Bioactivity in osseointegration of tantalum oxynitrides coatings for dental implants

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INTRODUCTION: Since decades, surface engineering plays a key role in the medical industry. Nowadays, coating technology research grows fast and offers novel solutions to improve the quality and durability of medical devices. Among new materials, metal oxynitrides are considered promising for applications in implantology due to their potential to accelerate early osseointegration [1]. The purpose of this study was to assess the osseointegration potential of sputtered tantalum oxynitride (TaOxNy) coatings with different nitrogen and oxygen contents grown on a standard dental implant material.

METHODS: TaOxNy coatings with different nitrogen and oxygen contents have been deposited by Magnetron Sputtering and High Power Impulse Magnetron Sputtering technologies onto micro-rough titanium and micro-rough stainless steel substrates. The coating thickness was set to 300 nm. Tailoring the coating composition can be performed with help of the target current hysteresis effect. Ion-induced secondary electron emission increases with the nitrogen flow while it decreases with the oxygen flow. Regarding surface preparation, Metal-Ion-Etching (MIE) clearly showed a modification of the titanium substrate micro-roughness. In some experiments, water vapor replaced oxygen in the process in order to bind hydroxyl groups at the coating surface. The micro-rough titanium surface was chosen as control and all obtained thin films were evaluated for their influence on cell proliferation with HOS osteoblast cells using a resazurin assay at days 4, 8, 14 and 21. Regarding the corrosion resistance, coated samples were tested in Ringer's solution + 0.2M sodium fluoride.

RESULTS: All developed coatings showed cell proliferation values comparable to the micro-rough titanium control and can therefore be considered cyto-compatible. The same coatings deposited onto micro-rough stainless steel showed significantly higher cell proliferation at days 14 and 21 than the uncoated control. The replacement of oxygen by water vapor demonstrated an improvement of the corrosion resistance in isotonic solution as well as a slight enhancement of cell adhesion compared to bare micro-rough titanium. It is worth noting that coated dental implants do not exhibit any significant damage during a screwing procedure into artificial bone (cellular foam).

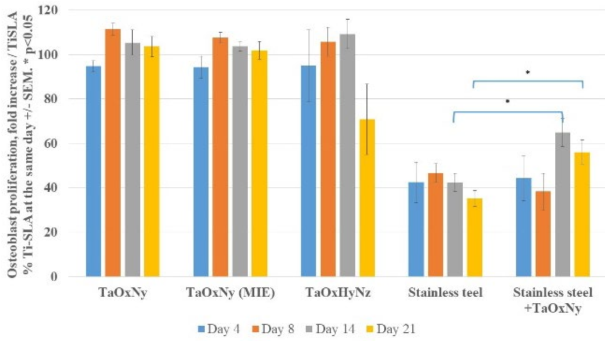

Fig. 1: Osteoblast proliferation assessed with a resazurin assay at days 4, 8, 14 and 21. Results were expressed as % of micro-rough titanium at the same day.

DISCUSSION & CONCLUSIONS: On micro-rough titanium samples, surface biocompatibility of coated samples was equal to bare control samples irrespective of the coating composition. The cell proliferation on micro-rough stainless steel was largely improved by tantalum oxynitride coatings. This shows a potential to apply tantalum oxynitrides coatings on other substrates than titanium (e.g. CoCr).

REFERENCES: [1] S. Durual, P. Rieder, G. Garavaglia, A. Filieri, M. Cattani-Lorente, S.S. Scherrer and A. Wiskott (2013) TiNOx coatings on roughened titanium and CoCr alloy accelerate early osseointegration of dental implants in minipigs, *Bone* **52**:230–7.

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Delayed delamination mechanisms of DLC coatings on articulating implants

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INTRODUCTION: Diamond-like carbon (DLC) coatings are promising materials for improving the wear resistance of articulating biomedical implants, due to their hardness and durability. However, despite successful in vitro high-force load testing, some DLC coated hip and knee replacements still failed after a few years in patients, mainly due to coating delamination induced by corrosion of the adhesion promoting interlayer, silicon (Si) [1]. Currently the performance of artificial joints is evaluated through articulating simulators that assess fatigue related problems, however these do not take into account slow corrosion processes, which may develop as a function of time in a corrosive media.

