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Modification of surface hardness, wear resistance and corrosion resistance of cold spray Al coated AZ31B Mg alloy using cold spray double layered Ta/Ti coating in 3.5 wt % NaCl solution



M. Daroonparvar^{a,b,*}, M.U. Farooq Khan^c, Y. Saadeh^c, C.M. Kay^a, A.K. Kasar^d, P. Kumar^b, L. Esteves^c, M. Misra^b, P. Menezes^d, P.R. Kalvala^b, H.R. Bakhsheshi-Rad^{e,f}, R.K. Gupta^{c,**}

^a Research and Development Department, ASB Industries. Inc, Barberton, OH, 44203, USA

^b Department of Chemical and Materials Engineering, University of Nevada, Reno, NV, 89501, USA

^c Department of Chemical, Biomolecular, and Corrosion Engineering, The University of Akron, Akron, OH, 44325, USA

^d Department of Mechanical Engineering, University of Nevada, Reno, NV, 89501, USA

^e Department of Materials, Manufacturing and Industrial Engineering, Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310, Johor Bahru, Johor, Malaysia

^f Advanced Materials Research Center, Department of Materials Engineering, Najafabad Branch Islamic Azad University, Najafabad, Iran

ARTICLE INFO	A B S T R A C T
Keywords: Magnesium Metal coatings Tantalum oxide EIS X-ray diffraction Passivity Pitting corrosion	In this research, cold sprayed Al coating layer on AZ31B Mg alloy was coated with cold sprayed Ti and Ta/Ti coatings, which noticeably reduced the wear rate of Al coated Mg alloy. Electrochemical corrosion tests and infinite focus 3D measurement results revealed that the high surface activity of commercially pure-Al coating, diffusion-controlled reactions, and formation of corrosion pits could be mitigated using Ti top coating. However, a dense layer of Ta on Ti coating exceptionally improved the corrosion resistance of Ti/Al coated AZ31B Mg alloy in neutral 3.5 wt.% NaCl solution This work gives a new strategy to considerably raise the wear and corrosion resistances of cold spray Al coated Mg alloys by double layered Ta/Ti coatings.

1. Introduction

Magnesium (Mg) based alloys owing to their low density and high specific strength became prospective for structural engineering applications. Such alloys have several unique attributes such as excellent recyclability, satisfactory electrical and thermal diffusivity, substantial castability, excellent weldability, and high capacity for damping [1–4]. However, poor creep, wear and corrosion resistance of Mg alloys limit their varied applications unless inhibited [4,5]. The inferior corrosion resistance of Mg and its alloys can primarily be attributed to their high surface reactivity and formation of loose and non-protective corrosion films on their surface [5,6].

Over the years, several methods have been developed to modify Mg alloys surface for mitigating the above-mentioned drawbacks. These include various conversion coatings, anodization process, plasma electrolytic oxidation (PEO), physical vapor deposition (PVD), electroless processes, air plasma spraying (APS) method, and ions implantation. All these techniques were targeted to enhance the corrosion resistance of Mg and its alloys [7-12] https://www.sciencedirect.com/science/artic le/abs/pii/S0042207X14001936 https://www.sciencedirect.com/sci ence/article/pii/S0272884215016430 https://www.sciencedirect.co m/science/article/pii/S0272884215015503 https://link.springer. com/article/10.1007/s11665-015-1543-9 https://link.springer. com/article/10.1134/S2070205118030231. A well-adhered coating with high denseness (low porosity) can exceptionally improve the corrosion resistance of the substrate. Nevertheless, these requirements may be met by a few of the above methods [13]. In comparison with the aforementioned techniques, the cold spray (CS) process is fairly new coating technology. This method (CS) uses kinetic energy to produce the coating layer rather than a combination of thermal and kinetic energies such as HVOF (high-velocity oxy-fuel) spray https://www.sciencedirect. com/science/article/abs/pii/S0010938X17322369 https://www.sci encedirect.com/science/article/pii/S0272884220316473. In the CS process, fine powder particles (5-50 µm) are propelled toward the

** Corresponding author.

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^{*} Corresponding author at: Research and Development Department, ASB Industries. Inc, Barberton, OH, 44203, USA.

E-mail address: mr.daroonparvar@yahoo.com (M. Daroonparvar).

substrate surface with supersonic velocity (300-1200 m/s). Upon impact, the particles undergo adiabatic heating and plastically deform at very high shear rates, which leads to flattening and helps bonding them strongly to the underlying surface (material jets) [14]. Better interface adhesion at the coating/substrate could be ascribed to elimination of the oxide scale on surface of substrate by powder particles (with high-speed impact) [15] and even metallurgical bonding at the particle/substrate interface [16]. Cold spray operational temperatures are relatively low when compared with those of thermal and plasma spray methods. The low operating temperature of cold spray together with the use of inert gas prevents oxidation of the particle surfaces, phase transformation, grain growth, and formation of undesirable phases in the coating during spraying. This can substantially help for the production of pure and dense coatings of oxidation-sensitive as well refractory metals. Moreover, microstructural damage of the heat-vulnerable substrates such as Mg alloys which are often observed in the alternative thermal and plasma spray methods can be prevented using the CS method [9,17–19]. In this method, preheating high-pressure propellant gas (with low molecular weight), which is injected into the cold spray gun, can increase the sonic velocity in the throat of the De-Laval nozzle. Preheating can considerably increase the powder particle velocity. Cold spray systems that worked with inexpensive and readily available N₂ gas were readily developed. Nowadays, gas temperatures up to 1100 °C can be achieved in such systems. In spite of the relatively high supply gas temperatures (in such systems), the propellant gas temperature substantially decreases as it expands in the divergent section of the De-Laval nozzle [16]. Hence, the dwell time of powder particles in high temperatures is only for a short time and they remain well below their melting point [16]. Moreover, the latest developments in the cold spray systems have led to process optimization using standard powders with high deposition efficiency.

Aluminum having excellent corrosion resistance, low density, and low standard reduction potential (SRP) mismatch with Mg alloys (minimum galvanic corrosion with Mg alloys) is used for the corrosion protection of Mg alloys [7,20-22]. In the CS process, N2 process gas with 230 °C and pressure of 1.6 MPa was employed to deposit pure Al coating on the AZ91D Mg alloy. Micro-sized cracks and pores were extensively observed in the coating microstructure [20]. Z. Jing et al. used a cold spray system (N2 was used as propellant gas with 400 °C and pressure of 3.5 MPa) to apply pure Al coating on S355 structural steel. However, this coating was post-spray processed using a laser remelting (LR) method, because of the presence of through porosities in the as-sprayed coating structure [23]. Nevertheless, more compact pure Al and Al alloy coatings on the Mg alloys were achieved using higher process gas (N₂) temperature (which could potentially increase the chance of nozzle clogging during process (substantial reduction of working efficiency [24])) and also expensive He (as propellant gas) [21,22,25]. However, Al and Al alloys (as a single layer) because of their high wear rate [26] and relatively low corrosion (localized corrosion) resistance in severe corrosive atmospheres can't be widely used as cold sprayed protective coatings on the Mg alloys [20,25,27,28]. In this regard, hard ceramic particles were added into the Al feedstock to enhance the mechanical properties of cold sprayed Al coatings [29,30]. However, Al/ceramic particle interface acted as quick channels for the infiltration of corrosive electrolyte. This deteriorated protective performance of ceramic particle reinforced Al-based composite coatings on Mg alloys [29,30]. Therefore, other efficient methods should be employed to mitigate the issues associated with the Al-based coatings substantially. Recently, multilayered materials including a cold sprayed Ti coating on the Al in place of titanium bulk has been suggested [31,32]. A balance between the cost reduction and better surface properties of Ti was achieved by using multilayered materials [31]. Ti and its alloys with good mechanical properties and excellent corrosion resistance (due to the formation of a firm protective oxide film on the metal surface when they are exposed to the aerated environment) can be used in severely corrosive environments such as offshore (salt water), aerospace, automotive, etc. [33-35].

Very low SRP between coating and substrate makes Ti coating as a good candidate for the corrosion protection of Al and its alloys. However, the production of cold sprayed Ti (with hcp crystal structure and low slip systems) deposits with no porosity is almost unachievable using current cold spray systems (with N_2 as propellant gas) [31,35–37]. Therefore, a post-cold spray process should be done on the Ti coating to further improve the coating properties [31,35]. On the other hand, Ta due to the quick formation of protective Ta₂O₅ film on its surface in aqueous media is known as a metal with phenomenal corrosion resistance [38] and thus has been extensively employed (as protective coating) to modify the surface of Ti substrates (due to low SRP mismatch between Ti and Ta) [39]. Dense cold sprayed Ta coatings (produced by optimized parameters, developed cold spray systems and suitable powders [40]) considerably reduced the corrosion rate of the substrate in corrosive solutions [41,42]. Motivated by the above-mentioned facts, it is expected that the drawbacks associated with CP-Al coatings could be mitigated with a Ti topcoat (very low SRP mismatch between Al and Ti layers). Additionally, a part of Ti coating thickness could be replaced by a dense layer of Ta to modify the surface properties of Ti coating. In this research, as-sprayed coatings were characterized by different analytical tools. The microstructural characteristics of Al, Ti/Al and Ta/Ti/Al coated Mg allovs were determined and compared. Wear performance of cold-sprayed coatings and bare Mg alloy substrate was examined by Rtec multifunctional tribometer at room temperature. Furthermore, the corrosion behavior of the proposed coatings was assessed by a set of electrochemical corrosion tests, immersion tests, SEM/EDS and IFM (infinite focus 3D measurement).

