Investigation of a Self-Organized TiO_2 Layer as Pre-treatment for Structural Bonding of Titanium

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ABSTRACT

Due to the increasing amount of composite materials used in the aircraft structure, new corrosion concepts have to be developed. In order to avoid galvanic corrosion, more titanium has to be used in aerospace (14 wt.-% in Airbus 350 XWB). To increase the efficiency and performance of the aircraft the connection between composite materials and titanium should be realized by adhesive bonding. However, it is well-known in aerospace industry that titanium materials exhibit critical issues in regard to long-term stable adhesion. Reflecting this, the surface treatment is the most important step to ensure durable bonds.

Within this work, a TiO_2-nanotube layer is formed by anodization. This anodization process is used as a pre-treatment for structural bonding of the titanium alloy Ti6Al4V. For reference, an alkaline etching process (Turco 5578) and a second anodizing procedure in an acidic anodizing electrolyte (sulphuric acid) are employed to evaluate the TiO_2-nanotube structure.

Using the TiO_2-nanotube process, the surface area could be enlarged by a factor of approximately 20, compared to the initial surface after alkaline etching. The mechanical tests (wedge test) show that the area enlargement due to the anodizing processes enhances the bonding durability in hot/wet conditions. The improved adhesion properties after the anodizing pre-treatment can be related to the contributions from the mechanical interlocking of the adhesive in porous oxide layers and the chemical and physical interactions between the hydroxylated surface and the epoxy film adhesive.

Using the TiO_2-nanotube anodizing at 5 V and 15 V, respectively, a high resistance against crack growth can be achieved. In comparison to the other treatments (sulphuric acid anodizing, alkaline etching) the TiO_2-nanotube anodizing leads to the lowest crack growth under hydrothermal conditions.

The investigations show that in principle the TiO_2-nanotubes can be used to achieve a long-term stable adhesion on Ti6Al4V even at combined mechanical and hydrothermal loads. Moreover the results confirm that the TiO_2-nanotubes can significantly improve the paint adhesion in comparison to sulphuric acid anodizing.

INTRODUCTION

In the aerospace industry new design concepts offering weight savings are high in demand. In the recent generation of aircraft (e. g. Airbus 350 XWB, Boeing 787), composite materials have shown new perspectives in terms of structural efficiency and performance. Due to the increasing amount of composite materials, new corrosion concepts have to be developed. Composite materials with carbon fibres can induce galvanic corrosion when attached to an aluminium structure. In order to avoid galvanic corrosion of aluminium in combination with carbon fibre reinforced materials, titanium alloys are used in aerospace. Titanium immediately forms a few nanometer thick oxide layer that protects the underlying bulk from further oxidation [1]. Once the oxide layer is damaged, it re-forms in the presence of oxygen or water [2, 3]. Therefore, the amount of titanium material employed rises to ensure galvanic compatibility to composite materials with carbon fibres.
It is known in literature that titanium surfaces exhibit some issues in regard to long-term stable adhesion [4]. One example is the loss of paint adhesion on titanium rivet heads [5]. In order to improve the adhesion between an adherend and an organic system surface pre-treatments are necessary. Therefore various treatments have been developed in the last years [6-8]. The resultant adhesion is mainly influenced by the following aspects:

- Production of contamination free surface
- Increasing the surface area by a nanoporous oxide layer
- Achieving a stable oxide layer with functional groups [7, 9]

Often wet-chemical treatments are employed to fulfil these aspects. Chemical treatments are often described as multi-step procedures. To remove organic contaminations usually alkaline cleaner or organic solvents are used. To generate a fresh oxide layers a chemical etching is mostly employed. For titanium either alkaline (e.g. based on sodium hydroxid) or acidic (e.g. based on hydrofluoric acid) solution could be applied. Such etching steps are also

discussed as a pre-treatment prior bonding [7]. However, these treatments give adequate dry bonding strength but poor durability and hot-wet conditions [7]. Mostly etching steps are applied prior anodizing. The composition and the morphology after the anodizing strongly depends on the electrolyte composition. For structural bonding of titanium chromic acid anodizing is used. After this process a surface with a significant amount of micro- and nanoroughness is formed. It is stated by Baldan [7] that chromic acid anodization leads to remarkable bond durability. However, the chemical stability of fresh oxide layers in moisture could also have an influence on the adhesion strength. Investigations on chromic acid anodized oxide layers in hot/wet conditions exhibit a transition from amorphous to crystalline titanium oxide [10, 11]. Moreover the use of chrome based processes is restricted by law due to environmental concerns. Therefore dry pre-treatments like plasma or laser have been investigated as pre-treatment for titanium. It is reported by Kurtovic et al. that the laser treatment of titanium leads to a nanostructured oxide layer which leads to long-term stable bonds [12]. Also plasma treatments could be employed to enhance the bond durability on titanium [9]. The use of dry pre-treatments for complex parts is challenging. For this reason this work focuses on the development and investigation of wet-chemical treatments. The literature overview shows that the resultant morphology strongly influences the durability of titanium bonds.
According to Venables et al. [10] and Liu et al. [13], there is a major correlation of surface morphology and durability of adhesive bonds. Venables classifies pre-treatments in three groups according to their influence on surface morphology [10].

Group 1: no micro / no macro-roughness
Group 2: macro-roughness / no or low micro-roughness
Group 3: micro-roughness

Pre-treatments like chromic acid anodizing lead to higher durability due to their high degree of micro roughness (Group 3) [11]. According to Group 3, the increase in surface area leads to an increased mechanical interlocking of the adhesive to the adherend. Meanwhile a Group 4 is introduced which represents treatments which lead to a nanostructure [9].
Reflecting this, new anodizing procedures should generate a nanostructured surface using environmental friendly ingredients. In the recent years the formation of self-organized porous structures on titanium is described in literature. Under optimized electrochemical circumstances self-organized TiO_2-nanotubes can be formed. In literature miscellaneous applications are described (e. g. gas sensing or biomedical) [14, 15]. At the moment no results exist, if the TiO_2-nanotubes can be used to improve the adhesion on titanium.
The TiO_2-nanotubes can be achieved by using fluoride based electrolytes and suitable anodization conditions. Ordered TiO_2-nanotubes can be formed,

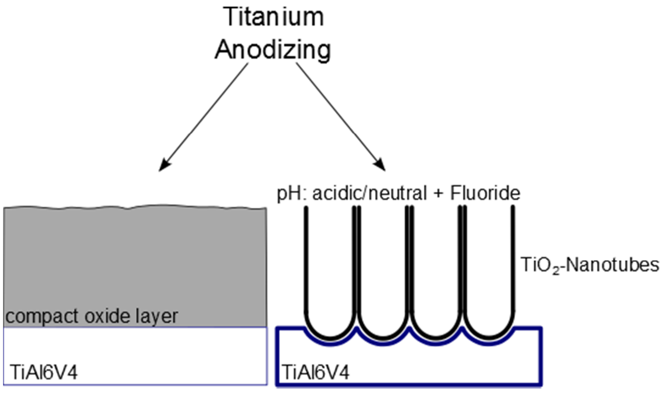


Figure 1: Schematic drawings of the oxide layer after anodizing. Depending on the electrolyte and the parameters the oxide layer can either be compact or nanostructured (acc. to [14])

as schematically shown in Figure 1. Highly ordered vertically oriented TiO_2-nanotubes are produced by using localised chemical dissolution (fluorine ions) with controlled field-assisted oxidation and dissolution reactions [14, 16]. The arrays of TiO_2-nanotubes are of great interest due to their high surface-to-volume ratio [17]
Aim of this work is to evaluate the applicability of TiO_2-nanotube anodizing as pre-treatment for titanium alloys. Within this study the morphology is investigated by means of SEM and resultant surface chemistry is inspected using XPS. For evaluation of the adhesion properties of the TiO_2-nanotube layer a bonding test (wedge test) and a paint adhesion test (cross cut test) was carried out.

Experimental

Material

For this study the titanium alloy Ti6Al4V was used. For the investigations concerning the bonding behaviour rectangular specimens with the dimensions of 150 x 150 mm and a thickness of 2.0 mm were employed. The paint adhesion was evaluated on titanium countersunk rivets with a diameter of 9 mm.

Surface preparation

All titanium samples were cleaned with the alkaline cleaner P3 Almeco 18, 30 g/l (Henkel AG & Co. KGaA, Dusseldorf) at 70 °C ± 3 for 15 min.
Subsequently, the samples were etched using the commercial etching bath Turco 5578 (Henkel AG & Co. KGaA, Dusseldorf) with a concentration of 500 g/l at 95 ± 3 for 5 min. The alkaline etching is also used as reference process. Therefore, some samples were not

submitted to anodizing procedure. Prior the sulphuric acid anodizing an acidic etching was conducted. After alkaline cleaning these samples were immersed in a solution containing 300 g/l nitric acid and 20 g/l hydrofluoric acid.

