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Electrochemical and DFT studies of laser-alloyed TiB₂/TiC/Al coatings on aluminium alloy

Dunja Ravnikar^{1,a}, Ravi Shanker Rajamure^{2,b}, Uroš Trdan^{1,c},

Narendra B. Dahotre^{2,d}, Janez Grum^{1,e,*}

¹ Faculty of Mechanical Engineering, University of Ljubljana, Askerceva 6, 1000 Ljubljana,
Slovenia

² Laboratory for Laser Aided Additive and Subtractive Manufacturing, Department of Materials
Science and Engineering, University of North Texas, 1155 Union Circle #305310, Denton, TX
76203-5017, USA

^adunja.ravnikar@fs.uni-lj.si, ^bravishanker76@gmail.com, ^curos.trdan@fs.uni-lj.si

^dnarendra.dahotre@unt.edu, ^ejanez.grum@fs.uni-lj.si,

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ABSTRACT

Microstructural and corrosion characteristic of laser-alloyed TiB₂/TiC/Al composite coatings on 6082-T651 aluminium substrate were investigated. Density functional theory was used to study the chemical bonding of TiC and TiB₂. The results confirmed a compact TiB₂/TiC/Al-coating with low porosity, without any cracks and with good long-term stability against corrosion. Moreover, EIS and CP results confirmed enhanced corrosion resistance of laser-alloyed TiB₂/TiC/Al coatings, with lower coating capacitance, increased polarisation resistance and reduced corrosion current density compared to the Al 6082 substrate. Although, all the laser-alloyed coatings experienced pitting attack, the intensity of pitting attack was substantially reduced compared to the substrate material.

Key words:

- A. Aluminium
- A. Ceramic
- B. Polarization
- B. Passive films
- C. Pitting corrosion

1. Introduction

The constantly increasing demand for light materials in the automotive and aerospace industries has led to considerable attention of researchers in the field of materials science regarding aluminium alloys. Some of the key properties that caused this great interest in aluminium alloys are their low specific weight, good corrosion resistance and high thermal conductivity [1]. However, in practical applications, their usage has often been restricted because conventional Al alloys are soft and known for their poor wear resistance [2]. Surface coating with ceramics is a highly promising approach to overcome this problem. By means of high-power lasers, very high temperatures can be attained in order to melt both the metal substrate and ceramic coating, which may lead to a strongly bonded ceramic/metal interface after re-solidification [3].

Despite several studies investigating wear of the laser coating of a ceramic-metal composite layer [4], [5], [6], there is a paucity of investigations devoted to the analysis of corrosion behaviour. The corrosion resistance of a material represents one of the key parameters affecting its potential applications in industry. Generally, the hard coatings possess high chemical resistance in corrosive media. Despite this very good chemical property, coated parts are often severely corroded, especially if the hard coating is deposited directly on to a less noble substrate [7]. The major problem in using protective coating in chemically aggressive environments is the possible presence of solution paths, i.e. open porosity and pinholes in the coatings, as the preferential paths for localized corrosion activity [8]. Pores and defects in the cathodic coating can lead to intensive localized corrosion attacks of the less noble/anodic substrate below the cathodic coating [9]. Therefore, the important characteristics of a good coating may be identified as the sound bonding with the substrate and free from metallurgical defects, such as porosity and cracks [10].

A number of authors have evaluated the corrosion behaviour of steel coated with NiTi [11], CrN, NbN, Cr/CrN [7], Ni-P/TiN, Ni-P/CrN, Cr/TiN, Cr/CrN [12], TiN, TiBN [9] and TiB₂ [9], [13]. However, there are only few reports concerning the corrosion behaviour of Ti₃AlC₂ [14] and Al₂O₃/TiB₂ [15]. Covino et al. [16] reported significantly higher corrosion resistance of Ti + TiC

composites in reducing mineral acid solution compared to the Ti + TiB₂ composites. Lekatou et al. [17] investigated the effect of the HVOF WC-17Co/Ni-5Al coating on Al7075. Their results confirmed high corrosion resistance of the coating in a salt spray chamber even with longer exposure over 49 days.

However, investigation devoted to corrosion behaviour of laser surface alloyed TiB₂/TiC/Al powder precursor coatings produced on Al 6082-T651 is very limited. Hence, in this investigation, the corrosion behaviour of laser-alloyed TiB₂/TiC/Al coatings was evaluated in 0.5 M NaCl solution via electrochemical methods. In order to obtain better understanding of the mechanism of the corrosion phenomenon, density functional theory (DFT) calculations were also carried out. Lately, DFT has become an attractive theoretical method, because it provides exact basic vital parameters for even complex molecules/compositions at relatively low cost [18]. DFT connects some traditional empirical concepts with quantum mechanical interpretations and can further shed the light on nature of chemical bonding of TiB₂ and TiC. In light of this, *ab initio* calculations were performed to evaluate the chemical bonding and hybridization of TiB₂ and TiC compounds using density of states (DOS) and elastic constants that in turn were correlated with the corrosion performance of these coating compounds.

2. Experimental procedure

2.1. Material and specimen preparation

Aluminium alloy 6082-T651 10 mm thick rolled plate was employed as the substrate material for laser alloying treatment. Its nominal chemical composition in wt.% is 0.87 Si, 0.72 Mg, 0.42 Mn, 0.3 Fe, 0.15 minor elements (Cu + Cr + Ni + Zn + Ti) and the remaining was Al. Prior to laser processing the specimens with a dimensions of 50 × 25 × 10 mm³ were produced using a water jet cutting process, and afterwards ground with 400 and 600-grit SiC papers. In order to avoid any undesirable effects of any grease/oil residues on the substrate surface during laser-matter interactions all specimens were thoroughly cleaned in an ultrasonic bath of distilled water followed by ethanol.