2. Experimental procedure

2.1. As-received powders and substrate

Commercially pure (CP) Al (H-15 Valimet Inc, California) powder (Fig. 1a) with particle size distribution (PSD) of $9-45 \,\mu\text{m}$, CP-Ti grade 1 (AP&C powder, Quebec, Canada) powder (Fig. 1b) with PSD of 10-45 µm, and high purity spherical Ta (Tekmat Pur (Tekna), Quebec, Canada) powder (Fig. 1c) with PSD of $10-25 \,\mu m$ were used as feedstock powder materials in this research. The substrates were cut from commercially available AZ31B Mg alloy plate (381 mm X 455 mm X 9.5 mm) which was procured from Magnesium EleKtron North America. The chemical composition of AZ31B Mg alloy is listed in Table 1. Prior to cold spray process, the substrate surface was grit blasted. The spray surface was blasted with 46 grit aluminum oxide blasting media with 0.41 MPa dry compressed air at an angle of $<45^{\circ}$ until the surface became a matte finish. The samples were sprayed with isopropyl alcohol and brushed with a nylon brush to remove any large contaminants and residue followed by additional cleaning of the surface with isopropyl alcohol and a lint-free rag.

2.2. Coating method

A high pressure cold spray system (Impact Innovation 5/11 system, GmbH Germany) at ASB Industries, Inc. was employed to spray metallic powders on the AZ31B Mg alloy. A water cooled SiC nozzle (convergingdiverging De Laval nozzle) with 160 mm long, 13 mm inlet diameter, 6 mm outlet diameter, and 5.6 expansion ratio was used to increase the velocity of the particle to supersonic velocity. Moreover, 25.4 mm was considered as a standoff distance between the nozzle exit and the sample surface. The temperature of the substrate and coatings was maintained less than 65 °C during the cold spray process. ABB robot was utilized to carry high pressure cold spray (HPCS) gun during spraying process. Apart from OM and SEM observations, coating thickness at different regions was checked by using calibrated micrometer (several times) during coating process. Moreover, cold spray parameters were tabulated in the Table 2. Hence, the following coatings were deposited on the AZ31B Mg alloy:



Fig. 1. SEM images from feedstock powders (a) CP-Al, (b) Ti, (c) Ta, (d) Al coating surface, (e) Ti coating surface, (f) Ta coating surface, (g) cross section of Al/Mg, (h) cross section of Ti/Al/Mg, and (i) cross section of Ta/Ti/Al/Mg systems after high pressure cold spray process, and (j-l) surface topography (3D) of as-sprayed coatings.

Table 1

Chemical composition of AZ31B Mg alloy (wt.%).

Alloy name	Mg	Al	Zn	Si	Mn	Fe	Cu	Ca	Ni	С
AZ31B Mg alloy	Balance	2.8	1.1	0.08	0.7	0.01	< 0.01	< 0.03	< 0.001	/

1 Al coating on AZ31B Mg alloy.

2 Ti/Al coating on AZ31B Mg alloy.

3 Ta/Ti/Al coating on AZ31B Mg alloy.

2.3. Characterization

Optical microscopy (Olympus IX70) was used to analyze the

Table 2

Cold spray process parameters.

Propellant gas	Sprayed material	Gas temperature (C°)	Gas pressure (MPa)	Spray angle (angle, degree)	Stand-off distance (mm)	Step size (mm)	Powder feed rate (RPM)	Powder carrier gas flow rate (m ³ /hr)	Type of Nozzle
N ₂	CP-Al	450-550	4.0-5.0	90°	25.4	0.508	2.0-3.0	3.0	SiC water cooled nozzle
N_2	CP-Ti	700-1000	4.0-5.0	90°	25.4	1.016	2.0 - 3.0	3.0	SiC water cooled nozzle
N ₂	Та	700-1000	4.0-5.0	90°	25.4	0.762	2.0-3.0	3.0	SiC water cooled nozzle

microstructure of polished cross-section of the as-sprayed coatings on the AZ31B Mg alloy. For this purpose, coated samples were cut, mounted, and polished using the Allied Metprep 3[™] grinder/polisher system (with standard metallographic procedures). ImageJ software was utilized to analyze the porosity level of the as-sprayed coatings (using ASTM E2109-01). The surface morphology, polished cross-sectional microstructures and chemical composition (elemental analysis) of developed coatings before and after immersion test were studied using TESCAN LYRA-3 model XUM integrated variable pressure focused ion beam-field emission scanning electron microscope (FIB-FESEM) and Hitachi TM-3030 scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). Moreover, the structural phases of as-sprayed coatings, bare AZ31B Mg alloy substrate and feedstock powders were analyzed using a Rigaku Ultima IV X-ray diffraction machine after grinding up to 1200 grit size sandpaper (for only bare and coated Mg alloys). The X-ray tube emits Cu-Ka radiation with an excitation voltage of 40 kV and excitation current of 35 mA. The samples were scanned at a rate of 1 deg/min with a step width of 0.04 degrees. The data were analyzed using X'Pert HighScore Plus software with the ICDD database. Furthermore, 2θ (as diffraction angle) range of 30° - 90° was employed to collect diffraction patterns of different samples.

The surface topography and average surface roughness (R_a) of the assprayed coatings before and after the grinding process were inspected during profilometry using Alicona Infinite Focus, a 3D measurement system which has a non-contact, optical measurement principle based on focus-variation. Prior to profilometry, the surface was cleaned with DI water using an ultrasonic cleaner. The brightness and contrast were adjusted at a range of focus to make sure all the features are within focus during the scan. The lateral resolution was set at 50 nm. R_a was measured using line scans across the IFM scan. At least five readings were collected for R_a to minimize standard deviation.

Electron backscattered diffraction (EBSD) on the polished crosssection of Ta coating was conducted utilizing the Oxford EBSD detector system attached to (SEM, JEOL-2100). For EBSD analyses, an operating voltage of 20 kV, a working distance of 10 mm, and a sample tilt angle of 70° was utilized. The data acquisition was performed with Integrated EDS/EBSD in AZtec software with a step size of 0.3 μ m. The EBSD analysis was performed with Channel 5 software. For grain analysis, >15 is considered the high angle grain boundaries. A Vickers hardness tester (Beuhler-Wilson Tukon 1202) was used to measure the micro-hardnesses of the substrate and the coatings, under the load of 0.245 N. It should be noted that the substrate hardness measurements were performed at the regions away from the interface between coating and the Mg alloy substrate. Additionally, ten (10) measurements were done on each sample and the average was reported as micro-hardness value.

Dry reciprocating sliding tests (according to ASTM G133) were performed using Rtech-Tribometer at room temperature (\sim 25 °C and 40–50 % relative humidity). Prior to sliding tests, all the coated surfaces were polished to achieve an average surface roughness of 0.2 \pm 0.05 μ m. E52100 steel ball with 6.35 mm diameter was used as a counterpart. All the reciprocating sliding tests were carried out with a track length of 15 mm and 1 mm/s velocity under a normal load of 4 N for a total

distance of 1000 mm. After the tests, the wear tracks on each sample were captured using optical profilometer and these wear profiles were analyzed to calculate the wear volume. So, the following formula was used for calculation of the wear rate [43]:

Wear rate
$$(\mu m3 / Nm) = \frac{Wear Volume (\mu m^3)}{Normal load (N) \times sliding distance (m)}$$
 (1)

2.4. Corrosion tests

2.4.1. Sample preparation for corrosion tests

As-cold sprayed coatings have a highly active surface [44], and their surface area is increased due to rough surface. It is general practice to eliminate the rough and porous surface of as-cold sprayed coatings before corrosion tests [20]. The samples for potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS) and immersion tests were ground up to 1200 grit size sandpaper (SiC abrasive papers) and cleaned with ethanol using an ultrasonic cleaner for 5 min.

2.4.2. Potentiodynamic Polarization (PDP) tests in 3.5 wt% NaCl solution

PDP tests were performed in a flat cell using VMP-300 Bio-logic potentiostat following a three-electrode setup. The standard calomel electrode, platinum electrode, and sample under test were connected as a reference electrode, counter electrode, and working electrode, respectively. Before the PDP test, the open circuit potential (OCP) was observed for 1 h to allow the system to achieve an equilibrium in the electrolyte. PDP tests were done in 3.5 wt.% NaCl (pH 6.7) at a scan rate of 1 mV/s from 200 mV_{SCE} below OCP to a current limit of 1 mA/cm² or a potential limit of 2.5 V_{SCE} at room temperature. In this work, there was a non-symmetrical polarization curve between the anodic and cathodic branches. Hence, the corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were calculated by the Tafel extrapolation of the cathodic polarization curve [27,45–48]. The results were then tabulated in Table 3.

2.4.3. EIS in 3.5 wt.% NaCl solution- 2days immersion

A three-electrode setup was used in a flat cell where standard calomel electrode, platinum electrode, and sample were connected as a reference electrode, counter electrode, and working electrode, respectively. The sample was kept immersed in 3.5 % NaCl (pH- 6.7) for 48 h exposing an area of 1 cm^2 at room temperature. EIS was performed at 1 h, 2 h, 6 h, 12 h, 24 h, 36 h, and 48 h. Prior to the first and subsequent EIS, the open circuit potential (OCP) was monitored to allow the system to achieve an equilibrium in the electrolyte. EIS was performed in the frequency range from 100 kHz to 10 mHz at OCP. For each EIS scan, ten

Table 3

The $E_{\rm corr}$ and $i_{\rm corr}$ for uncoated and coated Mg alloys calculated from the potentiodynamic polarization curves.