TiO_2-nanotube Anodizing

The TiO_2-nanotube anodizing was carried out in a 200 l bath. The anodizing was performed in electrolytes consisting of ammonium sulphate and ammonium fluoride using a three-electrode configuration with Ti6Al4V as cathode. The process was carried out with a voltage of 15 V and 5 V for 30 min at 25 °C.

Sulphuric Acid Anodizing (SAA)

As reference process the sulphuric acid anodizing process was investigated. The anodizing solution consists out of sulphuric acid in water with 200 g/l. The parts were fully immersed in solution. For anodizing a three-electrode configuration with stainless steel as cathode was used. The samples were anodized at 15 V for 15 min at 25 °C. The initial current density was approximately 0.2 A/dm².

Bonding

The adhesive used for the titanium joints was an epoxy based FM 73 supplied by Cytec Engineering Materials Inc. USA. The samples were bonded at 120 °C for 90 min in an autoclave at a pressure of 2.5 bar.

Painting

To observe the paint adhesion properties of the different surface treatments the countersunk rivets were installed in an aluminium plate and subsequently painted with a chromate free external epoxy primer system. Prior painting all rivets are cleaned with isopropanol.

Test methods

In order to evaluate the bonding strength und a combined mechanical and hydrothermal load the wedge test according to the German standard DIN 65448 was employed. The test was carried out in a climate chamber at 95 % rh and 50 °C. The initial crack length (a_0) and the crack propagation were measured. The rate at which the crack grows was microscopically monitored.
The paint adhesion was assessed using the cross cut test according to ISO 2409. Using this test the adhesion can be classified from GT 0, which represents a good adhesion, to GT 5 which characterizes a poor adhesion. The adhesion was measured in the initial state after painting and after 336 h immersion in deionized water at room temperature.

Surface characterization

X-ray photoelectron spectroscopy (XPS)

The chemical composition of the surfaces was obtained by using a Quantum 2000 spectrophotometer (Physical Electronics) equipped with an Al Kα (1486.6 eV) monochromatic source at base pressures less than 10^{-6} Pa with a 45° take-off angle. The spectra were obtained using a spot size of 200 µm, for the survey spectra a pass energy of 117.4 eV was used. Peaks were fitted (Gaussian/Lorentzian curves) after background subtraction (Shirley type) by using the MultiPak 8.2 software.

Scanning electron microscope (SEM)

The resultant morphology and the fracture surfaces were characterised by SEM, using a JEOL JSM-6320 SEM.

Results

The SEM pictures (Figure 2 - Figure 5) show the various morphologies obtained after the surface pre-treatments

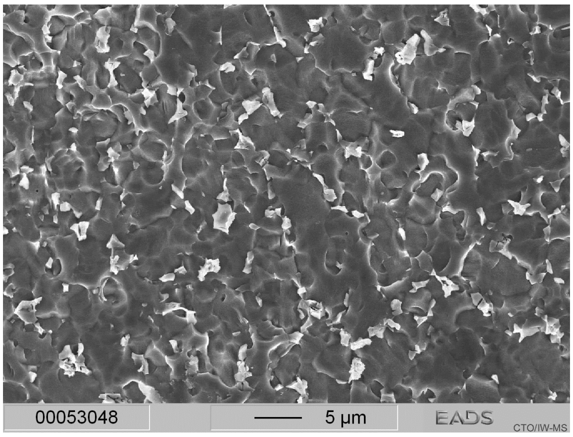


Figure 2: SEM micrograph after the treatment with Turco 5578 (Top view)

etching and anodizing. The titanium surface which is only treated by using Turco 5578 exhibits large amount of macro roughness (Figure 2).

The alkaline etching causes an oxide layer thickness between 20 nm and 35 nm. Only at higher magnifications a small amount of micro structure is visible. Similar to the morphology after the alkaline etching the surfaces after the sulphuric acid anodizing exhibit mainly macro structure (Figure 3) with a non-uniform growth of the oxide layer.

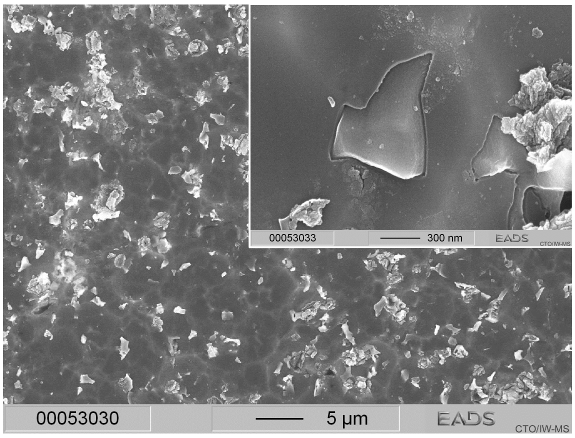


Figure 3: SEM micrograph after the sulphuric acid anodizing (Top view)

At higher magnification hardly any nanostructure could be observed. Using the SAA treatment for titanium an unstructured and approximately 50-70 nm thick oxide layer can be formed on the surface.
The anodizing of titanium in the ammonium sulphate and ammonium fluoride electrolyte at 15 V leads to a 300 – 350 nm thick oxide layer that features pore cell size of ≈ 40 – 50 nm (Figure 4). The reduction of voltage, down to 5 V, leads to a reduction in pore cell size (21.1 ± 3.5 nm). As shown in Figure 5 the anodizing at 5 V generates an oxide layer thickness of 181.5 ± 12.3 nm. The titanium substrate material is homogenously covered with this oxide layer. It is obviously that obtained TiO_2-nanotubes exhibit a large amount of nano roughness and hence an area enlargement.

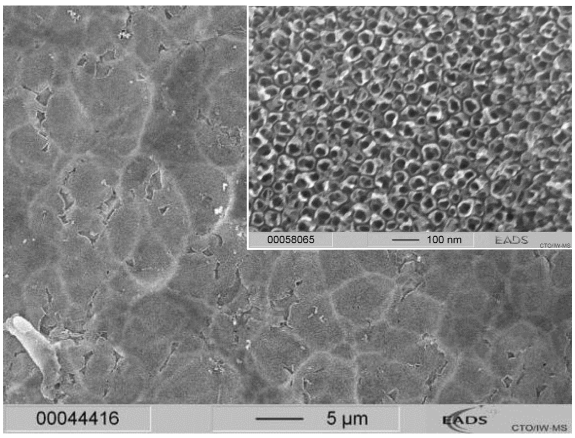


Figure 4: SEM micrograph after the TiO_2-nanotube anodizing at 15 V (Top view)

The calculated area enlargement for 5 V respectively 15 V lies in comparison to an alkaline etched surface between 19 – 20 times. This result features that due to the TiO_2-nanotube anodizing the mechanical and chemical interaction between the oxide layer and an organic system could be significantly increased.

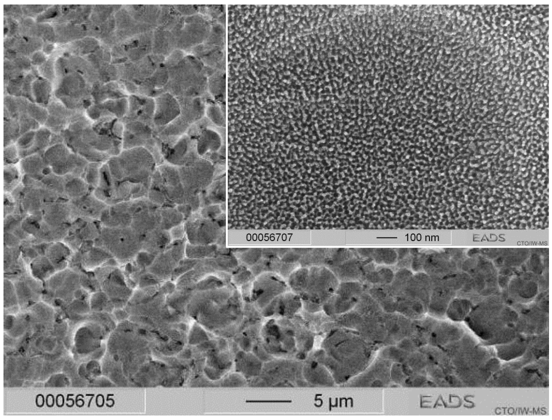


Figure 5: SEM micrograph after the TiO_2-nanotube anodizing at 5 V (Top view)

The chemical composition of the different surfaces was investigated by XPS. The results are summarized in Table 1.

