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Highly conformal thin-film coating on 3D-printed, open-porous structures using TiO_2 ALD

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Abstract:

Open-porous structures produced by Additive Manufacturing (AM) offer an excellent basis for patient-specific implants, scaffolds and medical devices. The interface of 3D structures produced by this technology can be improved by the thin-film technology of Atomic Layer Deposition (ALD), a highly modified form of Chemical Vapour Deposition. ALD allows to apply highly conformal coatings on complex geometries and coating of internal surfaces and channels. ALD is a versatile method, as it is compatible with AM. In this work, the conformity of the ALD coating on open-porous structures was investigated. Lattice type cubes of 10x10x10 mm^3 outer size and with square channels in all three orthogonal directions with widths of 2’000 µm and 750 µm and two, four or six open sides were produced using masked stereolithography. These additive manufactured open-porous structures were coated with a 75 nm thick titanium oxide (TiO_2) layer by ALD. The TiO_2 coating thickness was determined on different positions within channels using Scanning Electron Microscopy (SEM). The measurements revealed excellent coating conformity over the internal surfaces (82.1 ± 2.6 nm and 87.9 ± 3.8 nm in 2’000 µm and 750 µm channels, respectively) with a Uniformity Index of up to 7.8%: The results highlight the potential of combining 3D printing and ALD to overcome existing technical limitations and enhance the functionality, biocompatibility, and durability of advanced materials for medical applications.

Keywords: Atomic Layer Deposition; Additive Manufacturing; Open-Porous Structures; Titanium oxide; Conformal Coating

1 Introduction

The development of innovative biomaterials for medical applications faces the challenge of combining functionality, biocompatibility, and durability. Open-porous substrates, characterized by their large surface area and permeability, offer immense potential for implants, scaffolds, catalytic processes, or filtration materials. [1] These materials enable enhanced cell interaction and targeted substance release but are prone to chemical and mechanical degradation without suitable coatings. Therefore, in medical technology, coatings are applied to protect implants from corrosion and enhance biocompatibility. There is an urgent need for functional coatings that are thin, conformal and durable. [2]

Atomic Layer Deposition (ALD) is a cyclic coating process in which the layer-forming chemicals are introduced into the process chamber in separate process steps, where they can react with the surface in a self-limiting manner. [3] Through precise process control and selection of suitable precursors, any form of oxide, nitride or even metal can be deposited to conformally coat a bulk or porous materials. [4]

In this work, ALD on additively manufactured polymer scaffolds was investigated. The focus was on the conformity of the layers across internal pores within the lattice structure. TiO_2 was used as the ALD layer, known for its biocompatible properties as it supports the attachment of bone cells (osteoblasts) and promotes the formation of new bone tissue. [5] Its osseointegrative characteristics render TiO_2 especially valuable for medical applications, such as implant coatings, as it enhances the integration between implants and bone.

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2 Materials and Methods

For the investigation of the conformity of the coating, lattice-type cube structures were additively manufactured from a high-temperature resin and subsequently TiO_2 coated using ALD. The cubes were then embedded in epoxy resin, cut in half, and then ground at the cross-sectional area, 5 mm away from the surface. The layer thickness was determined on different positions within the channels by SEM.

2.1 Manufacturing of the cubes

For the open-porous structures, cubes with an outer edge length of 10 mm and square channels of 2’000 µm and 750 µm width in all three orthogonal directions were additively manufactured. These cubes were printed with 6, 4, and 2 open sides. Figure 1a) (right) illustrates an exemplary cube with 750 µm channel width and six open sides, and (left) a cube with 2’000 µm channel width and two open sides. For the manufacturing by masked stereolithography, a Saturn 3 Ultra 3D printer (Elegoo, Shenzen, China) was used with the high-temperature resin Phrozen TR300 (PHROZEN TECH CO., LTD., Hsinchu City, Taiwan) with a glass transition temperature of 220°C. For the initial lithographic exposure, 15 s were set, which were gradually reduced to the final exposure time of 1.5 s within 4 layers. The layer height during printing was 50 µm. Thus, the cubes were built up with 200 layers, see Figure 1c/d). After printing, the cubes were post-processed and UV-cured according to the manufacturer's instructions. Subsequently, the channel widths of the cubes were determined using a reflected-light microscope.

