PROPERTIES OF THERMOPLASTIC FIBRE METAL LAMINATES (FML) TITANIUM-PEEK INTERFACE

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Keywords: thermoplastic FML, metal-polymer interface, surface treatment, aging

Abstract
The properties of thermoplastic Fibre Metal Laminates (FML) composed of alternating stacked titanium foils and layers of carbon fibre reinforced polyetheretherketone (Ti/CF-PEEK laminates) are investigated. The adhesion between the polyetheretherketone (PEEK) matrix and titanium degrades by the influence of humidity. Physical, chemo-physical and chemical surface pre-treatments of the titanium layers were tested to improve the long-term behaviour of the interface. To compare the different surface treatments lap shear tests were conducted to determine the degradation of the initial strength by the influence of water. Concerning the physical pre-treatment the laser pre-treatment offers the highest magnitude of humidity resistance.

1 Introduction
Fibre Metal Laminates (FML) consisting of alternating stacked layers of polymer matrix composites and metallic foils as shown in figure 1 are considered for structures with high fracture toughness and good impact resistance in aeronautic applications. They join the advantages of polymer matrix composites, e.g. high specific stiffness and strength and the advantages of the metal, e.g. ductility, electrically conductive and superior bearing capabilities.

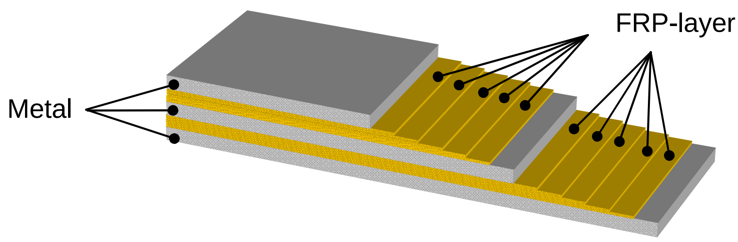


Figure 1. Composition of Fibre Metal Laminates

2 Materials and processing
The geometry of the lap shear specimens was chosen on the basis of the German standard DIN 1465 [1] as shown in figure 2. The titanium plates consisting of the alloy Ti-3Al-2.5V (length of 72.5 mm, width of 10 mm, and thickness of 1.6 mm) were pre-treated and

subsequently bonded with a 0.1 mm thick PEEK foil. In contrast to the German standard an adherent area of 5mm x 10mm is chosen. The lap shear specimens were manufactured in a laboratory furnace at a consolidation temperature of 400°C by using a positioning tool for ensuring reproducible specimens with uniform adherent areas. During the process of cooling the PEEK solidifies and adheres to titanium.