Type of sample	E _{corr} (mV _{SCE})	i_{corr} (µA cm ⁻²)
Bare AZ31B Mg alloy	-1488.440	23.303
Al coated Mg alloy	-714.185	0.402
Ti/Al coated Mg alloy	-351.104	0.218
Ta/Ti/Al coated Mg alloy	-218.805	0.019

measurements were recorded per decade, with an average of at least three points per measurement. Furthermore, sinusoidal AC perturbation with an amplitude of 10 mV (rms) was considered for all EIS tests. EC-lab 11 provided in the Bio-logic potentiostat was utilized to analyze PDP data whereas EC-Lab V11.21 and Z-view software were utilized to analyze the EIS data. Electrochemical corrosion tests were carried out three times to substantiate the repeatability of the results. After the immersion test, the samples were rinsed with DI water and subsequently dried in air.

2.5. Surface topography investigation of corroded surfaces after immersion test

The surface topography and average surface roughness (R_a) of the polished coatings and bare AZ31B Mg alloy substrate after immersion test were inspected using infinite focus 3D measurement (IFM). R_a was measured using line scans across the IFM scan. At least five readings were collected for R_a to minimize standard deviation. The maximum depth of the pits formed due to corrosion was also determined across the line scans.



Fig. 2. Photomicrographs from (a, b) Al layer on Mg at 100X and 200X magnifications, (c, d) Ti/Al layers on Mg at 100X magnification, (e) Al layer in Ti/Al/Mg system at 200X magnifications, (g, j) Ta layer in Ta/Ti/Al/Mg system at 100X and 400X magnifications, (i) Ti layer in Ta/Ti/Al/Mg system at 400X magnification, (k) Euler angle map from cross section of Ta layer in Ta/Ti/Al/Mg system, and (l) Microhardness of uncoated and coated AZ31B Mg alloys.

3. Results

3.1. Morphology of powders and microstructure of coatings

Figs. 1a-1c shows the morphology of powder particles of Al, Ti and Ta used in this research work. CP-Al (PSD (particle size distribution): $+9/-40 \mu$ m), CP-Ti (PSD: $+10/-45 \mu$ m), and Ta (PSD: $+10/-25 \mu$ m) powders all possess spherical morphology as depicted in Fig. 1a-c, respectively. Fig. 1d-f demonstrates the surface morphologies of assprayed Al, Ti, and Ta coatings, respectively. It's evidently seen that high impact energies led to the severe plastic deformation for the coatings. It should be noted that the bonding (in the cold spray process) can be created by ASI (adiabatic shear instability) or mechanical infiltration if the particle velocity to be between its critical velocity and erosion velocity [14,49].

Absence of any obvious micropores and the presence of more flattened particles (Fig. 11 and f) with noticeable material jetting on Ta coating (Fig. 1f, its inset) can be observed in contrast with Ti and particularly Al coatings (Fig. 1e and d, their insets). This can pertain to the intense plastic deformation of Ta powder particles upon impact [38]. Average surface roughness (R_a) of as-sprayed coatings was measured to be 2.81 μ m, 2.23 μ m and 1.89 μ m for Al, Ti, and Ta coatings, respectively (Fig. 1j-L). Lower R_a of Ta coating (Fig. 1l) could be ascribed to the more plastic deformation of Ta particles during high pressure cold spray process. Fig. 1g-i and 2 show the cross-sectional microstructure (by optical microscopy) of as-deposited coatings on the AZ31B Mg alloys at different magnifications. As-deposited Ta coating (with about 0.10 % porosity level) shows a dense microstructure with no noticeable micro-pores (Fig. 1i, f, g, and j). It is apparently seen that Ta top coating has tremendously improved the hardness of the Al coating surface compared to Ti top coating (Fig. 2l). It is reported that coating micro-hardness could be used to qualify the coating process parameters and extent of porosity in the coatings [16,32].

Moreover, Ti coating (with about 0.50 ± 0.20 % porosity level) indicated a slightly dense microstructure (Fig. 1h, d and g) with very limited micro-pores and the local deformation of Ti powder is apparent (Fig. 2i). The higher level of porosities was reported for cold sprayed Ti coating (2.7 %), warm sprayed Ti coatings (about 3.8–5.4 %) and Plasma sprayed Ti coatings (10.2 %) [37,50]. The higher level of porosities in warm sprayed Ti coatings substantially declined their corrosion resistance in 3.5 wt% NaCl solution and caused quick degradation of Mg substrate during long term corrosion (after 24 h immersion) [50].

In this research, CP-Al coating (with about 1.10 ± 0.20 % porosity level) depicted most porous coating (Figs. 1g and 2 a) compared to Ti (Figs. 1h and 2 d) and Ta (Fig. 1i and 2 g) coatings. The presence of a considerable number of micro-pores and even (worse) micro-cracks in the cold sprayed CP-Al coating microstructure (at inter-particle boundaries) on AZ91D Mg alloy was also reported by Y. Tao, et al. [20]. This



Ti hard particle



Fig. 3. Al layer densification in multilayer systems, (a, d) Al coated Mg alloy, (b, e) Ti/Al coated Mg alloy, and (c, f) Ta/Ti/Al coated Mg alloy.

could be attributed to a lower degree of localized plastic deformation (localized heating, stresses) [20] which resulted in an extensive formation of micro-defects at inter-particle boundaries. Electrochemical corrosion and immersion tests proved that Al coating with high denseness and sub-micron sized grains could considerably improve corrosion resistance compared to CP-Al bulk substrates [20,25]. It is interesting to note that Al layer compactness has been raised (Figs. 1g-1i) in the multilavered coating systems, in the order: mono-lavered Al (Figs. 2a, 2b, 3 a, and d), double-layered Ti/Al (Figs. 2c, 2e, 3 b, and e) and triple-layered Ta/Ti/Al (Figs. 2f, h, 3 c, f) coatings. Ti coating has deeply penetrated into the Al layer with substantial deformation, which is more noticeable in Ta/Ti/Al coated AZ31B Mg alloy (Figs. 1i, f, h, 3 c, f). This could be pertained to the densification of a softer substrate (Al) by hard particles (hammering effect) with high kinetic energy and also reduction of Al layer thickness ($150 \pm 35 \,\mu m$) in the triple-layered Ta/Ti/Al (Figs. 1i, 2f, 3 c, f) coating. This behavior is observed when hard particles (with high kinetic energy) are applied on the soft substrates (such as Al) [16,51,52]. Significant plastic deformation of powder particle (in the cold spray process) can originate from the high-velocity impact of the particle on the substrate or coating surface layer. Hence, the plastic deformation of the coating region (which is severely impacted by the particles) can lead to the tamping of outer and inner (subsurface) layers of the deposited coating during the spray process [53,54]. It is speculated that the compact Al inner barrier layer could protect the Mg substrate from a corrosive solution when it passes through from the top layers during extended long-term immersion in corrosive solution.

It is evident that Al particles are deeply infiltrated into the Mg alloy

substrates (Figs. 1g-1i, 2c and 2e). There were no micro-pores or microcracks observed at the layer/layer and the layer/substrate interfaces. The elemental analysis on polished cross-section for coated samples was performed using the EDS mapping (Fig. 4). Figs. 4a-4d indicate that monolayered coating on the Mg substrate is mainly composed of Al element. Moreover, the double-layered coating (Figs. 4e-i) on the Mg substrate is composed of Al (as the first layer) and Ti (as the second layer). However, the triple-layered coating (Figs. 4j-o) on the Mg substrate is constituted by Al (as the first layer) and Ti (as the second layer) and Ta (as topcoat or sealant layer). No evident interdiffusion of Al, Mg, Ti and Ta elements at the bonding interfaces are observed. This could be attributed to the low deposition time and very short exposure time of powder particles to the pre-heated propellant gas. The temperature of powder particles remains well below their melting point and the process gas significantly cools when it expands in the divergent section of the nozzle [16]. Figs. 5 and 6 show the XRD patterns of AZ31B Mg alloy substrate, as-received powders and as-sprayed coatings. XRD spectrum (Fig. 5a) indicates that the AZ31B Mg alloy substrate is mostly constituted by the α -Mg phase (H.C.P). Both powder and cold sprayed coating display the same phase structure and crystalline planes which are observable in Figs. 6b, 5 b, and 6 a. There is no evidence of phase transformation or oxidation in the cold sprayed coatings (Figs. 4–6). The obvious broadened peaks in the XRD patterns of Ti (Fig. 5b) and Ta (Fig. 6a) coatings are primarily related to the severe plastic deformation of powder particles in the coatings compared to Al coating (Fig. 6b) during spraying process [32,55]. Original phase and crystalline planes of powders were retained in their coatings which could be associated to the



Fig. 4. X-ray mapping from (a-d) Al coated Mg alloy, (e-i) cross section of Ti/Al coated Mg alloy, and (j-o) cross section of Ta/Ti/Al coated Mg alloy after high pressure cold spray process.



Fig. 5. XRD patterns of (c) AZ31B Mg alloy substrate, (b) as-received Ti powder and as-sprayed Ti coating.



Fig. 6. XRD patterns of (a) as-received Ta powder and as-sprayed Ta coating, (b) as-received Al powder and as-sprayed Al coating.

low temperature of spray process and substantial hammering effect of powder particles during cold spray process.

3.2. Wear rate of bare and coated AZ31B Mg alloys

A section of captured wear track is shown in Fig.7a along with their wear depth. It can be seen that a lower wear volume was observed for the Ta/Ti/Al coated surface in which the Ta coating was in contact with steel ball during sliding. Also, the associated depth of the wear track is around 4 μ m which is significantly lower than the other samples. Similarly, the wear depth on Ti/Al coated surface is about 7 μ m in which the Ti surface was in contact with the steel ball, whereas the Al coated surface resulted in the highest wear depth of ~70 μ m. The wear rate of the entire track, calculated using the wear depth, is plotted in Fig. 7b. The lowest wear rate was observed for the Ta/Ti/Al coating surface which is 2–3 orders of magnitude lower than all other surfaces. These results are also compared with bulk Mg samples that show superior wear resistance compared to the Al coating surface but lower wear resistance than the Ti/Al and Ta/Ti/Al coating surfaces.