TiB₂ (99.5% purity and average powder size of 45 μm), TiC (99.5% purity and average powder size of 2 μm) and Al (99.5% purity and average powder size of 45 μm) powders were used as the precursor. Aluminium powder was added to TiB₂-TiC ceramic precursor mixture to improve adhesion of the ceramic coating to the substrate. The powders were obtained from Global Tungsten & Powder Corp. Two different ratios of powder precursor material were used, i.e. 40 wt.% TiB₂/40 wt.% TiC/20 wt.% Al and 60 wt.% TiB₂/20 wt.% TiC/20 wt.% Al, respectively. Afterwards, the precursor powders were mixed with a water-based organic binder (LISI W 15853) and reducer (LISI W 15833) obtained from Warren Paint and Color Company (Nashville, TN, USA) and this precursor slurry was spray deposited onto the substrate with an average thickness of 150 ± 25 μm . Moisture from the precursor deposit on substrate was removed by air-drying for 24 hours.

2.2. Laser alloying of TiB₂/TiC/Al coatings

Laser alloying experiments of spray deposited TiB₂/TiC/Al coating were carried out using a 3 kW diode pumped ytterbium fiber laser (IPG YSL-3000) with a continuous wave and a wavelength of 1070 nm. The focused laser beam on the specimen surface had a uniform spot size of 1.0 mm diameter. The laser power and traverse speed were maintained constant at a 1200 W and 60 mm s⁻¹, respectively. Thus, the corresponding laser energy density was equal to 20 J mm⁻².

2.3. Microstructural analysis

The cross-sectional microstructural analysis was conducted by a FEI Quanta 200 scanning-electron microscope (SEM) and roughness measurements were conducted with a Surtronic 3+ profile meter (a product of Taylor/Hobson Peumo) using a Gaussian filter with a cut-off wavelength $\lambda_c = 0.8$ mm. The surface roughness value is given as the mean arithmetic value R_a , on the measuring length of $l = 12.5$ mm. The phases inside the TiB₂/TiC/Al laser-alloyed coatings were identified using X-ray diffractometry (XRD, Rigaku III Ultra) with Cu K α radiation of a 1.5418 Å wavelength

generated at 40 kV and 44 mA. The specimens were analysed in a 2θ range of 20° to 90° using a step size of 0.04° and scan speed of 3°min^{-1} .

2.4. Corrosion analysis

The electrochemical corrosion properties of laser-alloyed coatings and the substrate Al alloy (6082-T651) were carried out with a PAR Versastat-4 potentiostat/galvanostat/ZRA and controlled by Versa Studio software. A classic three-electrode cell (electrolyte volume 0.7 L) was used for the corrosion measurements, where the specimens of 15 mm diameter were embedded in a PAR Teflon holder, which served as the working electrode. A saturated calomel electrode (SCE) was employed as the reference electrode and a pair of graphite rods as the counter electrodes. The medium chosen for the investigation was naturally aerated, near natural ($\text{pH} = 7.3 \pm 0.5$) 0.5 M NaCl aqueous solution, prepared with deionised water. All the electrochemical experiments were carried out at room temperature ($T = 19.6 \pm 0.2^\circ\text{C}$) in a freshly prepared, unstirred electrolytic solution.

Immediately prior to each corrosion experiment, all specimens were cleaned and degreased in an ultrasonic bath of ethanol followed by deionised water for 3 min each. All specimens were prepared and cleaned in the same manner, with the utmost caution to obtain reliable measurements.

In this study, electrochemical techniques were performed in the following order:

- (i) open circuit potential ($E_{ocp} = f[t]$),
- (ii) electrochemical impedance spectroscopy (EIS) and
- (iii) cyclic polarization (CP).

Measurements of the open circuit potential E_{ocp} prior to EIS measurements were performed for 60 min in order to stabilize the surface [19][20][21], whereas at the end of the stabilization process the attained potential was referred to as the corrosion potential E_{corr} . In order to investigate the effect of laser alloyed specimens on long-term stability against corrosion, additional open circuit potential E_{ocp} measurements were conducted during 24 hour's immersion in aggressive chloride solution.

Followed by the initial stabilization delay time for 60 min at the equilibrium state at open-circuit potential (OCP) electrochemical impedance spectroscopy (EIS) measurements were carried out. The EIS measurements were performed at OCP by applying a sinusoidal 10 mV RMS perturbation signal at frequency ranging from 100 kHz down to 100 mHz. Impedance data was experimentally determined by fitting with ZsimpWin software, using different equivalent electrical circuits in order to obtain the most reasonable values with smallest possible error of fit.

Cyclic polarization (CP) tests were performed after the EIS measurements and additional 10 min stabilization at OCP. CP was conducted in anodic direction at 200 mV more negative than OCP towards anodic direction at a rate of 0.5 mV s^{-1} . Afterwards, the polarization scan was reversed to the cathodic direction at the switching potential (E_{sw}), which was obtained at a predefined current density threshold ($I_{th} = 1 \text{ mAcm}^{-2}$). For the CP experiments two sets of laser-alloyed specimens with different ratios of pre-deposited $\text{TiB}_2/\text{TiC}/\text{Al}$ coatings were prepared:

1. directly after laser alloying, in the “as is” condition,
2. laser-alloyed specimens with a subsequent grinding procedure.

Second set of specimens were chosen to investigate effect of surface topography/morphology (roughness) on corrosion behaviour and to eliminate the surface roughening due to laser alloying process and to obtain similar surface integrity as with the substrate material. Before each experiment the specimens were ground using deionized water starting with 320-grit SiC paper and continued with 500, 800, 1200, 2000 and 4000-grit papers (Struers ApS, Denmark). Between each paper change the specimens were rinsed with deionised water to remove abraded particles.

The corrosion parameters (E_{corr} and i_{corr}) were determined from cyclic potentiodynamic polarization via the Tafel extrapolation method by using a computer least square analysis with the smallest possible error of fit [19][20][21]. In order to evaluate corrosion morphology after CP test, the specimens were cleaned with alcohol, then rinsed gently with deionised water, dried and stored in a desiccator before SEM FEI Quanta 200 examination.

