Improved Bonding Strength Between Thermoplastic Resin and Ti Alloy with Surface Treatments by Multi-step Anodization and Single-step Micro-arc Oxidation Method: a Comparative Study

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Due to excellent specific mechanical and physical properties, titanium-based fibre metal laminates (FML) have attracted increasing attention in marine and defense for improved impact protection. Metal and composite interface (MCI) plays a pivotal role to determine the failure mode of FML. Surface treatment of metal is commonly carried out to improve the MCI properties. In this study, two different electrochemical surface treatments, anodization and micro-arc oxidation (MAO) were adopted. The tunable hierarchical structure observed after multiple physical and chemical surface treating processes, i.e., sandblasting, anodization, etching, and annealing on Ti6Al4V. In comparison single step MAO treatment shows more pores and craters on the surface with increasing anodic voltage. The results from lap shear experiment show that the adhesive strength between Elium[®] resin and titanium adherend by single-step MAO treatment has been improved compared to that by multi-step anodization. By increasing the anodic voltage of MAO treatment to 600 V, the highest shear strength of 18.4 MPa is achieved.

Keywords: Bonding strength; Surface treatment; Anodization; Micro-arc oxidation

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1. Introduction

Fibre metal laminate (FML) is a combination of metal, and composite sandwich layers which have the desirable impact damage resistance, superior strength, excellent fatigue resistance and decent corrosion resistance.^{1,2} The metal currently being used is either aluminium, titanium or magnesium alloy and the fibre-reinforced plastic layer is either kevlar-reinforced, carbon-reinforced, glass-reinforced composite. GLARE (GLASS Reinforced aluminium laminate) find its application in the upper fuselage of Airbus A380 aircraft.³ Apart from aerospace, FML used in marine⁴ and armor⁵ components due to their design resilience. Among metal, titanium alloy Ti-6Al-4V possesses many fascinating properties such as high fatigue strength, corrosion resistance, merchantability and weldability.⁶ Titanium-based FMLs attracted among the researchers and engineers due to its unique feature which includes high durability, decisive anti-permeability and assuring structural applications.⁷⁻⁹ To achieve the desired properties, excellent adhesion is a necessity between the titanium layer and fibre reinforced layer, which is very critical in determining the overall performance (fatigue, impact damage, and other mechanical properties) of titanium-based FML.

To improve the adhesion of Ti alloy to the polymer necessary surface treatment need to be carried out. Three major category of surface treatment are commonly followed they are (i) mechanical treatment - sandblasting¹⁰⁻¹² and shock peening,¹³ (ii) chemical treatment -

anodizing,^{14,15} etching^{16,17} and micro arc oxidation (MAO),^{18,19} and (iii) addition of interfacial layer - sol/gel methods,^{20,21} plasma-spray²² and coupling agent.^{23,24} He^{25,26} found higher shear strength by multi-step anodization i.e., sandblasting for 20sec, anodization at 40 °C for 15 min, NaOH etching for 24 hrs and annealing for 5 hrs at 600 °C leads to the formation of hierarchical macro to nanopores on Ti alloy surface. However, the improved shear strength was achieved after multiple steps. This inspires to develop a single-step Ti alloy surface treatment method to improve shear strength, work of fracture and wettability for polymer matrix. Another chemical treatment method, micro-arc oxidation (MAO) is a potential method to create a uniform ceramic-like TiO₂ film on Ti alloy metal surface by discharging sparks relatively at a high voltage. This action creates more pores and craters and also forms thick oxide film compared to the conventional anodization.²⁷ However, the ceramic-like oxide film, pore size depends on the parameters such as electrolytic solution, power supply (unipolar or bipolar), current density, the voltage of anode and cathode and the processing time.²⁸ The oxide film formed on the surface is derived from the electrolyte and the metal substrate during the MAO treatment.²⁹ The resultant oxide film comprised of amorphous-to-crystalline mixed phases.³⁰

