Buried interfaces – a systematic study to characterize an adhesive interface at multiple scales

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Abstract

A comparative study of a model adhesive interface formed between laser-pretreated Ti15-3-3 and the thermoplastic polymer PEEK has been carried out in order to characterize the interfaces' structural details and the infiltration of the surface nano-oxide by the polymer at multiple scales. Destructive approaches such as scanning and transmission electron microscopy of microsections prepared by focused ion beam, and non-destructive imaging approaches including laser scanning and scanning electron microscopy of pretreated surfaces

as well as synchrotron computed tomography techniques (micro- and ptychographic tomographies) were employed for resolving the large, μm -sized melt-structures and the fine nano-oxide substructure within the buried interface. Scanning electron microscopy showed that the fine, open-porous nano-oxide homogeneously covers the larger macrostructure features, which in turn cover the joint surface. The open-porous nano-oxide forming the interface itself appears to be fully infiltrated and wetted by the polymer. No voids or even channels were detected down to the respective resolution limits of scanning and transmission electron microscopy.

Keywords: Adhesive Bonding, Interface, Surface pretreatment, Serial sectioning, Synchrotron μ -Tomography, Ptychography.

1. Introduction

Adhesive bonding is a relevant technology for structural joining as well as for the production of modern lightweight multi-materials with tailored properties, e.g. fiber-metal laminates [1, 2]. One of the advantages of adhesive bonding is that it is not limited to particular material systems as in the case of welding of metals, and also reduces the thermal effects on the bonding substrates. Moreover, adhesive bonding enables larger joint areas and, thus, more homogenous load pathways as compared to mechanical joining: materials' damage, which are caused for example by drill holes required for riveting [3, 4] or by the plastic deformation occurring in clinching and lead to stress concentrations [5, 6] can be avoided. Furthermore, weight savings can be realized by eliminating the use of mechanical fasteners such as rivets. However, adhesive bonding can be a very demanding technology: service conditions in automobile or aeronautic applications often include a superposition of mechanical and environmental chemical loads, e.g. due to humidity, salt-water or deicing-agents, which have to be addressed for high-performance joints. Achieving sufficient mechanical performance simultaneously with high degradation and aging resistance depends on numerous factors, of which the joint pretreatment plays a key role [4, 7-12].

Especially for thermoplastic polymers like PEEK (poly-ether ether ketone) that are considered difficult to bond [12], the surface pretreatment is a key factor. Laser treating has gained much interest in the past decades for metallic surfaces since this technically simple and environmentally benign approach is highly efficient [9-12]. Lasers clean and restructure by ablating the surface [13-15] while, depending on the process atmosphere, they simultaneously chemically functionalize the surface by forming, for example, surface oxides, oxo-nitrides or nitride films [10, 16-18]. As a consequence, laser treatment enhances bond strengths and long-term stabilities of metal-polymer joints, though the fundamentals of this improvement remain under debate [19-23]. Improved wettability [24, 25], increased work of adhesion [25], better

means for mechanical interlocking [24], have been for example reported in several studies. Depending on material and laser process, nano-structured oxides with differing morphologies from microcolumnar oxide arrays [24] to finer, coral-like oxides of up to 200 nm thickness [19, 21, 23] can be formed.

The major challenge regarding adhesive joints besides the performance under mechanical load is usually the long-term resistance of the bonding against media including moisture, i.e. aging: joints often fail after a short period due to the influence of the service environment [11]. Several mechanisms can contribute to bonding. On the one hand, mechanical interlocking into rough surface structures can play a role ([7, 10] and refs. therein). Chemical bonding, on the other hand, can contribute to the joint strength [7, 9, 19, 21, 23, 26] and is sometimes even proposed to exceed the role of keying [10, 22, 24, 27]. However, most authors generally agree in attributing strength retention from aging to weakening of the chemical bonds [21, 23, 27], although also changes in the polymer (e.g. plastification, swelling etc.) can occur [11].

Relevant for degradation processes is also the structure of the interface region since the degradation mechanisms can be rate limited either by the reduction of bonds (e.g. displacement by water molecules or hydroxyls), by damage to the bonding interface (related to corrosion/unstable interface degradation) [28], or by the rate the chemical medium infiltrates the joint. Defects such as cracks may open additional pathways. Small channels or voids may remain after consolidation with the high-viscous thermoplastic polymer into the laser-nanostructure as result of poor wetting, air entrapment or shrinking. Water diffusion through such channels can be much faster than through water uptake of the polymer itself or along an oxide interface well-wetted by the adhesive. The H₂O diffusion rate of 1st layer adsorbed molecules was calculated in quantum chemical simulations e.g. at $\sim 1 \times 10^{-9} \text{ m}^2/\text{s}$ (at 300 K) [29] and $2 \times 10^{-10} \text{ m}^2/\text{s}$ (360 K) [30] on single-crystalline rutile TiO₂ surfaces (versus vacuum). Although the laser treated surfaces on various titanium substrates are not single-crystalline but consist of crystalline and amorphous oxides and suboxides [17, 22, 23, 31] that

affect the diffusion rate, the H₂O diffusion in the PEEK polymer bulk (amorphous: $D(22^{\circ}\text{C}) = 0.8 \times 10^{-12} \text{ m}^2/\text{s}$) [32, 33] is still orders of magnitude slower.

