Euro Hybrid Materials and Structures 2014
April 10 – 11
PFH – Private University of Applied Sciences,
Stade, Germany

LASER TREATMENTS OF TITANIUM SURFACES IN DIFFERENT ATMOSPHERES FOR IMPROVED ADHESION PROPERTIES

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ABSTRACT: We present a first study on the effects of the ambient gases of a laser pre-treatment on the interface and bond strength to a thermoplastic polymer, polyetheretherketone (PEEK). The pretreatments of titanium TiAl3V2.5 surfaces were performed with a pulsed Nd:YAG laser in air, oxygen, nitrogen and argon. SEM investigations showed macro-structuring at the micron scale and superimposed fine nanostructuring. We characterized the initial and residual bond strengths by means of single-lap shear experiments prior and after degradation for 7 days in 80°C hot H_2O, respectively. The initial strengths of the surfaces laser treated in air, oxygen and nitrogen were comparable at around 77 MPa, whereas for samples pretreated in Argon slightly lower strengths of 67±6 MPa were obtained. After degradation, the absolute strength loss varied from 11% (air) to 24% (Ar). While laser treatment in reactive gases still led to comparably high strengths (~64 MPa), the pre-treatment in Ar caused a significant loss of the residual strength (52 MPa). The shear strengths and degradation results correlated with changes in the nanostructures created by the laser irradiation, which was substantially less in case of argon compared to those obtained in reactive gases. The presence of titanium oxides was detected by EDX on all four surfaces.

KEYWORDS: Adhesion, adherend, surface pre-treatment, pulsed laser, ageing, titanium grade 9, TiAl3V2.5, thermoplastic polymer, polyetheretherketone (PEEK).

1 INTRODUCTION

Chemical and structural properties of joining surfaces are a major factor determining the strength and degradation resistance of adhesive joints. Especially for thermoplastic polymers like PEEK, which are commonly considered to bond only by comparably weak physical interactions and mechanically, the surface preparation is a key factor. Several reviews have been published on the topic of surface preparations to provide good adhesion,[1-3] particularly for titanium metal and alloy surfaces.[3-7] Their focus was geared mostly towards chemically reactive, thermosetting adhesives. A lot less is known about the requirements and effects of surface pretreatments suitable for primarily or purely physically consolidating thermoplastic polymers.[8-12]

Among the known surface preparation methods, the laser ablation treatment for surface cleaning and modification with continuous-wave or pulsed lasers has lately attracted great interest from both fundamental research and industrial application. Depending on the laser parameters and the gas atmosphere, e.g. air,[13-16] O_2,[13,17] N_2,[13,17] or inert gases[13] chemically and structurally different functional films can be formed on the metal. The films, in turn, influence the bonding, solidification and crystallization of the polymers and, thus, play a role for the stability of the near-interfacial region in the polymers.

Molitor et al. found that treatments of titanium surfaces with an excimer laser affected macroscopic roughness little, but led to improved wettability and work of adhesion of epoxy resins.[15] Applying an epoxy primer immediately after laser ablation was concluded to be important for the stability of the joint.

In one of the first studies of the structural and chemical properties of the functional layers created by laser irradiation, Baburaj et al. identified micro-columnar oxide arrays, which after in situ oxidation formed clusters of submicron-sized oxide particles with micro-pores.[18] These authors proposed that the structure allowed better mechanical interlocking and wettability.

Lavisse et al. studied the chemical composition of similar laser-induced oxide layers on Ti substrates with a pulsed Nd:YAG laser.[19] For small laser fluences (< 25 J/cm^2), the layers were colorless or pale yellow. From a combination of XPS and Raman measurements, titanium oxo-carbo-nitrides were identified. At higher laser fluence, rough sample surfaces with purple and blue colorations were obtained that showed increasing formation of anatase and rutile TiO_2 in Raman experiments.

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In a more recent study performed in a highly clean and well-controlled environment of a closed XPS/laser apparatus that allowed for in situ analysis without need of sample transfers through ambient air, the effects of pulsed Nd:YAG laser exposures in nitrogen and oxygen gases on Ti substrates were studied as a function of gas pressure and laser parameters by Ohtsu et al.[17] At low N_2 pressures (< 13.3 kPa), only non-stoichiometric titanium oxide layers with small amounts of nitrogen were observed. At higher pressures, an oxo-nitride layer was formed on top of stoichiometric titanium nitride. Repetition of the laser shots promoted the formation of the oxide layer, but the oxide layer formed by laser irradiation differed from that naturally formed on stoichiometric TiN in high-purity oxygen atmosphere.

