Coating of Additive Manufactured Dental Suprastructures and its Interaction with Veneering Resin

Alexander Rex

Master Thesis, 2016
Division of Material Chemistry | Department of Chemical Engineering
Faculty of Engineering LTH, Lund University
&
Dentsply Sirona Implants
Hasselt, Belgium

Coating of Additive Manufactured Dental Suprastructures and its Interaction with Veneering Resin

Author

Alexander Rex

Course name

Degree Project in Materials Chemistry for Engineers

Supervisors

Sebastian Bolling, Kevin Deprez, Jan-Olle Malm

Examiner

Staffan Hansen

Preface

This master thesis was done as the final stage of my studies in Biotechnology at Lund University, Faculty of Engineering. The thesis was conducted at Dentsply Implants in Hasselt, Belgium and with the department of Material Chemistry within the Faculty of Engineering, LTH.

I would like to give my special thanks to several people who helped enable this project and supporting me along the way;

Sebastian Bolling, my supervisor at Dentsply who has supported and worked with me on this project the entire way. Thank you for your active approach and commitment to this project and your knowledge of dentistry and additive manufacturing which was invaluable to complete the project. I would also like to thank Kevin Deprez who guided and supervised the project throughout the entire duration.

I would like to thank the management at Dentsply for allowing me to be involved in this project as well as the co-workers at the site in Hasselt for the good time and all the help and advice they gave me throughout my stay.

Finally I would like to thank my supervisor professor Jan-Olle Malm at Lund University who encouraged me to pursue this project and was always available for advice and support from back home.

Abstract

This study has investigated the possibilities of coating additive manufactured titanium dental prosthesis structures. Different coating alternatives were evaluated with the regards of esthetics, function and implementation possibilities. The coatings were applied on test samples and the adhesion between the printed titanium structures and the coating as well as to resin veneering applied on top was tested. The coating methods that were evaluated were anodization, plasma electrolytic oxidation, physical vapor deposition, sol-gel as well as a conventional opaque resin coating.

A so called Charpy test was conducted to evaluate if the different coatings affected the material strength, however the method proved unsatisfactory to study any differences caused by the coatings. The surface roughness was also tested for coated and non-coated samples. The possibility of implementing the coating at Dentsply were investigated by evaluating economic and technical aspects of the different coating methods. The shear bond test showed that the conventional method of opaque manual coating resulted in the highest bond strength, with anodization and PVD being the second best.

This study concluded that producing a large scale automated industrial method for coating titanium prosthetics before resin veneering poses several challenges. More development is needed in order to present an implementable solution.

Keywords: Additive manufacturing, 3D printing, dental prosthesis, coating.

Table of Contents

1 Introduction

This chapter presents the company where the project was executed and the background of the project. The goals and the scope is also presented.

1.1 Company

This master's thesis was performed at Dentsply Sirona Implants in Hasselt, Belgium (referred to as Dentsply). Dentsply has a 40 year history in the dental implant field, working with the motto "Restoring quality of life and happiness" they offer a wide range of products to meet the needs of dentists and lab technicians around the world. The production site in the Research Campus of Hasselt, Belgium employs approximately 60 people and specializes in production of dental prostheses and implant drill guides for a global market.

Dentsply is part of Dentsply Sirona, a multinational company listed on Nasdaq (XRAY) and the world's largest supplier of dental products and applications. The company has approximately 15,000 employees and operates globally in over 40 countries with sales in more than 120 countries, with its headquarters in York, Pennsylvania (Dentsply Sirona, 2016). During the project a merger between Dentsply (corporate) and Sirona was performed in order to strengthen the company portfolio of products and services.

1.2 Background

Dental prosthetics are made to help patients regain functionality and esthetic appearances that have been lost due to the loss of teeth. Today's dental industry not only develops prostheses but also solutions that enable and facilitate prosthetic procedures for dentists. Dentsply is divided into two units of operations ATLANTIS™ Suprastructures and SIMPLANT®[1]. This project is focused on the division of ATLANTIS™ Suprastructures that currently produce four different types of so called suprastructures which replace two or more teeth. These are categorized into bridges, bars, 2-in-1 and hybrid structures (see Figure 1.1) and each one is custom made to perfectly fit each customer.

---

[1] Business unit for drill guide production

Figure 1.1 Bridges (top left), bars (bottom left & right), 2-in-1 (center) and hybrid (top right) produced by Dentsply.

These structures are fixed into the patient's mouth by first inserting implants. These are screwed to the jawbone of the patient and act as attachments for the prosthesis. Potential existing implants from earlier abutments may also be used to help attach the prosthesis. Before inserting the suprastructures into the patient, they are sent to a dental laboratory were they are veneered with dental resins or alternatively in case of a bar structure a denture is created that can be attached to the structure. The finished prosthesis (see Figure 1.2) is then sent to the dentist who can insert it into the patient's mouth and fix it to the implants.

Figure 1.2 Example of a finished product showing a veneered hybrid prosthesis.

Within prosthetic dentistry there is an ongoing development and a strong innovative drive. A large focus is diverted to improving the materials of the prosthetic structures, the interaction of these materials with the human body and the design that will allow for a functional and esthetic result. One of these challenges involve the bonding of the veneering resin to the metal structure as well as the esthetics of the final product. Today opaque resin and metal primer is used to achieve the interface between the metal structure and the veneering resin in combination with other common surface treatment methods such as sandblasting. Apart from bonding the opaque resin has the important function to remove the mouse-grey color of the titanium metal allowing for a more natural result of the finished product.

Resins commonly contain methyl methacrylate which is extensively used within the dental industry for various applications. The resins are applied in molds as a flowing paste or by a brush and are subsequently cured either by light, heat or using a two-component cold-curing process. Veneering using ceramic materials that are baked at high temperatures is also commonly used, however this is out of the scope of this project.

1.3 Market Background

Today Dentsply does not coat its ATLANTIS Suprastructures however other products within the company are coated such as implants, abutments and screws. These are mainly anodized or coated with a titanium nitride (TiN) coating using a Physical Vapor Deposition (PVD) technique. Recently other actors on the market have begun offering coating options such as anodization and other surface treatments on titanium suprastructures (Panthera Dental, 2016), these however do not use structures produced by additive manufacturing (AM). The possibility of coating the suprastructures is an area of interest for Dentsply who are now looking at the opportunity to develop a coating that improves desired features of the suprastructures and simplifies production.

1.4 Aim and Objective

The objective of this master’s thesis is to investigate the possibilities of an efficient, esthetic and functional coating for titanium alloy AM products with a resin veneering and the way these coatings influence the final product. Feasibility of implementation should also be evaluated. The aim is to offer an improved option to conventional resin opaquing.

1.4.1 Objectives

- Define customer/production demands
- Investigate state of the art coatings
- Assess current market situation

- Produce coated samples
- Perform tests to compare conventional techniques with evaluated coatings
- Investigate implementation feasibility

1.5 Scope

The current market situation has been assessed and a literature study was conducted to acquire knowledge on possible coating materials and methodologies. The coatings were chosen and evaluated with defined user requirements in mind and were performed at Dentsply or by the help of a cooperating 3rd party company/institution.

To evaluate each coating based on the requirements a number of tests were defined and performed on coated surfaces and compared to non-coated surfaces as a controls. The goal was to find the most appealing coating to offer customers regarding esthetics, bonding and safety. Preserving the safety and reliability of the finished product even after the coating/colorization is essential and has also been taken into account when evaluating the methods and materials. The possibilities and limitations regarding implementation of the coating methods into the current process were evaluated, with regards to technical and financial limitations.

Both cobalt chrome and titanium-alloy suprastructures can be produced by AM or by conventional milling techniques however this project will only consider titanium Grade23 alloy (see Figure B.2 Appendix B) structures produced by AM and finished by composite veneering. Out of the four types of suprastructures produced by Dentsply (bridges, bars, 2-in-1 and hybrids), this project focuses on hybrids and bridges since these are produced by AM. Development of AM techniques is not within the scope of this project.

2 Pre-study

This chapter describes the basic concepts of the production at Dentsply and techniques used during this process. It also gives a background to the basic theory of the different coatings that were chosen as a result to the literature study.

2.1 Dental Prosthesis

The need for a dental prosthesis can have several reasons, such as tooth decay, gingivitis[2], or physical injury. Evidence has been found to support that dental surgery may be one of the oldest specializations within medicine dating back over 9000 years (Bower, 2006), and attempts to remove damaged parts or completely replace teeth with animal bones, shells or stones have been made. More modern solutions such as loose prostheses were the only available treatment in the past, however today modern dental implantation technology is available and rapidly becoming the standard treatment (Wijk, et al., 1998). The modern dental prosthesis consists of the implant which is fixed into the bone and the suprastructure that is in turn fixed onto the implant. The prosthetic structure consists of a metal base and a veneered surface made of ceramics or resin to replicate the lost teeth and gum line (see Figure 2.1). When replacing a single tooth an abutment is used instead of a suprastructure.

Figure 2.1 Clinical realization of an ATLANTIS™ Suprastructures bridge.

---

[2] Gum disease

2.2 Additive Manufacturing

The advancements within additive manufacturing (AM), also commonly known as 3D printing, have had revolutionizing effects on the production processes for many industries. Not least within the medical and dental field which has been the sector with the third largest adoption of the technique (Allison & Scudamore, 2014). AM can complement or replace conventional subtractive techniques, such as milling or turning. Additive manufacturing has several advantages over milling for the application of dental prostheses production:

- **Structure:** Complex and high precision design features can be created
- **Time effectiveness:** Batch process allows for several structures to be produced at once.
- **Material waste:** AM allows for a very low amount of waste to be generated compared to traditional subtractive techniques.
- **Net shape manufacturing**: What you see is what you get on structure level.
- **Light weight designs**: AM allows for light weight designs to be created with hollow or lattice matrixes which can maintain the structure strength while reducing the weight.

Drawbacks with using additive manufacturing compared to milling include:

- **Lower precision on standardized surfaces:** AM techniques are very precise on structure level but flat and standardized surfaces are less accurate than with traditional machining processes.
- **No standalone process:** For the application of dental prostheses AM cannot be used as a standalone process as the interface connections need very precise geometries.
- **Low throughput method:** Each batch is time consuming and the parts that can be put through each batch is limited.
- **Material limitations:** Not all materials can be used for AM. Many plastics can be used as well as some metals and ceramics.

At Dentsply the suprastructure production uses the best of both worlds by printing the structure with extra material around the interfaces and then using optimized milling programs and tools to finish the connections. Since the production of suprastructures can be considered a low throughput production this disadvantage is not a big issue, and the time effectiveness compared to individual milling of each complete structure is instead an advantage.

Regarding material limitations currently cobalt/chrome and titanium are the materials of interest, were cobalt chrome is currently in production and titanium will be produced in the near future. The titanium alloy that is used in the process at Dentsply is a titanium/aluminum/vanadium alloy often denoted Ti6Al4V which indicates the wt. 6% aluminum and wt. 4% vanadium present in the titanium (see Figure A.1 Appendix A for full data sheet information).

2.3 Biocompatibility

When discussing “biocompatibility” of a material different interpretations may be implied. For dental applications this word often describes four major functionalities.

- **Toxicity:** The material does not cause harm to humans even after prolonged contact. Human cells are not affected in a negative way and the material does not react undesirably in the oral environment.
- **Hard tissue compatibility:** Bone formation or osseointegration, is enhanced by the material.
- **Soft tissue compatibility:** Improved adhesion and growth of gingival epithelium cells are promoted by the material.
- **Antibacterial:** Material has properties that act to reduce growth of bacteria and reduces formation of biofilms.

Adhesion of gingival cells and the prevention of bacterial cell adhesion are two properties that contradict each other. These properties cannot be attributed to the metal itself however, but rather through surface modification (Hanawa, 2010). Hard tissue compatibility and gingival cell adhesion are properties that are more interesting for the surfaces of implants (Curto, et al., 2005). Since the suprastructures are not in contact with areas that need to promote these features adhesion of gingival and osteoblast cells is not of interest for this application, and are not included in the current definition.

In this thesis biocompatibility is referred to as a material that is non-toxic, non-degradable and possibly prevents or reduces the growth of bacteria or reducing biofilm formation.

2.4 Production Process

The production processes at Dentsply follows a well-defined path through the site in Hasselt. A simplified process flow for AM ATLANTIS™ suprastructures can be seen in Figure 2.2 and the process is described in further detail bellow.

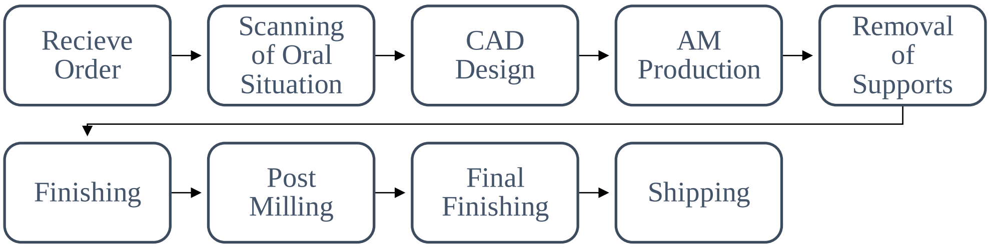


Figure 2.2 Simplified production flow at Dentsply.

When an order comes into Dentsply an inventory of the received materials is made, usually consisting of a stone model (casting of the teeth) with implant analogues and soft tissue replicas, or a digital file with pre-scanned model. In case of the stone model these are scanned using an Imetric scanner (see Figure 2.3) that creates a digital 3D model of the patient's oral situation, implant positions and the prosthetic situation.

Figure 2.3 Imetric 3D scanner used in the process.

The STL-files (typical CAD files) created by the 3D scanner are sent together with the customer requirements to the CAD-team who design each individual structure according to customer demands. Once the model is created the implant interfaces, which need to be milled for maximum precision in this critical area, are also modeled. The CAD models are then oriented on a virtual build plate and the data is sliced into several hundred layers creating 40 micron thick slices.