The oxide film formed on the MAO-treated metal surface comprises of two layers with a loose, porous outer layer and a thick inner dense layer. The outer porous layer creates an interlocking with the resin which contributes to improving the bonding strength. This shows the porous outer layer has a significant effect on the improvement of bonding strength.³¹ The porous layer formed on the MAO-treated surface increases in size by increasing voltage, this also contributes higher oxide thickness which improves the mechanical interlocking with a polymer resin.³² Hsieh³³ found an improved adhesive strength of TiNi shape memory alloy treated by MAO in 20 vol.% phosphoric acid electrolytic solution at pH of 4.1. Wu²⁷ demonstrated the pore size, the

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phase of the oxide layer depends on the applied voltage. Tang³⁴ highlighted pore size of the oxide surface film improves the bonding strength, increased pore size enhance mechanical interlocking and improves the stress distribution at the bonding interface. Gao³⁵ achieved improved lap shear strength by MAO surface treatment by modifying the concentration of Na_2SiO_3 in the electrolytic solution. This investigation aims to identify the shear strength, work of fracture, wettability, and surface roughness on multi-step conventional anodization treatment and to compare with single-step micro-arc oxidation treatment by increasing anodic voltage. The comparison study on two extreme conditions of low voltage anodization and high voltage MAO chemical surface treatment is first of its kind.

2. Experimental

2.1. Materials

Ti alloy (90 % Ti, 6 % Al, and 4 % V) of grade 5 with a thickness of 1.5 mm was used for surface treatment for both multi-step anodization and single-step MAO treatment. Elium[®]188 is a low viscous methyl methacrylate liquid thermoplastic resin which also has resin infusion capability was used as a polymer adhesive. Elium[®]188 resin undergo radical polymerization to complete the formation of toughening thermoplastic matrix, in which benzoyl peroxide (BPO) of 2 wt.% (weight ratio) is used to initiate the polymerization.

2.2. Surface treatment procedures

2.2.1. Anodization surface treatment process

The process of surface treatment started with grounding the Ti alloy by 2000 grid abrasive paper and cleaned with distilled water and ethanol separately in bath sonicator and dried after every hierarchical surface treatment process. Alumina powder of diameter 5–20 μm was used to clean the surface in sandblasting procedure. The anodization electrolyte solution is a combination of EDTA - 0.1 M (ethylene diamine tetra acetic acid) and Na-tartrate - 0.2 M which is used as the impurity and Ti-complexing agent respectively, also 7.5 M of NaOH (sodium hydroxide) added to the electrolytic solution. The Ti sample is anodized at 15 V and 40 °C for 15 min in as prepared electrolytic solution. As treated anodized sample is etched in 1 M of NaOH for 24 h at 60 °C. The etched Ti samples were placed in the hot furnace at 600 °C for 5 h to complete the annealing process. The sample were cut into a required dimension after each step of the surface treatment process for a single lap shear experiment.

2.2.2. MAO surface treatment process

The electrolytic solution is prepared by combining sodium pyrophosphate 5.0 g/L and sodium silicate 10.0 g/L in distilled water. After polishing and sandblasting of Ti alloy, the samples were cleaned with distilled water and ethanol separately before MAO process. MAO Ti alloy is processed at three constant voltage of 400 V, 500 V, and 600V for a constant time of 5 min each. One step voltage of 400 V for 2 min, 500 V for 2 min and 600 V for 1 min makes a total treating time of 5 min is also fabricated. This makes to compare with other MAO treated samples which are treated at constant voltage and constant time (5 min). Anodic voltage was selected based on few trails, where no arc is observed on the Ti alloy at 300 V and extensive arc observed at 600 V. Also, while treating at 600 V in Ti-MAO-Step sample, produces an intensified spark and prolonged activity (more than 2 min) makes difficult to the operator during fabrication. This similar intensified spark was also observed while treating Ti sample at constant 600 V for 5 min. This chooses to treat Ti-MAO-Step (5 min) sample for 2 min (400 V), 2 min (500 V) and 1 min (600 V).

2.3. Single-lap-shear sample preparation

Ti sample after different surface treatments (multi-step anodization and single-step MAO), were cut into the dimension of 25.4 mm $\times$ 100 mm $\times$ 1.5 mm to prepare single-lap-joint. Elium[®] resin was prepared carefully and spread on the Ti sample without any air bubble and well aligned to fix properly to make an overlap of 12.5 ± 0.25 mm. Fig. 1 shows the sample dimension for a single lap shear bonding experiment. The samples were cured at room temperature for 2 h and in the heating oven at 80 °C for 4 h. The thickness of the Elium[®] resin was maintained at 0.4 mm for all different surface treated samples. In accordance with ASTM standard D1002, single lap shear experiment were carried out in the universal testing machine with a crosshead speed of 1.3 mm/min, an average value with standard deviation reported.