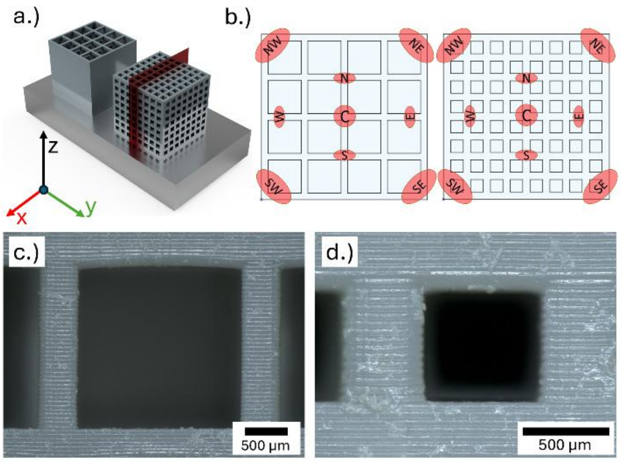

Figure 1: a) Representation of two 10x10x10 mm^3 cubes with two specific channel widths (2’000 µm and two open sides, resp. 750 µm and six open sides) as placed in the ALD-coating system. b) Cubes were cut in the XZ plane for layer thickness analysis at the indicated positions. Microscopic image of XZ plane of cube with c) 2’000 µm and d) 750 µm channel width.

2.2 Coating of the cubes

The cubes were then divided into two groups: One group was coated with Parylene-C using the Labcoater LC300 LV25 coating system (Plasma Parylene Systems, Rosenheim, Germany) before the ALD. For this purpose, 7.75 g of Parylene-C powder (Plasma Parylene Systems, Rosenheim, Germany) was used. The coating was carried out without any pretreatment of the PHROZEN substrate of the cubes and resulted in a Parylene-C film thickness of approximately 5 µm. The idea was that the Parylene-C layer on the PHROZEN substrate could be used to create a smoother interface so that the thickness of the TiO_2 layer could be measured more easily. The second group of cubes had no PARYLENE-C treatment. Subsequently, both groups were simultaneously ALD-coated using the radical-enhanced Atomic Layer Deposition process with the myPlas III coating system (Plasma Electronic GmbH, Neuenburg, Germany). For this purpose, the precursor titanium(IV)isopropoxide [$Ti(OCH(CH_3)_2)_4$, TTIP, >97%] (abcr GmbH, Karlsruhe, Germany) and an oxygen plasma as reactant was used. The coating temperature was 120°C which is well below the glass transition temperature of the substrate material PHROZEN TR300. A detailed description of the coating process can be found in [6]. In addition to the cubes, a silicon wafer with 10 x 10 mm^2 was also coated for layer thickness reference measurement. 1530 coating cycles were run, resulting in a layer thickness of approximately 75 nm TiO_2, which was measured using the reflectometer NanoCalc-XR (OceanOptics, Largo, FL, USA) on the silicon wafer. The growth per cycle (GPC) was calculated to 0.49 Å/cycle.

2.3 Investigation of the layer thickness

After coating, the cubes were embedded in epoxy resin and cured in vacuum for 24 hours. Subsequently, they were cut in half in the XZ plane, as shown in Figure 1a), red plane. For this purpose, the IsoMet low-speed precision saw (Buehler, Lake Bluff, IL, USA) was used. Then the cross-sectional area was first pre-ground with 2’000 grit sandpaper for 60 s and 350 RPM under constant water flow on a sanding disc and then fine ground with 4000 grit paper under the same parameters.

Approximately 5 nm of gold/palladium was sputtered onto the samples for the TiO_2 layer examination under the SEM (Gemini II CrossBeam 550L, Carl Zeiss AG, Oberkochen, Germany). The cross-sectional areas were aligned perpendicular to the electron-beam and the layer thicknesses were measured within the channels in the red-marked positions, as shown in Figure 1b).

3 Results and Discussion

Figure 1c) and d) show the reflected light microscope images of the outer surface of two cube types in the XZ plane. As expected, the struts of cubes with 2’000 channel width consist of 40 layers of 50 µm layer height (Fig. 1c, 40 x 50 µm = 2’000 µm) and of 15 layers at 70m µm channel width (Fig. 1d, 15 x 50 µm = 750 µm). In both cavities, a slight bending of the layers above the openings can be observed. This phenomenon can be attributed to the absence of a support structure within the channel, resulting in the formation of a printing artefact. The measurement of the channel widths revealed a deviation of the theoretical dimensions of 2’000 µm and 750 µm by approximately -5%.

The layer thickness measurement was carried out using SEM. All 6 cubes were analyzed in the carefully prepared XZ plane. As illustrated in Figure 2a) the thickness of the TiO_2 layer inside a channel of 750 µm width was measured to be 85 nm. Elemental confirmation of the TiO_2 was carried out by Energy Dispersive X-ray spectroscopy (EDX). The cracked structure on the surface is the gold/palladium layer. During the measurement, care was taken to take edges that are perfectly perpendicular to the viewing angle so that there is no perspective distortion that could distort the result.

The results of the TiO_2 layer thickness are listed in **Table 1**. The designation of e.g. 2’000/6 refers to the cube with a channel width of 2’000 µm and 6 open sides. The Uniformity Index (*UI*) was calculated according to formula (1) considering the local variation in coating thickness:

$$\boldsymbol{UI} = \left(\frac{(\boldsymbol{d_{max}} - \boldsymbol{d_{min}})}{\boldsymbol{2 * d_{avg}}}\right) * \boldsymbol{100} \tag{1}$$

Here, d_{max} and d_{min} are the maximum and minimum measured layer thicknesses and d_{avg} is the average layer thickness of all measurements of a cube.