The aim of this work is to gain a better understanding of the corrosive mechanisms responsible for coating delamination at an interlayer/interface, and to use this information to ultimately achieve a more accurate prediction of the implant`s lifetime.

METHODS: The buried interlayer/interface is revealed through low-angle flat milling with an ion beam, then by utilizing a micro-electrochemical technique (consisting of a glass micro-capillary that acts as a miniaturized electrochemical cell), the coating/substrate interface is targeted and locally attacked, providing electrochemical data which can be used to predict the speed of deterioration of the coating in the corresponding electrolyte (HyClone® Wear Test Fluid (WTF)).

RESULTS:

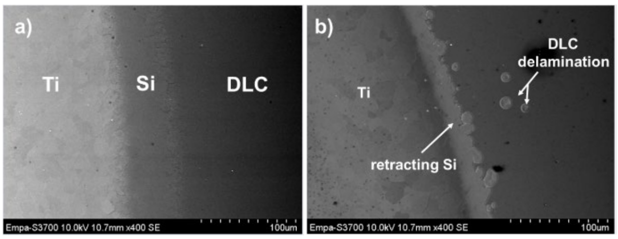

Fig. 1: a) SEM image of 1 µm DLC/100 nm Si/Ti flat-milled sample before immersion. b) SEM image of the same sample after immersion in HyClone® WTF for 1.5 years.

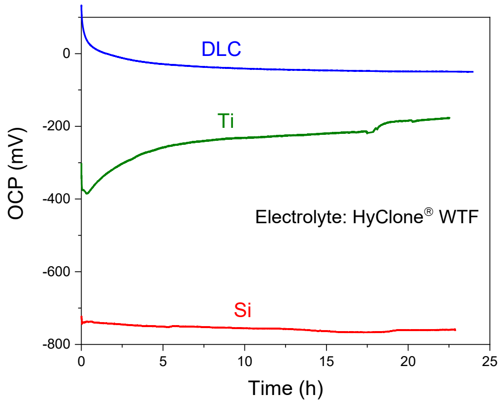

Fig. 2: Evolution of the OCP on DLC, Ti, and Si interlayer, measured with a 40 µm diameter capillary filled with HyClone® WTF.

DISCUSSION & CONCLUSIONS: Fig. 1a shows a SEM image of a flat-milled 1 µm DLC/100 nm Si/Ti sample, and Fig 1b shows the same sample after 1.5 years of immersion in HyClone® WTF. The initial Si interlayer has dissolved and the DLC has delaminated close to the interlayer interface. Contrary to lengthy immersion tests, Fig. 2 shows 24 h OCP measurements conducted on the initial flat-milled sample (Fig. 1a), with a 40 µm HyClone® WTF filled capillary. The DLC and Ti substrate show stable potentials plateauing at ca.-50 mV and -250 mV, respectively. While the Si interlayer shows a significantly lower potential, ca. -780 mV. The equilibrium potential of Si is ca.-1000 mV at ca. pH 7.4 (from the Si-H_2O Pourbaix system). The influence of proteins and additional species (phosphate, chloride, etc.) in HyClone® WTF can increase this equilibrium potential, narrowing the SiO_2 stability domain, so that a potential of ca. -780 mV results in SiO_2 dissolution. It can be concluded then that Si is an unstable interlayer in synovial-like fluid, and with micro-electrochemical characterization of the flat-milled sample, this conclusion can be reached much faster, as opposed to waiting 1.5 years with an immersion experiment.

REFERENCES: [1] R. Hauert, K. Thorwarth, and G. Thorwarth (2013) *Surf. Coatings Technol.* **233**:119–30.

Hydroxyapatite coating delamination – A case report 14 months after total hip arthroplasty

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INTRODUCTION: In uncemented total hip arthroplasty (THA) Hydroxyapatite (HA) coating has become very popular [1]. The increased porosity and specific surface topography of this coating might help accelerate integration into surrounding bone especially when compared to roughened titanium [2,3]. However, the interface between such a coating and the underlying metal represents a potentially weak zone. In the present case, the HA coating separated from the metal stem and this contributed to early failure after THA.