2.4. Surface characterization

SEM (scanning electron microscopy – JEOL-6390) was used to characterize the surface morphology after different surface treatment. SEI (secondary electron image) and BSE (backscattered electron) images operated at 20 kV were used to find the oxide layer thickness by taking the cross-sectional images of all differently treated samples. Average and standard deviation of surface roughness were reported from four different readings measured by optical profilometry (Bruker

Fig. 1 Ti-Elium[®] sample dimension geometries.

NPFLEX) with an area of 480 μm X 640 μm at a different location. The chemical composition of the oxide layer was detected by X-ray photoelectron spectroscopy (XPS, Axis-ultra, Kratos). An Al K α , the x-ray was used at 15 kV and 10 mA, and the C1s peak is shifted to 285.0 eV for energy calibration. The contact angle between resin and surface treated Ti was measured using contact angle measurement (Biolin Theta) with photo interval of 1 s.

3. Results & Discussions

3.1. The microstructure of treated Ti alloys

Fig. 2 and Fig. 3 shows SEM surface morphology of the metal after surface treatment of both the anodization and MAO process. In Fig. 2, for Ti-P, the surface shows microscopic and macroscopic bumps which disappear when the sample is anodized in Ti-PA. During the anodization process, the bumps were far more liable to be dissolved due to their contact with the electrolytic solution.³⁶ NaOH etching of Ti-PA sample has great influence on the surface morphology. After NaOH surface etching the surface becomes smoother than Ti-PA. But at higher magnification, the samples were shown with nano-structured bumps; this occurrence caused due to the chemical reaction in the corrosive NaOH solution at 60 °C. The chemical reaction between titanium and corrosive NaOH solution forms hydrated titanium oxide gel layer which contains Na⁺ ions on the surface of titanium.³⁷ This oxide gel layer contains an ample amount of water and hydrated ions, and it is mechanically unstable (Fig 2.c2). The heat treatment at 600 °C for 5h after the process of NaOH etching, dehydrate and densify the mechanically unstable gel layer, forming a porous network structure which makes the oxide layer to firmly bonded to the metal substrate³⁷ (Fig 2.d2). Annealing can influence the significance of the bonding strength on Ti alloy.³⁸ The formation of nanopores on the titanium surface enhances the bonding strength and wettability.^{25, 26}

In Fig. 3, the SEM images depict the surface of MAO treated Ti alloy at different anodic voltages and can be seen that increasing the anodic voltage the outer porous layer formed on the surface also increases. By increasing the anodic voltage, the pore size increases from 2 μm to 10 μm which will improve the wettability and more prone to mechanical interlocking when the Elium[®] resin is placed on the treated surface. On increasing anodic voltage in MAO surface treatment, the current transmits through the electrolyte provoke the spark initiation on the Ti alloy surface at high intensity. This intensified spark improves the Ti surface more rougher by creating regular growth mode of the volcano-shaped craters on the Ti surface.³⁹ From Table 1, the current requires for treating the samples was higher at initiation, and after 50 S the current stabilizes. The higher current required at the spark initiation of all MAO sample is due to the more power required to create initial melting on the pristine Ti alloy. Once spark initiation starts, the current stabilizes showing lesser power is adequate enough to create a spark when being compared to spark initiation. However, for step voltage the current requires is slightly less from the constant voltage samples. This phenomenon is due to the fact when treating the Ti-MAO-Step sample at 400 V it requires high current to create melt spark but on the consecutive voltage requires less current depicting the samples is already melted enough to form ceramic-like oxide layer. This shows that energy consumption is lower when treating the sample by a step voltage compared to constant voltage samples.