3.3. Electrochemical behavior of uncoated and coated samples

Before corrosion tests, the surface of bare, Al coated, Ti/Al coated, and Ta/Ti/Al coated Mg alloys were ground and polished to average surface roughness (R_a) <1 μ m, (Fig. 8a-8d). The electrochemical corrosion test results of coated and uncoated Mg alloys in 3.5 wt.% NaCl

solution are shown in Fig. 9 that represents the OCP of samples versus elapsed time. It is clearly seen that the OCP value for the bare and Al coated Mg alloys is relatively constant with the potential (mV_{SCE}) value stabilizing at -1590.21 mV and -727.50 mV, respectively after 1 h immersion in 3.5 wt.% NaCl solution. Al coating shows obvious OCP oscillation amplitude (Figs. 9a, 9b) compared to other samples in the NaCl solution. OCP oscillation could be ascribed to a passive film breakdown [56]. OCP for Ti/Al and Ta/Ti/Al coated Mg alloys was stabilized at around -249.84 mV_{SCE} and -168.59 mV_{SCE}, respectively. The results show that AZ31B Mg alloy substrate with more active potential (lower E_{OCP}) is much more vulnerable to corrosion than coated samples with higher E_{OCP}. However, it is evidently seen that Al coated Mg alloy is more active than Ti/Al and Ta/Ti/Al coated Mg alloys. Dynamic equilibrium dissolution between the formations of oxide scale (film) on the electrode surface can result in the final steady OCP [27,57]. In other words, the stable OCP of an electrode in a specific electrolyte can signifies the dynamic equilibrium potential of all electrode reactions taking place simultaneously on the electrode surface.

Fig. 9c demonstrates the potentiodynamic polarization curves of bare and coated Mg alloys (after stabilization of the OCP for 60 min) in 3.5 wt.% NaCl solution. Potentiodynamic polarization curve of Ta/Ti/Al coating is slightly analogous to that of the bulk Ta and also modified and impermeable cold sprayed Ta coatings per previous investigations [42]. It has been reported that a failure in the passive layer may lead to the formation of a pit [55]. However, the reparation in the passive layer at even higher potentials may take place when the pits are insignificant in



Fig. 7. (a) Wear tracks of bare and coated AZ31B Mg alloys (cross-sectional profiles and 3D surface profiles of wear tracks), and (b) wear rate of bare and coated AZ31B Mg alloys.



Fig. 8. (a-d) Surface topography (3D) and average surface roughness (R_a) of the polished coatings and bare AZ31B Mg alloy substrate before corrosion tests (using infinite focus 3D measurement).

size [55]. This behavior was also observed in the PDP curve of Ta/Ti/Al coated Mg alloy and also reported by Heli Koivuluoto et al. and Balani et al. [41,58]. Ta top layer retained linear passivation (passive layer formation) at even higher potentials (before breakdown potential, $E_b = 1356.66 \text{ mV}_{SCE}$). It is postulated that severe plastic deformation of Ta small particles upon impact (Fig. 2K) could lead to the significant duplication of dislocations, induction of lattice micro-strain, refined crystals and residual stresses in the coating microstructure [59–62]. These could influence the unique corrosion behavior of the high pressure cold spraved Ta layer.

Corrosion current density (i_{corr}) which is directly related to the corrosion rate [63,64], corrosion potential (E_{corr}) which is a measure of corrosion vulnerability [65] were obtained from potentiodynamic polarization curves (Fig. 9c), and were tabulated in Table 3. Ta/Ti/Al coated Mg alloy showed the lowest i_{corr} (0.019 μ A/cm²) and highest E_{corr} (-218.805mV_{SCE}) compared to i_{corr} and E_{corr} of the other samples (in this research, Table 3). H. Koivuluoto et al. reported lower i_{corr} (1.1 μ A/cm²) for compare to dense Ta coating than i_{corr} (7.1 μ A/cm²) for Ta coating (with through porosity) which showed no noticeable passivation behavior compared to dense Ta coating in 3.5 wt.% NaCl solution [42]. This indicates that the Ta layer (in this work) with a high propensity to passivation could seal the underneath transition layers in multilayered materials (coating systems) which will further be proven in this research work.

Potentiodynamic polarization curve of Ti/Al coated Mg alloy (anodic branch) shows the typical spontaneous passivation and pitting characteristics which is nearly analogs to the passivation behavior for the bulk Ti in 3.5 wt.% NaCl solution [36]. Ti top layer (in Ti/Al/Mg system) retained linear passivation (passive layer formation) at even higher potentials (before breakdown (pitting) potential, $E_b = 1293.05 \text{mV}_{SCE}$). Warm spray Ti coated Mg alloys showed negligible higher corrosion potentials and lower corrosion current densities compared to bare AZ91E Mg alloy [50]. This was attributed to the presence of through-thickness porosities in the warm sprayed Ti coatings which easily conducted the chloride containing solution towards the Mg surface [50]. Hence, they had to be sealed with three layers of epoxy-based

resin (as post-spray treatment). Moreover, D. Zhang et al. reported magnetron sputtered Ti coated AZ91D Mg alloy can only lower the i_{corr} to 26.60 µA/cm² from 162.70 µA/cm² for AZ91D Mg alloy and E_{corr} to (-1525 mV_{SCE}) from (-1570mV_{SCE}) for AZ91D Mg alloy [66]. In contrast, higher E_{corr} (-351.104) and lower i_{corr} (0.218 µA/cm²) were observed for Ti/Al coated AZ31BMg alloy (in this research work) than bare AZ31B Mg alloy with E_{corr} (-1488.440) and i_{corr} (23.303 µA/cm²). The active dissolution of AZ31B Mg alloy could be considerably lowered by Ti/Al coating. However, Ti/Al coated AZ31BMg alloy showed a higher average corrosion rate ($P_i = 22.85i_{corr}$ [67]) than Ta/Ti/Al coated AZ31B Mg alloy. This will be further discussed in the next parts of this research work.

Potentiodynamic polarization curve of Al coated Mg alloy (anodic branch, Fig. 9d) implies that the discontinuous hydroxide film (because of the existence of obvious pores in the Al coating) may cause pitting [28]. However, i_{corr} of bare AZ31B Mg alloy was lowered by about two orders of magnitude after applying Al coating on its surface. In other words, Al coating shows the slower degradation rate than bare Mg alloy in 3.5 wt.% NaCl solution. Nevertheless, the corrosion rate of AZ31B Mg alloy can further be reduced using Ti/Al coating and particularly Ta/Ti/Al coating.

The protective efficiency of coatings, in the short-term test, was calculated using the following Eq. (2) [68].

$$%PE = \frac{icorr of bare Mg alloy - icorr of coated Mg alloy}{icorr of bare Mg alloy} \times 100$$
(2)

Hence, the protective efficiency of Al, Ti/Al and Ta/Ti/Al coatings was calculated to be 98.274 %, 99.064 %, and 99.92 %, respectively. This shows the highest protective efficiency for Ta/Ti/Al coating.

Electrochemical impedance spectroscopy (EIS) of coated and uncoated Mg alloys was measured at their OCP to further elucidate the influence of multilayer cold sprayed coatings on the corrosion resistance of Mg alloy. Figs. 10 and 11 demonstrate the Nyquist and bode plots. In Figs. 10a-10c, the symbols correspond to the experimental impedance data and the solid lines are the fit. Moreover, the equivalent electrical circuits (Fig. 11: models A, B, and C) were employed to fit the impedance



Fig. 9. Electrochemical corrosion test results of coated and uncoated Mg alloys in 3.5 wt.% NaCl solution, (a, b) OCP for 1 h, (c, d) Potentiodynamic polarization curves.



Fig. 10. (a-c) Nyquist plots of coated and un-coated Mg alloys at OCP.

spectra. The Nyquist plot of uncoated Mg alloy (Fig. 10a) is comprised of one capacitive loop (at high frequency) and also one inductive loop (at a low frequency) which is in harmony with the previous researches [27, 69]. The characteristic of an electrical double layer (at the electrode/electrolyte interface) was ascribed to the capacitive loop (at higher and intermediate frequency regions) [70]. On the other side, the characteristic property of protective corrosion surface film (partially formed) can be associated with the inductive loop at lower frequency regions [69,71–73]. The bode phase plot of AZ31B Mg alloy (Fig. 11a) apparently indicates the maximum phase angle of about -55° at high-intermediate frequencies. This could be ascribed to the capacitive behavior with weak dielectric characteristics. On the contrary, bode



Fig. 11. (a, b) Bode plots of coated and un-coated Mg alloys at OCP, and electrical equivalent circuits (EEC) to fit the impedance spectra of (c) bare (model A), (d) Al coated Mg alloy (model B), and (e) Ti/Al and Ta/Ti/Al coated Mg alloys (model C).

phase plots (Fig. 11a) were considerably enlarged and broadened (their aperture) after cold spraying protective metallic coatings on the AZ31B Mg alloys. This occurrence pertained to the shielding ability of coatings [19,74]. In this regard, Al, Ti/Al and Ta/Ti/Al coated Mg alloys depicted maximum phase angle about -75 (at middle frequency), -74 (at a relatively low-intermediate frequency) and -80 (at a low-intermediate frequency), respectively. Nonideal capacitance was attributed to the phase angles below -90 [75]. Hence, constant phase elements (CPE or Q) is widely used for replacing the capacitance (C) in the equivalent electrical circuits (EEC), when the system is non-ideal due to the hererogeineities, roughness, porosity, and other non-ideal dielectric properties [26]. The impedance response of the Q can be obtained from the following equation [76,77]:

$$Z_{CPE} = \frac{1}{Q(j\omega)^n}$$
(3)

Where, n is a CPE exponent which measures the heterogeneity or roughness of the surface and the CPE simulates an ideal capacitor when n = 1, an ideal resistor for n = 0 and an ideal inductor for n = -1 [78]. Furthermore, the values of n when 0.6 < n < 1 could be ascribed to the heterogeneous charge distribution (at the surface) or heterogeneous distribution of the properties (inside the coating) [79].