Table 1: Chemical composition of the surfaces after the different pre-treatment processes

Elements		Ti	Al	V	O	C	Others
Turco 5578	[At.-%]	12.0	5.4	1.2	46.2	28.4	6.8
SAA	[At.-%]	15.2	2.4	0.9	48.5	31.0	2.0
TiO_2-Nanotube Anodizing (5 V/15 V)	[At.-%]	19.2	2.6	1.0	55.0	15.9	6.3
Indentification		TiO_2/Hydroxide	Al_2O_3	V_2O_5	Oxide/ Hydroxide/ Contaminations	Contaminations	-

According to Table 1 all surfaces feature independent from the pre-treatment process the alloying elements of the TI6Al4V alloy used. Most likely the different alloying elements (Ti, Al, V) are present at the surface as oxides or hydroxides. All processes lead to a high level of oxygen on the surface which can be attributed to the formed oxides, hydroxides or contaminations. Table 1 shows that the TiO_2-nanotube anodizing causes the highest amount of oxygen at the surface due to the low carbon content at the surface (15.9 at.-%). Using alkaline etching (Turco 5578) or SAA a carbon content of approximately 30 at.-% could be measured. This carbon is most likely caused by contaminations. The detected contamination on the surfaces after alkaline etching (Turco 5578) or SAA could also affect the adhesion properties.
The analysis of the XPS results shows that the amount of oxygen after the TiO_2-nanotube anodizing is higher in comparison to the other treatments. Hence, the amount

of functional groups (e .g. hydroxyl groups) which could interact with an organic system is higher. Moreover due to surface enlargement after the TiO_2-nanotube anodizing, more functional groups are available in nanostructure (s. Figure 6)

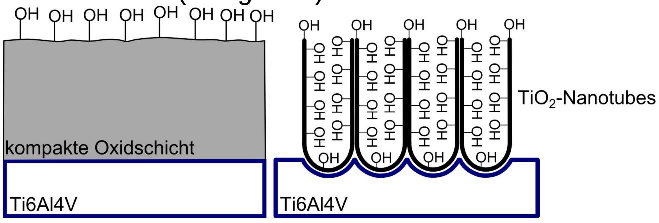


Figure 6: Comparison between the amount of hydroxyl groups on a compact oxide layer and after TiO_2-Nanotube anodizing

The long-term durability was assessed using wedge test. All treatments lead to a comparable initial crack length and bonding strength, respectively. The initial crack length(a_o) was for all treatments between 24 and 28 mm. Due to this, for all joints the initial failure loci was similar. The failure was initiated in a cohesive manner in the middle of the adhesive. After introduction of the joints into the climate chamber the failure was transferred within 75 min close to the titanium surface. The results indicate that the TiO_2 nanotube anodization, independent from the applied voltage, leads to good resistance against crack growth. After 1000 h exposure to 95 % rh and 50°C the titanium samples treated with TiO_2-nanotube anodizing process at 15 V feature a crack length of 30.3 mm ± 2.2. The TiO_2-nanotube process at 5 V leads to comparable results after 1000 h exposure. The samples feature an average crack length of 31.0 mm ± 1.8. The joints treated with Turco 5578 show a crack length of 72.8 mm ± 4.3.

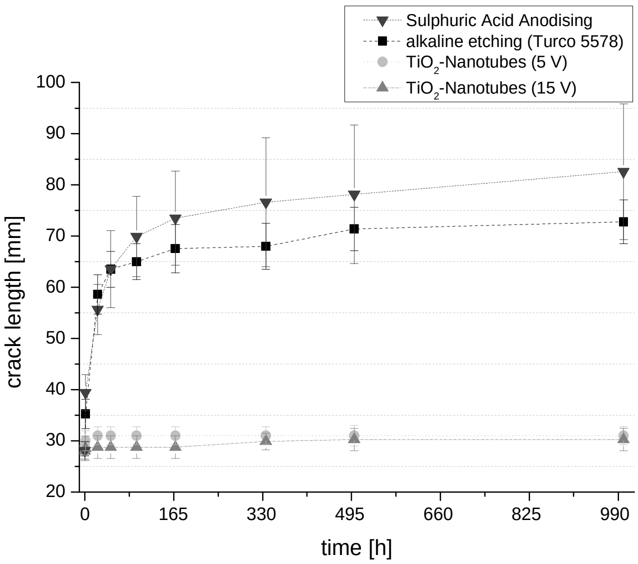


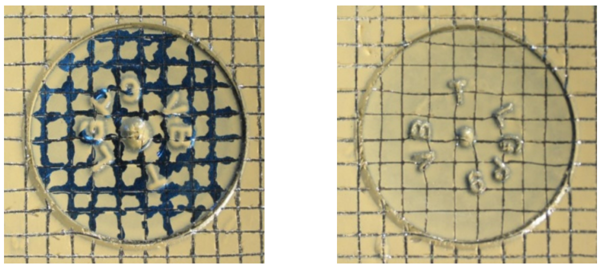
Figure 7: Comparison between the amount of hydroxyl groups on a compact oxide layer and after TiO_2-Nanotube anodizing

The worst results feature the samples treated with the SAA process. After 1000 h exposure the samples exhibit a crack length of 82.6 mm ± 13.2. The analysis of the fracture surfaces show, that the samples treated with the alkaline etching or the SAA process feature interfacial failure. Samples pre-treated with the TiO_2-nanotube anodizing show cohesive failure. However the failure loci are transferred close to oxide layer interface. The wedge test results show that using the TiO_2-nanotube anodizing a high resistance against crack growth under hot/wet conditions can be achieved. The difference in growth can be related to the obtained morphologies after pre-treatments. The high degree of nano roughness after TiO_2-nanotube anodizing led to good durability compared to macro roughness or micro roughness after Turco 5578 treatment or the SAA process.

One potential application of the TiO_2-nanotube anodizing could be the pre-treatment of titanium rivets prior painting to overcome the adhesion problems (see Figure 8)

Figure 8: Titanium countersunk rivets treated with the TiO_2-nanotube anodizing

Therefore the paint adhesion is measured on rivet heads pre-treated with SAA or TiO_2-nanotube anodizing at 15 V. In

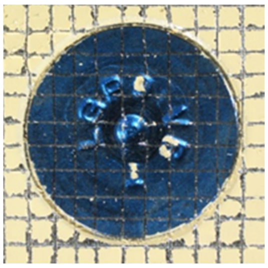


a) b)

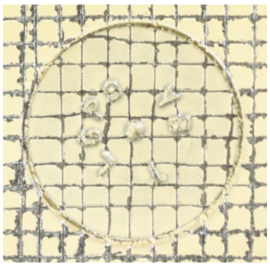
Figure 9: Paint adhesion on titanium rivet heads in the initial state without ageing after cross cut test acc. ISO 2409; a) Titanium countersunk rivet treated with SAA process; b) Titanium countersunk rivet treated with the TiO_2-nanotube anodizing at 15 V

Already in the initial state the sulphuric acid anodizing leads to inadequate paint adhesion (see Figure 9 a). According to ISO 2409 the adhesion can be classified with GT3. In contrast to the rivets treated with the SAA process no loss of paint adhesion could be detected after the pre-treatment with the TiO_2-nanotube anodizing.

After immersion in deionized water for 336 h the paint adhesion on rivets treated with the SAA process degrades. As shown in Figure 10 a) the rivets feature a complete loss of paint adhesion (GT 5).



a)



b)

Figure 10: Paint adhesion on titanium rivet heads after 336 h immersion in water after cross cut test acc. ISO 2409; a) Titanium countersunk rivet treated with SAA process; b) Titanium countersunk rivet treated with the TiO_2-nanotube anodizing at 15 V

Using the TiO_2-nanotube anodizing at 15 V the paint adhesion can be significantly improved (Figure 10 b). Even after immersion in water the samples show a good paint adhesion which can be classified with GT 0 – 1. Likewise to the results after bonding test the good paint adhesion after the TiO_2-nanotube anodizing can be attributed to the optimized morphology and surface chemistry. Paints or adhesives are able to penetrate the nanoporous structure and this enables an enhanced mechanical and chemical anchoring.

CONCLUSION

It has been demonstrated that the anodizing of TiO_2-nanotubes could be a promising treatment for titanium to enhance the adhesion.
Using the TiO_2-nanotube anodizing, the surface area could be enlarged, compared to the surfaces after the alkaline etching or the SAA process. The mechanical test (wedge test) shows that the area enlargement due to the TiO_2-nanotube anodizing process enhances the bonding durability in hot/wet conditions. The results obtained, confirm the correlation between the morphology and the bond strength. The improved adhesion properties after the TiO_2-nanotube anodizing can be related to the contributions from the mechanical interlocking of the adhesive in porous oxide layers and the chemical and physical interactions between the hydroxylated surface and the epoxy film adhesive. The results show that the good adhesion properties after TiO_2-nanotube anodizing are independent broad ranges independent from the film thickness and the pore cell size.
Moreover it is possible to apply the TiO_2-nanotube anodizing to titanium rivets. The paint adhesion results demonstrate that not only the bonding strength could be enhanced, but also the paint adhesion.
The investigations show that in principle the TiO_2-nanotubes can be used to achieve a long-term stable adhesion on Ti6Al4V even at combined mechanical and hydrothermal load.