Cross-section of the oxide layer formed on the Ti surface after anodization and MAO treatment is shown in Fig. 4. The thickness of the oxide layer for all anodization treatment with further processing is relatively low when compared to the MAO samples which are treated at higher anodic voltage. It is found that the thickness of oxide layer was 1 μm , 1.7 μm , 3.1 μm , for Ti-PA, Ti-PAE, and Ti-PAEA respectively. This shows anodization with further treatment of etching and annealing

Table 1 Surface treatment of samples prepared by anodization and micro-arc oxidation.

Sample code	Description	Time	Current (A)		Duty (%)	Frequency (Hz)
			Start	End		
Ti-P	Sandblasting only	20s	-	-	-	-
Ti-PA	Sandblasting + Anodization	20s + 15min	-	-	-	-
Ti-PAE	Sandblasting + Anodization + NaOH	20s + 15min + 24h	-	-	-	-
	Etching					
Ti-PAEA	Sandblasting + Anodization + NaOH	20s + 15min + 24h + 5h	-	-	-	-
	Etching + Annealing					
Ti-MAO-400	Micro-arc oxidation at 400V	5min	12.5	7.2	20	1000
Ti-MAO-500	Micro-arc oxidation at 500V	5min	18	13.9	20	1000
Ti-MAO-600	Micro-arc oxidation at 600V	5min	30.9	27.2	20	1000
Ti-MAO-Step	Micro-arc oxidation step 400V + 500V + 600V	2min +	12.5	7.1	20	1000
		2min +	16.2	13.3		
		1min	28.9	26.5

Fig. 2 SEM images of Ti-P (a1, a2), Ti-PA (b1, b2), Ti-PAE (c1, c2), Ti-PAEA (d1, d2).

Fig. 3 SEM images of (a) Ti-MAO-400, (b) Ti-MAO-500, (c) Ti-MAO-600, (d) Ti-MAO-Step.

Fig. 4 Cross-sectional oxide layer SEI and BSE images of (a)Ti-PA, (b) Ti-PAE, (c) Ti-PAEA, (d) Ti-MAO-500, (e) Ti-MAO-600, (f) Ti-MAO-Step.

Fig. 5 Surface roughness of the treated Ti-alloy.

Fig. 6 XPS-Chemical compositions on the treated Ti alloy surfaces.

improves the oxide layer thickness. The oxide layer thickness of MAO treated Ti alloy are 10.1 μm , 20.6 μm , 43.5 μm , 37.5 μm for Ti-MAO-400, Ti-MAO-500, Ti-MAO-600, and Ti-MAO-Step respectively. The result shows that increasing anodic voltage from 400 V to 600 V in MAO treatment can increase the thickness of oxide layer which in turn improves the wettability of Elum[®] resin and improves the shear strength.

Fig. 5 depicts the surface roughness of Ti-PAEA has a higher surface roughness among anodization samples which is crucial in improving the bonding strength. On the other hand, Ti-PA and Ti-PAE show less roughness compared to Ti-P which is due to the dissolution of macroscopic and microscopic bumps in the electrolytic solution during the anodization and etching process respectively. However, the surface roughness of the MAO samples is much higher compared to the anodization process and has increased roughness on increasing the

anodic voltage. The improved surface roughness is due to intensified spark on the surface at higher anodic voltage.

3.2. Chemical composition and phase analysis

To find out the chemical composition on the surface treated Ti alloy, XPS experiment is used, and the results are shown in Fig. 6 and Table 2. In Fig. 6, dotted lines at the two-different peak of binding energy 459.0 eV and 464.7 eV shows the phase difference corresponds to pristine titanium alloy (Ti-P). Table 2 Shows the binding energy of Ti alloy surface treated by both anodization and MAO surface treatment, and TiO_2 were observed for all samples with stable Ti^{4+} at two different spectral lines of $2\text{P}_{3/2}$ and $2\text{P}_{1/2}$. Two factors were attributed towards the observation of glassy amorphous nature of MAO treatment. First, MAO is a quenching process, i.e., rapid solidification in the electrolyte occurs when the substrate surface is locally melted during micro-arc discharge

Table 2 Binding energy tabulation from XPS for the treated Ti alloy surfaces.