The two capacitive loops (at high and low frequency regions) could be considered for the coated AZ31B Mg alloys in this research. The introduced electrical equivalent circuits (Figs. 11c-11e) acceptably fitted the impedance spectra of coated samples and also confirmed this statement. Figs. 11c-11e portray the used electrical equivalent circuits for fitting the impedance spectra of bare AZ31B Mg alloy (A), Al/Mg (B), Ti/Al/Mg (C), and Ta/Ti/Al/Mg (C) systems. The equivalent circuit used for the substrate consists of R_{ct} (charge transfer resistance across the electric double layer at electrode/electrolyte interface), Rs (solution resistance), Qdl (CPE related to electric double layer), L (adsorption inductance) and R_L (adsorption resistance). Accordingly, the model could be portrayed as Rs(QdlRct(RLL)). This equivalent circuit for the bare AZ31B Mg alloy has also been reported in the previous researches [27,48,69]. The low-frequency inductive loop is described by R_L and L, which represent onset of pitting corrosion [48]. Model B used for Al coated Mg alloy includes Rs, Rct (charge transfer resistance across the

inner electrical double layer at electrode/electrolyte interface), Qdl (CPE related to electrical double layer (inner)), Zw (Warburg diffusive impedance), Qc (CPE for surface film (outer)), and Rc (resistance which includes the resistance of the oxide film/corrosion products and the electrolyte resistance inside the pores [80]). Hence, the model could be depicted as $R_s(Q_cR_c)(Q_{dl}(R_{ct}Z_w))$. This model has also been employed for the Al coated AZ91D Mg alloy [20]. Likewise, Model (8B) has been reported by the other researchers [20,26,81]. The Nyquist spectra of Al coated Mg alloy (Fig. 10c (2)) shows an approximately straight line at a low frequency range which is characteristic of diffusion-controlled reaction [82,83]. This indicates that reactants diffusion (such as oxygen) can be easily done through profound and slender defects and also the solution layer in this stage (mass transfer stage) [83,84]. This phenomenon was also attributed to the rapid corrosion due to the formation of non-protective scale during corrosion [85]. Moreover, partial mass transfer of oxygen through a loose layer of corrosion products formed in the pores has been reported [26,84,86]. Warburg impedance because of the diffusion process has been mostly observed in the coatings with low denseness [26,38,41,50,85,87]. Moreover, for the cold sprayed Al coatings, some contribution of diffusion was also attributed to the increment of the impedance modulus values at low frequency regions (about < 0.1 Hz) as the frequency reduced [80,88].

Model C used for Ti/Al and Ta/Ti/Al coated Mg alloys consists of Rs, Qc (CPE for surface film (outer)), Rpo (pore resistance (resistance of the electrolyte in the pore)), Rct (charge transfer resistance across the inner electrical double layer at electrode/electrolyte interface) which is not in series with $Z_{\rm w}$ element, and $Q_{\rm dl}$ (CPE related to electric double layer (inner)). Therefore, the model could be described as $R_s(Q_c(R_{po}(Q_{dl}R_{ct})))$. This model has also been reported in the previous researches [27,38,41, 50]. The impedance spectra of all samples were perfectly fitted to the above-mentioned EECs. Table 4. indicates the results from fitting the impedance spectra via electrical equivalent circuits (models A, B, and C in Fig. 11). Uncoated substrate disclosed the worst corrosion resistance amongst four (4) samples. This deduction is attributed to the lower R_{ct} (182.9 Ω cm²) for uncoated AZ31B Mg alloy. This proves the low protective performance of the corrosion surface layer (film) formed on Mg alloys in chloride containing solutions. Nevertheless, R_{ct} values for Al, Ti/Al and Ta/Ti/Al coated Mg alloys are 56.1 k Ω cm², 150.41 k Ω cm² and 2350k Ω cm², respectively. This shows that Al, Ti/Al and Ta/Ti/Al

EIS fitted results for uncoated and coated Mg alloys in 3.5 wt%NaCl solution.

Samples	R _s (Ω cm ²)	Z _w (Ω cm ²)	R _{ct} (Ω cm ²)	Q_{dl} (F cm ⁻² s ⁿ⁻¹)	n	R _c (Ω cm ²)	Q _c (F cm ⁻² s ⁿ⁻¹)	n	R_L (Ω cm ²)	L (H cm²)	$\begin{array}{l} Z _{f=0.01Hz} \\ \text{(}\Omega \text{ cm}^2\text{)} \end{array}$
Bare AZ31B Mg alloy	15.38		182.9	3.30×10^{-5}	0.92				60.36	53.81	5.78×10^2
Al coated Mg alloy	16.82	17,626	5.61×10^4	1.27×10^{-4}	0.79	1.81×10^4	1.26×10^{-5}	0.88			6.31×10^4
Ti/Al coated Mg alloy	14.55		1.50×10^{5}	7.10×10^{-5}	0.60	2.49×10^{3}	$3.55 \cdot 10^{-5}$	0.92			4.84×10^{4}
Ta/Ti/Al coated Mg alloy	17.02		2.35 × 10 ⁶	5.45 × 10 ⁻⁶	0.65	372.7	2.0 × 10 ⁻⁵	0.91			3.33 × 10 ⁵

coatings can act as protective coatings on Mg alloys. However, R_{ct} value for the Ta/Ti/Al coated Mg alloy is roughly 42 times the value of R_{ct} for the Al coated Mg alloy and 16 times the value of R_{ct} for the Ti/Al coated Mg alloy. R_{ct} can predominantly control the rate of electrochemical processes at the electrode/electrolyte interface (across the electrical double layer) [89,90]. Therefore, larger R_{ct} can considerably decelerate the electrochemical dissolution process and could result in the higher corrosion resistance [91]. In fact, corrosion rate is typically conversely proportionate to the Rct [27]. In addition, Ta/Ti/Al coated AZ31B Mg alloy showed highest R_{ct} and lowest Q_{dl} (Table 4) which indicates that this coating has the highest corrosion resistance amongst the coated samples (Ta/Ti/Al coated Mg alloy > Ti/Al coated Mg alloy > Al coated Mg alloy) [92].

In this regard, Nyquist plots of warm sprayed Ti coated AZ91E Mg alloy presented diffusion tail at low frequency range. Moreover, these coatings showed small values of R_{ct} (1–6 $k\Omega$ $cm^2)$ and accelerated the dissolution of Mg substrate (due to galvanic cell formation between coating and substrate) in 3.5 wt.% NaCl solution [50]. In contrast, Ti/Al coated Mg alloy (in this research) depicted large value of R_{ct} (150.41 k Ω cm^2) and noticeable passivation behavior (Fig. 9c (3)). In this regard, R_{ct} value for Ti and its alloys (as passivating materials) is reported to be about 100–1000 k Ω cm² in 3.5 wt.% NaCl solution [93]. Larger R_{ct} value (2350 k Ω cm²) for Ta/Ti/Al coated Mg alloy could be ascribed to the presence of the Ta sealant top layer which could exceptionally reduce the rate of electrochemical processes at the electrode/electrolyte interface. The corrosion rate of the samples can also be evaluated with impedance modulus ($|Z|_{f=0.01Hz}$) at low frequency [89,90,94,95] (by bode magnitude plots (Fig. 11b)). Likewise, $(|Z|_{f=0.01Hz})$ is often used to assess the protection capability of the coating systems [26]. It is conspicuously seen that impedance modulus $(|Z|_{\rm f=0.01 Hz})$ at low frequency for the bare Mg alloy (Fig. 11b (1)) is lower than that of coated Mg alloys. However, Ta/Ti/Al coated Mg alloy showed the highest $|\mathbf{Z}|_{f=0.01Hz} at$ low frequency range than the other coated samples (Fig. 11b). The above-mentioned results reveal that a layer of Ta (with high denseness and excellent anti-corrosion properties) could remarkably improve the surface hardness and the corrosion protection performance (shielding effect) of the bi-layered Ti/Al coating on Mg alloys in corrosive solutions. It is expected that this significant improvement (corrosion rate reduction) could be retained during longer immersion times.

It is interesting to note that the double layer capacitance (C_{dl}) can be estimated from the constant phase element value (CPE or Q) using the Brug's formula [96–98].

$$C_{dl} = Q_{dl}^{1/n} \left(\frac{1}{R_s} + \frac{1}{R_{ct}} \right)^{\frac{1-n}{n}}$$
(4)

Where,

 $Q_{dl} = \text{Double layer CPE}$

 $R_s = solution \ resistance$

R_{ct} = charger transfer resistance

 $n = exponent \ coefficient \ of \ Q_{dl}$

The calculated C_{dl} (F cm⁻²) for AZ31B Mg Alloy, Al coated Mg alloy,

Ti/Al coated Mg alloy and Ta/Ti/Al coated Mg alloy was $1.11\times 10^{-5}, 5.52\times 10^{-6}, 2.04\times 10^{-8},$ and $1.74\times 10^{-9},$ respectively. Lower capacitance indicates the less charge accumulation at the surface. The lowest Cdl value for Ta/Ti/Al coated Mg alloy is in harmony with highest Rct and $|Z|_{f=0.01Hz}$ values obtained for Ta/Ti/Al coated Mg alloy.