Hence, methods to study the structure of buried interfaces and detect voids, defects and open channels, in which these dynamic processes can occur, are of key importance. Buried joint interfaces between metals or thin metal oxide films and polymers can be characterized by conventional materialographic techniques such as e.g. scanning electron microscopy (SEM) and transmission electron microscopy (TEM). With the establishment of the focused-ion beam (FIB), preparation for TEM from thinly polymer-covered “model joints” (or fracture surfaces with thin residual polymer layers) with high local selectivity as well as serial sectioning tomography with sub- μm resolution is possible.

However, these techniques are destructive and do not allow investigating buried interfaces without potentially causing artifacts. On the other hand, laboratory X-ray tomography and parallel beam synchrotron micro-tomography (μCT) can provide non-destructive 3D imaging but their limited spatial resolution ($\sim 0.5 - 1 \mu\text{m}$) is not sufficient to resolve details of the interface. Furthermore, the large difference in attenuation coefficients between polymers and metals can result in reconstruction artefacts at their interface in the case of X-ray-absorption-based techniques. These disadvantages can be overcome combining the phase contrast capabilities offered by some synchrotron sources with focusing optics to obtain spatial resolutions well below sub- μm range [34]. Magnified holographic-tomography [35] and, more recently, the developments in ptychographic X-ray computed tomography (PXCT) [36] allow unprecedented access to nano-sized structures such as adhesive joint interfaces. In particular PXCT can provide spatial resolutions of few tens nm [37], which is decisive to further our understanding of metal- and oxide-polymer bonding structures.

We report here on the 2D and 3D multi-scale characterization of a metal oxide-polymer interface carried out on a laser-pretreated Ti-15V-3Cr-3Sn-3Al alloy bonded to PEEK. Different methods were employed for characterizing the buried interface and the laser-

pretreated surfaces prior to bonding and were compared with regard to complementary information that can be obtained as well as specific methodological drawbacks encountered in the investigation.

2. Material and methods

2.1. *Ti15-3-3-3 and PEEK sample preparation: laser pretreatment and bonding procedure, bonded specimen and fracture surfaces covered by nm-thin PEEK layers*

The metastable β -titanium alloy Ti-15V-3Cr-3Sn-3Al (hereafter Ti15-3-3-3) obtained from *Timet GmbH* (Germany) as rolled sheets of 1.6 mm was used for the investigations. After cleaning the surface with acetone, a laser pre-treatment was performed in ambient air on rectangular stripes ($72.5 \times 10 \times 1.6 \text{ mm}^3$) using a pulsed Nd:YAG laser *CL20* (*Clean-Lasersysteme GmbH*, Herzogenrath) with a wavelength of 1064 nm, pulse length of 110 ns and a Gaussian intensity profile. The Ti15-3-3-3 substrates were pretreated with an average laser power of 20 W, a frequency of 40 kHz, a velocity of 3000 mm/s and a line spacing of 45 μm , resulting in an energy area density of 14.8 J/cm^2 . These parameters were deduced in a prior study and transferred to this alloy [20].

For investigation of the Ti15-3-3-3/PEEK interface morphology and the polymer infiltration, butt-joint and lap-shear specimens were prepared. Specimen geometries were chosen for optimal accessibility by the respectively employed characterization methods. For micro-tomography a Ti15-3-3-3/PEEK/Ti15-3-3-3 butt-joint sample (square bonding area, $1 \times 1 \text{ mm}^2$) was chosen. For FIB/SEM, TEM and PXCT analysis, fracture surfaces of single lap-shear specimens (described further in Ref. [20]) were employed, which in conjunction with the laser-pretreatment had consistently failed cohesively within the polymer. They were, thus, covered homogenously with a thin residual PEEK layer of a few 10 nm to a few 100 nm thickness which still gave access to the interfacial properties while also being ideally suited

for sample preparation by FIB milling.