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Investigation of a Self-Organized TiO_2 Layer as Pre-treatment for Structural Bonding of Titanium

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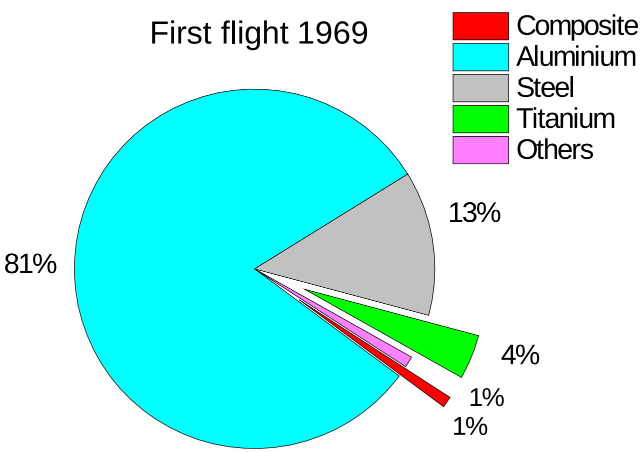
Material breakdown


[Source: Website Boeing]


[Source: Website Airbus]

Boeing 747

First flight 1969

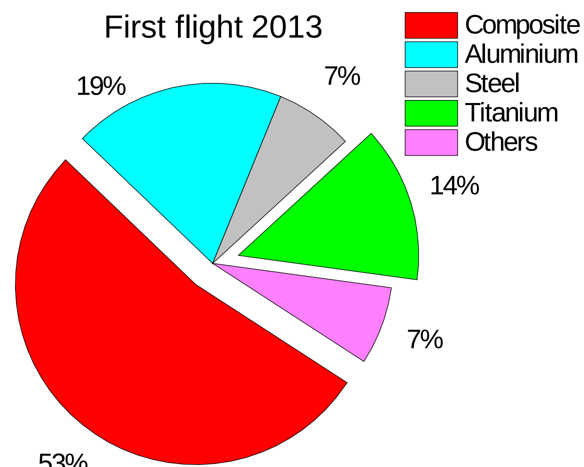


All values in wt%

Source: Starke*2

A 350 XWB

First flight 2013



All values in wt%

Source: Gaudin*1

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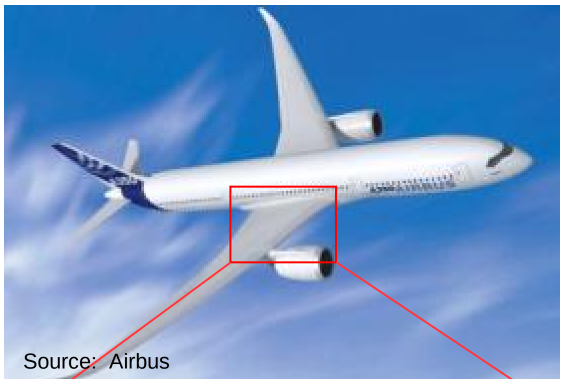
*1 J. Gaudin, AIAA CASI MAO Conference, Victoria, September 2008

*2 E.A. Starke et al. / Prog. Aerospace Sci. 32, (1996), 131-172.

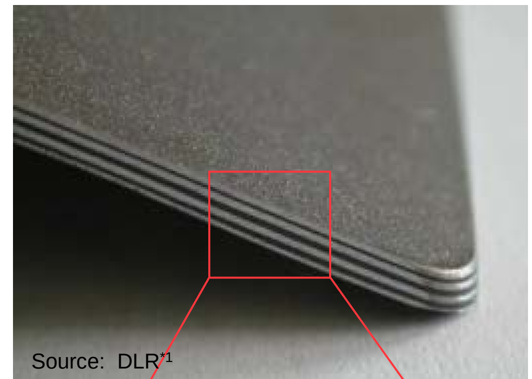
The Issue – Loss of Adhesion on Titanium

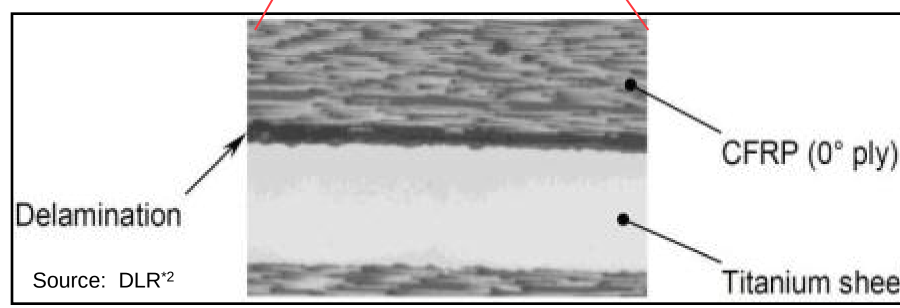
Paint Adhesion



Rivet rash on titanium rivet heads

Bonding





Delamination of fiber metal laminates (Ti/CFRP)

Long-term stable adhesion on Titanium is known to be critical!

[*1]: Hausmann, J., Hybride Werkstoffe und Strukturen für die Luftfahrt, Werkstoff Kolloquium 2006.
[*2]: Wilmes, H., CFK/Titan, ein Hybridwerkstoff zur verbesserten Kopplung von Faserverbundstrukturen, Congress Intelligente Leichtbau Systeme 2002.

Objectives

- Creation of fundamental understanding about the long-term durability and degradation mechanisms
- Overcoming of limitations for structural bonding of Titanium by proving durable and long-term stable surfaces
- Ensure long-term stable adhesion
- Provide cost efficient and environmentally benign processes for series production

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Enabler for future CFRP-Titanium hybrid structural concepts offering weight saving

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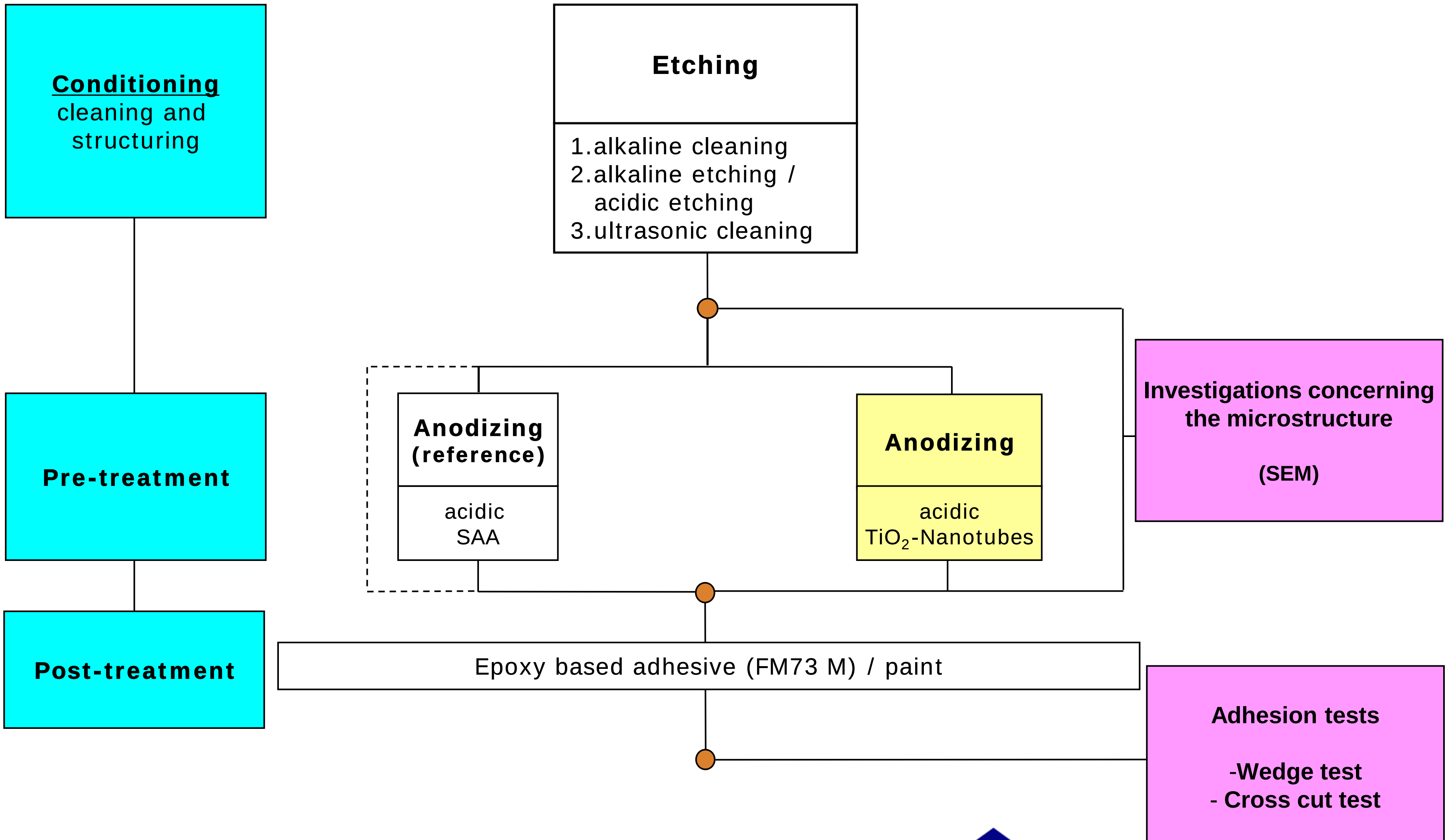
Work flow – pre-treatment



