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Atomic Layer Deposition as an Alternative Surface Finishing Technique: Characterisation of Oxide Layer Composition and Corrosion Behaviour

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Introduction

Nitinol is an important material for medical implants due to its super elastic behaviour and since its mechanical properties mimic biological materials. The surface of nitinol implants is commonly covered with a thin titanium dioxide (TiO_2) layer which acts both as a passivating layer to increase the corrosion resistance and as a barrier layer to address the toxicological concerns of long-term nickel release into the biological tissue. Even though nitinol undergoes a natural passivation when exposed to air, various thermal, chemical, and electrochemical surface finishing techniques are applied during manufacturing to replace the native oxide layer by uniform TiO_2 layers of controlled thickness. The properties of these oxide layers depend on the surface finishing technique and the process parameters.

Electropolishing is the surface finishing method of choice for nitinol devices which are passivated after shape setting is completed. This technique combines surface levelling, the removal of potentially contaminated surface layers and defects (e.g. Beilby layer, microfractures) [1,2] and the formation of a passivating oxide layer in one processing step. Atomic layer deposition (ALD) is another promising technology to produce TiO_2 layers through a series of alternating, self-limiting chemical reactions [3] of at least two precursor substances (e.g. titanium tetrachloride & water) in the gas phase. A sketch of an ALD sequence with $TiCl_4$ and H_2O is shown in Figure 1 (A-D). Upon every ALD-cycle one monolayer of stoichiometric TiO_2 is deposited and the desired oxide layer thickness can be tuned with high precision by the number of applied ALD-cycles. Due to the self-limiting reactions the deposition rate of the oxide growth is governed by the saturation of the surface with the precursor molecules [4] rather than the uniformity of the gas inflow. Therefore, ALD produces smooth and homogeneous layers with high contour accuracy even in spatially constrained structures. Processing of titanium tetrachloride ($TiCl_4$) and water (H_2O) at low temperatures is known to produce amorphous TiO_2 layers free of defects [5], which can be crystallised to the anatase structure upon thermal annealing.

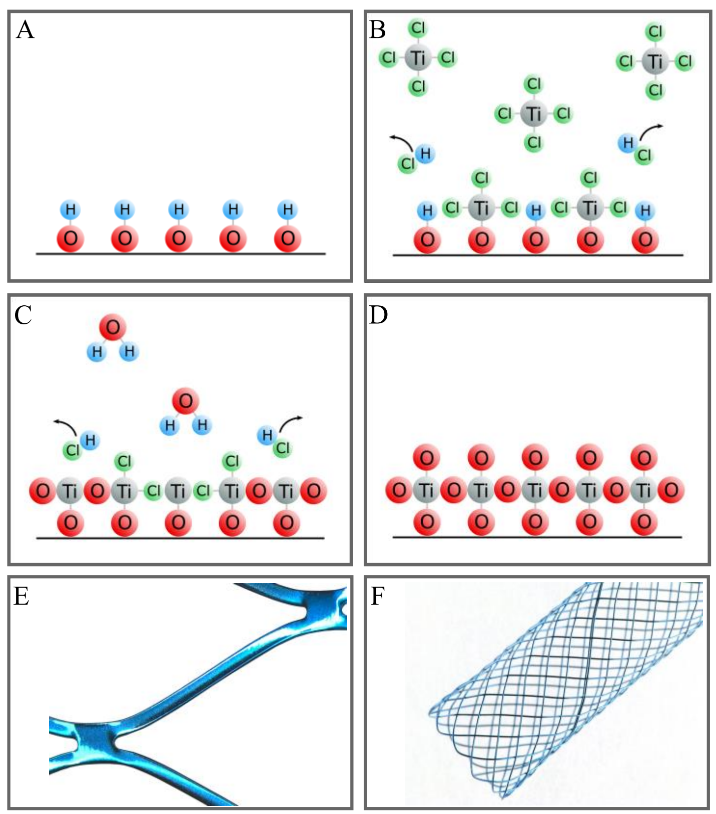

Figure 1: Atomic layer deposition mechanism as a series of alternating reactions of $TiCl_4$ and H_2O on a substrate surface (A-D) and ALD-TiO_2 covered heart valve frame (E) and braid (F).

The ALD-TiO_2 layer composes of titanium and oxygen atoms from the precursor gases, which means that the passivating layer gets coated onto the surface from an external source instead of being generated by consuming titanium from the workpiece like in the other surface finishing methods mentioned above. This is a mayor difference, since the surface modification by titanium consumption can lead to nickel enriched zones [6] underneath the oxide layer.

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Within this study ALD-TiO_2 was applied on both laser-cut and braided devices (heart valve frame in Figure 1 (E), braid in Figure 1 (F)) and initial characterisation of the composition, structure and corrosion behaviour have been performed on nitinol sheets and wires.