The bonding of the butt-joint and single lap-shear samples was carried out using 100 μm thick PEEK foils (“*LITE TK*” from *Lipp-Terler GmbH*, Germany), which were cleaned in acetone prior to bonding. The consolidation of both sample types was performed in ambient air in a laboratory furnace (model *P330* by *Nabertherm*) with a small pressure of 0.01 MPa applied through weights. The sample setup was heated up to 668 ± 5 K (395 °C, i.e. above the PEEK melting temperature) with a roughly linear heating rate of ~ 3.5 K/s (i.e. the technically limited maximum heating rate) and was annealed at this temperature for 15 minutes and cooled down passively to room temperature. Further details on the bonding procedure and lap-shear sample geometry can be found in Ref. [20].

2.2. Confocal Laser Scanning Microscopy (LSM)

The topology of the laser-induced macrostructure on the surface of the Ti15-3-3-3 alloy was characterized by confocal laser scanning microscopy (LSM) with a *Zeiss LSM 700* (laser $\lambda = 405$ nm) instrument. A tile scan consisting of 3×3 tiles ($358.6 \times 358.6 \mu\text{m}^2$) was measured at a 500-times nominal magnification with a 12.1 mm pinhole setting. This resulted in a height resolution of $\sim 0.11 \mu\text{m}$ with an overall height range scanned of 22 μm . A 3D-heightmap was recorded and the 3D roughness parameters S_{dr} (developed interfacial area ratio), S_z (maximum height) and S_a (arithmetic mean height) were computed with the *Zeiss ConfoMap®* software.

2.3. Scanning Electron Microscopy (SEM)

The investigations of the laser-induced structures on different length scales were conducted with a *Zeiss Ultra 55* field emission scanning electron microscope at a primary beam energy of 5 keV and a working distance of 7.8 mm employing the installed secondary electron (SE2; Everhart-Thornley) detector. Prior to SEM investigation, a thin Pt layer (~ 3 nm) was

deposited with a sputter-coater (*Baltec SCD 500*) on the laser-treated Ti15-3-3-3 surface to avoid charging effects.

2.4. Transmission Electron Microscopy (TEM)

In order to obtain a better insight into the morphology of the laser-generated nanostructure and the infiltration by the polymer, a lamella of the infiltrated laser structure (fracture surface of Ti15-3-3-3/PEEK lap shear specimen) was prepared via FIB milling for a TEM investigation. This was done with a dual-beam *FIB FEI Helios 600i* (FEI, Hillsboro, USA; *Tomahawk* Ga⁺ ion beam column, 30 kV). The fracture surface was covered locally with a ~2 µm thick, ion-beam deposited Pt-layer to prevent alteration or damage to the interface by the ion milling. A ~1 µm wide lamella was dissected from the covered region in several milling steps. The lamella was then thinned with a Ga beam until electron transparency was reached (< 0.5 µm, in specific areas down to 0.05 µm). The lamella was afterwards transferred into the *Philips Tecnai F30* analytical transmission electron microscope (Philips Electron Optics, Eindhoven, The Netherlands) equipped with field emission gun (acceleration voltage of 300 keV) and a Gatan 2002 GIF (Gatan, Pleasanton, USA).

2.5. Synchrotron microtomography (µCT)

Synchrotron microtomography with a parallel beam setup was carried out for the Ti15-3-3-3/PEEK joint at beamline P05 of the synchrotron source Petra III at DESY, Hamburg. 900 projections were recorded for reconstruction with an x-ray energy of 23 keV. A sample with a square bonding area of ~1 × 1 mm² and a 100 µm PEEK layer was centred within a field of view of 1.78 × 1.78 mm² at a sample-detector distance of 30 mm. An effective voxel size of 1.2 × 1.2 × 1.2 µm³ was used.

2.6. Ptychographic tomography (PXCT)

The PXCT experiments were carried out at the ID16A beamline of the European Synchrotron Radiation Facility (ESRF), Grenoble. FIB was used to extract a cylinder of $\sim 19 \mu\text{m}$ diameter and $\sim 40 \mu\text{m}$ length out of a fracture surface of a Ti15-3-3-3/PEEK lap shear specimen (Fig. 1 (a)). Prior to FIB milling, the fracture surface was protected by depositing a Pt cover layer. The sample was welded to a tungsten needle that was mounted onto a sample holder.

