ESRF	**Experiment title: Three dimensional structure of Ti interfaces for bonding with polymers in thermoplastic hybrid materials**	**Experiment number**: MA2783
Beamline: ID16A-NI	**Date of experiment**: from: 10 Oct 2015 to: 14 Oct 2015	**Date of report**: 05 Mar 2018
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Report:

Results of this experiment haven been published in:

J. Haubrich, M. Löbbecke, P. Watermeyer, F. Wilde, G. Requena, J. da Silva, "Buried interfaces – a systematic study to characterize an adhesive interface at multiple scales", Appl. Surf. Sci. 433 (2018), 546-555.

A comparative study of a model adhesive interface formed between laser-pretreated Ti15-3-3-3 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, PXCT) were employed for resolving the large, µm-sized melt-structures and the fine nano-oxide substructure within the buried interface.

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 ~19 µm diameter and ~40 µm 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)). A FreLoN Kodak indirect CCD detector [38], with a GGG:Eu scintillator and effective pixel size of 4.8 μm, binned 4 × to obtain 19.2 μm, was employed to record complex valued absorption and phase-contrast images with a pixel size of 13.06 nm. The tomography measurements were performed using a binary acquisition strategy described by Kaestner with 4 subtomographies over a range of 180 degrees. 360 projections were acquired with angular step of 0.5 degrees. Given the projections are complex-valued, the absorption and phase-contrast tomograms were calculated independently from the same dataset. This resulted in 3D images of the refractive index decrement, δ(r), and of the absorption index, β(r), of the sample with dimension of 20 × 20 × 3 μm3 (Fig. 1(c) and Fig. 1(d), respectively).

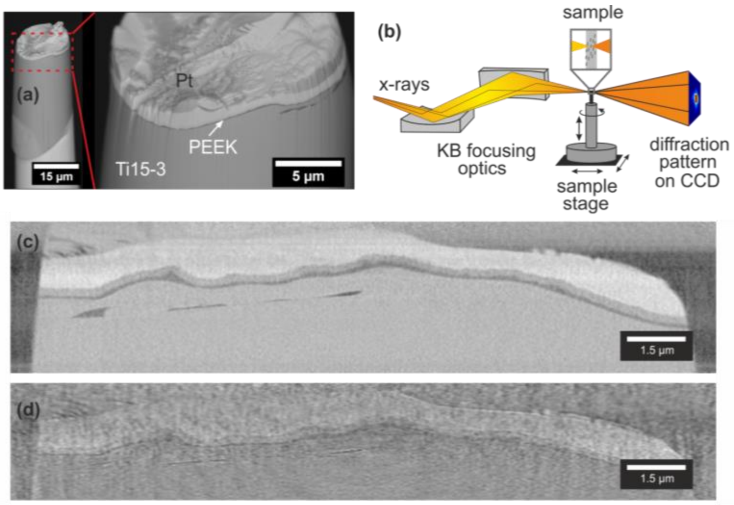

Fig. 1. (a) SEM image of the sample prepared from a Ti15-3-3-3/PEEK fracture surface by FIB milling for the PXCT measurements (TLD). Different material contrasts allow to distinguish the bulk Ti alloy, the PEEK-infiltrated bonding layer, and the protective Pt layer deposited prior to ion milling. (b) 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.

The key findings of this study include:

- SEM, LSM and μCT 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.
- 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.

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 works.