This model is then printed, layer by layer, by selective laser melting (SLM) with a Renishaw AM250 printer (see Figure 2.4). This technique uses a high powered laser to melt fine metal powder in these thin layers onto a build plate (see Figure 2.5). The laser melts the metal powder for each thin layer allowing it to bond within the current layer as well as with the previous layer, creating a coherent and dense structure. In contrast to selective laser sintering, which is a similar process were the metal power is only partially melted across the surface of the particles, a close to 100% density can be achieved with SLM giving reproducible properties and non-porous structures (Bremen, et al., 2012).

Figure 2.4 Renishaw AM 250 used for production at Dentsply.

In order to achieve these 40 micron thin layers a powder bed fusion technology is used which utilizes a sieve that spreads a thin layer of the powder over the build plate. The laser which is guided by a scanning system melts the layer and then the build station piston is lowered and a new layer of powder is applied. This process is repeated for all layers until the structures are completed after which excess powder can be removed and reused.

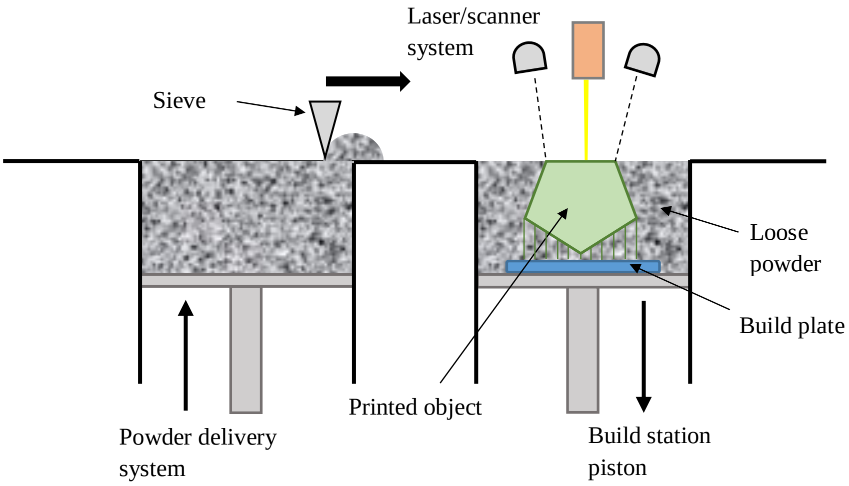


Figure 2.5 Schematic illustration of AM process used to produce test specimens (Referera till Titanium Powder Metallurgy boken? sparad som länk).

During the SLM process required support structures are created onto which the structures are then printed. These also help transport heat away from the structure created by the melting process, preventing it from over-heating during the process. After the complete structure has been printed these supports must thus be removed, which is done by a band-saw and manual removal or polishing. Each suprastructure is printed with a hub that allows for the structure to be post-milled using a 5-axis milling machine (see Figure 2.6). In this step the implant interface connections are created with very high precision for an optimal fit. Finally the hub is removed and the product is finished manually by sandblasting and polishing desired areas. The product is finally analyzed by quality control before shipping to the customer, which in Dentsply’s case is the dental laboratories.

Figure 2.6 Milling machine used to mill implant interfaces.

2.5 User Requirements

Properties that are sought for when producing a dental prosthesis is corrosion resistance, biocompatibility, high strength and light weight. Cobalt chrome is excellent for the first three properties, but has a higher density (~8.5g/cm^3) compared to titanium (~4.5 g/cm^3) resulting in a heavier final structure. Titanium instead has a much lower tensile strength and worse tribological features than cobalt chrome, something however that can be improved upon by adding a thin film coating (Catauro, et al., 2014).

Other demands exist on dental prostheses that determine the final esthetics of the product. Finding a correct structure fit and performing veneering to match the patient’s gingiva and tooth colors are crucial in order to produce a good prosthesis.

To have a base for evaluating the different coatings that were to be investigated a set of requirements were defined (see Table 2.1). The importance of each requirement was also rated on a scale from 1 – 5.

Table 2.1 List of defined user requirements, the effect if these are not fulfilled and the importance of each requirement.

Requirement	User requirement	Non-compliance Effect	Imp.
Functional	Excellent bonding to titanium alloy (grade 23)	Failure of metal-coating interface	5
	Excellent bonding between coating and resin	Failure of coating-resin interface	5
	Compatible with all resin types (cold, heat, light)	Not compatible with products on market	4
	Surface macro/(micro) structure should be retained	Failure in interface	5
	Not affect material strength negatively	Reduced life-length of product	5
	Corrosion resistant	Reduced life-length of product	4
Esthetic	Opaque, pinkish color to cover mouse-grey titanium surface	Dead/dull final impression of product	5
	Visual appealing product	Less attractive for customers	3
Safety	Biocompatible coating	Danger to patient health or reduced life-length of product	5
	Withstand steam sterilization	Sterilization will damage coating	5
	Process risks taken into account	Improper handling of machines and materials	5
Technical	Easy to implement in-house	Costly implementation/ ineffective workflow	5
	Cheap process	Inefficient process	4
	Suitable for automation	Costly labor required	4
	Suitable for CoCr &/or Ti	Coating cannot be used for process	5
	Suitable for rough/porous surfaces	Coating less effective	4

The first requirement is for the coating to improve the esthetics of the structure, removing the grey color of the metal causing a dead and unnatural look of the final prosthesis. Since the largest part of the prosthesis is within the gingiva region a pink colored coating or a warm color such as yellow/gold would be optimal for this purpose. The second requirement is for the coating to bond well to the metal structure as well as to the denture resin. This is important to minimize the risk of failure and the development of micro-gaps between the coating and resin due to curing shrinkage. Additional requirements is for the coating to be compatible with all types of curing resins used in the field, such as heat-curing or light-curing resins, it should not reduce the endurance limit of the structure and it should be biocompatible to ensure a safe product.

The coating process should also meet certain requirements, related to technical and financial demands. The process should be feasible to implement in-house at Dentsply taking into account space limitations and process flow as well as automation. The process should handle a throughput of 30 units per day to ensure the process is not a bottleneck in production. The capital investment of the coating process as well as the coating price per unit should be estimated in order to calculate the ROI.

2.6 Coatings

Within the area of thin film surface coating a lot has happened in the recent years and development is steadily ongoing. The available coating materials and techniques are constantly being improved upon and are becoming cheaper. This development is driven by increasing consumer demands and extensive government investments within growing industries such as aerospace, renewable energy and medicine (MarketsandMarkets, 2014).

The literature on optimizing coatings for dental prostheses is quite limited, and the commercially available coatings for this application are simple. A combination of these factors form an opportunity to innovate the surface treatment/coating of dental suprastructures, with the benefits of esthetics and reliability of the final product for the customer as well as an interesting business case for Dentsply.

Based on these requirements possible metal coatings and metal coating techniques were evaluated. Through an internal selection process four coatings were deemed the most interesting candidates for further pursuit. These were anodization, plasma electrolytic oxidation (PEO), titanium carbon nitride (TiCN) applied by PVD, and a hybrid sol-gel coating. Anodization and PEO coatings are conversion coatings, meaning that the base material is converted to form a coating layer, while PVD and sol-gel are deposition techniques, meaning that a material is deposited to form a coating layer.

2.6.1 Anodization

Anodization is used widely within the dental industry in order to improve the esthetics, color code, or add functional properties to metals like aluminum, magnesium and titanium metal pieces. The special color anodizing without pigments is however only possible to perform on titanium. Indeed even anodized suprastructures exist on the market, for example the hybrid structure seen in Figure 2.7 from Panthera Dental, however these are milled with a fine polished surface.

Figure 2.7 Anodized milled hybrid bar from Panthera Dental.

Anodization is an electrolytic passivation process that increases the naturally occurring conversion of titanium into titanium dioxide (TiO_2) on the surface of the metal. This process forms a protective layer preventing further corrosion and improves wear resistance. The TiO_2 layer formed by anodization on titanium substrates causes a colored appearance by light interference, such as the effect seen with thin oil spills on water. This effect is not seen on aluminum or magnesium and pigments are commonly used in these cases. Through the effect of cancelling and reinforcement of different wavelengths of light and in different amounts the white light that hits the surface will be visualized as a color after passing through the titanium dioxide surface layer. This gives the grey metal surface a colored appearance. For example if the blue wavelengths are reinforced and the red wavelengths are cancelled out the color you see is blue.

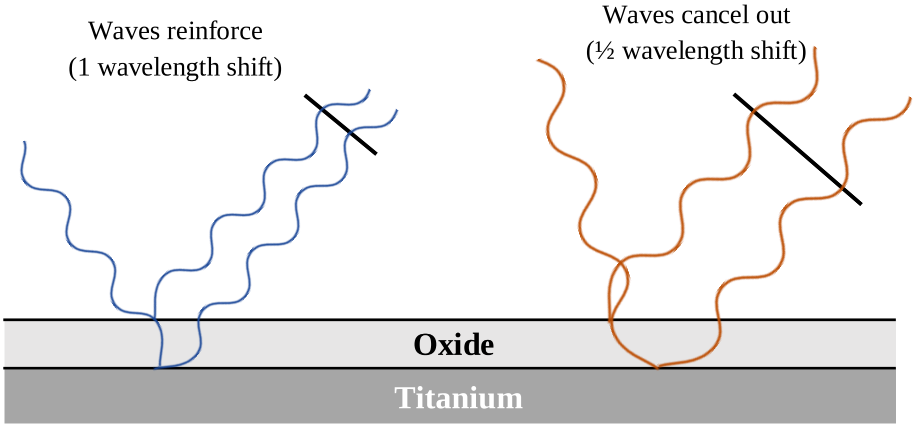


Figure 2.8 Light interference effect caused by reflection and wavelength shifts due to the oxide layer.

Through this method a wide range of colors, dependent on the anodized layer thickness, can be achieved and may be used to greatly improve the product esthetics (Wadhwani, et al., 2015). Most interesting colors for this project such as yellow, gold and even pink are possible to achieve on titanium and titanium-alloys, however white is not achievable with this method. The thickness of the oxide layer formed by anodization is typically a few microns and can be optimized by the process parameters, especially through the potential applied were increasing potentials create thicker oxide layers. Anodizing typically uses potentials from 10 – 100V but can go as high as 200V. Acidic electrolytes are commonly used for the process, such as sulfuric or phosphoric acid.

Anodization has the limitation of only being applicable to titanium and titanium-alloys, which prevents the use of this method on CoCr products. Also since the color is not an absorption color from the material itself but an interference color, creating a consistent color will depend on controlling the process carefully to achieve a uniform layer thickness. According to Vermesse el al. (2013) anodization of the titanium-alloy Ti6Al4V causes an endurance limit decrease of approximately 2.9% compared to a turned sample, which would need to be avoided through process optimization or compensated for in the design of the prosthesis in order to maintain the same strength for coated prostheses.

Titanium is well known for its biocompatibility and anodization of titanium has shown in many studies to further increase proliferation of human cells (Singh, et al., 2013) (Chen, et al., 2009). Anodization is also used within a various medical and dental applications further supporting the safety and reliability of this technique for the application described. Also the availability and simplicity make anodization an interesting choice of coating method to investigate.

2.6.2 Plasma Electrolytic Oxidation

Plasma electrolytic oxidation (PEO), also commonly known as micro-arc oxidation, is an electrochemical surface treatment not very different from anodization. Similarly it creates oxide coatings but uses higher potentials (>200 V) to create plasma by discharges occurring on the surface of the metal. Common electrolytes for PEO coating on titanium include aluminate, phosphate and silicate (Lugovskoy & Zinigrad, 2013). The electrolytes used also often contain a strong base or acid to alter the pH of the solution.

The coatings produced are much thicker than from anodization ranging from tens to hundreds of micrometers in thickness. Metals like aluminum, titanium or magnesium are suitable for this method and can receive greatly increased hardness, wear resistance and corrosion resistance (Yerokhin, et al., 1999).

Important ways of modifying the PEO process include varying the electrolyte composition or voltage. Also the substrate can be of great importance for example different titanium alloys such as Ti6Al4V or Ti6Al7Nb were shown to exhibit different surface structures after PEO treatment with identical process parameters (Cimenoglu, et al., 2011). The reason for this is differences in the reactions with vanadium and niobium. The coating parameters in combination with the substrate material are also something that can greatly affect the coating in terms of structure and color. A reason for this is that the electrolyte is partially incorporated into the coating layer, thus changing the electrolyte will affect the exact composition of the coated layer.

Cimenoglu et al (2011) concluded that PEO coated titanium alloys showed increased biocompatibility compared to the uncoated titanium alloys by showing a significant increase in growth of human osteosarcoma cells on these coated substrates. The potential of PEO coatings to coat complex 3D structures in a simple manner while giving enhanced properties makes this method interesting to investigate.

2.6.3 Physical Vapor Deposition

Physical vapor deposition (PVD) is a thin film coating method that vaporizes a solid material by high temperature vacuum, a gaseous plasma or by high-current discharges and allows these vapors to be deposited onto the substrate. Several methods to apply PVD films are available. A well know technique is cathodic arc deposition or Arc-PVD which relies on a high-current low-voltage discharge occurring between two metallic electrodes. Other well-known PVD technologies include thermal evaporation and sputtering and can in principle work just as good, however these will not be described in-depth since cathodic arc was the focus in this project.

The current between the two electrodes will create a discharge once ignited and will start forming a small number of spots on the cathode target with a very short residence time. New daughter spots are rapidly created on the edges of parent spots. This causes a typical movement of the arc beam across the cathode target surface allowing different areas of the cathode target to be eroded. To allow the cathode target to be evenly eroded however, magnetic fields can be used to control the arc and move the discharge spots across the surface.