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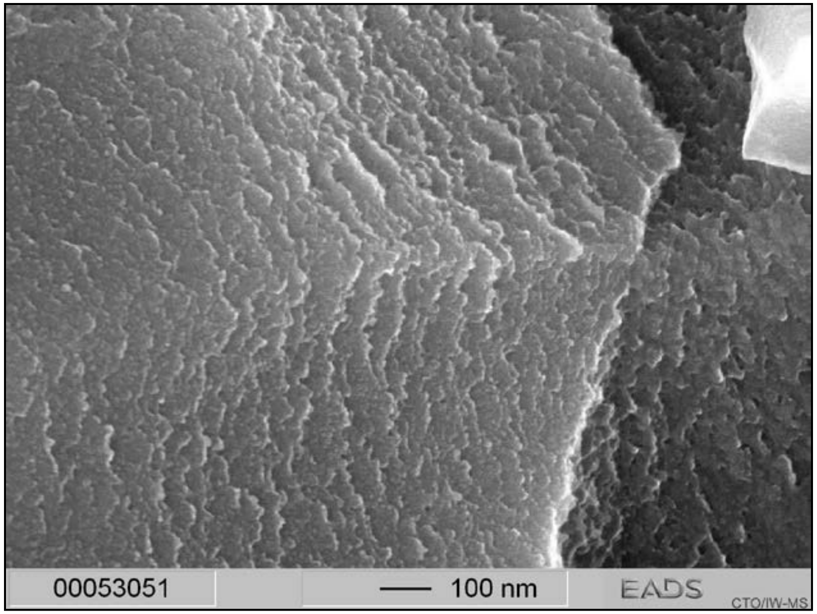
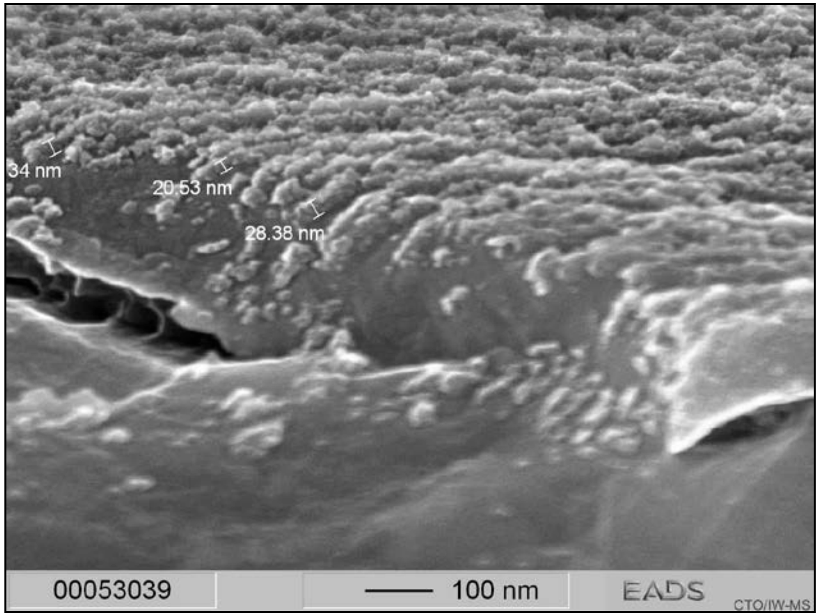
SEM- Investigations - Morphology

Titanium surface after the alkaline etching (Turco 5578):





- The Titanium surface which is only treated by using Turco 5578 exhibit large amount of macro roughness
- After the alkaline etching the oxide layer is ≈ 20 – 30 nm thick
- Only at higher magnifications a small amount of micro structure can be detected

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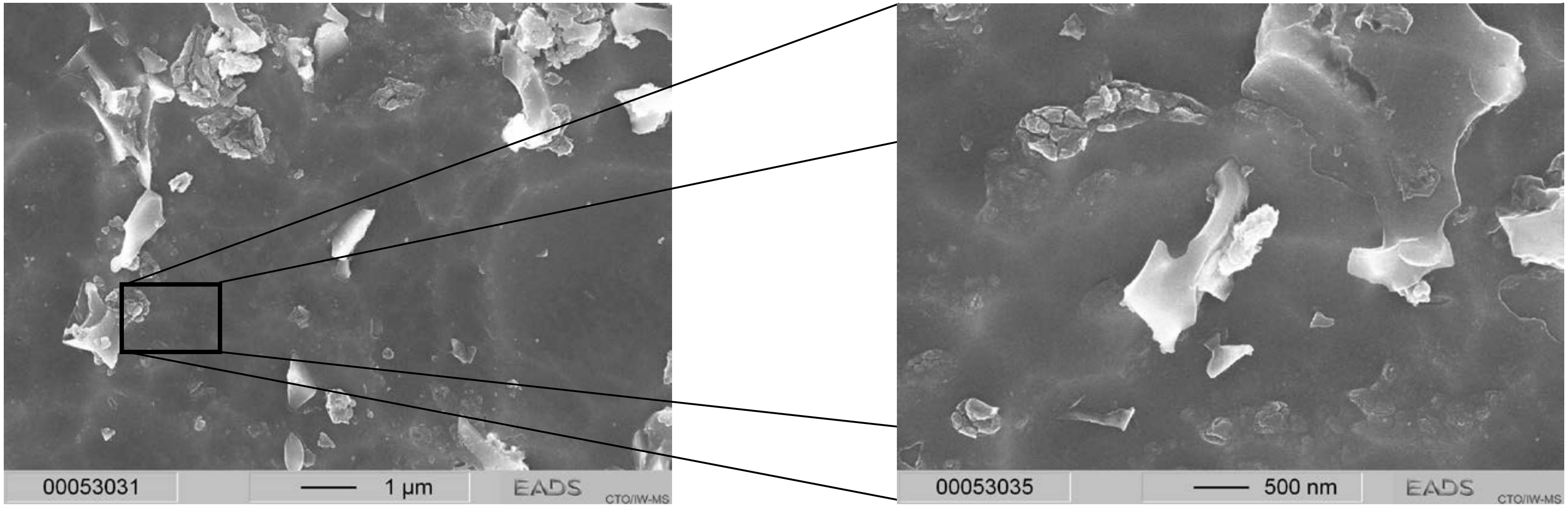
SEM - Morphology



- The SAA-Process applied cause app. 50 nm thick oxide layer without any micro structure
- Due to the smooth surface only a few chemical and mechanical interactions with a paint are possible
- Partially a non-uniform growing of the oxide layer could be detected

  → Probably the indifferent growing can be related to the α + β alloy (Ti6Al4V) used

How can be nanostructured oxide layer realized ?

Anodizing in acidic electrolytes:

Anode reaction:

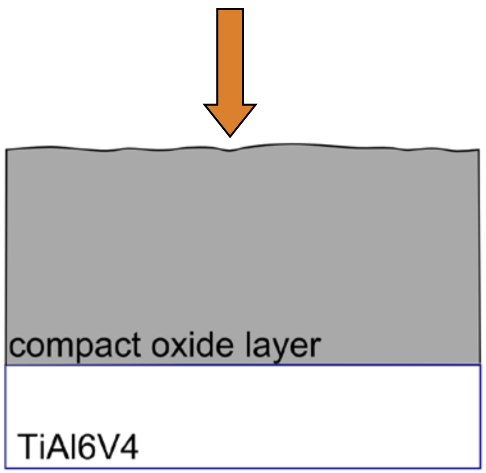
$$Ti \longleftrightarrow Ti^{4+} + 4e^{-}$$

Cathode reaction:

$$2H_2O + 4e^{-} \longleftrightarrow 2O^{2-} + 2H_2 \uparrow$$

Complete reaction:

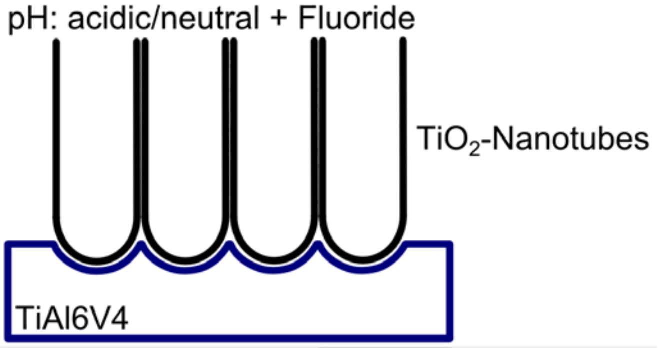
$$Ti + 2H_2O \longleftrightarrow TiO_2 + 2H_2$$



Anodizing in acidic electrolytes with complexing agents:

Due to the complexing agents in the electrolyte the compact oxide layer can partially be dissolved:

$$TiO_2 + 6F^{-} \xrightarrow{H^{+}} [TiF_6]^{2-} + 2H_2O$$



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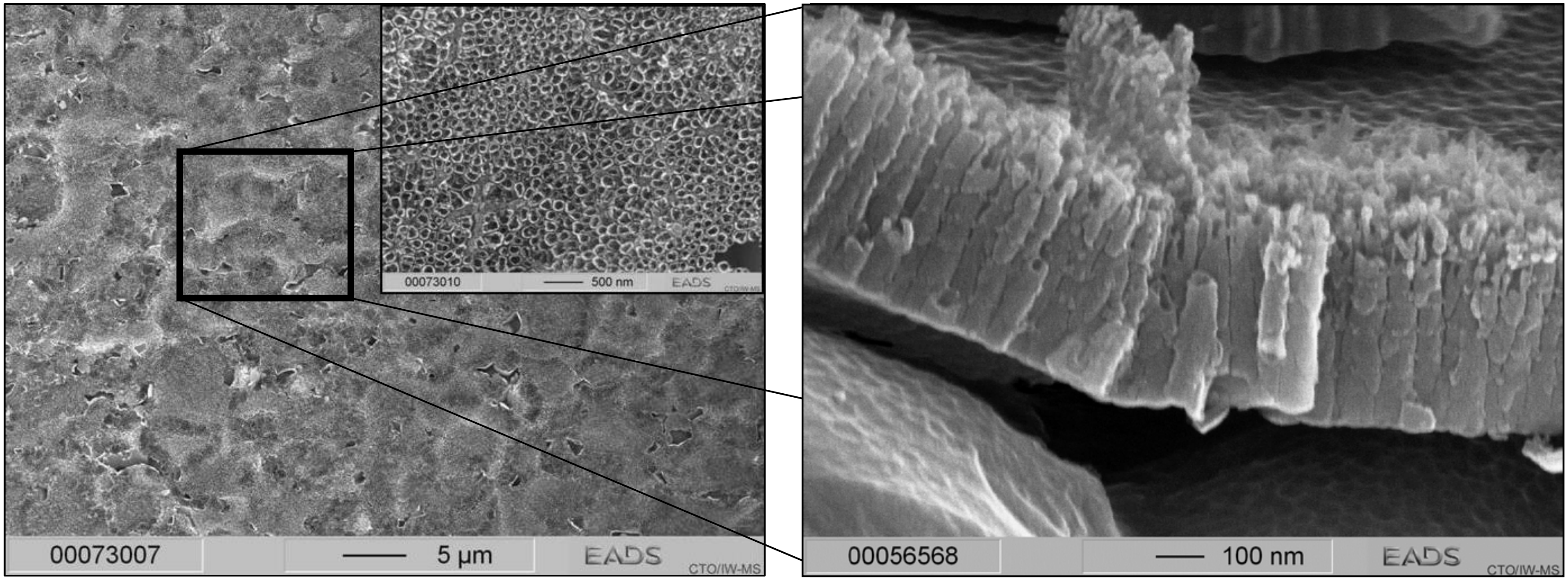
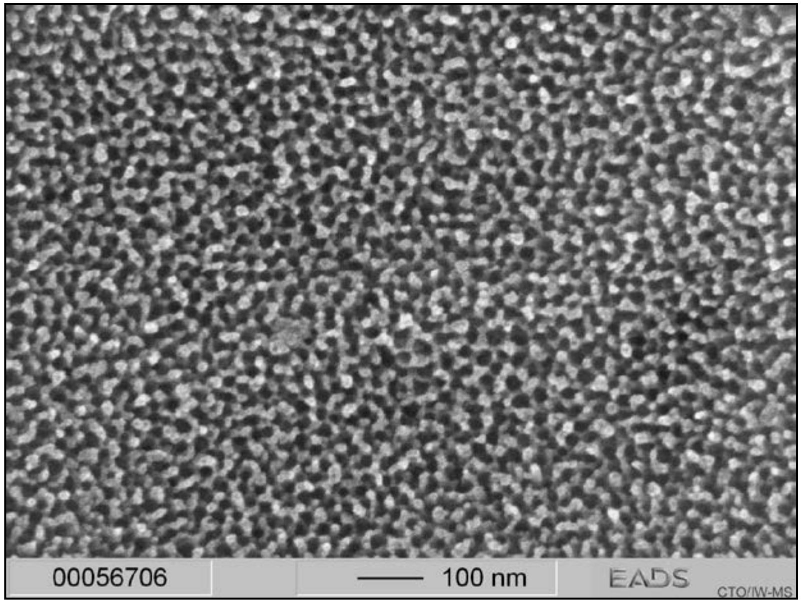
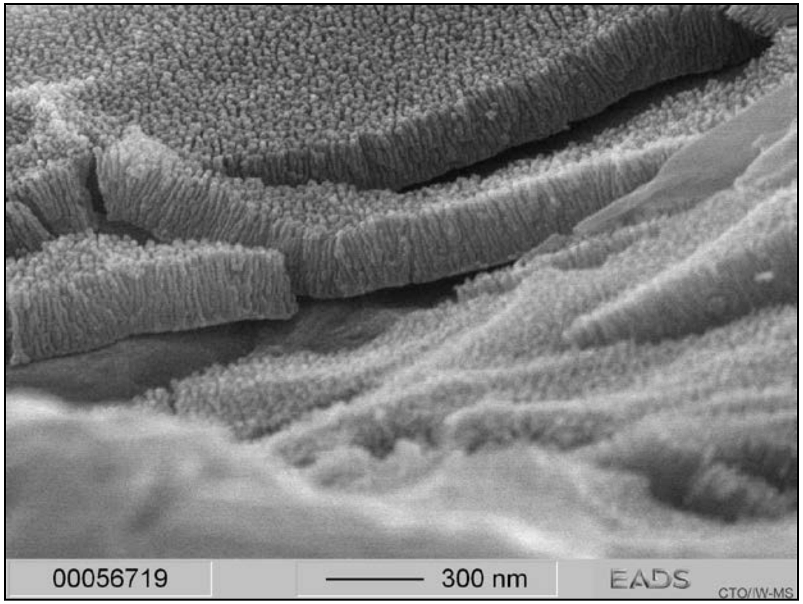
SEM- Investigations - Morphology



- The anodizing of titanium in the ammonium sulphate and ammonium fluoride electrolyte at 15 V leads to a 300 – 400 nm thick oxide layer
- The oxide layer features a pore cell size of ≈ 40 – 50 nm
- The TiO_2-Nanotube anodizing leads to a large amount of nano roughness

SEM- Investigations - Morphology





- The anodizing of titanium in the ammonium sulphate and ammonium fluoride electrolyte at 5 V leads to a 180 – 220 nm thick oxide layer
- The oxide layer features a pore cell size of ≈ 20 – 25 nm
- The TiO_2-Nanotube anodizing leads to a large amount of nano-roughness

XPS – Investigations

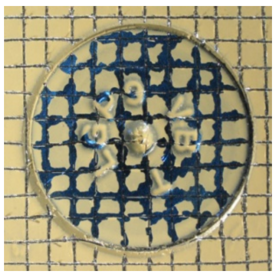
Elements		Ti	Al	V	O	C	Others
Turco 5578	[At.-%]	12.0	5.4	1.2	46.2	28.4	6.8
SAA	[At.-%]	15.2	2.4	0.9	48.5	31.0	2.0
TiO_2-Nanotube Anodizing (5 V/15 V)	[At.-%]	19.2	2.6	1.0	55.0	15.9	6.3
Identification		TiO_2/ Hydroxide	Al_2O_3	V_2O_5	Oxide/ Hydroxide/ Contaminations	Contaminations	-

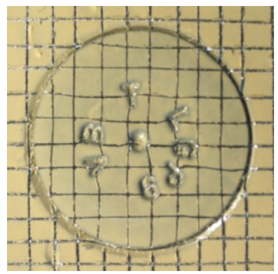
- The XPS-Investigations show that surfaces feature different oxides (TiO_2; Al_2O_3; V_2O_5) which could be related to the Ti6Al4V alloy used
- Using alkaline etching (Turco 5578) or SAA a carbon content of approximately 30 at.-% could be measured → This carbon is most likely caused by contaminations
- The detected contaminations on the surfaces after alkaline etching (Turco 5578) or SAA could also affect the adhesion properties
- After the TiO_2-Nanotube anodizing the amount of functional groups (e .g. hydroxyl groups) which could interact with an organic system is higher