Sample no	Sample name	Binding energy (eV)	Species (2P _{3/2})	Reference	Binding energy (eV)	Species (2P _{1/2})	Reference
1	Ti-P	459.0	TiO ₂	40	464.7	TiO ₂	41
2	Ti-PA	458.7	TiO ₂	42	464.4	TiO ₂	43
3	Ti-PAE	459.0	TiO ₂	40	464.7	TiO ₂	41
4	Ti-PAEA	458.7	TiO ₂	42	464.3	TiO ₂	44
5	Ti-MAO-400	459.1	TiO ₂	45	464.9	TiO ₂	46
6	Ti-MAO-500	459.2	TiO ₂	47	464.9	TiO ₂	48
7	Ti-MAO-600	458.9	TiO ₂	46	465.2	TiO ₂	49
8	Ti-MAO-Step	459.2	TiO ₂	47	465.5	TiO ₂	50

Fig. 7 (a) Wettability between treated Ti alloy and resin (b) Static contact angle images for resin droplets on the treated Ti alloy surfaces at time of 0, 50, 100 and 150 s (from left to right in each group of images) as mentioned in table 1 (c) Schematic wetting diagram of Ti-P, Ti-PAEA and Ti-MAO-600.

on the surface. The total cooling time is too small which allow atoms to migrate to appropriate lattice sites in the micro arc oxidized film. Also, the pores are interconnected each other from the outer surface to the inner surface in the MAO film. These interconnected films allow the electrolyte to infiltrate through MAO film and allows the rapid cooling rate to the inner MAO film. Second, a significant amount of phosphate in the electrolyte is introduced in the MAO which attributes to the changes in stoichiometry and crystallinity of the TiO_2 .³³

3.3. Wettability between treated Ti surface and resin

Good wettability is crucial in improving the adhesion of Elium® to Ti alloys. The dynamic wetting behavior of different surface treated samples was evaluated by measuring the contact angle between the resin and treated Ti surface from 0s to 150 s with photo interval of 1s. In general, Elium® resin is MMA which dries very fast when a small droplet exposes to the atmospheric air. In this case, commercial epoxy which has a similar viscosity of Elium® resin is used to evaluate the wettability.

Fig. 7a shows plot of resin contact angle for all treated samples from 0s to 150 s. From figure, it is obvious that anodized treated with post-treatment of etching and annealing showing poor wettability performance compared to all MAO treated samples. The wettability for Ti-PA and Ti-PAE seems relatively similar. However, the decrement of the contact angle is much faster for Ti-PAE sample showing NaOH etching after anodization has improvement in the wettability. Among all the anodization and post-treated samples, Ti-PAEA shows very lower contact angle with improved wettability for resin. MAO treated sample shows improved wettability between the treated Ti and resin by increasing the anodic voltage of 400 V, 500 V, and 600 V, but for the case of step voltage, the wettability performance is in between the sample 500 V and 600 V. This shows that the porous structure formed on the sample Ti-MAO-Step is capable enough to improve wettability relative to 500 V but less compared to sample treated at 600 V. Among, MAO treated samples, Ti-MAO-600 shows improved wettability due to the large porous structure on the treated Ti alloy. Fig. 7b shows the typical images of the resin droplet at different time interval with their average contact angle measured during the experiment. It is obvious to found that all MAO treated samples possess improved wettability

compared to anodization treated samples. Among all the treated samples, Ti-MAO-600 showed the best wettability of $\sim 7^\circ$ after 150 s. Fig. 7c represents the schematic diagram of the wettability of resin on Ti-P, Ti-PAEA and Ti-MAO-600. In Fig. 7c, Ti-P shows no oxide layer and poor wettability, but for Ti-PAEA shows nanopores and they are close to one another. For Ti-MAO-600, the pores are larger which can withhold more resin and creates mechanical interlocking.