Another comparative study of laser treatment in different atmospheres carried out by Ciganovic and co-workers showed the formation of a variety of morphological features with generally increased roughness.[13] Structures formed in air or oxygen were smoother, periodical and dome-like oxides according to SEM/EDX, while the ones obtained in nitrogen were porous. A local EDX analysis of the "cone" tips of these porous structures indicated only the presence of titanium and nitrogen, suggesting that a titanium nitride was formed. Formations produced in helium atmosphere were distinctively different in the sense that micro-holes/pores and cracks dominated the surface, but also here oxides were detected.

Zimmermann et al. performed XPS and XRD investigations of oxide layers formed by a laser treatment in air for the purpose of improving the adhesion to a one-component, hot-curing epoxy-based adhesive.[16] The removal of surface contaminants as well as the formation of a nanostructured top layer exhibiting a large effective surface and nanometer roughness was observed. This functional surface consisted of a nanoporous, coral-like oxide of ca 200 nm thickness and near-TiO_2 stoichiometry after several treatment repetitions. After a single irradiation cycle, a fraction of nitrogen in an effective charge state close to a nitride on titanium was measured. XRD, however, showed only crystalline α-TiO and Ti_2O suboxide phases, suggesting that the outer TiO_2, and TiO_xN_y layers were amorphous. This is consistent with studies by del Pino, who observed crystalline TiO and Ti_2O with XRD below amorphous Ti_2O_3 and TiO_2 layers detected with Raman.[20] The laser induced oxidation leads to the presence of a surface layer with cracks but improved, hydrothermally stable adhesion properties.[16]

A related coral-like but homogeneous nano-structured oxide layer was reported by Kurtovic and co-workers, who also found a much cleaner surface after laser treatment compared to chemical processing (e.g. alkaline etching) with XPS experiments.[14] Wedge test and floating roller peeling measurements indicated that the nano-structured oxide formed allowed a better long-term stable adhesion.

A correlation between the laser fluence or ablation efficiency (duty cycle and power) and the final adhesion properties of the PETI-5 polyimide was first searched by Palmieri et al.[21] Single-lap shear experiments showed increasing strength and durability with increasing laser ablation duty cycle and power. While changes in surface chemistry were concluded to be the origin of the significant improvements in apparent shear strength below 400mW ablation power, less significant improvements occurring at higher powers were traced back to steeply increasing surface roughness. These results supported previous observations that surface roughness is a secondary factor influencing the bond strength of a lap shear specimen prepared by laser ablation less than the surface chemistry for this reactive, "pseudo-thermoplastic" resin.

Vide infra, this not only underlines the importance for a detailed analysis of the chemical, structural as well as the mechanical and degradation properties of the functional interface of the adherend, but also the need for a similarly detailed fundamental understanding of the polymer's interface region. Even in case of thermoplastic materials, the surface chemistry is a key factor that can e.g. strongly influence coordinative and ionic bonding of organic functional groups such as carbonyls, alcohols or imides common to adhesive compounds.

Previous studies by our group have shown that laser-treatments allow the formation of strong Titanium-PEEK-interfaces with high initial strengths and favorable degradation resistance against humidity.[22,23] The formation of a nano-oxide with tightly packed, vertical columnar structures of broad size distribution (0.5-1 µm length and 0.1-0.2 µm in diameter) was concluded from TEM micro-sections. TEM/EELS suggested that the core of the columns consisted of TiO and separate XPS experiments confirmed that the upper layer corresponded to TiO_2. Both micro-mechanical adhesion to this porous nanostructure and macro-mechanical bonding to undercuts and large macro-features were observed.

Fracture surfaces of single-lap shear samples evidenced primarily ductile failures in the interfacial region of the polymer, often leaving behind traces of the polymer. However, the failure occurred also in and beneath the columnar oxide layer. The mechanism of micro mechanical adhesion appeared largely unaffected at high mode I load, whereas fracture surfaces tested at high mode II load showed rather large amounts of residual PEEK within undercuts. The two mechanical interlocking mechanisms decreased by the hydrothermal aging.