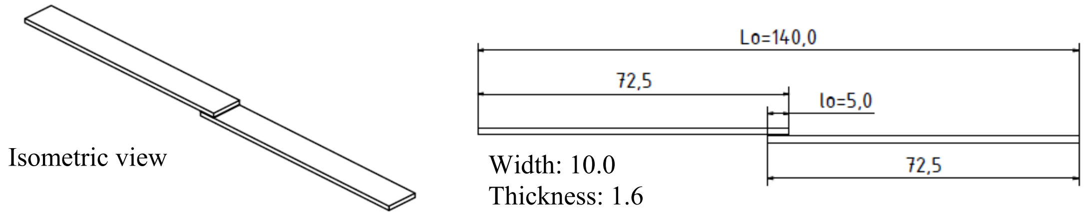


Figure 2. Lap shear specimen

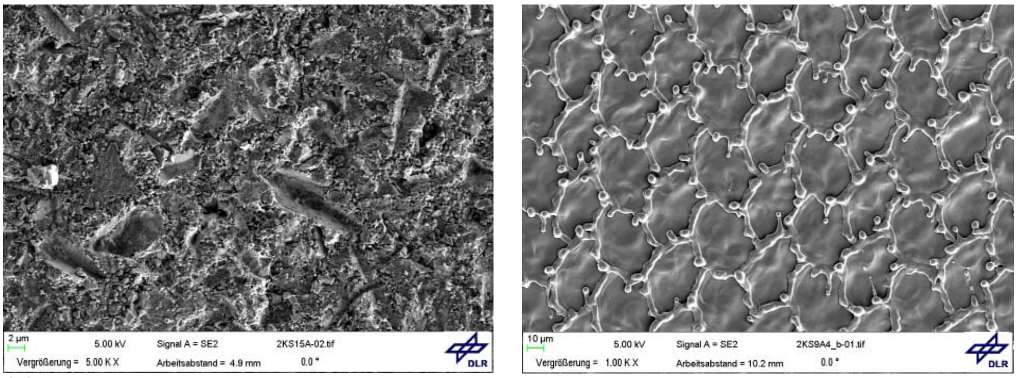
3 Experimental procedures

The first step of this investigation consisted in determining the best physical pre-treatment, subsequently the chemo-physical and also the chemical pre-treatment were applied on the best physical pre-treatment. The third step consisted in investigating the long-term behaviour of the most promising surface pre-treatment by aging in hot water.

3.1 Surface pre-treatment

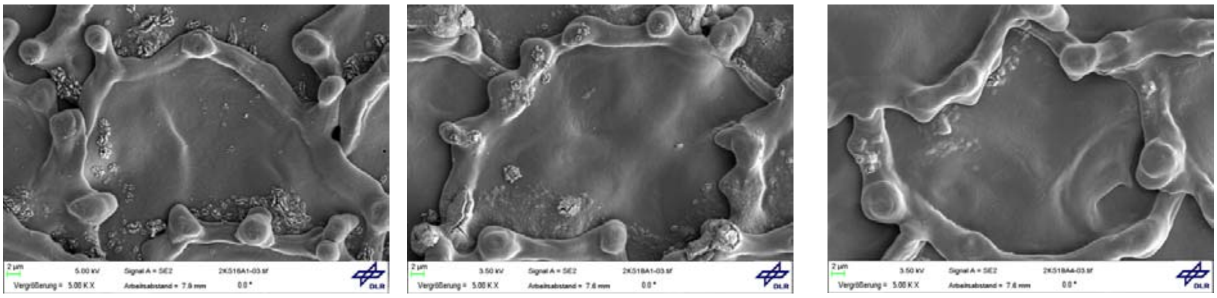
The objective of physical pre-treatments of titanium is to create a macro structured surface for enhanced specific surface and for mechanical interlocking. Physical pre-treatment was performed by wet grinding, grit blasting, and laser treating. The process of wet grinding was performed by SiC sandpaper with a grit size of P320. The ground surface just exhibits scattered grinding grooves which marginally vary in depth. After wet grinding the titanium plates were cleaned to remove contamination on the surface and subsequently the lap shear samples were made of it. The process of grit blasting was performed by alumina with a grit size of 180-250µm at a pressure of 0.8 bar and a working distance of 8 cm. Thereby, a sharp-edged surface roughness including penetrated grit particles was formed as shown in figure 3a. The grit blasted surface exhibits scattered indentations which vary in length, width and depth as well as in the kind of wedge profile, i.e. more or less sharp-edged. After grit blasting the titanium plates were cleaned to remove contamination and subsequently the lap shear samples were made of it. The laser treatment was performed by a cleaning laser with a spot size of 56µm and an energy density of 8.61 J/cm². Thereby, a reproducible surface structure including welding beads obtained as shown in figure 3b. In comparison to the ground and grit blasted surface the laser treated surface exhibits evenly arranged cups which marginally vary in size, i.e. in length, width, and depth. The surface doesn't exhibit sharp edges, neither at the cups nor at their border strips. The process of laser treatment cleans the surface as well, that no further cleaning steps were necessary. The lap shear samples were made of the laser treated titanium plates.

The objective of the chemo-physical pre-treatments is to create a micro structured oxide layer on the titanium surface for enhanced specific surface and for enhanced mechanical interlocking. The process of electrolytic passivation, the so called anodising, increases the thickness and stability of the natural oxide layer on the surface. Anodising increases corrosion resistance and provides better adhesion for paint primers and glues than bare metal. Anodising of titanium can be performed in an alkaline and acid electrolytic solution. For this investigation laser treated titanium plates (best physical pre-treatment) were anodised in 5M NaOH (15V for 10 minutes), in 1M H_2SO_4 (40V for 3 minutes) and 1M H_3PO_4 (60V for 3 minutes). By means of the alkaline anodisation a structured oxide layer was formed as shown in figure 4a. By means of the acidic anodisation in H2SO4 a structured oxide layer was formed as shown in figure 4b. By means of the acidic anodisation in H3PO4 a marginally structured oxide layer was formed as shown in figure 4c.