CASE REPORT: In another clinic a HA coated hip stem was implanted without cement in a 68 years old osteoporotic, deaf and dumb male patient for treating a femoral neck fracture. Following a minor trauma 14 months later, a periprosthetic fracture required a removal of the loose stem. The stem could be recovered without any instrumentation and a new implant was set. Early postoperative recovery and rehabilitation for now 14 months followed without adverse events.

METHODS: Clinical follow-up x-rays documented the reaction of the mineralized tissue around the implant. Tissue specimens removed during operation from the medullary cavity of the proximal femur have been examined by µ-CT and PMMA histology. Cut and ground undecalcified sections were stained with Giemsa-Eosin. The crystallographic phases of the HA coating were determined by X-ray diffraction (XRD) methods.

RESULTS: Conventional x-rays identified a thin and dense line parallel to the medial edge of the implant. Analysis of the corresponding tissue samples by µ-CT identified this as the HA coating which seemed well attached to the bone (Fig. 1). Histologically, this could be confirmed and the bone appeared viable with numerous nuclei in the osteocyte lacunae. No adverse reaction to either metal or HA particles could be observed. HA was the main crystallographic phase determined by X-ray diffraction in the coating layers that were attached to stem and bone.

DISCUSSION & CONCLUSIONS: Selection of an obviously under-sized stem at primary uncemented THA in an osteoporotic bone contributed to the fracture which followed the minor trauma [4]. The tissue samples obtained during the reoperation showed that bone was intimately grown to and connected with the HA coating. This could be documented with µ-CT as well as with histological investigations. However, delamination of a HA coating from a metal stem after only 14 months in situ is a fairly poor result for a permanent implant. Although the biomechanical situation with an under-sized stem might be more challenging than with a suitably sized implant, this type of failure required more attention. Further investigations of the interface between the hip stem and the coating and the bonding strength of the coating phases are needed. It is also necessary to closely monitor patients with comparable implant designs in order to get further information on the long-term durability of these coatings.

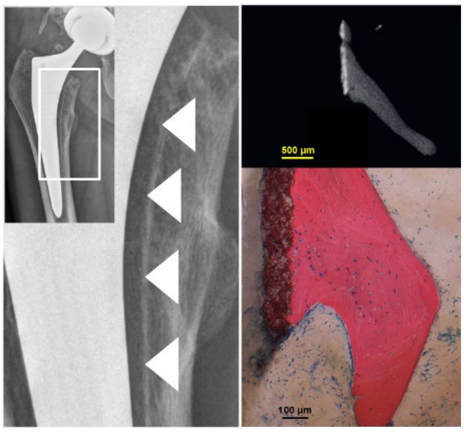

Fig. 1: In the clinical x-ray, the bright line (marked with arrows) of the delaminated HA coating is clearly visible. In the µ-CT image the coating (bright grey) with an on-grown trabecular bone (grey) could be shown and in the histological section the osteocyte nuclei (blue dots within red bone) can be seen.

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Cleaning of 3D-printed titanium implants

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INTRODUCTION: The interests in printing metals grew in the last few years, while the techniques start to be mature enough to generate reproducible and reliable results. Parts produced using these techniques can now rely on qualified equipment and highly reproducible powders. Such high quality of equipment and raw materials allowed the development of 3D-printing for medical device applications [1], as well as for other industries.

While 3D-printing is often seen as a tool where no limits are given, the post-processing of the parts remains as of today challenging. The obtained surfaces often present high roughness and a high number of half-embedded particles, which could be the origin of critical issues during further applications, in particular for medical implants made from metals.

Approaches for cleaning 3D-printed parts of different metals and geometry are presented.

METHODS: Grid samples and sponge-like structure of selective laser melting 3D-printed titanium alloy Ti6Al4V ELI were received either as printed or after a heat treatment. The samples were first pre-cleaned in an ultrasonic bath with an alkaline cleaner. A further treatment with an aqueous solution of proprietary composition and proprietary parameters was performed to remove the half-embedded powder remains. Surface topography was further analyzed using SEM (Hitachi, TM3000) or light microscopy. Roughness measurements were performed using a Hommel Tester T1000 (Jenoptik).

RESULTS: The use of ultrasound alone does not achieve the removal of half-embedded particles, and this independently of the used frequency (Figure 1a and 1b). The new wet process developed by KKS Ultraschall AG enables the removal of the surface embedded particles on all exposed surfaces and generates fully clean surfaces (Figure 1a and 1c). This surface treatment allows to remove particles in any complex geometry such as grids or bone-like meshes.