In order to obtain quantitative information a protective efficiency (P_{EF}) was calculated using the following equation:

$$P_{EF}(\%) = \frac{i_{corr,0} - i_{corr,N}}{i_{corr,0}} \quad (1)$$

where $i_{corr,0}$ represents corrosion current density of the as received substrate and $i_{corr,N}$ represents the corrosion current density of laser-alloyed coatings produced with different powder precursor mixtures.

2.5. Computational methodology

In this study, the elastic constants and density of states calculations (DOS) were carried out using the highly efficient Vienna ab initio simulation package (VASP) code, which is based on density functional theory (DFT) [22], [23]. The exchange and correlation potential were treated using the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerh (PBE) method optimized by Perdew [24], [25] and the hybrid exchange-correlation functional (HSE06) [26], [27], [28]. The plane wave cut-off energies for TiB₂ and TiC are used as 371 eV and 422 eV, respectively, for all the calculations. The integration over the Brillouin Zone was done with the help of a Monkhorst-pack k -point mesh size of 9×9×7 (TiB₂) and 13×13×13 (TiC) [29]. The linear tetrahedron method incorporating Blöchl's corrections was used for calculation of density of states (DOS). All the atoms were relaxed to a maximum force below 0.01 eV Å⁻¹, and the maximum stress and displacement between the cycles converged to below 0.01 GPa and 0.001 Å, respectively.

3. Results and discussion

3.1. Microstructural analysis

Fig. 1 shows cross-section SEM images of the laser-alloyed coatings with 40/40/20 and 60/20/20 TiB₂/TiC/Al ratios of powder precursor materials. The coating pre-deposition method (air spray deposition of precursor slurry) resulted in the anticipated coating thickness deviations. The average

laser-alloyed coating thickness of 40/40/20 and 60/20/20 TiB₂/TiC/Al powder precursor ratio material were $110 \pm 8 \mu\text{m}$ and $100 \pm 6 \mu\text{m}$, respectively. Quantitative microstructure analysis indicates that reinforcement particles occupy approximately 60–65% of the total volume in the coating. Evidently, both laser-alloyed coatings are free of cracks with low content of porosity, showing a sound bonding with the continuous and smooth interface between the coating and the substrate material. The reinforced particles in the coating are multimodal in size, and relatively uniformly distributed in the Al matrix.

Fig. 1. Cross-section SEM micrographs of the laser-alloyed coating with different ratios of TiB₂/TiC/Al powder precursor material; (a) 40/40/20 and (b) 60/20/20.

In addition to the quality of the coating (pores, density, adhesion, etc.), the topography/morphology (roughness) of the coated layer directly affects the oxidation process and corrosion resistance. A typical surface topography of laser-alloyed coating depends on the method of laser operation, the laser input energy density and the beam overlapping. The mean arithmetic roughness R_a of coated specimens processed with 40/40/20 and 60/20/20 TiB₂/TiC/Al ratios of powder precursor materials were $2.1 \mu\text{m}$ and $2.2 \mu\text{m}$, whereas with the uncoated, i.e. substrate material it was much lower and equalled to $0.8 \mu\text{m}$. Similar roughness values of the coated specimens are rather reasonable, since only two different ratios of powder precursor material were spray coated and subsequently laser alloyed using the constant laser parameter processing.

Nonetheless, it should be noted that one of the major disadvantages associated with laser surface alloying is that they create significant rippling and roughening of the treated surface. This rippling results from two major factors, namely the fluid flow resulting from the shear stresses on the molten film caused by the gradient in surface tension of the liquid film and the vapour pressure above the molten film which depresses the liquid film [30].

Due to the fact that the flat and smooth surface is likely to be chemically less active compared to the rough surface and since surface finish plays a crucial role in industrial applications, all specimens were additionally fine-grinded to enhance the corrosion resistance in an aggressive environment. Mean arithmetic roughness was 0.7 μm for both coated specimens and 0.2 μm for uncoated specimen.

XRD patterns of the laser-alloyed coating produced with 40/40/20 and 60/20/20 TiB₂/TiC/Al ratios of powder precursor material are shown in Fig. 2. XRD analyses after laser coating have confirmed the presence of the following expected phases: TiB₂, TiC, Al, B₂O₃, Al₄C₃, Al₂O₃ and TiO₂. TiB₂, TiC primarily via the following possible reactions [31], [32], [33], [34], [35], [36]:

A thin passive Al₂O₃ film was formed spontaneously on aluminium in oxidizing media according to the reaction (2) [31], [32]. Titanium dioxide (TiO₂) generally formed by the oxidation of the TiC or TiB₂ according to the reaction (3) and (4), while B₂O₃ was formed by the oxidation of the TiB₂ according to the reaction (4) [33], [34]. Furthermore, it is assumed that after the decomposition of TiC, carbon reacted with aluminium to form aluminium carbide Al₄C₃ according to the reaction (5) [35], [36]. Kennedy et al. [35] reported that reaction (5) can take place at about 705°C, while the melting point of TiC is much higher, i.e. 3067°C [37].

Fig. 2. XRD patterns of laser-alloyed TiB₂/TiC/Al coatings.

The corrosion resistance mainly depends on the general coating integrity and quality based on the aspects such as but not limited to adhesion, porosity, roughness, coating passive film, kinetics of the passive film formation and its resistance. When titanium diboride is immersed in NaCl solution at room temperature, it behaves like a passive metal due to the formation of a surface oxide film (hydrated titanium dioxide), whose protectivity decreases with the temperature and completely vanishes at 65 °C [15], [38]. In salt rich ocean water, a white film of tetravalent oxide titanium TiO₂-H₂O is formed, which hinders the material dissolution [13], [38]. Titanium carbide is relatively stable in mineral acids and alkali solutions, but decomposes in the presence of oxidizing acids [39].