The energy of the incoming X-ray beam was set at 17.05 keV with a moderate monochromaticity of about 1% using a multilayer mirror. Such a beam was focused by a set of Kirkpatrick-Baez (KB) mirrors (Fig. 1 (b)). The aperture right before the KB mirrors were set to $27 \times 60 \mu\text{m}^2$ (H $\times$ V), which provides a beam divergence of 0.6 mrad. The sample was positioned at 2.3 mm downstream the focus, where the beam size is $1.4 \mu\text{m}$. A pair of horizontal slits at 143.5 m upstream the KB mirrors was close to $50 \mu\text{m}$ to increase the transverse coherence of the beam. A FreLoN Kodak indirect CCD detector [38], with a GGG:Eu scintillator and effective pixel size of $4.8 \mu\text{m}$, binned $4 \times$ to obtain $19.2 \mu\text{m}$, was positioned 1.2 m downstream of the sample. The scan of the sample was performed using a circular shell grid with a radial step of $0.6 \mu\text{m}$ and with 5 points in the first inner shell to avoid the pathology grid of ptychography [39]. Thus, the sampling ratio was $1/\alpha\beta = 7.6$, where $\alpha = 0.43$ is the ratio step-size/beam-size and $\beta = 0.31$ is the inverse of the oversampling factor in the reciprocal space, respectively [40]. The resulting field-of-view of the image was about $20 \times 3 \mu\text{m}^2$, which corresponds to 142 diffraction patterns of 320×320 pixels (after binning) acquired with 0.5 s exposure time each. This resulted in complex valued images (absorption and phase-contrast) with a pixel size of 13.06 nm. The phases were retrieved using 300 iterations of Difference Map algorithm [41] followed by 100 iterations of Maximum Likelihood algorithm [42] using the Python package Ptypy [43]. Additionally, an orthogonal mode decomposition of the probe in 3 modes to take into account any partial coherence effects was used [44]. The tomography measurements were performed using a binary

acquisition strategy described by Kaestner et al. [45] with 4 subtomographies over a range of 180 degrees. Each projection represents a ptychography experiment and 360 projections were acquired with angular step of 0.5 degrees. Before the actual tomography reconstruction, the projections were processed and aligned according to Guizar-Sicairos et al. [46]. The tomographic reconstructions were performed using a modified filtered back-projection algorithm (FBP) suitable for wrapped phase. Given the projections are complex-valued, the absorption and phase-contrast tomograms were calculated independently from the same dataset. To mitigate noise in the reconstruction, a Hanning filter was used with 0.3 and 0.9 normalized cut-off frequency for the absorption and phase-contrast projection. This resulted in 3D images of the refractive index decrement, $\delta(r)$, and of the absorption index, $\beta(r)$, of the sample with dimension of $20 \times 20 \times 3 \mu\text{m}^3$ (Fig. 1(c) and Fig. 1(d), respectively).

2.7. 3D tomography by focused ion-beam sectioning and SEM imaging

A small volume of the PXCT sample was characterized further using serial sectioning tomography consisting of alternating steps of FIB slicing and SEM recording with the dual-beam *FIB FEI Helios 600i*. First, a more massive protection layer of gold (thickness $\sim 3.5 \mu\text{m}$) was deposited on top of the sample's Pt layer. For alignment and drift correction, a small Pt pad was deposited on the gold layer into which a cross was milled. Serial sectioning was carried out parallel to the length of the sample by ion beam milling (30kV, 0.77 nA). A minimum distance between two consecutive FIB slices of 10 nm (z-direction) was achieved. After each slicing step, a SEM image was recorded via electron beam with the TLD-detector in electron backscatter mode. The resulting voxel size of the serial sectioning tomography was $1.35 \times 1.71 \times 10 \text{ nm}^3$. The recorded images were registered with the ImageJ [47] software package FIJI [48] to minimize remaining drift effects.

The slicing was performed from one side of the sample measured previously with PXCT so

that an exact comparison of the data was enabled. The region sampled within ~ 48 h of measurement time extended ~ 3 μm from the border of the cylinder into the volume. A reduced rectangular volume element was selected from the raw data for presentation, leaving out regions that due to drift were not recorded for the whole stack.

3. Results and Discussion

3.1. Two-dimensional studies of laser-pretreated joining surfaces

After pretreatment with the Nd:YAG pulsed-laser the surface of Ti15-3-3-3 exhibits characteristic structures at the μm - and nm-levels (Fig. 2): larger, μm -sized melt-structures covered by a much smaller, homogeneous coral-like nanostructure [19, 20, 23]. The mechanisms of laser-substrate interactions, which depend on the introduced energy (fluence) include melt and plasma formation, are well-understood [49, 50].

The micro-level structuring is easily accessible by both SEM (Fig. 2 (a) and (b)) and confocal LSM (Fig. 2 (c)), which show that the laser pretreatment creates meandering tracks of partially overlapping spots with diameters of ~ 75 μm on the surface. Preceding and receding laser vectors lead to neighboring tracks of melt-structures that are separated by the line distance that was set at 45 μm (Fig. 2 (b)). SEM in secondary electron (SE) mode is easily capable of resolving quantitatively the lateral details of this structure. The observed features consist of overlapping “spots” from the solidification of the melt pools created by the laser pulses that are framed by melt splats and rims. On several samples prepared in the same fashion, different locations were investigated and showed similar morphologies, indicating that the laser pretreatment leads to a homogeneous structuring of the surface.