In this preliminary study we focus on the mechanical shear strength achievable with laser pre-

treatment in different process gas atmospheres and the degradation properties of these so formed interfaces. We report scanning-electron investigations of these laser-formed nanoporous functional films, which show different degrees of nanostructured rough and porous ("coral-like") surfaces that are ideal for the intrusion and bonding of polymers.

2 EXPERIMENTAL DETAILS

2.1 SAMPLE MATERIALS

All investigations were carried out with the titanium alloy TiAl3V2.5 (commercial grade 9). SEM experiments were carried out on laser pre-treated surfaces of rectangular 72×10 mm^2 titanium stripes of 1.6 mm thickness. The titanium material was obtained from Timet Germany GmbH. It was polished with grade 320 SiC polishing paper and cleaned with acetone prior to laser treatment.

For the determination of the bonding strength in the lap-shear experiments, we chose the thermoplastic polymer PEEK (poly-ether ether ketone) as model adhesive compound. PEEK foil with high crystallinity (LITE TK procured from Lipp-Terler GmbH, thickness 100 µm) was cleaned in isopropanol and acetone.

The oxygen, nitrogen and Ar gases used to flush the laser cell during the pre-treatment were of purity 5.0 (99.999%).

2.2 LASER TREATMENT

The laser pre-treatment was performed with a pulsed Nd:YAG laser "CL20" (1064 nm, pulse length 110 ns, Gauss laser profile) with an average laser power of 20 Watts manufactured by Clean-Lasersysteme GmbH, Herzogenrath. The employed laser process parameters were:

- Power: 60%
- Frequency: 70 KHz
- Duty cycle: 40%
- Line distance (y): 0.03 mm
- Scan speed (x): 3000 mm/s
- Repeats: 1

An average fluence of 5.17 J/cm^2 and laser intensity of 4.7×10^7 W/cm^2 was, thus, affecting the surface. The overlap resulting from scan speed and line-distance was ca 34% in x (scanning) and ca 54% in y (transverse) direction.

Each sample was placed in a small laser-cell that was flushed with as process gas at a high flow rate for the pre-treatment. The laser beam penetrated a window transparent at 1064 nm on the top of the laser cell before impinging on the surface. After the laser treatment, the samples were removed from the cell and quickly transferred through ambient air into vacuum storage (ca 10^{-3} mbar). This accounted for the formation of surface oxides on the samples laser treated in Ar atmosphere, but did not affect the interface properties of the other samples any further. It was tested and found that samples pre-treated with the laser in air and subsequently stored on air at room temperature for 7 days did not show differences in the morphology or adhesive properties. Hence, also all kind of surface reactivity conceivable in air at room temperature (e.g. reactions of "reduced" defects like oxygen vacancies or Ti interstitials encountered in imperfect, rough/amorphous or sputtered TiO_2,[24] as well as reduced Ti ions from suboxides like Ti_2O_3 and TiO with O_2 or H_2O) is quenched very quickly after the laser treatment.

2.3 BONDING, DEGRADATION AND LAP SHEAR EXPERIMENTS

Single-lap shear samples were produced from pairs of the laser-treated titanium stripes, which were bonded together with an overlapping area of ca 10×5 mm^2 using PEEK foil with a homogeneous thickness of 100 µm (Fig. 1). The dimensions of our lap-shear samples have been derived according to German standard DIN EN 1465. This standard is convenient for the testing of adhesive bonds glued with thermosetting based adhesives.

However, the bond strength between titanium and PEEK foil is generally about three times higher compared to bonding strength between metals and thermosetting adhesives, hence leading to much higher loads and stresses for the specimen. In order to reduce stress concentrations, and avoid plastic deformations or even the failure within the titanium stripes of the lap shear specimen, the joint area was, thus, reduced.

The lap-shear samples were assembled in an appropriately formed tool with a small brass weight put right on-top (ca 35 g on each joint), to which thermocouples were attached. No additional pressure was applied during the bonding process.