The type of coating applied is dependent on the arc source material as well as the gas atmosphere inside the chamber. Sputtering targets of several materials can be used such as titanium, aluminum, zirconium, and more. The coating is generated by energy transferring from the arc into the cathode target material dislodging atoms. The dislodged atoms are directed towards the substrate and condensate onto the substrate surface.

If a gas, such as CH_4 and N_2 which is used to create TiCN, is also introduced these will react on the way towards impacting the substrate. To change the composition of the deposited film different cathode materials can be used as well as introducing different reactive gases into the reaction chamber.

A problem with arc deposition is that undesired macro particles and neutral particles that adhere poorly to the substrate will be dislodged from the cathode. This can however be solved by using a magnetic duct that effectively can filter out large and uncharged particles allowing only desired plasma to be directed towards the substrate (see Figure 2.9).

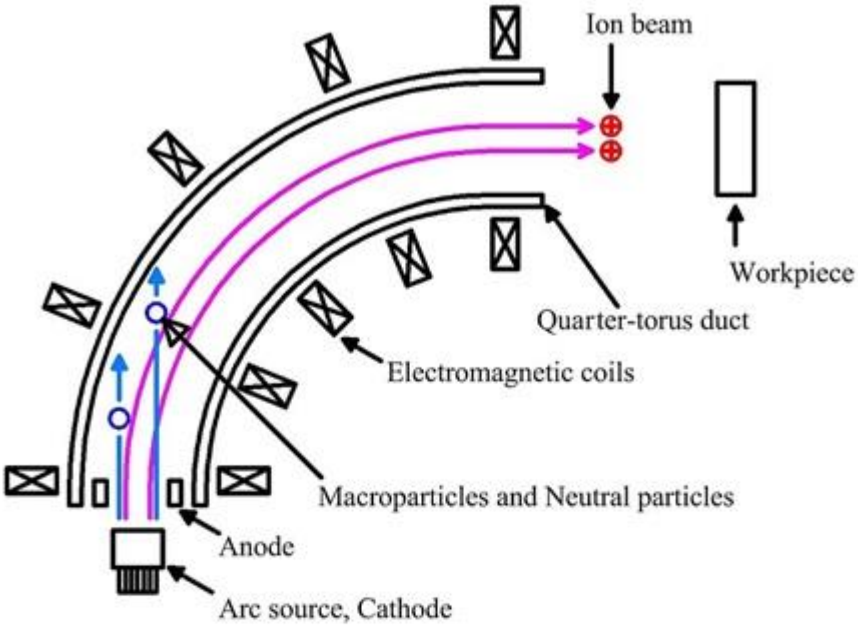


Figure 2.9 I. I. Aksenov’s quarter-torus macroparticle filter used to filter undesired particles in Arc-PVD (Sunyataburus, 2010).

PVD coatings have several industrial applications today including coatings for drill tips, automotive parts and many accessories that require both strength and an esthetic appearance. This technique is also used today to coat dental abutments with a TiN coating since titanium has very low tribological properties with a micro hardness ranging between 250-300 HV for Ti6Al4V (Marin, et al., 2014) were TiN has a Vickers hardness of 2400.

There have been many studies which bring up and show the effectiveness and benefits of TiN for the use as dental material coatings. However these studies have been in *vitro* and thus very few studies regarding in vivo effects have been conducted. Coated orthodontic archwires and abutments are two of the few commercial products that currently utilize this coating type in the dental field (Jabbari, et al., 2012).

An achievable coating with PVD is TiCN which has a brownish, pinkish or grey color and similar functional properties as TiN. It is also biocompatible and has an even harder surface than TiN (coefficient of friction 0.32-0.45).

The benefits of this method are also accompanied by some downsides such as high investment costs, large equipment and advanced technical requirements. The method is also based on a line-of-sight coating procedure which is troublesome for very complex or porous 3D designs. This makes it difficult to access the entire part and to create an even coating. A PVD coating unit can cost somewhere between € 30 000 to € 300 000 and occupy several m^3 weighing several tons, making not only the cost of the machine itself an issue but also the allocation of space. Since the size of the machine is partly dependent on the size of the reaction chamber and the parts to be coated are small and in low quantity it can be expected to be sufficient with a smaller variant. The process requires quite a lot of power both for the controlling computers and for the management of the sputtering reactions.

2.6.4 Sol-gel

Sol-gel is a broad definition of methods that involve a solvent-gelation process and in different ways allow for production of ceramic or glassy coatings and materials to be made in a unique low-temperature way. For example it allows for the production of inorganic-organic hybrid materials otherwise impossible to create due to the differences in reaction temperatures of the materials. It is common for sol-gel methods to utilize metal alkoxides which gel by hydrolysis and polycondensation reactions of these metal alkoxide precursors. Depending on the formulation these types of materials can be used for a vast amount of applications including protective, adhesive and esthetic coatings.

The most common application methods of sol-gel coatings is dip coating, spin coating and spray coating. Dip coating involves dipping the substrate into the coating liquid in a controlled manner and drying the coating to form an even thin layer. Spin coating involves applying the coating liquid onto the substrate while it is in a spinning motion allowing excess liquid to be removed, forming a thin even layer. A spray coating is applied by a spray brush to the desired thickness.

The coating method that will be in focus for this process is dip coating which allows for a relatively simple way to coat complex 3D structures. Even though coating by dipping the substrate into a liquid and then letting it dry may seem trivial, this process needs to be optimized and controlled just as well. Dipping speed, dwell time in the liquid and the drying process are all parameters that in the end determine coating thickness and uniformity, not to mention the viscosity and flowing properties of the coating liquid. Increasing the speed that the dipping is performed increases the thickness of the coating (Source, maybe even explain since it seems a bit counter intuitive). The dwell time affects how well the coating can wet the surface of the substrate. The curing of the coating however is the most critical part and will determine the uniformity of the coating.

3 Materials and Methods

This chapter describes the work process of the master thesis including the materials and methods used during this project.

3.1 Project Charter

To plan and continuously evaluate the project a project charter was continuously updated with information. To assess the time required for the different parts of the project a time-plan was created and continuously revised throughout the project.

3.2 Pre-study

The pre-study consisted of familiarizing with the production site and the product as well as performing a literature study involving coating materials and methodologies. The pre-study results is presented in chapter 2.

The purpose of the literature study was to assess the coating possibilities on a broad front before narrowing down on a few candidates to proceed with further investigation and testing. The technical and practical aspects of the different methods deemed most interesting is also part of the literature study. The current products on the market and gathering of knowledge on different coating materials and methods was also part of the focus. It also covers the production processes and techniques used at Dentsply such as AM and milling.

3.3 Business Case

A business case was also constructed in order to evaluate the financial aspects of each coating. These calculations were based on assumptions regarding the investment costs for each coating process, the production costs of each coating and of the sales numbers provided by Dentsply. Due to competitive reasons these numbers were confidential and thus only the conclusions and general outlines of the business case is presented in the report (chapter 6).

3.4 Sample Preparation

Four coating types were prepared on titanium AM test specimens as well as reference plates consisting of both a conventional metal alloy and opaque resin coating and uncoated test specimens. In order to perform a delamination test, a Charpy impact test (used to test material strength) and a surface roughness comparison, two types of samples were prepared. Below is described how the samples were coated and prepared.

3.4.1 Sample Modeling

For the delamination test, plates were designed in CAD according to the ISO 10477 with the standard dimensions *20*10*2* mm^3 (see Figure 3.1:A). These plates were also used to determine the surface roughness as well as the visual examination. For the Charpy v-notch test bars according to EN 10 045 were designed in CAD with the standard dimensions *55*10*10* mm^3 containing a 2 mm deep v-notch with a 45° angle and a radius of the base curvature of 25 mm, in the center of the piece (see Figure 3.1:B). Both structures were modeled using x-shaped supports.

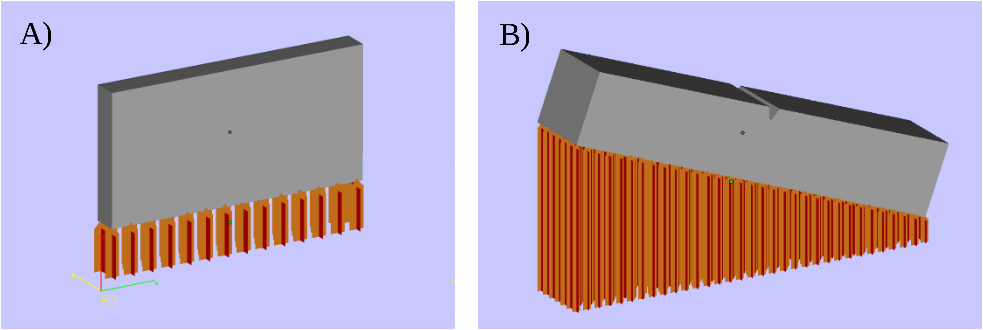


Figure 3.1 CAD models of A) Plate test specimen and B) Charpy test specimen.

Next these structures were modeled onto a virtual build plate (see Figure 3.2) along with five bridges and two artifacts. The artifacts are present on each build and are used to validate the process by density measurements and spherical measurements. A total of 60 delamination plates and 20 of the Charpy bars were modeled onto the build plate. Finally the prepared build plate file was sent to the milling machine and printed.

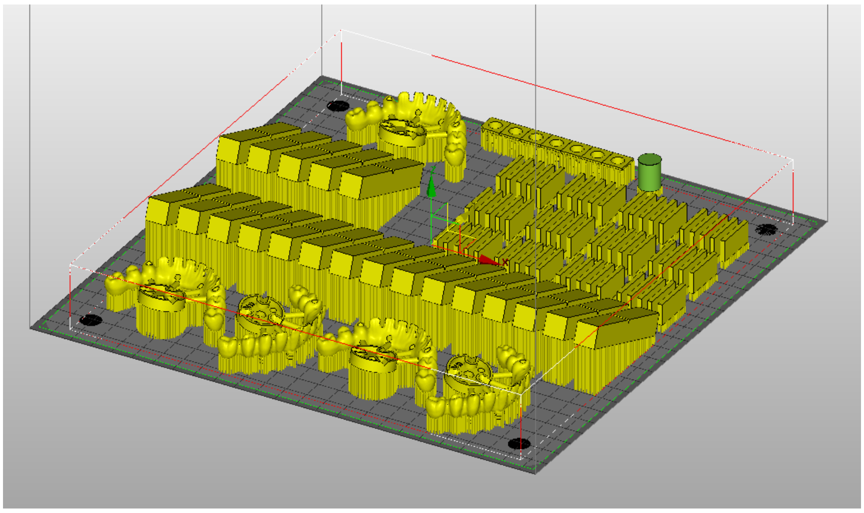


Figure 3.2 Build plate CAD model containing sample test plates and bridges as input for AM. Two artifacts can also be seen.

3.4.2 Sample Production

The structures were printed on the build plate (Figure 3.3) using a Renishaw AM250 machine with titanium Grade 23 powder (Appendix A). The build took approximately 24 h to complete after starting the AM process. Once completed excess powder was removed from the build plate to be re-used. The build plate was removed from the printer and hardened in an argon filled oven for 8h wrapped in a metal foil to reduce spontaneous oxidation of the titanium caused at the elevated temperature.

Once hardened the build was let to cool in room temperature. Thereafter the structures were removed from the build plate by cutting of the structures using a band saw and the remaining supports attached to the structures were easily removed by hand. The roughest areas were manually polished and then the entire structures were sandblasted in an automatic sandblasting apparatus for 20 min.

Figure 3.3 Printed build plate measuring 250 mm x 250 mm, showing five bridge structures with hubs, 20 Charpy samples, and 60 small plates as well as two artifacts to the far right of the picture.

The Charpy sample bars were then marked with numbers on each short side and the density for each bar as well as the density artifact, was measured using Sartorius YDK03 Density Determination Kit. This kit uses Archimedes principle to determine the density of the sample were the density of the water (ρ(*fl*)), the weight of the sample in air (W(*a*)) and submerged in water (W(*fl*)) was measured. A correction was also done for the buoyancy in air giving the following equation (1). The density of air for standard conditions at 20˚C and 1 atm was used (ρ(*a*) = 1.2 mg/cc).

$$\rho = \frac{W(a)*[\rho(fl)-\rho(a)]}{W(a)-W(fl)} + \rho(a) \tag{1}$$

3.4.3 Coating

After preparing the samples they were coated with the assistance of third party companies as well as within Dentsply (see Table 3.1). For each coating type 4 Charpy bars were coated and 11 small plates. Only the smaller plates were coated by the conventional coating. The coating procedures followed for each method is described below.

Table 3.1 Table of third party companies performing the coatings.

Company	Coating	Material
Dentsply Sirona, Mannheim	Anodization	TiO_x conversion
Meotec	PEO	TiO_x conversion
DOT coating	PVD	TiCN
Sirris	Sol-gel	Hybrid silica
Dentsply Sirona Implants, Hasselt	MMA	Alloy primer + opaque resin

3.4.3.1 PEO Coating Procedure

The PEO coating was performed by Meotec according to the following procedure:

- Samples were pretreated with 96% ethanol and rinsed with de-ionized water (DIW)
- A small thread was drilled in one end and a titanium was screwed into the hole. The rod was coated with a plastic shrinking tube so it had no contact with the electrolyte.
- The parts were submersed into the coating liquid called Irox 1, which is a sodium silicate based electrolyte with a pH value of 1.
- A pulsed DC current was used with a maximum voltage of 400 V.
- The coating time was around 15 minutes and slightly longer for the larger bars.
- After the coating the parts were cleaned using DIW rinsed in ethanol and dried using compressed air.

3.4.3.2 Sol-gel Coating Procedure

The sol-gel coating was prepared together with Sirris. The process steps of the sol-gel coating were as follows:

- Mixing of ethanol and acid catalyst in the silane mixture until the ethanol has dissolved.
- Add the silica suspension during slow mixing for 45 minutes to hydrolyze
- Add the organic metal complex during stirring and stir for 10 minutes.