3.4. Shear strength of Elium® by Single lap shear

Fig. 8a and 8b present the load-displacement, shear strength and work of fracture for adhesively joint bonded Ti-Elium® assembled specimens. Compared with Ti-P, Ti-PAEA and Ti-MAO-600 show 309.6 % and 558.9 % improvement observed from the result of four tested samples from each configuration. This trend shows treating the Ti alloy after MAO treatment has a significant improvement in the shear strength compared to anodization with the further process of etching and annealing. After anodization and etching process, the shear strength was improved but not very significantly; this indicates just anodization and etching process does not influence the shear strength improvement even though their wettability is better than Ti-P. Fig. 9a and 9b present fractographic images after the shear strength experiment. Ti-P, Ti-PA, and Ti-PAE shows entirely adhesive failure. However, after the annealing process, Ti-PAEA sample has a significant improvement in the shear strength; this is due to the mechanical interlocking of Elium® resin in the nanopores on the Ti surface. However, the failure was a combination of both adhesive and cohesive failure which is shown in Fig. 9a. SEM of Ti-PAEA shows the shear failure at the fracture region in Fig. 9b, where other anodization treated sample does not have a shear failure. Compared to Ti-PAEA, all other anodization treatment and pristine Ti shows adhesive failure which can be confirmed by Fig. 9b. Only after multiple surface treatment of anodization the shear strength has significant improvement. Even though Ti-PAEA has higher shear strength among all other anodization sample, all MAO treatment has superior improvement in shear strength. Ti-MAO-600 has 558.9 % increment with Ti-P and 163 % increment with Ti-MAO-400. Among all MAO treated sample, Ti-MAO-600 has the highest shear strength and work of fracture.

For all MAO treated samples, the failure is a combination of both

Fig. 8 (a) Load-displacement curve of Ti treated with Elium® resin (b) Shear strength and work of fracture of Ti treated with Elium® resin.

Fig. 9. (a) The fractographies of adhesive bonded Ti alloy joints (b) SEM fractography after lap-shear experiment ((a1, b1 – Ti-P); (a2, b2 – Ti-PA); (a3, b3 – Ti-PAE); (a4, b4 –Ti-PAEA); (a5,b5 –Ti-MAO-400); (a6,b6 – Ti-MAO-500); (a7,b7 – Ti-MAO-600); (a8,b8 – Ti-MAO-Step)).

adhesive and cohesive and resin de-bonded mostly at the edges. The shear failure was confirmed with SEM pictures showing the direction of shear in Fig. 9b. In Fig. 9a the de-bonded resin at the corners for all MAO treated samples were clearly shown. Ti-PAEA and Ti-MAO-400 have a more similar failure, but the work of fracture for Ti-PAEA is slightly higher than Ti-MAO-400 due to the surface morphology of nanopores for anodization and macroporous structure for MAO. Even though Ti-MAO-600 has the highest shear strength and work of fracture; it is worth to note that energy consumption is higher than treating Ti-MAO-Step.

4. Conclusions

In this electrochemical surface treatment investigation, results were systematically compared between multi-step anodization and single-step micro-arc oxidation. The wettability and shear properties show better performance in single-step MAO method. The main conclusions are

(1) Improved surface roughness was achieved for MAO treated Ti alloy with increasing anodic voltage from 400V to 600V, whereas the measured surface roughness on all anodization samples was relatively low compared to the MAO surface treatment.

(2) Ti-PAEA with a hierarchical macro to nanostructure by multi-steps showed a lower contact angle between the resin and treated Ti metal. However, the improved oleophilic surface was obtained on all MAO treated Ti alloy with relatively very lower resin contact angle. This concludes MAO surface treatment is superlative to anodization.

(3) Shear strength of MAO treated Ti alloy at a higher voltage of 600 shows the highest shear strength among all the surface treated samples. Even though multiple steps of anodization increase the shear strength among anodization, single-step MAO is superlative which improves the shear strength on increasing the anodic voltage. This confirms increasing anodic voltage in MAO treatment process increases the pore size and thus improves the mechanical interlocking with Elum[®] resin.

(4) Regarding energy consumption for treating the Ti alloy, MAO sample treated by step voltage consumes less energy than treating at constant 600 V. However, Shear strength of Ti-MAO-600 is 18.4 MPa which is 12.8 % higher than that of Ti-MAO-Step. Developing a large structure of FML also involves the cost of surface treatment of Ti alloy. Lower energy consumption on surface treating Ti alloy will reduce the fabrication cost for such a large structure. This concludes, to save energy MAO step is the right choice but need to compensate in shear

strength and work of fracture slightly.

Conflict of interest

There are no conflicts to declare

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