(a) (b)

Figure 3. SEM image of grit blasted titanium surface (a) and laser treated titanium surface (b)



(a) (b) (c)

Figure 4. SEM image of laser treated titanium surfaces anodized in 5M NaOH electrolyte (a), in 1M H_2SO_4 electrolyte (b), and in 1M H_3PO_4 electrolyte (c)

The objective of the chemical pre-treatment is to create chemical bonds at the interface between titanium and PEEK. Therefore, laser treated titanium plates (best physical pre-treatment) were coated with organic functional silane and organic titanium acetylacetonate (TAA). At this investigation bifunctional glycidoxypropyltrimethoxysilane of DowCorning® Z-6106 [2] and titanium acetylacetonate of DuPontTM Tyzor® AA-105 [3] was used. Since a very thin layer of the adhesion promoter has to be deposited on the titanium surface both adhesion promoters were solved in isopropanol. The mixed solvents have concentrations of 0.2vol% and 0.02 vol%, alternatively. The laser treated titanium plates were dipped in the solvent for 1 hour in an ultrasonic bath and subsequently dried for 1 hour at 80°C. Lap shear specimens were made of the coated titanium plates.

3.2 Lap shear experiments

The quasi-static lap shear experiment was carried out on the basis of the German standard DIN 1465 [1] with a cross-head displacement rate of 1 mm/min. The machine used is a 10 tons Instron testing machine equipped with a 10 kN load cell to measure the load for lap shear fracture. The cross-head displacements and load histories were recorded. Six specimens per surface pre-treatment were tested for assuring output data accuracy. Thereof three specimens were tested at the initial status and three specimens were tested after exposure to deionised water for 72 hours at 80°C to determine the degradation of the initial shear strength (= bonding strength) by influence of water. This procedure has been proven as accelerated aging test showing similar effects as longer exposures to humidity of ambient air. The laser pre-treated specimens (most promising surface pre-treatment) were tested after exposure to 80°C deionised water for up to 17 days.

4. Results

4.1 Lap shear experiment

The results of physical, chemo-physical and chemical treated lap shear specimens are summed up in figure 5. Figure 6 shows the decrease of bonding strength of the laser treated specimens (most promising pre-treatment) as a function of long-time exposure to 80°C deionised water.

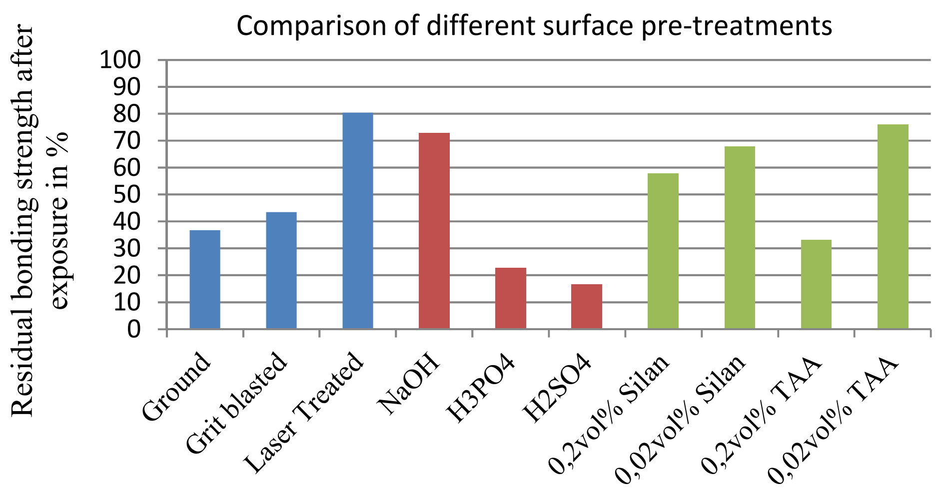


Figure 5. Residual bonding strength in % of the initial bonding strength after exposure to hot water of different titanium-PEEK interfaces