- Add 0.1% of the total weight of flow additive during stirring.
- Set the gloss as desired by adding a matting agent (max 5% of total weight)
- Rinse parts in isopropanol.
- Dry in oven for 10 minutes at 60˚C.
- Dip the parts in the sol gel suspension and let excess coating liquid run off.
- Dry in oven for 10 minutes at 60˚C.
- Harden for 20 minutes at 160˚C in the oven and let cool in room temperature.

3.4.3.3 Anodization Coating Procedure

The Anodization process was performed by Dentsply in Mannheim and the process include the following steps:

- Cleaning by ultra-sonication in an ultrapure water (UPW) and detergent bath for 3 minutes.
- Parts removed from the bath and rinsed with UPW.
- Isopropanol bath, pivot at least 10 times.
- Remove the parts and dry for 30 minutes in 80˚C.
- Pickling procedure allowing for a fresh non-oxidized surface to be present prior to the anodization process.
- Anodize bath for 5-30 seconds depending on color to be achieved and surface properties of the substrate.
- Rinsing with isopropanol and UPW.

3.4.3.4 PVD Coating Procedure

The TiCN PVD coating was performed by DOT GmbH with the following steps:

- Samples were mounted within the PVD coater's vacuum chamber.
- The coating was applied during rotation of the piece.

3.4.3.5 Conventional Procedure

The conventional coating was performed at Dentsply in Hasselt and includes the following steps:

- Steam clean the surface using steam gun.
- Dry the surface completely.

- Apply two drops of metal alloy primer to completely cover the surface.
- Allow the primer to dry.
- Apply the opaque resin using a brush in an even layer.
- Let dry completely

3.5 Test Methods

The shear bond strength, Charpy impact strength and surface roughness parameters were tested. Microscopic images of the surface were also taken. The coating thickness was of interest, however due to the rough surface and lack of precise equipment it was not possible to measure the thickness accurately.

3.5.1 Shear Bonding

For shear bond testing the ISO 10477: chapter 7.7 ‘Bond Strength’ was used as guidance when preparing the samples, but with some changes. 5 samples with dimensions in accordance to the ISO standard as described above, were coated for each coating type. 5 samples were also produced and prepared with alloy primer from Kuraray Dental and OVS II pink opaque resin from DeguDent to be used as a reference. The test method involves applying a resin plug onto the substrate to be tested and then applying a force onto the plug until it delaminates. The force required for this procedure is then measured.

In order to apply the resin plug onto each coated plate with the dimensions specified in ISO 10477 a silicon mold was created. Technosil NT silicon from Bredent medical was used together with two test plates and 3D printed resin pins to create the form of the plug and a funnel (see Figure 3.4). Once the mold had dried the pins and plates were removed and the mold was complete. To apply the resin plugs the plates were fixed in the mold and Selectaplus resin from DeguDent was prepared and applied through the funnel. The mold was then inserted into a pressure pot at ~2 bar with hot water (30-40 C) for 15 minutes to cure. The mold was gently dried with a paper towel and the plates were removed from the mold. Excess resin left in the funnel was removed and the top of the plug was carefully grinded down to a smooth surface.

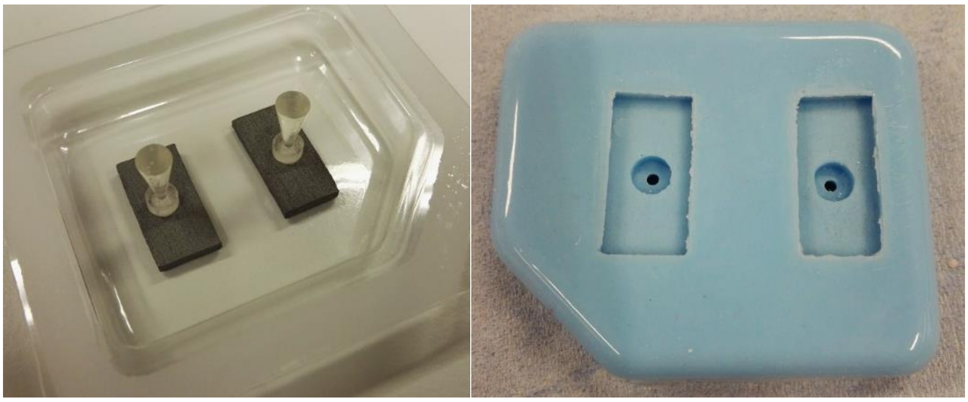


Figure 3.4 Setup of creating the mold for the resin plugs.

To measure the bond strength the prepared sample plate was placed on top of a brass cylinder. Over the metal plate a hollow brass holder was attached firmly against this plate (see Figure 3.5). In the guillotine pipe there is a fastening screw to ensure that the cutting knife does not slip. The increasing force of the rod from the Lloyds machine continues until the sample is cut from the plate. The force is recorded with Neygen software pc-program.

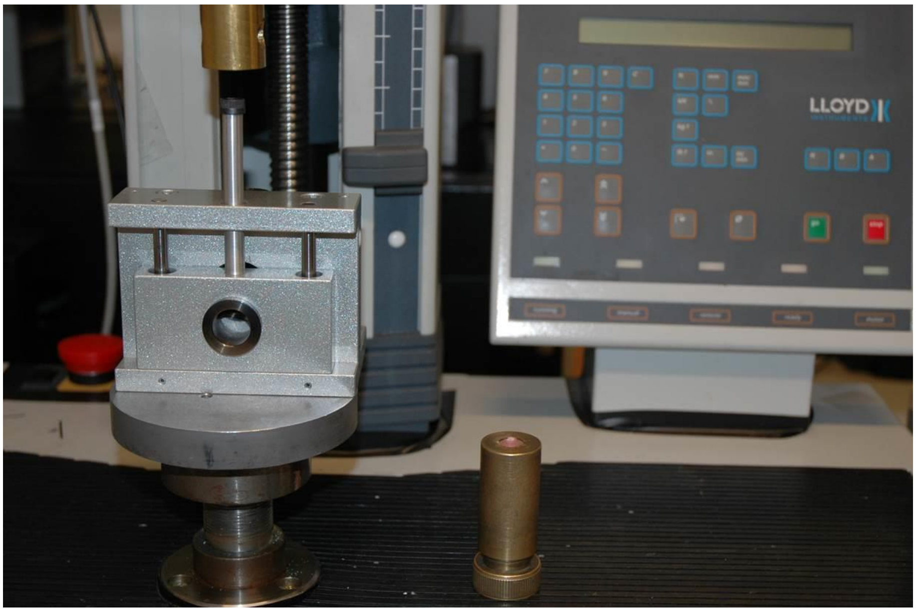


Figure 3.5 Bond strength testing setup.

3.5.2 Charpy Impact Test

The Charpy impact test is a test to determine the fracture strength of a material when exposed to a large impact force. The setup consists of a pendulum with a known weight and length and an anvil to which the sample to be tested can rest. There is also a meter which is used to determine the energy that is required to fracture the sample (see

Figure 3.**6**). The pendulum is released from a measured height and the loss in energy caused by the impact is measured by the height difference of the hammer before and after the impact.

Four bars were produced according to the above specifications in accordance with EN 10 045 and were coated on all sides. Each Charpy bar was placed in a central position between the two anvils with the V-notch facing away from the impact point (see Figure 3.7). The 14.7 Nm pendulum was raised to its resting location and the meter was set to 0. The pendulum was then released and the meter was read. The Charpy test procedure was executed four times for each coating to get a mean result.

Figure 3.6 Charpy impact setup with 14.7 Nm pendulum.

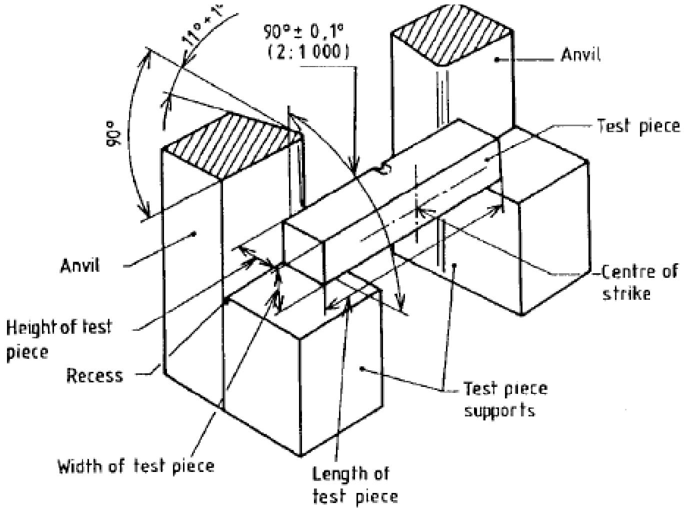


Figure 3.7 Charpy test piece with anvil.

3.5.3 Surface Roughness

The surface roughness was measured using a Mitutoyo Surftest SJ-500, which uses a contact stylus. A program was created to measure the roughness parameters across the surface of the plates in three different locations and calculate the mean value for each parameter.

3.5.4 Images

For all coatings a surface image was taken at x200 magnification using a Keyence VHX-500 FE digital microscope. The fracture interface of the Charpy samples were also photographed in the microscope to visualize the fracture area.

4 Results

This chapter describes the results achieved through the different tests performed.

4.1 Test Structures

The test plates and bars produced by AM were successfully produced. It was noted for the Charpy impact bars that they were slightly curved however. This is thought to be an effect of the rather compact parts and not enough heat transfer during production. This was also kept in regard when evaluating the results for the Charpy impact test results.

4.1.1 Density Measurement

The density of all the Charpy test bars and the artifact cylinder were > 98% of the titanium Grade23 theoretical values provided by the supplier for all samples. This indicates a structure with low porosity and validates the performance of the AM process.

4.2 Surface Coatings

The visual result varied from each coating, from transparent to dark pink (see Figure 4.1). The sol-gel coating produced did not have any added pigments, something that could potentially be improved in the future, and was thus transparent. The PEO coating had a beige color which was completely covering the surface. The PVD coating had a light pink color. The anodized coating had a dark pink color.

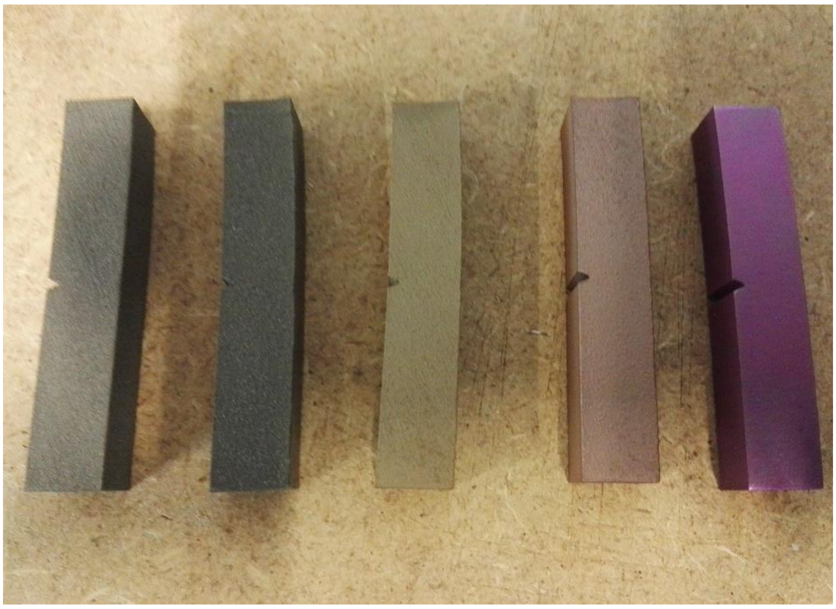


Figure 4.1 Charpy bars with four coatings. From the left; uncoated, sol-gel, PEO, PVD and anodized.

Images were also taken by a microscope on the surface of the plates for each coating type. The resolution allowed to better visualize the macro structure of the surface as well as the color. The pictures were taken at a 200 times magnification.

In the uncoated surface, the base titanium color can be seen and the macro structure of the surface can clearly be visualized with ridges and valleys creating a complex surface landscape (see Figure 4.2).

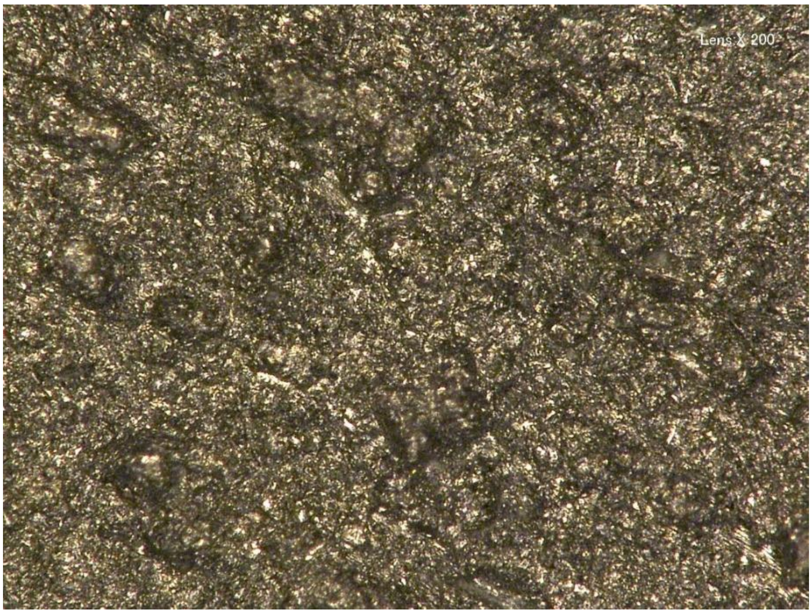


Figure 4.2 Uncoated surface at x200 magnification.

