750	10	2.5	90%Zr+10% TiC
2	750	10	2.5	80%Zr+20 %TiC
3	750	10	2.5	70%Zr+30 %TiC
4	750	10	2.5	60%Zr+40% TiC



**Figure 1.** Variation of hardness value for coaxial nozzle at 1.4 kW laser power



**Figure 2.** Variation of hardness of MMCs without coaxial nozzle at 750 W laser power

### 3.2 Electrochemical corrosion behavior of the MMCs

The potentiodynamic polarization test was carried out in 0.1 M H<sub>2</sub>SO<sub>4</sub> + 3.75 % NaCl solution. The data of the potentiodynamic tests for Ti6Al4V/Zr + TiC, Ti6Al4V/Ti + TiC laser cladded with coaxial nozzle and Ti-6Al-4V/Zr + TiC cladded without coaxial nozzle (Tables 1, 2 and 3). The value of corrosion current density, *i*<sub>corr</sub>, was extrapolated from the polarization curves and the results are summarized in Tables 4, 5 and 6. The positive shift of *E*<sub>corr</sub> to -0.34375 (mV) for Ti6Al4V/ 80%Zr + 20% TiC indicates better corrosion resistance of the Zr + Ti coatings on Ti6Al4V as shown in Figure 5. The corrosion current is reduced to 0.000429 (mm/yr), as indicated in Table 4. The same electrode cell assembly that was used for the potentiodynamic polarization experiments was also employed for the OCP investigations. When the sample is immersed in the electrolyte the defects in the coating provide the direct diffusion path for the corrosive media [10].

The corrosion potential (*E*<sub>corr</sub>) for Zr 80% + TiC 20% does not change with voltage noticeably as the OCP in the working electrolyte does (see Table 4 and Figure 3) which means that the electrochemical behaviour of 80% Zr + 20 %TiC and 70% Zr + 30 %TiC coatings in 0.1 M H<sub>2</sub>SO<sub>4</sub> + 3.75% NaCl solution is less sensitive to changes in structure in the working electrolyte. The coatings however improved the corrosion resistance of the Ti6Al4V substrate, although the improvement is not significant. This indicates that coatings are favourable for the substrate material, but must be limited to an appropriate level, or else, the compactness of the inner layer will decrease, hence property may be affected adversely.

For the Ti6Al4V laser cladded (with coaxial nozzle) at 750 kW with Zr+TiC powder, with increasing concentration, *E*<sub>corr</sub> shifts positively and *i*<sub>corr</sub> decreases; thereby increasing the corrosion resistance of the Ti6Al4V alloy.

**Table 4.** The electrochemical parameters of (Ti-6Al-4V) and Ti-6Al-4V/Zr +TiC composites electrodes in NaCl + H<sub>2</sub>SO<sub>4</sub> with coaxial nozzle

Electrodes	<i>E</i> <sub>corr</sub> (mV)	<i>i</i> <sub>corr</sub> A/cm <sup>2</sup>	β <sub>a</sub>	β <sub>c</sub>	LPR (kΩ)	CR (mm/yr)
Ti-6Al-4V substrate	-0.54016	1.76E-07	0.021028	0.019955	25283	0.006233
Ti-6Al-4V /90%Zr +10% TiC	-0.53924	1.28E-07	0.012558	0.015199	23258	0.002123
Ti-6Al-4V /80%Zr +20% TiC	-0.60207	2.33E-08	0.023692	0.048269	295950	0.000429
Ti-6Al-4V /70%Zr +30% TiC	-0.60207	4.20E-06	0.38409	0.16245	11817	0.0050398

**Table 5.** The electrochemical parameters of (Ti-6Al-4V) and Ti-6Al-4V/Ti +TiC composite electrodes in NaCl + H<sub>2</sub>SO<sub>4</sub> with coaxial nozzle