A stable surface is only achieved after heat treatment, which then allows color-coding.

The roughness of the treated parts is slightly decreased by the treatment, as shown in Figure 2.

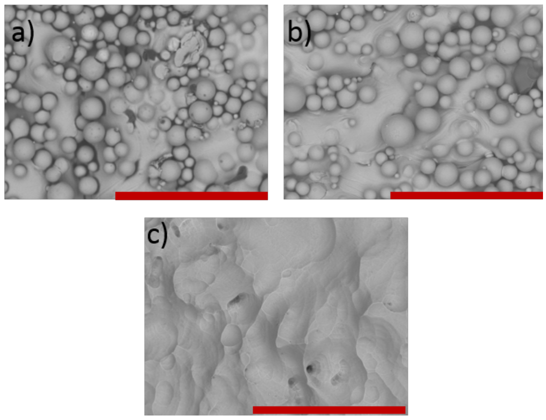

Fig. 1: SEM micrographs of titanium 3D-printed parts. a) As received after printing, b) after ultrasonication and c) after KKS surface treatment. Scale bar is 200 µm.

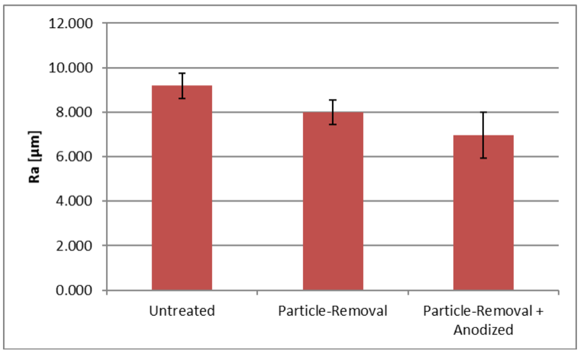

Fig. 2: Ra Value of 3D-printed titanium before and after treatment as well as after anodization.

DISCUSSION & CONCLUSIONS: It is shown that application of ultrasound of different frequencies is able to remove remaining loosely attached metal powder but not the half-embedded particles coming from the selective laser melting process. The developed proprietary method enables the removal of the surface-embedded particles remaining after 3D-Printing. The method is based on a wet process which allows the cleaning of parts even of very complex geometry, and a further color-coding. In contrast, standard techniques such as sand-blasting or electropolishing do not allow the removal of the half-embedded particles due to their line-of-sight effects.

REFERENCES: [1] https://www.fda.gov/MedicalDevices/ProductsandMedicalProcedures/3DPrintingofMedicalDevices/ucm500539.htm, accessed 14/12/2017.

Experimental mapping of contact stresses related to hip arthroplasty using dual mobility cup

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INTRODUCTION: The concept of dual mobility developed by Prof. Gilles Bousquet concerning total hip prostheses has shown its clinical interest concerning the reduction of hip dislocation risk. However, there is the problem of implants wear which is one of the main causes of long-term failures. The study of dual mobility explants revealed specific wear of the polyethylene insert of dual mobility prostheses. The objective of the study is therefore to establish the causal link between the distribution of the stresses applied on the polyethylene insert and the wear observed on the explants. The experimental model was based on the use of a pressure sensor placed between the acetabular cup and the polyethylene insert, first time concerning Hip prosthesis.

METHODS: The first step of our study was to demonstrate the reproducibility and the repeatability of the experimental model using a pressure sensor in static conditions. Secondarily, the consequences of the different artifices constituting the experimental model to support dynamic stresses were analysed. These results were then compared with the explants wear to determine the relevance of the model. Finally, the analysis of an interface protein suspension was investigated to determine the consequence of physical mechanisms induced by the adsorption phenomenon.

The experimental model was based on the use of an MTS 855 Bionix walking simulator equipped with a standard dual mobility prosthesis with an ultra-high molecular weight polyethylene and a 22.2 mm metal femoral head. The stresses distribution and values were collected using the TEKSCAN® piezoelectric pressure sensor 4402 K-Scan placed between the insert and the acetabular cup. To analyse the effect of adsorption phenomenon, a protein suspension was applied between the insert and the sensor.