In the sol-gel coated surface the coating can be distinguished in the valleys of the surface, “filling” these areas to create a smoother surface. This effect is expected to clearly affect the surface retention properties unless there is some chemical bonding between the sol-gel coating and denture resin, as in the case of the opaque resin. The sol-gel coating used was colorless and the titanium color can be seen through the coating (see Figure 4.3).

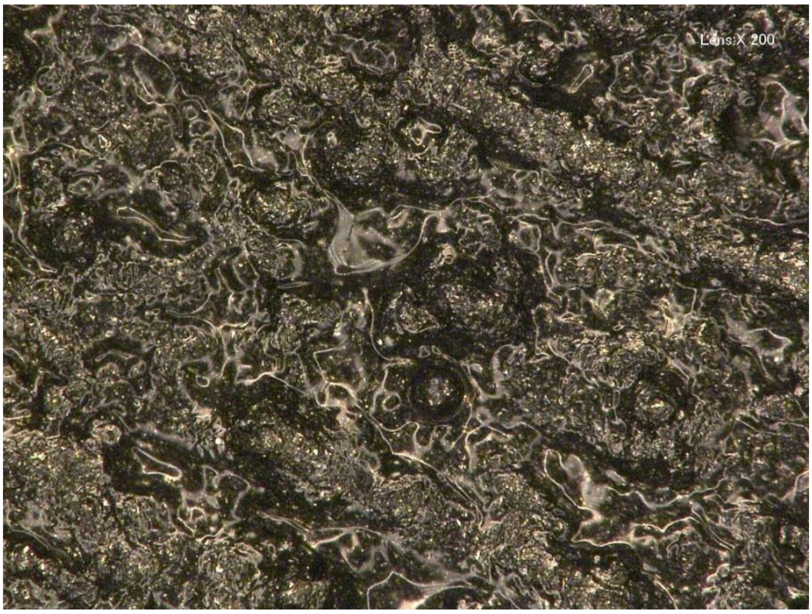


Figure 4.3 Sol-gel coated surface at x200 magnification.

In the anodized sample the interference colors created by the TiO_2 layer formed by the process can be seen clearly. It can also be noted that the color is not uniform across the sample but spots of blue, purple and golden colors can be seen giving the final appearance of the coating (see Figure 4.4).

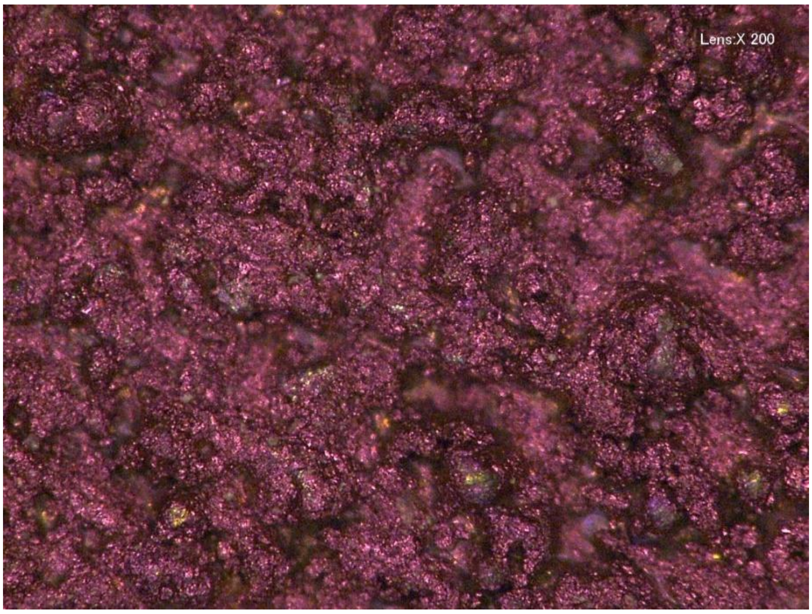


Figure 4.4 Anodized surface at x200 magnification.

The PVD applied TiCN coating shows a subtle pink color covering the entire surface (see Figure 4.5). The macro structure of the surface looks exactly like the one for the pure titanium surface which is expected since the coating should be a very thin deposited layer.

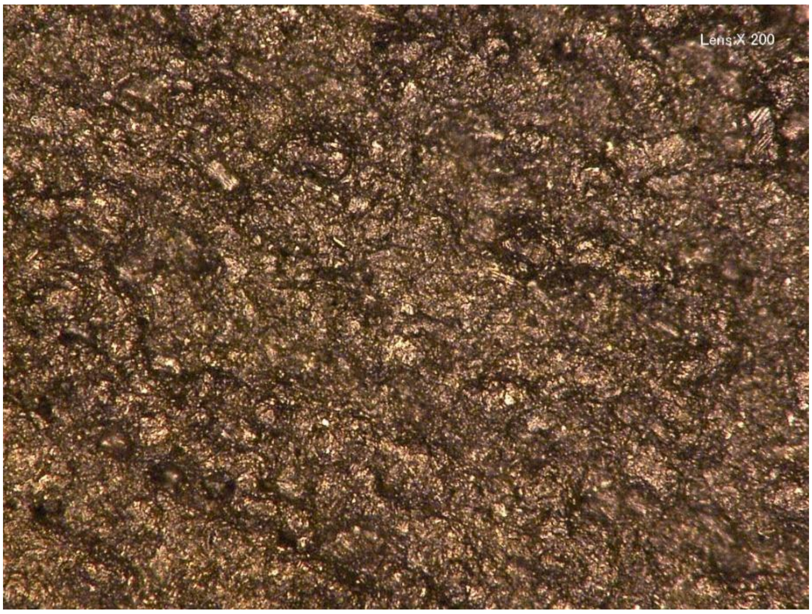


Figure 4.5 PVD coated surface at x200 magnification.

In the PEO coated sample a well-covered surface can be seen with dull yellow color. Some points of chipping can be seen on the more exposed ridges, possibly due to the handling of the samples (Figure 4.6).

Figure 4.6 PEO coated surface at x200 magnification.

The opaque resin surface shows a matte pink surface that is covering the metallic surface (see Figure 4.7). White grains can also be seen that are apparently suspended in the resin coating liquid possibly intended to increase the surface roughness to add mechanical retention.

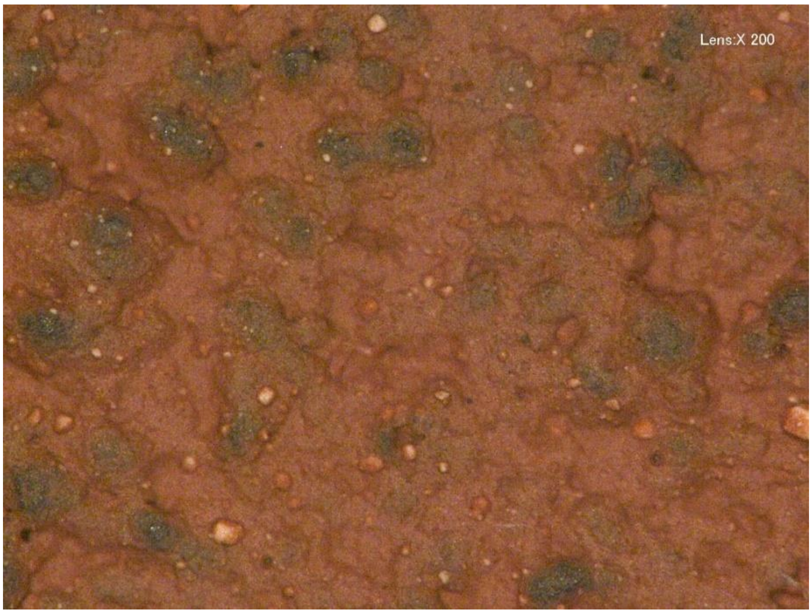


Figure 4.7 Opaque resin coating at 200x magnification.

4.3 Shear Bonding Test Results

The shear bonding test showed a clear difference in bonding strength between the different coatings (see Figure 4.8). The coating with the strongest bonding strength was the opaque resin reference with a bond strength of 18.3 (2.8) MPa. The coating with the least good bonding was the sol-gel coating with an average bond strength of 2.2 (1.7) MPa. The anodized surface and PVD coated surface showed similar bond strengths of just under 14 MPa and the PEO coating had a bond strength of 9.3 (3.5) MPa. The full data sets can be seen in Table C. in Appendix C.

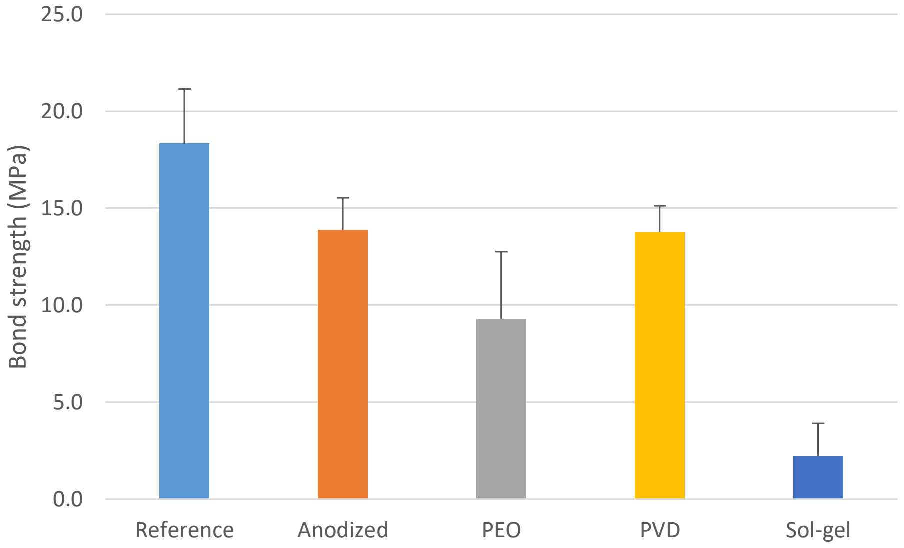


Figure 4.8 Average bond strength comparison between the different coating types.

The shear bond test showed that the delamination occurred between the coating and resin interface for most of the tested coatings, see Figure 4.9. This was true for PVD, anodization and sol-gel. For PEO the results varied with two samples delaminating in the coating to resin interface completely, one sample delaminating in the titanium to coating interface and two samples had partial delamination in the titanium coating interface. For the conventional coating the delamination occurred in the titanium to coating interface. Notably some of the resin stayed on the samples and was “chipped” off from the rest of the resin plug.

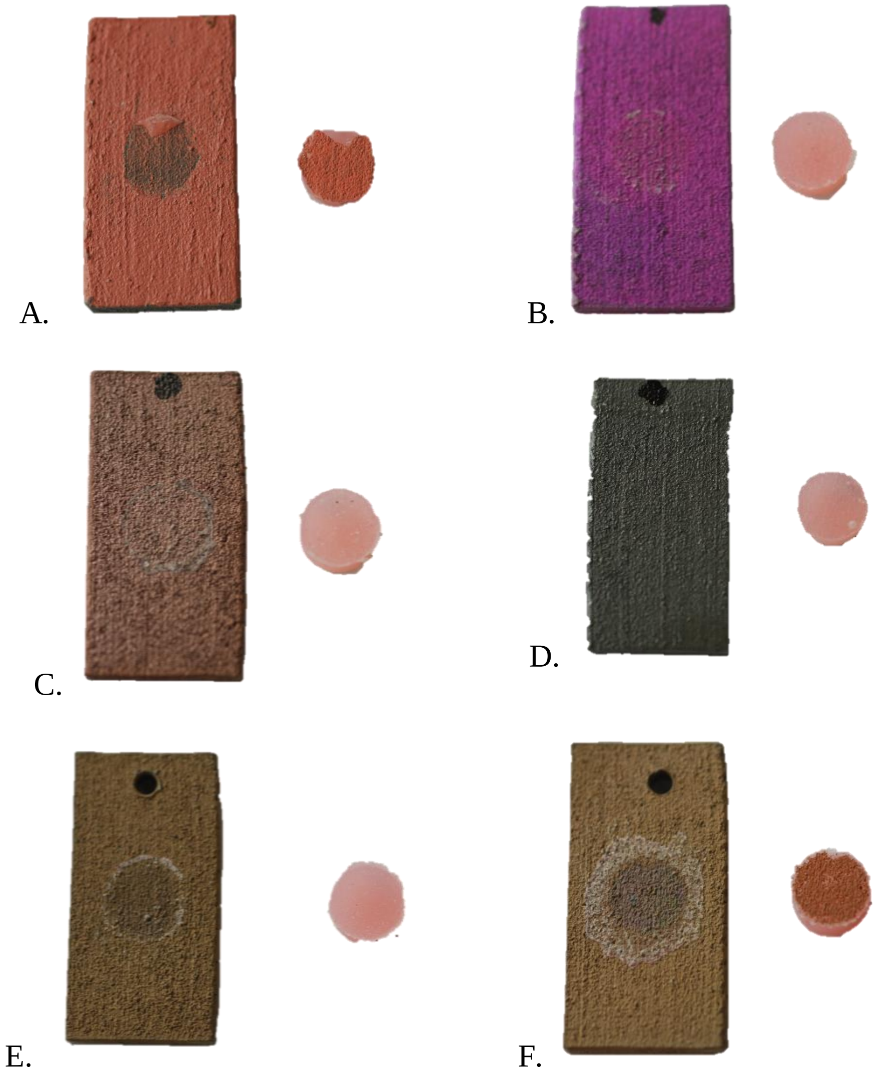


Figure 4.9 Delamination samples after delamination test was performed. A. Conventional opaque resin, B. Anodized sample, C. PVD coated sample, D. Sol-gel coated sample, E. PEO coated sample with coating staying on plate, F. PEO coated sample with coating being removed form plate.

4.4 Charpy Impact Test Results

It was not possible to see a significant difference in impact strength between the groups of coated samples. The difference in impact strength within each coating group showed a large variance (Figure 4.10). The entire range of impact values were between 95 – 145 kJ/m^2.