The three-dimensional morphology information gained by LSM matches that from SEM closely (Fig. 2 (c)). However, while SEM cannot provide quantitative height information, con-

focal LSM can resolve this complimentary information: it quantitatively resolves corrugations down to $\sim 0.1 \mu\text{m}$. The surface corrugation (maximum height) determined from a measurement area of $350 \times 350 \mu\text{m}^2$ after Gaussian low pass filtering (filter wavelength-cutoff $\lambda_c = 0.8 \mu\text{m}$) is $S_z = 22.1 \mu\text{m}$ (arithmetic mean height $S_a = 1.42 \mu\text{m}$), which leads to a small enhancement of the effective surface area of the substrate of about 29%. The typical corrugation from melt pool bottom to melt rim top was in the range of 8 to 12 μm .

Nonetheless, LSM cannot access the much smaller nanostructures that SEM reveals on the whole surface of the micro-structured substrate: a homogeneous, open-porous film of fine oxide (Fig. 2 (d)). From a top perspective, the structures appear to consist of interconnected particles measuring on average less than 20 nm in size. As shown in previous studies, these fine, homogeneous nanostructures are detected whenever the mechanical characterization of correspondingly pretreated and aged lap-shear specimens indicate a high residual strength, i.e. a high degradation resistance of the joints [20, 51].

3.2. TEM analysis of an interface lamella

The bright field (BF) TEM images of the interface in the fracture surface of a Ti15-3-3-3/PEEK joint (Fig. 3) provide further details of the porous nano-oxides' structure. Below a thinner nanostructure region (Fig. 3, label A), thicker structure features (B) extending in height only some 30 – 40 nm above two closed layers (C-D) are found with BF-TEM. The two dense layers are imaged with different contrast compared to that of the Ti15-3-3-3 bulk: a layer of $\sim 10 - 12 \text{ nm}$ in thickness (Fig. 3, label C) is observed directly below the porous structures and is separated from the metallic part by a $\sim 1 - 2 \text{ nm}$ layer (Fig. 3, label D), which is recognized by its darker contrast. The latter implies that a different phase or composition is present between the metal and the oxide phases above. EFTEM, EELS, and SAED are to be employed in future studies for identifying the chemical or structural nature of the dense layers.

Above the thicker features of the nano-oxide, the nanostructure thins out and forms a rather homogeneous porous network of connected small particles (<5 nm). The finer nanostructures extend for ~ 150 nm, which results in a total layer thickness of the porous layer of roughly 200 nm. Importantly, TEM shows that these features are fully infiltrated by the polymer PEEK and no voids are visible. Assuming that no preparation artifacts have closed any potential voids, even pores smaller than 1 nm should be recognizable due to increased contrast between the different material phases in the BF imaging mode.

3.3. Tomographic synchrotron studies of buried interfaces: micro-scale structures

μ CT allows non-destructive access to the buried interface after consolidation and, thus, to the analysis of defects at the μ m-scale as well as the assessment of the bond line in the sampled volume (Fig. 4 (a)). Importantly, no defects or voids are detected in the near-interfacial region based on intensity (gray scale) analysis down to $\sim 2^3 \mu\text{m}^3$. Hence, no large void networks exist at this scale that would allow penetration of media into the bond line. The bond line thickness was found to vary by less than 10 μm around a mean value of $\sim 80 \mu\text{m}$ on the whole butt joint area.

The corrugation due to laser micro-structuring and the tracks of overlapping spots is generally resolved by micro-tomography, though at a lower resolution (voxel size $= 1.2^3 \mu\text{m}^3$; the overall height of the melt features is on average less than 6 to 10 voxels) than LSM (Fig. 4 (b)). The different refraction indexes of PEEK and Ti15-3-3-3 result in edge enhancement at the interface due to phase contrast that provokes a contrast increase particularly at the sharp spikes of the metallic tracks. This gradient in the gray values of the reconstructed slices at the metallic side of the interface PEEK/Ti15-3-3-3 has been used in Fig. 4(a) to generate a colored 3D visualization that clearly shows the topography of the micro-structured surface.

μ CT can be considered a non-destructive characterization method capable of deducing the three-dimensional structure within the bonding region, while LSM or SEM cannot gain direct access to buried interfaces. μ CT thus allows accessing the homogeneity of the bond line and the presence of larger defects such as voids in a larger sampling volume. In case of hybrid engineering materials such as fiber-metal laminates, also the distribution of the reinforcement fibers, potential fiber-joint contacts or delamination defects can be detected. On the other hand, from a technical perspective, the need to prepare small samples from a real joint and the limitations imparted on the sample size by μ CT limit the use of this technique as a non-destructive testing method in a manufacturing and engineering sense.