3.2. Open-circuit potential measurements

The open circuit potential (OCP) curves of laser-alloyed TiB₂/TiC/Al powder precursor materials and a substrate Al 6082 alloy in a 0.5 M NaCl water solution are presented in Fig. 3. As noticed from the potential-time behaviour the substrate material exhibits the most negative values with a gradual

potential decrease. On the contrary, both laser-alloyed coatings shows relatively stable and higher potential values. Furthermore, the potential transients indicate that laser-alloying process enables potential ennoblement in the first stage of immersion. This fact is most likely associated with the passivation/re-passivation process of the oxide layer and its thickening caused by the interaction of passive layer with the electrolyte [40]. In the second stage of immersion in an aggressive chloride solution laser-alloyed coating exhibit a slow potential decrease which remained almost constant with slight fluctuations. The potential fluctuations of laser-alloyed coatings probably associated with increased active surface due to the micro-roughening effect during laser alloying process or mutual reaction between film formation and partial dissolution of corrosion products [14]. Nevertheless, both laser-alloyed coatings exhibited higher potential E_{corr} values at the end of the stabilization process compared to the substrate Al alloy (-755 mV_{SCE} and -764 mV_{SCE} vs. -786 mV_{SCE}).

Although, on the basis of 1 h immersion test it is impossible to foresee long-term stability against corrosion, all specimens achieved steady-state potential after approximately 30 min, indicating an equilibrium state at which the rate of oxidation equals that of reduction. Moreover, long-term stability results during 24 h immersion in a 0.5 M NaCl solution (inset in Fig. 3) clearly demonstrate that with laser alloying process of TiB₂/TiC/Al powder precursor materials onto Al 6082 alloy a chemically stable, durable and corrosion resistant coatings are achieved, with superior long-term corrosion stability is obtained showing a stable/steady state and nobler potential compared to the Al 6082 substrate material. On the contrary, the substrate specimen exhibited the most active behaviour with sharp OCP drop from the very beginning in the test solution. With longer exposure time the OCP continued to drop and further moved towards more negative values indicating a rupture of the oxide film and corrosion propagation.

Fig. 3. Open circuit potential of different specimens in 0.5 M NaCl solution over a period of 1 hour (Inset: OCP recordings during longer, i.e. 24 h exposure time).

However, since only the potential-time measurements do not reveal the underlying corrosion mechanism and kinetics, this statement will be either confirmed or rejected after electrochemical impedance spectroscopy, cyclic polarization and surface morphology evaluation in the next sections.

3.3. Electrochemical impedance spectroscopy

To further investigate the corrosion process, EIS plots were recorded in a 0.5 M NaCl solution at OCP. Fig. 4a and b shows the EIS results presented as Nyquist and Bode plots, respectively. From a comparison of Nyquist plots in Fig. 4a it can be seen that there are differences not only in the shape but also in the size of the respective Nyquist plots. The diameter of the capacitive semicircle of a measured Nyquist spectrum is closely related to the corrosion rate [41]. A larger diameter of capacitive loop implies a larger charge transfer resistance. A reduced charge transfer reflects a lower corrosion rate of a metal in a corrosive solution [42]. Obviously, the coated specimens with the large capacitive loop exhibit higher resistance to the tested solution resistance compared to the uncoated Al alloy specimen. Furthermore, the EIS response in Nyquist plot of the uncoated specimen (inset in

Fig. 4a) indicates a feature of Warburg impedance. This effect can be attributed to a diffusion control of ions from the electrode to the bulk solution [15].

Fig. 4. EIS spectra presented as (a) Nyquist plot and (b) Bode plots in 0.5 M NaCl solution
(19.6 ± 0.2 °C, $\text{pH } 7.3 \pm 0.5$).

Bode plots in Fig. 4b clearly shows higher absolute impedance value $|Z|$ of the coated specimens in the low frequency region. The phase angle modulus of the coated specimens was close to 90° over a wide frequency range, confirming the interaction of at least two time constants [40]. Such capacitive response of the coated aluminum alloy is expected due the high polarization resistance of the coating [9] indicating a more stable barrier of protection in an aggressive chloride environment for the coated specimens compared to the bare/uncoated Al alloy specimen. In contrast,

the modulus of the phase angle maxima of the uncoated specimen was lower than 45°. Such behavior can be interpreted as a deviation from ideal capacitor behavior [43] [44].

In order to interpret electrochemical behaviour further, EIS data were fitted in complex plane by using various equivalent electrical circuits (EEC) models. Based on the smallest error of fit, i.e. lowest chi-square value obtained (avg. $\chi = 1.93 \times 10^{-3}$) the final EEC presented in Fig. 4a was chosen. In this electrical circuit, the components are as follows, R_s is the solution resistance, the electrical circuit parameter group Q_c and R_{po} represents the reactions at the outer interface and is assigned to the areas covered with the porous passive film at higher frequencies. The parameter groups Q_{dl} and R_{ct} represent the charge-transfer reaction at the electrolyte/dense passive film interface (inner barrier processes) at lower frequency ranges.

Instead of the ideal electrical capacitance a constant phase element – CPE was used because it better describes depressed semicircle behaviour due to the non-perfectly smooth surface having heterogeneities in microstructure and chemical composition. The impedance of CPE (Z_{CPE}) is given as [45]:

$$Z_{CPE(\omega)} = 1/(Q_o j \omega^n) \quad (6)$$

where ω represents the angular frequency; j is the complex operator ($j^2 = -1$), Q_o is a fit parameter and n represents an empirical exponent ($0 \leq n \leq 1$). In the ideal case when $n = 1$, the CPE acts like a capacitor associated with a perfectly smooth surface, when $n = 0$ the CPE represents a resistor and when $n = 0.5$ the CPE represents the Warburg impedance, respectively [43].

The coating (C_c) and double-layer (C_{dl}) capacitance were calculated from the CPE (Q) and afterwards the total resistance R_t and total capacitance C_t were determined by using the following equations [43][46][47]:

$$C = (QR)^{1/n} / R \quad (7)$$

$$R_t = R_{po} + R_{ct} \quad (8)$$

$$C_t = (1/C_c + 1/C_{dl})^{-1} \quad (9)$$

where R , Q and C correspond to the parameter of the specific group (outer/inner process), respectively.