The CPE is purely mathematical description without physical process meaning for this reason the film capacitance (C_c) is extracted from the film CPE (Q_c) using the expression developed by Hsu and Mansfeld [77] and Hirschorn, et al. [79,98].

$$C_c = Q_c^{1/\alpha} R_c^{(1-\alpha)/\alpha}$$
⁽⁵⁾

The film capacitance (C_c) should be related to film thickness (δ) according to [79,98,99]:

$$C_c = \frac{\varepsilon_0 \varepsilon_\gamma}{\delta} \tag{6}$$

Where,

 $C_c = capacitance of the film (F cm⁻²)$

 $\epsilon_0 =$ electrical permissivity of vacuum (8.854 \times 10⁻¹⁴ F/cm) [100]

 $ε_{\gamma}$ = dielectric constant of the thin oxide film = The dielectric constant value ranges from 9 for a dry oxide layer [101–104] to 40 for a partially hydrated layer [101–104] for aluminum oxide films. The estimated values of the oxide-layer thickness (δ) for the cold sprayed Al coating using a relative dielectric constant (ε) of 9 [101–104] and 40 [101–104], were between 0.78 nm (ε = 9) and 3.47 nm (ε = 40). Additionally, δ at ε = 15 [104,105] was calculated to be 1.30 nm. Ferreira et al. [102] reported that the hydration of oxide layer (Al₂O₃·xH₂O) upon immersion can lead to the increment of $ε_{\gamma}$ value which caused the propensity for capacitance rise and thus reduction of the corrosion performance of the materials over time. This behavior was also observed by J. A. Moreto, et al. [106].

On the other hand, 40 was considered for titanium oxide [107,108], and 25 was assumed for tantalum oxide film [107–109].

 δ = Film thickness (cm).

Film capacitance (C_c) and thickness (δ) of oxide films formed on the coated Mg alloys in 3.5 wt% NaCl solution were tabulated in Table 5. The calculated values are in agreement with those values reported in the previous researches, that typically range from 1 to 3 nm (passivation film thickness) in such cases [110–112].

3.4. Immersion test in 3.5 wt.% NaCl solution

3.4.1. Electrochemical tests

Figs. 12a, 13 a and b exhibit the Nyquist and bode plots of Ta/Ti/Al

Table 5

Film capacitance (C_c) and thickness (δ) of oxide films formed on the coated Mg alloys in 3.5 wt% NaCl solution.

Specimen	C_{c} (F. cm ⁻²)	δ (nm)
Al coated Mg alloy	1.02E-05	1.30
Ta/Ti/Al coated Mg alloy	2.87E-05 1.23E-05	1.23

coated Mg alloy at different immersion periods. Moreover, the equivalent electrical circuit (Fig. 11e) was employed to fit the impedance spectra. It is clearly seen that the values of R_{ct} and $R_{po}+R_{ct}$ ($R_{ct}>>R_{po}$) for the Ta/Ti/Al coated Mg alloy have increased after 48 h of immersion (Fig. 12b). This indicates that the rate of electrochemical processes at the electrode/electrolyte interface could further be lowered (considerable increment of Rct) in the course of time. Nyquist plots of Ti/Al coated Mg alloy at different immersion times (after 1 h, 12 h and 48 h) are shown in Fig. 14a. Fitting values (using the electrical equivalent circuit (Fig. 11e: model C)) of R_{ct} and $R_{po}{+}R_{ct}$ for the Ti/Al coated Mg alloy have reduced after 48 h of immersion (Fig. 14b). The decrease of R_{ct} (after 12 h) can lead to a noticeable decline of $R_{\text{po}} + R_{\text{ct}}$. This indicates that the total resistance [113-115] is mainly controlled by the R_{ct} (R_{ct}>>R_{po}). The electrolyte could infiltrate the underneath coating through the non-connected limited micro-pores (leading to Rct reduction). However, porous warm sprayed Ti coatings on Mg alloy showed very low protective performance with R_{ct} value (1000–6000 Ω cm²) after 2 h of immersion. R_{ct} much further reduced to 125–175 Ω cm² for warm sprayed Ti coating during immersion [50]. This was mainly related to the presence of through-thickness porosities in the warm spraved Ti coatings, which eventually formed a galvanic couple with the Mg alloy (with no Al bond coat) [50].

Nyquist plots of Al coated Mg alloy at different immersion times are shown in Fig. 14a, as well. At short immersion times, the formation of corrosion products on the active regions [80] can lead to the increase of R_c+R_{ct} and R_{ct} values (Fig. 15a). As a matter of fact, aluminum corrosion products can rapidly occlude the pinholes and defects in the aluminum layer [26]. This temporarily hinders the electrolyte access and postpones the further dissolution of aluminum [103]. This phenomenon can cause the resistance for the diffusion of reactants (e.g. oxygen) by enhancing the conductivity at the interface of coating/corrosion products [116, 117]. Entire this process is also known as plugging effect [26,118]. It is evident that the slope of curves at low frequency tends to decline in the course of immersion time (Fig. 14a for Al coated Mg alloy (2)) which was mainly correlated to the corrosion acceleration over immersion time [119].

The values of R_{ct} and $R_{c}+R_{ct}$ for the Al coated Mg alloy has dramatically reduced after 12 h of immersion (Fig. 15a). This indicates that pits (from pitting corrosion at more active sites) and coating microdefects (prevention of a uniform passive film formation [41]) can easily conduct the electrolyte into the inner regions of the Al coating. Moreover, the corrosion process includes the diffusion of reactants which could also be due to the presence of un-connected micro-sized and nano-sized pores in the Al coating [20]. Furthermore, partial mass transfer of oxygen through a loose layer of corrosion products formed in the pores has been reported [84,86]. These phenomena could lead to a sizable decrease in Z_w after 12 h. However, as immersion time goes by, R_c+R_{ct} and Z_w values reduced slightly (Fig. 15a), this could be attributed to the accumulation of electrolyte in the defects inside the Al coating and loose corrosion products formed in the pores [26,103] which could slightly slow the solution infiltration rate into the more inner regions of the Al coating and nearly restrict the oxygen diffusion paths (Figs. 15a, and 15b).

3.4.2. Morphological characteristics of the uncoated and coated AZ31B Mg alloys after immersion in 3.5 wt.% NaCl solution

Fig. 16 shows the surface morphological characteristics of polished bare and coated Mg alloys after immersion (in 3.5 wt.% NaCl solution for 2 days). The surface of bare AZ31B Mg alloy is very rough after 2 days of immersion (Figs. 16a, 18 a). The bare AZ31B Mg alloy surface is entirely covered by uneven corrosion products with micro-cracks [48] (Figs. 16a and 17 a). In fact, dehydration of corrosion products and surface contraction can lead to the formation of micro-cracks on the Mg alloy surface after immersion test. As shown in Figs. 16e and 17 b, corrosion products are chiefly constituted by Mg, O, Cl as well as Al, Na and C elements. Several mechanisms have been proposed to explain the Mg corrosion [120-122], which involves the formation of unstable intermediates like magnesium hydride (MgH₂), monovalent magnesium (Mg^+) , diffusion of Mg^{2+} that generates absorbed intermediates such as magnesium hydroxides and oxides (Mg(OH)₂ and MgO) [123]. The anodic dissolution of magnesium is accompanied by an anomalous phenomenon called the negative difference effect (NDE), where the hydrogen evolution reaction (HER) rate increases with increasing potential [121,124]. The mechanism of Mg dissolution can be represented by the following reactions [121]:

$$2H^+ + 2e^- \rightarrow H_2 \text{ (cathodic partial reaction)}$$
 (Reaction 1)

$$2M_g \rightarrow 2M_g^+ + 2e^-$$
 (anodic partial reaction) (Reaction 2)

$$2Mg^+ + 2H_2O \rightarrow 2Mg^+ + 2OH^- + H_2$$
 (chemical reaction NDE

$$2Mg + 2H^{+} + 2H_2O \rightarrow 2Mg^{2+} + 2OH^{-} + 2H_2 \text{ (overall reaction)}$$
(Reaction 4)

$$Mg^{2+} + 2OH^{-} \rightarrow Mg(OH)_2(corrosion \ product \ formation)$$
 (Reaction 5)

Severe Cl⁻ adsorption and Mg dissolution (simultaneously) can be accelerated, when concentration of Cl- (more than 30 mmol/L) is very high in the corrosive electrolyte. This phenomenon could lead to the formation of pits on the Mg alloy surface (Fig. 19a) and followed by formation of MgCl₂ or Mg(OH)₂ (as corrosion products) at the vicinity of pits [125,126].

Nevertheless, after applying cold sprayed Al coating on AZ31B Mg alloy, the lower corrosion current density, higher R_{ct} , and |Z|at low frequency were obtained for the Mg alloy. Before the immersion test, aspolished Al coating surface (with Ra: 124.02 nm) only portrayed scratches (grinding tracks) (Fig. 8b). After immersion in 3.5 wt% NaCl



Fig. 12. (a) Nyquist plots of Ta/Ti/Al coated Mg alloy during 2 days of immersion; (b) R_{ct} and R_{po}+R_{ct} values versus immersion time for Ta/Ti/Al coated Mg alloy.



Fig. 13. (a, b) Bode plots of Ta/Ti/Al coated Mg alloy during 2 days of immersion.



Fig. 14. (a) Nyquist plots of Al coated Mg alloy (2) and Ti/Al coated Mg alloy (3) during 2 days of immersion; (b) R_{ct} and $R_{po}+R_{ct}$ values versus immersion time for Ti/Al coated Mg alloy.