3.4. Ptychographic tomography analysis of buried interfaces: submicron scale

PXCT provides a more detailed non-destructive analysis of the interface region, permitting to clearly distinguish several layered regions based on phase and absorption contrasts (Fig 1 (c) and (d), respectively). We will concentrate on the analysis of the phase-contrast tomogram, since it shows a better contrast between the materials than the absorption tomogram. A spatial resolution on the 3D phase-contrast image of about 3 pixel size is estimated, which corresponds to about ~ 40 nm. The Ti15-3-3-3 metal substrate, a homogeneous layer consisting of the nano-oxide layer infiltrated by PEEK, and the two protective Pt layers that were deposited on top by electron and Ga ion beams by FIB, respectively can be seen in Fig. 5 and Fig. 6 (a)-(b).

Several voids are observed in the Ti15-3-3-3 bulk material at distances of ~ 750 nm to $1.5 \mu\text{m}$ below the laser-generated bonding interface (Fig. 5, pore shown in blue). The elongated, crack-like shape of the voids indicate that they are also caused by the laser-pretreatment. While most are smaller than $0.5 \mu\text{m}$ in their largest horizontal axis, two large voids with diameters of ~ 3.5 and $\sim 4 \mu\text{m}$ are found within the sampled cylinder.

Neither in the phase nor the absorption contrast data of the PXCT experiment, an unambiguous differentiation between the nano-oxide layer and the PEEK polymer is possible, preventing a detailed structural analysis of the nanostructure and the identification of voids or channels <40 nm (Fig. 6 (a) and (b)). Only a homogeneous mixed phase is detected that varies between 100 and 200 nm in thickness (on average ~ 150 nm; Fig. 6 (b)), which is slightly thinner than the laser-generated films of ~ 164 nm thickness measured on Ti6Al4V by Kurtovic et al. [19] or ~ 200 nm measured on pure titanium reported by Zimmermann et al. [23], respectively.

The mixed interface layer does not exhibit larger voids or channels, i.e. $\geq \sim 40$ nm in the PXCT analysis. Hence, the nanostructures appear fully infiltrated by PEEK down to this size scale. Although it is still quite coarse compared to the average separation distance of the fine nanostructures deduced from the SEM images (smaller than $\sim 10 - 20$ nm; Fig. 2), at least larger defects can be excluded unambiguously and non-destructively with this method. Spatial resolution could be improved by increasing the number of projections and measurement time during PXCT scans. Longer measurement times of 72 to 96 h per experiment would be worthwhile to fully exploit the potential of this new technique.

3.5. 3-dimensional analysis using FIB tomography

FIB serial sectioning tomography provides the highest resolution and the best detail on the PEEK-infiltrated titanium oxide nanostructure interface by enabling a clear distinction between the organic and inorganic phases (Fig. 6 (c)-(d)). The backscattered electron detection mode gives high material contrast between the different phases and significantly higher lateral resolution (voxel size = $1.35 \times 1.71 \times 10$ nm³) than achieved in the PXCT experiments, albeit destructively and with only an even smaller volume that can effectively be investigated.

FIB tomography was carried out on the same sample measured previously with PXCT to compare both tomography results in an identical sample region. Overall, the volume that was sampled by FIB tomography within a measurement time of ~ 48 h is significantly smaller (depth of ~ 3 μm as compared to the diameter of the PXCT data of 18.3 μm) since the highest resolution setting is used. Corresponding volume elements are chosen in the FIB and the PXCT measurements and are displayed in Fig. 6 (a) and (c).

While the PXCT data is equally well resolved in all three spatial directions (Fig. 6 (a)) down to about 40 nm, the FIB tomography data is better resolved in the image plane (width and height directions of the stack) than in the “depth” (Fig. 6 (b)): On the front side of the measured volume, the structural features of the nm-sized, porous oxide film can be easily recognized and correlate well to the results obtained from the SEM top view images (top view, Fig. 2) and the TEM lamella (Fig. 3). Here a resolution of ~ 5 nm is achieved. On the side of the volume, however, a lower depth resolution of 10 nm prevents resolving the nanostructure details.

Moreover, the long measurement and slicing times in this experiment also led to significant drift in the FIB image stack, which was corrected only partly by the auto-alignment function that re-centers on the calibration cross on the Pt layer prior to taking a new SEM image. This resulted in a slight residual drift, which can be recognized on the side face of the volume. Although this can be further improved by registration corrections, this was omitted since the lack of lateral resolution in this direction hindered further 3D analysis of the FIB tomography data. This and the fact that material re-deposition during slicing may “hide” the presence of small voids are severe drawbacks of this approach in comparison to the μCT and PXCT.