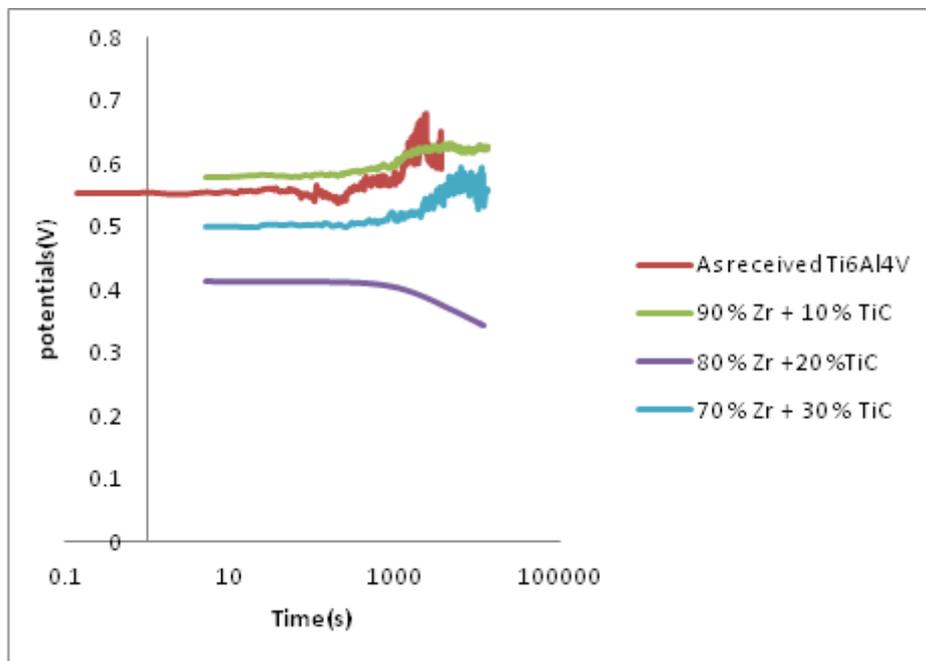
Electrodes	E corr (mV)	I <sub>corr</sub> A/cm <sup>2</sup>	β <sub>a</sub>	β <sub>c</sub>	LPR (kΩ)	CR (mm/yr)
Ti-6Al-4V substrate	-0.54016	1.76E-07	0.021028	0.019955	25283	0.006233
Ti-6Al-4V-90%Ti +10% TiC	-0.55271	2.16E-07	0.015789	0.045577	23611	0.003311
Ti-6Al-4V-80%Ti +20% TiC	-0.64993	4.84E-06	-0.64847	0.03664	3487.4	0.074245
Ti-6Al-4V-70%Ti+30% TiC	-0.28426	1.83E-08	0.005395	0.024315	104880	0.00022

**Table 6.** The corrosion parameters of (Ti-6Al-4V) and different coated composition of Ti-6Al-4V/Zr +TiC alloy (without coaxial nozzle) electrodes in the same concentration of NaCl + H<sub>2</sub>SO<sub>4</sub>