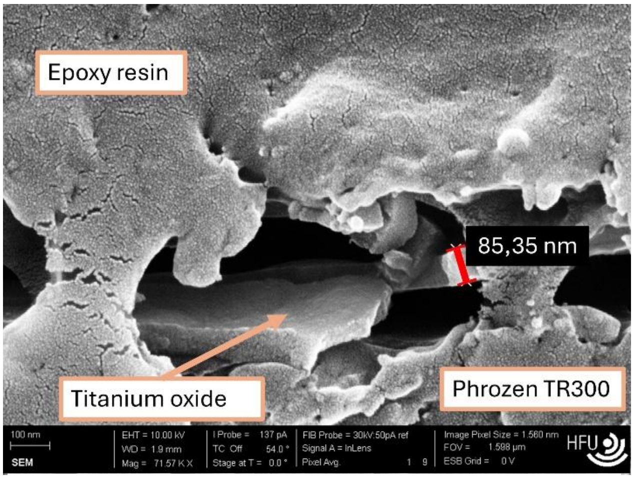

Figure 2: SEM analysis for the determination of the ALD-titanium oxide layer thickness (85 nm) on a 3d-printed Cube made of Phrozen TR300 resin (channel width 750 µm, 6 open sides, Position *West*).

Table 1: Thickness of the ALD TiO_2-coating (in nm) at different positions and Uniformity Index (*UI*, in %) of the cubes with channel width 750 µm, resp. 2’000 µm and with two, four or six open sides.

Position	750/2	750/4	750/6	2’000/2	2’000/4	2’000/6
C	80	80	80	92	89	89
N	82	80	82	88	82	84
E	81	80	89	90	84	89
S	79	82	80	90	86	91
W	80	80	85	90	86	91
NE	83	83	83	81	83	90
NW	86	84	81	90	80	86
SE	86	79	87	94	89	89
SW	82	81	82	95	86	91
AVG	**82**	**81**	**83**	**90**	**85**	**89**
SD	**2.5**	**1.7**	**3.2**	**4.0**	**3.0**	**2.4**
UI	**4.3**	**3.1**	**5.4**	**7.8**	**5.3**	**3.9**

The average layer thicknesses in **Table 1** are always thicker than the expected 75 nm measured on the silicon wafer. Since the cut surface was sputter-coated with approximately 5 nm of gold/palladium, the increasing in the layer thickness could be attributed to the sputter coating. The average thickness of the TiO_2 layer within the 750 µm channels of 87.9 ± 3.8 nm was slightly higher compared to the 2’000 µm channels (82.1 ± 2.6 nm). The enhanced accessibility during the ALD process is a possible contributing factor. However, it appears that the layer thickness is not influenced by the number of open sides of the cube. Similarly, no layer thickness gradient was identified between the central and peripheral regions.

The measurements revealed excellent coating conformity over the internal surface with a Uniformity Index *UI* of maximum 7.8%. The data indicates that there is a marginal improvement in the values for the *UI* in the 2000 µm channels (5.7 ± 1.9%) when compared with those in the 750 µm channels (4.3 ± 1.2%). It is also conceivable that the reason is to be found in enhanced accessibility in the wider channels.

Unfortunately, the idea of using a Parylene-C protection layer to optimize cutting and analysis was not feasible. The Parylene-C probably smeared during grinding and thus covered the thin TiO_2 layer.

4 Conclusion

The production of open-porous cubes was well achievable using AM. Although the channel widths were slightly smaller than the theoretical dimensions, this could be reduced with further improvement of the printing parameters. The uniform ALD coating of the internal channels using Parylene-C and TiO_2 was also possible. Irrespective of the number of open sides, reproducible layer thicknesses were measured even at a depth of 5 mm within the channels. It has been demonstrated that the ALD method is therefore applicable for the deposition of a homogeneous layer deep within porous structures. Central and peripheral areas exhibited an equivalent coating thickness. The actual layer thicknesses measured are slightly greater than those expected. Furthermore, the increase in channel widths from 750 µm to 2’000 µm was found to result in a slight augmentation of the coating thickness.

5 Outlook

The coating of open-porous structures produced by AM offers great potential, particularly in the field of medical technology. For example, patient-specific implants or scaffolds for the bone augmentation could be additively manufactured from PEEK and subsequently coated with ALD to ensure optimized biocompatibility and osseointegration.

This study showed that the ALD TiO_2-layer thickness is reproducible, homogeneous and conformal even in high aspect ratio cavities in porous additive manufactured structures.

Author Statement

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