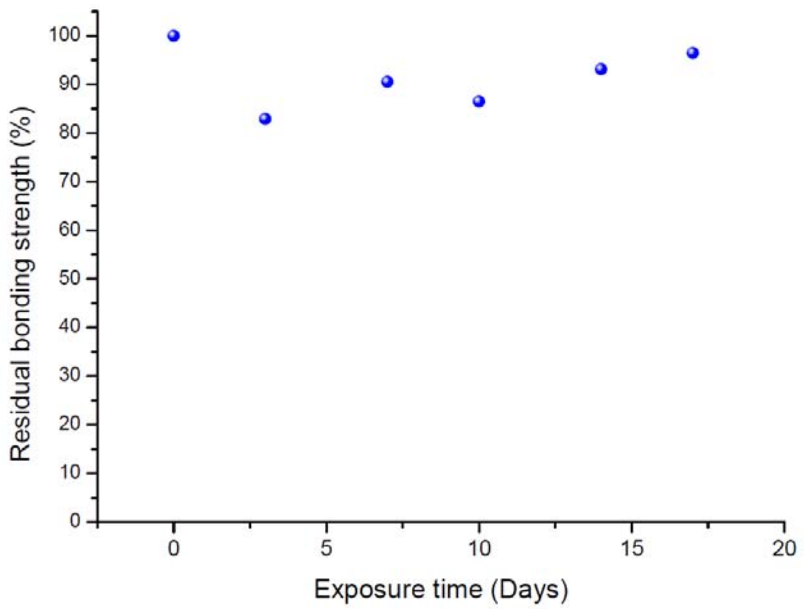


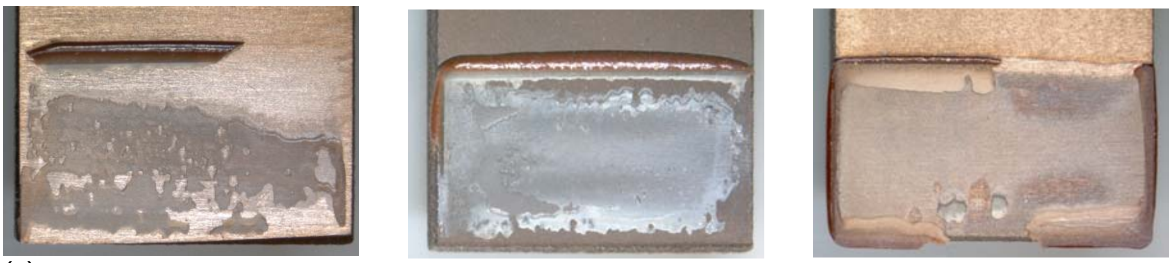
Figure 6. Residual bonding strength of laser pre-treated lap specimen in % of the initial bonding strength after long-term exposure to water (each dot represents average of three specimens)

The process of laser pre-treatment causes the highest bonding strength after exposure to water (τ = 62.27 MPa) and the lowest magnitude of degradation of the bonding strength by the influence of humidity. In comparison to the laser treated specimens the anodised specimens exhibit decreased bonding strength at the initial and exposed status. In addition, the anodised lap shear specimens show increased degradation of the bonding strength by the influence of humidity. In comparison to the laser pre-treated specimens by the usage of adhesive promoter the initial bonding strength doesn't change significantly but the degradation of the bonding strength increases by influence of humidity. Thus, the strength after exposure to water is even much lower.

Concerning the long-time exposure to 80°C deionised water the laser pre-treated specimens offer superior resistance against moisture. Apart from a marginally decrease of the bonding strength at the beginning of the exposure to hot water the bonding strength retain a high level constantly.

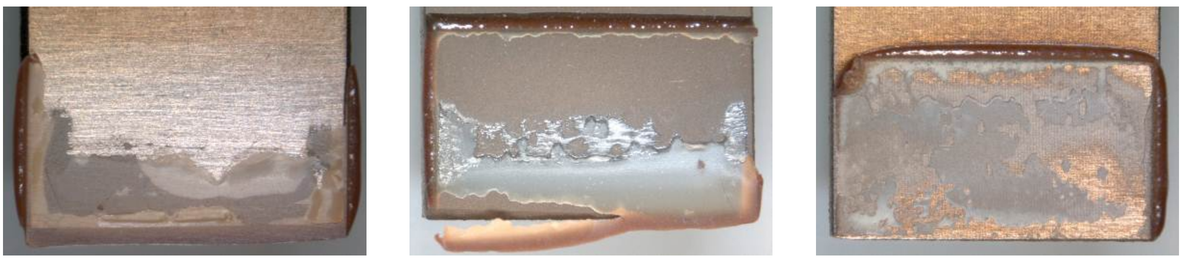
4.2 Failure analysis

Figure 7a-c show the fracture surface of the physical treated lap shear samples at the initial status. Figure 8a-c show the fracture surface of the physical lap shear samples after exposure to hot deionised water.