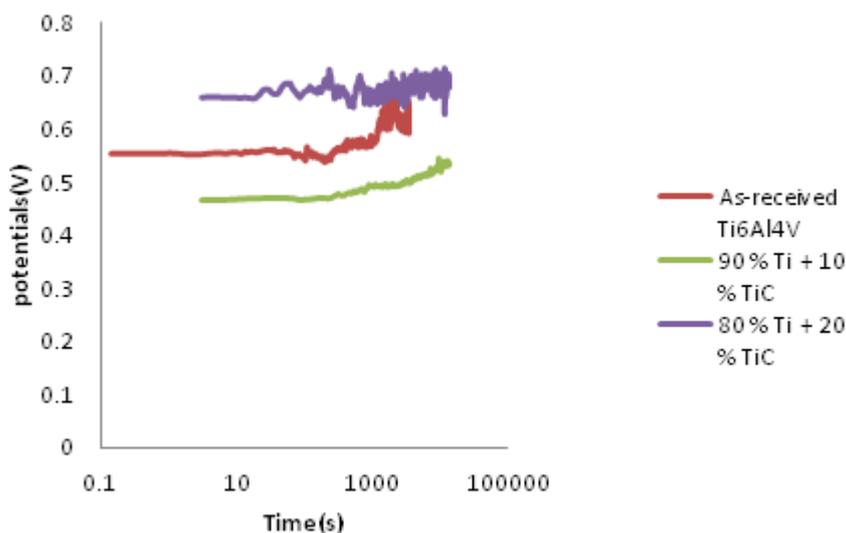
Electrodes	E corr (mV)	I <sub>corr</sub> A/cm <sup>2</sup>	β <sub>a</sub>	β <sub>c</sub>	LPR (kΩ)	CR (mm/yr)
Ti-6Al-4V substrate	-0.54016	1.76E-07	0.021028	0.019955	25283	0.006233
Ti-6Al-4V /90%Zr +10% TiC	-0.65746	1.69E-06	0.30669	0.013985	3442.5	0.0034716
Ti-6Al-4V /80%Zr +20% TiC	-0.64918	2.73E-06	0.031158	0.025512	2228.6	0.0050321
Ti-6Al-4V /70%Zr +30% TiC	-0.30167	3.77E-09	0.013559	0.035574	1131600	0.000062297
Ti-6Al-4V /60%Zr +40% TiC	-0.2525	1.44E-08	0.025688	0.023545	369300	0.00016239

This means that the discharge damage noticed in the as-received could be minimized by developing coating on it. It can be seen that the results of the potentiodynamic polarization test agree well with the open circuit polarization value in the working electrolyte. This means that polarization data measured from working electrolyte can also be used to evaluate the corrosion resistance of the coating. Table 2 shows a shift in the corrosion potential of the Ti6Al4V substrate. For Ti6Al4V/70%Zr + 30% TiC which is at the same corrosion potential with 80 % Zr + 20 % TiC giving the best corrosion resistance. The corrosion rate of Ti6Al4V is generally greater than those of Ti6Al4V/Zr +

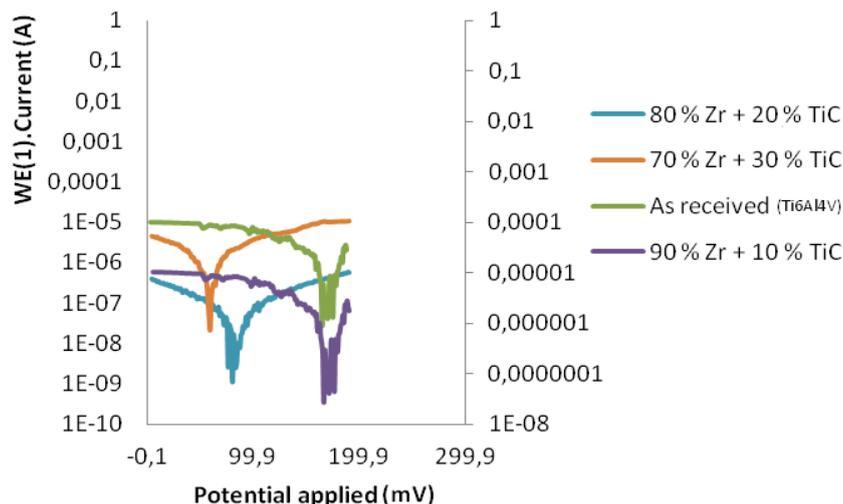
TiC MMCs systems. The corrosion current was reduced significantly to 0.00022 (mm/yr), as indicated in Table 5 (Figures 4 and 6). The corrosion potential of the laser cladded Ti6Al4V alloy without coaxial nozzle increased from -0.618636 (mV) for the substrate to -0.28503 (mV) as noticed for Ti-6Al-4V-70%Zr + 30% TiC.