Experimental Procedure and Results

The aim of this study is to evaluate the feasibility of atomic layer deposition of TiO_2 on nitinol as a novel passivation process for the manufacturing of medical devices. Therefore, the chemical composition, structure, and corrosion behaviour of the oxide layer are investigated by means of Auger electron spectroscopy, transmission electron microscopy, scanning electron microscopy, corrosion testing according to ASTM F2129-19a and long-term monitoring of the resting potential under simulated physiological conditions. To mimic the thermal load during shape setting, post-annealing is performed and the influence on the mentioned properties is studied. Special interest is set on defects in the oxide layer, the film thickness and homogeneity, and the distribution of nickel. Long-term monitoring of the resting potential during immersion in phosphate buffered saline (PBS) is used to study the stability of the passive oxide layer under simulated physiological conditions. Gaining insight on the value and evolution of the resting potential is also beneficial regarding the current debate on the lack of corrosion acceptance criteria [7] given in ASTM F2129-19a.

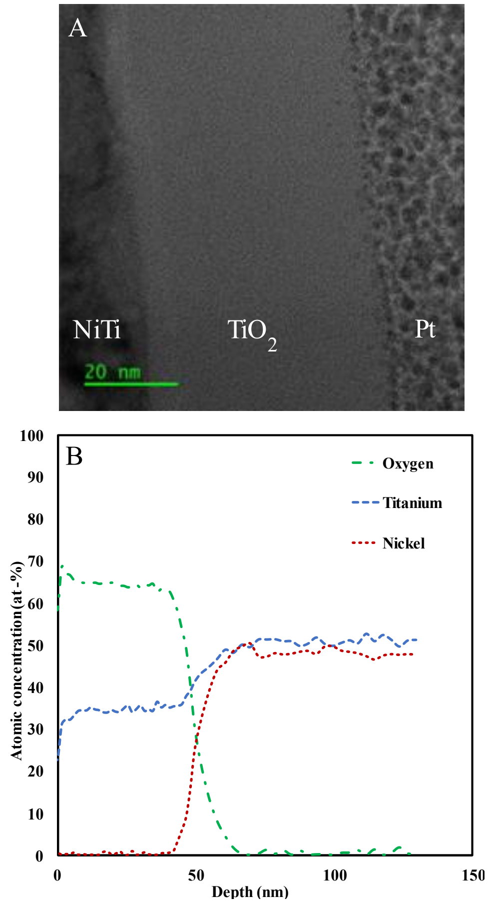

Figure 2: TEM image (A) and Auger electron spectrum (B) of ALD-TiO_2 on nitinol.

In the following, some exemplary results are shown. As demonstrated in Figure 2 (A) ALD-TiO_2 forms an amorphous layer with a homogeneous film thickness and a smooth surface. No defects are observed at the nitinol-to-oxide interface. According to the depth profile in Figure 2 (B) the oxide layer comprises of pure TiO_2 (33 at-% Ti, 67 at-% O) with a thickness of about 50 nm and no Ni-enriched zone is observed underneath the oxide layer. In corrosion testing according to ASTM F2129-19a the ALD-TiO_2 coating reveals passivating behaviour (not shown here).

References

[1] G. Yang, *et al.*, "Electropolishing of surfaces: theory and applications", *Surface Engineering*, Vol. 33 No. 2 (2017), p. 149-166. doi: 10.1080/02670844.2016.1198452

[2] R. Rokicki, *et al.*, "Enhanced oxidation-dissolution theory of electropolishing", *Transactions of the IMF*, Vol. 90 No. 4 (2012), p. 188-196. doi: 10.1179/0020296712z.00000000031

[3] M. Leskelä, *et al.*, "Atomic Layer Deposition Chemistry: Recent Developments and Future Challenges", *Angew. Chem. Int. Ed.*, Vol. 42 (2003), p. 5548-5554. doi: 10.1002/anie.200301652

[4] S.M. George, „Atomic Layer Deposition: An Overview", *Chem. Rev.*, Vol. 110 (2010), p. 111-131. doi: 10.1021/cr900056b

[5] B. Liao, *et al.*, "Excellent *c*-Si surface passivation by low-temperature atomic layer deposited titanium oxide", *Applied Physics Letters*, Vol. 104 (2014). doi: 10.1063/1.4885096

[6] S. Shabalovskaya, *et al.*, "Critical overview of Nitinol surfaces and their modifications for medical applications", *Acta Biomaterialia*, Vol. 4 (2008), p. 447-467. doi: 10.1016/j.actbio.2008.01.013

[7] L.E. Eiselstein *et al.*, "Acceptance Criteria for Corrosion Resistance of Medical Devices: Statistical Analysis of Nitinol Pitting in In Vivo Environments", *Journal of Materials Engineering and Performance*, Vol. 18 (2009), p. 768-780. doi: 10.1007/s11665-009-9420-z

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