Results of the EIS fitted parameters (Table 1) confirm superior corrosion resistance of both TiB₂/TiC/Al laser-alloyed coating, with lower coating capacitance C_c values than with the substrate Al-alloy. The lowest value was obtained with 40/40/20 TiB₂/TiC/Al laser-alloyed coating, which was 45-times lower than with the BM sample ($1.22 \mu\text{F cm}^{-2}$ vs. $13.71 \mu\text{F cm}^{-2}$), indicating thicker passive surface film. Furthermore, double-layer capacitance C_{dl} of this specimen was lower more than 863-times ($7.84 \mu\text{F cm}^{-2}$ vs. 6.77 mF cm^{-2}) and charge-transfer resistance R_{ct} higher more than 4-times ($6.38 \text{ k}\Omega \text{ cm}^2$ vs. $1.45 \text{ k}\Omega \text{ cm}^2$) as a consequence of decreased metal area in contact with the electrolyte and lower ion adsorption, respectively.

Table 1. Circuit parameters obtained from simulation of EIS measurements using EEC.

Parameter	Substrate Al alloy	40/40/20 coating	60/20/20 coating
$R_s [\Omega \text{ cm}^2]$	4.36	1.97	2.84
$Q_c [\text{S cm}^{-2} \text{ s}^n]$	5.52×10^{-5}	1.22×10^{-6}	1.22×10^{-5}
$n-(Q_c) [/]$	0.82	1	0.86
$C_c [\text{F cm}^{-2}]$	13.71×10^{-6}	1.22×10^{-6}	7.43×10^{-6}
$R_{po} [\Omega \text{ cm}^2]$	36.02	57.39	4198
$Q_{dl} [\text{S cm}^{-2} \text{ s}^n]$	2.66×10^{-3}	2.16×10^{-5}	1.57×10^{-3}
$n-(Q_{dl}) [/]$	0.59	0.66	0.48
$C_{dl} [\text{F cm}^{-2}]$	6.77×10^{-3}	7.84×10^{-6}	2.01×10^{-3}
$R_{ct} [\Omega \text{ cm}^2]$	1.45×10^3	6.38×10^3	0.80×10^3
$R_t [\Omega \text{ cm}^2]$	1.49×10^3	6.43×10^3	5.01×10^3
$C_t [\text{F cm}^{-2}]$	13.68×10^{-6}	1.05×10^{-6}	7.40×10^{-6}

Moreover, by comparing the total resistance R_t and total capacitance C_t values it can be concluded that the corrosion resistance of the investigated specimens is the following order: 40 TiB₂/40 TiC/20 Al coating > 60 TiB₂/20 TiC/20 Al coating > BM –substrate Al alloy. Further, the above results clearly show that the OCP monitoring/results cannot serve as an ultimate in determination of corrosion resistance, especially when different materials/coatings are compared

among themselves. Despite the fact that 60/20/20 TiB₂/TiC/Al laser alloyed coating achieved nobler OCP recording than 40/40/20 coating during the initial 60 min and 24 h immersion, the latter show more corrosion resistant surface with long-term stability and reduced kinetics, which can successfully inhibit the corrosion process in chloride solution.

3.4. Cyclic polarization scans

Cyclic polarization techniques provide a qualitative view of pitting corrosion mechanisms and can determine the tendency of a material to undergo surface pitting or crevice corrosion when placed in a specific corrosive environment [48]. Cyclic polarization (CP) curves corresponding to laser-alloyed specimens with 40/40/20 and 60/20/20 TiB₂/TiC/Al ratios of powder precursor material, in the as-is condition (without surface grinding), are shown separately in Fig. 5a and b, respectively. For the sake of better comparison, the CP curves of laser-alloyed coatings are presented together with the substrate Al alloy.

CP curves in Fig. 5 indicate similar behaviour, with higher current density in the reverse cathodic scan direction, whereas the cathodic curve intersects the forward anodic scan, regardless of the specimen condition. This fact confirms that the substrate materials as well as both laser-alloyed coating in the as processed condition are susceptible to pitting corrosion [13]. A similar result was also found in the work of Darabara et al. [13] who found that TiB₂ and TiB₂ + N alloyed layers are susceptible to pitting corrosion in 3.5 wt.% NaCl and 1 N H₂SO₄ solution. Further, one should note that although TiC and TiB₂ coating itself exhibits good passivation behaviour in a NaCl solution the Al part of the coatings prevented a passive region plateau, as the potential continuously increases with increasing current density. In addition, the polarization curves of laser-alloyed coating have the same form as that substrate, i.e. the uncoated Al 6082 alloy.

Fig. 5. Cyclic polarization curves of Al 6082 substrate and laser-alloyed TiB₂/TiC/Al coatings in 0.5 M NaCl solution ($19.6 \pm 0.2^\circ\text{C}$, $\text{pH } 7.3 \pm 0.5$); (a) 40/40/20 and (b) 60/20/20 ratios of precursor material.

Electrochemical parameters, such as corrosion potential (E_{corr}), switching potential (E_{sw}), the potential at which pits repassivate on reverse scan (E_{prot}) and corrosion current density (i_{corr}) derived from the polarization curves are given in Table 2.

Analysis showed that the noblest corrosion potential E_{corr} was obtained with the substrate Al alloy and 60/20/20 laser-alloyed coating ($-744 \text{ mV}_{\text{SCE}}$), while the 40/40/20 TiB₂/TiC/Al laser-alloyed coating exhibited the most negative E_{corr} value ($-751 \text{ mV}_{\text{SCE}}$). However, it should be noted that due to small difference of corrosion potential values and the variability of the coating porosity, a direct conclusion on the relative nobility of the different coatings solely on the basis of E_{corr} cannot be drawn [9]. However, the corrosion current density i_{corr} of 40/40/20 laser-alloyed coating was found to be

almost 5 times lower than the substrate specimen ($6.0 \mu\text{A cm}^{-2}$ vs. $29.9 \mu\text{A cm}^{-2}$). A similar result was also obtained for the laser-alloyed coating with a 60/20/20 ratio of powder precursor material, which achieved corrosion current of $7.9 \mu\text{A cm}^{-2}$, indicating 3.8 times lower value compared to the substrate Al alloy. Clearly, both $\text{TiB}_2/\text{TiC}/\text{Al}$ laser-alloyed coatings improve corrosion resistance of Al 6082 alloy. It seems that dissolution of TiB_2 and TiC results in the formation of an insoluble hydrated titanium dioxide film on the aluminium substrate, which further reduces the corrosion rate. Moreover, the protection efficiently (Eq. 1) results indicate an obvious beneficial effect of the laser alloying process with both ratios of powder precursor material, with the highest value of almost 80%. These results are consistent with results reported by Alkhateeb et al. [9], where it was shown that boron content inside Ti-based coatings is highly beneficial in increasing a coating corrosion resistance.