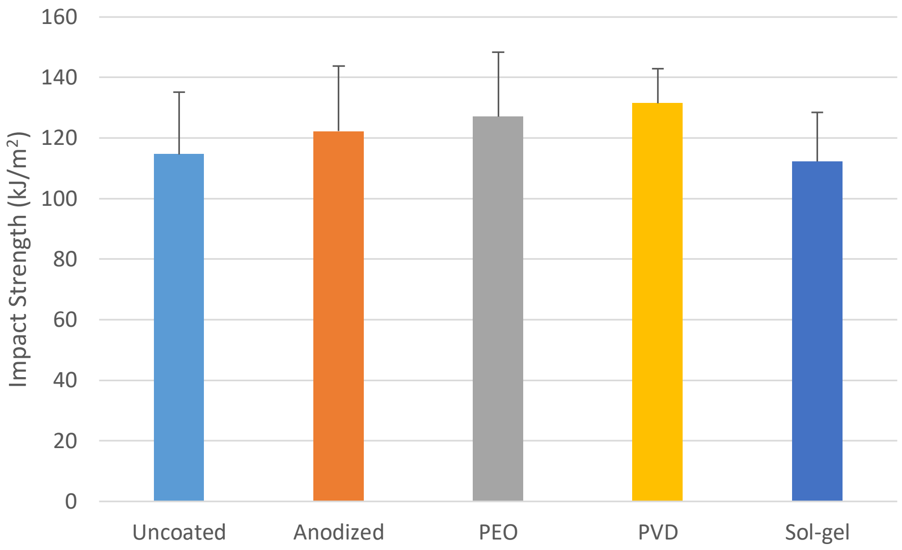


Figure 4.10 Average impact strength for each coating type.

The fracture of all samples was a brittle fracture since no deformation of the samples around the fracture was present. It could however be seen that the fracture surfaces had different appearances between the samples, regardless of what coating was applied. It was thus hypothesized that there would be a correlation between these differences and the impact strength. All the samples were categorize as either as rough, medium or smooth and then the average impact strength of each group was compared (see Figure 4.11). The rough group had an average of 101 (7.9), the medium group 113 (16.3) and the smooth group 135.8 (7.4). Thus a significance can be shown between the rough and smooth group, were the middle group seem to have characteristics of both. The density of each structure was compared to the impact strength however no significant correlation was found between the differences in density and the impact strength of the bars. The full data can be found in Table C.2 in Appendix C.

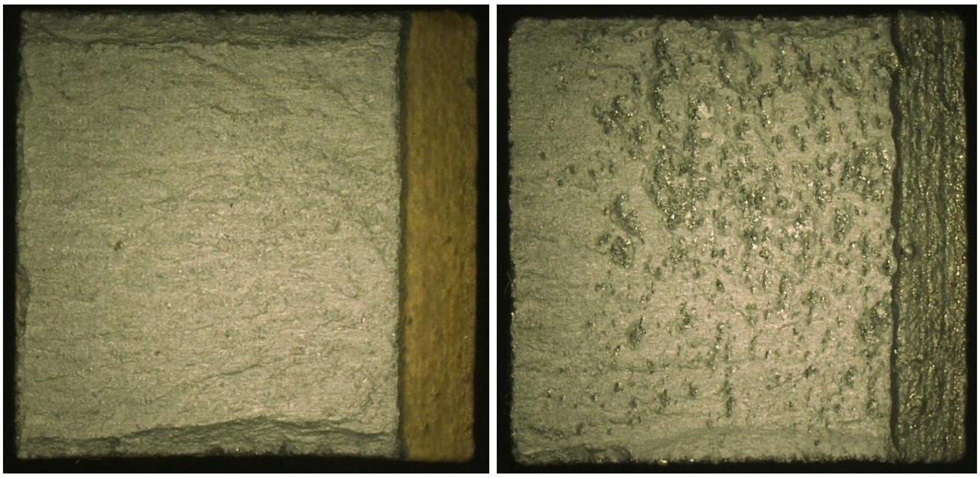


Figure 4.11 Comparison between smooth and rough impact fracture.

4.5 Surface Roughness

Several surface parameters were measured on each coating type including the conventional opaque resin coating and uncoated titanium samples. A surface profile was also made which can be seen in Figure 4.12, showing one replica from a resin coated sample.

Since there is not yet a standard set to what roughness the titanium surface should optimally be the results can only be used comparatively between one another and not compared to a preset standard. The coated roughness parameters were compared to the pure titanium sample parameters.

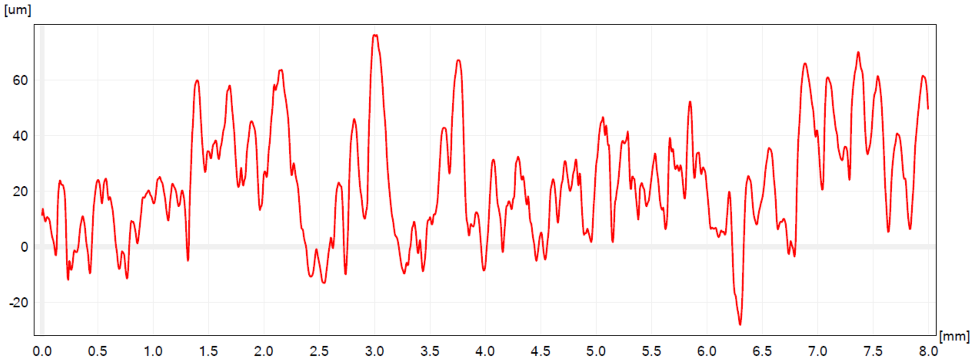


Figure 4.12 Surface roughness profile for opaque resin coating.

The average roughness, R_a can be seen in Figure 4.13 showing PEO to have the highest roughness and sol-gel the lowest. The roughness of the opaquer coating however was not significantly higher than the sol-gel coating suggesting that the bonding properties cannot solely be explained by the roughness of the material.

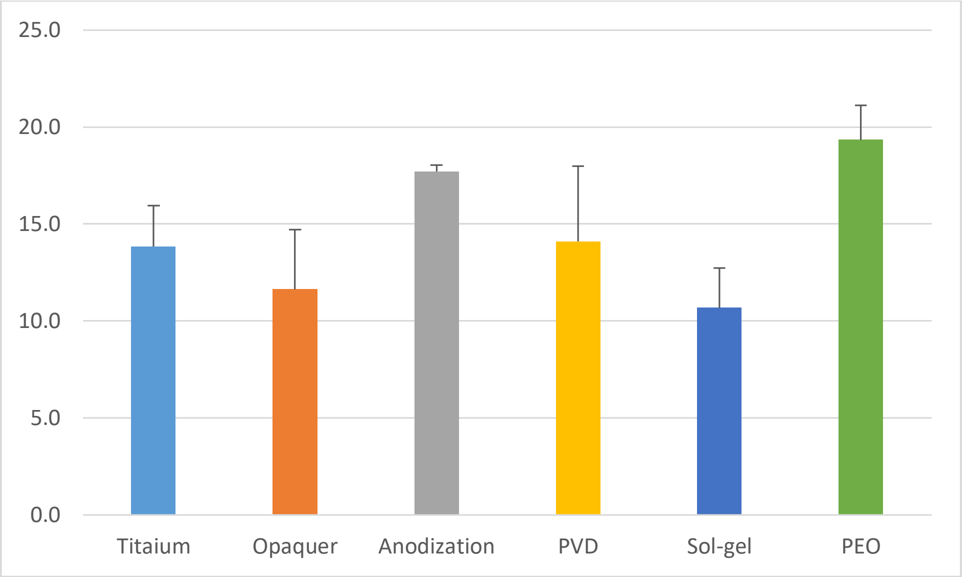


Figure 4.13 The roughness average, R_a.

The maximum peak height R_p seen in Figure 4.14 show similar results for pure titanium, opaque resin, anodization, and PVD coating. The sol-gel coating shows varying results possibly caused by the uneven thicker coating layer. The PEO coating showed the highest R^p value suggesting a rougher structure is being created by this process. A comparison between the different maximum valley depth parameters, R_v (see Figure 4.15), shows that these remain relatively similar for pure titanium, opaque resin, anodization, and PVD coating. However Sol-gel shows a significant reduction in maximum valley depth which is expected after visualizing the surface in the microscope. For PEO coating an increase can be seen. The reason for this could be pores created by the PEO process.

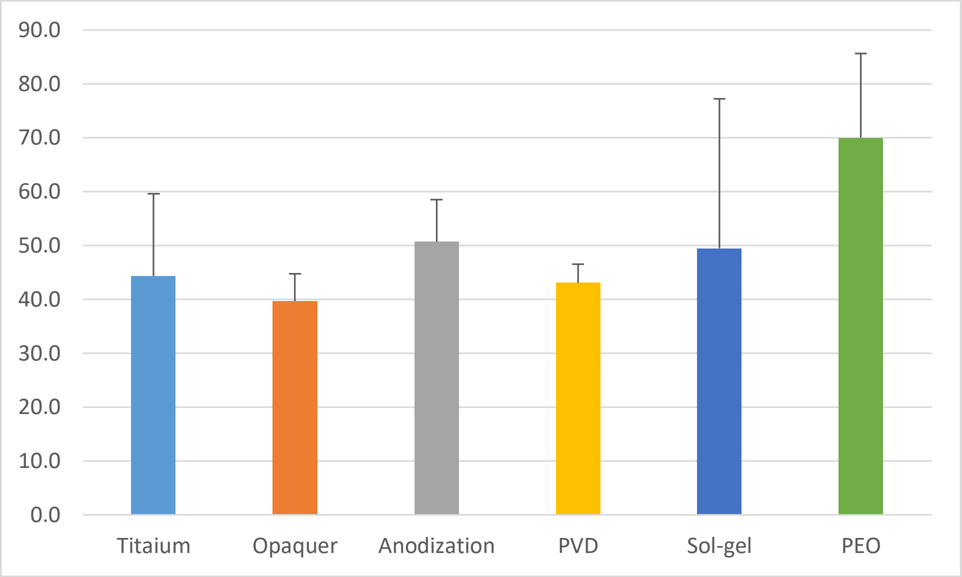


Figure 4.14 The maximum peak height, R_p.

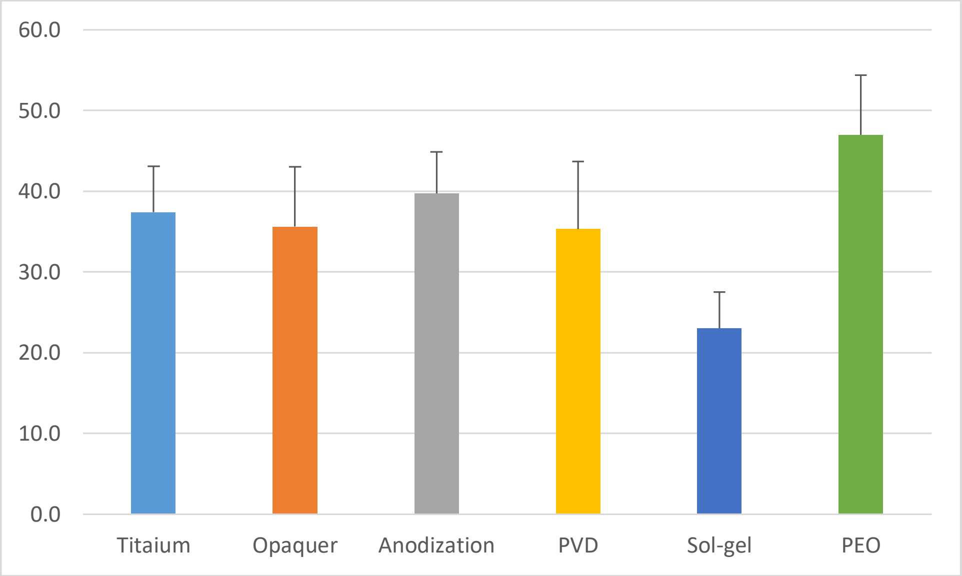


Figure 4.15 The maximum valley depth, R_v.

5 Process Implementation

This chapter describes the possible implementations of the coating methods described with regards to technical aspects and limitations realized by the process work-flow at Dentsply as well as the product of interest.

5.1 Implementation Challenges

One of the challenges with applying a coating to a dental prosthesis is the integration of this process step into the process flow. Currently the veneering and opaquing is done at dental laboratories after the product has been shipped from Dentsply. Integrating the coating step in an earlier phase of the process may allow more complex coating methods, as well as automation. This presents new difficulties however and may require changes to the current process.

To achieve a successful coating process the method used should meet certain requirements. It should be possible to create a uniform coating and it should not affect the implant connections or other areas that are desired to remain uncoated. Also the coating process should be as automated as possible. These requirements may seem fairly simple but the fact that every structure is unique and has a complex 3D geometry, impacts the difficulty of achieving these criteria.

5.2 Integration

When observing the process flow two possible options for integrating the coating process step can be found. The first possible option is to coat the suprastructure before the post-milling of the implant interfaces. This approach allows for a simple way to avoid coating the interfaces and simplifies the possibilities of automating the coating process. However it also means that the hub must be removed prior to post- milling in order to coat the entire structure as well as limiting the amount of finishing that can be done subsequent to the coating. The coating in this case must also be unaffected by the milling procedure.

An alternative approach to these problems could be an automated coating process using the hub as a handle during the procedure and accepting that small spots will remain uncoated on the suprastructure, alternatively coating these spots manually after post-milling (possible for wet chemical coating). Procedures regarding finishing would be required to change as the finishing steps such as removal of supports, polishing and sandblasting would need to be completed before coating and post milling.