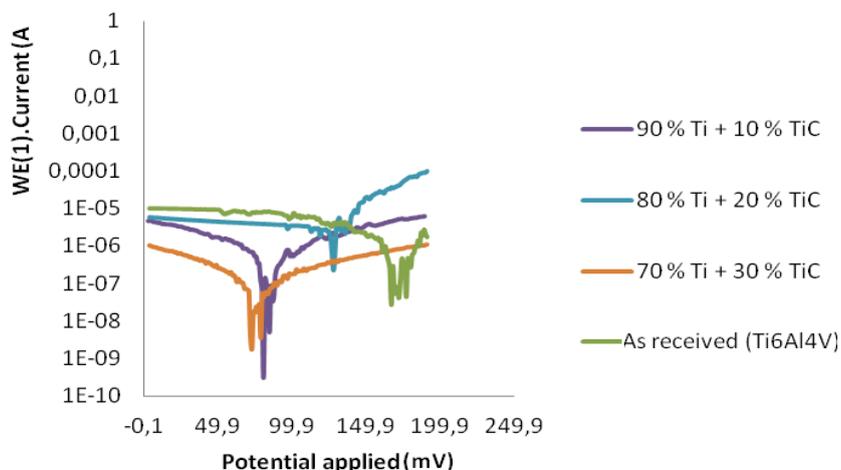
**Figure 3.** The OCP curve for Ti6Al4V and laser cladded Ti6Al4V/Zr+TiC composite fabricated with coaxial nozzle in a NaCl + H<sub>2</sub>SO<sub>4</sub> solution at room temperature



**Figure 4.** The OCP curve for Ti6Al4V and laser cladded Ti6Al4V/Ti+TiC composite with coaxial nozzle in a NaCl + H<sub>2</sub>SO<sub>4</sub> solution at room temperature

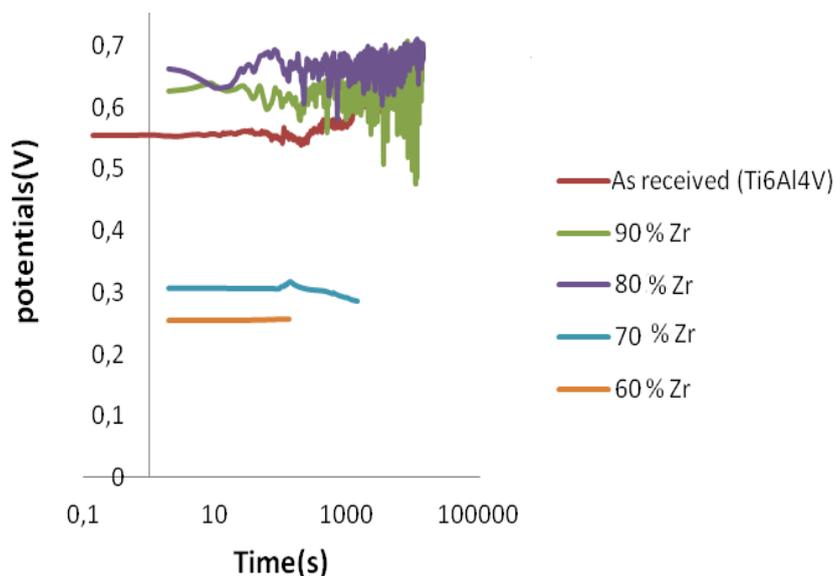


**Figure 5.** Potentiodynamic polarization curves of Ti6Al4V and laser cladded Ti6Al4V/Zr+TiC composite in a 3.75% NaCl + 0.1 M H<sub>2</sub>SO<sub>4</sub> solution at room temperature