(a) (b) (c)

Figure 7. Fracture surface of ground (a), grit blasted (b), and laser treated lap shear specimens (c) at initial state



(a) (b) (c)

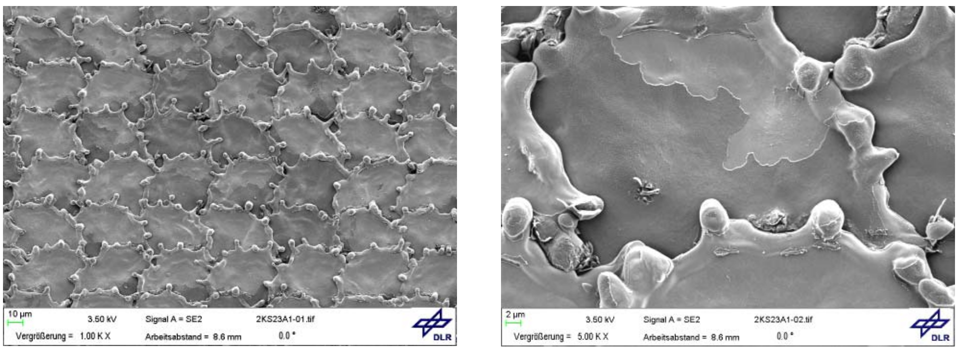
Figure 8. Fracture surface of ground (a), grit blasted (b), and laser treated lap shear specimens after exposure to deionised water

At the initial status the grit blasted and laser treated samples offer a higher magnitude of cohesive fracture and higher values of initial bonding strength than that of the ground samples. The grit blasted and laser treated samples offer a higher magnitude of surface roughness than that of the ground samples. Thus, increased surface roughness causes a higher magnitude of mechanical interlocking of polymer to the roughened surface, a higher content of cohesive fracture and thus higher values of initial bonding strength. The ground samples not only offer a lower magnitude of cohesive fracture and bonding strength at the initial state but also after exposure to water. Although the grit blasted and laser treated samples offer increased surface roughness the magnitude of cohesive fracture and as well as the bonding strength of the laser treated samples are two times higher than that of the grit blasted samples. That indicates that not only the magnitude of surface roughness but also the kind of surface roughness plays an important role. In comparison to the grit blasted samples the surface of laser treated samples exhibit cups and border strips without any sharp edges. On the one hand surface roughness causes mechanical interlocking and enhanced initial bonding strength. On the other hand it causes stress peaks at the interface during cooling and correspondingly increased degradation of the initial bonding strength by influence of humidity.

Figures 9a-c show the fracture surface of the anodised lap shear samples at the initial state. A loss of the interference colour at the fracture surface is observable. The fracture surfaces of the anodised samples were investigated by means of Scanning Electron Microscope (SEM). Independent of the used electrolyte all anodised specimens fail in the same way. As an example of the samples anodised in 1M H_2SO_4 the result will be described. The figures 10a-b show SEM images of the discoloured fracture surface. The discoloured fracture surface exhibits removed and remaining oxide layer which indicates that the failure occurred partly at the titanium – oxide interface. The figures 11a-b show the SEM images of the PEEK surface. Oxides adhere partly on the PEEK surface which indicates that the oxide layer is removed by the PEEK. A high fraction of oxide layer is removed by PEEK as shown in figure 11a as well. This result indicates that the adhesion between titanium oxide and PEEK is stronger than the adhesion between titanium and its oxide.