RESULTS: The experimental values were reproducible and repeatable under static conditions (typically 15 % and in the best case about 2 % of difference). There was no statistically significant difference when analyzing the insert position using a polyvinylidene chloride film. During the dynamic simulations we were able to observe the displacement of the stress peak maximum reproducing wear zones described on the explants (high stress means high wear). The presence of a suspension also didn't show any statistically significant difference.

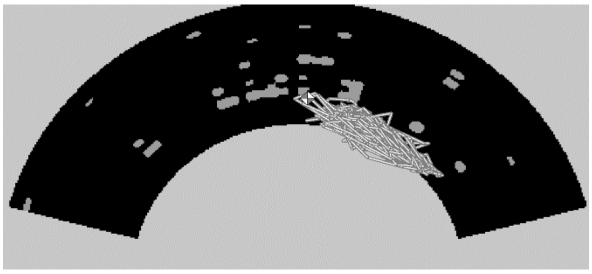

Fig. 1: Displacement of the maximum of the pressure peak (grey mark) on the film, running conditions.

DISCUSSION & CONCLUSIONS: The experimental model allowed reproducing the wear pattern on the explants. The study of the effects of a protein suspension didn't reveal any difference. However, many other settings should be analysed to optimize the model. Furthermore, the sensor fixation to the cup should be improved to support hip natural movements and stresses by any operator. The development of an experimental model for dual mobility hip arthroplasty will allow understanding more the wear phenomena. The experimental measurements are assessing the wear patterns isolated on explants [1]. By evaluating all parameters potentially involved in wear, it will allow improving the design and the material choice concerning the insert.

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Bridging cartilage defects: Could a metal foam/polymer-compound be an option?

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INTRODUCTION: Small cartilage defects in the knee might be bridged temporarily by a metal foam /polymer compound. An osteoconductive titanium foam acts as an anchoring material in the subchondral bone. The infiltrated UHMWPE functions as gliding material in contact with the remaining natural cartilage.

METHODS: Titanium foam cylinders (Ø 38 mm) with porosities ranging from 57 % to 77 % were produced by powder metallurgy [1] with two different grain sizes of the space holder (fine: 340 ± 110 µm, coarse: 530 ± 160 µm). The sintered titanium foam cylinders were infiltrated with UHMWPE powder (P) on one end and bulk (B) at the other end, at two different temperatures (160 °C, 200 °C) using a constant pressure of 20 MPa for 15 minutes.

Smaller cylinders (Ø 16 mm) were retrieved from the compound material by water jet cutting. The infiltration depths were determined by optical microscopy. The mechanical anchoring of the UHMWPE was measured by a shear test and the mechanical properties of the titanium foam were verified by a subsequent compression test.

The tribological behaviour was investigated using a cartilage pin sliding against a UHMWPE disc with a simulated gap.

RESULTS: Figure 1 shows a titanium foam cylinder with infiltrated UHMWPE after water jet cutting and after a shear test at one end. The only statistical differences in infiltration depth (Table 1) were found between fine and coarse pores (student's t-test, $p < 0.01$).

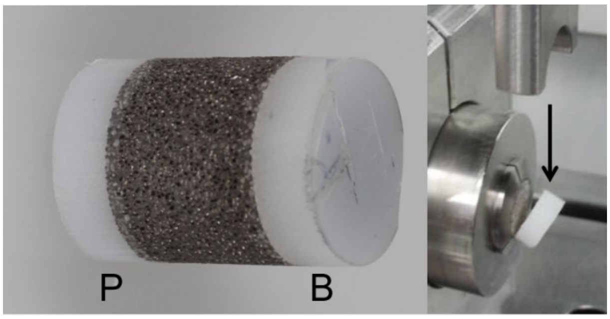

Fig. 1: Titanium foam cylinder (Ø 16 mm / left) infiltrated with UHMWPE as powder (P) and as bulk (B). Compound after a shear test (right).

The shear strength of the compounds exceeded the values obtained for a UHMWPE-cylinder alone with maximum forces ranging from 2800 - 4000 N.