Table 2. Electrochemical parameters obtained from the CP curves in 0.5 M NaCl solution (19.6 ± 0.2 °C, pH 7.3 ± 0.5).

Specimen designation	R_a [μm]	E_{corr} [mV _{SCE}]	E_{sw} [mV _{SCE}]	E_{prot} [mV _{SCE}]	i_{corr} [$\mu\text{A cm}^{-2}$]	P_{EF} [%]	$E_{\text{sw}} - E_{\text{corr}}$ [mV]	$E_{\text{corr}} - E_{\text{prot}}$ [mV]
Substrate Al alloy	0.8	-744	-701	-795	29.9	/	43	51
40/40/20 coating	2.1	-751	-717	-773	6.0	79.93	34	22
60/20/20 coating	2.2	-744	-705	-766	7.9	73.58	40	22
Substrate Al alloy + grinded	0.2	-778	-740	-800	10.2	65.88	37	24
40/40/20 coating + grinded	0.7	-766	-572	-818	1.1	96.32	192	52
60/20/20 coating + grinded	0.7	-797	-577	-823	2.0	93.31	219	26

Despite the fact, that both laser-alloyed coatings improve the corrosion resistance of the Al 6082 alloy, no passive behaviour of $\text{TiB}_2/\text{TiC}/\text{Al}$ coating could be detected. In view of this, additional evaluation of corrosion resistance of these specimens after subsequent surface grinding was conducted. The second set of CP curves in Fig. 6 indicates a significant influence of grinding procedure emphasizing the important role of surface homogeneity and roughness in reducing corrosion susceptibility. In contrast to CP curves of the laser-alloyed coatings directly after laser

processing (Fig. 5), where a sharp current increase during anodic polarization was present, subsequent grinding contributed to partial passivation behaviour (Fig. 6). Afterwards, a sharp increase in anodic current due to a stable pit growth or pit propagation is observed with a well-defined hysteresis in the reverse, i.e. cathodic scan.

Fig. 6. Cyclic polarization curves of Al 6082 substrate and laser-alloyed $\text{TiB}_2/\text{TiC}/\text{Al}$ coatings after subsequent grinding procedure in 0.5 M NaCl solution (19.6 ± 0.2 °C, $\text{pH } 7.3 \pm 0.5$); (a) 40/40/20 and (b) 60/20/20 ratios of precursor material (inset: comparison of CP curves prior and after subsequent grinding for each $\text{TiB}_2/\text{TiC}/\text{Al}$ coatings).

Moreover, as can be clearly seen from Fig. 6 and Table 2 subsequent grinding further enhances the corrosion resistance of both laser-alloyed $\text{TiB}_2/\text{TiC}/\text{Al}$ coatings. A superior corrosion resistance compared to the grinded Al 6082 substrate, with a considerably lower corrosion current density over all the potential range scanned can be seen, with less abrupt current increase in anodic direction from

E_{corr} to E_{sw} . Although, CP curves of both coated specimens in Fig. 6 show some amount of scattering in the Tafel region, the reduction of i_{corr} is clearly apparent. Nonetheless, in order to achieve the most accurate readings, i_{corr} of grinded coated specimens were obtained by the intersection of the Tafel lines extrapolations by ± 150 mV around E_{corr} , starting 50 mV away from E_{corr} , taking into consideration the IR drop. Afterwards, the best linear part was chosen for analysis. To obtain the smallest possible error of fit, the values were constantly monitored and several repetitions were performed, whereas the E_{corr} difference (actual vs. fitted) did not exceed ± 3 mV. The highest i_{corr} reduction was experienced with 40/40/20 TiB₂/TiC/Al laser-alloyed coating with i_{corr} value of $1.1 \mu\text{A cm}^{-2}$. Laser-alloyed coating with 60/20/20 ratio of powder precursor material experienced a corrosion current density of $2.0 \mu\text{A cm}^{-2}$. Hence, the highest protection efficiency of 96.32% was obtained with a specimen coated with the same TiB₂ and TiC content, whereas the value of protection efficiency for a specimen coated with higher TiB₂ content was 93.31%.

It is also noteworthy, that the substrate Al alloy after subsequent grinding exhibited almost 3 times lower corrosion current density than in the as received condition ($10.2 \mu\text{A cm}^{-2}$ vs. $29.9 \mu\text{A cm}^{-2}$). These indicate almost linear inverse correlation with surface roughness of these two specimens ($0.2 \mu\text{m}$ vs. $0.8 \mu\text{m}$). Such results clearly emphasizes that surface roughness wields a tremendous effect on corrosion resistance. This is rather logical since higher roughness reflects in larger active area and higher sensitivity to localized corrosion attack compared to specimens with lower surface roughness. Increased roughness also affects the passive/oxide film resistance, which can cause easier penetration of water molecules, oxygen, and Cl^- ions into isolated regions of inhomogeneities (surface craters, passive film defects, pores, etc.) [43].

