Materials Science Engineering, Symposium B6 - Hybrid Structures

The stability of different titanium-PEEK interfaces against water

K. Schulze\textsuperscript{a*}, J. Hausmann\textsuperscript{a}, B. Wielage\textsuperscript{b}

\textsuperscript{a}German Aerospace Center (DLR), Institute of Materials Research, 51147 Cologne, Germany
\textsuperscript{b}Chemnitz University of Technology, Institute of Materials Science and Engineering (IWW), 09107 Chemnitz, Germany

Abstract

Fibre Metal Laminates (FML) consisting of alternating stacked layers of polymer matrix composites and metallic foils are considered for structures with high fracture toughness and good impact resistance in aeronautic applications. The properties of thermoplastic Fibre Metal Laminates composed of titanium and carbon fibre reinforced polyetheretherketone (Ti/CF-PEEK laminates) are under investigation at DLR. 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 specimens were prepared and partly exposed to hot water (80°C). 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 because of the magnitude and kind of surface roughness. Concerning the chemo-physical pre-treatment, the anodization offers reduced initial bonding strength and reduced humidity resistance caused by the created oxide layer. Concerning the chemical pre-treatment, the usage of adhesion promoter causes enhanced initial bonding strength but also reduced humidity resistance.

© 2013 The Authors. Published by Elsevier Ltd. Open access under CC BY-NC-ND license.
Selection and peer-review under responsibility of Conference organizers (MSE-Symposium B6).

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

* Corresponding author. Tel.: +49 (0) 2203 601-3160; fax: +49 (0) 2203 696480.
E-mail address: karola.schulze@dlr.de
**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_0$</td>
<td>bonding strength before ageing</td>
</tr>
<tr>
<td>$\tau_{aged}$</td>
<td>bonding strength after ageing</td>
</tr>
</tbody>
</table>

### 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 aeronautical applications. They combine the advantages of polymer matrix composites, e.g. high specific stiffness and strength and the advantages of the metal, e.g. isotropic properties, electrically conductive and superior bearing capabilities. In comparison to GLARE® (Glass fibre reinforced aluminium), carbon fibre reinforced polymers combined with titanium foils offer higher strength and stiffness. When using thermoplastics for the matrix, further advantages such as formability, weldability and environmental friendliness arise. Thermoplastic Fibre Metal Laminates composed of titanium and carbon fibre reinforced polyetheretherketone (Ti/CF-PEEK laminates) are under investigation.

![Fig. 1. Composition of Fibre Metal Laminates](image)

However, the degradation of the bonding strength between the PEEK matrix and titanium is an issue. Especially humidity is a critical factor for the ageing of Ti/CF-PEEK laminates. Therefore, the main objective of this investigation is to improve the long-term behaviour and resistance against humidity of the PEEK - titanium interface by various pre-treatments of titanium layers.

### 2. Materials and processing

The geometry of the lap shear specimens was chosen on the basis of the German standard DIN EN 1465 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, the adherent has an area of 5 mm x 10 mm. 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.
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 ageing in hot water.

3.1. Surface pre-treatment

The main 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 with SiC (P320) sandpaper. 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. Alumina (180-250 μm) was used as abrasive material during the grit blasting process at a pressure of 0.8 bar and a working distance of 80 mm.

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 56 μm and an energy density of 8.61 J/cm². Thereby, a reproducible surface structure including welding beads was 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. During the process of laser treatment energy was induced into the surface and gave an activation of this. Thus, the surface energy was improved. The lap shear samples were made of the laser treated titanium plates.

![Image](image1.png)

![Image](image2.png)

![Image](image3.png)

Fig. 4. SEM image of laser treated titanium surfaces anodized in 5M NaOH electrolyte (a), in 1M H₂SO₄ electrolyte (b), and in 1M H₃PO₄ electrolyte (c)

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. Ingram and Ramani, 1997 show improved long-term behavior of adhesively bonded titanium (Ti-6Al-4V) and polyetherketoneetherketoneketone (PEKEKK) by previous grit blasting and sodium hydroxide anodisation (SHA) of titanium. Sharma, 1992 investigate anodic oxide coatings on Ti-6Al-4V obtained by anodisation in sulphuric acid. He demonstrated the stability of the anodic oxide coating on titanium against humidity,
repetitive heating and thermal cycling. For this investigation, laser treated titanium plates (best physical pre-treatment) were anodised in 5M NaOH (15V for 10 minutes), in 1M H₂SO₄ (40V for 3 minutes) and in 1M H₃PO₄ (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.

Fig. 5. Molecule structure of glycidoxypropyltrimethoxysilane according to DowCorning® Z-6106 (a) and condensed polysiloxane on titanium surface (b) according to Habenicht, 2009 and Matinlinna et al., 2004

Fig. 6. Molecule structure of titanium acetylacetone according to Tyzor® AA-105 (a) and their chemical bond to titanium surface according to Bieleman, 2008 (b)

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 and titanium acetylacetone of DuPontTM Tyzor® AA-105 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 EN 1465 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 before ageing and three specimens were tested after exposure to 80°C deionized water for 72 hours (accelerated ageing) to determine the moisture resistance. The determined shear stress is assumed as equivalent to the bonding strength between titanium and PEEK.