Test – Paint adhesion

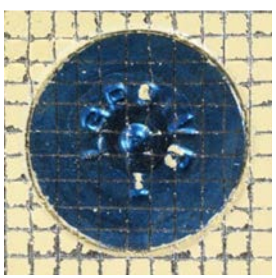
Cross cut test acc. to ISO 2409:

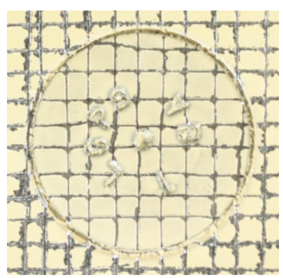
Initial state (0 h):





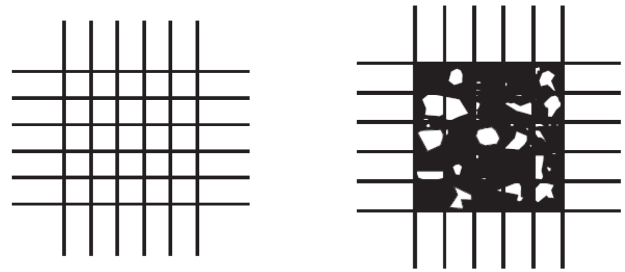
After water immersion (336 h):





Classification of area removed

GT 0 GT 5

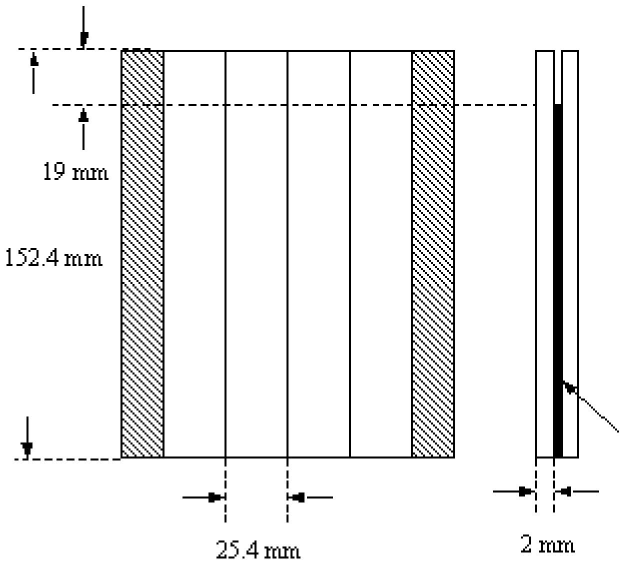


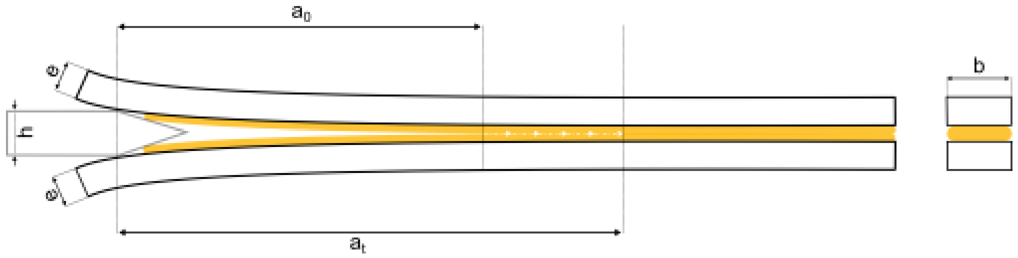
- Already in the initial state the sulphuric acid anodizing leads to inadequate paint adhesion
- After 336 h water immersion the SAA process causes a complete loss of paint adhesion
- Using the TiO_2-Nanotube anodizing at 15 V the paint adhesion can significantly improved

Results- Wedgetest (DIN 65448)

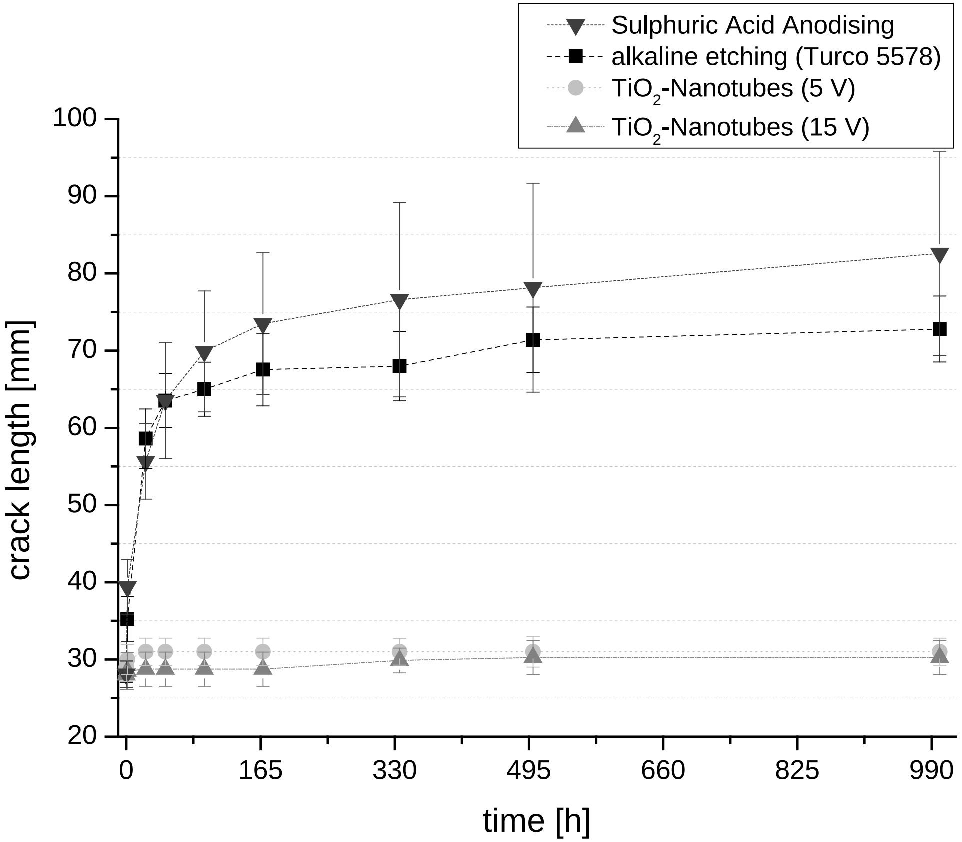
Parameter:

- Temperature: 50 °C
- Humidity: 95 %
- Inspection: 75 min, 24 h, 48 h, 96 h, 168 h, 336 h, 500 h, 1000 h





Wedge-Test (DIN 65448) - Titanium



- The Turco 5578 pre-treatment for titanium leads to a high crack propagation within hot/wet conditions (72.8 mm ± 4.3).
- After 1000 h exposure the samples treated with SAA exhibit a crack length of 82.6 mm ± 13.2
- After 1000 h exposure to 95 % rh and 50°C the titanium samples treated with TiO_2-Nanotube anodizing process at 15 V feature a crack length of 30.3 mm ± 2.2
- The TiO_2-Nanotube process at 5 V leads to comparable results after 1000 h exposure

The TiO_2-Nanotubes can be used to achieve a long-term stable adhesion on Ti6Al4V !

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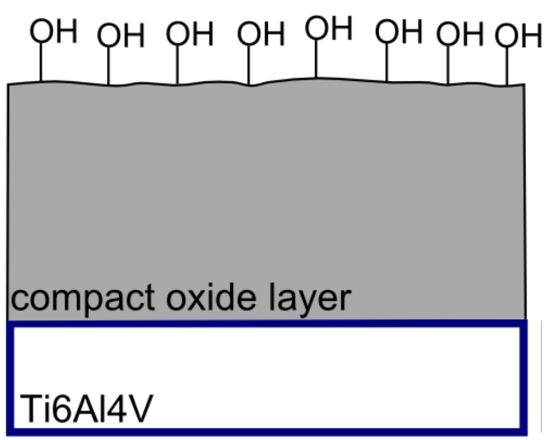
How does the morphology influences the adhesion?

What is the advantage of a nanostructured surface ?