Closer inspection of the sectioning images, e.g. the front face being shown in Fig. 6 (d), finally resolves the vertical detail of the nanostructures oxide film: The fracture in the PEEK polymer of the joint apparently occurred almost directly (within $\sim 10 - 20$ nm) above the topmost nanostructure features. The film itself shows an average height of ~ 100 to 200 nm,

comparable to the result from PXCT, and appears denser at the base while thinning out to the top. The structures themselves consist of larger column- or particle-shaped features that are typically around $\sim 20 - 30$ nm in width and extend roughly $50 - 60$ nm in height, where they fan-out into distinct but connected particles. Also note that the features are not imaged with sharp rims in the SEM images, thus probably leading to a slight overestimation of the dimensions.

3.6. Combined insights into the buried interface – a comparison of methods

Combining the LSM and SEM analysis provides a detailed description of the micro- and nanostructures formed by the pulsed Nd:YAG laser on the Ti15-3-3-3 surface. Both are local techniques that require analyzing several regions of the samples to ascertain that the observed features are representative. The laser-generated surface oxide film was imaged with high lateral resolution from the top perspective with SEM, but this does not provide quantitative information of the vertical structure.

The interface after bonding and, thus, the infiltration behavior of PEEK into the open, porous (“coral-like”) nano-oxide network was in turn characterized by SEM on the FIB slices, and by a TEM lamella prepared by FIB milling. However, the latter procedure necessitated the samples to exhibit no more than a few μm PEEK thin-layers in order to render FIB milling efficiently feasible; it is also a local and destructive approach. Both techniques generally allow high resolutions, TEM down to a few nm, and even allow analytic extensions such as EDX, EELS, or SAED to be employed for chemical and phase analysis.

The SEM images of the FIB slices show an interphase region with a height of up to 200 nm that consists of a PEEK percolated nanostructure film. These column- and particle-shaped features of $\sim 20 - 30$ nm width are denser at the base and split up and thin out roughly $50 - 60$ nm above, where the imaged nanostructure tends to appear like interconnected particles. The

lateral width and shape of the rather homogeneously distributed oxide nanostructures coincides with the SEM images recorded from the top view.

Complementary TEM bright field images of a lamella of a Ti15-3-3-3/PEEK interface show similar nanostructure features: denser up to ~ 50 nm and fanning/thinning out into a homogenous, network structure of connecting small particles. The porous structures are fully infiltrated by PEEK and are separated from the metallic bulk by two dense layers, one of 10 – 12 nm thickness that rests on a thinner region of $\sim 1 - 2$ nm. The overall thickness of the porous nanostructure layer is on average 200 nm as judged from TEM. Compared to previous studies, the thickness of the porous region measured here (on average ~ 150 nm from SEM, ~ 200 nm from TEM) appears to be generally in line with films of ~ 164 nm thickness formed by laser-treatment on Ti-6Al-4V (Kurtovic et al. [19]), or ~ 200 nm reported by Zimmermann et al. on cp-titanium [23].

Importantly, neither TEM nor the SEM images of the FIB slices evidence any voids or channels. However, one major drawback when analyzing the polymer distribution and infiltration into the nanostructure based on SEM, TEM or FIB/SEM stems from the micro-section preparation: Especially with the FIB technique the redeposition of material during milling can lead to closure of small voids and open features, which may lead to wrong conclusions. This limits the use of these high resolution imaging destructive techniques and requires the use of non-destructive tomographic experiments to access the buried interfaces without suffering from such sample preparation artifacts.

Synchrotron μ CT with resolution at the order of μ m proves to be sufficient for detection of the melt-structures and of larger defects. A sizable joint sample of 1×1 mm² cross-section is still feasible to be measured. The results show that no defects above ~ 47 μ m³ ($3 \times 3 \times 3 = 27$ voxel), particularly no air entrapments were present in the bond line.

Although tomographic reconstruction of a 3D volume of the interface region by FIB serial sectioning tomography with the lateral resolution of the SEM imaging should in principle give access to a 3-dimensional characterization of the oxide nanostructures, this approach suffers from a limited resolution in the slicing direction due to requiring a slice thickness of at least several nanometers (i.e. 10 nm here). This renders this method to be of limited use for deducing a “true” three-dimensional model of the laser nanostructure, but it allowed for a volume reconstruction with asymmetric voxel size ($1.35 \times 1.71 \times 10 \text{ nm}^3$).