The bonding was performed in ambient air in a laboratory furnace (model P330 by Nabertherm) under temperature control with type K thermocouples touching the top metal strip above the bonding end.

With a roughly linear heating rate of 3.5 K/s the sample setup was annealed to 668±5 K (395±5°C). The temperature was held for 15 minutes and before passively cooling back to room temperature in the furnace (at ca 0.5 K/min down to ca 130°C, thereafter at ca 2 K/min).

For each laser atmosphere, minimal statistical sets of 3 samples were prepared for initial strength characterization and 3 for degradation experiments. The degradation of the adhesive interface was carried out in 353K (80°C) hot deionized H_2O. Each 3-sample set of the all four atmospheres were exposed in this medium for nearly 7 days (161h).

The measurements of the maximum shear strengths were carried out with an Instron model 5566A

universal testing instrument equipped with a 10 kN load cell (series 2525, model 804). The accuracy of the measured maximal stresses at fracture was better than 0.5%. A slow extension rate of 1mm/min. was chosen, which corresponds to quasi static conditions. Since PEEK as a visco-elastic material, its elastic and failure properties depend on the rate of perturbation.

For the correct calculation of the bonding strengths, the true adhesion area of each sample was determined by averaging the fracture surfaces of both sample parts. The fracture surfaces were measured with a Zeiss stereo-microscope model SteREO Discovery V12.

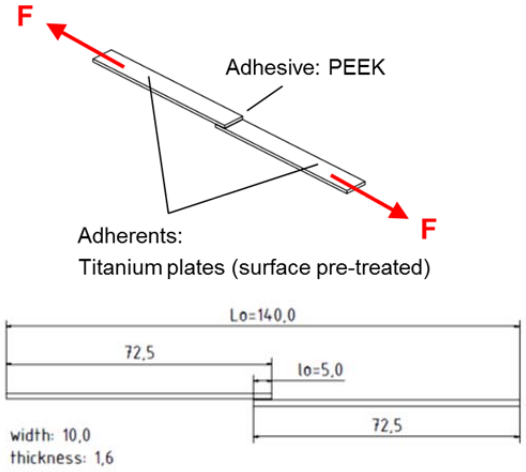

Fig. 1 *Lap-shear specimen used for rapid characterisation of bond strength.*

2.4 SCANNING-ELECTRON MICROSCOPY

Prior to SEM and EDX investigation, a ca 0.6nm thin Pt layer was deposited with a sputter-coater (Baltec SCD 500) on each laser-treated titanium reference surface and the fracture surfaces of the lap-shear samples.

The SEM investigations were conducted with a Zeiss Ultra 55 scanning electron microscope equipped with Gemini electron column and an Oxford Instruments Penta FETx3 EDX analyser (analysis software INCA). The imaging was conducted with primary beam energies of 10 and 15 keV employing the installed SE2, InLens and the AsB detectors.

3 RESULTS AND DISCUSSION

3.1 INITIAL BOND STRENGTH

Sets of 6 lap-shear samples have been prepared by laser pre-treatment of the joining surface in each of the four atmospheres (air, O_2, N_2 and Argon) and subsequent bonding with the PEEK foil at ca 395°C as described before. Additionally, metal stripes of the same titanium material were laser-treated without subsequent gluing identically to provide reference surfaces for SEM investigations of the effects induced by the laser.

Of each set of samples, 3 samples were tested without hydrothermal ageing in a lap-shear experiment to characterize the initial bonding strength of the created joint (Fig. 2).

Single-lap shear experiments provide a simple and quick means to study bond strength. However, two disadvantages are inherent to this experiment setup, i.e. the superposition of mode II and mode I stresses,[25] and the occurrence of mechanical stress peaks at the two ends of the joints,[25] but they do not alter our conclusions. No significant plastic deformation of the metal stripes was detected.

We found that the laser treatment in air (75±6 MPa) leads to equivalent initial strengths as treatments in O_2 (77±3 MPa) or N_2 gas (78±5 MPa). Only the pre-treatment in Ar atmosphere fell off slightly below this level with 67±6 MPa. This implies that the reactive gases play an important role in the morphological and chemical surface modification. The irradiation of the pure (clean) but structurally modified metal substrate from the treatment in Ar subsequently to air does likely also lead to an immediate oxidation of the rough metal, but this functional joining surface is poorer in its properties. Microscopic and spectroscopic investigations give insight in structural differences, depth and chemical nature of the functional surfaces (Chap. 3.3).