Fig. 15. (a) R_{ct} and R_c+R_{ct} values versus immersion time for Al coated Mg alloy, and (b) Z_w value versus immersion time for Al coated Mg alloy.

solution for 2 days, Fig. 18b discloses a completely various figure from the corroded Al coating surface (with Ra: 74.17 nm) which shows some obvious signs of localized corrosion (at more active sites) (Figs. 16b, 17 c, 19 b and 20). No scratches are discernible anymore (reduction of Ra to 74.17 nm from 124.02 nm). In fact, the most surface area of Al coating is influenced by general corrosion. Some of the pits (as localized corrosion) look to be filled up with oxygen-rich corrosion products that could probably be hydroxides and/or oxides (Fig. 17c and d). The electrochemical reactions during corrosion of the Al coating could be as follows:

Al \rightarrow Al³⁺ + 3e⁻ Anodic reaction (localized anodic dissolution of Al coating) reaction (6)

$$2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH$$
- reaction (7)

 $2H_2O + 4e^+ + O_2 \rightarrow 4OH^-$ Cathodic reaction reaction (8)

Reactions (7) and (8) may be considered as cathodic reactions in this research. Al^{3+} as metallic cations react with OH^- to form $Al(OH)_{3\downarrow}$



Fig. 16. Morphological characteristics of polished bare and coated AZ31B Mg alloys after immersion in 3.5 wt.% NaCl solution for 2 days (part I), (a) bare AZ31B Mg alloy surface, (b) Al coated Mg alloy surface, (c) Ti/Al coated Mg alloy surface, (d) Ta/Ti/Al coated Mg alloy surface, EDS analysis of A (e), B (f), C (g), and D (h).

(white precipitate) in reaction (9).

$$Al^{3+} + 3OH^{-} \rightarrow Al(OH)_{3\downarrow}$$
 reaction (9)

It has also been reported that $Al(OH)_3\downarrow$ can be transformed to Al_2O_3 in reaction (10) [127].

$$2\text{Al}(\text{OH})_3 \downarrow \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \text{ reaction}$$
(10)

Happening of pitting corrosion can further be accelerated by Cl^- in the chloride containing solutions [128]. $Al(OH)_3\downarrow$ would react with Cl^- to form $Al(OH)_2Cl$ (reaction 11). $Al(OH)_2Cl$ would again react with Cl^- to form Al(OH) Cl₂ (reaction 12). This compound would then continually react with Cl- to eventually form $AlCl_3$ (reaction 13) [23]. This compound can considerably interfere with the formation of a stable oxide on the Al surface [128].

$$Al(OH)_{3\downarrow} + Cl^{-} \rightarrow Al(OH)_{2}Cl + OH - reaction$$
 (11)

$$Al(OH)_2Cl^- + Cl \rightarrow Al(OH) Cl_2 + OH^- reaction$$
(12)

$$Al(OH) Cl_2 + Cl^- \rightarrow AlCl_3 + OH\text{- reaction}$$
(13)

EDS analysis (Figs. 16f and 17 d) from Al coated Mg alloy surface after 2 days disclosed that the corrosion products are mainly constituted by Al and O as well as Cl, Na, C, and Si elements. But, no Mg element was detected on the corroded Al coating surface. This indicates that the Al coating can separate the Mg alloy surface from the corrosive electrolyte during immersion for 2 days. This was also observed for the cold sprayed Al coating (with non-interconnected pores and fine-grain structure) on the AZ91D Mg alloy after immersion test (in 3.5 wt% NaCl solution) which showed the formation of corrosion pits with low depth and absence of net-cracks of corrosion products on the cold sprayed Al coating surface compared to Al bulk [20]. It was also proven than cold sprayed Al coatings have higher localized corrosion resistance than Al



Fig. 17. Surface morphological characteristics of coated Mg alloys after immersion in 3.5 wt.% NaCl solution for 2 days (Part II), (a) bare AZ31B Mg alloy surface, (c) Al coated Mg alloy surface, and EDS analysis of A (b), B (d).



Fig. 18. (a-d) Surface topography (3D) and average surface roughness (R_a) of the polished coatings and bare AZ31B Mg alloy substrate after immersion test (using infinite focus 3D measurement).

bulk [20]. It is worth mentioning that no galvanic corrosion was seen at the Al coating/AZ31B Mg alloy interface (Fig. 21a) after the immersion test in 3.5 wt% NaCl solution.

Noticeable corrosion pits and the other localized corrosions were not detected on the Ti layer surface after immersion (Figs. 16c and 18 c). Likewise, scratches (grinding tracks) are discernible (Figs. 16c and 18 c) even after the reduction of Ra to 123.43 nm from 197.59 nm. As shown

in Fig. 16g, corrosion products are mainly constituted by Ti and O elements which may correspond to the existence of titanium-oxides [34] on the Ti layer surface. No Mg and Al elements were detected on the corroded Ti layer surface. This reveals that the Ti layer can isolate the Al coated Mg alloy surface from the electrolyte during immersion for 2 days. Furthermore, no visible change was seen on the Ti layer surface (after 2days of immersion, Fig. 22c) in comparison with as-polished



Fig. 19. 3D corrosion appearances of the (a) bare AZ31B Mg alloy surface, (b) Al coated Mg alloy surface after immersion in 3.5 wt.% NaCl solution for 2 days.



Fig. 20. Cross-sectional profiles and 2D surface profiles of the corroded surface of Al coated AZ31B Mg alloy after immersion in 3.5 wt.% NaCl solution for 2 days.

Ti/Al coated Mg alloy. No corrosion products (formation and accumulation) were seen at the Ti layer /Al layer and Al layer/AZ31B Mg alloy interfaces (Fig. 21b) after the immersion test in 3.5 wt% NaCl solution. This indicates that the Ti layer (in this research) with even some unconnected micro-pores (at inter-particle boundaries) and high surface activity (compared with bulk Ti [129]) could nearly modify the corrosion behavior of Al coated Mg alloy in chloride-containing solutions. As previously stated in the introduction, production of cold sprayed Ti (with H.C.P crystal structure and low slip systems) deposits with no porosity is almost unachievable using cold spray process (with N₂ as propellant gas) [36]. So, a post-cold spray process should be done on Ti coating to further improve the coating properties [31,35]. A layer of Ta could exceptionally improve the corrosion resistance of Ti/Al coated AZ31B Mg alloy. Pitting and other localized corrosions were not



Fig. 21. EDS line scan from cross section of coated AZ31B Mg alloys after surface polishing and then immersion test in 3.5 wt.% NaCl solution, (a) Al coated AZ31B Mg alloy, (b) Ti/Al coated AZ31B Mg alloy, and Ta/Ti/Al coated AZ31B Mg alloy.

detected on the Ta layer surface after immersion (Figs. 16d and Fig. 18d). Moreover, scratches (grinding tracks) are still detectable (Figs. 16d and Fig. 18d) on the surface. Ra was relatively stable during immersion. Corrosion products are largely comprised of Ta and minor O which may correspond to the existence of Ta-oxide on the corroded Ta layer surface. No Mg, Al and Ti elements were identified on the corroded Ta layer surface (Fig. 16h). Likewise, no noticeable change was observed on the Ta layer surface (after 2days of immersion, Fig. 22d) compared to as-polished Ta/Ti/Al coated Mg alloy. It is also clearly seen that the multilayered coating is still attached to Mg alloy and corrosion products (formation and accumulation) weren't observed at the Ta layer /Ti layer, Ti layer /Al layer and Al layer/AZ31B Mg alloy interfaces (Fig. 21c) after immersion test in 3.5 wt% NaCl solution. This discloses that the Ta layer can separate the Ti/Al coated Mg alloy surface from the electrolyte during immersion (Fig. 22a).

4. Discussion

As mentioned earlier, Al and Al alloys (as a single layer) due to their high wear rate [26] and relatively low corrosion (localized corrosion) resistance in severe corrosive atmospheres can't be extensively used as cold sprayed protective coatings on the Mg-based alloys [20,25,27,28]. Hardness and wear resistance of the cold sprayed Al coatings improved when ceramic particles were added into the Al feedstock [29,30]. Nevertheless, protective performance of the ceramic particle reinforced Al-based composite coatings on Mg alloys was deteriorated by Al/ceramic particle interfaces which acted as quick channels for the infiltration of corrosive electrolyte [29,30]. In this research, a novel method was employed to alleviate the issues related to the cold sprayed Al-based coatings substantially. Above-mentioned drawbacks associated with cold sprayed CP-Al coatings were lessened using Ti top coating. Never-theless, wear and corrosion resistances were outstandingly improved when a part of Ti (from group 4B) top coating thickness (in Ti/Al coating) was replaced by a layer of Ta (from group 5B).

4.1. Surface modification of Ti/Al coated AZ31B Mg alloy by a dense layer of Ta

In this work, severe plastic deformation of Ta powder particles (with bcc crystal structure and more slip system than Ti with hcp crystal structure) upon impact can lead to the tight bonding at highly deformed particle/particle interface (Figs. 1j and 1k) [41] and substantial strain hardening in the coating microstructure [130]. Higher microhardness in Ta coating signifies tremendous plastic deformation (high amount of dislocations) at inter-particle boundaries which led to the increase in coating denseness [16,25]. So, a part of Ti coating thickness was replaced by a dense layer of Ta to modify the surface properties of Ti coating (in Ti/Al coating). Corrosion resistance of the metal coated Mg-based alloys is majorly determined by the coating compactness.

The previously shown hardness results (Fig. 2l) justify the observed trend in the wear. The surface with higher hardness i.e. Ta/Ti/Al coating provides a lower wear rate followed by Ti/Al coating, Mg bulk, and Al coating surfaces, respectively. This indicates that Ti/Al and Ta/Ti/Al coatings significantly increase the surface hardness and wear resistance of Al coated AZ31B Mg alloys. This also showed a good potential of the cold sprayed Ta/Ti coatings for the wear protection of the Al coated Mg-based alloys surface.