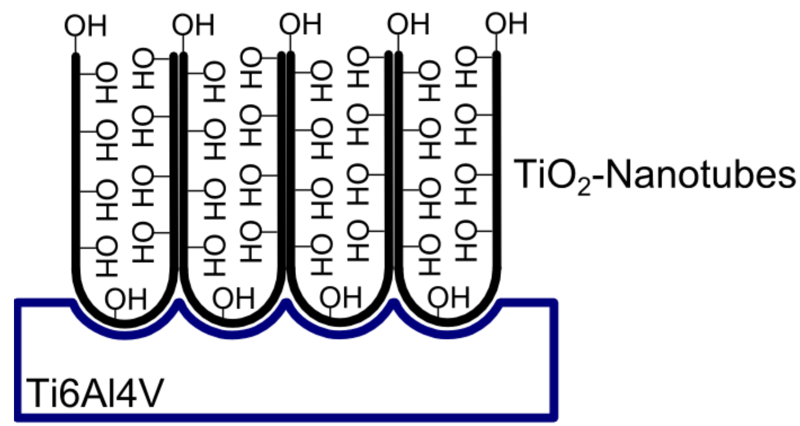
- Organic systems can infiltrate a nanostructured surface and this causes a mechanical anchoring
- Due to the surface enlargement after the TiO_2-Nanotube anodizing, more functional groups are available in nanostructure

Alkaline etching / SAA



Area enlargement: 1.4 times

TiO_2-Nanotube Anodizing



Area enlargement: 20 times

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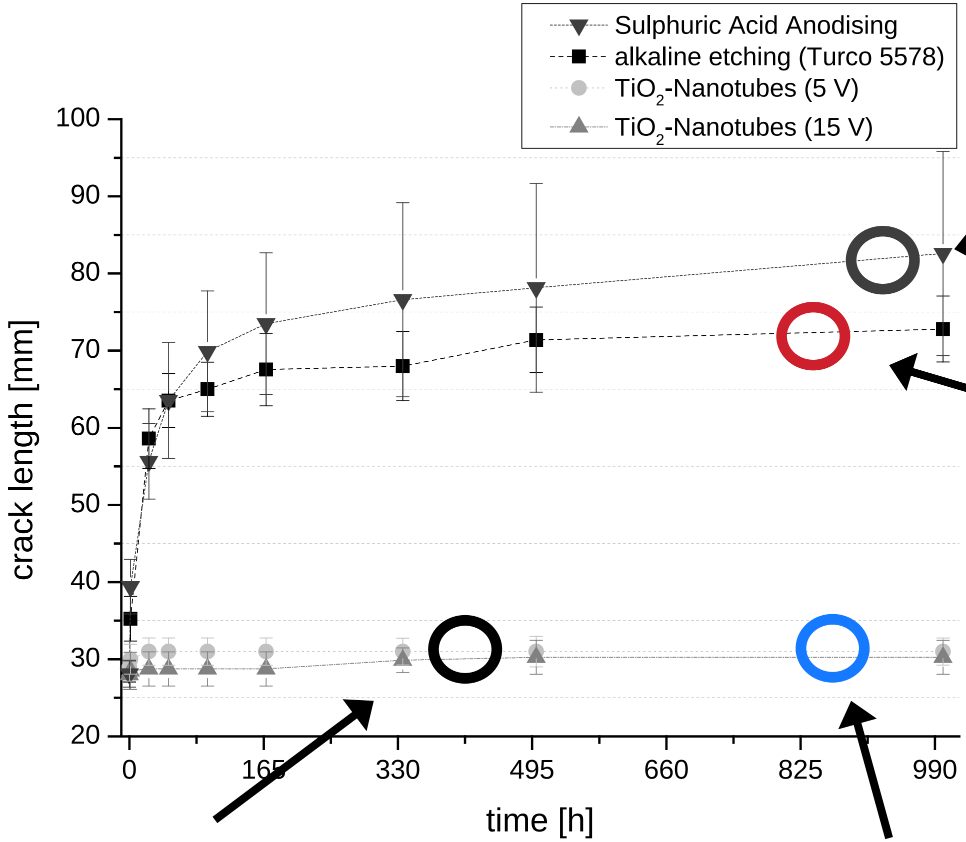
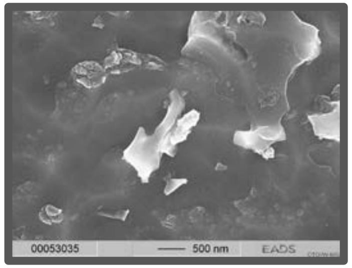
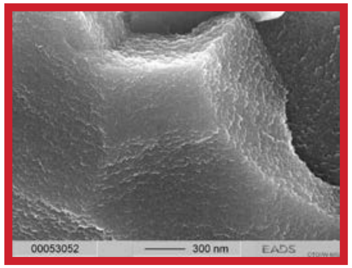
How does the morphology influence the bonding results?

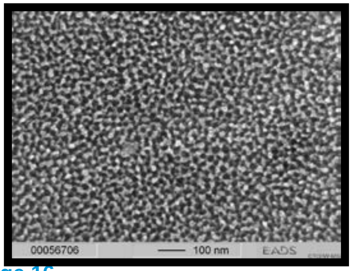




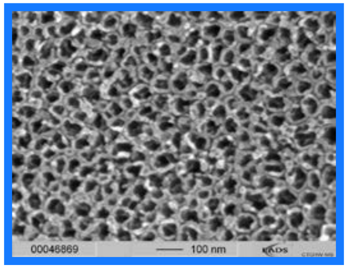
Microstructure / no nanostructure



Microstructure / no nanostructure



Microstructure / nanostructure



Microstructure / nanostructure

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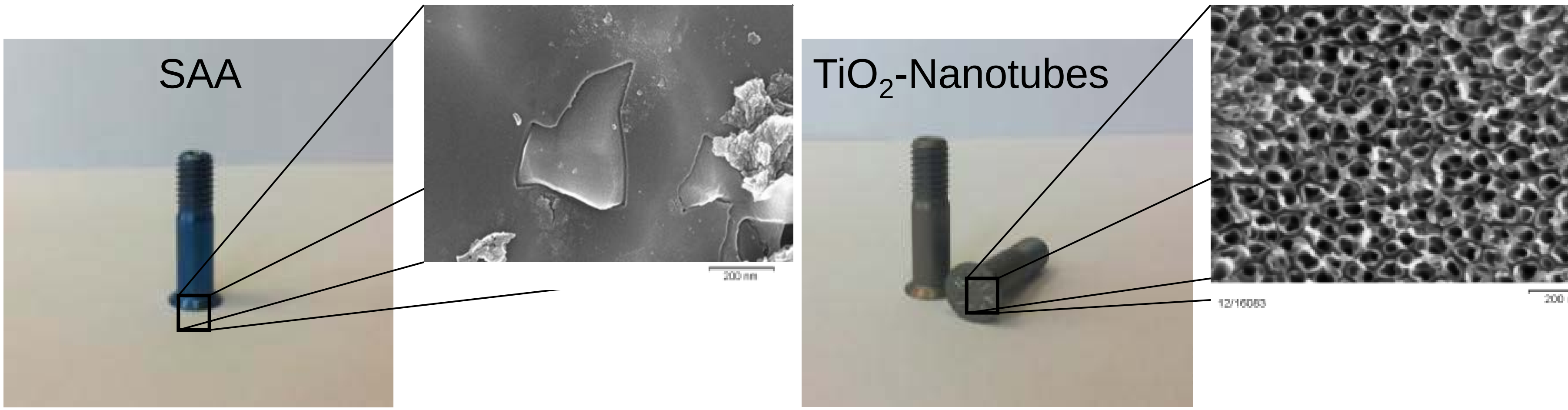
The way forward … potential applications

Anodizing of Titanium rivets:



- Using the standard process for Titanium rivets a blue coloured rivet with compact oxide layer can be achieved
- With the new pre-treatment for Titanium parts a nano-porous oxide layer is generated which leads to a mechanical and chemical interlocking of paints in the nanotubes

Summary

What are the main drivers for a long-term stable adhesion on Titanium?

- **The morphology extremely influences the resultant bonding strength**

  → Best adhesion results are obtained with porous morphology structures below 100 nm

- **Using the TiO_2-Nanotube anodizing the paint adhesion can significantly improved in comparison to sulphuric acid anodizing**

  → The new anodizing procedure will help to overcome the rivet rash phenomena

- **The bonding test show**

  → that only alkaline etching and the SAA leads to inadequate bonding results

  → that the TiO_2-Nanotube anodizing leads to long-term stable adhesive bonds due to a chemical and mechanical anchoring in the tubes

  → that a high degree of nano-roughness enhance the bonding strength

The TiO_2-Nanotube anodizing is a promising process for pre-treatment of Titanium to enhance the adhesion !

Thank you !

Dr. Tobias Mertens

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