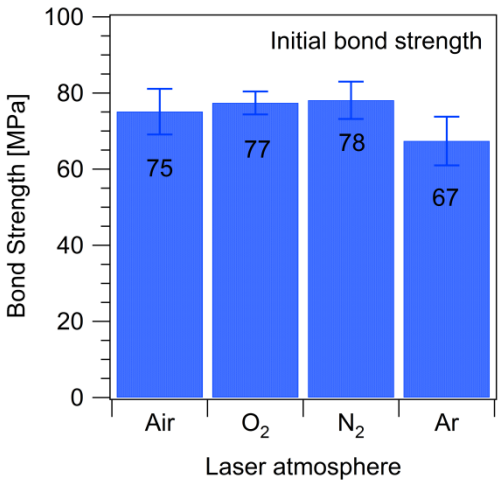

Fig. 2 *Initial bond strengths [MPa] measured for the single lap-shear samples from titanium-PEEK bondings after laser treatment of the metal joining surfaces in various gaseous media.*

The standard deviations are rather sizable, which can be traced back partially to the mechanical polishing of the metal specimen before exposure to the laser. The comparably low reproducibility of manual polishing leads to differences in the surface quality, and, hence, in the local reflectivi-

ty/absorption of the laser energy, which in turn strongly affects the efficiency of the surface modification. Larger sample sets will have to be considered in our future work to improve the statistics of the obtained results.
Stereo-microscopic analysis of the fracture surface were performed to determine the true area of adhesion (Fig. 3), which commonly varied less than 5% around the size of the PEEK slips cut for bonding (5×10 mm^2).
The optical images suggested in most cases that the dominant fracture mechanism was an adhesive failure at the interface, whereas cohesive failure mechanisms contributed only to a minor degree. Large, characteristic PEEK features left behind on one side of the sample corresponded to identically shaped areas on the other metal specimen where essentially no polymer was seen (Fig 2). However, a bluish-grey coloration in large parts of these "PEEK bare" areas compared to the laser treated areas outside the joining region was observed. This is due to a thin PEEK layer remaining after fracture on the whole adhesion surface as imaged with SEM.[26] The results of optical microscopy are qualitatively misleading and this method should not be relied on for a correct understanding of fracture and adhesion phenomena.

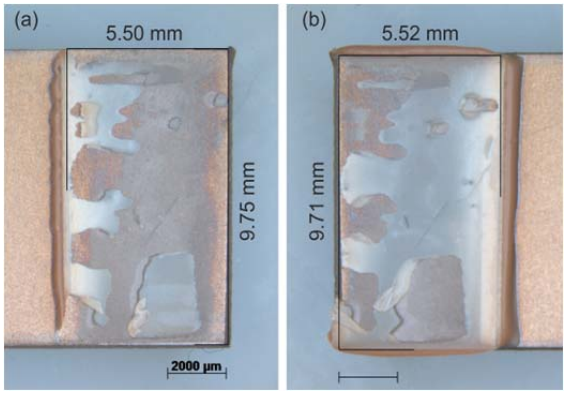

Fig. 3 *Example of a stereo-microscopic image of the fracture surfaces on a titanium specimen laser treated in air (note the patterning the laser creates outside the joining area). For easier comparison, the right sample image has been mirrored along the metal stripe axis. Clearly the mirror-like features of thick PEEK layers on one side correspond to "nearly" bare areas on the laser treated surface of the opposite metal substrate. Given are the values that are measured for determining the true joint area.*