4.2. Corrosion mechanism of Al, Ti/Al and Ta/Ti/Al coated AZ31B Mg alloys

Al coating showed the slower degradation rate than bare Mg alloy in 3.5 wt.% NaCl solution. Nevertheless, the corrosion rate (directly related to i_{corr}) and also the corrosion vulnerability of AZ31B Mg alloy can further be reduced using Ti/Al coating and particularly Ta/Ti/Al coating. This indicates that the dense Ta layer with a high propensity to passivation could seal the underneath transition layers in multilayered materials (coating systems). This could also be attributed to the in-situ localized grain refinement of impinged powder particles (during cold spray process) mainly due to rotational dynamic recrystallization which has been frequently reported for the cold sprayed metallic coatings (e.g. Ta, Ti, Ni, etc.,) [131–133]. A dense cold sprayed Ni coating (as a passive metal) considerably increased the corrosion resistance of Mg alloy in neutral aqueous corrosive solution. This improvement was related to the in-situ localized grain refinement of impacted particles and also compressive residual stresses caused by peening effect (by powder particles with high kinetic energy) [27,133]. It has been reported that compressive stresses can close the micro-cracks that are vertical to the surface of coating and thus cause the corrosion resistance improvement [134].

The impedance modulus $(|Z|_{f=0.01Hz})$ at low frequency for the bare Mg alloy (Fig. 11b (1)) was improved when the coatings were applied on the AZ31B Mg alloy. Nevertheless, Ta/Ti/Al coated Mg alloy depicted the highest $|Z|_{f=0.01Hz}$ at low frequency range than the other coated samples (Fig. 11b). The preliminary results of EIS test disclosed that a layer of Ta (with high denseness and excellent anti-corrosion properties) could remarkably improve the surface hardness and also the corrosion protection performance (shielding effect) of the bi-layered Ti/Al coating on Mg alloys in corrosive electrolyte.



Fig. 22. (a) Schematic illustration of Ta/Ti/Al coated AZ31B Mg alloy in 3.5 wt.% NaCl solution, (b) E-pH diagram of Ta, (c) photos of Ti/Al coated Mg alloy, and (d) Ta/Ti/Al coated Mg alloy after immersion in 3.5 wt.% NaCl solution.

After applying cold sprayed Al coating on AZ31B Mg alloy, the lower corrosion current density, higher $R_{ct,}$ and |Z|at low frequency were attained for the Mg alloy. However, plugging effect led to the temporarily prevention of the electrolyte access and delay of the further aluminum dissolution [26]. This also caused the obvious resistance (Z_w) for the diffusion of reactants (e.g. oxygen) during corrosion process of the Al coating. The reduction of R_{ct} and R_c + R_{ct} values for the Al coated Mg alloy (after 12 h of immersion (Fig. 15a)) indicated that pits and coating micro-defects can easily conduct the electrolyte into the inner regions of the cold sprayed Al coating. This reduction was also attributed to the dissolution and porosity of the corrosion products in the course of immersion time [88]. In general, Al coating with the lowest R_{ct} (Fig. 15a) compared to the other multi-layered coatings (Figs. 12b, 14b), should be protected by the protective top layers.

The drawbacks associated with CP-Al coating were mitigated with Ti (from group 4B) top layer (with very low standard reduction potential (SRP) mismatch (between Al and Ti layers) and high passivation propensity). However, the corrosive electrolyte infiltrated the underneath coating through the non-connected limited micro-pores which led to the reduction of Rct after 48 h of immersion. Nonetheless, Ti/Al coated Mg alloy (with higher value of R_{ct}, Fig. 14b) showed lower corrosion rate than Al coated Mg alloy even after 2days of immersion (Fig. 15a) in 3.5 wt% NaCl solution. This could be attributed to the lower presence of micro-pores in the cold sprayed Ti top layer (in Ti/Al coating) compared to cold sprayed Al coating. S. Kumar et al. [135] reported that the stable oxide formation along the inter-particle boundaries of as-cold sprayed Ti deposit can hampers the further aggressive attack of corrosive electrolyte in the course of time. Likewise, the absence of Mg and Al elements on the corroded Ti layer surface disclosed that Ti layer with even some unconnected micro-pores (at inter-particle boundaries) and high surface activity (compared with bulk Ti [129]) is able to somewhat modify the corrosion behavior of Al coated Mg alloys. Moreover, the benefits of the bi-layered coatings compared to the mono-layer coatings have already been reported in previous researches [136]. In contrast to cold sprayed Ti/Al coating (in this research, Fig. 22c), porous warm sprayed Ti coatings (having through thickness pores) formed a galvanic cell with

the AZ91E Mg substrate. This led to the formation and accumulation of corrosion products at the Ti coating/Mg interface and premature rupture of the coatings after only 1 day of immersion in 3.5 wt% NaCl solution [50]. This adverse behavior was not observed in the Ti/Al coated Mg alloys.

A layer of Ta exceptionally lowered the corrosion rate of Ti/Al coated AZ31B Mg alloy (sizable increment of Rct, Fig. 12b). H. Koivuluoto et.al [41] showed that the presence of a stable thin passive (corrosion) film between a dense (almost impermeable) cold sprayed Ta coating (consisting of very fine grain structure at inter-particle boundaries of Ta deposit [41], (Fig. 2K)) and the electrolyte can significantly slow the electrochemical dissolution process (leading to substantial increment of R_{ct} [137]). The formation of oxides can be aided by the stored energy (because of high strain rate deformation in the as-cold sprayed deposits) [135]. Passivation of some metals is influenced by pH and the potential [138]. However, at almost all pH values, the highly protective oxide layer of Ta could remain stable (concerning the potential values) [138]. Based on the E-pH diagram of Ta (Fig. 22b) [139], and OCP value of Ta/Ti/Al coated Mg alloy after immersion (Fig. 22b), it is postulated that an oxide layer of Ta is probably existent between Ta layer (in this research) and the electrolyte at all pH values.

The parameter which could characterize the corrosion resistance is the polarization resistance at the corrosion potential (R_{pol}). The polarization resistance values for Ti/Al and Ta/Ti/Al coated Mg alloys were calculated according to the following equation under EEC (Model C) in Fig. 11e [113,115,140–142].

$$Rpol = Rpo + Rct \tag{7}$$

It is conspicuously seen that the Mg sample coated with Ta/Ti/Al coating (Fig. 12b) shows the much better corrosion resistance at all immersion times (1, 12 and 48 h) than Ti/Al coated Mg alloy in 3.5 wt% NaCl solution (Fig. 14b). It is anticipated that this significant improvement could be retained even during longer immersion times.

5. Conclusions

4–**1**- Al, Ti/Al, and Ta/Ti/Al coatings were successfully applied on the AZ31BMg alloy using high pressure cold spray system. The surface with higher hardness i.e. Ta/Ti/Al coating provided a lower wear rate followed by Ti/Al coating, Mg bulk, and Al coating surfaces, respectively. This indicated that Ti/Al and Ta/Ti/Al coatings significantly elevated the surface hardness and wear resistance of Al coated AZ31B Mg alloy.

4–**2-** Protective efficiency of Al, Ti/Al, and Ta/Ti/Al coatings was calculated to be 98.27 %, 99.06 %, and 99.92 %, respectively. This shows the highest protective efficiency for Ta/Ti/Al coating.

4—**3-** No galvanic corrosion was seen at the Al coating/AZ31B Mg alloy interface after immersion test in 3.5 wt% NaCl solution. However, the drawbacks associated with CP-Al coating could be mitigated with the Ti top layer. Obvious corrosion pits and the other localized corrosions were not detected on the surface of Ti layer after immersion. The Nyquist spectra of Ti/Al coated Mg alloy didn't show straight line at low frequency range (characteristic of diffusion-controlled reaction). Likewise, No Mg and Al elements were detected on the corroded Ti layer surface. This revealed that the Ti layer not only lowers the wear rate of Al coated Mg alloy, but also can isolate the Al coated Mg alloy surface from the electrolyte during immersion.

4–**4**- A dense layer of Ta on the Ti/Al coating exceptionally improved the corrosion resistance of Ti/Al coated AZ31B Mg alloy. Ta/Ti/Al coated AZ31B Mg alloy showed the highest $|Z|_{f=0.01Hz}$ at low frequency range than the other coated samples. Likewise, the values of R_{ct} for the Ta/Ti/Al coated Mg alloy increased after 48 h of immersion. This indicated that the rate of electrochemical processes at the electrode/ electrolyte interface could be further lowered in the course of time.

CRediT authorship contribution statement

M. Daroonparvar: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing original draft, Supervision, Project administration, Writing - review & editing. M.U. Faroog Khan: Methodology, Validation, Visualization, Data curation, Formal analysis, Writing - review & editing. Y. Saadeh: Methodology, Validation, Visualization, Writing - review & editing. C. M. Kay: Funding acquisition, Project administration, Resources, Writing - review & editing. A.K. Kasar: Data curation, Formal analysis, Methodology, Writing - review & editing. P. Kumar: Methodology, Validation, Visualization, Writing - review & editing. L. Esteves: Writing review & editing. M. Misra: Funding acquisition, Project administration, Resources, Writing - review & editing. P. Menezes: Project administration, Resources, Writing - review & editing. P.R. Kalvala: Project administration. H.R. Bakhsheshi-Rad: Writing - review & editing. R.K. Gupta: Data curation, Formal analysis, Writing - review & editing, Funding acquisition, Project administration, Supervision.

Declaration of Competing Interest

The authors declare no conflict of interest.

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