4. Results

4.1. Lap shear experiment

The determined bonding strength of physical, chemo-physical and chemical treated lap shear specimens before and after ageing are summed up on table 1. The moisture resistance of physical, chemo-physical and chemical treated lap shear specimens, calculated according to equation (1), is summed up in figure 7.

\[
\text{Moisture resistance} = \frac{\tau_{\text{aged}}}{\tau_{\text{o}}} \cdot 100\%
\]  

(1)

The process of laser pre-treatment causes the highest bonding strength after ageing and the highest moisture resistance. In comparison to the laser treated specimens, the anodised specimens exhibit decreased bonding strength before and after ageing. In addition, the anodised lap shear specimens show decreased moisture resistance. In comparison to the laser pre-treated specimens, the bonding strength of the laser pre-treated specimens with an additional adhesive promoter treatment doesn’t change significantly before ageing. Yet, the moisture resistance decreases and the strength after ageing is even much lower.

Table 1: Bonding strength of the different surface pre-treatments before and after ageing

<table>
<thead>
<tr>
<th>Surface pre-treatment</th>
<th>Bonding strength before ageing $\tau_0$ [MPa]</th>
<th>Bonding strength after ageing $\tau_{\text{aged}}$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground</td>
<td>$50,21 \pm 6,85$</td>
<td>$18,44 \pm 0,84$</td>
</tr>
<tr>
<td>Grit blasted</td>
<td>$70,23 \pm 4,30$</td>
<td>$30,56 \pm 3,96$</td>
</tr>
<tr>
<td>Laser-treated</td>
<td>$77,42 \pm 1,38$</td>
<td>$62,27 \pm 10,19$</td>
</tr>
<tr>
<td>Anodized (NaOH)</td>
<td>$54,61 \pm 3,39$</td>
<td>$39,72 \pm 5,40$</td>
</tr>
<tr>
<td>Anodized (H$_3$PO$_4$)</td>
<td>$39,70 \pm 4,93$</td>
<td>$9,03 \pm 3,01$</td>
</tr>
<tr>
<td>Anodized (H$_2$SO$_4$)</td>
<td>$43,44 \pm 6,06$</td>
<td>$7,24 \pm 1,96$</td>
</tr>
<tr>
<td>Adhesive promoter (0.2vol% TAA)</td>
<td>$78,70 \pm 3,70$</td>
<td>$25,99 \pm 0,81$</td>
</tr>
<tr>
<td>Adhesive promoter (0.02vol% TAA)</td>
<td>$75,27 \pm 2,26$</td>
<td>$57,31 \pm 1,27$</td>
</tr>
<tr>
<td>Adhesive promoter (0.2vol% Silane)</td>
<td>$88,70 \pm 1,43$</td>
<td>$51,59 \pm 1,60$</td>
</tr>
<tr>
<td>Adhesive promoter (0.02vol% Silane)</td>
<td>$74,03 \pm 2,65$</td>
<td>$50,13 \pm 4,95$</td>
</tr>
</tbody>
</table>

Figure 8 shows the moisture resistance of the laser treated specimens (most promising pre-treatment) as a function of long-time exposure to 80°C deionised water. 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 strengths retain a high level constantly.

Fig. 7. Comparison of the moisture resistance of different titanium-PEEK interfaces in % (calculated by equation 1)

Fig. 8. Moisture resistance of laser pre-treated lap specimen in %
4.2. Failure Analysis

Figure 9a-c show the fracture surface of the physical treated lap shear samples before ageing. Figure 10a-c show the fracture surface of the physical lap shear samples after ageing.

Before ageing, 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 before ageing. The ground samples not only offer a lower magnitude of cohesive fracture and bonding strength before ageing but also after ageing. 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 both, that not only the magnitude of surface roughness but also the kind of surface roughness and that the surface energy 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. The altered surface energy improves both the surface wettability and the formation of attractive intermolecular forces at the titanium – PEEK interface.
Figures 11a-c show the fracture surface of the anodised lap shear samples before ageing. 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$_2$SO$_4$, the result will be described. The figures 12a-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.

![Fig. 11. Fracture surface of samples anodised in 5M NaOH electrolyte (a), in 1M H$_2$SO$_4$ electrolyte (b), and in 1M H$_3$PO$_4$ electrolyte (c) before ageing](image1)

![Fig. 12. SEM images of discoloured fracture surface of anodised specimens in 1M H$_2$SO$_4$ electrolyte before ageing](image2)
The figures 13a-b show the SEM images of the PEEK surface. Oxides adhere partly on the PEEK surface which indicates that the titanium-oxide layer is removed by the PEEK. A high fraction of oxide layer is removed by PEEK as shown in figure 13a as well. This result indicates that the adhesion between PEEK and titanium oxide is stronger than the adhesion between titanium and its oxide. Figures 14 a-c show the fracture surface of the anodised lap shear tests after ageing. 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 titanium-oxide PEK interface is weakened by humidity and that the failure occurred at the titanium-oxide PEK interface.

Figures 15 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 up to 28 days. The fracture surfaces offer a high magnitude of cohesive fracture before ageing 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 15a), the long-time exposed samples (figure 15b and 15c) 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 surface. In contrast to that, the fracture surface exhibits no interference colour. Thus, the laser pre-treated surface acts likely as a moisture barrier.
5. Conclusions

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 kind of surface roughness and the surface energy. 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 at low cycle times. In future works, the improved adhesion between titanium and PEEK and their resistance against humidity will be investigated more detailed.

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 more detailed.

References

Bieleman, J., 2008. Additives for coatings, Wiley-VCH, p.120
DIN EN 1465:2009 Adhesives - Determination of tensile lap-shear strength of rigid-to-rigid bonded assemblies
Ingram, C., Ramani, K., 1997. The effect of sodium hydroxide anodization on the durability of poly(etherketoneetherketoneketone)
Material data sheet of Dow Corning® Z-6106 Silane, 2004
  vinyltrisopropoxysilane blend and tris(3-trimethoxysilylpropyl)isocyanurate on the shear bond strength of composite resin to
titanium metal, Dental Materials 20(9), p. 804-813