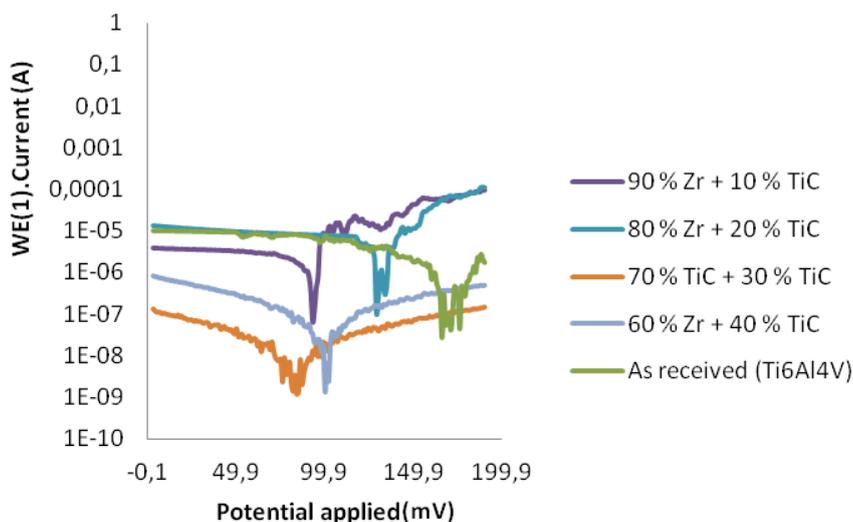


**Figure 6.** Potentiodynamic polarization curves of Ti6Al4V and laser cladded Ti6Al4V/Ti+TiC alloy in NaCl + H<sub>2</sub>SO<sub>4</sub> solution at room temperature with coaxial nozzle

The corrosion current however reduced significantly to 0.000062297 (mm/yr), as indicated in Table 6 which has positive effects on the polarization resistance of 1131600 kΩ. The 80%Zr addition with the substrate indicated higher corrosion potential than other compositional blend in the same group of analysis without coaxial nozzle (see Figure 7). The polarization resistance of the Zr/TiC system laser cladded without coaxial nozzle seems to favour higher corrosion resistance of the MMCs (Figure 8). This may be attributed to oxidation noticed on the surface of the modified surface as a result of the non-shielding which may allow the penetration of oxygen into the surface of the modified Ti6Al4V alloy. The more positive shift in corrosion potential noticed in the Zr/TiC system contributed to a significant increase in the corrosion rate as well as the polarization resistance as high as 1131600 kΩ.



**Figure 7.** The OCP curve for as-received (Ti6Al4V) and laser cladded Ti6Al4V/Zr alloy in a NaCl + H<sub>2</sub>SO<sub>4</sub> solution at room temperature without coaxial nozzle



**Figure 8.** Potentiodynamic polarization curves of Ti6Al4V and laser cladded Ti6Al4V/Zr+TiC composite without coaxial nozzle in a NaCl + H<sub>2</sub>SO<sub>4</sub> solution at room temperature

#### 4. CONCLUSIONS

Electrochemical and hardness studies showed that combination of ceramic and metallic powders has significant influence on the property enhancement of surface-modified Ti6Al4V alloy. The following conclusions can be drawn:

- ❖ A moderate amount of ceramic coatings can increase the surface properties of Ti6Al4V alloy. However, a larger amount of zirconium favours the chemical performance of Ti6Al4V thereby increasing the corrosion and polarization resistance of the MMCs.

❖ There is a direct relationship between the hardness and corrosion/polarization resistance of the developed MMCs. It is generally noticed that as the hardness increases, the corrosion and polarization resistance also increases.

❖ Laser cladding with and without coaxial nozzle with respect to laser power does have a significant difference in terms of hardness behaviour.

❖ The potentiodynamic polarization showed that the Zr/TiC coatings (deposition without coaxial nozzle at 750 W) on Ti6Al4V exhibited superior corrosion resistance and high polarization resistance compared to the Ti+TiC and Zr+TiC coatings (deposition with coaxial nozzle at 1.4 kW) and that of the Ti6Al4V substrate.

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