Table 1. Average infiltration depth (± standard deviation) of UHMWPE into titanium foams with different porosities (n = 4)

pore size	temp.	infiltration depth /mm powder	bulk
fine	160 °C	1.26±0.08	1.27±0.13
	200 °C	1.20±0.04	1.26±0.11
coarse	160 °C	1.72±0.08	1.67±0.19
	200 °C	1.57±0.13	1.51±0.18

Mechanical properties of the titanium foam obtained during uniaxial compression were in the expected range [1]. Strength and stiffness values were depending on porosity but not on pore size. All samples could be compressed to at least 50 % of their initial height without the appearance of macroscopically visible cracks (Figure 2).

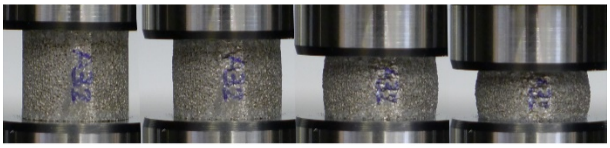

Fig. 2: Compression test of a Ø 16 mm titanium foam cylinder with sheared-off UHMWPE ends.

Preliminary tribological tests were carried out in order to prove the feasibility of the current concept.

DISCUSSION & CONCLUSIONS: The feasibility of a titanium foam / UHMWPE-compound material to gap small cartilage defects in the knee was tested *in vitro*. A pre-clinical study with an adequate animal model [2] will be needed to investigate safety and performance of the present concept.

REFERENCES: [1] T. Imwinkelried (2007) Mechanical properties of open-pore titanium foam. *J Biomed Mater Res A* **81(4)**:964-70. [2] B.B. Christensen et al. (2015) Experimental articular cartilage repair in the Göttingen minipig: the influence of multiple defects per knee. *J Exp Orthop* **2**:13.

Increasing the primary stability of cementless monoblock cups

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INTRODUCTION: Cementless, macro structured, modular acetabular cups proved to be safe and effective implants with excellent clinical results. Their production costs are significantly lower than those of porous coated or 3-D printed cups. Thus, macro structures are the design of choice, especially for thin-walled shells, in markets with high volumes but low budgets.

This is why the proven PrimeFit macro structure (Fig. 1) has been proposed for so-called monoblock designs, applied especially to cementless dual mobility shells and factory assembled ceramic monoblocks consisting of a metal back and a ceramic insert (Fig. 2). For both designs, the goal is to offer the largest possible ball head diameter for good joint stability which implies the use of shells with minimum wall thickness.

CHALLENGE: In some high volume markets, such as India and China, it is state-of-the-art to secure a modular press fit cup with 2 bone screws. The excellent primary stability of the proven PrimeFit structure alone could not convince orthopaedic companies. But, as a matter of fact, monoblock designs do not offer the opportunity to place screw holes. The only way to overcome this dilemma was to modify the implant design, without changing instrumentation and handling.

SOLUTION: Our development lead to an arc-shaped macro structure, trademarked PrimeFit Arcus (Fig. 3). It can be impacted like any other press fit cup, with identical reaming and impaction procedure. During impaction the shell performs a slight turn of less than 5°, and the surgeon neither feels this little twist nor a change of impaction force.

But how is primary stability affected? PrimeFit Arcus was tested against a market leading macro structured cup with identical press fit in PU blocks, density 15 PCF, regular and with defects.

RESULTS: Mean push out force was 822 N vs 550 N (+49%, N=4). Lever out moments were 37 Nm vs 23 Nm (+61%, N=2) and in blocks with defects 14 Nm vs. 7 Nm (+100%, N=4) in the direction of the defect (worst case). These results have been confirmed in a client's lab.

CONCLUSION: If a cup has the characteristics of a screw, even though with a small turn, the discussion to set additional bone screws becomes obsolete. This is valid for monoblock designs as well as modular primary acetabular cups. Handling and instrumentation remain unchanged, and being able to avoid bone screws saves costs and OT time.

Fig. 1: The PrimeFit structure, developed by Jossi Orthopedics, has been adopted by 3 orthopaedic companies. So far, approx. 15'000 PrimeFit cups have been implanted.

Fig. 2a (left): Design proposition for a dual mobility shell with PrimeFit structure. Fig. 2b (right): PrimeFit Monoblock, a project with CeramTec.

Fig. 3: PrimeFit Arcus, an arc-shaped macro structure, with doubled primary stability compared to a market leading macro structured cup under worst-case conditions.