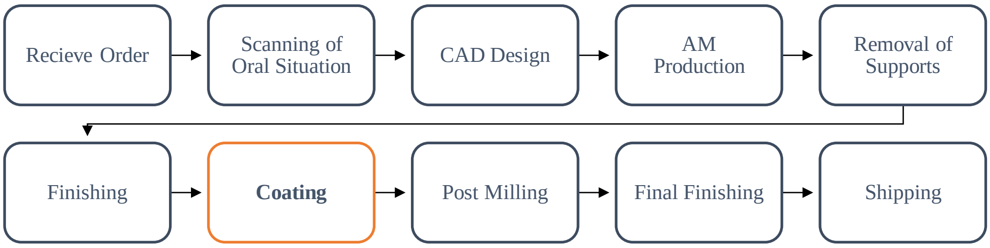


Figure 5.1 AM process flow with coating step before post milling.

A second option is to perform the coating after the post-milling, this however will most likely require the interface connections to be covered/protected in some manner. Possibilities here are either to physically protect them for example by mounting the part using the interface when coating or to chemically protect them, for example protecting certain areas from oxidation. The downside of this approach is that protecting each individual implant interface connection would require manual labor and automation would increase in difficulty.

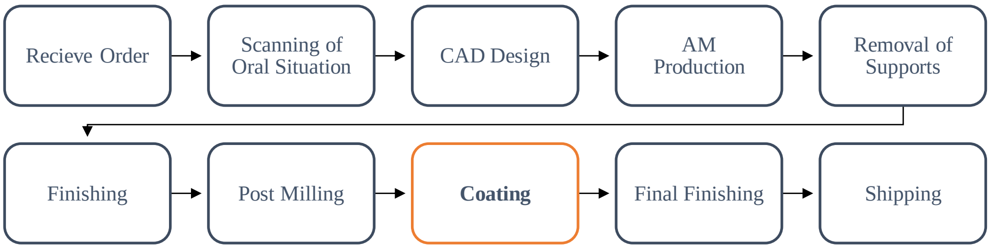


Figure 5.2 AM process flow with coating step after post milling.

5.3 Method Specifics

A second part in this discussion is more specified to the differences in the methods used. This includes space required, investment costs and running costs. These parameters vary greatly among the methods studied.

Anodization and dip coating, used for applying sol-gel coatings, seem to be the cheapest methods available starting at a few thousand euros in investment costs, with a seemingly simple/easy to learn setup. The investment costs increases for PEO and even more for PVD. As for the running costs the dip coating is relatively cheap compared to the other methods, the only requirements are to heat up the oven and to resupply new coating liquid when this is used up. Anodization is also a wet process requiring consistent replacing of different liquids in the anodizing line. Here more power is used to heat liquids and to perform the anodization itself. For PEO a large amount of power is used, this also contains a bath with chemicals that need to be replaced every so often. For PVD large amounts of power are required to keep the vacuum, sputtering potential/arc and computers running. Titanium sputtering targets need to be provided to produce the films. This is also one of the more technically requiring methods and well trained labor is a necessity.

5.4 Cleaning

The implementation of a coating step within the process will set higher demands on cleaning the structure during the process. Currently cleaning is not a big focus in the process at Dentsply since this responsibility is given to dental laboratories who perform the veneering and finally send the product to the end customer.

5.4.1 Reasons for Cleaning

Cleaning should be performed for two reasons, first to offer a safe product without residual particles, fatty contaminants or microorganism remaining on the product. The second important reason is to achieve a good surface to be coated. Most coating processes require clean surfaces for an optimal and reproducible result. Thus the cleaning should be performed before coating of the suprastructures and should remove any loose particles, fatty contaminations and microorganisms to a certain extent to ensure that these are not stuck in the coating layer and leak out during usage of the product or affect the coating procedure.

5.4.2 Current Cleaning

Cleaning is something that is not currently a big part of the production site in Hasselt. A steam gun is available at Dentsply that is used to remove particles during the finishing process. After finishing and QC the prostheses are sent directly to the dental laboratory to be veneered. Thus the responsibility for proper cleaning of the prostheses lies on the dental lab. A suitable cleaning procedure should be developed depending on the coating method to be implemented.

5.4.3 Cleaning Solutions

There are several methods to perform cleaning of metal surfaces that can be considered prior to the coating process. The cleaning process should naturally involve the cleaning itself but also rinsing and drying. Cleaning methods that are interesting for this application are ultrasonic cleaning, steam cleaning, or the use of organic solvents. Isopropanol and ethanol are organic solvents commonly used as a pre-cleaning step to remove fat from the surface. Rinsing should be performed by DI water or UPW. Drying can be done in vacuum, by hot air or infrared light.

Several companies supply equipment to facilitate cleaning and sterilization, however this should be regarded in the cost of implementation in this project since the equipment is not currently present. If purchasing an anodization line or a PEO coating line the pre-cleaning baths and liquids would most likely be included in the setup. For PVD and sol-gel coating equipment this is most likely not the case.

6 Business Case

This chapter highlights the economic feasibility of coating titanium AM prostheses, regarding investment and potential return that can be expected.

6.1 Assumptions

A business case was created to assess the economic feasibility of each coating method. Investment costs were estimated for each coating process with the regards of required coating equipment and further R&D costs. The gross margin was calculated based on expected sales price, the cost of goods and sales volumes, including expected growth.

For each coating method the payback time was calculated and compared to the other methods. A three year payback period or better is expected in order to consider the project economically feasible.

6.2 Evaluation

The business case showed that sol-gel would have the lowest payback period of 2.11 years, followed by Anodization at 2.13 years, PEO 2.52 years and finally PVD at 4.79 years. It can thus be seen that PVD does not meet the requirements to be considered economically feasible. The most attractive method according to this business case is the sol-gel method which comes for lower expected investment costs as well as a lower production cost compared to the other methods. It should also be noted that the product mix as well as the customer demand for such a coating would affect the payback period for all the coating alternatives.

7 Discussion

The test results showed that the investigated coatings did not meet the bonding strength of the conventional opaque resin and metal primer treatment used as a reference. Anodization and TiCN coating showed similar results in the bond strength test, however, significantly lower than the reference. The PEO coating showed roughly half of the strength compared to the conventional technique and the sol-gel coating was by far the worst with eight times lower bonding strength compared to the reference.

Of all the samples it was also seen that for the reference sample the coating delaminated in the metal coating interface whereas the other coatings delaminated in the coating to resin interface. It would thus be important to consider the coating to resin bonding mechanisms in order to increase the bond strength of the coatings.

It was also acknowledged during the production of both PVD, PEO and anodization coatings that the color is not necessarily easy to change/optimize. The sol-gel coating was not colored however it is believed to be relatively easy to perform such a pigmentation in the future. For the PEO coating the manufacturers noted that the vanadium present in Ti Grade 23 could pose a problem since it caused a brownish discoloration not seen when coating Ti Grade 4 objects.

7.1 Impact Strength

The Charpy impact tests could not be used to show an effect of the material strength when comparing the different coated and non-coated samples. The differences seen within the groups of identical coating showed large variances, thought to be caused by the method accuracy as well as differences related to the AM process. The fracture in the titanium bars that was seen was a brittle fracture, which is expected for titanium at room temperature (Chemistry Explained, 2016). The fact that the coatings are expected to be only a few microns thin would indicate that the Charpy impact test is not precise enough to show variations in material strength. In order to characterize the material strength effects it is possible that a more sensitive test method could give results. It is also believed that the potential weakening caused by anodization or PEO would not affect the impact strength of the structure but might however affect the surface integrity leading to cracks, causing a reduced fatigue resistance.

The tests did show differences for the samples however this was seen in the cross section images and did not depend on the coating applied. It is believed that these differences were due to the AM process and that a smoother fracture was associated with a higher impact strength.

The hypotheses was that PEO and anodization could potentially have a weakening effect since these are conversion coatings and could affect the surface integrity. To better evaluate this parameter an endurance limit test is most likely more interesting to perform than Charpy testing.

7.2 Surface Structure

The surface of the AM and sandblasted titanium metal is a very rough one, with both macro sized and micro sized retention mechanisms, which act to add mechanical retention that anchors the resin onto the surface. The surface produced by AM is quite different from a traditionally milled surface which is much smoother and lacks these macro elements.

Although proven beneficial to adhering resin to the surface, the roughness can pose a challenge to certain coating techniques, for example anodization. As the coating thickness is responsible for the color having a very uneven surface will pose a challenge when looking to achieve a coherent color. Another challenge is purely process technical and arises when moving the substrates between different baths. Achieving a thorough rinse between each bath can pose a challenge and would increase the cost of the process compared to anodizing a smoother surface. This increase in cost arises from the increased processing time and also through the risk of contaminating the different baths.

For the sol-gel coating it was seen that the coating remained in the valleys of the rough surface after dip-coating. Also it could be seen that the coating thickness was quite varying over the surface depending on how the plate had been dried with the area facing downward during the drying a much thicker coating was seen than areas facing upwards. This causes very smooth regions and regions with more retained surface roughness.

8 Conclusion

Coating of titanium AM structures is an interesting opportunity and a natural step in product development for ATLANTIS suprastructures. The potentials include improved esthetics, functionality and diversification on the market. This project should be considered a first investigation of the potential into coatings for titanium AM prostheses which showed that alternative methods for coating would still require development in order to be successfully implemented into the process.

Regarding the investigated methods anodization and sol-gel methods are the ones that should be considered for further investigations, however for different reasons. It is believed that anodizing products could lead to a more attractive product appearance for customers. The sol-gel method has room for improvement, both regarding the composition and the application method these are areas that should be further investigated. The coating should be develop to allow covalent bonding between the coating and the resin. PEO is not considered a feasible method due to difficulties in achieving a color that is desired for the final product. It is also exhibiting very low bond strengths with delamination occurring both at the metal/coating interface as well as the coating/resin interface. Regarding the PVD this coating method also poses several difficulties with high investment costs, and doubtful benefits for the final product.

8.1 Project conclusions

The goal of the project was to investigate the development of a coating for AM titanium suprastructures and the effects of veneering.

Achieving a pink color proved to be a challenge with most of the investigated methods. Also adjusting the color can be quite challenging since this requires a change in materials or other process conditions. For the sol-gel the simplest way to achieve a desirable color would be to add pigments. These could also be replaced to get different colors or nuances. For the PVD coating a rather good color as achieved, however the process of changing this would be to experiment with different composition of the final material. For the anodized surface the colors were easy to change however not all colors can be created.

8.2 Future Work

The future work should focus on developing a coating which has the possibility to bond with the resin. Efforts to implement methods such as anodization could be possible but this would likely only serve as a design feature to the customer and to add color the product, however efforts to get a good bonding would still need to be performed.

One of the most crucial questions to analyze and develop further is how to automate the process, since the suprastructures are unique 3D structures this is a very complex issue that will require special installations depending on what coating method is used. To aim for a fully automated coating process is most likely not feasible within the financial limitations.

References

Allison, A. & Scudamore, R., 2014. *Additive Manufacturing: Strategic Research Agenda,* s.l.: AM Sub-platform.

Bower, B., 2006. Mystery Drilling. *Science News,* 169(14), p. 213.

Bremen, S., Diatlov, A. & Meiners, W., 2012. Selective Laser Melting. *Laser Technik Journal: A manufacturing technology for the future?,* Volume 2, pp. 33-38.

Catauro, M. et al., 2014. Corrosion behavior and mechanical properties of bioactive sol-gel coatings on titanium implants. *Materials Science & Engineering,* August, 78(2), pp. 375-382.

Chemistry Explained, 2016. *Chemistry Explained.* [Online]
Available at: http://www.chemistryexplained.com/elements/T-Z/Titanium.html
[Accessed 25 August 2016].

Chen, Z. X., Y Takao, W. X. W., MAtsubara, T. & Ren, L. M., 2009. Surface characteristics and in vitro biocompatibility of titanium anodized in a phosphoric acid solution at different voltages. *Biomedical Materials,* 4(6), pp. 1-8.

Cimenoglu, H. et al., 2011. Micro-arc oxidation of Ti6Al4V and Ti6Al7Nb alloys for biomedical applications. *Materials Characterization,* Volume 62, pp. 304-311.

Curto, B. D. et al., 2005. Decreased Bacterial Adhesion to Surface-treated Titanium. *The international Journal of Artificial Organs,* 28(7), pp. 718-730.

Dentsply Sirona, 2016. *About Dentsply Sirona.* [Online]
Available at: https://www.dentsplysirona.com/en/company/about-dentsply-sirona.html
[Accessed 30 May 2016].

Hanawa, T., 2010. Rev. of Biofunctionalization of Titanium for Dental Implant. *Japanese Dental Science Review,* 46(2), pp. 93-101.

Jabbari, Y. S. A. et al., 2012. Titanium Nitride and Nitrogen Ion Implanted Coated Dental Materials. *Coatings,* pp. 160-178.

Lugovskoy, A. & Zinigrad, M., 2013. Plasma Electrolytic Oxidation of Valve Metals. In: Y. Mastai, ed. *Materials Science - Advanced Topics.* Ariel: InTech, pp. 85-102.

Marin, E. et al., 2014. Hybrid diffusive/PVD treatments to improve the tribological resistance of Ti-6Al-4V. *Bio-Medical MAterials and Engineerinh,* Volume 24, pp. 581-592.

MarketsandMarkets, 2014. *marketsandmarkets.* [Online]
Available at: http://www.marketsandmarkets.com/Market-Reports/thin-film-material-market-232915487.html
[Accessed 18 April 2016].

Panthera Dental, 2016. *Metal Implant Bar.* [Online]
Available at: https://www.pantheradental.com/metalbar
[Accessed 9 May 2016].

Singh, A. et al., 2013. Effect of anodization on corrosion behaviour and biocompatibility of Cp-titanium in simulated body fluid. *Bulletin of Materials Science,* 36(5), pp. 931-937.

Sunyataburus, 2010. *Wikipedia, the free encyclopedia.* [Online]
Available at: https://en.wikipedia.org/wiki/Cathodic_arc_deposition
[Accessed 23 May 2016].