3.2 INVESTIGATION OF THE BOND DURABILITY

The remaining 3 samples of each set underwent an accelerated degradation for 7 days in 80°C hot deionized H_2O before mechanical testing and microscopic characterization. This procedure provides a first estimate for environmental aging of bond joints by humidity or direct water exposure and serves as a well-controlled model experiment to study the occurring degradation mechanisms.
The absolute residual strength (Fig. 4, left axis) of the lap shear joints followed the same general trend already observed for the unaffected specimen, but the discrepancy between reactively gas atmospheres and inert Ar was enhanced further: while the laser treatment in air (67±6 MPa), O_2 (61±5 MPa) or N_2 (63±1 MPa) lead to consistently stable results around the average of 64 MPa, the aged specimen pre-treated in Ar gas achieved only values of 52±4 MPa.
For surfaces pre-treated in air, the joint was found to be very stable after the exposure to the degradation medium (Fig. 4, right axis/black triangles): 89% of the initial bond strength was retained. The joint surfaces laser treated in nitrogen and oxygen exhibited slightly smaller residual stability (81 and 79%). The slight difference between the laser pre-treatment in air, and those in O_2 and N_2 is likely not significant and can be attributed due to the limited sample sets used and to reproducibility.

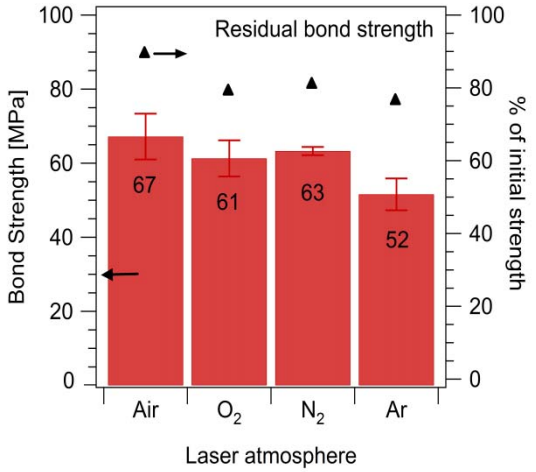

Fig. 4 *Residual bond strengths [MPa] and relative fraction of initial value [%, right axis] measured after degrading the laser pre-treated single lap-shear samples for 7 days in 80°C hot H_2O.*

It seems unlikely that neither of the two pure gases, N_2 and particularly O_2, would lead to a joining surface matching that formed by laser irradiation in air more closely (although it cannot be generally be ruled out that the chemistry may deviate due to the presence of the both components or even other gases, e.g. CO_2). Preliminary SEM and EDX data support this expectation since only small differences in the spectra and morphologies were found (Chap. 3.3).
From a purely technical perspective, there is no advantage to be gained in terms of strength or resistance against humidity by performing the

surface pre-treatment in oxygen, nitrogen, or even inert gas atmospheres versus a pre-treatment in air. This, however, does not rule out that other properties may be positively affected e.g. the stability of the attachment of the functional TiO_xN_y interface created in using nitrogen to the metal substrate (exploit properties of wear resistant coatings) below towards cyclic stress or the resistance against more corrosive media.

3.3 SURFACE MORPHOLOGY

SEM investigations were carried out with the pristine titanium alloy reference surfaces modified by laser treatment analogous to that for the lap shear joints.

A macro structure is observed at the micron scale with average feature sizes between 1 and 60 µm (size of the laser spot) consistent with our previous results (Fig. 5).[22,23] It appears independent of the gas atmosphere. It is characterized by large droplets, depressions, rims and undercuts. Scanning velocity and line distance of our process lead to multiple irradiations of parts of each laser spot (~28% 1×, 56% 2× and 16% 3×), causing a half-moon like pools surrounded by rims. The formation of the macro structure is governed by the material properties (naturally) and by pulse duration and energy absorption.[27,28] Formation of topography is due to an interplay of heat and mass diffusion, capillary forces at the surface of the melt pool (*Marangoni* effect) and compositional gradients.[28]

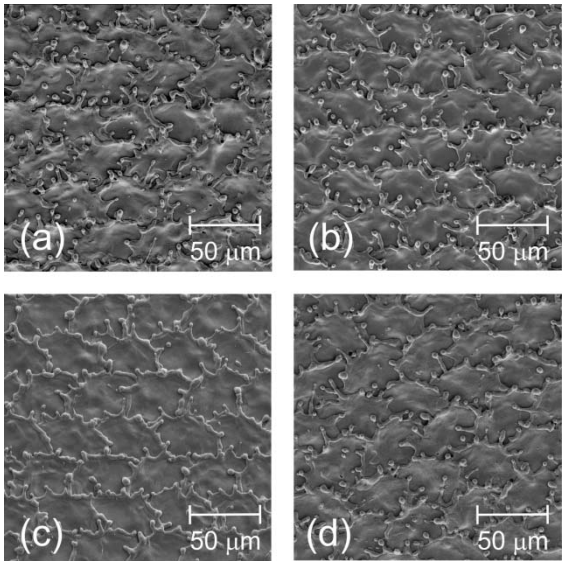

Fig. 5 *SEM images (SE2, 10kV) of a TiAl3V2.5 titanium surfaces laser irradiated in (a) air, (b) O_2, (c) N_2, and (d) Argon. The laser-induced macro-structuring at the micron scale is a clearly distinguishable feature.*