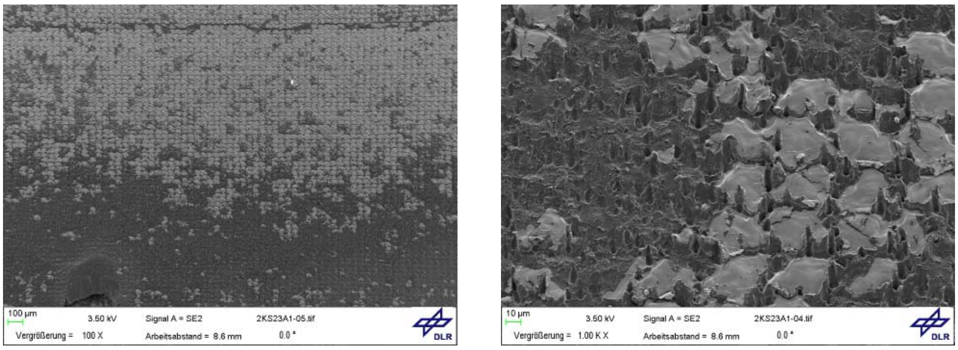
(a) (b) (c)

Figure 9. Fracture surface of samples anodised in 5M NaOH electrolyte (a), in 1M H_2SO_4 electrolyte (b), and in 1M H_3PO_4 electrolyte (c) at the initial state



(a) (b)

Figure10. SEM images of discolored fracture surface of anodised specimens in 1M H_2SO_4 electrolyte at the initial state



(a) (b)

Figure 11. SEM images of PEEK surface of anodised specimens in 1M H_2SO_4 electrolyte at the initial state

Figures 12 a-c show the fracture surface of the anodised lap shear tests after exposure to water. In comparison to the samples which were tested at the initial status there is no loss of interference colour at the fracture surface. That indicates that the oxide – PEEK interface is weakened by humidity and that the failure occurred at the oxide – PEEK interface.

(a) (b) (c)

Figure 12. Fracture surface of samples anodised in 5M NaOH electrolyte (a), in 1M H2SO4 electrolyte (b), and in 1M H3PO4 electrolyte (c) after exposure to 80°C deionised water

Figures 13 a-c show the fracture surface of laser pre-treated lap shear tests at the initial status and after long-time exposure to 80°C deionised water. The fracture surfaces offer a high magnitude of cohesive fracture at the initial status as well as after long-time exposure. The observed high content of cohesive fracture after long-time exposure fits to the results of the lap shear tests which are described in chapter 4.1. In comparison to unexposed samples (figure 13a) the long-time exposed samples (figure 13c) exhibit a clearly defined borderline between the fracture surface (metallic colour) and the area out of the fracture surface (blue colour). The blue (interference) colour which arose during the exposure to water indicates an oxide growth onto the laser pre-treated laser surface. In contrast to that the fracture surface exhibits no interference colour. Thus, the laser pre-treated surface acts likely as a moisture barrier.

(a) (b) (c)

Figure 13. Fracture surface of laser treated surface at the initial state (a) and after exposure to 80°C deionized water of 7 days (b) and 17 days (c)

5 Conclusion

Concerning the physical pre-treatment the process of laser pre-treatment offers the highest initial bonding strength and the highest magnitude of humidity resistance even after long-time exposure to hot water. The enhanced titanium – PEEK interface properties are induced by both the magnitude and the kind of surface roughness. In comparison to wet grinding and grit blasting the process of laser pre-treatment offers the highest degree of automation. Thus, it is appropriate to the series production of Fibre Metal Laminates. Since laser treated titanium surfaces don't require subsequently cleaning steps Fibre Metal Laminates can be produced with low cycle times. In future works the improved adhesion between titanium and PEEK and their resistance against humidity will be investigated in more detail.

In comparison to the laser pre-treatment the process of anodisation leads to reduced initial bonding strength and reduced humidity resistance. The declined properties of the titanium – PEEK interface are induced by the created oxide layer. In comparison to the laser pre-treatment the usage of adhesion promoter causes high values of initial bonding strength but reduced humidity resistance. The subsequent process of anodisation and the subsequent usage of adhesion promoters, respectively don't enhance the titanium – PEEK interface properties. Thus, they don't need to be investigated in more detail.

References

[1] DIN EN 1465, Adhesives - Determination of tensile lap-shear strength of rigid-to-rigid bonded assemblies (1994)
[2] Material data sheet of Dow Corning® Z-6106 Silane (2004)
[3] Material data sheet of DuPont™ Tyzor® AA-105 (2008)