Wadhwani, C. P. K., O'Brien, R., Kattadiyil, M. T. & Chung, K.-H., 2015. Laboratory technique for coloring titanium abutments to improve esthetics. *The Journal of Prosthetic Dentistry,* pp. 1-3.

Vermesse, E., Mabru, C. & Arurault, L., 2013. Surface integration after pickling and anodization of Ti-6Al-4V titanium alloy. *Applied Surface Science,* Volume 285P, pp. 629-637.

Wijk, P. v. d. et al., 1998. The Cost of Dental Implants as Compared to That of Conventional Strategies. *The International Journal of Oral & Maxillofacial Implants,* 13(4), pp. 546-553.

Yerokhin, A. et al., 1999. Review: Plasma electrolysis for surface engineering. *Surface & Coatings Technology,* Issue 122, pp. 73-93.

Appendix A: Material Data Sheets

Data sheet

RENISHAW
apply innovation™

Ti6Al4V ELI-0406 powder for additive manufacturing

Process specification

Powder description	Titanium alloy powder
Layer thickness	30 µm
Laser power	200 W
Additive manufacturing system	AM250

Material description

Ti6Al4V ELI-0406 alloy comprises titanium mass fraction up to 90% alloyed with aluminium up to 6.75% and vanadium up to 4.5%, along with other minor elements. Ti6Al4V grade 23 is otherwise referred to as ELI or Extra Low Interstitial with regards to the interstitial impurities oxygen, carbon, and nitrogen. It is a higher purity version of the most commonly used titanium alloy Ti6Al4V grade 5. The reduced interstitial elements in grade 23 lead to an increase in both ductility and fracture toughness.

Ti6Al4V ELI-0406 has excellent specific strength (strength to weight ratio) which makes it an ideal choice where weight saving load structures are required. It has good corrosion resistance, it is also biocompatible, so can be used for a range of surgical and dental applications.

Material properties

- High specific strength
- High corrosion resistance
- Excellent biocompatibility
- Good osseointegration
- Low thermal expansion
- Low thermal conductivity

Applications

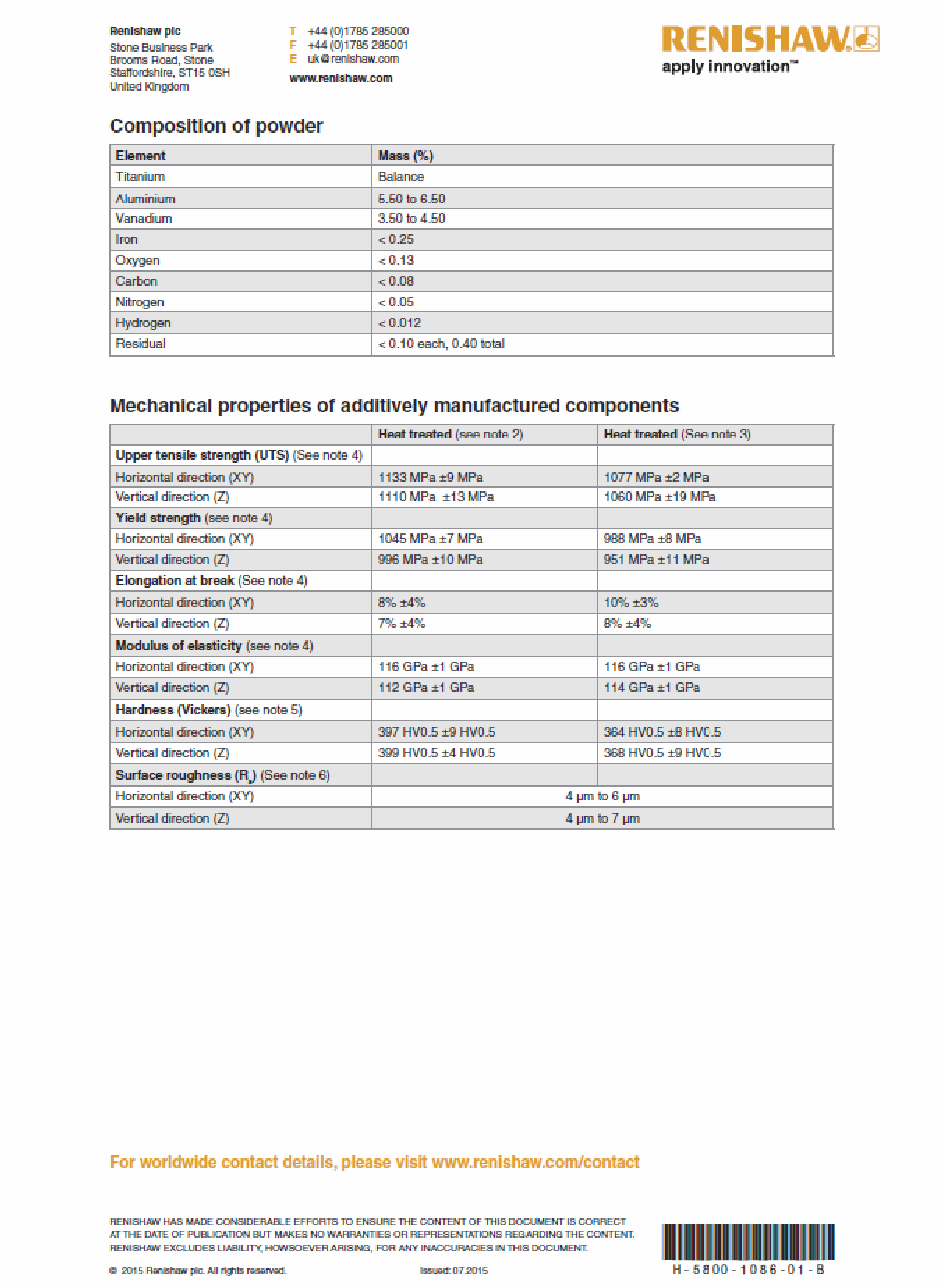
- Medical implants
- Surgical tools
- Aerospace and defence
- Motor sport
- Jewellery and art
- Maritime applications
- High-end sports equipment

Generic data - wrought material

Density	4.42 g/cm^3
Thermal conductivity	6 W/mK to 8 W/mK
Melting range	1635 °C to 1665 °C
Coefficient of thermal expansion (see note 1)	$8\ 10^{-6}\ K^{-1}$ to $9\ 10^{-6}\ K^{-1}$

Note 1 In the range of 0 °C to 100 °C.
Note 2 Annealed at 730 °C for 1 hr.
Note 3 Annealed at 850 °C ±10 °C for 1 hr.
Note 4 Tested at ambient temperature by Nadcap and UKAS accredited independent laboratory. Test ASTM E8. Machined before testing.
Note 5 Tested to ASTM E384-11. As built, after polishing.
Note 6 Tested to JIS B 0601-2001 (ISO 97). As built after bead blasting.

For further information or support please contact Renishaw or visit **www.renishaw.com/additive**



Renishaw plc
Stone Business Park
Brooms Road, Stone
Staffordshire, ST15 0SH
United Kingdom

T +44 (0)1785 285000
F +44 (0)1785 285001
E uk@renishaw.com
www.renishaw.com

RENISHAW
apply innovation™

Composition of powder

Element	**Mass (%)**
Titanium	Balance
Aluminium	5.50 to 6.50
Vanadium	3.50 to 4.50
Iron	< 0.25
Oxygen	< 0.13
Carbon	< 0.08
Nitrogen	< 0.05
Hydrogen	< 0.012
Residual	< 0.10 each, 0.40 total

Mechanical properties of additively manufactured components

	Heat treated (see note 2)	**Heat treated** (See note 3)
Upper tensile strength (UTS) (See note 4)		
Horizontal direction (XY)	1133 MPa ±9 MPa	1077 MPa ±2 MPa
Vertical direction (Z)	1110 MPa ±13 MPa	1060 MPa ±19 MPa
Yield strength (see note 4)		
Horizontal direction (XY)	1045 MPa ±7 MPa	988 MPa ±8 MPa
Vertical direction (Z)	996 MPa ±10 MPa	951 MPa ±11 MPa
Elongation at break (See note 4)		
Horizontal direction (XY)	8% ±4%	10% ±3%
Vertical direction (Z)	7% ±4%	8% ±4%
Modulus of elasticity (see note 4)		
Horizontal direction (XY)	116 GPa ±1 GPa	116 GPa ±1 GPa
Vertical direction (Z)	112 GPa ±1 GPa	114 GPa ±1 GPa
Hardness (Vickers) (see note 5)		
Horizontal direction (XY)	397 HV0.5 ±9 HV0.5	364 HV0.5 ±8 HV0.5
Vertical direction (Z)	399 HV0.5 ±4 HV0.5	368 HV0.5 ±9 HV0.5
Surface roughness (R_a) (See note 6)		
Horizontal direction (XY)	4 µm to 6 µm	
Vertical direction (Z)	4 µm to 7 µm	

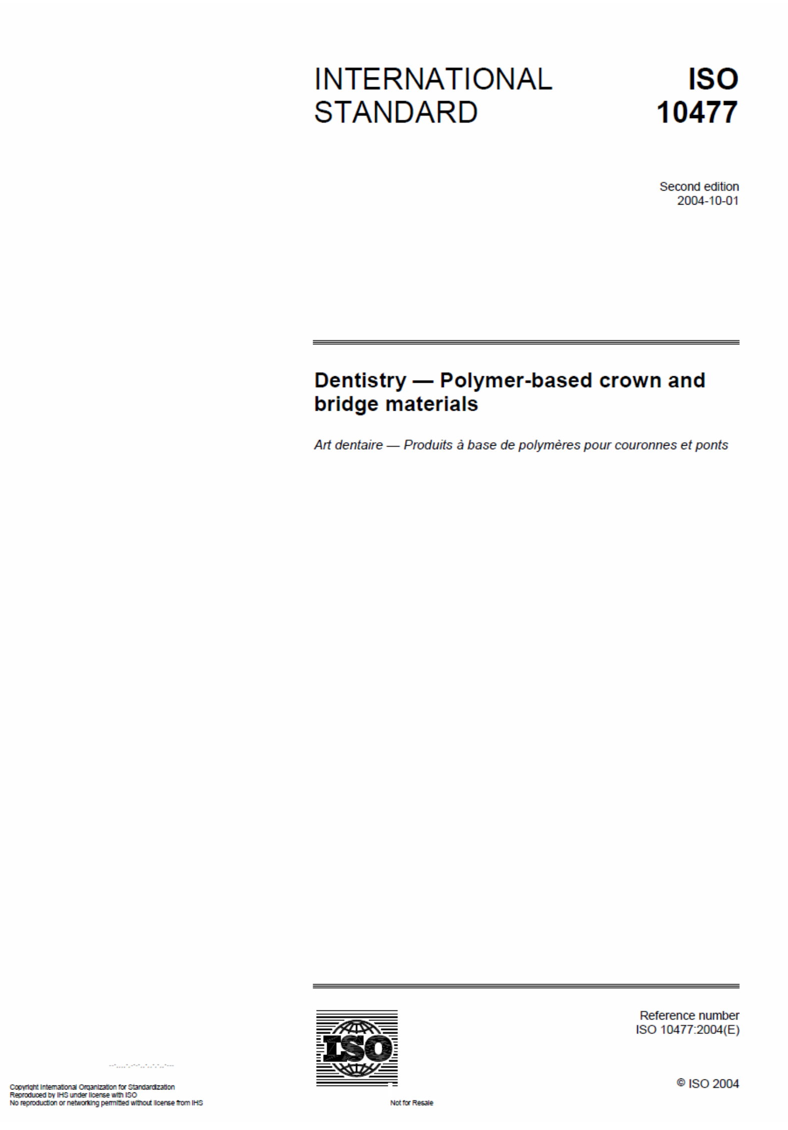
For worldwide contact details, please visit www.renishaw.com/contact

Issued: 07.2015

H-5800-1086-01-B

Figure A.1 Renishaw Ti-alloy powder data sheet

Appendix B : ISO 10477



INTERNATIONAL STANDARD

ISO 10477

Second edition
2004-10-01

Dentistry — Polymer-based crown and bridge materials

Art dentaire — Produits à base de polymères pour couronnes et ponts

Reference number
ISO 10477:2004(E)

Figure B.2 ISO 10477 used for delamination testing.

Appendix C: Raw Data

Table C.1 Bond strengths in MPa obtained by delamination test performed by NIOM.

Coating type	Bond strength (MPa)					
	1	2	3	4	5	Average (σ)
Opaque Resin (ref.)	19.2	17.5	22.8	16.2	15.9	18.3 (2.8)
Anodized	15.0	12.4	15.6	11.8	14.5	13.9 (1.7)
PEO	6.7	7.9	10.1	15.0	6.7	9.3 (3.5)
PVD	14.9	12.5	15.4	13.6	12.4	13.8 (1.4)
Sol-gel	0.7	2.5	2.6	4.7	0.6	2.2 (1.7)

Table C.2 Charpy impact strength test results for the four coated samples and reference.

Coating type	Charpy impact strength (kJ/m^2)				
	1	2	3	4	Average (σ)
Uncoated (ref.)	100	141	120	97	115 (21)
Anodized	117	144	95	133	122 (21)
PEO	96	131	140	142	127 (21)
PVD	134	139	115	138	132 (11)
Sol-gel	98	129	99	123	112 (16)

Table C.3 Mean surface roughness measurements for different roughness parameters.

Roughness parameters	Titanium	Opaquer	Anodization	PVD	Sol-gel	PEO
Ra	13.8	11.6	17.7	14.1	10.7	19.3
Rq	17.3	14.4	22.0	17.2	14.4	24.5
Rp	44.3	39.7	50.7	43.1	49.4	70.0
Rv	37.4	35.6	39.7	35.3	23.0	47.0
Rz	81.7	75.3	90.4	78.4	72.6	116.9
Rt	81.7	75.3	90.4	78.4	72.6	116.9
RPc	28.5	24.2	27.4	30.3	23.0	22.3