At the nanometer scale, a fine structure with varying degrees of porosity can be observed. The size distribution and homogeneity of this coral-like, comparably open structuring with various pores and trenches is very close for the surfaces pre-treated in air and O_2 (Fig. 6 (a) and (b)), whereas the structure imaged on the specimen irradiated in N_2 atmosphere seemed slightly finer (Fig. 6 (c)). The features on the joining surface pre-treated in inert Argon gas were substantially different: much less dense, much smaller clusters or disordered layers (Fig. 6 (d)). In fact, imaging these fine structures particularly on the latter samples was quite demanding since beam damage due to the scanning electron beam affected the visible structures within a few minutes despite using small beam currents and changed the detected appearance towards large, coalescing features.

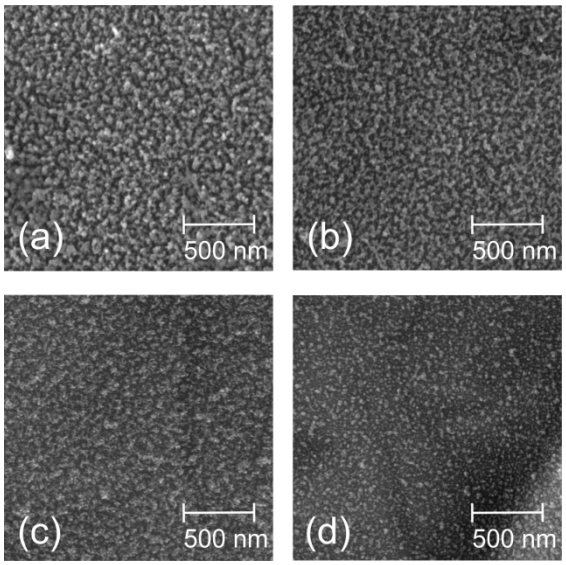

Fig. 6 *SEM images (SE2, 10kV) of a TiAl3V2.5 titanium surfaces laser irradiated in (a) air, (b) O_2, (c) N_2, and (d) Argon showing the laser-induced nanostructuring of the functional adhesive interface.*

First, EDX investigations of the surfaces created by laser irradiation in the four gas atmospheres showed the formation of TiO_x layers. Due to the information depth of EDX being much larger than the height of the formed functional films, and the unknown thickness thereof, a determination of the stoichiometry of the surface compounds was not possible with this method. Notably, no clear indication of any sizable amount of nitrogen was on the surfaces treated in nitrogen due to insufficient instrumental resolution of the N/Ti/O signals between 401, 497 and 532 eV. While this behaviours related to behaviours reported by Zimmermann et al.[16] or Ohtsu et al.[17], the formation of an oxide or oxo-ntride contradicts the reports by Ciganovic and co-workers[13], who observed a pure nitride layer. XPS measurements with optimal surface sensitivity will be carried out in the future to determine whether oxides, or oxo-nitrides were formed.

It can be expected that on the surfaces treated in Argon, much thinner oxide films form on the titanium metal upon transfer into ambient air (at room temperatures) compared to oxidation of molten titanium in reactive gas atmospheres during the laser irradiation. Sputter-profiling XPS, SIMS or TEM/EELS measurements will allow the determination of chemical nature of the lower layers.

SEM imaging of the fracture surfaces (further publication in preparation[26]) confirmed that the failure mode under the superimposed mode I and mode II loading is pseudo-adhesive, i.e. fracture of the bonding layer occurs in the near-interface region of PEEK close the functional layer on the metal. This holds consistently true for all surface treatments. Only very rarely small parts of oxide or oxo-nitride layers from the underlying interface were recognized on residual PEEK layers of the opposite fracture surface, suggesting that the laser-formed functional layers are strongly attached to the titanium alloy below.