Several authors [11], [43], [49], [50], [47] have proposed the necessity of ΔE trend determination for the prediction of localized corrosion susceptibility of Al alloys in chloride-containing solutions. A larger value of $E_{\text{sw}} - E_{\text{corr}}$, indicates a lower degree of anodic dissolution of material, while a smaller value of $E_{\text{corr}} - E_{\text{prot}}$ presents an improved ability for material repassivation. From the ΔE trend results in Fig. 7, it can be confirmed that in the as-is condition (no grinding) the substrate Al alloy provided

a lower degree of anodic dissolution, while the laser-alloyed coatings provided a better and faster ability for repassivation. This confirms that the substrate Al alloy surface is, compared to TiB₂/TiC/Al laser-alloyed coatings, slightly more resistant only at the beginning of the corrosion process. In contrast, both coated specimens provided lower advance of corrosion, with much smaller corrosion current and improved ability for repassivation with 2.4 times lower $E_{\text{corr}} - E_{\text{prot}}$ value compared to the substrate Al alloy. On the contrary, after subsequent grinding both laser-alloyed coatings achieved more than 5 times higher value of $E_{\text{sw}} - E_{\text{corr}}$, than the rest of the specimens indicating the lowest degree of anodic dissolution in an aggressive chloride environment.

Fig. 7. Comparison of ΔE trend as a function of specimens in 0.5 M NaCl solution (19.6 ± 0.2 °C, pH 7.3 ± 0.5).

The above mentioned phenomenon can be clearly seen in [Fig. 8](#), wherein the substrate Al alloy surface exhibits a widespread pitting attack with large and small pits. In contrast, the surface morphology of the laser-alloyed coatings after the CP test revealed that the size and number of pits are reduced.

Fig. 8. Surface morphology of the specimens' surface after CP corrosion test in 0.5 M NaCl solution ($19.6 \pm 0.2^\circ\text{C}$, $\text{pH } 7.3 \pm 0.5$); (a) Al 6082 substrate (b) 40 TiB₂/40 TiC/20 Al laser-alloyed coating and (c) 60 TiB₂/20 TiC/20 Al coating.

Rajamure et al. [47] reported that important factor influencing the susceptibility to localized corrosion attack is the microstructure evolved during laser surface alloying. According to the nature of inhomogeneities, the common susceptible sites for pits may be classified as inclusions, second phase particles, grain boundaries, processing defects such as pores, cracks, etc. [11], [43]. After the breakdown of the passive layer on aluminium alloy, the pitting attack is associated with the second-

phase intermetallic particles such as Si, Mg₂Si, Al_x(Si, Mn, Mg, Fe), Al_x(Zn,Mn,Fe,Cu), and Al_x(Mn,Fe) in Al 6082 alloy [51], [52]. Hence, the microstructural heterogeneity and the presence of inter-metallic phases of various compositions can drastically increase the susceptibility of Al alloy to local corrosion attack in an aggressive Cl⁻ environment [49]. In fact, minor defects, which are often unavoidable with laser alloying process owing to melting and rapid solidification, and overlapping of melt tracks could have a similar effect. Although in general, these defects might not seriously affect the cavitation erosion resistance, they might affect the integrity of the passive film, i.e. its formation, kinetics and resistance, resulting in increased susceptibility to pitting attacks in the proximity of the defect [11]. Moreover, as seen in Fig. 8 pitting attack on the laser-alloyed coatings is mainly confined to the isolated regions associated with uneven distribution of phases and the regions of compositional variation [47].

From the CP results and surface examination after corrosion, good correlation with EIS results was obtained. All results clearly show that the laser coating improves the pitting resistance of the aluminum alloy with TiB₂/TiC/Al coating. The formation of passive films on the laser-treated coating in air can act as a protective barrier and effectively reduce the rate of corrosion [42]. However, as the dissolution of the coated specimens is often localized in the pores and defects in the coatings, the average corrosion rate and impedance values measured directly depends on the size and number of the defects [9]. Thus, for high corrosion resistance, the compactness coating without cracks and pores must be achieved.

3.5. Prediction of Chemical bonding using Cauchy pressure and Density Functional Theory

In order to predict the nature of chemical bonding and hybridization of TiB₂ and TiC, the Cauchy pressure, and total and partial density of states were calculated (Table 3 and Fig. 9). Pettifor [53] showed that nature of chemical/atomic bonding in a material can be classified by using the magnitude of the Cauchy pressure (C₁₂–C₄₄). Furthermore, this relationship also relates brittle and ductile characteristics in a material to the nature of atomic bonding. In general, for the metallic materials, the

Cauchy pressure is positive; in contrast, for covalent materials, the Cauchy pressure is negative. Considering this criteria for TiB₂ ($C_{12} - C_{44} = -205$) and TiC ($C_{12} - C_{44} = -72$), it can be clearly seen that both compounds are highly covalent in nature. Additionally, the nature and type of covalent bonding can be understood from the density of states.

Table 3. Calculated elastic constants (in GPa) using VASP.

Phase	C11	C12	C13	C33	C44
TiB ₂	683.01 ± 4.23	58.83 ± 4.23	91.88 ± 2.99	479.50 ± 4.23	264.25 ± 5.99
TiC	512 ± 7.21	129 ± 7.21	/	/	201 ± 10.19

In Fig. 9, the Fermi level is scaled to zero and the various regions in the valence and conduction bands are dominated by Ti d states, B s, p states and C s, p states. Considering the valence electron domination, the valence and conduction bands are separated into three regions. For TiB₂ and TiC, the lower part of the valence band is mainly dominated by B s states and C s states, the upper part of the valence band is mainly dominated by B p states, C p states and Ti d states, where as the whole conduction band is dominated by TiB₂ (Ti d states and B p states) and TiC (Ti d states and C p states). Furthermore, for both compounds, a strong hybridization near the Fermi level between Ti d and B p states for (TiB₂) and Ti d and C p states for (TiC) exists. Hence, due to the presence of strong hybridization in vicinity of the Fermi level, the whole region can be divided into bonding and anti-bonding regions, and the presence of quasi gap at the Fermi level separates the high and low energy bonding regions. Previously, Kumar et al. [54] and Kavitha et al. [55] carried out the first principle calculations on TiB₂ and TiC, and the results of their study were in close agreement with the present calculations performed using hybrid functional (HSE06).