Ptychographic X-ray computed tomography PXCT provides a highly resolved 3D structure of the interface and allows distinguishing the PEEK-infiltrated nanostructure as a ~150 nm thick layer above the metal substrate and below the two protective Pt layers. The finer details including nanostructure $< 40 \text{ nm}$, however, remain unresolved. Recording more projections with higher exposure times might significantly enhance resolution and contrast, although requiring significantly more than the 36 h measurement time used for this data set.

From the TEM, FIB/SEM and the PXCT data we conclude that the nanostructures are fully infiltrated and well wetted by PEEK and that no voids or channels down to the respectively achieved resolutions are present. Therefore, we can exclude that water will enter the bond line during aging by means of defects networks and channels larger than ~3-5 nm.

4. Conclusions

The structural details of the adhesive interface formed between laser-pretreated Ti15-3-3-3 and the thermoplastic polymer PEEK have been characterized with different destructive and non-destructive 2D/3D imaging techniques. The following conclusions can be drawn from the investigations:

- SEM, LSM and μ CT showed that the pulsed Nd:YAG laser treatment on air led to partial melting of the metal substrate. Melt-structures with a corrugation of 8 to 12 μm

enhanced the effective bonding surface of the joint by ~29%. Moreover, a fine, open porous nanostructure homogeneously covered the entire surface, including the melt-structures, and results in a more significant surface area increase.

- The porous nanostructure consisted of thicker and thinner regions, which have been formed on top of two dense layers separating the interface region from the metallic bulk, as revealed by TEM and FIB tomography in bonded Ti15-3-3-3/PEEK samples. Both characterization techniques suggested excellent wetting and full infiltration of the nanostructures by PEEK down to resolutions of 3-5 nm, respectively.
- The highly resolved, non-destructive PXCT allowed for a distinction between various layers from the substrate metal, over the fully PEEK-infiltrated nanostructure region to the Pt protection layers deposited on top. Also this technique did not detect any channels or larger defects in the interface region down to the achieved resolution of ~40 nm.

Thus, we conclude that no voids or channels larger than 3 nm (i.e. above TEM and SEM/FIB detection limits) were present in the samples' interfaces through which water diffusion might take place. This provides further support for the benefits of the laser surface treatment for the long-term resistance exhibited by the PEEK-Ti15333 joints reported in a previous work [20].

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FIGURES

Fig. 1. (a) SEM image of the sample prepared from a Ti15-3-3/PEEK fracture surface by FIB milling for the PXCT measurements (TLD). Different material contrasts allow to distinguish the bulk Ti alloy, the PEEK-infiltrated bonding layer, and the protective Pt layer deposited prior to ion milling. (b) Sketch of the experimental setup for PXCT at ID16A/ESRF Grenoble; (c) example of a reconstructed slice from the phase contrast data (d) from absorption contrast data.

Fig. 2. Imaging analysis of the laser-pretreated Ti15-3-3-3 surfaces at different length scales: (a) SEM image of microstructure, (b) magnified SEM image of microstructure, (c) LSM image of microstructure with height information, (d) SEM nanostructure (laser pretreated at $p = 100\%$, $v = 40$ kHz, $v = 3000$ mm/s, $d = 45$ μm). The arrow indicates the laser advancing direction, the circle the position of laser spots to indicate the overlap (hatch distance = 45 μm). The red squares in the SEM images (a) and (b) indicate the magnification regions for (b) and (d), respectively.

Fig. 3. Energy-filtered BF TEM image of FIB-prepared lamellae of a buried adhesive interface between laser-pretreated Ti15-3-3-3 and PEEK. (A) porous nanostructure, (B) denser nanostructure layer, (C) and (D) closed layers above metal substrate.

Fig. 4. (a) μ CT reconstruction of the laser-treated Ti15-3-3-3 joint surface inside the buried adhesive interface of a butt-jointed specimen bonded with PEEK, (b) 3-dimensional representation of the LSM data of a laser-pretreated Ti15-3-3-3 open surface.

Fig. 5. Measured and segmented PXCT volume of the adhesive interface between laser-pretreated Ti15-3-3-3 and PEEK: The Ti15-3-3-3 bulk (green), the PEEK infiltrated titanium oxide nanostructure (red), a pore generated by the laser pretreatment (blue), and the two Pt protection layers deposited with

the electron beam (yellow) and Ga ion beam (silver) segmented based on phase contrast in the PXCT data.

Fig. 6. PXCT (a-b; phase contrast) and FIB/SEM (c-d) reconstructions of the adhesive interface between laser-pretreated Ti15-3-3-3 and PEEK: (a) magnification of a selected PXCT volume element recorded at ID16A and (b) frontal view. (c) FIB volume element and (d) frontal view.