Correlating the measured mechanical shear strength with the observed nanostructures confirms that it fills a key role for obtainable bond strengths. This is consistent with previous studies.[14,16,22,23] Since the macro-structuring is comparable in all four cases, the key differences must arise from the chemical and morphological nature of the respective nanostructures. The role of macro- and micro-structuring for the bonding has been classified by Venables.[3] Besides mechanical interlocking with features at both size scales, the nanoscale has been found to be at least as important for the joint properties.[29] Moreover, especially the nanostructuring causes a strong enhancement of the effective surface area which increases the number of surface sites available for specific chemical (e.g. covalent, coordinative or hydrogen bonds) or physical bonding (dispersive interactions, e.g. Van der Waals).

The initial strength of the adhesive bonding is found to be less sensitive to the process gas during the laser irradiation. The residual strength after degradation, however, is affected much stronger. Clearly, the resilience of the adhesive interface and bonds towards water is much lower for the pre-treatment in Argon, which correlates to the lower degree of nanostructuring. The role of the chemical composition, atomic structure, thickness and stability of the functional oxide and oxo-nitrides, which affect e.g. H_2O diffusion into the joint and dissociation and, hence, bond displacements of PEEK bonds such as coordinative interactions from the carbonyl groups ($RR'C{=}O{\rightarrow}Ti^{\delta+}$),[30,31] will need to be considered in future work to develop a better fundamental of the adhesive bonding and degradation mechanisms and compare the role of the nanostructure to that of its chemistry.

4 CONCLUSIONS

We present a first study on the effects of the different ambient gases used in a laser pre-treatment on the mechanical properties and the interface morphology for adhesive bonding to a thermoplastic polymer, PEEK. The laser pre-treatments of coarse-polished titanium alloy TiAl3V2.5 surfaces were performed with a pulsed Nd:YAG laser in air, oxygen, nitrogen and argon atmospheres using identical laser process parameters.

SEM experiments of the morphology of the surfaces showed a simultaneous macro structuring at the micron scale and a superimposed fine nanostructuring. The nanostructure appears coral shaped and does not exhibit flat and ordered surfaces down to the achievable resolution of ca 10 nm.

We characterized the initial and the residual bond (shear) strength by means of single-lap shear experiments prior and after degradation of the adhesive interface for 7 days in 353K (80°C) hot H_2O, respectively. The initial strengths of the adherend surfaces laser treated in air, oxygen and nitrogen were comparable at on average 77 MPa, whereas the lap shear samples pre-treated in Ar atmosphere showed slightly lower strengths of ca 67±6 MPa. After degradation in aqueous environment, the absolute strengths decreased on average between 11% and 24%, pronouncing the trend of the pre-treatments further. While laser treatment in air (67 MPa, i.e. 89% of initial value), nitrogen (63 MPa, 81%) and oxygen (61 MPa, 79%) resulted in comparable, small strength losses and very sizable residual bonding strengths, the laser pre-treatment in unreactive Ar gas lead to significantly inferior interface strength (52 MPa). Although the relative loss was only slightly larger (24%) in this case, the pre-treatment under inert gas environment led to the poorest measured absolute strength and, thus, provided no advantages.

Preliminary EDX measurements confirmed the formation of similar titanium oxides on all four surfaces, although a small contribution of nitrogen (oxo-nitrides) on the surfaces laser treated in air or nitrogen cannot be ruled out.

The trend in the bonding strengths of the four sample groups correlates with the differences observed in the nanostructuring, yet effects from changes of the chemical composition of the pre-treated surfaces and the structure on the atomic scale need to be considered in our future work as they can also strongly affect or even determine the properties of the adhesive interface.

From the technical point of view it can be concluded that the additional effort for surface pre-treatment in special gases is not necessary; laser treatment in ambient air provides best properties for adhesion. However, the study presented is a basis to elaborate the mechanisms of polymer adhesion at laser treated metal surfaces.

5 ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of U. Fuchs and R. Nodeh-Farahani from the "Mechanics of Materials Testing" group for the preparation of the testing setup for the lap shear experiments.

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