For TiB₂ and TiC, the number of total DOS values ($N(E_f)$) are 0.1 and 0.5 states/ev/atom, which indicate that these compounds are stable structures [56], [57], [58]. Moreover, the fact that both compounds are structurally stable, is mainly attributed to the presence of wide energy gap and the

presence of the Fermi level in narrow valley of the bonding region [59], [60], [61]. However, for TiB₂ the amount of covalency is higher, mainly due to the hybridization, and the nature of the pseudo-gap is widest at the Fermi level when compared with TiC. Indeed, this suggests that the amount of covalency is highly dependent on nature of pseudo-gap at the Fermi level and also the total number of density of states at the Fermi level [56], [57], [58], [59], [60], [61].

Fig. 9. Density of states for (a) TiB₂, (b) TiC calculated using HSE06 functional.

It is apparent from the comparison of the EIS and CP results (Figs. 4 to 6, Table 1 and 2) that aluminium alloy 6082 substrate has inferior corrosion resistance compared to the laser-alloyed coatings. Although the laser surface alloyed samples did not show the passive behaviour, a substantial enhancement in the corrosion resistance compared to the uncoated Al specimen was confirmed. It is interesting to note that the increase in corrosion resistance after laser processing is mainly attributed to cathodic suppression towards lower current densities. This further implies that the cathodic reduction reaction was suppressed by the presence of TiB₂ and TiC phases within the microstructure, thereby enhancing its corrosion resistance. Moreover, DFT results confirm good agreement with CP results in the investigated chloride solution. It is generally believed that the corrosion resistances of TiB₂ and TiC are higher, and this is mainly due to the nature of the covalent bonding.

However, it should be noted that in the case of laser-alloyed coatings in the un-altered condition (no grinding) the Al part of these coatings is somehow detrimental to their performance since the coating behaviour resembles the behaviour of the substrate. However, the specimens with subsequent grinding exhibit substantial enhancement in the corrosion resistance with partial passivation, lower corrosion current density and lower anodic dissolution compared to substrate 6082 Al alloy.

In general, the electrochemical behaviour of any surface is mainly dictated by the presence of local heterogeneity in the microstructure over different length scales such as 1) mesoscale (degree of surface roughness and waviness, which affect the real active surface), 2) macroscale (variation in the grain size, distribution or segregation of intermetallic phases and their composition), and 3) nano-scale (dislocation density, its transition and configuration, grain refinement). During laser surface alloying, the high rate of heating, remelting, and solidification cycles contribute to generation of morphological and microstructural features at various scales described above.

Therefore, understanding the mechanism of bonding and electronic structural characteristics, such as the Fermi level and density of states of TiB₂ and TiC is highly critical and yields significant insight into their electrochemical nature. In this study, the enhancement in the corrosion resistance is most likely attributed to reduction in the cathodic current and to the low cathodic activity due to the effect of laser processing. This implies that the relative amount of electron density of states for TiB₂ and TiC at the Fermi level is very low (Fig. 9) and the presence of wide pseudo-gap further indicates that energy at the Fermi level is also low [62]. Besides, the valence electron charge densities maps of TiB₂ and TiC are presented elsewhere [63][64][65][66][67][68] also indicate the presence of covalent bonding and existence of strong hybridization. From all the above mentioned, it is clear that strong covalent bonding of TiB₂ and TiC are highly preferable for corrosion applications, contributing to the retardation of the specimen dissolution due to reduced penetration of water molecules, oxygen and Cl⁻ ions.

4. Conclusions

Investigation of corrosion resistance in the 0.5 M NaCl solution of 6082-T651 Al alloy coated with TiB₂ and TiC with the addition of aluminium powder using laser based techniques was conducted. The laser-alloyed coatings were produced using two different ratios of powder precursor material, i.e. 40 wt.% TiB₂/40 wt.% TiC/20 wt.% Al (40/40/20) and 60 wt.% TiB₂/20 wt.% TiC/20 wt.% Al (60/20/20). Based on the results obtained the following conclusions can be drawn:

- 1.) The laser-alloyed TiB₂/TiC/Al compound coatings mainly consisted of blocky reinforcements, possessed sound metallurgical bond with the substrate, low porosity, and no cracks, which are necessary to achieve good corrosion resistance.
- 2.) OCP transients confirmed stable and more positive potential values of laser-alloyed TiB₂/TiC/Al coatings. On the contrary, lowest long-term stability was confirmed with the substrate Al 6082 alloy, which achieved the most active behaviour with sharp decrease of OCP over the period of 24 h, indicating the lowest corrosion resistance.
- 3.) Furthermore, the results of electrochemical impedance spectroscopies (EIS) demonstrated superior corrosion resistance of TiB₂/TiC/Al laser-alloyed coatings compared to the substrate material. Despite lower OCP value of 40 TiB₂/40 TiC/20 Al laser alloyed coating (than 60 TiB₂/20 TiC/20 Al coating) this specimen achieved the highest corrosion resistance with 863 times lower double-layer capacitance C_{dl} and more than 4 times higher charge-transfer resistance R_{ct} than the substrate material.
- 4.) SEM results after CP measurements confirmed pitting attack on both, i.e. substrate and laser alloyed specimens. However, the latter ones showed improved corrosion resistance with lower intensity of pitting attack. Although Al inside the powder precursor material improved adhesion of the ceramic coating to the substrate, the Al part in the as-processed condition also resembles the behaviour of the substrate material. However, due to the formation TiO₂, B₂O₃ and Al₂O₃ on the specimens' surface satisfactory corrosion resistance is achieved. Moreover, the subsequent grinding exhibit substantial enhancement in the corrosion resistance with partial passivation, lower corrosion current density and lower anodic dissolution.

- 5.) The highest protection efficiently value of 96.32% was experienced with a 40/40/20 TiB₂/TiC/Al laser-alloyed coating after substantial grinding.
- 6.) The presence of wide energy gap for TiB₂ and TiC near the Fermi level indicated the directionality of covalent bonding which further enhanced the corrosion resistance, compared to the pure metallic bonding in the substrate aluminium specimen.

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